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

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Abstract: The synthesis of the reactive PN(C) ligand 2-di([tert-butylphosphanomethyl]-6-phenylpyridine (1ª) 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-PN-1₃Me)] (5). Variable-temperature NMR spectroscopy indicates the involvement of a RhIII intermediate through formal oxidative addition to give trans-[Rh(C₃H₅)(CH₃)(CO)](κ²-PN,C-1) prior to C–C reductive elimination. The RhIV-trans-diiodide complex [Rh(CO)(L)₂(κ²-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 RhIII species.[3] Isolated high-oxidation state RhIV complexes that feature a cyclometalated phenylpyridine ligand or substrate scaffold are well-documented.[4] Well-characterized examples of low-oxidation state RhII cyclometalated complexes are rare (Figure 1).[5,6] 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 RhI 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(phosphanomethyl)benzene (PCP) pincer system reported by

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Milstein and co-workers, wherein a Rh(C–H) bond was detected as an intermediate toward the oxidative addition of the C–H bond. 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, and reversible cyclometalation has been postulated as a possible ligand-mediated mechanism in catalysis, primarily based on theoretical calculations. 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. 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 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 arene Rh(C–H) agostic complex. We also describe the first case of facile methylation of a cyclometalated Rh–arene through the reductive elimination of a [RhIII(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 species

Addition of ligand 1H to 0.5 molar equivalents of [{Rh(µ-Cl)(CO)}₂] yielded a yellow solid, which displays a doublet in the ³¹P NMR spectrum at δ = 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)(µ-Ph–H)] (2; Figure 2). The most striking feature of the molecular structure is the flaming phenyl ring that strongly points out of the Rh coordination plane (Rh1-N1–C5-C15 = 19.32(18)°) to accommodate the Cl ligand, which also results in a somewhat acute P1-Rh1-Cl1 angle of 162.983(15)°.

Figur 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-N1 81.95(3), P1-Rh1-C21 93.75(3), N1-Rh1-Cl1 93.75(3); torsion angle N1-C5-C15-C16 = 38.6(2).

Notably, the reaction of 1H with [Rh(acac)(CO)]₂ results in the red complex 3 with very different spectroscopic features relative to 2. ³¹P 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 ³¹P NMR spectrum showed a doublet at δ = 76 ppm with a significantly smaller coupling constant (J_Rh,P = 101 Hz), which indicates the presence of a strong o-donor trans to the phosphane group. Furthermore, the ³¹P NMR spectra with relevant coupling constants for Rh complexes 2–5.

Figure 3. ³¹P NMR spectra with relevant coupling constants for Rh complexes 2–5.
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 complexes, involves proton transfer from the base and with internal bases (for example, acac). However, this dearomatized 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.

$\text{PMe}_3$ 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.

We resorted to DFT calculations to understand the observed reaction sequence of the initial deprotonation at the $\cdots$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 into a high lying transition state $\text{TS}_{2-3}$ of 29.5 kcal mol$^{-1}$ (Figure 5). Therefore, the mechanism most likely involves proton shuttling through tBuOH$_2$, which gives a very low barrier of only approximately 1 kcal mol$^{-1}$ ($\text{TS}_{2-\text{H}2\text{BuOH}}$).

Reactivity of the cyclometalated Rh complex toward acid: Formation of an aromatic C$-$H agostic Rh$_2$ species

As mentioned in the Introduction, pincer ligands with a flanking phenyl group are scarce, especially in contrast to the arachetypical 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 $1^\text{th}$ 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
solid in CD$_2$Cl$_2$ yielded a doublet at $\delta = 121$ ppm ($\Delta \delta = 45.1$ ppm vs. 3) in the $^3$P NMR spectrum, with a coupling constant $J_{\text{HH}}$ of 202 Hz ($\Delta J = 101$ 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 CH$_2$Cl$_2$/pentane, and the resulting X-ray structure of complex 4 (Figure 6) shows a distinct Rh(η$^2$-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 $\delta = 4$ ppm for the respective proton in the $^1$H NMR spectrum. Furthermore, the $J_{\text{CH}}$ value should decrease due to the weakening of the C–H bond. In case of 4, the phenyl group shows local C$_\text{sp}$ symmetry by $^1$H NMR spectroscopic analysis, even at $-90^\circ$C, thus indicating fast rotation around the C$_\text{sp}$–C$_\text{py}$ bond. The signal for the two ortho-C-H bonds shows an upfield shift to $\delta = 117$ ppm in the $^1$C NMR spectrum relative to complex 2, but the $J_{\text{CH}}$ 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$_4$],[8] 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 [(PCHP)Rh(CO)][BF$_4$], 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).[24]

**Methylation of the cyclometalated Rh complex:**

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

Reactivity of a Rh–phenyl fragment toward MeI 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 MeI 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 abase to major species, with adoublet at as documented for the low-valent situation. We are currently this Rh reductive elimination process. Conversion into complex adoublet of doublets at igated relative to positions. The I1-Rh1-I2 angle is rather acute at 161.345(12).

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, HBF₄ and Mel. This reactivity towards electrophiles could be caused by the ring strain (see the Supporting Information). When [D₂]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(phenyl)–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 can act as a reactive flexideterminate ligand, which switches between bis- 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–C₃ bond is selectively cleaved by one molar equivalent of HBF₄ to result in the formation of the rare agostic...
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×) and the organic phases were combined and dried over MgSO₄. The solvents were evaporated under reduced pressure to yield the product as a yellow-white solid (0.47 g, 150 mmol, 97%).

H NMR (300 MHz, CDCl₃): δ = 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 = 3.3 Hz, 2H; CH₃P), 1.20 ppm (d, J = 11.0 Hz, 18H; CH(C₃H₅)₂P); ¹³C NMR (75 MHz, [D₆]acetone): δ = 162.99 (d, J = 14.0 Hz; CO), 156.36 (d, J = 5.3 Hz; Py-CH), 140.37 (s; Ph-CH), 137.67 (s; Py-CH), 129.52 (Ph-CH₃), 129.38 (s; 2CH-Ph), 127.45 (s; 2CH-Ph), 123.18 (d, J = 8.1 Hz; Py-CH), 117.51 (s; Py-CH), 32.67 (d, J = 16.8 Hz; CH₃P), 32.34 (d, J = 14.9 Hz; CH(C₃H₅)₂P), 10.30 ppm (d, J = 13.8 Hz; CH(C₃H₅)₂P); HRMS (FAB): m/z calcd for C₈H₁₁N(CO)P: 34.0342 [M⁺]; found: 34.0345.

Synthesis of [Rh(C₃H₅)₂(CO)]⁺ (1): A solution of [Rh(C₃H₅)₂(CO)]⁺ (0.012 g, 0.032 mmol) in CH₂Cl₂ (3 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 yellow powder (0.022 g, 72%). Single crystals suitable for an X-ray crystal structure determination were obtained by slow diffusion of pentane into a solution of 2 in CH₂Cl₂. H NMR (300 MHz, [D₆]acetone): δ = 8.15–8.07 (m, 2H; Ph), 7.98 (dd, 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 = 9.3 Hz, 2H; CH₂P), 1.41 ppm (d, J = 4.7 Hz, 18H; CH(C₃H₅)₂P); ¹³C NMR (121 MHz, [D₆]acetone): δ = 150.35 (s; Ph-C), 140.37 (s; Ph-CH), 137.67 (s; Py-CH), 129.52 (Ph-CH₃), 129.38 (s; 2CH-Ph), 127.45 (s; 2CH-Ph), 123.18 (d, J = 8.1 Hz; Py-CH), 117.51 (s; Py-CH), 32.67 (d, J = 16.8 Hz; CH₃P), 32.34 (d, J = 14.9 Hz; CH(C₃H₅)₂P), 10.30 ppm (d, J = 13.8 Hz; CH(C₃H₅)₂P); HRMS (FAB): m/z calcd for C₈H₁₄N(CO): 384.0496 [M⁺]; found: 384.0493.

Synthesis of [Rh(C₃H₅)₂(CO)]⁺ (1): A solution of [Rh(C₃H₅)₂(CO)]⁺ (0.012 g, 0.032 mmol) in CH₂Cl₂ (3 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 yellow powder (0.022 g, 72%). Single crystals suitable for an X-ray crystal structure determination were obtained by slow diffusion of pentane into a solution of 2 in THF. H NMR (500 MHz, [D₆]acetone): δ = 8.15–8.07 (m, 2H; Ph), 7.98 (dd, 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 = 9.3 Hz, 2H; CH₂P), 1.41 ppm (d, J = 4.7 Hz, 18H; CH(C₃H₅)₂P); ¹³C NMR (121 MHz, [D₆]acetone): δ = 150.35 (s; Ph-C), 140.37 (s; Ph-CH), 137.67 (s; Py-CH), 129.52 (Ph-CH₃), 129.38 (s; 2CH-Ph), 127.45 (s; 2CH-Ph), 123.18 (d, J = 8.1 Hz; Py-CH), 117.51 (s; Py-CH), 32.67 (d, J = 16.8 Hz; CH₃P), 32.34 (d, J = 14.9 Hz; CH(C₃H₅)₂P), 10.30 ppm (d, J = 13.8 Hz; CH(C₃H₅)₂P); HRMS (FAB): m/z calcd for C₈H₁₄N(CO): 384.0496 [M⁺]; found: 384.0493.

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 Å 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 Å. The intensity data were integrated with the Eval15 software [30] 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 [31]. Least-squares refinement was performed with SHELXL-2013 [33] for 2, 4, 6, and SHELXL-97 [33] 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: C18H22ClO3P=CNOPh-CH2Cl, M. = 564.70, yellow needle, 0.06 x 0.07 x 0.27 mm, monoclinic, P2_1/c (No: 14), a = 8.47689(19), b = 13.4570(4), c = 20.4259(5) Å, β = 90.141(1)°, V = 2468.41(11) Å³, Z = 4, Dc = 1.509 g cm⁻³, μ = 0.19 mm⁻¹; 4672 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 5235 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 and wR2 (I > 2σ(I)): 0.0189/0.0459; R1 and wR2 (all refl.): 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: C18H22ClO3P=N=CNOPh3, 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 = 1.465 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 and wR2 (I > 2σ(I)): 0.0161/0.0418; R1 and wR2 (all refl.): 0.0189/0.0427; S = 1.047; residual electron density between –0.33 and 0.31 e Å⁻³.

4: [C16H28N2O8P=CF3], M. = 531.13, orange block, 0.08 x 0.20 x 0.25 mm, triclinic, P(T) (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 and wR2 (I > 2σ(I)): 0.0260/0.0632; R1 and wR2 (all refl.): 0.0331/0.0659; S = 1.034; residual electron density between –0.70 and 0.91 e Å⁻³.

5: C18H15N2O3PF=CF3, M. = 697.11, red-orange block, 0.18 x 0.08 x 0.05 mm, triclinic, P(T) (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 = 1154.94(9) Å³, Z = 2, Dc = 2.005 g cm⁻³, μ = 3.49 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 optimized with the Turbomole program package[38] coupled to the P05 Baker optimizer[39] via the B05 package[40] at the unrestricted DFT level using the B88[41] functional and the resolution-of-identity B3 method.[41] We optimized the geometries of all stationary points at the def2-TZVP basis-set level[42] and at 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. 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[43] were calculated from the Turbomole output files by using the AOMix program.[44]

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Keywords: C–H activation · metallocycles · pincers · reactive ligands · rhodium


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