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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(CO)3 ligand 2-dialkylphosphonomethyl-6-phenylpyridine (1) and its versatile coordination to a Rh center is described. Facile C–H activation occurs in the presence of an (internal) base, thus resulting in the new cyclometalated complex \([\text{Rh}(\text{CO})(\kappa^1,\kappa^3,\kappa^1-PN,C-1)]\) (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 \([\text{Rh}(\text{CO})(\kappa^1,\kappa^3,\kappa^1-PN,C-1)(\kappa^2,\kappa^1-PN,C-1)])\) (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 \([\text{Rh}(\text{CO})(\kappa^1,\kappa^3,\kappa^1-PN,C-1)])\) (5). Variable-temperature NMR spectroscopy indicates the involvement of a Rh[III] intermediate through formal oxidative addition to give trans-[\text{Rh}(\text{CH})_3(\text{CO})((\kappa^1,\kappa^3,\kappa^1-PN,C-1))] prior to C–C reductive elimination. The Rh[III]-trans-diiodide complex \([\text{Rh}(\text{CO})(\kappa^1,\kappa^3,\kappa^1-PN,C-1)])\) (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–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 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[II] cyclometalated complexes are rare (Figure 1).[5,6] As a consequence, the potential reactivity of the metallacyclic Rh[II]–C bond and the scope for follow-up chemistry is unexplored.

Figure 1. Overview of known cyclometalated Rh[III] complexes.

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 σ* 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 flexidentine 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(phosphonophenethyl)benzene (PCP) pincer system reported by...
Milstein and co-workers, wherein a Rh(C\textsubscript{Ph}-H) bond was detected as an intermediate toward the oxidative addition of the C-H bond.\textsuperscript{[8,9]} Examples of structurally characterized complexes with an agostic C-arene-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,\textsuperscript{[10–12]} and reversible cyclometalation has been postulated as a possible ligand-mediated mechanism in catalysis,\textsuperscript{[13]} primarily based on theoretical calculations.\textsuperscript{[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.\textsuperscript{[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\textsuperscript{i} 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 complex. We also describe the first case of facile methylation of a cyclometalated Rh-arene through the reductive elimination of a [Rh\textsuperscript{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\textsuperscript{i} species**

Addition of ligand 1\textsuperscript{H} to 0.5 molar equivalents of [Rh(p-CI)(CO)]\textsubscript{3} yielded a yellow solid, which displays a doublet in the \textsuperscript{31}P NMR spectrum at \(\delta = 104\) ppm (\(J_{Rh-P} = 160\) Hz; Scheme 2). X-ray crystal structure determination confirmed the square-planar geometry expected for this complex, formulated as [RhCl(CO)(k\textsuperscript{2}-PN-1\textsuperscript{H})] (2; Figure 2). The most striking feature of the molecular structure is the phenyl ring that strongly points out of the Rh coordination plane (\(\tau\); Rh1-N1-C5-C15 = 19.32(18)\textdegree) to accommodate the Cl ligand, which also results in a somewhat acute P1-Rh1-Cl1 angle of 162.983(15)\textdegree.

Notably, the reaction of 1\textsuperscript{H} with [Rh(acac)(CO)]\textsubscript{2} (acac = acetlyacetonate) results in the red complex 3 with very different spectroscopic features relative to 2. \textsuperscript{31}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 \textsuperscript{31}P NMR spectrum showed a doublet at \(\delta = 76\) ppm with a significantly smaller coupling constant (\(J_{Rh-P} = 101\) Hz), which indicates the presence of a strong \(\sigma\)-donor trans to the phosphane group. Furthermore, the


$^{13}$C NMR spectrum contained a doublet of doublets at $\delta = 177$ ppm ($J_{\text{HH-C}} = 82, J_{\text{H-P}} = 37$ 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 (η$^3$-P,η$^3$-C)-coordination mode of the ligand in this unusual Rh$^+$ cyclometalated complex was unambiguously confirmed by X-ray structure determination (Figure 4). The cyclometalated ligand structure bears considerable strain, with $\gamma: P1-Rh1-C1 = 162.47(4)$ and $\gamma: N1-Rh1-C1 = 80.26(5)$.

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–C2 1.8144(16); P1-Rh1-N1 82.87(3), P1-Rh1-C1 81.37(4), P1-Rh1-C2 99.92(4), N1-Rh1-C1 80.26(5); torsion $\gamma: C1-C6-C7-N1 = 0.79(17)$.

**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 catalysts, proceeds through a six-membered transition state where the non-coordinated acetate oxygen atom of the $\eta^1$-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 Rh$^+$ and Ir$^+$ species. Based on this precedent, we speculate that a similar mechanism is plausible for the Rh$^+$ 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(phosphonamidophenyl)dilutidine (PNP) ligand. Apart from a distinct darkening of the solution upon dearomatization of the pyridine fragment, deuterium experiments (that is, the use of DCl results in selective deuteration at the $-CH_2(P)$ position; see the Supporting Information) are indicative for methylene reactivity. However, this deaeromatized 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 is 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 $-78$ °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.

We resorted to DFT calculations to understand the observed reaction sequence of the initial deprotonation at the $-CH_2P$ 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 $T_D$ of 29.5 kcal mol$^{-1}$ (Figure 5). Therefore, the mechanism most likely involves proton shuffling through tBuOH; obtained from protonation of KOtBu, which gives a very low barrier of only approximately 1 kcal mol$^{-1}$ ($T_D$).

**Reactivity of the cyclometalated Rh$^+$ complex toward acid:**

**Formation of an aromatic C–H agostic Rh$^+$ 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. The unique structure of ligand 1 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...
Reactivity of Rh complex 3 with one molar equivalent of HBF₄ thus resulting in the rare ᵃ⁻[C–H] agostic species 4.

solid in CD₂Cl₂ yielded a doublet at δ = 121 ppm (Δδ = 45.1 ppm vs. 3) in the ¹³C NMR spectrum, with a coupling constant ¹JC₇H₈ 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[η³-C–H] interaction, with a Rh1–C11 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.[7]

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 ¹JC₆H 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-C₇ bond. The signal for the two ortho-C₆H₆ atoms does show an upfield shift to δ = 117 ppm in the ¹³C NMR spectrum relative to complex 2, but the ¹JC₆H 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 [(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[24] 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[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⁺ intermediate

Reactivity of a Rh₂-phenyl fragment toward Mel to induce selective methylation has been reported for a [(PC₃)Rh(μ-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...
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 spectroscopic analysis, with an almost identical chemical shift ($\delta = 105$ ppm) and coupling constant ($J_{d_{\text{ax}},d_{\text{ax}}} = 102$ 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 $[\text{Rh}(\text{CO})(\text{I})(\text{PN})]^+$, in which 1$^{16}$m is the ortho-tolyl variant of ligand 1$^6$. The pathway for the formation of this complex presumably involves metal-centered oxidative addition of Mel to give $[\text{Rh}^{18}(\text{CO})(\text{I})(\text{Me})]^+$ (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$^{18}$ species could be detected at $-20$ °C as the major species, with a doublet at $\delta = 52$ ppm ($J_{d_{\text{ax}},d_{\text{ax}}} = 66$ Hz) in the $^{31}$P NMR spectrum and the methyl ligand appearing as a doublet of doublets at $\delta = 0.73$ ppm ($J_{d_{\text{ax}},d_{\text{ax}}} = 5.0, J_{d_{\text{ax}},h_{\text{ax}}} = 2.4$ 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$^{18}$ 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 $J_{d_{\text{ax}},d_{\text{ax}}} = 69$ 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$^{18}$ center (Scheme 5). The structure of the neutral complex $[\text{Rh}^{18}(\text{CO})(\text{I})]^+$ (11) was confirmed by X-ray diffraction studies. The molecular structure (Figure 7) displays a distorted octahedral Rh$^{18}$ center, with the two iodo ligands in the axial positions. The I1-Rh1-I2 angle is rather acute at 161.345(12)° as a result of steric interference with the bulky Bu groups of the phosphane arm. The Rh1–P1 bond length is significantly elongated relative to 3 ($\Delta \rho = 0.18$ 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$^{18}$ 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$^{18}$ complex 6 does not react with, for example, HBF$_4$.

Reversible cyclometalation as potential for cooperative bond activation

During the course of our investigations, we noticed that the Rh–C bond in complex 3 can be selectively activated, as illustrated by the smooth and facile reactions with HCl, HBF$_4$, and Mel. This reactivity towards electrophiles could be caused by the ring strain ($\gamma$; N1-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, proposedly generating the formate complex $[\text{Rh}(\text{CO})(\text{I})(\text{PN})]^{-}$ (7; see the Supporting Information). When [D$_2$]formic acid (HCOOD) is used, both ortho positions of the phenyl group are deuterated within minutes, which indicates that the cyclometalation at the Rh$^3$ 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 H$_2$ (20 bar, room temperature) was not observed, thus suggesting that dehydrogenation of a putative Rh(PNC)$_2$–hydride 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$^6$ can act as a reactive flexiendate 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 phenyl-pyridine fragment on a low-valent Rh$^{18}$ complex. The ligand backbone displays dual-site proton-responsive reactivity. The cyclometalated species reacts rapidly with various (protic) electrophiles. The Rh–C$_\text{Ph}$ bond is selectively cleaved by one molar equivalent of HBF$_4$ to result in the formation of the rare agostic...
[Rh(1\textsuperscript{+})(CO)]	extsuperscript{+} species (4), which has been structurally characterized. Rapid methylation of the phenyl ring was observed by reaction of 3 with Mel to give species 5 selectively, which has hitherto not been reported for a cyclometalated Rh complex. This reaction likely proceeds by oxidative addition to generate a Rh\textsuperscript{II} intermediate, as indicated by VT-NMR spectroscopic analysis. Model complex [Rh(CO)(II)(1)] (6) has also been characterized, including by X-ray diffraction studies. These results have provided insight into and control over the reactivity of the Rh–C bond in this unique cyclometalated Rh\textsuperscript{I} complex renders it a competent species in cooperative dehydrogenation catalysis.

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 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{13}C\text{H}, \textsuperscript{31}P, \textsuperscript{31}P\text{H}, \textsuperscript{19}F, and \textsuperscript{11}B) were measured on a Varian INOVA 500 MHz, a Bruker AV400s or a Varian MERCURY 300 MHz spectrometer. IR spectra (ATR) were recorded with a Bruker Alpha-p FTIR spectrometer. IR spectra were measured on an ATR platinum diamond 1 Refl. spectrometer. High-resolution (HR) mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer, with 3-nitrobenzyl alcohol as the matrix for FAB-MS.

Synthesis of ligand 1\textsuperscript{+}: This is a modified procedure\textsuperscript{[27]} to BuLi (1.6 \text{mmol}, 0.6 mL, 1.54 mmol, 1 equiv) was added to a solution of 2-phenyl-6-methylpyridine\textsuperscript{[20]} (0.26 g, 1.54 mmol) in THF (10 mL) cooled to –78 °C. The solution was stirred at –78 °C for 2 h and Li(Bu)\textsubscript{2}Cl (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 room temperature overnight. The reaction mixture was quenched with degassed water (10 mL), and the organic phase was separated. The water layer was washed with pentane (2 \times) and the organic phases were combined and dried over MgSO\textsubscript{4}. The solvents were evaporated under reduced pressure to yield the product as a yellow-white solid (0.47 g, 1.50 mmol, 97%).

1\textsuperscript{H} NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 8.04–7.98\) (m, 2H), 7.60 (app t, J = 7.7 Hz, 1H), 7.50–7.32 (m, 5H), 3.16 (d, \(J_{\text{H-H}} = 3.3\) Hz, 2H; CH\textsubscript{2}P), 1.20 ppm (d, \(J_{\text{H-P}} = 11.0\) Hz; CH\textsubscript{3}CP); \textsuperscript{13}P NMR (121 MHz, CDCl\textsubscript{3}): \(\delta = 36.88\) ppm; \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta = 162.99\) (dd, \(J_{\text{C-P}} = 14.6\) Hz; Py-C), 156.36 (dd, \(J_{\text{C-P}} = 5.3\) Hz; Py-C), 140.37 (s; Ph-C), 137.67 (s; Py-CH\textsubscript{2}), 129.52 (Ph-CH\textsubscript{2}), 129.38 (s; 2C; Ph-CH\textsubscript{2}), 127.45 (s, 2C; Ph-CH), 123.18 (dd, \(J_{\text{C-P}} = 8.1\) Hz; Py-CH), 117.51 (s; Py-CH), 32.67 (d, \(J_{\text{C-P}} = 16.8\) Hz; CH\textsubscript{2}P), 32.34 (d, \(J_{\text{C-P}} = 14.9\) Hz; CH\textsubscript{3}CP), 30.10 ppm (d, J = 13.8 Hz; CH\textsubscript{2}P); HRMS (FAB): m/z calcd for C\textsubscript{12}H\textsubscript{17}P: 314.2053 [M\textsuperscript{+}] – found; 314.2053.

Synthesis of [Rh(Cl)(CO)(\textsuperscript{13}C\text{H}(\text{II})(\text{I})\text{P}(\text{N})(\text{C}(\text{H})\text{P}))\text{BF}_{4}(4)]: \(\text{HBF}_{4}\) (54 wt\% in Et\textsubscript{2}O, 3.7 mg, 23 \mu L) was added to a solution of 3 (10 mg, 23 \mu mol) in Et\textsubscript{2}O (5 mL) so that the desired solution of a yellow solid. After 15 min, the reaction mixture was quenched with 1 mL 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,
CDCl₃): δ = 8.23–8.15 (m, 3H), 7.93–7.84 (m, 3H), 7.83–7.77 (m, 2H), 3.89 (d, J = 10.0 Hz, 2H; CH₂P); 1.43 ppm (d, J = 15.6 Hz, 6H; CH₃). (C Tabs 3 and 5).

X-ray crystallography studies

X-ray intensities were measured on either a Bruker Kappa Apex II diffractometer with a sealed tube and Triumph monochromator (Ω = 0.1073 Å) at 150(2) K for 2–4 or on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (Ω = 0.71073 Å) and a CMOS Photon 50 detector at 150(2) K for 6. The intensity data were integrated with the Eval15 software[29] or the Bruker APEX2 software.[31] Absorption correction and scaling was performed with SADABS.[32] The structures were solved with the programs SHELXT[33] for 2, SHELXS-97[34] for 3 and 4, or SHELXTL for 6.[35] Least-squares refinement was performed with SHELXL-2013[36] for 2, 4, and 6 or SHELXL-97[35] for 3 against F² for 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.[37] CCDC 966973 (2), 966735(3), 966376 (4), and CCDC 1035861 (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: C₃H₇H₂CNOPPRH₂CH₂, M. = 564.70, yellow needle, 0.06 x 0.07 x 0.02 mm crystal, monoclinic, P2₁/c (No: 14), a = 8.47689(19), b = 13.4570(4), c = 20.4259(5) Å, β = 90.149(1)°, V = 2486.41(11) Å³, Z = 4, D = 1.1962 g/cm³, μ = 1.09 mm⁻¹; 4670 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/wR2 (I > 2σ(I)) = 0.0189/0.0459; R1/wR2 (all refl.:) = 0.0223/0.0473; S = 1.051; twin fraction BASF = 0.01959(18); residual electron density between −0.60 and 0.68 eÅ⁻³.

3: C₅H₀NPRH₄, M = 443.32, red needle, 0.08 x 0.17 x 0.044 mm crystal, 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, D = 1.456 g/cm³, 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/wR2 (I > 2σ(I)) = 0.0161/0.0418; R1/wR2 (all refl.:) = 0.0189/0.0427; S = 1.047; residual electron density between −0.33 and 0.31 eÅ⁻³.

4: [C₅H₀NPRH₄][BF₄]_, M = 531.13, orange block, 0.08 x 0.20 x 0.25 mm, triclinic, P(1) (No: 2), a = 8.0624(3), b = 11.5108(4), c = 12.8859(3) Å, α = 108.1431(1), β = 95.8561(1), γ = 96.4800(1)°, V = 1117.18(6) Å³, Z = 2, D = 1.579 g/cm³, 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/wR2 (I > 2σ(I)) = 0.0260/0.0632; R1/wR2 (all refl.:) = 0.0331/0.0659; S = 1.034; residual electron density between −0.70 and 0.91 eÅ⁻³.

5: C₅H₀NPRH₂, M = 697.11, red-orange block, 0.18 x 0.08 x 0.05 mm, triclinic, P(1) (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, D = 2.050 g/cm³, 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;
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Keywords: C–H activation · metallacycles · pincers · reactive ligands · rhodium

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