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Investigation of the Dynamic Solution Behavior of Chloro(diene)rhodium(I) Phosphine Complexes with a Pendant Unsaturated Heterocycle at Phosphorus (2-pyridyl, 2-imidazyl; diene = COD, NBD)

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Reaction of chloro(diene)rhodium(I) dimer with 2-pyridyl- and 2-imidazylphosphines resulted in the formation of the four-coordinate, square-planar complexes chloro(diene)rhodium-κ^1-P-phosphine [diene = 1,5-cyclooctadiene (COD), bicyclo[2.2.1]hepta-2,5-diene (NBD)]. The nitrogen in the β-position to phosphorus provoked a fast exchange of the olefin sites in solution. Influences on this system were investigated through variation of the substituents on the phosphorus, the diene, the metal, and the heterocycle and the substitution pattern of the heterocycle. Additional isotopic labeling experiments were performed with a deuterium (**1-*d*$_1$**) or a trideuteromethyl group (**1-Me-*d*$_3$**) in the *ortho*-position to nitrogen in **1** and one deuterium in each of the olefinic positions of COD (**1-COD-*d*$_2$**). These findings resulted in an inverse kinetic isotope effect (KIE) in the case of **1-Me-*d*$_3$** and **1-COD-*d*$_2$**. No KIE was found by complete line-shape analysis when the pyridyl-nitrogen was labeled with ^{15}N. The temperature dependence of T_1 relaxation times for the *para*-proton in the pyridyl moiety was found to be a diagnostic criterion for an interaction of the pyridyl moiety with the rest of the complex, allowing the estimate of the strength of the attractive part of this interaction. No ground-state experimental proof (X-ray structure, scalar coupling constants in NMR spectroscopy) was found for this kind of interaction. DFT calculations support the nonexistence of ground-state complexes with Rh-coordinated pyridyl-nitrogen. Calculations on the pathway of the dynamic behavior in comparison to the experimental results exclude an interaction of the pyridyl-nitrogen with the COD double bonds and speak in favor of a temporary coordination of the pyridyl nitrogen to the metal center in a transition state. The calculated and measured kinetic data (including the KIEs) are in good agreement with this mechanism.

Introduction

Chelating diolefin complexes of Rh(I) and Ir(I) are well-known precursors for the synthetic coordination chemistry and the application of these metals as catalysts.[1] In several cases a fluxional behavior of the chelating diolefin (site exchange of the coordinated double bonds) has been observed on the spectral NMR time scale in this type of complex.[2] Proposals of why this occurs have included an intramolecular rotation of the chelating diolefin in a tetracoordinated complex via a pseudotetrahedral intermediate, a dissociative exchange of spectator ligands via a T-shaped three-coordinated intermediate, or an associative pseudorotation within a pentacoordinated intermediate. Despite numerous reports, the mechanism of this fluxional behavior is still under dispute.

In this contribution we report new insight into the mechanism using multinuclear VT-NMR spectroscopy, X-ray analysis, and DFT calculations concerning the fluxional behavior of group 9 complexes [diolefin]M^{I}(PR$_2$Py)(X), shown in Scheme 1 as type B.

Thus, the focus of our studies is set on the influence of a nitrogen atom in *ortho*-position of the aryl group connected to the P donor (1P,3N relation)[3a−c] on the fluxional behavior of the chelating diolefin ligand. The behavior of the nitrogen-free analogues (type A in Scheme 1) is discussed in a separate paper.[13]

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(1) (a) Jalon, F. A.; Manzano, B. R.; Caballero, A.; Carrion, M. C.; Santos, L.; Espino, G.; Moreno, M. *J. Am. Chem. Soc.* **2005**, *127*, 15364. (b) Drent, E.; Arnoldy, P.; Budzelaar, P. H. *J. Organomet. Chem.* **1993**, *455*, 247. (c) Drent, E.; Arnoldy, P.; Budzelaar, P. H. *J. Organomet. Chem.* **1994**, *475*, 57. (d) Grotjahn, D. B.; Lev, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 12232. (e) Grotjah, D. B.; Kragulj, E. J.; Zeinalipour-Yazdi, C. D.; Miranda-Soto, V.; Lev, D. A.; Cooksy, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 10860. (f) Labonne, A; Kribber, T.; Hintermann, L. *Org. Lett.* **2006**, *8*, 5853. (g) Kribber, T.; Labonne, A.; Hintermann, L. *Synthesis* **2007**, 2809.

(2) (a) Cesar, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Eur. J. Inorg. Chem.* **2004**, 3436. (b) Cesar, V.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Chem.—Eur. J.* **2005**, *11*, 2862. (c) Weller, A. S.; Mahon, M. F.; Steed, J. W. *J. Organomet. Chem.* **2000**, *614−615*, 113. (d) Miranda-Soto, V.; Prez-Torrente, J. J.; Oro, L. A.; Lahoz, F. J.; Martin, M. L.; Parra-Hake, M.; Grotjahn, D. B. *Organometallics* **2005**, *25*, 4374. (e) Haarman, H. F.; Bregman, F. R.; Ernsting, J.-M.; Veldman, N.; Spek, A. L.; Vrieze, K. *Organometallics* **1997**, *16*, 54.

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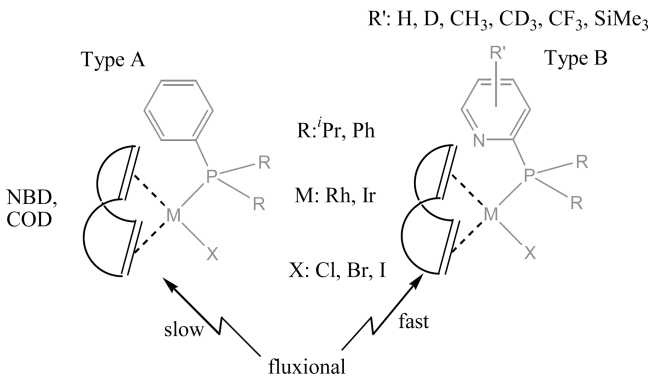
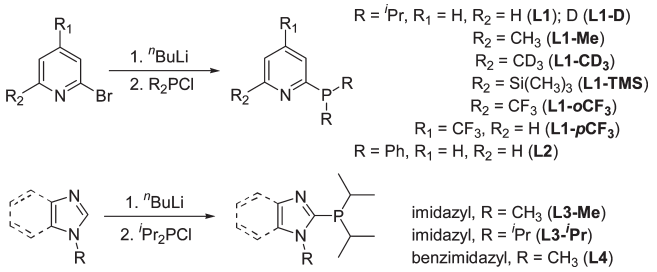
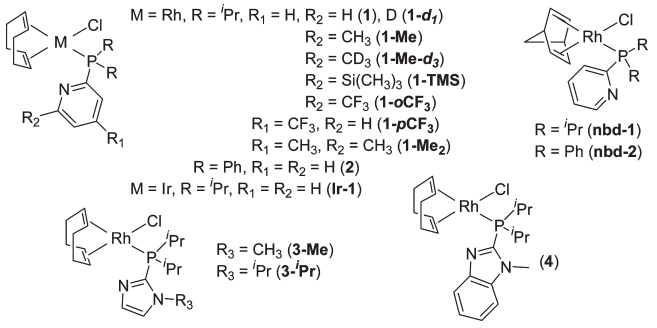
Scheme 1



Scheme 2. Synthesis of the Ligands



Scheme 3. Complexes Used in This Study



Results and Discussion

Synthesis of the Ligands and Complexes. The pyridine-containing ligands used in our study were synthesized starting from the corresponding 2-bromopyridine derivatives by lithiation with *n*-butyllithium (^{n}BuLi) followed by a reaction with chlorodiisopropylphosphine (^{i}Pr$_2$PCl) or chlorodiphenylphosphine (Ph$_2$PCl) (Scheme 2).[3d−g] The imidazole-containing ligands were synthesized in a similar manner by deprotonation of the N-alkylated imidazoles at the C2 position with *n*-butyllithium and further reaction with chlorodiisopropylphosphine.

The rhodium and iridium complexes (Scheme 3) were obtained in very good yields by stirring 1 equiv of [(diolefin)MCl]$_2$ with 2 equiv of the ligand in dichloromethane.

In the case of **1-*p*CF$_3$**, the use of the crude ligand (**L1-*p*CF$_3$**) was not sufficient due to the formation of 20−30% of the bromo derivative (**Br-1-*p*CF$_3$**) of the complex. This can be explained by elimination of lithium bromide in the ligand synthesis and further extraction by coordination to **L1-*p*CF$_3$**. The **1-*p*CF$_3$** and **Br-1-*p*CF$_3$** complexes can be distinguished in the ^{31}P{^{1}H} NMR spectrum by a shift of the doublet from 44.6 ppm ($^1J_{PRh}$ = 148.5 Hz) for the chloro compound to 46.1 ppm ($^1J_{PRh}$ = 145.5 Hz) for the bromo compound. Both compounds are identical in the ^{1}H NMR spectra. The second compound can be assigned to be the bromo compound by X-ray analysis of **1-*p*CF$_3$** and **Br-1-*p*CF$_3$** mixed single crystals (ratio Cl/Br = 2:1, redissolving of the crystals resulted in the same ^{31}P{^{1}H} and ^{1}H NMR spectra). As the halide did not show a high impact on the dynamic behavior of the studied system, no further effort was undertaken to purify **1-*p*CF$_3$** and **Br-1-*p*CF$_3$**.

Since ^{15}N NMR spectroscopy was presumed to provide insight into the solution behavior of the pyridyl moiety in general, and eventually to interactions between nitrogen and other groups of the complex by direct coupling, we synthesized the ^{15}N-labeled ligand diisopropyl(4,6-dimethyl-2-pyridyl)phosphine, **^{15}N-Me$_2$-L1**, and the ^{14}N counterpart **Me$_2$-L1** for direct comparison of the solution behavior of the final complexes (Scheme 4).[4,5] A palladium-catalyzed coupling of aryl and binaphthyl triflates with diphenylphosphine oxide and subsequent reduction of the phosphine oxide with trichlorosilane was applied. In addition to ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{15}N{^{1}H} NMR spectroscopy, elemental analysis, and mass spectroscopy, crystals suitable for X-ray diffraction were obtained from a saturated acetone solution, confirming the structure of complex **1-Me$_2$**.

The abstraction of chloride in **1** with silver tetrafluoroborate resulted in complex **1-BF$_4$**, which is static on the spectral time scale of ^{1}H NMR spectroscopy (Scheme 5). The nitrogen coordinates to the rhodium, resulting in a four-membered ring. In addition to the absence of line broadening for the COD signals in the ^{1}H NMR spectrum, the ring formation is accompanied by a typical upfield shift in the ^{31}P NMR from 43.3 ppm to −11.9 ppm and a reduction of the coupling constant $^1J_{PRh}$ from 144.7 Hz to 120.9 Hz. **1-BF$_4$** and its derivatives were stable only in solution and decomposed during isolation and crystallization attempts, showing the weak coordination in this unfavorable four-membered ring system.

Addition of 1 equiv of *para*-toluenesulfonic acid (*p*-TsOH) to a NMR sample of **1** in CDCl$_3$ resulted in deceleration of the olefin exchange rate (*vide infra*) and, thus, a sharpening of the olefin signals, and a slight broadening of the pyridyl signals in combination with a low-field shift of the *ortho*-proton from 8.67 ppm to 9.40 ppm. The protonation of the nitrogen also resulted in a low-field shift in the ^{31}P NMR from 43.3 ppm to 48.7 ppm and an increase in the $^1J_{RhP}$ coupling constant from 144.7 Hz to 151.5 Hz. The same result is obtained when first quantitively protonating the ligand and then applying it to [(COD)RhCl]$_2$.

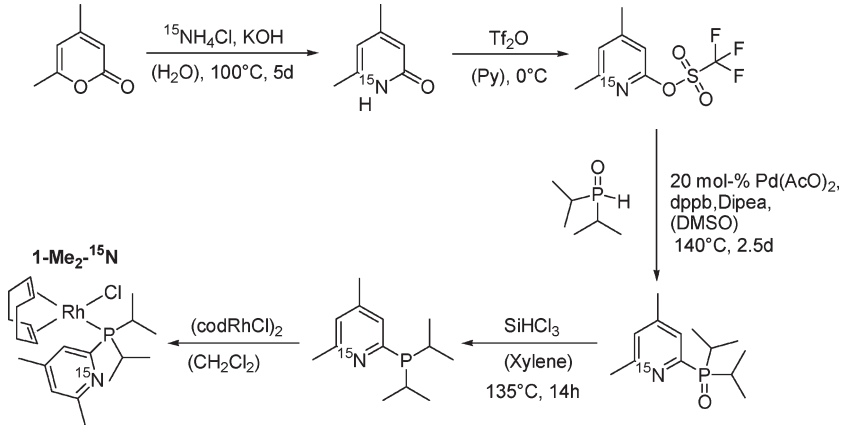
We find evidence for a hydrogen bond in **1-H$^+$**, as shown in Scheme 5, by the following facts: (i) The change in ^{31}P chemical shift to higher ppm is in accordance with the

(3) (a) Newkome, G. R. *Chem. Rev.* **1993**, *93*, 2067. (b) Grotjahn, D. B. *Dalton Trans.* **2008**, 6497. (c) Zhang, Z. Z.; Cheng, H. *Coord. Chem. Rev.* **1996**, *147*, 1. (d) Spencer, L. P.; Altwer, R.; Wie, P.; Gelmini, L.; Gauld, J.; Stephan, D. W. *Organometallics* **2003**, 3841. (e) Jansen, A.; Pitter, S. *J. Mol. Catal. A* **2004**, *217*, 41. (f) Gros, P.; Younes-Millot, C. B.; Fort, Y. *Tetrahedron Lett.* **2000**, *41*, 303. (g) Scrivanti, A.; Beghetto, V.; Matteoli, U. *Adv. Synth. Catal.* **2002**, *344*, 543.

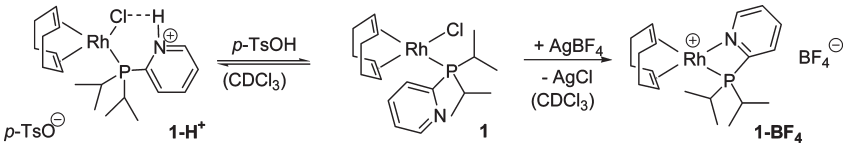
(4) (a) Anschütz, R.; Bendix, P.; Kerp, W. *Anal. Chem.* **1890**, *256*, 148. (b) Ritter, K. *Synthesis* **1993**, 735. (c) Schwan, A. L. *Chem. Soc. Rev.* **2004**, *33*, 218.

(5) Beletskaya, I. P.; Kazankova, M. A. *Russ. J. Org. Chem.* **2002**, *38*, 1391.

Scheme 4. Synthetic Route to the ^{15}N-Labeled Ligand ^{15}N-Me$_2$-L1 and Further Reaction to the Rhodium Complex 1-Me$_2$-^{15}N (and Their Unlabeled Counterparts Me$_2$-L1 and 1-Me$_2$)



Scheme 5



formation of a six-membered ring; (ii) a broad peak at 16.2 ppm in ^{1}H NMR spectroscopy resolved at −60 °C; (iii) samples of **1-H**$^+$ were not stable in solution and decomposed completely within a few hours. ^{31}P NMR reaction control showed that one of the intermediate decomposition products is the corresponding cationic rhodium complex to **1-BF$_4$**, indicating the release of HCl within the course of decomposition. Similar hydrogen bonding behavior has previously been reported.[6]

VT 1D NMR Studies. The starting point in this study was the complex chlorocycloocta-1,5-diene(diisopropyl-2-pyridylphosphine)rhodium (**1**). At room temperature (298 K), all signals in the ^{1}H NMR spectrum (400.13 MHz) were sharp and at the expected chemical shifts except for the olefinic protons, which vanished in the baseline. Additionally, the allylic signals in the ^{13}C{^{1}H} NMR (100.6 MHz) spectrum showed up as one very broad signal at about 31 ppm. At the same time, the ^{31}P{^{1}H} NMR spectrum (161.1 MHz) showed a sharp doublet at 43.3 (d, $^1J_{PRh}$ = 144.7 Hz) ppm.

^{1}H VT NMR measurements in $CDCl_3$ through the temperature range from 213 to 323 K (Figure 1) in 10 deg steps were performed. The olefinic protons showed two sharp signals at 3.33 and 5.23 ppm at 213 K, which broadened upon warming to 273 K (the two ^{1}H signals within each double bond are equivalent). Between 283 and 303 K, these signals could be observed only by enlargement of the spectrum, so that a coalescense temperature T_c of 298 K could be determined (T_c concerns the coalescence temperature of the olefinic proton resonances in the COD ligand throughout the whole paper). At higher temperatures, a very broad singlet around 4.28 ppm was obtained. A ^{1}H VT NMR series in toluene-d_8 in the temperature range from 183 to 373 K showed the same overall behavior, with a general shift to higher temperatures (T_c = 318 K) so that even at 373 K no sharp signals were detected. The decrease in line-width broadening of the olefinic signals was also observable in the ^{13}C{^{1}H} NMR spectra (Figure 2), so that below 253 K two broad singlets at about 70 and 103 ppm in $CDCl_3$ were obtained. Upon further cooling to 213 K, the broad signals developed into a doublet at 69.5 ppm ($^1J_{CRh}$ = 13.2 Hz) for the olefinic group *cis* to phosphorus and a weakly resolved doublet of doublets at 102.8 ($^1J_{CRh}$ = 11.0 Hz, $^2J_{CP}$ = 7.3 Hz) for the olefinic group *trans* to phosphorus. The allylic groups showed one very broad signal at about 32 ppm at room temperature, which sharpened into a broad singlet at 328 K and split into two singlets at 28.4 and 32.7 ppm below 253 K.

The whole process is reversible, and the VT NMR measurements could be repeated several times without change in the dynamic behavior of the COD signals and without decomposition of the sample. At this point we must explicitely state that the doublet in the ^{31}P{^{1}H} NMR spectrum did not undergo any change in shape or coupling constant upon cooling or warming.

This fluctuation of the COD is a more general phenomenon for substituted pyridines.[7] We investigated the influences on the system by changing the substituents on the pyridine ring, the heterocycle itself, the additional substituents on the phosphorus ligand, the metal, and the diolefin. In addition to T_c, complete line-shape analysis for the determination of the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, E_a)

(6) (a) Camus, J. M.; Andrieu, J.; Poli, R.; Richard, P.; Baldoli, C.; Maiorana, S. *Inorg. Chem.* **2003**, *42*, 2384. (b) Selent, D.; Baumann, W.; Kempe, R.; Spannenberg, A.; Röttger, D.; Wiese, K.-D.; Börner, A *Organometallics* **2003**, *22*, 4265. (c) Andrieu, J.; Camus, J.-M.; Richard, P.; Poli, R.; Gonsalvi, L.; Vizza, F.; Peruzzini, M. *Eur. J. Inorg. Chem.* **2006**, 51.

(7) (a) Tejel, C.; Ciriano, M. A.; Bravi, R.; Oro, L. A.; Graiff, C.; Galassi, R.; Burini, A. *Inorg. Chim. Acta* **2003**, *347*, 129. (b) Grassi, M.; De Munno, G.; Nicolo, F.; Lo Schiavo, S. *J. Chem. Soc., Dalton Trans.* **1992**, 2367. (c) Arena, C. G.; Rotondo, E.; Faraone, F. *Organometallics* **1991**, *10*, 3877. (d) Chan, A. S. C.; Chen, C.-C.; Cao, R. *Organometallics* **1997**, *16*, 3469. (e) Kurtev, K.; Ribola, D.; Jones, R. A.; Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 55. (f) Arena, G. C.; Faraone, F.; Lanfranchi, M.; Rotondo, E.; Tiripicchio, A. *Inorg. Chem.* **1992**, *31*, 4797. (g) Casares, J. A.; Espinet, P.; Martin-Alvarez, J. M.; Santos, V. *Inorg. Chem.* **2006**, *45*, 6628.

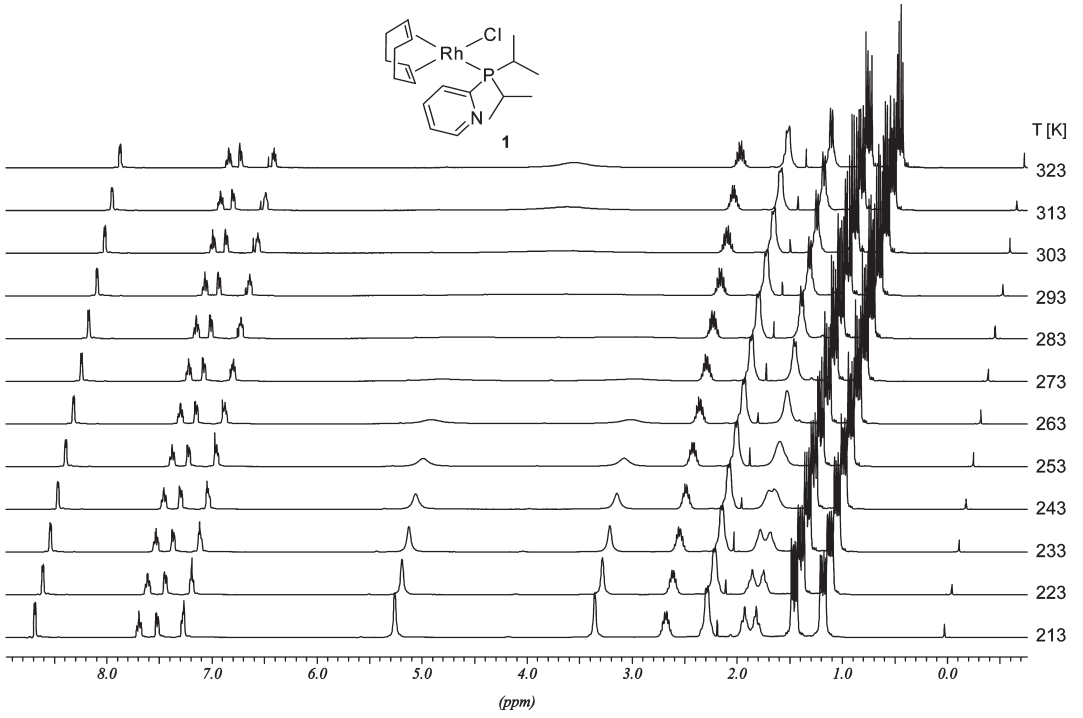


Figure 1. ^{1}H VT NMR spectra of **1** in the temperature range from 213 to 323 K.

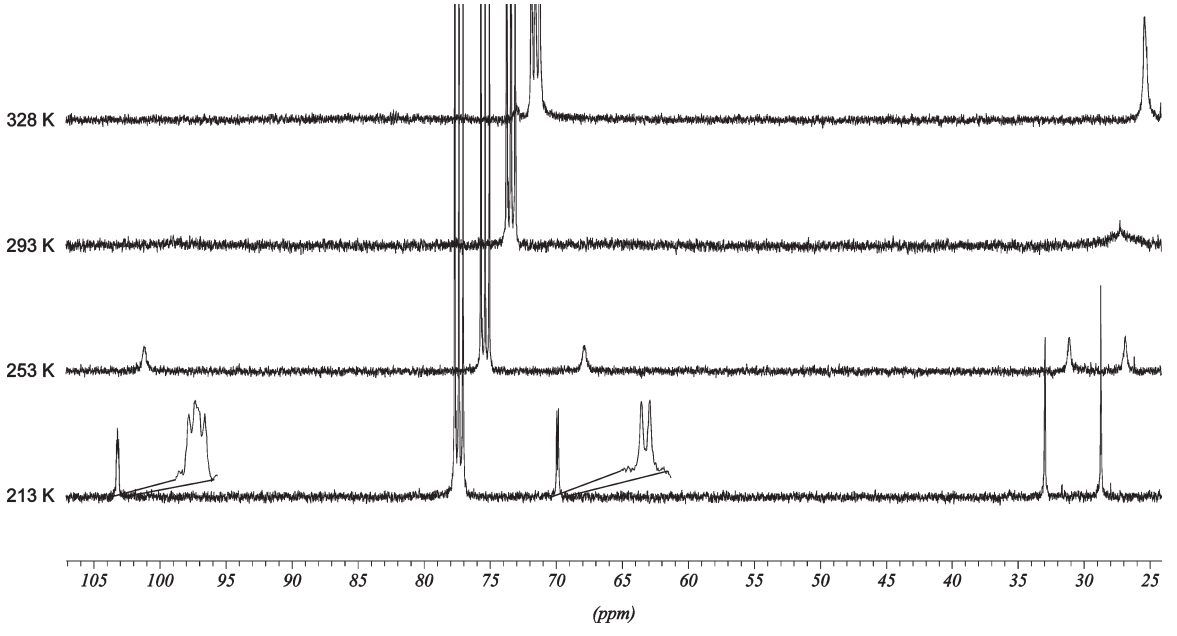


Figure 2. $^{13}C\{^{1}H\}$ VT NMR spectra of **1** at 213, 253, 293, and 328 K in $CDCl_3$. Only the dynamic COD section is shown in the range from 25 to 105 ppm.

was performed. Another descriptive value is T_0, which represents the lowest temperature in the 10 K step VT series *without* broadening of the signal. The VT NMR measurements of one sample were performed three times at three different concentrations (typically 20 mg of complex in 0.5, 1.0, and 1.5 mL of $CDCl_3$). The variations of the three activation parameters for each sample were usually small (1−2 kJ/mol for $\Delta H^{\ddagger}$), so that the dynamic process is independent of the concentration, and a first-order kinetic approach is proposed. An exemplary Eyring plot for the determination of the activation parameters of **1** is depicted in Figure 3. Complex **1** served as a benchmark for

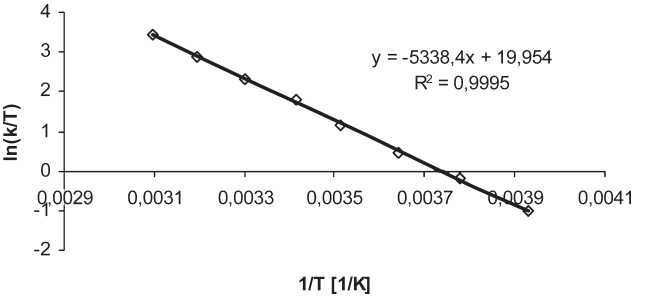


Figure 3. Eyring plot of the dynamic behavior in **1**.

Table 1. Activation Parameters for the Pyridine Derivatives

	solvent	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/(mol K)]	E_a [kJ/mol]	T_0 [K][a]	T_c [K][b]
1	$CDCl_3$	44.6 ± 0.7	−31 ± 195	45.9 ± 0.7	233	298
1	Tol-d_8	49.4 ± 0.8	−29 ± 195	52.0 ± 0.8	253	318
1	C_6D_6	51.9 ± 1.2	−21 ± 194	53.9 ± 1.3		318
1-d_1	$CDCl_3$	45.8 ± 0.5	−25 ± 196	46.6 ± 0.5	233	290
1-COD-d_2	$CDCl_3$	39.9 ± 0.6	−47 ± 196	41.1 ± 0.6	223	293
I-1	$CDCl_3$	45.1 ± 0.8	−31 ± 194	45.9 ± 1.0	233	298
1-Me	$CDCl_3$	42.4 ± 0.9	−46 ± 194	43.3 ± 0.8	233	306
1-Me-d_3	$CDCl_3$	37.6 ± 0.3	−59 ± 196	38.7 ± 0.4	223	299
1-Me_2	$CDCl_3$	35.4 ± 0.6	−63 ± 195	36.8 ± 0.6	223	288
1-Me_2-^{15}N	$CDCl_3$	35.6 ± 0.7	−63 ± 195	36.8 ± 0.8	223	288
1-*p*CF_3	$CDCl_3$	44.1 ± 0.7	−41 ± 195	45.0 ± 0.7	243	303
Br-1-*p*CF_3	$CDCl_3$	42.9 ± 0.7	−44 ± 195	43.9 ± 0.7	243	303
Ir-1	$CDCl_3$	40.8 ± 0.6	−44 ± 195	41.9 ± 0.6	223	288
nbd-1	$CDCl_3$	42.2 ± 0.8	−20 ± 194	43.4 ± 0.8	≤213	248
2	$CDCl_3$	36.0 ± 0.8	−46 ± 195	37.3 ± 0.8	213	258
nbd-2	CD_2Cl_2	28.3 ± 0.7	−54 ± 195	29.8 ± 0.6	< 173	233

[a] T_0: first temperature without line-broadening. [b] T_c: coalescence temperature.

the comparison with other derivatives (enthalpy of activation $\Delta H^{\ddagger}$ of 44.6 ± 0.67 kJ/mol and T_c of 298 K).

Influence of the Solvent. The change of solvent from $CDCl_3$ to toluene-d_8 or benzene-d_6 resulted in an increase of T_c by about 20 K to 318 K and $\Delta H^{\ddagger}$ to 49.4 ± 0.83 and 51.9 ± 1.2 kJ/mol, respectively (for a comparison of all activation parameters see Table 1).

Influence of *ortho*-Substituents to the Pyridyl-Nitrogen. The change from a proton to a methyl group (**1-Me**) had a very small effect on the activation enthalpy ($\Delta H^{\ddagger}$ = 42.4 ± 0.91 kJ/mol), but T_c (306 K) slightly increased. However, the substitution of the proton by a more sterically demanding, electron-withdrawing trifluoromethyl (**1-*o*CF_3**) or a trimethylsilyl group (**1-TMS**; minimum group van der Waals radii $r_{v,min}$: Me, 1.715; CF_3, 2.107; $SiMe_3$, 2.60[8]) resulted in complete loss of the aforementioned line-broadening in the temperature range from 213 to 328 K in the 1D NMR spectra.

To answer the question whether the inhibition of the dynamic behavior of **1-*o*CF_3** was solely a steric effect of the *ortho*-CF_3 group or a combination of steric and electronic properties, a CF_3 group was introduced in the *para*-position to nitrogen (**1-*p*CF_3**). Even though **1-*p*CF_3** could not be obtained in pure form, the chloro/bromo mixture showed a slight shift of the dynamic process to higher temperatures (T_0 = 243 K, T_c = 303 K) but almost identical activation parameters compared to **1**, underlining that the decelerating effect of the CF_3 group in the *ortho*-position is mainly steric in nature. A comparison of the activation parameters of **1-Me** and **1-Me_2** showed that a substituent in the *para*-position does have a significant influence, indicating that electron-releasing groups accelerate the dynamic behavior. We propose that in the case of **1-Me** the steric (decelerating, more crowded) and electronic (accelerating, more electron-releasing) effects cancel out each other, leading to almost no difference in the dynamics between **1** and **1-Me**.

Influence of the Halide. To test the influence of the halide in this system, a **1-*p*CF_3** NMR sample was transformed into the bromo compound **Br-1-*p*CF_3** by abstracting the halide with silver tetrafluoroborate ($AgBF_4$; 1.1 equiv) and further reaction with LiBr. The successful exchange was proven by ^{31}P NMR spectroscopy. The VT measurements were repeated after filtration, and the obtained activation parameters and temperatures (T_0; T_c) were identical within the accuracy of the measurements. To further investigate the influence of the halide, complex **1** was transformed into its iodo derivative (**I-1**) through a similar procedure using $AgBF_4$ and NaI. The determined activation parameters and temperatures for **1** and **I-1** were again identical, supporting the assumption that the halide plays a minor role in influencing the dynamic behavior. Additionally, NMR experiments were performed with *n*-tetrabutylammonium chloride as additive, which should shift a possible dissociative equilibrium to the side of the neutral species and eventually stop or slow the exchange rate if a dissociation of the halide is involved. The obtained activation parameters and temperatures were very similar to the results without excess halide.

Influence of the Additional Substituents on the Phosphorus. Substitution of the isopropyl groups (**1**) on the phosphorus by phenyl groups (**2**) had an accelerating effect on the dynamic process (Table 1), so that T_0 reduced to 213 K and T_c to 258 K. This was accompanied by a decrease of the activation parameters, e.g., $\Delta H^{\ddagger}$ dropped to 36.0 ± 0.79 kJ/mol ($\Delta\Delta H^{\ddagger}$ = 8.6 kJ/mol).

Influence of the Diene. A similar shift of T_0 and T_c was caused by substitution of cycloocta-1,5-diene (**1**) for norborna-2,5-diene (**nbd-1**), even though the activation enthalpy remained similar ($\Delta\Delta H^{\ddagger}$ = 2.4 kJ/mol). The accelerating effect of the phenyl fingers on phosphorus (**2**) and the norborna-2,5-diene (**nbd-1**) is additive: The room-temperature ^{1}H NMR spectrum of **nbd-2** exhibited for the first time one sharp singlet for both olefinic groups at 4.24 ppm. The VT NMR measurements in CD_2Cl_2 did not lead to separated sharp signals for both olefinic groups (T_0 < 173 K), and a coalescense temperature T_c of 233 K was obtained. This cooperative effect also resulted in the lowest enthalpy of activation ($\Delta H^{\ddagger}$ = 28.3 ± 0.68 kJ/mol; $\Delta\Delta H^{\ddagger}$ = 16.3 kJ/mol compared to **1**) of this study.

Influence of the Metal Center. The change of the rhodium metal center of **1** to iridium (**Ir-1**) resulted in a shift of the dynamic values T_0 and T_c of 10 K to lower temperatures and a reduction of the enthalpy of activation $\Delta H^{\ddagger}$ of ca. 4 kJ/mol.

Influence of Isotopic Labeling. Scheme 6 contains the labeled compounds that have additionally been examined (see Tables 1 and 2). The deuterium substitution of the methyl group in **1-Me** resulted in a decrease of T_0 to 223 K, T_c to 299 K, and $\Delta H^{\ddagger}$ to 37.6 ± 0.34 kJ/mol ($\Delta\Delta H^{\ddagger}$ = 4.8 kJ/mol to **1-Me**). In comparison, the introduction of deuterium in *ortho*-position (**1-d_1**; deuteration grade

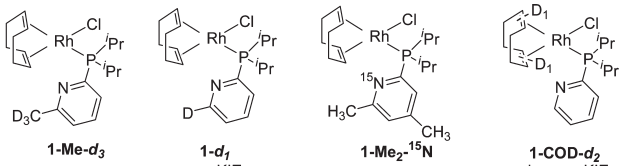
(8) Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 1552.

Table 2. KIE Data for the Fluctuation in 1-Me-d_3 and 1-COD-d_2 (measurement uncertainty of k values is ±8%)

	temperature [K]									
	233	243	253	263	273	283	293	303	313	328
1-Me (k_H) [Hz]	< 2	8	43	101	200	345	681	1294	2283	3902
1-Me-d_3 (k_D) [Hz]	12	39	91	181	336	613	1031	1777	2903	4824
k_H/k_D	< 0.16	0.2	0.48	0.56	0.60	0.56	0.66	0.73	0.79	0.81
$\mathbf{k_1}$ [Hz]	< 2	16	86	198	388	633	1304	2469	4444	7617
$\mathbf{k_{1\text{-}COD\text{-}d2}}$[Hz][a]	12	53	141	250	513	907	1591	2939	4999	8325
$\mathbf{k_1/k_{1\text{-}cod\text{-}d2}}$	< 0.17	0.30	0.60	0.79	0.76	0.73	0.82	0.84	0.89	0.91

[a] Deuteration grade about 75%; ^{2}H NMR VT series provided in the Supporting Information.

Scheme 6



LSA: Line Shape analysis

approximately 85%) did not affect the rate of the dynamic behavior, although a slightly lower T_c (290 K) was obtained (deuterium scrambling was not observed in a $CDCl_3$ solution over a period of approximately 2 weeks). A comparison of the rate constants k_H and k_D is presented in Table 2. T_0 of **1-Me-d_3** (223 K) is 10 K lower than for **1-Me** (233 K), and thus the value of the inverse kinetic isotope effect is lowest for low temperatures.

The origin of an inverse KIE can be referred to sterics (deuterium is slightly smaller than protium) and electronics (deuterium is slightly more electron-donating than protium; also a hybridization change of a C−H/D bond during the rate-determining step causing a decrease of the p-amount in the hybrid orbital is more favorable for protium than it is for deuterium and *vice versa*). The stronger +I effect of the CD_3 group in comparison to a CH_3 group (making the pyridyl nitrogen more nucleophilic) and its smaller size (making the pyridyl nitrogen more accessible) would explain the inverse KIE found for **1-Me-d_3**. Of course, the same effect would influence **1-d_1** in the same way, but since secondary KIEs are additive, the change of only one protium into deuterium does not seem to induce a difference in the nonlabeled compound. One might also argue that in **1** the small *ortho*-H-substituent is not yet in a critical steric level. Thus, reducing its size by changing to deuterium will have no accelerating effect. Deuteration of one of the two olefinic protons of the coordinated COD ligand also resulted in an inverse KIE almost as large as that found for **1-Me-d_3**, again supporting the additive character of a secondary KIE. Since a change of protium to deuterium in **1-d_1** did not show any KIE, we propose that the secondary KIE in **1-COD-d_2** is not caused by sterics but due to a change of the hybridization of the olefinic C−H/D bond in the rate-determining step with an increase in p character. This would be an indicator for the mechanistic interpretation that during the dynamic process some of the coordinated olefinic COD carbons change in the rate-determining step from sp^{2+x} (coordinated) to sp^3 hybridization.[9]

The pyridyl-nitrogen was also labeled with ^{15}N, but no KIE was found by complete line-shape analysis. (It must be stated that a $^{14/15}$N KIE may be too small to be detected, especially in the case of an asymmetric and bent transition state concerning the X−N···Y moiety; reported $^{14/15}$N KIEs are in the range 0.994 to 1.003, which is smaller than our measurement uncertainty. In nucleophilic addition reactions, an inverse KIE is attributed to a late transition state of the nitrogen's lone pair nucleophilic attack resulting from contributions of an equilibrium isotopic effect when changing from an sp^2 to an sp^3 carbon center.[10]) At no temperatures (higher than 173 K) was a ^1J-coupling observed between the ^{15}N nucleus and the ^{103}Rh nucleus ($^3J_{RhN}$ = 2.7 Hz). The chemical shift of the pyridyl-nitrogen in **1-Me$_2$-^{15}N** (−65.8 ppm) was temperature-independent down to 173 K and indicated that no interaction of the free lone pair with a Lewis acid (i.e., the Rh center) occurs (Figure 4a).

In contrast if the cationic compound [**1-Me$_2$-^{15}N**][**BF$_4$**] is generated by addition of $AgBF_4$, a $^1J_{RhN}$ ($^1J_{RhN}$ = 11.9 Hz) is detected and the chemical ^{15}N-shift (−135.1 ppm) is in a range typically found for protonated or Rh-coordinated pyridyl moieties.[11] Thus, by ^{15}N labeling of the pyridyl-nitrogen, we must state that no evidence for an interaction of the pyridyl-nitrogen with the metal center can be detected in the neutral complexes.

We additionally determined the T_1 relaxation times (inversion recovery) of the protons in **1-Me$_2$-^{15}N** and **1-Me$_2$** at high and low temperatures in the range with and without the fluxional behavior present on the spectral NMR time scale. The results along with the activation energies of molecular motion determined by a $\ln(T_1)$ vs $1/T$ plot for each proton are given in the Supporting Information.

The following observations can be highlighted concerning these measurements:

- In the low-temperature range without visible line broadening in the spectra, no difference is found in the T_1 times between the two compounds.
- In the high-temperature range below 373 K, **1-Me$_2$-^{15}N** shows significantly smaller T_1 times than **1-Me$_2$** (most pronounced for CH_{COD}, CH_p; intermediate for CH_o, Me_a, CH_{iPr}; much less pronounced for Me_{iPr}, CH_2, Me_b), an effect

(9) (a) Kohen, A.; Limbach, H.-H. *Isotope Effects in Chemistry and Biology*; CRC Press, 2006; p 956. (b) Hoffmann, R. W. *Aufklärung von Reaktionsmechanismen*; Thieme Verlag, 1976; p 74. (c) Krumbiegel, P. *Isotopeneffekte*; Akademie-Verlag, 1970; p 131.

(10) Kohen, A.; Limbach, H.-H. *Isotope Effects in Chemistry and Biology*; CRC Press, 2006; p 908.

(11) (a) Carlton, L.; Weber, R. *Inorg. Chem.* **1996**, *35*, 5843. (b) Meji, R.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1979**, *164*, 353. (c) Bose, K. S.; Abbott, E. H. *Inorg. Chem.* **1977**, *16*, 3190. (d) Appleton, T. G.; Cox, M. R. *Magn. Reson. Chem.* **1991**, *29*, 80. (e) Rentsch, G. H.; Kozminski, W.; Philipsborn, W.; Asaro, F.; Pellizer, G. *Magn. Reson. Chem.* **1997**, *35*, 904. (f) Heaton, B. T.; Jacob, C.; Heggie, W.; Page, P. R.; Villax, I. *Magn. Reson. Chem.* **1991**, *29*, 21. (g) Dilworth, J. R.; Donavan-Mtunzi, S.; Kann, C. T.; Richards, R. I. *Inorg. Chim. Acta* **1981**, *53*, 161. (h) Carlton, L.; Belciug, M.-P. *J. Organomet. Chem.* **1989**, *378*, 469. (i) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1988**, *27*, 4435. (j) Preetz, W.; Peters, G.; Vogt, J.-U. *Z. Naturforsch.* **1993**, *48b*, 348.

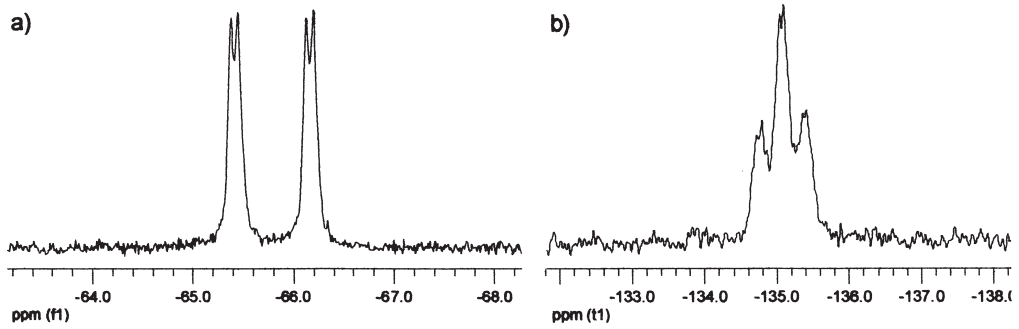


Figure 4. $^{15}N\{^1H\}$ NMR spectra at 298 K of (a) **1-Me$_2$-^{15}N** and (b) **[1-Me$_2$-^{15}N]BF$_4$**.

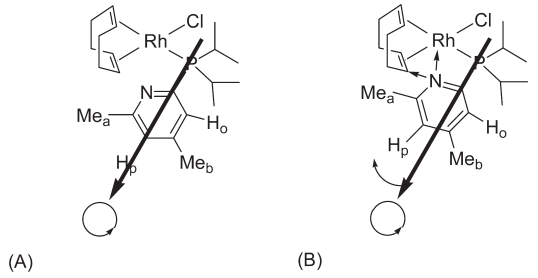


Figure 5. (A) Main rotation axis in **1-Me$_2$** about $C_{py}-P$ with proton H_p on it. (B) In the case of an interaction of the pyridyl-nitrogen with the metal center or a coordinated double bond of the COD, H_p is bent out of the main rotation axis.

that disappears at temperatures above 373 K. (We note that the T_1 values of $CH_{COD,cis}$ and $CH_{COD,trans}$ in the low-temperature range are almost equal. Thus, we conclude that a mixing of the two T_1 times caused by the dynamic exchange in the high-temperature range will not perturb the data.)

- A plot of $\ln(T_1)$ vs $1/T$ (the slope of which is a measure of the activation energy of molecular motion) results in excellent straight lines over the complete temperature range for **1-Me$_2$**, while in contrast for **1-Me$_2$-^{15}N** in the case of the CH_{COD}, CH_p, CH_o, and Me_a protons two separate straight lines must reasonably be fitted for the high- and low-temperature range, respectively.
- The T_1 relaxation time of H_p is by far the longest of all protons in both compounds. On the other hand the increase of T_1 with increasing temperature is by far least pronounced for H_p in comparison to all other protons.

We draw the following conclusions from these experimental results:

- The significantly longer relaxation time of H_p is attributed to the fact that this proton (as the only one) is positioned on a main rotational axis of the molecule **1-Me$_2$** (rotation of the pyridine moiety about the $C_{Py}-P$ axis), and thus, it experiences less magnetic fluxionality than the other protons do (Figure 5).

The less intense increase of T_1 for the H_p proton with the temperature compared to that of the T_1 values of all other protons in **1-Me$_2$** can be regarded as an indicator (but not a proof) that a bending of the pyridyl moiety occurs out of the main rotation axis. We propose that this behavior results from an interaction of the pyridyl nitrogen either with the metal center or with a coordinated COD double bond.

- In **1-Me$_2$-^{15}N** an isotopic effect must be present concerning the T_1 relaxation behavior in the high-temperature range, where the fluxionality is observed for the COD ligand, since significantly lower T_1 times are measured for **1-Me$_2$-^{15}N** compared to **1-Me$_2$** at 363, 368, and 373 K concerning especially the CH_{COD}, CH_p, and the Me_a protons. We propose that there is a relationship between the bending mode in Figure 5 and the isotopic effect found for the T_1 times. Through the bending, the COD-olefinic protons and the Me_a protons come closer together, giving rise to more efficient relaxation via $^1H_{dipole}-{}^1H_{dipole}$ interaction. Thus, a longer lifetime of the bent mode depicted in Figure 5 in **1-Me$_2$-^{15}N** would explain the experimental data, although it does not help to decide whether the inducing interaction is between the nitrogen and the metal center or between the nitrogen and the coordinated COD double bond.

Influence of the Heterocyclic Fragment. The substitution of the heterocycle to *N*-methylimidazole (**3-Me**) slowed down the dynamic process, so that at room temperature two broad singlets for the olefinic groups were obtained and the exchange of the olefin sites was frozen out at 263 K (T_0) in $CDCl_3$. At lower temperatures ($T < 223$ K) a second dynamic process was observed, which was further investigated by changing the solvent to CD_2Cl_2 (Figure 6). We ascribe the first fluxional process at higher temperatures to freezing out the rotation about the Rh−P axis (thus, this rotation occurs more easily in the imidazyl complexes than in the pyridyl ones), while the second fluxional process of the imidazyl derivatives is due to freezing out the rotation about the $P-C_{imidazyl}$ bond.

VT $^{13}C\{^1H\}$ measurements showed the same behavior for the carbon nuclei; for example, the olefinic sites *cis* to phosphorus were obtained at 173 K as two doublets around 69 ppm and the olefinc sites *trans* to phosphorus at 104 ppm as an unresolved multiplet. The diverse signals could be assigned by 2D HC−COSY measurements at 213 and 173 K. The phosphorus signal in the $^{31}P\{^1H\}$ NMR spectra again remained unaffected by the temperature (21.4 ppm, $^1J_{PRh}$ = 142.7 Hz). The relatively high activation temperatures (T_0 = 263 K; $T_c \geq 328$ K) for the COD olefin exchange process (> 263 K) in $CDCl_3$ also resulted in decisively larger activation enthalpies ($\Delta H^{\ddagger}$ = 60.9 kJ/mol) compared to **1** ($\Delta\Delta H^{\ddagger}$ = 16.3 kJ/mol). The determined activation parameters for the second fluxional process below 223 K are approximately 10 kJ/mol lower than for the first dynamic process and are thus in accordance with the VT NMR profile. The benzimidazole derivative **4** showed a similar behavior in the VT NMR measurements to that found for **3-Me**. The sterically more demanding isopropyl group (**3-^{i}Pr**) had a greater influence on the dynamic VT NMR profile than the benzannulated phenyl ring in derivative **4**. In this case both fluxional processes intersected in the temperature range from 233 to 253 K in $CDCl_3$ (see Supporting Information for the VT

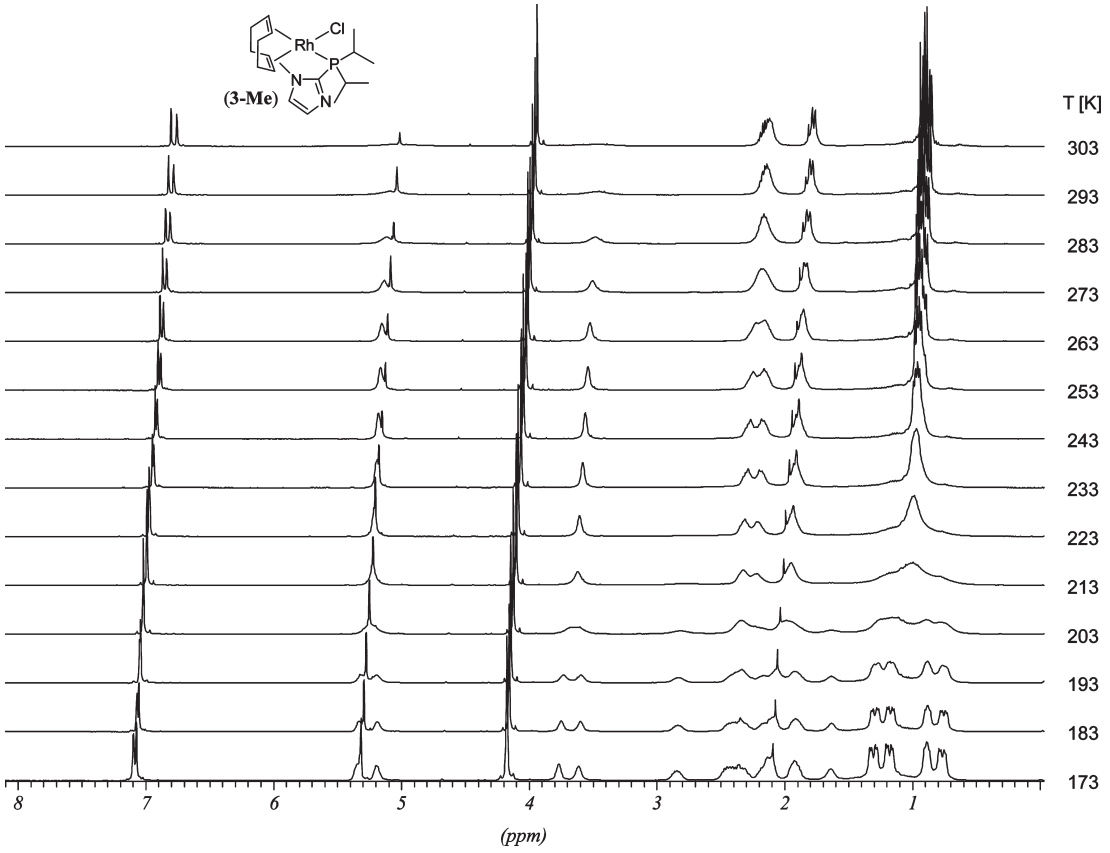


Figure 6. ^{1}H VT NMR series of **3-Me** in CD_2Cl_2 in the temperature range from 173 to 303 K.

Table 3. Activation Parameters of codRhCl^{i}Pr$_2$P-Imidazyl Derivatives

	solvent	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/(mol K)]	E_a [kJ/mol]	T_0 [K]^a	T_c [K]^b
			COD Exchange Process			
3-Me	$CDCl_3$	60.9 ± 2.0	−24.0 ± 191	61.5 ± 1.3	263	≥328
3-^{i}Pr	$CDCl_3$	49.5 ± 0.6	−25.4 ± 196	50.1 ± 0.4	253	313
4	$CDCl_3$	58.6 ± 4.2	−11.5 ± 83	59.4 ± 3.4	263	>328
			Ligand Rotation			
3-Me	CD_2Cl_2	50.9 ± 6.2	48.8 ± 167	52.3 ± 6.1	<173	203
3-^{i}Pr	CD_2Cl_2	48.6 ± 3.5	−27.8 ± 181	50.5 ± 15.1	183	218
4	CD_2Cl_2	57.0 ± 8.4	72.0 ± 156	58.6 ± 8.4	≤173	203

^{a} T_0: first temperature without line-broadening. ^{b} T_c: coalescence temperature.

NMR spectra). This overall behavior is also reflected by the activation enthalpies, which are slightly lower for the second dynamic process at lower temperatures (Table 3).

Phase-Sensitive 2D Exchange-Spectroscopy Studies.[12] We used ^{1}H−^{1}H EXSY measurements to test our complexes for olefin exchange processes outside the range of line-broadening in 1D NMR, i.e., **1** at 213 K (and 183 K) and the "static" complexes **1-*o*CF$_3$** and **1-TMS** at 298 K. To this purpose, the spin−lattice relaxation times T_1 were first determined to set the evolution time d_1 in the EXSY measurements to 4 times T_1.

When complex **1** was measured at 213 K in $CDCl_3$ with an evolution time d_1 of 2.2 s and a mixing time τ_m of 1 s, exchange cross-peaks for the olefin sites were obtained besides various NOE cross-peaks. The acquired 2D spectrum in CD_2Cl_2 at 183 K (d_1 = 2.2s; τ_m = 1s) showed slightly less intense exchange cross-peaks and therefore a reduced exchange rate at 183 K. ^{1}H,^{1}H−COSY measurements assured that scalar couplings did not interfere with the exchange cross-peaks. In general, rate constants of exchange processes can be estimated by variation of the mixing time τ_m and fitting of the obtained cross-peak (a_{cross}) to diagonal-peak (a_{diag}) amplitude ratios to the equation $\tanh(k\tau_m) \approx (a_{cross}/a_{diag})$, valid for small mixing times.

By this method an exchange rate of 0.88 s^{-1} at 213 K was determined for complex **1**, which is in accordance with the kinetic data obtained from the 1D NMR measurements ($k_{\mathbf{1}}$ = 0.99 s^{-1} by calculation using the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at 213 K; Figure 7). The *ortho*-substituted complexes **1-TMS** and **1-oCF$_3$** also showed exchange cross-peaks in the EXSY spectra at room temperature.

(12) (a) Levitt, M. H., *Spin Dynamics*; Wiley and Sons, 2001; p 500. (b) Perrin, C. L.; Dwyer, T. *J. Chem. Rev.* **1990**, *90*, 935.

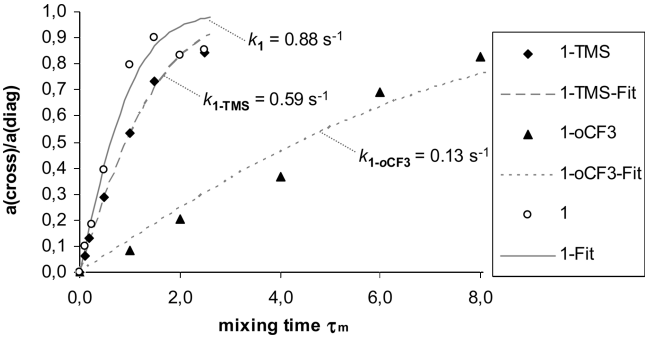


Figure 7. Quantitative evaluation of the ^{1}H,^{1}H-EXSY measurement with **1** (at 213 K), **1-TMS** (at 298 K), and **1-oCF$_3$** (at 298 K).

The exchange rate of 0.59 s^{-1} for **1-TMS** at 298 K is lower than for **1** at 213 K, as expected by the 1D VT NMR measurements (no line broadening up to 328 K). The bulky and electron-withdrawing CF_3 group in **1-*o*CF$_3$** with 0.13 s^{-1} led to a further deceleration of the olefin exchange rate. Despite the bulkiness of these groups, the general accelerating effect of the nitrogen within the ring was still perceivable compared to the unsubstituted non-nitrogen-containing phenyl derivative.[13]

The abstraction of the chloride in **1** with $AgBF_4$ led to the cationic complex **1-BF$_4$**, which is static on the spectral NMR time scale according to the 1D ^{1}H NMR spectra. However, the 2D EXSY spectra showed an exchange of the olefin sites, which can be explained by the weak coordination and de- and recoordination of the nitrogen to the rhodium center in the unfavorable four-membered ring system. Additionally, an intermolecular exchange with chloro-1,5-cyclooctadienerhodium(I) dimer (if added in traces) was observed. Such dynamic processes were reported earlier in similar Rh(I) complexes by Pregosin et al.[21] Addition of CODRhCl dimer to a NMR sample of **1** also showed an intermolecular exchange between the neutral complexes and the dimer. As this is not directly connected to the solution dynamics of the pure neutral complexes, no further attempts were undertaken to provide insight into these intermolecular processes.

Crystal Structure Determination. Single crystals for X-ray diffraction were obtained for the complexes **1**, **1-Me**, **1-Me$_2$**, **1-*o*CF$_3$**, **Ir-1**, **2**, and a bromo-chloro (Br/Cl = 1:2) mixture of **1-*p*CF$_3$** and **4** from saturated dichloromethane or acetone solutions (see Experimental Section for details). Selected data are provided in the Supporting Information (Table 7, Supporting Information II). This table also contains the corresponding data for the two non-nitrogen-containing complexes (COD)RhCl(PPh_3) (**1-PPh$_3$**, taken from the literature[14]) and (COD)RhCl(PPh^iPr_2) (**1-PPh^{i}Pr$_2$**, determined by us[13]).

There are only slight differences between the structures of **1** and **1-PPh^{i}Pr$_2$**. No hint for an interaction between the pyridyl nitrogen and the Rh metal center or the coordinated COD is found by X-ray analysis. The structures of a molecule in the solid state of **2** and **4** deviate decisively from those found for **1** and **1-PPh^{i}Pr$_2$**. In both first mentioned molecules the nitrogen atom prone to an interaction with the metal center is even pointed away from it. In **2** this can be judged by evaluation of the bond lengths. In regard to the thermodynamic ground state of these molecules an attractive interaction of the Lewis-basic nitrogen with the metal center is not found. There is some indication of an intermolecular interaction between the pyridyl nitrogen and the coordinated COD in **2** insofar as the pyridyl nitrogen is exclusively found in a position directed toward one of the coordinated COD double bonds of a neighboring molecule. The anisotropic ellipsoids for this part of the COD are decisively larger than for the remaining portion of the ligand, and they are decisively larger than found in any other structure presented in this paper. A similar intermolecular equilibrium was postulated in low-temperature experiments of dichloro-η^2-ethylenepyridineplatinum(II) with an excess of pyridine. In these NMR experiments, pyridine attacks intermolecularly the coordinated ethylene moiety to form up to 40% σ complex at 223 K in solution.[19] Still, there is no abnormally short distance found between these nitrogens and the COD double bond with the more extended anisotropic ellipsoids (and the dynamic behavior of **2** found in solution is concentration-independent as for all other complexes).

Mechanistic Considerations. We first list a summary of the experimental results.

- Blocking the pyridyl nitrogen by protonation or (even more rigorous) by exchange of the nitrogen through a CH moiety drastically slows the dynamic process. Thus, the nitrogen is the origin of the acceleration.
- The addition of 1 equiv of pyridine to a sample of **1-PPh(iPr)$_2$** results in no line-broadening of the NMR spectra. Therefore the intramolecular fixation of the nitrogen is crucial for the induction of the fluctuation. (For **1-PPh$_3$** with 5 equiv of pyridine a slight line broadening was observed, but not comparable to **2**.)
- The dynamic process is first order in the complexes (concentration-independent kinetics).
- *ortho*-Substituents at the pyridyl moiety have a strong steric and a significant electronic influence on the fluctuation. The more sterically demanding the substituent, the slower the fluctuation. The more electron-donating the substituent, the faster the fluctuation.
- Polar coordinating solvents change the mechanism toward the temporary dissociation of the halide.
- The cationic complex **1-BF$_4$** shows a decisively slower COD fluctuation than found for **1**.
- Excess halide does not influence the dynamic behavior.
- Excess diene does not influence the dynamic behavior.
- Excess P-ligand does not influence the dynamic behavior (no line-broadening either in ^{1}H or in ^{31}P NMR spectroscopy).
- No evidence for an interaction of the pyridyl-nitrogen with the metal center was found through X-ray analysis. ^{15}N NMR spectroscopy provides no evidence for a N···Rh or N···C=C contact through visible coupling. However, T_1 relaxation measurements indicate that a pyridyl/complex interaction, related to the dynamic behavior of the COD ligand, exists that is connected with a bending of the

(13) Paper in preparation.
(14) Horn, Q. L.; Jones, D. S.; Evans, R. N.; Ogle, C. A.; Masterman, T. C. *Acta Crystallogr.* **2002**, *E58*, m51–m52.
(15) (a) Perera, S. D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1995**, 633. (b) Crociani, B.; Antonaroli, S.; Di Vona, M. L.; Licoccia, S. *J. Organomet. Chem.* **2001**, *631*, 117. (c) Valentini, M.; Selvakumar, K.; Wörle, M.; Pregosin, P. S. *J. Organomet. Chem.* **1999**, *587*, 244. (d) Bookham, J. L.; Smithies, D. M.; Pett, M. T. *J. Chem. Soc., Dalton Trans.* **2000**, 975. (e) Mikhel, I. S.; Rüegger, H.; Butti, P.; Camponovo, F.; Huber, D.; Mezzetti, A. *Organometallics* **2008**, *27*, 2937. (f) Espinet, P.; Casares, J. A. *Fluxional Organometallic and Coordination Compounds*; John Wiley & Sons, 2004; p 131.

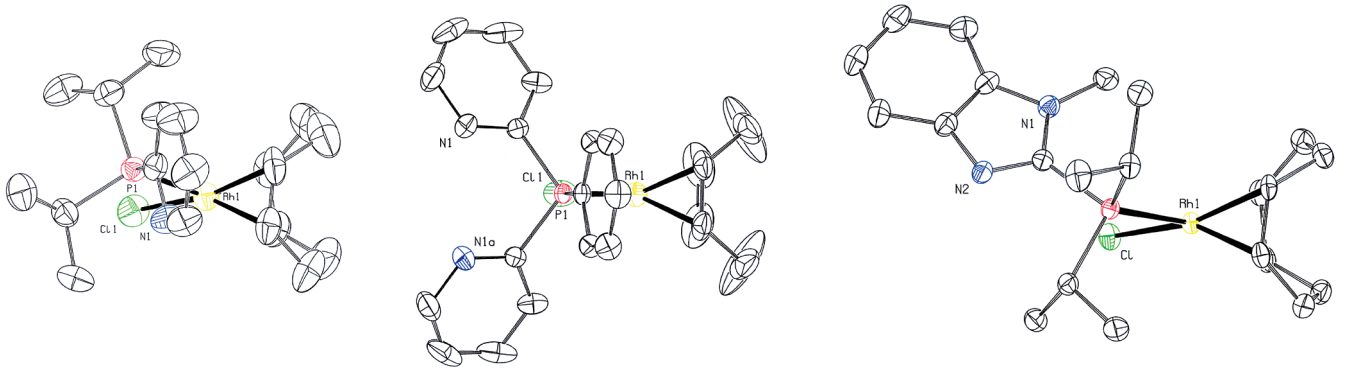
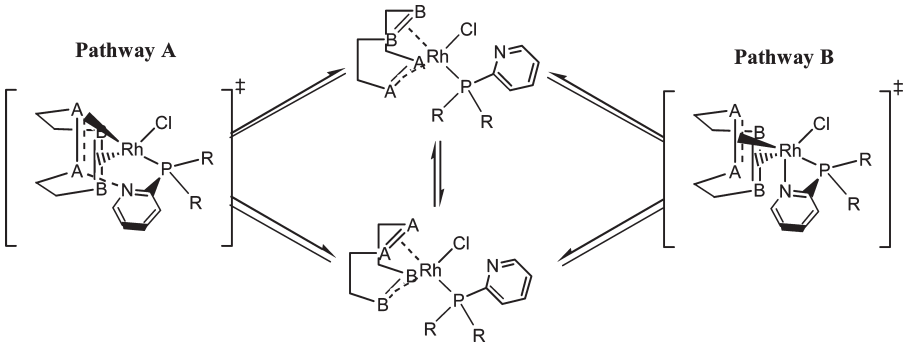


Figure 8. Depiction of a molecule in the solid state of **1**, **2**, and **4**.

Scheme 7



pyridylphosphane ligand. The strength of the attractive part of it can be estimated to be about 4 kJ/mol (comparison of activation energies of molecular motion determined by T_1 measurement with the temperature of H_p and H_o in the pyridyl moiety).

- Deuterium labeling at the coordinated olefinic C−H/D groups in COD supports a change of hybridization of this bond in the rate-determining step from lower to higher p-character (inverse KIE).
- The dynamic process is faster for NBD than it is for COD.
- A $Ph_2P(Py)$ ligand (Rh−P bond length 2.2871(8) Å in the solid state) in comparison to a $^iPr_2P(Py)$ ligand (Rh−P bond length 2.3203(16) Å in the solid state) decisively accelerates the fluctuation.
- A change of the heterocyclic moiety from pyridyl to imidazyl slows the dynamic process of the diene. Additionally, a second fluxional behavior is found at lower temperatures. The rotation about the Rh−P axis is easier for $^iPr_2P$(imidazyl) than it is for $^iPr_2P(Py)$. The latter is static on the spectral NMR time scale even at room temperature concerning the rotation about this axis.

Evaluation of Mechanisms. We concentrate on two particularly interesting mechanisms shown in Scheme 7. Pathway B might seem to be the most intuitive one, while the novel pathway A has yet to be considered.

Both of them are quite similar to each other. Still pathway A (if real) would be of fundamental interest since, in contrast to pathway B, the COD ligand is activated, which might play a yet unconsidered role when applying pyridyl phosphanes as a ligand in catalysis. A single similar behavior (attack of pyridyl nitrogen on coordinated olefin) has been mentioned before with a Pt^{II}(ethen) complex.[19]

On the other hand there is only one known example of an intramolecular four-membered-ring formation in neutral complexes bearing pyridyl phosphanes,[17] although the temporary coordination of the pyridyl nitrogen to the metal center (pathway B) was suspected as intermediate in some cases (without experimental evidence though).

At first, we must state that on the basis of ground-state criteria (X-ray analysis, NMR coupling constants) no evidence can be found for either interaction. The extended anisotropic ellipsoids and the direction of the pyridyl nitrogens found by X-ray analysis are not pronounced enough to serve as unequivocal proof of an interaction between the nitrogen and the coordinated double bond. We still have the kinetic data that must conform to the real mechanism.

- An activation enthalpy of about 50 kJ/mol and a slightly negative activation entropy were found. This will be addressed in the DFT calculations in the next section.
- No ^{15}N-KIE was found that would be out of the range $0.99 < KIE < 1.01$ (measurement uncertainty).
- An inverse KIE was found in the case of deuteration of the olefinic protons in **1**.
- The T_1-relaxation behavior especially of the *para*-proton in the pyridyl ring shows peculiarities. Thus, for the first time an indirect experimental criterion can be established for an additional interaction of the pyridyl moiety with the complex

(16) Rotondo, E.; Battaglia, G.; Arena, C. G.; Faraone, F. *J. Organomet. Chem.* **1991**, *419*, 399.
(17) Olmstead, M. M.; Maisonhat, A.; Farr, J. P.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 4060.
(18) Hawkes, K. J.; Cavell, K. J.; Yates, B. F. *Organometallics* **2008**, *27*, 4758.
(19) Kaplan, P. D.; Schmidt, P.; Orchin, M. *J. Am. Chem. Soc.* **1968**, *90*, 4175.

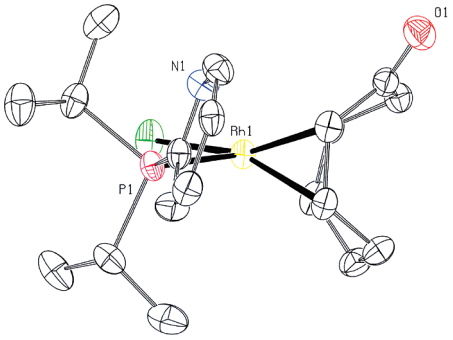


Figure 9. Depiction of a molecule of **1-C=O** in the solid state, determined by X-ray analysis.

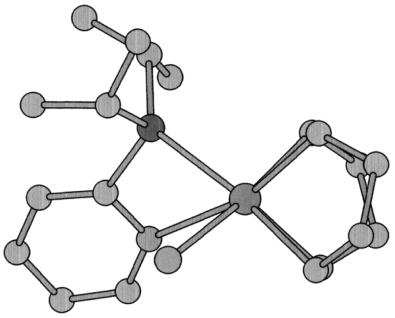


Figure 10. Calculated geometry for the transition state of pathway B with **1**.

rather than just suspecting it. The strength of its attractive part can even be estimated using this new method.

To find clear evidence for the interaction proposed in pathway A, compound **1-C=O** was synthesized with the aim to trap and detect the interaction between the pyridyl nitrogen and, in this case, the electron-poor double bond (Michael interaction, Figure 9).

1-C=O is completely static on the ^{1}H NMR time scale, but its X-ray structure does not provide the anticipated proof for the proposed interaction, which means in this case a measurable intramolecular Micheal-type interaction of the pyridyl nitrogen with the electron-poor C=C-double bond (the complex analogous to **1-CO** with a CH group instead of the nitrogen behaves statically, too).

DFT Calculations. DFT calculations using B3PW91/LanL2DZ were performed. The structure parameters calculated for **1** and **1-PPh(iPr)$_2$** were in good agreement with those determined by X-ray analysis. (We know that this does not allow us to tell whether calculated energies are accurate as well.)

No ground-state structure could be found that contains the pyridyl nitrogen coordinated to Rh. On this basis we exclude a coordination/decoordination equilibrium preceded by the rotation of the COD ligand. The geometry calculated for the transition state of pathway B is shown in Figure 10.

In the case of **1** a normal ^{15}N KIE of 1.0002 and an inverse ^{2}H KIE of 0.99 for **1-COD-d$_2$** were calculated for this pathway and transition state, both in qualitative accordance with the experimental results. In particular the small calculated ^{15}N KIE value supports that despite the formation/cleavage of a metal—N bond in the rate-determining step this effect is not large enough to be detectable by our measurements. The inverse ^{2}H KIE can be explained by a more electron-rich

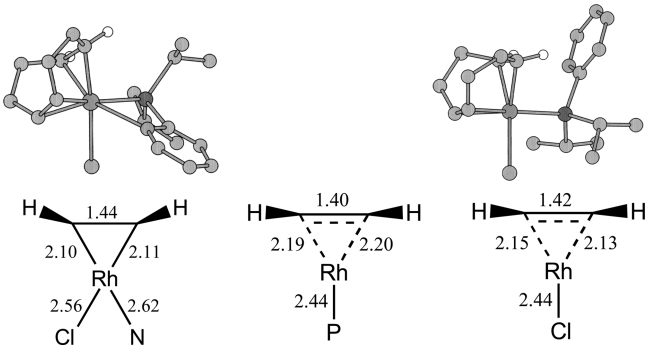


Figure 11. Calculated geometries of the coordinated double bond *trans* to the Cl ligand for the transition state (left) and the ground state (right) of **1** in comparison to the coordinated double bond *trans* to the P ligand (middle), which is almost the same in both cases.

metal center due to the additional coordination of the pyridyl-nitrogen leading to a more pronounced back-bonding into the π^* orbital of the coordinated double bond of the COD *trans* to the Cl ligand, thus yielding in an interaction closer to a metallacyclopropane for this double bond. This is supported by the calculated geometries (Figure 11).

An elongation of the coordinated double bond *trans* to the Cl ligand is found along with a shortening of the M−C bonds and a stronger pyramidalization (which means hybridization toward sp^3) of the carbon centers in this double bond in the transition state compared to the calculated ground state. The coordinated double bond *trans* to the P ligand is almost uneffected.

The calculated values of $\Delta H^{\#} = 55.8$ kJ/mol and $\Delta S^{\#} = -41.1$ J/(mol K) for this case are in good agreement with the measured ones.

Calculated transition states involving an intramolecular attack of the coordinated COD by the pyridyl nitrogen resulted in activation energies 3 times as large as the ones found experimentally and can, thus, be neglected. A pathway with a pseudotetrahedral transition state and without a Rh−N interaction resulted in a calculated activation enthalpy twice as large as found experimentally (about 95 kJ/mol).

Conclusion. We can prove that the most intuitive mechanism, namely, the temporary coordination of the pyridyl nitrogen in a transition state, is the reason for the induced dynamic behavior of the coordinated COD ligand in the complexes of this work. We could exclude a competitive mechanism concerning an interaction of the pyridyl nitrogen with the coordinated COD. We could also, for the first time, find indirect experimental evidence of the pyridyl/metal interaction using the temperature-dependence of the T_1 relaxation times of the *para* hydrogen in the pyridyl moiety as a diagnostic criterion, and we can use this method to estimate the strength of the attractive portion of this interaction.

Experimental Section

General Procedures. Manipulations and experiments were performed under an argon atmosphere using standard Schlenk techniques and/or in an argon-filled glovebox if not otherwise stated. Diethyl ether, pentane, acetonitrile, dichloromethane, and toluene were dried and degassed using a two-column drying system (MBraun) and stored under an argon atmosphere over molecular sieves. Deuterated solvents used in NMR studies, including $CDCl_3$, toluene-d_8, and benzene-d_6 were stored under

argon over molecular sieves. Carbon monoxide 2.5 was purchased from Messer Griessheim and used without further purification. Metal precursors, $RhCl_3 \cdot$hydrate and $IrCl_3 \cdot$hydrate from Strem Chemicals were used as received. Chlorodiisopropylphosphane, chlorodiphenylphosphine, $^{15}NH_4Cl$, COD, NBD, 2-Br-pyridine, imidazole, *n*-butyllithium (2.5 M hexanes), *sec*-butyllithium (1.3 M hexane/benzene), *tert*-butyllithium (1.6 M heptane), 2-bromo-4-trifluoromethylpyridine, 2-bromo-6-trifluoromethylpyridine, 2,6-dibromopyridine, trimethylsilyl chloride, deuterium oxide, and trideuteromethyl iodide were purchased from Aldrich and used without further purification.

NMR measurement was performed on a Bruker AMX400: ^{1}H NMR (7.24 ppm, 400 MHz) and ^{13}C NMR (77.0 ppm, 100 MHz). Chemical shifts are given in ppm relative to the solvent signal for $CDCl_3/C_6D_6/C_7D_8$. ^{31}P NMR (161 MHz) used 85% H_3PO_4 as an external standard, and ^{15}N NMR (40.54 Hz) used ^{15}N-urea in DMSO-d_6 at −304.3 ppm as external standard. The FTIR spectra were measured on a JASCO FI7IR-460plus spectrometer using KBr pellets or in a KBr cell as a CH_2Cl_2 solution.

Dibromo-1,5-cyclooctadiene,[22] 2,6-cyclooctadienone,[23] and 2-bromo-6-methylpyridine[24] were synthesized according to literature procedures. The 2-bromopyridine derivatives were synthesized by procedures described in the Supporting Information.

VT-NMR Calibration and Evaluation. The temperature control unit of the NMR machine was calibrated with a sample of 1,2-ethanediol.[25] The line-broadening was quantified using the program suite DNMR7.1[26] as described in the literature citation. The olefinic COD signals were fitted as an AB system ($W_a = W_b = 12$ Hz, %a = 50).

DFT Calculations. The DFT calculations were performed using the program suite Gaussian 03.[27] All molecular geometries were fully optimized. Transition states were obtained using the OPT2 or OPT3 function implemented in the program suite and were proven to be one-dimensional saddle points by frequency analysis in each case. KIEs were calculated by employing the X(iso=n) function, implemented in the program suite. The DFT method used includes Becke's three-parameter hybrid exchange functional in combination with the correlation functional of Perdew and Wang (B3PW91). Geometry calculations and frequency calculations were performed using the valence double-ζ LANL2DZ basis set.

General Procedure for the Synthesis of 2-Pyridylphosphines Starting from 2-Bromopyridines (except L1-TMS). To a stirred, cold (−78 °C; 2-propanol + dry ice) solution of 1 equiv of 2-bromopyridine in diethyl ether (approximately 10 mL/2.5 mmol) was added 1 equiv of a 1.6 M *n*-butyllithium solution in *n*-pentane. After stirring the mixture for 30 min (if not mentioned otherwise; see experimental data of the ligand), 1 equiv of R_2PCl (R = ^{i}Pr, Ph) was added via syringe. The reaction mixture was allowed to warm slowly to room temperatur overnight. Removing the solvent under vacuum resulted in a white suspension. The product was separated from inorganic salts by extracting and cannula-filtering with *n*-pentane. Removing the solvent yielded the ligand as a colorless to yellowish liquid. The ligands were used without further purification.

Diisopropyl-2-pyridylphosphine (L1). Yield: 93%. ^{1}H NMR ($CDCl_3$, 298 K): 0.91 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 12.0 Hz, 6H, CHC*H*$_3$), 1.11 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 14.6 Hz, 6H, CHC*H*$_3$), 2.26 (dsept, $^3J_{HH}$ = 8.5 Hz, $^2J_{HP}$ = 2.8 Hz, 2H, C*H*CH$_3$), 7.14−7.18 (m, 1H, CH$_{Py}$), 7.47−7.50 (m, 1H, CH$_{Py}$), 7.56 (tt, $^3J_{HH}$ = 8.5 Hz, J = 1.9 Hz, 1H, CH$_{Py}$), 8.68 (d, $^3J_{HH}$ = 4.8 Hz, 1H, NCH). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): 15.0 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): 19.3 (d, $^2J_{CP}$ = 9.9 Hz, CH*C*H$_3$), 19.6 (d, $^2J_{CP}$ = 16.0 Hz, CH*C*H$_3$), 23.1 (d, $^1J_{CP}$ = 11.1 Hz, *C*HCH$_3$), 122.5 (s, CH$_{Py}$), 130.9 (d, $^2J_{CP}$ = 33.3 Hz, PC*C*H$_{Py}$), 134.6 (d, $^3J_{CP}$ = 8.6 Hz, CH$_{Py}$), 150.0 (d, $^3J_{CP}$ = 6.2 Hz, NCH), 161.9 (d, $^1J_{CP}$ = 14.8 Hz, CP$_{Py}$).

Diisopropyl-3-deutero-2-pyridylphosphine (D-L1). Yield: 84%. ^{1}H NMR ($CDCl_3$, 298 K): 0.91 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 11.7 Hz, 6H, CHC*H*$_3$), 1.10 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 14.7 Hz, 6H, CH$_3$), 2.22−2.31 (m, 2H, C*H*CH$_3$), 7.15 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH$_{Py}$), 7.47 − 7.50 (m, 1H, CH$_{Py}$), 7.57 (t, $^3J_{HH}$ = 7.5 Hz, 1H, CH$_{Py}$) [residual *o*H: 8.68 (d, $^3J_{HH}$ = 4.7 Hz, 0.14H)]. ^{2}H NMR ($CDCl_3$, 298 K): 8.71 (s, NCD). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): 19.3 (d, $^2J_{CP}$ = 9.2 Hz, CH*C*H$_3$), 19.6 (d, $^2J_{CP}$ = 16.5 Hz, CH*C*H$_3$), 23.1 (d, $^1J_{CP}$ = 11.0 Hz, *C*HCH$_3$), 122.4 (s, CH$_{Py}$), 130.9 (d, $^2J_{CP}$ = 33.1 Hz, PC*C*H$_{Py}$), 134.6 (d, $^3J_{CP}$ = 9.2 Hz, CH$_{Py}$), 149.9 (d, $^3J_{CP}$ = 5.5 Hz, residual-NCH), 161.7 (d, $^2J_{CP}$ = 12.9 Hz, CP$_{Py}$). *C*D was not detected. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): 15.0 (s).

Diisopropyl-(6-methyl-2-pyridyl)phosphine (L1-Me). Yield: 83%. ^{1}H NMR ($CDCl_3$, 298 K): 0.92 (dd, $^3J_{HH}$ = 6.2 Hz, $^3J_{HP}$ = 11.1 Hz, 6H, CHC*H*$_3$), 1.10 (dd, $^3J_{HH}$ = 6.2 Hz, $^3J_{HP}$ = 13.5 Hz, 6H, CHC*H*$_3$), 2.19−2.28 (m, 2H, C*H*CH$_3$), 2.53 (s, 3H, CH$_{3;Py}$), 6.99 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH$_{Py}$), 7.26 (d, $^3J_{HH}$ = 4.9 Hz, 1H, CH$_{Py}$), 7.44 (t, $^3J_{HH}$ = 7.4 Hz, 1H, CH$_{Py}$). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): 12.8 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): 19.4 (d, $^2J_{CP}$ = 9.9 Hz, CH*C*H$_3$), 19.6 (d, $^2J_{CP}$ = 17.3 Hz, CH*C*H$_3$), 23.1 (d, $^1J_{CP}$ = 12.3 Hz, *C*HCH$_3$), 24.8 (s, CH$_{3;Py}$), 120.0 (s, CH$_{Py}$), 127.2 (d, $^2J_{CP}$ = 28.4 Hz, PC*C*H$_{Py}$), 134.6 (d, $^3J_{CP}$ = 7.4 Hz, CH$_{Py}$), 158.3 (d, $^3J_{CP}$ = 7.4 Hz, *C*CH$_3$), 161.1 (d, $^1J_{CP}$ = 8.6 Hz, CP$_{Py}$).

Diisopropyl-(6-trideuteromethyl-2-pyridyl)phosphine (D$_3$-L1-Me). Yield: 75%. ^{1}H NMR ($CDCl_3$, 298 K): 0.92 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 12.1 Hz, 6H, CHC*H*$_3$), 1.10 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 14.2 Hz, 6H, CHC*H*$_3$), 2.24 (dhept, $^3J_{HH}$ = 7.1, $^2J_{HP}$ = 2.8 Hz, 2H, C*H*CH$_3$), 6.99 (dt, J_{HH} = 1.3 Hz, $^3J_{HH}$ = 7.6 Hz, 1H, CH$_{Py}$), 7.26 (dt, J_{HH} = 1.3 Hz, J = 3.8 Hz, 1H, CH$_{Py}$), 7.44 (dt, $^3J_{HH}$ = 7.6 Hz, J = 1.8 Hz, 1H). ^{2}H NMR ($CDCl_3$, 298 K): 2.51 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): 19.4 (d, $^2J_{CP}$ = 10.3 Hz, CH*C*H$_3$), 19.6 (d, $^2J_{CP}$ = 16.1 Hz, CH*C*H$_3$), 23.1 (d, $^1J_{CP}$ = 11.7 Hz, *C*HCH$_3$), 120.0 (s, CH$_{Py}$), 127.2 (d, $^2J_{CP}$ = 28.6 Hz, PC*C*H$_{Py}$), 134.6 (d, $^3J_{CP}$ = 8.1 Hz, CH$_{Py}$), 158.3 (d, $^3J_{CP}$ = 8.8 Hz, *C*CH$_3$), 161.1 (d, $^1J_{CP}$ = 8.8 Hz, CP$_{Py}$). *C*D$_3$ was not detected. ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): 13.9 (s).

Diisopropyl-(6-trifluoromethyl-2-pyridyl)phosphine (L1-*o*CF$_3$). The reaction mixture was stirred for 15 min after addition of

(20) Phillips, A. D.; Bolano, S.; Bosquain, S. S.; Daran, J.-C.; Malacea, R.; Peruzzini, M.; Poli, R.; Gonsalvi, L. *Organometallics* **2006**, *25*, 2189.
(21) Filipuzzi, S.; Männel, E.; Pregosin, P. S.; Albinati, A.; Rizzato, S. *Organometallics* **2008**, *27*, 4580.
(22) Detert, H.; Rose, B.; Mayer, W.; Meier, H. *Chem. Ber.* **1994**, *127*, 1529.
(23) Echter, T.; Meier, H. *Chem. Ber.* **1985**, *118*, 182.
(24) Schubert, U. S.; Eschbaumer, C.; Heller, M. *Org. Lett.* **2000**, *2*, 3373.
(25) (a) van Geet, A. L. *Anal. Chem.* **1970**, *42*, 670. (b) Friebolin, H.; Schilling, G.; Pohl, L. *Org. Magn. Reson.* **1979**, *12*, 569. (c) Piccinni-Leopardii, C.; Fabre, O.; Reisse, J. *Org. Magn. Reson.* **1976**, *8*, 233. (d) Köhler, F. H.; Xie, X. *Magn. Reson. Chem.* **1997**, *35*, 487. (e) Raiford, D. S.; Fisk, C. L.; Becker, E. D. *Anal. Chem.* **1979**, *51* (12), 2050.
(26) http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm.
(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2004.

n-BuLi. Yield: 65%. ^{1}H NMR ($CDCl_3$, 298 K): 0.92 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 11.7 Hz, 6H, CHCH_3), 1.10 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 14.7 Hz, 6H, CH_3), 2.32 (dhept, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 2.4 Hz, 2H, CHCH$_3$), 7.53 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.64 (m, 1H, CH_{Py}), 7.73 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 15.6 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 19.1 (d, $^2J_{CP}$ = 9.5 Hz, CHCH$_3$), 19.4 (d, $^2J_{CP}$ = 16.1 Hz, CHCH$_3$), 23.0 (d, $^1J_{CP}$ = 11.0 Hz, CHCH$_3$), 118.9 (q, $^3J_{CF}$ = 2.4 Hz, CH_{Py}), 118.9 (q, $^1J_{CF}$ = 274.4 Hz, CF_3) 133.2 (d, $^2J_{CP}$ = 33.4 Hz, PCCH$_{Py}$), 135.6 (d, $^3J_{CP}$ = 8.8 Hz, CH_{Py}), 148.2 (dq, $^2J_{CF}$ = 4.4 Hz, $^3J_{CP}$ = 34.4 Hz, CCF$_3$), 163.6 (d, $^2J_{CP}$ = 18.3 Hz, CP). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K): −69.3 (s).

Diisopropyl-(4-trifluoromethyl-2-pyridyl)phosphine (L1-*p*CF$_3$). The reaction mixture was stirred for 15 min after addition of *n*-BuLi. The product was not pure. Yield: ca. 58%. ^{1}H NMR ($CDCl_3$, 298 K): 0.95 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 11.9 Hz, 6H, CHCH_3), 1.16 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 14.7 Hz, 6H, CHCH_3), 2.35 (dhept, $^2J_{HP}$ = 2.3 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, CHCH$_3$), 7.42 (d, $^3J_{HH}$ = 5.1 Hz, 1H, HCCF$_3$), 7.72 (d, J = 4.3 Hz, 1H, HCCP), 8.92 (d, $^3J_{HH}$ = 5.1 Hz, 1H, NCH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 16.7 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 19.2 (d, $^2J_{CP}$ = 9.5 Hz, CHCH$_3$), 19.4 (d, $^2J_{CP}$ = 16.1 Hz, CHCH$_3$), 23.2 (d, $^1J_{CP}$ = 11.7 Hz, CHCH$_3$), 117.9 (br d, $^3J_{CF}$ = 3.7 Hz, CH_{Py}), 122.9 (q, $^1J_{CF}$ = 273.7 Hz, CF_3) 125.8 (dq, $^3J_{CF}$ = 3.4 Hz, $^2J_{CP}$ = 35.1 Hz, PCCH$_{Py}$), 137.1 (dq, $^2J_{CF}$ = 8.8 Hz, $^3J_{CP}$ = 34.4 Hz, CCF$_3$), 150.5 (d, $^3J_{CP}$ = 4.4 Hz, CH_{Py}), 163.5 (d, $^2J_{CP}$ = 23.4 Hz, CP). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 293 K): −65.9 (s).

Diphenyl-2-pyridylphosphine (L2). Off-white solid. Yield: 55%. ^{1}H NMR ($CDCl_3$, 298 K): 7.05 (d, $^2J_{HH}$ = 8.6 Hz, 1H, CH_{Py}), 7.15 (m, 1H, CH_{Py}), 7.31−7.39 (m, 10H, CH_{Ph}), 7.53 (m, 1H, CH_{Py}), 8.70 (d, $^2J_{HH}$ = 4.9 Hz, 1H, NCH_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): −3.9 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 122.1 (s, CH_{Py}), 127.8 (d, $^1J_{CP}$ = 14.7 Hz, PC_{Ph}), 128.6 (d, $^2J_{CP}$ = 7.4 Hz, CH_{Py}), 129.0 (s, CH_{Ph}), 134.1 (s, CH_{Ph}), 134.3 (s, CH_{Ph}), 135.7 (d, $^3J_{CP}$ = 1.8 Hz, CH_{Py}), 136.1 (d, $^2J_{CP}$ = 11.3 Hz, CH_{Ph}), 150.3 (d, $^2J_{CP}$ = 12.8 Hz, CH_{Py}), 164.0 (d, $^2J_{CP}$ = 12.8 Hz, CH_{Py}).

Diisopropyl-(6-trimethylsilyl-2-pyridyl)phosphine (L1-TMS). To a stirred, cold (−78 °C; 2-propanol + dry ice) solution of 1.63 mL (2.61 mmol) of a 1.6 M *tert*-butyllithium solution (in *n*-petane) in approximately 8 mL of diethyl ether was added dropwise a solution of 0.3 g (1.30 mmol) of 2-bromo-6-(trimethylsilyl)pyridine in 2 mL of diethyl ether via syringe. The resulting clear and yellowish solution was stirred for 3 h at −78 °C, followed by addition of 0.21 mL (1.30 mmol) of chlorodiisopropylphosphine via syringe. The reaction mixture was allowed to warm slowly to room temperature overnight. After removing the solvent under vacuum, the product was extracted with *n*-pentane (3 × 8 mL). Removal of the solvent under vacuum yielded the product as light yellow liquid (0.31 g; 89%). The ligand was used without further purification. ^{1}H NMR ($CDCl_3$, 298 K): 0.27 (s with Si-sat., $^2J_{HSi}$ = 40.5 Hz, 9H, $SiCH_3$), 0.90 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 11.7 Hz, 6H, CHCH_3), 1.10 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 14.7 Hz, 6H, CH_3), 2.25−2.40 (m, 2H, CHCH$_3$), 7.32−7.36 (m, 2H, CH_{Py}), 7.41−7.45 (m, 1H, CH_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 13.1 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): −1.9 (s, $SiCH_3$), 19.0 (d, $^2J_{CP}$ = 8.8 Hz, CHCH$_3$), 19.6 (d, $^2J_{CP}$ = 16.8 Hz, CHCH$_3$), 22.8 (d, $^2J_{CP}$ = 10.3 Hz, CHCH$_3$), 126.8 (s, CH_{Py}), 129.9 (d, $^2J_{CP}$ = 38.1 Hz, PCCH), 160.9 (d, $^3J_{CP}$ = 11.7 Hz, CP), 168.2 (d, $^3J_{CP}$ = 3.7 Hz, CSiCH$_3$).

General Procedure for the Synthesis of *N*-Alkyl-2-imidazyl-phosphines. To a stirred, cold (−78 °C; 2-propanol + dry ice) solution of 1equiv of *N*-alkylimidazole in diethyl ether (approximately 10 mL/2.5 mmol) was added 1 equiv of a 1.6 M solution of *n*-butyllithium. The mixture was stirred for 1 h at this temperature followed by addition of 1 equiv of chlorodiisopropylphosphine. The reaction mixture was allowed to warm slowly to room temperature overnight. Removing the solvent under vacuum resulted in a white suspension. The product was separated from inorganic salts by extracting and cannula-filtering with *n*-pentane. Removing the solvent yielded the ligand as a colorless to yellowish liquid. The ligands were used without further purification.

***N*-Methyl-2-imidazyldiisopropylphosphine (L3-Me).** Yield: 84%. ^{1}H NMR ($CDCl_3$, 298 K): 0.93 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 12.3 Hz, 6H, CHCH_3), 1.06 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHCH_3), 2.25−2.34 (m, 2H, CHCH$_3$), 3.78 (s, 3H, NCH_3), 6.93 (s, 1H, CH_{imid}), 7.17 (s, 1H, CH_{imid}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): −19.3 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 19.2 (d, $^2J_{CP}$ = 7.4 Hz, CHCH$_3$), 19.9 (d, $^2J_{CP}$ = 17.3 Hz, CHCH$_3$), 24.2 (d, $^1J_{CP}$ = 11.1 Hz, CHCH$_3$), 33.9 (d, $^3J_{CP}$ = 14.8 Hz, NCH_3), 122.6 (s, CH_{imid}), 130.6 (s, CH_{imid}), 146.4 (d, $^1J_{CP}$ = 14.8 Hz, PC_{imid}).

***N*-Isopropyl-2-imidazyldiisopropylphosphine (L3-^{i}Pr).** Yield: 62%. ^{1}H NMR ($CDCl_3$, 298 K): 0.93 (dd, $^3J_{HH}$ = 7.4 Hz, $^2J_{HP}$ = 12.3 Hz, 6H, PCHCH_3), 0.93 (dd, $^3J_{HH}$ = 7.4 Hz, $^2J_{HP}$ = 15.9 Hz, 6H, CHCH_3), (d, $^3J_{HH}$ = 6.1 Hz, 6H, NCHCH_3), 2.26−2.35 (m, 2H, PCHCH$_3$), 5.05−5.14 (m, 1H, NCHCH$_3$), 7.05 (s, 1H, CH_{imid}), 7.21 (s, CH_{imid}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): −19.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 19.4 (d, $^2J_{CP}$ = 9.9 Hz, PCHCH$_3$), 20.0 (d, $^2J_{CP}$ = 17.3 Hz, PCHCH$_3$), 23.9 (s, NCHCH$_3$), 24.4 (d, $^1J_{CP}$ = 4.9 Hz, PCH-CH$_3$), 47.8 (d, $^1J_{CP}$ = 17.3 Hz, NCHCH$_3$), 116.8 (s, CH_{imid}), 130.6 (s, CH_{imid}), 145.3 (d, $^1J_{CP}$ = 12.3 Hz, CP_{imid}).

***N*-Methyl-2-methylbenzimidazyldiisopropylphosphine (L4).** Yield: 67%. ^{1}H NMR ($CDCl_3$, 298 K): 0.98 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 12.9 Hz, 6H, CHCH_3), 1.12 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHCH_3), 2.42−2.50 (m, 2H, CHCH$_3$), 3.93 (s, 3H, NCH_3), 7.21−7.27 (m, 2H, CH_{imid}), 7.31−7.34 (s, 1H, CH_{imid}), 7.79−7.82 (m, 1H, CH_{imid}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): −13.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 19.5 (d, $^2J_{CP}$ = 8.6 Hz, CHCH$_3$), 19.9 (d, $^2J_{CP}$ = 18.1 Hz, CHCH$_3$), 24.2 (d, $^1J_{CP}$ = 7.8 Hz, CHCH$_3$), 31.2 (d, $^3J_{CP}$ = 16.4 Hz, NCH_3), 109.5 (s, CH_{imid}), 119.9 (s, CH_{imid}), 122.0 (s, CH_{imid}), 122.6 (s, CH_{imid}), 136.4 (s, NC), 144.1 (s, NC), 154.7 (d, $^1J_{CP}$ = 19.8 Hz, PC_{imid}).

4,6-Dimethyl-1*H*-pyridin-2-one. 4,6-Dimethylpyrone (2.7 g, 21.7 mmol), 2.1 g (38.3 mmol) of ammonium chloride, and 1.7 g (30.3 mmol) of potassium hydroxide in a 20 mL Schlenk tube were suspended in 10 mL of water, sealed, and heated at 100 °C for 5 days. After cooling, the water phase was washed 3× with 20 mL of ethyl acetate. The combined organic phases were dried over magnesium sulfate and filtered, and the solvent was removed *in vacuo*. The crude product was purified over a short silica gel column (EtOAc/methanol = 9:1; R_f = 0.5) to yield 0.77 g (14−19%) of the product as a beige solid. ^{1}H NMR ($CDCl_3$): 2.19 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 5.84 (s, 1H, CH_{Py}), 6.13 (s, 1H, CH_{Py}), 13.10 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): 18.8 (s, CH_3), 21.5 (s, CH_3), 108.5 (s, CH_{Py}), 115.1 (s, CH_{Py}), 144.6 (s, CCH$_3$), 153.6 (s, NCCH$_3$), 165.9 (s, CO).

^{15}*N*-4,6-Dimethyl-1*H*-pyridin-2-one. ^{1}H NMR (298 K, $CDCl_3$): 2.14 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 5.89 (s, 1H, CH_{Py}), 6.18 (s, 1H, CH_{Py}), 12.91 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): 18.8 (s, CH_3), 21.5 (s, CH_3), 108.6 (s, CH_{Py}), 115.1 (d, $^2J_{CN}$ = 5.1 Hz, CH_{Py}), 144.6 (d, $^1J_{CN}$ = 11.7 Hz, NCCH$_3$), 153.7 (s, CCH$_3$), 165.9 (d, $^1J_{CN}$ = 11.7 Hz, CO). ^{15}N NMR (298 K, $CDCl_3$): −206.7 (s).

Trifluoromethanesulfonic Acid (4,6-Dimethyl-2-pyridyl) Ester. Trifluoromethanesulfonic anhydride (1.1 mL, 1.86 g; 6.6 mmol) was added dropwise to a cold (ice bath) solution of 0.74 g (6.0 mmol) of 2,4-dimethyl-1*H*-pyridone in 5 mL of dry pyridine. The mixture was allowed to warm slowly overnight and stirred for an additional 48 h at RT. Excess pyridine was removed *in vacuo*, and the residue was dissolved in dichloromethane and filtered over a short silica gel column (R_f = 0.78). Removal of the solvent *in vacuo* yielded the product as yellowish liquid (0.77 g; 50%). ^{1}H NMR ($CDCl_3$): 2.36 (s, 3H, CH_3),

2.47 (s, 3H, *o*-CH_3), 6.76 (s, 1H, CH_{py}), 7.01 (s, 1H, CH_{py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 20.9 (s, CH_3), 23.6 (s, CH_3), 112.3 (s, CH_{Py}), 118.6 (q, $^1J_{CF}$ = 320.5 Hz, CF_3), 124.3 (s, CH_{Py}), 153.0 (s, CCH_3), 155.5 (s, $NCCH_3$), 158.3 (s, CO). ^{19}F NMR ($CDCl_3$): −74.2 (s). EI-MS (*m*/*z*): 255.0 (M, correct isotope pattern, 69%), 227.0 (34%), 161.9 (F_3CSO_3CH, 42%), 147.9 (12%), 107 ($M + H^+ - F_3CSO_3$, 7%), 106 ($M - F_3CSO_3$, 38%), 106 ($M - F_3CSO_3H$, 100%), 103.9 ($M - F_3CSO_3H - H^+$,69%), 93.9 (64%), 77.9 (46%), 68.9 (60%), 52.9 (79%), 38.9 (18%).

^{15}*N*-Trifluoromethanesulfonic Acid (4,6-Dimethyl-2-pyridyl) Ester. ^1H NMR ($CDCl_3$): 2.36 (s, 3H, CH_3), 2.47 (d, $^3J_{NH}$ = 3.6 Hz, 3H, *o*-CH_3), 6.76 (s, 1H, CH_{Py}), 7.01 (s, 1H, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 20.9 (s, CH_3), 23.6 (d, $^2J_{CN}$ = 3.6 Hz, *o*-CH_3), 112.3 (s, CH_{Py}), 118.6 (q, $^1J_{CF}$ = 319.8 Hz, CF_3), 124.7 (s, CH_{Py}), 153.0 (s, CCH_3), 155.5 (d, $^1J_{CN}$ = 8.9 Hz, $NCCH_3$), 158.3 (s, CO). ^{19}F NMR ($CDCl_3$): −74.2 (s). ^{15}N NMR ($CDCl_3$): −98.8 (s). EI-MS (*m*/*z*): 256.0 (M, correct isotope pattern, 73%), 228.0 (35%), 162.9 (F_3CSO_3CH, 44%), 148.9 (12%), 108.0 ($M + H^+ - F_3CSO_3$, 7%), 107.0 ($M - F_3CSO_3$, 36%), 105.9 ($M - F_3CSO_3H$, 100%), 104.9 ($M - F_3CSO_3H - H^+$, 70%), 94.9 (64%), 78.0 (41%), 68.9 (60%), 52.9 (80%), 38.9 (18%).

Diisopropylphosphine Oxide. Diisopropylphosphine (2.1 mL, 2 g, 13.1 mmol) was dissolved in 30 mL of acetonitrile and 2 mL of water. The solution was refluxed for 4 h, dried with magnesium sulfate, and filtered, and the solvent was removed *in vacuo*. The liquid was destilled over a Kugelrohr still, yielding 1.4 g (86%) of the product at 0.1 mbar and 100 °C as a colorless liquid. The product was presumed to be hygroscopic and stored under argon. ^1H NMR ($CDCl_3$, 298 K): 1.27 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 15.0 Hz, 6H, $CHCH_3$), 1.31 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 13.0 Hz, 6H, $CHCH_3$), 2.08−2.16 (m, 2H, $CHCH_3$), 6.41 (dt, $^3J_{HH}$ = 3.2 Hz, $^1J_{HP}$ = 449.3 Hz, 1H, PH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 14.9 (d, $^2J_{CP}$ = 3.7 Hz, $CHCH_3$), 16.2 (s, $CHCH_3$), 25.0 (d, $^1J_{CP}$ = 64.4 Hz, $CHCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 56.3 (s).

2-(Diisopropylphosphinoyl)-4,6-dimethylpyridine. Trifluoromethanesulfonic acid (4,6-dimethyl-2-pyridyl) ester (0.68 g, 2.66 mmol), 0.39 g (2.93 mmol) of diisopropylphosphine oxide, 0.12 g (0.53 mmol) of palladiumacetate, and 0.24 g (5.59 mmol) of 1,4-bisphenylphosphinobutane (dppb) were suspended in ca. 25 mL of dry dimethylsulfoxide and 4.4 mL (26.6. mmol) of *N*, *N*-diisopropylethylamine in a Schlenk tube and heated at 130 °C for 2.5 days. After cooling, the solvent was removed *in vacuo*, the residue was dissolved in 20 mL of dichloromethane and washed twice with 5 mL of water, and the organic phase was subsequently dried over magnesium sulfate. The solvent was removed after filtration and the brown-black residue was distilled over a Kugelrohr still . The product was isolated at 160 °C and ca. 1×10^{-1} mbar as a yellowish, viscous liquid (0.38 g; 61%). ^1H NMR ($CDCl_3$, 298): 1.04 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, $CHCH_3$), 1.17 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 15.3 Hz, 6H, $CHCH_3$), 2.32 (s, 3H, $CH_{3;Py}$), 2.42−2.48 (m, 2H, CH), 2.48 (s, 3H, $CH_{3;Py}$), 6.98 (s, 1H, CH_{Py}), 7.68 (d, *J* = 4.9 Hz, 1H, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298): 15.0 (d, $^2J_{PC}$ = 4.8 Hz, $CHCH_3$), 16.1 (d, $^2J_{PC}$ = 4.8 Hz, $CHCH_3$), 20.8 (s, $CHCH_3$), 24.3 (s, $CHCH_3$), 24.7 (s, $CH_{3;Py}$), 25.3 (s, $CH_{3;Py}$), 125.4 (d, J_{CP} = 3.0 Hz, CH_{Py}), 127.3 (d, $^2J_{CP}$ = 16.7 Hz, $PCCH_{Py}$), 146.9 (d, $^3J_{CP}$ = 7.9 Hz, CCH_3), 153.8 (d, $^1J_{CP}$ = 111.2 Hz, CP), 158.2 (d, $^3J_{CP}$ = 18.7 Hz, $NCCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298): 50.3 (s). EI-MS (*m*/*z*): 197.0 ($M - {}^i$Pr, 22%), 153.9 [$M - ({}^i Pr)_2$, correct isotope pattern, 100%], 149.0 (15%), 106.9 ($M - PO({}^i Pr)_2$, 16%).

^{15}*N*-2-(Diisopropylphosphanoyl)-4,6-dimethylpyridine. ^1H NMR ($CDCl_3$, 298 K): 1.03 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 15.3 Hz, 6H, $CHCH_3$), 1.17 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 15.3 Hz, 6H, $CHCH_3$), 2.31 (s, 3H, $CH_{3;Py}$), 2.38−2.48 (m, 2H, $CHCH_3$), 2.47 (s, 3H, $NCCH_{3;Py}$), 6.97 (s, 1H, CH_{Py}), 7.67 (d, *J* = 4.9 Hz, 1H, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 15.1 (s, $CHCH_3$), 16.1 (s, $CHCH_3$), 20.8 (s, $CHCH_3$), 24.3 (d, $^1J_{CP}$ = 8.9 Hz, $CHCH_3$), 24.7 (s, $CH_{3;Py}$), 25.4 (s, $CH_{3;Py}$), 125.3 (d, J_{CP} = 8.9 Hz, CH_{Py}), 127.3 (dd, $^2J_{CN}$ = 7.4 Hz, $^2J_{CP}$ = 16.3 Hz, $PCCH_{Py}$), 146.9 (d, $^3J_{CP}$ = 5.9 Hz, CCH_3), 153.8 (d, $^1J_{CP}$ = 112.9 Hz, CP), 158.2 (d, $^3J_{CP}$ = 17.8 Hz, $NCCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 50.1 (d, $^2J_{PN}$ = 28.4 Hz). $^{15}N\{^1H\}$ NMR ($CDCl_3$, 298 K): −73.5 (d, $^2J_{NP}$ = 28.4 Hz). EI-MS (*m*/*z*): 198.0 ($M - {}^i$Pr, 23%), 154.9 [$M - ({}^i Pr)_2$, correct isotope pattern, 100%], 150.0 (15%), 107.9 ($M - PO({}^i Pr)_2$, 14%).

Diisopropyl-(4,6-dimethyl-2-pyridyl)phosphine. Trichlorosilane (0.7 mL, 0.94 g; 6.93 mmol) was added dropwise to 0.33 g (1.36 mmol) of 2-(diisopropylphosphinoyl)-4,6-dimethylpyridine in ca. 20 mL of xylene (mixture of isomers) and ca. 4 mL (ca. 7.0 mmol) of triethylamine in a 150 mL Schlenk tube. This resulted in immediate formation of a white precipitate. The mixture was first stirred for 1 h at RT and then slowly (1 h) heated to 135 °C for 14 h. After cooling, the mixture was filtered over a silica gel column and the column washed 5× with a 1:0.5 mixture of dichloromethane/triethylamine. The solvent was removed *in vacuo*, yielding the product as a colorless liquid (66%). ^1H NMR (298 K, $CDCl_3$): 0.91 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 12.5 Hz, 6H, $CHCH_3$), 1.09 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, $CHCH_3$), 2.17−2.25 (m, 2H, $CHCH_3$), 2.25 (s, 3H, $CH_{3\text{-}Py}$), 2.48 (s, 3H, $NCCH_{3\text{-}Py}$), 6.83 (s, 1H, $NCCH_{Py}$), 7.09 (s, 1H, $PCCH_{Py}$). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): 19.4 (d, $^2J_{CP}$ = 8.9 Hz, $CHCH_3$), 19.7 (d, $^2J_{CP}$ = 17.8 Hz, $CHCH_3$), 20.9 (s, $CHCH_3$), 23.1 (s, $CHCH_3$), 23.2 (s, $CH_{3\text{-}Py}$), 24.5 (s, $NCCH_3$), 123.1 (s, $NCCH_{Py}$), 128.1 (d, $^2J_{CP}$ = 29.7 Hz, $PCCH_{Py}$), 146.9 (d, $^3J_{CP}$ = 8.9 Hz, $NCCH_3$), 153.8 (d, $^1J_{CP}$ = 8.9 Hz, CP), 158.2 (d, $^2J_{CP}$ = 8.9 Hz, $NCCH_3$). $^{31}P\{^1H\}$ NMR (298 K, $CDCl_3$): 13.3 (s).

^{15}*N*-Diisopropyl-(4,6-dimethyl-2-pyridyl)phosphine. ^1H NMR (298 K, $CDCl_3$): 0.91 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 11.6 Hz, 6H, $CHCH_3$), 1.09 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 13.5 Hz, 6H, $CHCH_3$), 2.17−2.25 (m, 2H, $CHCH_3$), 2.25 (s, 3H, $CH_{3\text{-}Py}$), 2.48 (d, $^3J_{HN}$ = 2.4 Hz, 3H, $NCCH_{3\text{-}Py}$), 6.83 (s, 1H, $NCCH_{Py}$), 7.08 (d, $^3J_{HN}$ = 2.4 Hz, 1H, $PCCH_{Py}$). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): 19.4 (d, $^2J_{CP}$ = 8.9 Hz, $CHCH_3$), 19.7 (d, $^2J_{CP}$ = 17.8 Hz, $CHCH_3$), 20.9 (s, $CHCH_3$), 23.1 (s, $CHCH_3$), 23.2 (s, $CH_{3;Py}$), 24.5 (d, $^2J_{CP}$ = 8.9 Hz, $NCCH_3$), 123.1 (d, *J* = 8.9 Hz, $NCCH_{Py}$), 128.3 (d, $^2J_{CP}$ = 29.7 Hz, $PCCH_{Py}$), 145.3 (d, $^3J_{CP}$ = 5.9 Hz, $NCCH_3$), 153.0 (d, $^1J_{CP}$ = 6.0 Hz, CP), 160.5 (br s, $NCCH_3$). $^{31}P\{^1H\}$ NMR (298 K, $CDCl_3$): 12.1 (d, $^2J_{PN}$ = 21.7 Hz). $^{15}N\{^1H\}$ NMR (298 K, $CDCl_3$): −65.3 (d, $^2J_{NP}$ = 21.7 Hz).

General Procedure for the Synthesis of CODMCl(P−N) (1−4; M = Rh, Ir). In a 50 mL Schlenk flask, 1 equiv of $(CODMCl)_2$ and 2.2 equiv of the N−P ligand were dissolved in dichloromethane and stirred for 1 h at room temperature. After removal of the solvent *in vacuo*, the yellow powders were washed with *n*-pentane (3×) and dried *in vacuo*.

Chlorocycloocta-1,5-diene(diisopropyl-2-pyridylphosphine)-rhodium(I) (1). Yellow powder (95%). **1** can be crystallized overnight from a saturated acetone solution. ^1H NMR ($CDCl_3$, 293 K): 1.20 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 13.5 Hz, 6H, $CHCH_3$), 1.49 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, $CHCH_3$), 1.89 (br d, *J* = 8.6 Hz, 4H, CHH'), 2.30 (br d, *J* = 9.8 Hz, 4H, CHH'), 2.68−2.78 (m, 2H, $CHCH_3$), 7.22 (d, $^3J_{HH}$ = 5.5 Hz, 1H, CH_{Py}), 7.52 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.61−7.66 (m, 1H, CH_{Py}), 8.67 (d, $^3J_{HH}$ = 3.7 Hz, 1H, NCH_{Py}). ^1H NMR ($CDCl_3$, 213 K): 1.16 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, $CHCH_3$), 1.43 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 14.7 Hz, 6H, $CHCH_3$), 1.76−1.81 (m, 2H, CHH'_{cisCP}), 1.90−1.93 (m, 2H, $CHH'_{transCP}$), 2.26 (br d, *J* = 7.4 Hz, 4H, CHH'), 2.60 − 2.70 (m, 2H, $CHCH_3$), 3.33 (s, 2H, $CH_{COD;cisCP}$), 5.23 (s, 2H, $CH_{COD;transCP}$), 7.25 (d, $^3J_{HH}$ = 6.1 Hz, 1H, CH_{Py}), 7.49 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.64−7.69 (m, 1H, CH_{Py}), 8.66 (d, $^3J_{HH}$ = 4.9 Hz, 1H, NCH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.3 (s, $CHCH_3$), 19.9 (d, $^2J_{CP}$ = 4.4 Hz, $CHCH_3$), 24.2 (d, $^1J_{CP}$ = 22.0 Hz, $CHCH_3$), 123.3 (d, $^4J_{CP}$ = 1.5 Hz, CH_{Py}), 128.6 (d, $^2J_{CP}$ = 16.1 Hz, $PCCH_{Py}$), 134.6 (d, $^3J_{CP}$ = 5.9 Hz, CH_{Py}), 149.5 (d, $^3J_{CP}$ = 11.7 Hz, NCH_{Py}), 155.5 (d, $^1J_{CP}$ = 45.4 Hz,

CP_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 19.3 (s, $CHCH_3$), 19.9 (d, $^2J_{CP}$ = 2.2 Hz, $CHCH_3$), 23.4 (d, $^1J_{CP}$ = 22.0 Hz, $CHCH_3$), 28.4 (s, CH_2), 32.7 (s, CH_2), 69.5 (d, $^1J_{CRh}$ = 13.2 Hz, $CH_{COD;cisCP}$), 102.8 (dd, $^1J_{CRh}$ = 11.0 Hz, $^2J_{CP}$ = 7.3 Hz, $CH_{COD;transCP}$), 123.3 (s, CH_{Py}), 128.6 (d, $^2J_{CP}$ = 16.8 Hz, PC-CH_{Py}), 134.6 (d, $^3J_{CP}$ = 5.9 Hz, CH_{Py}), 149.5 (d, $^3J_{CP}$ = 10.2 Hz, NCH_{Py}), 155.5 (d, $^1J_{CP}$ = 45.4 Hz, CP_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 43.3 (d, $^1J_{PRh}$ = 144.7 Hz). Anal. Calcd for $C_{19}H_{30}NClPRh$: C 51.65, H 6.84, N 3.17, Cl 8.02, P 7.01. Found: C 51.50, H 6.87, N 3.11, Cl 8.02, P 6.94. FAB-MS *m*/*z*: 406.2 (M^+ − Cl, 100%), 333.1 (M^+ − COD, 7.5%), 298 (M^+ − COD − Cl, 3.5%).

Chloro-1,5-cyclooctadiene[diisopropyl-(6-deutero-2-pyridyl)-phosphine]rhodium(I) (1-*d*$_1$). Yellow powder (89%). This can be crystallized from a saturated acetone solution (yellow-orange crystals). Deuteration grade ≈ 85%. ^1H NMR ($CDCl_3$, 293 K): 1.21 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, $CHCH_3$), 1.50 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 15.6 Hz, 6H, $CHCH_3$), 2.30 (br d, *J* = 8.0 Hz, 4H, CHH'), 2.69 (br d, *J* = 5.5 Hz, 4H, CHH'), 2.70−2.77 (m, 2H, $CHCH_3$), 7.21 (d, $^3J_{HH}$ = 6.8 Hz, 1H, CH_{Py}), 7.49−7.52 (m, 1H, CH_{Py}), 7.61−7.66 (m, 1H, CH_{Py}), [residual *ortho*-H: 8.67, d, *J* = 8.0 Hz, 0.14H)]. ^1H NMR ($CDCl_3$, 213 K): 1.15 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, $CHCH_3$), 1.42 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 15.3 Hz, 6H, $CHCH_3$), 1.78 (br d, *J* = 8.6 Hz, 2H, CHH'_{cisCP}), 1.91 (br d, *J* = 9.8 Hz, 2H, $CHH'_{transCP}$), 2.65 (br d, *J* = 4.9 Hz, 4H, CHH'), 3.32 (s, $CH_{COD;cisCP}$), 5.23 (s, $CH_{COD;transCP}$), 7.25 (d, *J* = 8.6 Hz, CH_{Py}), 7.50 (d, *J* = 7.4 Hz, CH_{Py}), 7.65−7.68 (m, 1H, CH_{Py}) [residual *ortho*-CH: 8.66 (d, *J* = 3.7 Hz, 0.14H)]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.2 (s, $CHCH_3$), 19.8 (d, $^2J_{CP}$ = 22.1 Hz, $CHCH_3$), 24.3 (d, $^1J_{CP}$ = 22.7 Hz, $CHCH_3$), 31.0 (br s, CH_{allyl}), 70.0 (br s, $CH_{COD;cisCP}$), 103.0 (br s, $CH_{COD;transCP}$), 123.2 (s, CH_{Py}), 128.5 (d, $^2J_{CP}$ = 18.4 Hz, $PCCH_{Py}$), 134.8 (d, $^3J_{CP}$ = 6.4 Hz, CH_{Py}), 149.2 (dt, $^1J_{CD}$ = 26.7 Hz, $^3J_{CP}$ = 12.9 Hz, CD_{Py}; overlaps with residual *ortho*-CH_{Py}: 149.5, d, $^3J_{CP}$ = 12.0 Hz), 158.1 (d, $^1J_{CP}$ = 45.1 Hz, PC_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 43.4 (d, $^1J_{PRh}$ = 146.9 Hz). ^2H NMR ($CDCl_3$, 293 K): 8.72 (s). FAB-MS (*m*/*z*): 406.7 (100%, M − Cl, correct isotope pattern), 298.8 (2.1%, M − Cl − COD). Anal. Calcd for $C_{19}H_{29}DNClPRh$: C 51.54, H 7.06, N 3.16. Found: C 51.59, H 6.65, N 3.03.

Chlorocycloocta-1,5-diene[diisopropyl-(6-methyl-2-pyridyl)-phosphine]rhodium(I) (1-Me). Yellow powder (91%). This can be crystallized overnight from a saturated acetone solution. ^1H NMR ($CDCl_3$, 293 K): 1.22 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, $CHCH_3$), 1.54 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, $CHCH_3$), 1.87 (d, *J* = 7.4 Hz, 4H, CH_2), 2.28 (d, *J* = 8.6 Hz, 4H, CH_2), 2.52 (s, 3H, $CH_{3;Py}$), 2.64−2.79 (m, 2H, $CHCH_3$), 7.04 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.26 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.51 (dt, $^3J_{HH}$ = 7.4 Hz, *J* = 2.5 Hz, CH_{Py}). ^1H NMR ($CDCl_3$, 213 K): 1.21 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 13.5 Hz, 6H, $CHCH_3$), 1.50 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 14.7 Hz, 6H, $CHCH_3$), 1.80 (d, *J* = 11.0 Hz, 2H, CHH'_{cisCP}), 1.94 (d, *J* = 11.0 Hz, 2H, $CHH'_{transCP}$), 2.29 (br s, 4H, CH_2), 2.55 (s, 3H, $CH_{3;Py}$), 3.38 (s, 2H, $CH_{COD;cisCP}$), 5.24 (s, 4H, $CH_{COD;transCP}$), 7.10 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.29 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.57 (t, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.3 (s, $CHCH_3$), 19.9 (d, $^2J_{CP}$ = 4.4 Hz, $CHCH_3$), 24.3 (d, $^1J_{CP}$ = 22.7 Hz, $CHCH_3$), 24.6 (s, $CH_{3;Py}$), 122.7 (s, CH_{Py}), 125.2 (d, $^2J_{CP}$ = 15.4 Hz, $PCCH_{py}$), 134.8 (d, $^3J_{CP}$ = 6.6 Hz, CH_{Py}), 154.5 (d, $^1J_{CP}$ = 46.8 Hz, CP_{Py}), 158.1 (d, $^3J_{CP}$ = 10.2 Hz, $CCH_{3;Py}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 19.1 (s, $CHCH_3$), 19.4 (d, $^2J_{CP}$ = 3.7 Hz, $CHCH_3$), 23.7 (d, $^1J_{CP}$ = 22.7 Hz, $CHCH_3$), 24.7 (s, $CH_{3;Py}$), 28.4 (s, CH_2), 32.7 (s, CH_2), 69.4 (d, $^1J_{CRh}$ = 13.9 Hz, $CH_{COD;cisCP}$), 102.2 (dd, $^2J_{CP}$ = 8.1 Hz, $^1J_{CRh}$ = 11.0 Hz, $CH_{COD;transCP}$), 122.9 (s, CH_{Py}), 124.9 (d, $^2J_{CP}$ = 15.4 Hz, $PCCH_{Py}$), 134.8 (d, $^3J_{CP}$ = 6.6 Hz, CH_{Py}), 153.4 (d, $^1J_{CP}$ = 48.3 Hz, CP_{Py}), 158.0 (d, $^3J_{CP}$ = 13.2 Hz, $CCH_{3\text{-}Py}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 41.6 (d, $^1J_{PRh}$ = 144.7 Hz). Anal. Calcd for $C_{20}H_{32}ClNPRh$: C 52.7, H 7.08, N 3.07, Cl 7.78, P 6.79. Found: C 52.63, H 7.31, N 2.96, Cl 7.82, P 6.71. FAB-MS *m*/*z*: 420.2 (M − Cl, 100%), 347.1 (M − COD, 51%), 312.1 (M − Cl − COD, 9%).

Chloro-1,5-cyclooctadiene-[diisopropyl-(3-trideuteromethyl-2-pyridyl)phosphine]rhodium(I) (1-CD$_3$). Yellow powder (92%). This can be crystallized from a saturated acetone solution (yellow crystals). ^1H NMR ($CDCl_3$, 293 K): 1.22 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, $CHCH_3$), 1.53 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, $CHCH_3$), 1.87 (d, *J* = 7.4 Hz, 4H, CHH'), 2.28 (br s, 4H, CHH'), 2.68−2.74 (m, 2H, $CHCH_3$), 3.52 (vbr s, 2H, $CH_{COD;cisCP}$), 5.08 (vbr s, 2H, $CH_{COD;transCP}$), 7.04 (d, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{Py}), 7.27 (d, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{Py}), 7.49−7.52 (m, 1H, CH_{Py}). ^1H NMR ($CDCl_3$, 213 K): 1.17 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 13.4 Hz, 6H, $CHCH_3$), 1.47 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 15.9 Hz, 6H, $CHCH_3$), 1.77 (d, *J* = 13.5 Hz, 2H, CHH'_{cisCP}), 1.91 (d, *J* = 9.8 Hz, 2H, $CHH'_{transCP}$), 2.26 (br s, 4H, CHH'), 2.60−2.70 (m, 2H, $CHCH_3$), 3.34 (s, 2H, $CH_{COD;cisCP}$), 5.21 (s, 2H, $CH_{COD;transCP}$), 7.06 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{py}), 7.25 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.53 (dt, $^3J_{HH}$ = 7.4 Hz, *J* = 2.9 Hz, 1H, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.3 (s, $CHCH_3$), 19.9 (d, $^2J_{CP}$ = 3.7 Hz, $CHCH_3$), 24.3 (d, $^1J_{CP}$ = 22.7 Hz, $CHCH_3$), 31.0 (vbr s, CH_{allyl}), 69.0 (vbr s, $CH_{COD;cisCP}$), 102.5 (vbr s, $CH_{COD;transCP}$), 122.8 (s, CH_{Py}), 125.2 (d, $^2J_{CP}$ = 15.4 Hz, $PCCH_{Py}$), 134.8 (d, J_{CP} = 5.9 Hz, CH_{Py}), 154.5 (d, $^1J_{CP}$ = 46.8 Hz, CP_{Py}), 158.1 (d, $^3J_{CP}$ = 12.4 Hz, CCD_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 18.9 (s, $CHCH_3$), 19.3 (d, $^2J_{CP}$ = 3.7 Hz, $CHCH_3$), 23.5 (d, $^1J_{CP}$ = 22.7 Hz, $CHCH_3$), 28.3 (s, CH_{allyl}), 32.5 (s, CH_{allyl}), 69.2 (d, $^1J_{CRh}$ = 16.6 Hz, $CH_{COD;transCP}$), 102.5 (dd, $^1J_{CRh}$ = 10.6 Hz, $^2J_{CP}$ = 7.0 Hz, $CH_{COD;transCP}$), 122.7 (m, CH_{Py}), 124.8 (m, $PCCH_{Py}$), 134.6 (m, CH_{Py}), 153.4 (d, $^1J_{CP}$ = 49.0 Hz, CP_{Py}), 157.7 (d, $^3J_{CP}$ = 12.4 Hz, CCD_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 42.3 (d, $^1J_{PRh}$ = 144.7 Hz). ^2H NMR ($CDCl_3$, 293 K): 2.50 (s). Anal. Calcd for $C_{20}H_{29}D_3NClPRh$: C 52.35, H 7.69, N 3.05. Found: C 51.67, H 7.32, N 2.89. FAB-MS (*m*/*z*): 423.2 (M^+ − Cl, 100%), 458.2 (M 2%).

Chloro-1,5-cyclooctadiene[diisopropyl-(4,6-dimethyl-2-pyridyl)-phosphine]rhodium(I) (1-Me$_2$). Yellow powder (99%). This can be crystallized from a saturated acetone solution (yellow-orange crystals). ^1H NMR ($CDCl_3$, 293 K): 1.21 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 14.1 Hz, 6H, $CHCH_3$), 1.53 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 14.7 Hz, 6H, $CHCH_3$), 1.86 (br d, *J* = 8.6 Hz, 4H, CHH'), 2.29 (br s, 7H, CHH', $CH_{3;Py}$), 2.46 (s, 3H, $CH_{3;Py}$), 2.61−2.75 (m, 2H, $CHCH_3$), 6.86 (s, 1H, CH_{Py}), 7.04 (s, 1H, CH_{Py}). ^1H NMR ($CDCl_3$, 213 K): 1.17 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 14.1 Hz, 6H, $CHCH_3$), 1.48 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$ = 15.3 Hz, 6H, $CHCH_3$), 1.77 (br d, *J* = 13.5 Hz, 2H, CHH'_{cisCP}), 1.90 (br d, *J* = 12.3 Hz, 2H, $CHH'_{transCP}$), 2.22−2.32 (m, 4H, CHH'), 2.29 (s, 4H, $CH_{3;Py}$), 2.46 (s, 3H, $CH_{3;Py}$), 2.56−2.69 (m, 2H, $CHCH_3$), 3.36 (br s, 2H, $CH_{COD;cisCP}$), 5.19 (br s, 2H, $CH_{COD;transCP}$), 6.89 (s, 1H, CH_{Py}), 7.01 (s, 1H, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.3 (s, $CHCH_3$), 19.9 (s, $CHCH_3$), 21.2 (s, $CHCH_3$), 24.2 (s, $CH_{3\text{-}Py}$), 24.4 (s, $CHCH_3$), 24.5 (s, $CH_{3\text{-}Py}$), 30.3 (vbr s, CH_2), 69.7 (vbr s, $CH_{COD;cisCP}$), 102.2 (vbr s, $CH_{COD;transCP}$), 123.8 (s, $NCCH_{Py}$), 125.8 (d, $^2J_{CP}$ = 14.9 Hz, $PCCH_{Py}$), 145.7 (d, $^3J_{CP}$ = 5.9 Hz, $CCH_{3\text{-}Py}$), 154.2 (d, $^1J_{CP}$ = 47.5 Hz, PC), 157.8 (d, $^3J_{CP}$ = 14.6 Hz, $NCCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 19.2 (s, $CHCH_3$), 19.5 (s, $CHCH_3$), 21.3 (s, $CHCH_3$), 23.7 (s, $CH_{3\text{-}Py}$), 23.9 (s, $CHCH_3$), 24.5 (s, $CH_{3;Py}$), 28.5 (br s, CH_2), 32.7 (br s, CH_2), 69.7 (d, $^2J_{CRh}$ = 14.9 Hz, $CH_{COD;cisCP}$), 102.2 (pseudo-t, $^1J_{CRh}$ = 8.9 Hz, $^2J_{CP}$ = 8.9 Hz, $CH_{COD;transCP}$), 123.9 (s, $NCCH_{Py}$), 125.5 (d, $^2J_{CP}$ = 14.9 Hz, $PCCH_{Py}$), 145.8 (d, $^3J_{CP}$ = 5.9 Hz, $CCH_{3;Py}$), 153.4 (d, $^1J_{CP}$ = 47.5 Hz, PC_{Py}), 157.6 (d, $^3J_{CP}$ = 11.9 Hz, $NCCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 41.1 (d, $^1J_{PRh}$ = 145.5 Hz). FAB-MS: 433.6 (M − Cl, 100%, correct isotope pattern), 360.6 (M − COD, 30%, correct isotope pattern). Anal. Calcd: C 53.68, H 7.29, N 2.98, Cl 7.55. Found: C 53.57, H 7.36, N 2.76, Cl 7.42.

^{15}N-Chloro-1,5-cyclooctadiene[diisopropyl(4,6-dimethyl-2-pyridyl)phosphine]rhodium(I) (1-Me$_2$-^{15}N). Yellow powder (99%). ^1H NMR ($CDCl_3$, 293 K): 1.21 (dd, $^3J_{HH}$ = 6.1 Hz,

$^3J_{HP}$ = 13.5 Hz, 6H, CHC*H*$_3$), 1.53 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 15.3 Hz, 6H, CHC*H*$_3$), 1.85 (br d, *J* = 7.4 Hz, 4H, C*H*H'), 2.29 (br s, 7H, CH*H*', CH$_{3;Py}$), 2.46 (s, 3H, CH$_{3;Py}$), 2.62−2.73 (m, 2H, C*H*CH$_3$), 6.86 (s, 1H, CH$_{Py}$), 7.03 (s, 1H, CH$_{Py}$). ^{1}H NMR (CDCl$_3$, 213 K): 1.16 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 14.1 Hz, 6H, CHC*H*$_3$), 1.47 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$ = 15.3 Hz, 6H, CHC*H*$_3$), 1.77 (br d, *J* = 12.3 Hz, 2H, C*H*H'$_{cisCP}$), 1.90 (br d, *J* = 11.0 Hz, 2H, C*H*H'$_{transCP}$), 2.22 − 2.33 (m, 4H, CH*H*'), 2.29 (s, 4H, CH$_{3\text{-}Py}$), 2.45 (d, $^3J_{HN}$ = 2.5 Hz, 3H, CH$_{3;Py}$), 2.56−2.69 (m, 2H, C*H*CH$_3$), 3.36 (br s, 2H, CH$_{COD;cisCP}$), 5.19 (br s, 2H, CH$_{COD;transCP}$), 6.88 (s, 1H, CH$_{Py}$), 7.00 (s, 1H, CH$_{Py}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): 19.3 (s, CH*C*H$_3$), 19.9 (s, CH*C*H$_3$), 21.2 (s, *C*HCH$_3$), 24.2 (s, CH$_{3\text{-}Py}$), 24.4 (s, *C*HCH$_3$, CH$_{3\text{-}Py}$), 30.8 (vbr s, CH$_2$), 69.9 (vbr s, CH$_{COD;cisCP}$), 102.0 (vbr s, CH$_{COD;transCP}$), 123.8 (d, ^3J = 8.9 Hz, NC*C*H$_{Py}$), 125.8 (m, PC*C*H$_{Py}$), 145.7 (s, *C*CH$_{3\text{-}Py}$), 154.1 (d, $^1J_{CP}$ = 47.5 Hz, PC), 157.8 (d, $^2J_{CP}$ = 11.9 Hz, N*C*CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 213 K): 19.2 (s, CH*C*H$_3$), 19.5 (s, CH*C*H$_3$), 21.3 (d, $^1J_{CP}$ = 8.9 Hz, *C*HCH$_3$), 23.7 (s, CH$_{3\text{-}Py}$), 23.9 (s, CH$_{3\text{-}Py}$), 24.4 (t, d, *J* = 8.9 Hz, *C*HCH$_3$), 28.5 (br s, CH$_2$), 32.7 (br s, CH$_2$), 69.5 (d, $^2J_{CRh}$ = 11.9 Hz, CH$_{COD;cisCP}$), 102.1 (br s, CH$_{COD;transCP}$), 123.9 (d, *J* = 5.9 Hz, NC*C*H$_{Py}$), 125.5 (m, PC*C*H$_{Py}$), 145.7 (d, $^3J_{CP}$ = 5.9 Hz, *C*CH$_{3\text{-}Py}$), 153.2 (d, $^1J_{CP}$ = 50.5 Hz, PC), 157.6 (d, $^3J_{CP}$ = 14.9 Hz, N*C*CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): 40.1 (dd, $^1J_{PRh}$ = 145.5 Hz, $^2J_{PN}$ = 22.3 Hz). ^{15}N{^{1}H} NMR (CDCl$_3$, 293 K): −65.8 (dd, $^2J_{PN}$ = 22.3 Hz, $^3J_{RhN}$ = 2.7 Hz). FAB-MS: 434.6 (M − Cl, 100%, correct isotope pattern), 361.6 (M − COD, 37%, correct isotope pattern).

Chlorocycloocta-1,5-diene[diisopropyl-(6-trimethylsilyl-2-pyridyl)phosphine]rhodium(I) (1-TMS). Yellow powder (86%). ^{1}H NMR (CDCl$_3$, 298 K): 0.29 (s, 9H, SiCH$_3$), 1.20 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 4.9 Hz, 6H, CHC*H*$_3$), 1.58 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{HP}$ = 7.4 Hz, 6H, CHC*H*$_3$), 1.77−1.82 (m, 2H, C*H*H'$_{cisCP}$), 1.92−1.95 (m, 2H, C*H*H'$_{transCP}$), 2.28 (br s, 4H, CH*H*'), 2.65 − 2.75 (m, 2H, C*H*CH$_3$), 3.36 (s, 2H, CH$_{COD;cisCP}$), 5.27 (s, 2H, CH$_{COD;transCP}$), 7.34−7.40 (m, 2H, CH$_{Py}$), 7.50−7.55 (m, 2H, CH$_{Py}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): −1.9 (s with Si satellites, $^1J_{CSi}$ = 53.0 Hz, SiCH$_3$), 19.3 (s, CH*C*H$_3$), 20.1 (d, $^1J_{CP}$ = 3.7 Hz, CH*C*H$_3$), 24.5 (d, $^1J_{CP}$ = 22.2 Hz, *C*HCH$_3$), 28.7 (s, CH$_2$), 32.8 (s, CH$_2$), 69.2 (d, $^1J_{CP}$ = 14.8 Hz, CH$_{COD;cisCP}$), 102.5 (dd, $^2J_{CP}$ = 7.4 Hz, $^1J_{RhC}$ = 11.1 Hz, CH$_{COD;transCP}$), 126.7 (d, $^2J_{CP}$ = 14.8 Hz, PC*C*H$_{Py}$), 127.7 (s, CH$_{Py}$), 132.7 (d, $^3J_{CP}$ = 6.2 Hz, CH$_{Py}$), 155.8 (d, $^1J_{CP}$ = 46.9 Hz, CP$_{Py}$), 168.4 (d, $^3J_{CP}$ = 11.1 Hz, NCSi). ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): 41.6 (d, $^1J_{PRh}$ = 144.7 Hz). ^{29}Si{^{1}H} NMR (CDCl$_3$, 298 K): −12.0 (s). Anal. Calcd for C$_{22}$H$_{38}$NClOPRhSi: C 51.41, H 7.45, N 2.73. Found: C 50.36, H 7.69, N 2.51. FAB-MS *m*/*z*: 513.2 (M$^+$, 5%), 478.2 (M$^+$ − Cl, 98%), 405.1 (M$^+$ − Cl − TMS, 100%).

Chlorocycloocta-1,5-diene[diisopropyl-(6-trifluormethyl-2-pyridyl)phosphine]rhodium(I) (1-*o*CF$_3$). Yellow powder (90%). This can be crystallized overnight from a saturated acetone solution (orange crystals). ^{1}H NMR (CDCl$_3$, 293 K): 1.22 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, CHC*H*$_3$), 1.51 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHC*H*$_3$), 1.84−1.91 (m, 2H, C*H*H'$_{cisCP}$), 1.96−1.98 (m, 2H, C*H*H'$_{transCP}$), 2.23−2.32 (br s, 4H, CH*H*'), 2.70−2.78 (m, 2H, C*H*CH$_3$), 3.32 (s, 2H, CH$_{COD;cisCP}$), 5.35 (s, 2H, CH$_{COD;transCP}$),), 7.59 (d, $^3J_{HH}$ = 7.3 Hz, 1H, CH$_{Py}$), 7.76 (d, $^3J_{HH}$ = 8.6 Hz, 1H, CH$_{Py}$), 7.81−7.85 (m, 2H, CH$_{Py}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): 19.1 (br s, CH*C*H$_3$), 19.7 (d, $^2J_{CP}$ = 4.4 Hz, CH*C*H$_3$), 24.3 (d, $^1J_{CP}$ = 22.0 Hz, *C*HCH$_3$), 28.6 (s, CH$_2$), 32.9 (s, CH$_2$), 69.2 (d, $^1J_{RhC}$ = 13.9 Hz, CH$_{COD;cisCP}$), 103.5 (dd, $^1J_{RhC}$ = 11.7 Hz, $^2J_{CP}$ = 7.3 Hz, CH$_{COD;transCP}$), 119.9 (s, CH$_{Py}$), 128.6 (s, CH$_{Py}$), 131.2 (d, $^3J_{CP}$ = 15.3 Hz, *C*CF$_3$), 136.1 (d, $^2J_{CP}$ = 5.9 Hz, PC*C*H$_{Py}$), 147.7 (dq, $^1J_{CF}$ = 35.1 Hz, *J* = 11.7 Hz, CF$_3$), 157.2 (d, $^1J_{CP}$ = 40.3 Hz, CP$_{Py}$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): 46.1 (d, $^1J_{PRh}$ = 144.7 Hz). ^{19}F{^{1}H} NMR (CDCl$_3$, 293 K): −69.4 (s). Anal. Calcd for C$_{20}$H$_{29}$NClF$_3$PRh: C 47.12, H 5.73, N 2.75. Found: C 47.04, H 5.59, N 2.97. FAB-MS *m*/*z*: 508.9 (M$^+$, 11%), 473.9 (M$^+$ − Cl, 100%).

Chlorocycloocta-1,5-diene[diisopropyl-(4-trifluoromethyl-2-pyridyl)phosphine]rhodium(I) (1-*p*CF$_3$). ^{1}H NMR (CDCl$_3$, 298 K): 1.21 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, CHC*H*$_3$), 1.51 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 15.2 Hz, 6H, CHC*H*$_3$), 1.84−1.91 (m, 2H, C*H*H'$_{cisCP}$), 1.89 (d, *J* = 7.8 Hz, 2H, C*H*H'$_{transCP}$), 2.25−2.32 (m, 4H, CH*H*'), 2.67−2.83 (m, 2H, C*H*CH$_3$), 3.31 (vbr s, 2H, CH$_{COD;cisCP}$), 5.33 (vbr s, 2H, CH$_{COD;transCP}$), 7.44 (d, $^3J_{HH}$ = 4.9 Hz, 1H, CH$_{Py}$), 7.67 (d, $^3J_{HH}$ = 12.2 Hz, 1H, CH$_{Py}$), 8.87 (d, $^3J_{HH}$ = 5.4 Hz, 1H, NCH$_{Py}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): 19.2 (s, CH*C*H$_3$), 19.7 (d, $^2J_{CP}$ = 3.7 Hz, CH*C*H$_3$), 24.3 (d, $^1J_{CP}$ = 22.0 Hz, *C*HCH$_3$), 31.2 (vbr s, CH$_2$), 69.8 (vbr s, CH$_{COD;cisCP}$), 103.4 (v.br s, CH$_{COD;transCP}$), 118.7 (s, CH$_{Py}$), 124.0 (q, $^1J_{CF}$ = 273.7 Hz, CF$_3$), 123.7 (dq, $^3J_{CF}$ = 3.4 Hz, $^2J_{CP}$ = 16.8 Hz, PC*C*H$_{Py}$), 137.1 (dq, $^3J_{CP}$ = 6.6 Hz, $^2J_{CF}$ = 34.4 Hz, *C*CF$_3$), 150.3 (d, $^3J_{CP}$ = 11.7 Hz, NCH), 158.4 (d, $^1J_{CP}$ = 41.0 Hz, CP$_{Py}$). ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): 44.6 (d, $^1J_{PRh}$ = 148.5 Hz). ^{19}F{^{1}H} NMR (CDCl$_3$, 298 K): −65.8 (s). FAB-MS (*m*/*z*): 663.8 [RhCl(PN)$_2^+$, 14%], 628.8 [Rh(PN)$_2^+$, 22%], 508.8 (M$^+$, 7%), 473.9 (M − Cl, 100%), 400.8 (M$^+$ − COD, 56%).

Bromocycloocta-1,5-diene[diisopropyl-(4-trifluoromethyl-2-pyridyl)phosphine]rhodium(I) (Br-1-*p*CF$_3$). ^{1}H NMR (CDCl$_3$, 298 K): 1.22 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, CHC*H*$_3$), 1.55 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHC*H*$_3$), 1.87 (br s, 4H, C*H*H'), 2.27 (d, *J* = 8.6 Hz, 4H, CH*H*'), 2.76−2.85 (m, 2H, C*H*CH$_3$), 7.43 (d, $^3J_{HH}$ = 4.9 Hz, 1H, CH$_{Py}$), 7.67 (s, 1H, CH$_{Py}$), 8.87 (d, $^3J_{HH}$ = 6.1 Hz, 1H, NCH$_{Py}$). ^{1}H NMR (CDCl$_3$, 213 K): 1.18 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, CHC*H*$_3$), 1.50 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHC*H*$_3$), 1.72−1.76 (m, 2H, C*H*H'$_{cisCP}$), 1.91−1.96 (m, 2H, C*H*H'$_{transCP}$), 2.23−2.28 (m, 4H, CH*H*'), 2.69 − 2.75 (m, 2H, C*H*CH$_3$), 3.26 (s, 2H, CH$_{COD;cisCP}$), 5.38 (s, 2H, CH$_{COD;transCP}$), 7.48 (d, $^3J_{HH}$ = 4.9 Hz, 1H, CH$_{Py}$), 7.62 (s, 1H, CH$_{Py}$), 8.90 (d, $^3J_{HH}$ = 4.9 Hz, 1H, NCH$_{Py}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): 19.4 (s, CH*C*H$_3$), 20.1 (d, $^2J_{CP}$ = 3.7 Hz, CH*C*H$_3$), 25.2 (d, $^1J_{CP}$ = 22.0 Hz, *C*HCH$_3$), 118.7 (s, CH$_{Py}$), 123.5 (d, $^3J_{CP}$ = 16.8 Hz, *C*CF$_3$), 122.7 (q, $^1J_{CF}$ = 273.7 Hz, CF$_3$), 137.1 (d, $^2J_{CP}$ = 40.5 Hz, PC*C*H$_{Py}$), 150.2 (d, $^1J_{CP}$ = 11.7 Hz, CH$_{Py}$), 158.8 (d, $^1J_{CP}$ = 39.5 Hz, PC$_{Py}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 213 K): 19.2 (s, CH*C*H$_3$), 19.5 (s, CH*C*H$_3$), 24.5 (d, $^1J_{CP}$ = 22.2 Hz, *C*H-CH$_3$), 28.7 (s, CH$_2$), 32.4 (s, CH$_2$), 70.5 (d, $^1J_{RhC}$ = 14.8 Hz, CH$_{COD;cisCP}$), 102.8 (dd, $^1J_{RhC}$ = 11.1 Hz, $^2J_{CP}$ = 6.2 Hz, CH$_{COD;transCP}$), 118.9 (s, CH$_{arom}$), 122.3 (q, $^1J_{CF}$ = 273.7 Hz, CF$_3$), 136.8 (d, $^2J_{CP}$ = 34.5 Hz, PC*C*H$_{Py}$), 150.2 (d, $^1J_{CP}$ = 11.7 Hz, CH$_{Py}$), 157.7 (d, $^1J_{CP}$ = 41.9 Hz, PC$_{Py}$). ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): 46.1 (d, $^1J_{PRh}$ = 145.5 Hz). ^{19}F{^{1}H} NMR (CDCl$_3$, 298 K): −65.8 (s).

Chlorocycloocta-1,5-diene(diisopropyl-2-pyridylphosphine)-iridium(I) (Ir-1). Yellow powder (91%). This can be crystallized from a saturated acetone solution. ^{1}H NMR (CDCl$_3$, 298 K): 1.2 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 13.2 Hz, 6H, CHC*H*$_3$), 1.43 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHC*H*$_3$), 1.65 (d, *J* = 7.4 Hz, 4H, C*H*H'), 2.14 (d, *J* = 8.6 Hz, 4H, CH*H*'), 2.87−3.01 (m, 2H, C*H*CH$_3$), 7.26 (d, $^3J_{HH}$ = 4.9 Hz, 1H, CH$_{Py}$), 7.60−7.62 (m, 1H, CH$_{Py}$), 7.67−7.71 (m, 1H, CH$_{Py}$), 8.71 (d, $^3J_{HH}$ = 4.9 Hz, 1H, NCH). ^{1}H NMR (CDCl$_3$, 213 K): 1.13 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 13.2 Hz, 6H, CHC*H*$_3$), 1.33 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 3H, CHC*H*$_3$), 1.51 (br d, *J* = 8.6 Hz, 2H, C*H*H'$_{cisCP}$), 1.69 (br d, *J* = 8.6 Hz, 2H, C*H*H'$_{transCP}$), 2.14 (br d, *J* = 6.1 Hz, 4H, CH$_2$), 2.87−3.01 (hept, $^3J_{HH}$ = 7.4 Hz, 2H, C*H*CH$_3$), 3.01 (s, 2H, CH$_{COD;cisCP}$), 4.84 (s, 2H, CH$_{COD;transCP}$), 7.28 (d, $^3J_{HH}$ = 4.9 Hz, 1H, CH$_{Py}$), 7.58−7.62 (m, 1H, CH$_{Py}$), 7.68−7.72 (m, 1H, CH$_{Py}$), 8.70 (d, $^3J_{HH}$ = 3.7 Hz, 1H, NCH). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): 18.9 (br s, CH*C*H$_3$), 19.3 (d, $^2J_{CP}$ = 2.8 Hz, CH*C*H$_3$), 23.7 (d, $^1J_{CP}$ = 28.5 Hz, *C*HCH$_3$), 123.8 (s, CH$_{Py}$), 129.8 (d, $^2J_{CP}$ = 18.4 Hz, PC*C*H$_{Py}$), 134.4 (d, $^3J_{CP}$ = 7.4 Hz, CH$_{Py}$), 149.5 (d, $^3J_{CP}$ = 12.0 Hz, NCH), 153.3 (d, $^1J_{CP}$ = 55.2 Hz, CP$_{Py}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 213 K): 19.0 (s, CH*C*H$_3$), 19.4 (s, CH*C*H$_3$), 23.6 (d, $^1J_{CP}$ = 22.7 Hz, *C*HCH$_3$), 28.4 (s, CH$_2$), 32.7 (s, CH$_2$), 69.5 (s, CH$_{COD;cisCP}$),

102.8 (d, $^2J_{CP}$ = 7.7 Hz, $CH_{COD;transCP}$), 123.8 (s, CH_{Py}), 129.8 (d, $^2J_{CP}$ = 18.4 Hz, PCCH_{Py}), 134.4 (d, $^3J_{CP}$ = 7.4 Hz, CH_{Py}), 149.5 (d, $^3J_{CP}$ = 12.0 Hz, NCH), 153.3 (d, $^1J_{CP}$ = 55.2 Hz, CP_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 32.1 (s). Anal. Calcd for $C_{19}H_{30}NClPIr$: C 42.97, H 5.67, N 2.64, Cl 6.69, P 5.69. Found: C 42.18, H 5.94, N 2.48, Cl 7.10, P 5.69. FAB-MS (*m*/*z*): 531.1 (M^+, 12%), 496.0 (M^+ − Cl, 100%), 531.1 (M^+, 12%).

Chlorocycloocta-1,5-diene(diphenyl-2-pyridylphosphine)-rhodium(I) (2). Yellow powder (88%). This can be crystallized overnight from a saturated acetone solution (orange crystals). ^1H NMR ($CDCl_3$, 298 K): 2.00 (br d, $^3J_{HH}$ = 8.6 Hz, 4H, C*H*H′), 2.39 (br s, 4H, CH*H*′), 4.46 (br s, 4H, CH_{COD}), 7.25 (d, $^3J_{HH}$ = 4.9 Hz, 1H, CH_{Py}), 7.38−7.42 (m, 6H, CH_{Ph}), 7.66 (dt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, NCHC*H*$_{Py}$), 7.83−7.92 (m, 5H, CH_{Ph+Py}), 8.71 (d, $^3J_{HH}$ = 4.9 Hz, 1H, NCH_{Py}). ^1H NMR ($CDCl_3$, 213 K): 1.98 (br s, 2H, CH_2), 2.36 (s, 4H, CH_2), 3.32 (br s, 2H, $CH_{COD;cisCP}$), 5.54 (br s, 2H, $CH_{COD;transCP}$), 7.27 (m, 1H, CH_{Py}), 7.37−7.45 (m, 6H, CH_{Ph}), 7.67 (t, $^3J_{HH}$ = 6.8 Hz, 1H, NCHC*H*$_{Py}$), 7.80−7.88 (m, 5H, CH_{Ph+Py}), 8.70 (d, $^3J_{HH}$ = 3.7 Hz, 1H, NCH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 30.9 (br s, CH_2), 123.6 (s, CH_{Py}), 128.1 (d, $^3J_{CP}$ = 10.3 Hz, CH_{Ph}), 130.3 (d, $^4J_{CP}$ = 2.2 Hz, CH_{Ph}), 131.4 (d, $^1J_{CP}$ = 43.9 Hz, CP_{Ph}), 131.7 (d, $^2J_{CP}$ = 24.9 Hz, PCCH_{Py}), 135.3 (d, $^2J_{CP}$ = 11.7 Hz, PCCH_{Ph}), 135.4 (d, $^3J_{CP}$ = 11.0 Hz, CH_{Py}), 149.7 (d, $^3J_{CP}$ = 13.2 Hz, NCH_{Py}), 157.4 (d, $^1J_{CP}$ = 60.8 Hz, CP_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 28.6 (br s, CH_2), 32.8 (br s, CH_2), 70.5 (br s, $CH_{COD;cisCP}$), 105.4 (br s, $CH_{COD;transCP}$), 123.7 (s, CH_{Py}), 128.0 (d, $^3J_{CP}$ = 10.3 Hz, CH_{Ph}), 130.3 (d, $^4J_{CP}$ = 5.9 Hz, CH_{Ph}), 131.5 (d, $^1J_{CP}$ = 39.5 Hz, CP_{Ph}), 134.9 (d, $^2J_{CP}$ = 11.7 Hz, CH_{Ph}), 135.5 (d, $^3J_{CP}$ = 8.8 Hz, CH_{Py}), 149.7 (d, $^3J_{CP}$ = 13.9 Hz, CH_{Py}), 156.5 (d, $^1J_{CP}$ = 61.5 Hz, CP_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 28.5 (d, $^1J_{PRh}$ = 150.6 Hz). Anal. Calcd for $C_{25}H_{26}NClPRh$: C 58.90, H 5.14, N 2.75. Found: C 58.54, H 5.17, N 2.62. FAB-MS (*m*/*z*): 509.1 (M^+, 509.1, 12%), 474.1 (M^+ − Cl, 100%), 401.0 (M^+ − COD, 26%), 365.1 (M^+ − COD − Cl, 4%).

Chloronorborna-2,5-diene(diisopropyl-2-pyridylphosphine)-rhodium(I) (nbd-1). Yellow powder (85%). ^1H NMR ($CDCl_3$, 298 K): 1.14 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, CHCH_3), 1.30 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 15.3 Hz, 6H, CHCH_3), 1.36 (s, 2H, CH_2), 2.48−2.58 (m, 2H, C*H*CH$_3$), 3.74 (s, 2H, CH_{allyl}), 4.31 (br s, 4H, CH_{nbd}), 7.21 (m, $^3J_{HH}$ = 4.9 Hz, *J* = 2.4 Hz, 1H, CH_{Py}), 7.61−7.67 (m, 2H, CH_{Py}), 8.66 (d, $^3J_{HH}$ = 3.7 Hz, 1H, NCH). ^1H NMR ($CDCl_3$, 213 K): 1.07 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 13.8 Hz, 6H, CHCH_3), 1.22 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 16.1 Hz, 6H, CHCH_3), 1.35 (s, 2H, CH_2), 2.39−2.44 (m, 2H, C*H*CH$_3$), 3.52 (br s, 2H, $CH_{nbd;cisCP}$), 3.77 (s, 2H, CH_{allyl}), 5.10 (br s, 4H, $CH_{nbd;transCP}$), 7.26 (m, 1H, CH_{Py}), 7.60 (m, 2H, CH_{Py}), 8.66 (d, $^3J_{HH}$ = 4.6 Hz, 1H, NCH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 18.7 (s, CH*C*H$_3$), 19.1 (s, $^2J_{CP}$ = 4.4 Hz, CH*C*H$_3$), 23.1 (d, $^1J_{CP}$ = 22.0 Hz, *C*HCH$_3$), 50.7 (s, CH_2), 63.8 (d, *J* = 4.4 Hz, CH_{allyl}), 123.5 (s, CH_{Py}), 130.4 (d, $^2J_{CP}$ = 21.2 Hz, CH_{Py}), 134.7 (d, $^3J_{CP}$ = 8.1 Hz, CH_{Py}), 149.6 (d, $^3J_{CP}$ = 11.0 Hz, CH_{Py}), 154.1 (d, $^1J_{CP}$ = 46.8 Hz, CP_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 18.3 (s, CH*C*H$_3$), 18.8 (d, $^2J_{CP}$ = 4.9 Hz, CH-*C*H$_3$), 22.3 (d, $^1J_{CP}$ = 22.2 Hz, *C*HCH$_3$), 50.6 (br s, $CH_{nbd;cisCP}$), 50.8 (s, CH_2), 63.9 (d, *J* = 4.9 Hz, CH_{allyl}), 83.7 (br s, $CH_{nbd;transCP}$), 123.8 (s, CH_{Py}), 130.9 (d, $^2J_{CP}$ = 22.2 Hz, CH_{Py}), 134.8 (d, $^3J_{CP}$ = 7.4 Hz, CH_{Py}), 149.5 (d, $^3J_{CP}$ = 12.0 Hz, NCH_{Py}), 152.8 (d, $^1J_{CP}$ = 46.9 Hz, CP_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 44.5 (d, $^1J_{PRh}$ = 166.5 Hz). Anal. Calcd for $C_{18}H_{26}NClPRh$: C 50.78, H 6.16, N 3.29, Cl 8.33, P 7.28. Found: C 49.93, H 6.04, N 3.22, Cl 8.41, P 6.78. FAB-MS (*m*/*z*): 425.1 (M, 12%), 390.2 (M^+ − Cl, 100%), 333.1 (M^+ − nbd, 37%).

Chloronorborna-2,5-diene(diphenyl-2-pyridylphosphine)-rhodium(I) (nbd-2). Yellow powder (85%). ^1H NMR ($CDCl_3$, 298 K): 1.36 (s, 2H, CH_2), 3.71 (s, 2H, CH_{allyl}), 4.24 (s, 4H, CH_{nbd}), 7.25 (m, 1H, CH_{Py}), 7.36−7.41 (m, 6H, CH_{Ph}), 7.63 (t, $^3J_{HH}$ = 7.4 Hz, CH_{Py}), 7.74 (t, $^3J_{HH}$ = 9.2 Hz, CH_{Ph}), 7.82 (t, $^3J_{HH}$ = 7.7 Hz, CH_{Py}), 8.69 (d, $^3J_{HH}$ = 4.9 Hz, CH_{Py}). ^1H NMR (CD_2Cl_2, 183 K): 1.26 (s, 2H, CH_2), 3.06 (br s, $CH_{nbd;cisCP}$), 3.67 (s, 2H, CH_{allyl}), 5.21 (s, 4H, $CH_{nbd;transCP}$), 7.23 (br s, 1H, CH_{Py}), 7.33−7.39 (m, 6H, CH_{Ph}), 7.61−7.70 (m, 6H, CH_{Py}, CH_{Ph}), 8.62 (d, $^3J_{HH}$ = 3.7 Hz, NCH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 50.6 (s, CH_2), 63.7 (d, *J* = 5.2 Hz, CH_{allyl}), 68.5 (br s, CH_{nbd}), 123.6 (s, CH_{Py}), 128.2 (d, $^3J_{CP}$ = 10.4 Hz, CH_{Ph}), 130.2 (s, CH_{Ph}), 131.2 (d, $^1J_{CP}$ = 43.1 Hz, CP_{Ph}), 134.0 (br s, CH_{Py}), 134.7 (br s, PCCH_{Ph}), 134.8 (d, $^2J_{CP}$ = 10.4 Hz, PCCH_{arom}), 135.6 (br s, CH_{Py}), 150.0 (m, NCH_{Py}), 157.0 (d, $^1J_{CP}$ = 60.3 Hz, CP_{Py}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 178 K): 50.5 (s, CH_2), 51.8 (br s, $CH_{COD;cisCP}$), 63.6 (CH_{allyl}), 86.1 (br s, $CH_{COD;transCP}$), 123.7 (s, CH_{Py}), 128.0 (d, $^3J_{CP}$ = 10.2 Hz, CH_{Ph}), 130.2 (s, CH_{Ph}), 130.5 (d, $^1J_{CP}$ = 43.2 Hz, CP_{Ph}), 130.8 (d, $^2J_{CP}$ = 24.2 Hz, PCCH_{Py}), 134.5 (d, $^2J_{CP}$ = 12.5 Hz, PCCH_{Ph}), 135.7 (d, $^3J_{CP}$ = 8.1 Hz, CH_{Py}), 149.8 (m, NCH_{Py}), 155.8 (d, $^1J_{CP}$ = 60.7 Hz, CP_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 29.5 (d, $^1J_{PRh}$ = 169.3 Hz). FAB-MS (*m*/*z*): 457.6 (M − Cl, 38%), 400.6 (M − nbd, 7%).

***N*-Methylchlorocycloocta-1,5-diene(diisopropyl-2-imidazyl-phosphine)rhodium(I) (3-Me).** Yellow powder (90%). ^1H NMR ($CDCl_3$, 298 K): 1.16 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHCH_3), 1.24 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 13.9 Hz, 6H, CHCH_3), 2.05 (d, $^3J_{HH}$ = 8.5 Hz, 4H, C*H*H′), 2.35 − 2.49 (m, 6H, C*H*CH$_3$, CH*H*′), 3.67 (br s, 2H, $CH_{COD;cisCP}$), 4.26 (s, 3H, NCH_3), 5.44 (br s, 2H, $CH_{COD;transCP}$), 7.02 (s, 1H, CH_{arom}), 7.15 (s, 1H, CH_{arom}). ^1H NMR (CD_2Cl_2, 173 K): 0.77 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HP}$ = 15.9 Hz, 3H, CHCH_3), 0.90 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HP}$ = 9.8 Hz, 3H, CHCH_3), 1.19 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HP}$ = 15.9 Hz, 3H, CHCH_3), 1.31 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HP}$ = 17.2 Hz, 3H, CHCH_3), 1.65 (m, 1H, C*H*CH$_3$), 1.89−1.94 (m, 2H, CH_2), 2.10−2.20 (m, 3H, CH_2), 2.31−2.48 (m, 3H, CH_2), 2.83−2.87 (m, 1H, C*H*CH$_3$), 3.62 (br s, 1H, CH_{COD}), 3.77 (br s, 1H, CH_{COD}), 4.18 (s, 3H, NCH_3), 5.20 (br s, 1H, CH_{COD}), 5.35 (br s, 1H, CH_{COD}), 7.08 (s, 1H, CH_{arom}), 7.10 (s, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 18.8 (s, CH*C*H$_3$), 19.7 (d, $^2J_{CP}$ = 4.4 Hz, CH*C*H$_3$), 24.2 (d, $^1J_{CP}$ = 24.2 Hz, *C*HCH$_3$), 28.5 (s, CH_2), 33.2 (s, CH_2), 37.2 (d, *J* = 2.9 Hz, NCH_3), 69.7 (br s, CH_{cisCP}), 104.6 (br s, $CH_{transCP}$), 104.6 (s, CH_{arom}), 129.6 (d, *J* = 8.1 Hz, CH_{arom}), 139.1 (d, $^1J_{CP}$ = 59.3 Hz, CP_{arom}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 173 K): 15.6 (s, CH*C*H$_3$), 15.6 (d, $^2J_{CP}$ = 7.4 Hz, CH*C*H$_3$), 19.5 (s, CH*C*H$_3$), 20.6 (d, $^1J_{CP}$ = 24.7 Hz, *C*HCH$_3$), 25.2 (d, $^1J_{CP}$ = 27.1 Hz, *C*HCH$_3$), 27.4 (s, CH_2), 28.9 (s, CH_2), 31.9 (s, CH_2), 33.6 (s, CH_2), 37.3 (s, NCH_3), 69.3 (d, $^1J_{CRh}$ = 14.8 Hz, $CH_{COD;cisCP}$), 69.7 (d, $^1J_{CRh}$ = 12.3 Hz, $CH_{COD;cisCP}$), 104.3−104.5 (m, $CH_{COD;transCP}$), 124.1 (s, CH_{arom}), 128.8 (d, *J* = 7.4 Hz, CH_{arom}), 138.8 (d, $^1J_{CP}$ = 61.7 Hz, CP_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 21.4 (d, $^1J_{PRh}$ = 142.7 Hz). Anal. Calcd for $C_{18}H_{31}N_2ClPRh$: C 48.61, H 7.03, N 6.30, Cl 7.97, P 6.96. Found: C 48.12, H 7.14, N 5.60, Cl 8.49, P 6.79. FAB-MS (*m*/*z*): 444.1 (M^+, 2%), 409.1 (M^+ − Cl, 100%), 336.0 (M^+ − COD, 30%) 301.0 (M^+ − COD − Cl, 8%).

***N*-Isopropylchlorocycloocta-1,5-diene(diisopropyl-2-imidazyl-phosphine)rhodium(I) (3-^{i}Pr).** Yellow powder (89%). ^1H NMR ($CDCl_3$, 298 K): 1.19 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 14.7 Hz, 6H, PCHCH_3), 1.33 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 14.7 Hz, 6H, PCHCH_3), 1.56 (d, $^3J_{HH}$ = 6.1 Hz, 6H, NCHCH_3), 2.02 (d, $^3J_{HH}$ = 8.6 Hz, 4H, C*H*H′), 2.34 (br s, 4H, CH*H*′), 2.53−2.59 (m, 2H, PC*H*CH$_3$), 6.25−6.32 (m, 1H, NC*H*CH$_3$), 7.13 (s, 1H, CH_{arom}), 7.17 (s, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 19.5 (s, PCH*C*H$_3$), 20.4 (s, PCH*C*H$_3$), 24.6 (s, NCH*C*H$_3$), 25.1 (d, $^1J_{CP}$ = 23.4 Hz, P*C*HCH$_3$), 28.9 (vbr s, CH_2), 33.2 (vbr s, CH_2), 37.2 (d, *J* = 2.9 Hz, NCH_3), 49.7 (d, $^3J_{CP}$ = 4.4 Hz, N*C*HCH$_3$), 69.5 (vbr s, $CH_{COD;cisCP}$), 103.9 (vbr s, $CH_{COD;transCP}$), 118.7 (s, CH_{arom}), 130.4 (d, $^3J_{CP}$ = 8.8 Hz, CH_{arom}), 139.5 (d, $^1J_{CP}$ = 59.3 Hz, CP_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 17.7 (d, $^1J_{PRh}$ = 142.6 Hz). Anal. Calcd $C_{20}H_{35}N_2ClPRh$: C 50.80, H 7.46, N, 5.92. Found: C 50.27, H 7.40, N 5.64. FAB-MS (*m*/*z*): 436.6 (M^+ − Cl, 100%).

***N*-Methylchlorocycloocta-1,5-diene(diisopropyl-2-benzimidazyl-phosphine)rhodium(I) (4).** Must be washed with *cold n*-pentane in the workup. Yellow powder (84%). ^1H NMR ($CDCl_3$,

298 K): 1.23 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 15.9 Hz, 6H, CHCH_3), 1.32 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.1 Hz, 6H, CHCH_3), 2.07 (br d, $^3J_{HH}$ = 8.6 Hz, 4H, CH_2), 2.43 (br s, 4H, CH_2), 2.61−2.68 (m, 2H, CHCH$_3$), 3.74 (br s, 2H, $CH_{COD;cisCP}$), 4.41 (s, 3H, NCH_3), 5.50 (br s, 2H, $CH_{COD;transCP}$), 7.24−7.31 (m, 2H, CH_{arom}), 7.37 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{arom}), 7.79 (d, $^3J_{HH}$ = 8.6 Hz, 1H, CH_{arom}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 19.1 (s, CHCH$_3$), 19.8 (s, CHCH$_3$), 24.4 (d, $^1J_{CP}$ = 24.2 Hz, CHCH$_3$), 28.6 (br s, CH_{2allyl}), 33.3 (br s, CH_{2allyl}), 34.7 (s, NCH_3), 70.0 (br s, $CH_{COD;cisCP}$), 105.1 (br s, $CH_{COD;transCP}$), 109.9 (s, CH_{arom}), 120.1 (dd, J = 9.9 Hz, J = 4.9 Hz, CH_{arom}), 122.3 (s, CH_{arom}), 123.3 (s, CH_{arom}), 137.1 (s, NC), 143.2 (s, NC), 147.1 (d, $^1J_{CP}$ = 51.8 Hz, CP_{arom}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 23.6 (d, $^1J_{PRh}$ = 142.6 Hz). FAB-MS (m/z): 485.5 (M − Cl, 100%), 385.5 (M^+ − COD). Anal. Calcd for $C_{22}H_{33}N_2ClPRh$: C 53.40, H 6.72, N 5.66, Cl 7.16, P 6.26. Found: C 53.79, H 6.93, 5.40, Cl 6.91, P 6.10.

Chloro-2,6-cyclooctadienone(diisopropyl-2-pyridylphosphine)-rhodium(I). Yellow powder (95%). This can be crystallized from a saturated acetone solution (orange-red crystals). ^1H NMR ($CDCl_3$, 298 K): 1.05 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.1 Hz, CHCH_3), 1.25 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 15.3 Hz, CHCH_3), 1.44 (d d, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 9.8 Hz, CHCH_3), 1.50 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HP}$ = 16.5 Hz, CHCH_3), 1.59−1.63 (m, 1H, CH_2), 1.87−1.94 (m, 1H, CH_2), 2.28−2.31 (m, 1H, CH_2), 2.47−2.52 (m, 1H, CH_2), 2.63−2.68 (m, 1H, CHCH$_3$), 2.71−2.80 (m, 2H, CHCH$_3$, COCHH′), 2.87−2.93 (dd, $^3J_{HH}$ = 7.3 Hz, $^2J_{HH}$ = 17.1 Hz, 1H, COCHH′), 3.03 (br s, 1H, CH_{COD}), 3.90 (br s, 1H, CH_{COD}), 4.99 (br s, 1H, CH_{COD}), 5.55 (br s, 1H, CH_{COD}), 7.20 (s, 1H, CH_{Py}), 7.43 (d, $^3J_{HH}$ = 7.4 Hz, CH_{Py}), 7.61−7.63 (m, 1H, CH_{Py}), 8.64 (d, $^3J_{HH}$ = 3.7 Hz, NCH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 18.6 (d, $^2J_{CP}$ = 2.2 Hz, CHCH$_3$), 18.6 (d, $^2J_{CP}$ = 2.9 Hz, CHCH$_3$), 19.9 (s, CHCH$_3$), 18.6 (d, $^2J_{CP}$ = 3.7 Hz, CHCH$_3$), 18.6 (d, $^1J_{CP}$ = 8.8 Hz, CHCH$_3$), 18.6 (d, $^1J_{CP}$ = 9.5 Hz, CHCH$_3$), 28.5 (s, CH_2), 31.6 (s, CH_2), 41.4 (s, $COCH_2$), 70.1 (br s, CH_{COD}), 70.9 (br s, CH_{COD}), 84.2 (br s, CH_{COD}), 107.5 (br s, CH_{COD}), 123.8 (d, $^4J_{CP}$ = 2.2 Hz, CH_{Py}), 128.1 (d, $^2J_{CP}$ = 14.6 Hz, CH_{Py}), 135.2 (d, $^3J_{CP}$ = 5.9 Hz, CH_{Py}), 149.8 (d, $^3J_{CP}$ = 13.2 Hz, NCH_{Py}), 154.2 (d, $^1J_{CP}$ = 51.2 Hz, CP_{Py}), 205.4 (d, J = 3.7 Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): 45.5 (d, $^1J_{PRh}$ = 145.5 Hz). FAB MS (m/z): 520.3 [(O−CODRhCl)$_2^+$, 25%], 492.3 [(Rh(NP)$_2$)$^+$, 100%], 419.4 (M^+ − Cl, 81%), 332.5 (M^+ − COD, 37%). IR (KBr pellet): 3058 (m), 2960 (m), 2925 (m), 2867 (m), 1680 (vs, CO), 1571 (m), 1563 (m), 1449 (m), 1420 (m), 1381 (w), 1362 (w), 1334 (w), 1303 (w), 1262 (w), 1243 (m), 1184 (w), 1161 (w), 1132 (w), 1102 (w), 1089 (w), 1062 (w), 1032 (w), 987 (m), 696 (w), 930 (vw), 883 (w), 865 (vw), 809 (w), 772 (w), 748 (w), 720 (w), 657 (w), 633 (w), 617 (w), 526 (m).

Chloro-2,6-cyclooctadienonerhodium(I) Dimer. One equivalent of chlorodicyclooctenerhodium(I) dimer was stirred with 3 equiv of 2,6-cylooctadienone in dichloromethane for 1 h. Removal of the solvent *in vacuo* and washing of the crude product twice with *n*-pentane yielded the product as a yellow powder (80%). ^1H NMR ($CDCl_3$, 298 K): 1.48−1.53 (m, 1H, CH_2), 1.86−1.91 (m, 1H, CH_2), 2.41−2.52 (m, 2H, CH_2), 2.72−2.99 (m, 1H, CH_2), 2.99−3.06 (m, 1H, CH_2), 4.05−4.08 (m, 2H, CH), 4.56−4.61 (m, 2H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 29.3 (s, CH_2), 31.2 (s, CH_2), 41.4 (s, CH_2), 60.4 (d, $^1J_{CP}$ = 13.2 Hz, CH), 77.9 (d, $^1J_{CP}$ = 14.6 Hz, CH), 79.3 (d, $^1J_{CP}$ = 15.4 Hz, CH), 84.9 (d, $^1J_{CP}$ = 13.2 Hz, CH), 206.4 (s, CO). FAB-MS (m/z): 520.1 (M, 5%, correct isotope pattern). FT-IR (KBr pellet): 2996 (w), 2940 (m), 2886 (w), 2830 (w), 1688 (vs, CO), 1482 (w), 1467 (w), 1434 (w), 1418 (w), 1375 (w), 1351 (w), 1332 (w), 1300 (w), 1274 (w), 1240 (w), 1227 (w), 1183 (w), 1132 (w), 1063 (w), 1033 (w), 975 (m), 877 (w), 853 (w), 827 (w).

1,5-Cyclooctadieneiodo(diisopropyl-2-pyridylphosphine)-rhodium(I) (I-1). Silver tetrafluoroborate (9 mg, 0.05 mmol) was added to 20 mg (0.045 mmol) of chloro-1,5-cyclooctadiene-(diisopropyl-2-pyridylphosphine)rhodium(I) (**1**) in a Schlenk flask, suspended in 5 mL of dichloromethane, and stirred for 1.5 h at room temperature. Then 2 mg (0.13 mmol) of solid sodium iodide was added, and the reaction mixture stirred overnight. After filtration and removal of the solvent *in vacuo*, the crude product was washed 3× with *n*-pentane and dried *in vacuo* to yield a yellow powder (63%). ^1H NMR ($CDCl_3$, 293 K): 1.21 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, 6H, CHCH_3), 1.56 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, 6H, CHCH_3), 1.75 (br s, 4H, CHH′), 2.17 (br d, J = 7.4 Hz, 4H, CHH′), 2.78−2.91 (m, 2H, CHCH$_3$), 7.21 (t, $^3J_{HH}$ = 6.1 Hz, 1H, CH_{Py}), 7.46 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.61−7.66 (m, 1H, CH_{Py}), 8.67 (d, $^3J_{HH}$ = 3.7 Hz, 1H, NCH_{Py}). ^1H NMR ($CDCl_3$, 213 K): 1.17 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 12.2 Hz, 6H, CHCH_3), 1.51 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 14.3 Hz, 6H, CHCH_3), 1.57−1.61 (m, 2H, CHH′$_{cisCP}$), 1.87−1.91 (m, 2H, CHH′$_{transCP}$), 2.10−2.19 (m, 4H, CHH′), 2.74−2.80 (m, 2H, CHCH$_3$), 7.56 (d, $^3J_{HH}$ = 6.1 Hz, 1H, CH_{Py}), 7.46 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.66−7.70 (m, 1H, CH_{Py}), 8.67 (d, $^3J_{HH}$ = 4.9 Hz, 1H, NCH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.5 (s, CH_3), 20.5 (s, CH_3), 26.5 (d, $^1J_{CP}$ = 23.4 Hz, CHCH$_3$), 30.9 (vbr s, CH_2), 123.3 (s, CH_{Py}), 128.1 (d, $^2J_{CP}$ = 13.9 Hz, PCCH$_{Py}$), 134.5 (d, $^3J_{CP}$ = 5.9 Hz, CH_{Py}), 149.4 (d, J = 12.4 Hz, NCH_{Py}), 156.4 (d, $^1J_{CP}$ = 44.6 Hz, CP). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 19.4 (s, CH_3), 20.5 (s, CH_3), 25.9 (d, $^1J_{CP}$ = 22.7 Hz, CHCH$_3$), 29.3 (s, CH_2), 32.1 (s, CH_2), 72.8 (d, $^1J_{CRh}$ = 12.4 Hz, $CH_{COD;cisCP}$), 100.3 (dd, $^2J_{CP}$ = 6.6 Hz, $^1J_{CRh}$ = 12.4 Hz, $CH_{COD;transCP}$), 123.4 (s, CH_{Py}), 128.0 (d, $^2J_{CP}$ = 13.9 Hz, PCCH$_{Py}$), 134.7 (d, $^3J_{CP}$ = 5.9 Hz, CH_{Py}), 149.4 (d, $^3J_{CP}$ = 12.4 Hz, NCH_{Py}), 155.4 (d, $^1J_{CP}$ = 45.4 Hz, CP). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 47.5 (d, $^1J_{PRh}$ = 140.7 Hz). FAB-MS: 425.0 (M − COD, 7.5%), 406.2 (M^+ − I, 100%).

Dideutero-1,5-cyclooctadiene. To a cold solution (ca. −100 °C; 2-propanol + liquid N_2) of 4.3 mL of *tert*-butyllithium in heptane (1.6 mol/L; 6.4 mmol) and 20 mL of tetrahydrofuran (THF) was added 0.57 g (2.13 mmol) of dibromocyclooctadiene in 5 mL of THF. The solution immediately turned dark, and the mixture was stirred for another 5 min. Then 1.9 mL (10.6 mmol) of deuterium oxide was added quickly, and the mixture was allowed to warm slowly overnight, while a white precipitate (LiOH) was formed. The solvent was removed *in vacuo* and the product was extracted with diethyl ether (3× 10 mL). The combined organic fractions were dried with magnesium sulfate and filtered, and the solvent was removed *in vacuo*, yielding 0.08 g (34%) of product as a light yellow liquid. The product was used without further purification. ^1H NMR ($CDCl_3$, 298 K): 2.35 (s, 8H), 5.57 (s, 2.5H; deuteration grade ca. 75%). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): 27.9 (s, CH_2), 28.0 (s, CH_2), 128.2 (m, CD), 128.5 (s, CH), 128.7 (s, CH). One data set for each isomer (1,5-dideutero- + 1,6-dideutero-1,5-cyclooctadiene). ^2H NMR ($CDCl_3$, 298 K): 5.6 (s).

Chlorodideutero-1,5-cyclooctadiene(diisopropyl-2-pyridylphosphine)rhodium(I) (1-COD-d_2). One equivalent of chlorodicyclooctenerhodium(I) dimer was stirred with 3 equiv of dideutero-1,5-cylooctadiene in dichloromethane for 1 h. After removal of the solvent *in vacuo*, 2.1 equiv of the ligand was added and the mixture stirred for another hour in dichloromethane. Removal of the solvent *in vacuo*, washing the crude product twice with *n*-pentane, and crystallization from a saturated acetone solution yielded the complex as yellow crystals (50%). The deuteration grade is ca. 75% due to integrals of the olefinic groups in ^1H NMR. ^1H NMR ($CDCl_3$, 293 K): 1.21 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 14.1 Hz, 6H, CHCH_3), 1.51 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 15.3 Hz, 6H, CHCH_3), 1.88 (d, $^3J_{HH}$ = 7.4 Hz, 4H, CHH′), 2.28 (br d, $^3J_{HH}$ = 8.6 Hz, 4H, CHH′), 2.68−2.78 (m, 2H, CHCH$_3$), 7.21 (d, $^3J_{HH}$ = 6.1 Hz, 1H, CH_{Py}), 7.50 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.61−7.65 (m, 1H, CH_{Py}), 8.67 (d, $^3J_{HH}$ = 4.9 Hz, 1H, NCH_{Py}). ^1H NMR ($CDCl_3$, 213 K): 1.17 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, 6H, CHCH_3), 1.45 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, 6H, CHCH_3), 1.79 (d, $^3J_{HH}$ = 8.6 Hz, 2H, CHH′), 1.93 (d, $^3J_{HH}$ = 8.6 Hz, 2H, CHH′), 2.30 (br d, $^3J_{HH}$ = 8.6 Hz, 4H, CHH′), 2.62−2.71 (m, 2H, CHCH$_3$), 3.34

(s, 1H, CH_{COD}), 5.25 (s, 1H, CH_{COD}), 7.26 (d, $^3J_{HH}$ = 5.5 Hz, 1H, CH_{Py}), 7.51 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{Py}), 7.65−7.70 (m, 1H, CH_{Py}), 8.67 (d, $^3J_{HH}$ = 3.7 Hz, 1H, NCH_{Py}). ^{2}H NMR ($CDCl_3$, 293 K): 4.36 (br s, CD_{COD}). ^{2}H NMR ($CDCl_3$, 213 K): 3.38 (s, $CD_{COD;cisCP}$), 5.28 (s, $CD_{COD;transCP}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.2 (s, $CHCH_3$), 19.8 (s, $CHCH_3$), 24.1 (d, $^1J_{CP}$ = 22.1 Hz, $CHCH_3$), 30.6 (vbr s, CH_{allyl}), 69.8 (vbr s, CH_2), 102.8 (vbr s, CH_2), 123.3 (s, CH_{Py}), 128.5 (d, $^2J_{CP}$ = 16.6 Hz, $PCCH_{Py}$), 134.6 (d, $^3J_{CP}$ = 6.4 Hz, CH_{Py}), 149.5 (d, $^3J_{CP}$ = 12.9 Hz, NCH_{Py}), 155.4 (d, $^1J_{CP}$ = 46.9 Hz, CP_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 213 K): 18.9 (s, $CHCH_3$), 19.3 (s, $CHCH_3$), 23.5 (d, $^1J_{CP}$ = 22.1 Hz, $CHCH_3$), 28.4 (s, CH_2), 32.6 (s, CH_2), 69.4 (d, $^1J_{CRh}$ = 12.9 Hz, $CH_{COD;cisCP}$), 102.8 (m, $CH_{COD;transCP}$), 123.5 (s, CH_{Py}), 128.5 (d, $^2J_{CP}$ = 14.7 Hz, $PCCH_{Py}$), 134.8 (s, CH_{Py}), 149.5 (d, $^3J_{CP}$ = 12.0 Hz, NCH_{Py}), 154.3 (d, $^1J_{CP}$ = 45.4 Hz, CP_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 40.4 (d, $^1J_{PRh}$ = 145.5 Hz). FAB-MS (*m*/*z*): 407.8 (M^+ − Cl, 100%, correct isotope pattern).

Chloro-1,5-cyclooctadien-(diisopropyl-2-pyridiniumylphosphane)-rhodium(I) 4-Methylphenylsulfonate (1-H$^+$). To a NMR solution of **1** was added 1 equiv of *para*-toluenesulfonic acid. ^{1}H NMR ($CDCl_3$, 298 K): 1.20 (t, $^3J_{HH}$ = 7.7 Hz, 12H, $CHCH_3$), 2.05 (d, $^3J_{HH}$ = 9.2 Hz, 4H, CHH'), 2.36 (s, 3H, $C_{Ph}CH_3$), 2.47 (s, 4H, CHH'), 2.61 (h, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$), 3.79 (s, 2H, CH_{COD}), 5.49 (s, 2H, CH_{COD}), 7.18 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_{arom}), 7.81 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_{arom}), 7.96 (t, $^3J_{HH}$ = 6.7 Hz, 1H, CH_{Py}), 8.31 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH_{arom}), 8.39 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH_{Py}), 9.46 (d, $^3J_{HH}$ = 5.9 Hz, 1H, CH_{Py}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 48.7 (d, $^1J_{PRh}$ = 151.5 Hz).

***cis*-1,5-Cyclooctadiene(-κ^2-*N*,*P*-diisopropyl-2-pyridylphosphine)-rhodium(I) Tetrafluoroborate (1-BF$_4$).** Silver tetrafluoroborate (1.1 equiv) was added to a NMR sample of **1** in $CDCl_3$. The mixture was heated for 1 h at 50 °C and directly filtered in a second NMR tube. The compound was stable in solution for several days, but isolation attempts resulted in complete decomposition. ^{1}H NMR ($CDCl_3$, 293 K): 1.23−1.26 (m, 6H, $CHCH_3$), 1.30 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 2.5 Hz, 6H, $CHCH_3$), 2.11−2.22 (m, 4H, CH_2), 2.41−2.58 (m, 6H, $CHCH_3$, CH_2), 4.64 (s, 2H, CH_{COD}), 5.35 (s, 2H, CH_{COD}), 7.69−7.74 (m, 2H, CH_{Py}), 8.10−8.16 (m, 2H, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 19.1 (s, $CHCH_3$), 19.3 (d, $^2J_{CP}$ = 6.6 Hz, $CHCH_3$), 22.8 (d, $^2J_{CP}$ = 6.6 Hz, $CHCH_3$), 28.5 (s, $CH_{2;allyl}$), 29.7 (s, CH_2), 32.3 (s, CH_2), 78.0 (d, $^1J_{CP}$ = 11.7 Hz, $CH_{COD;cisCP}$), 98.9 (pseudo-t, $^1J_{CRh}$ = 8.8 Hz, $^2J_{CP}$ = 8.8 Hz, $CH_{COD;transCP}$), 127.9 (s, CH_{Py}), 131.0 (s, CH_{Py}), 140.5 (s, CH_{Py}), 148.6 (d, $^2J_{CP}$ = 11.7 Hz, NCH_{Py}), 155.5 (d, $^1J_{CP}$ = 40.3 Hz, J = 5.1 Hz, CP). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): −11.9 (d, $^1J_{PRh}$ = 120.9 Hz).

^{15}N-1,5-Cyclooctadiene[κ^2-*N*,*P*-diisopropyl-(3,5-dimethyl-2-pyridylphosphine]rhodium(I) Tetrafluoroborate [1-Me$_2$-^{15}N]BF$_4$. Silver tetrafluoroborate (1.1 equiv) was added to a NMR sample of ^{15}N-chloro-1,5-cyclooctadiene[diisopropyl(3,5-dimethyl-2-pyridyl)phosphine]rhodium(I) in $CDCl_3$. The mixture was heated for 1 h at 50 °C and directly filtered in a second NMR tube. The compound was stable in solution for several days, but isolation attempts resulted in complete decomposition. ^{1}H NMR ($CDCl_3$, 293 K): 1.24 (d, $^3J_{HH}$ = 7.4 Hz, 6H, $CHCH_3$), 1.28 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 2.5 Hz, 6H, $CHCH_3$), 2.08 (d, $^3J_{HH}$ = 8.6 Hz, 4H, CH_2), 2.32 (br d, J = 2.5 Hz, 3H, $CH_{3;Py}$), 2.42−2.56 (m, 6H, $CHCH_3$, CH_2), 2.44 (s, 3H, $CH_{3;Py}$), 4.43 (s, CH_{COD}), 5.64 (s, CH_{COD}), 7.22 (s, CH_{Py}), 7.33 (s, CH_{Py}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 18.6 (s, $CHCH_3$), 19.0 (d, $^2J_{CP}$ = 3.9 Hz, $CHCH_3$), 21.4 (s, $CH_{3;Py}$), 22.0 (s, $CH_{3;Py}$), 24.4 (d, $^1J_{CP}$ = 19.7 Hz, $CHCH_3$), 28.9 (s, CH_2), 32.0 (s, CH_2), 73.3 (d, $^1J_{CP}$ = 12.8 Hz, $CH_{COD;cisCP}$), 101.0 (pseudo-t, $^1J_{CRh}$ = 7.9 Hz, $^2J_{CP}$ = 7.9 Hz, $CH_{COD;transCP}$), 107.4 (d, J_{CP} = 7.9 Hz, CH_{Py}), 128.8 (d, J = 31.5 Hz, CH_{Py}), 152.8 (t, J = 3.9 Hz, CH_{Py}), 159.9 (d, J_{CP} = 11.7 Hz, J_{CN} = 12.3 Hz, CH_{Py}), 155.5 (d, $^1J_{CP}$ = 44.3 Hz, J_{CN} = 4.9 Hz, CP). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): −13.1 (dd, $^1J_{PRh}$ = 121.8 Hz, J = 11.9 Hz). $^{15}N\{^1H\}$ NMR ($CDCl_3$, 293 K): −135.1 (pseudo-t, $^1J_{NRh}$ = 11.9 Hz, J_{NP} = 11.9 Hz).

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