DOI: 10.1002/chem.200700805

Solvent-Dependent Interconversions between Rh^{I}, Rh^{II}, and Rh^{III} Complexes of an Aryl–Monophosphine Ligand

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Abstract: Reaction of the aryl-monophosphine ligand α^2-(diisopropylphosphino)isodurene (**1**) with the Rh^{I} precursor $[Rh(coe)_2(acetone)_2]BF_4$ (coe = cyclooctene) in different solvents yielded complexes of all three common oxidation states of rhodium, depending on the solvent used. When the reaction was carried out in methanol a cyclometalated, solvent-stabilized Rh^{III} alkyl-hydride complex (**2**) was obtained. However, when the reaction was carried out in acetone or dichloromethane a dinuclear η^6-arene Rh^{II} complex (**5**) was obtained in the absence of added redox reagents. Moreover, when acetonitrile was added to a solution of either the Rh^{II} or Rh^{III} complexes, a new solvent-stabilized, noncyclometalated Rh^{I} complex (**6**) was obtained. In this report we describe the different complexes, which were fully characterized, and probe the processes behind the remarkable solvent effect observed.

Keywords: arene complexes · C–H activation · oxidation state · phosphanes · rhodium · solvent effects

Introduction

Complexes of divalent rhodium have been studied extensively since the discovery of the prototypical rhodium(II) carboxylates in the 1960s.[1] Since then, hundreds of dinuclear and polynuclear species of Rh^{II}, as well as a smaller number of mononuclear species, have been isolated and characterized. Many of them, especially dinuclear complexes, have also been utilized for catalytic applications.[2]

Rh^{II} complexes are usually accessible by oxidation of Rh^{I} or reduction of Rh^{III} complexes, both processes being accomplished by the use of appropriate redox reagents.[3] Only rarely do Rh^{II} species form spontaneously from monovalent or trivalent rhodium complexes, without the addition of external redox reagents. Such transformations may be accomplished by either *disproportionation* of Rh^{I} complexes, as recently reported by Willems and co-workers,[4] or *comproportionation* of Rh^{I} and Rh^{III} complexes, as reported by several other groups.[5]

Herein, we describe a cationic rhodium–monophosphine system which undergoes facile conversion between mononuclear Rh^{I} and Rh^{III} species, but, more intriguingly, also yields a dinuclear Rh^{II} species without the addition of an external redox reagent. Moreover, these interconversions were found to be strongly influenced by the coordinating ability of the solvent. In fact, we found that it is possible to funnel the system into just one of the oxidation states simply by use of the appropriate solvent.

The rhodium–monophosphine system is based on the ligand α^2-(diisopropylphosphino)isodurene (ligand **1**, Scheme 1a), which was previously reported by our group in the context of cyclometalation by neutral Pt^{II} complexes.[6,7] Similar cyclometalation was also found to occur upon reaction of ligand **1** with the cationic Rh^{I} precursor $[Rh(coe)_2(acetone)_2]BF_4$ (coe = cyclooctene). However, in contrast to the Pt^{II} system, the present cyclometalation reaction was found to be highly reversible, resulting in the interesting valence interconversions described in this work.

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Results and Discussion

Reaction of ligand 1 with $[Rh(coe)_2(acetone)_2]BF_4$—effect of solvent on the product: When ligand **1** was allowed to react with one equivalent of the Rh^{I} precursor $[Rh(coe)_2$-

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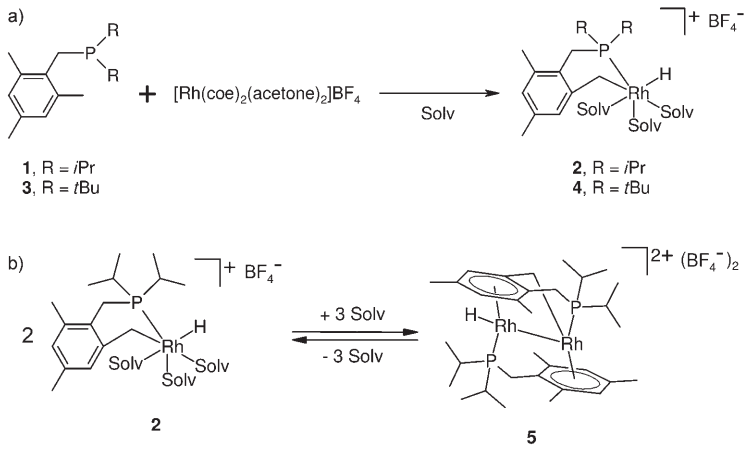

Scheme 1. a) Formation of the solvent stabilized alkylrhodium(III) hydride complexes (**2a**/**4a**: Solv = methanol; **2b**/**4b**: Solv = acetone). b) Formation of dimeric complex **5** (Solv = acetone, CH_2Cl_2).

(acetone)$_2$]BF_4 in methanol a facile C–H activation reaction took place yielding the yellow complex **2a**, a methanol-stabilized alkyl-hydride Rh^{III} species (Scheme 1a). This complex is analogous to a previously reported complex obtained with ligand **3**, complex **4a**.[8] The only structural difference between the two systems is the size of substituents of the phosphine group (isopropyl groups in **2a** compared with *tert*-butyl groups in **4a**). The new complex was found to be highly stable in methanol at room temperature and even at 80 °C, just like its bulkier analogue. The solution structure was confirmed by NMR techniques, as detailed below in the Experimental Section. The $^{31}P\{^1H\}$ NMR spectrum of complex **2a** exhibits a doublet at $\delta = 111.85$ ppm ($^1J(Rh,P) = 193.0$ Hz) and the ^1H NMR spectrum shows a characteristic hydride signal at $\delta = -24.72$ ppm (dd, $^1J(Rh,H) = 29.4$ Hz, $^2J(P,H) = 21.9$ Hz). Such a high-field signal is typical of a hydride situated *trans* to a vacant coordination site or to a loosely coordinated ligand (in this case, methanol). The methylene group attached to the metal center gives rise to two multiplets in the ^1H NMR spectrum, at $\delta = 2.73$ (dd, $^2J(H,H) = 8.8$ Hz, $^2J(Rh,H) = 3.0$ Hz) and 2.56 ppm (unresolved), and one multiplet in the $^{13}C\{^1H\}$ NMR spectrum, at $\delta = 13.65$ ppm (dd, $^1J(Rh,C) = 25.4$ Hz, $^2J(P,C) = 7.4$ Hz). This is consistent with a nonsymmetrical, cyclometalated structure, as shown in Scheme 1a. The number of coordinated solvent molecules in **2a** could not be determined directly due to difficulties in its isolation in pure solid form.[9] Nonetheless, examination of the crystal structure of its tetramethylethylenediamine adduct (see below), as well as analogy with complex **4a**,[10] leads us to conclude that three solvent molecules are coordinated.

When the reaction between **1** and [Rh(coe)$_2$-(acetone)$_2$]BF_4 was carried out in acetone, a very similar complex, **2b**, which is stabilized with acetone instead of methanol molecules, was rapidly obtained. However, when the acetone solution was kept at room temperature for a few hours, or warmed at 60 °C for a few minutes, a pronounced color change from light yellow to dark blue-violet was observed. The visible change was also accompanied by significant changes in the NMR spectra of the solution. In the $^{31}P\{^1H\}$ NMR spectrum the signal at $\delta = 111.81$ ppm (d, $^1J(Rh,P) = 190.6$ Hz), attributed to complex **2b**, slowly decreased and two new signals appeared (with a 1:1 integral ratio): a double doublet at $\delta = 86.69$ ppm ($^1J(Rh,P) = 151.1$ Hz, $^2J(Rh,P) = 20.7$ Hz) and a double triplet at $\delta = 56.73$ ppm ($^1J(Rh,P) = 161.7$ Hz, $^2J(Rh,P) \approx {}^2J(P,H) = 21.7$ Hz). In the ^1H NMR spectrum, the hydride signal of complex **2b**, which appears in acetone as a double doublet at $\delta = -23.99$ ppm ($^1J(Rh,H) = 31.0$ Hz, $^2J(P,H) = 20.1$ Hz), gave way to a new hydride multiplet at $\delta = -12.63$ ppm (td, $^2J(P,H) \approx {}^1J(Rh,H) = 26.1$ Hz, $^3J(P,H) = 7.7$ Hz). Other changes included the appearance of four aromatic signals instead of the original two and redistribution of the signals of the methylene groups (from $\delta = 2.5$–2.9 to 2.4–3.9 ppm) with significant low-field shifts (≈ 1 ppm). Furthermore, electrospray mass spectrometry showed that the primary product of the above reaction was a doubly charged species with a mass of 706.5 g mol^{-1}, which is exactly twice the mass of complex **2b**, excluding the solvent molecules and counterion. This indicated that the new product was some dimeric form of complex **2**. Indeed, full characterization, including X-ray crystallography (see below), revealed the product, complex **5**, to be a dimeric structure made up of two units of complex **2**. It must be noted that the rapid formation of this new complex from **2** is in marked contrast to the behavior of complex **4**, which was found to be stable in acetone for days at room temperature.[8,11] It appears that the primary reason for the differences between the two systems is the difference in their steric bulk (see below).

Molecular structure of dimeric complex 5: The unique features of complex **5** became clearly apparent upon X-ray diffraction crystallographic analysis. Suitable crystals of complex **5** were grown from tetrahydrofuran (THF) at room temperature. The crystal structure parameters are given in Table 1. The unit cell contains four asymmetric units, each of which comprises the dicationic complex **5**, two BF_4^- counterions and one noncoordinated solvent molecule. The cationic complex itself, the structure of which is shown in Figure 1, possesses a chiral structure (with two asymmetric centers at the metal atoms) and crystallizes as a racemic mixture. The complex is made up of two molecules of ligand **1** that bridge together two Rh^{II} centers (the oxidation state was inferred from a formal electron count). As can be seen in Figure 1, each ligand is bound to one metal center via the phosphine group and to the second metal center via the aromatic moiety (in an η^6 fashion).[12] Furthermore, one of the

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Table 1. Crystallographic data for complexes **5** and **7**.

	5 (from THF)	**5** (from acetone)	**7**
formula	$C_{36}H_{62}B_2F_8OP_2Rh_2$	$C_{35}H_{60}B_2F_8OP_2Rh_2$	$C_{22}H_{45}BF_4N_2OPRh$
F_W [g mol^{-1}]	959.24	938.21	574.29
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
crystal system	monoclinic	monoclinic	monoclinic
a [Å]	10.174(2)	10.217(2)	11.645(2)
b [Å]	31.348(6)	31.049(6)	11.209(2)
c [Å]	12.688(3)	12.679(3)	20.688(4)
α [°]	90.0	90.0	90.0
β [°]	92.70(3)	92.16(3)	102.95(3)
γ [°]	90.0	90.0	90.0
cell volume [Å^3]	4042(1)	4019(1)	2631.7(9)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	1.565	1.550	1.449
μ [mm^{-1}]	0.961	0.965	0.755
T [K]	120(2)	120(2)	120(2)
radiation	$Mo_{K\alpha}$ ($\gamma = 0.71073$ Å)	$Mo_{K\alpha}$ ($\gamma = 0.71073$ Å)	$Mo_{K\alpha}$ ($\gamma = 0.71073$ Å)
$R(F)$ [%]	5.64	3.92	5.64
$R(\omega F^2)$ [%]	9.42	8.97	12.38

ligands is also bound to the metal center (Rh1) through a methylene bridge that extends from the aromatic ring. The second metal atom (Rh2) bears a hydride ligand,[13] consistent with the above NMR data.

The metal-to-metal distance in the crystal structure is 2.6708(9) Å, which falls within the range of known Rh–Rh single bonds.[14] Support for the existence of this bond in solution was provided by both $^{31}P\{^1H\}$ and ^1H NMR experiments in which a large ^2J coupling was observed between the phosphorus and rhodium nuclei ($^2J(Rh,P) \approx 21$–22 Hz), as well as coupling of the hydride nucleus to both of the phosphorus nuclei ($^2J(P,H) = 26.1$ Hz, $^3J(P,H) = 7.9$ Hz; confirmed by an $^1H\{^{31}P\}$ NMR experiment). Furthermore, the existence of a Rh–Rh bond is consistent with the diamagnetic nature of the complex, as judged by the various NMR spectra of complex **5**. As for the exact location of the hydride ligand in solution, the fact that it is attached only to one metal center, which is different from the one binding the methylene bridge, was confirmed by a combina-

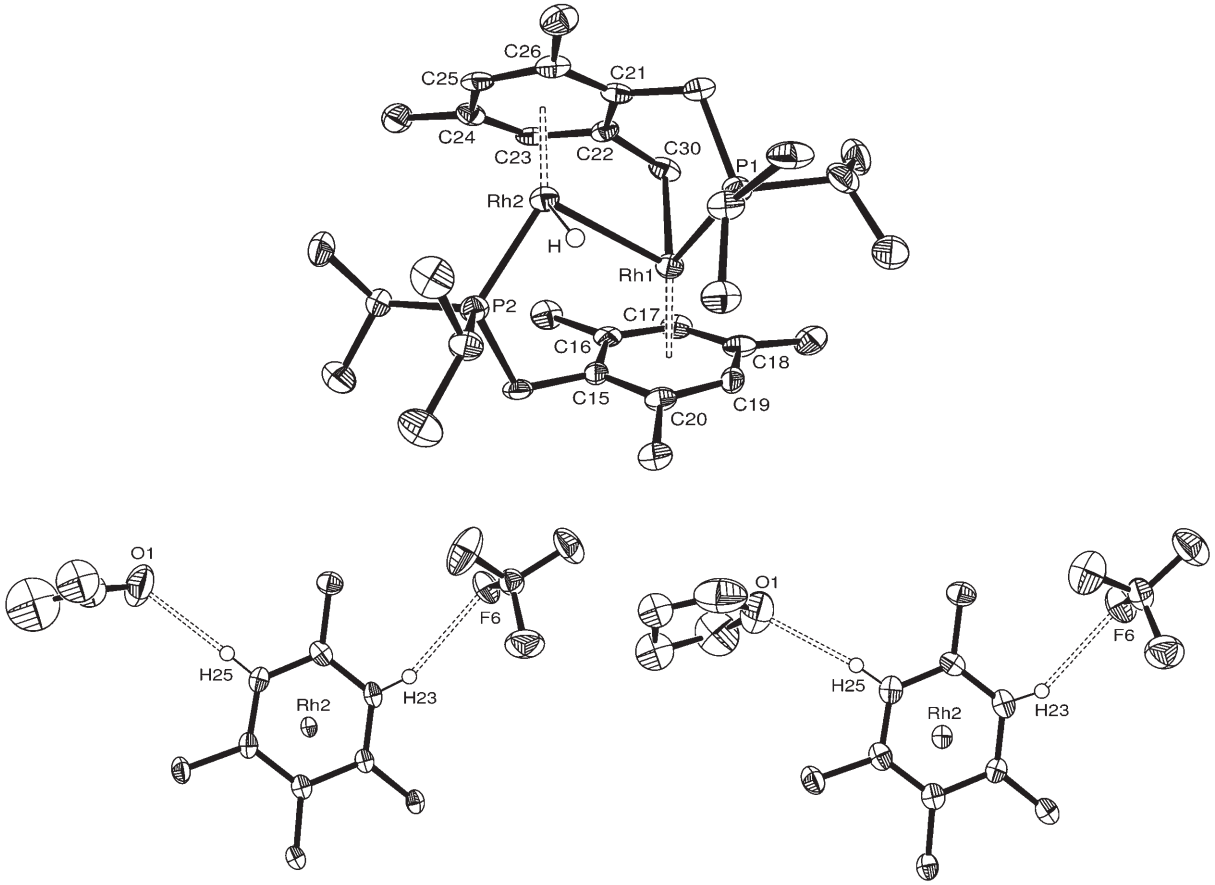

Figure 1. Top: Crystal structure of complex **5** (isolated from THF). All hydrogen atoms (except for the hydride), two BF_4^- counterions, and one THF molecule were omitted for clarity. Bottom: View of ring C21–C26 along the b axis of the unit cell in crystals isolated from THF (right) and acetone (left), showing the interactions with the BF_4 counterion and solvent molecule. The THF molecule on the right is partly disordered.

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tion of ^{103}Rh–^{1}H and ^{103}Rh–^{31}P correlation spectroscopy experiments on a CD_2Cl_2 solution of **5**. These experiments also confirmed the existence of two magnetically inequivalent rhodium atoms (as seen in the crystal structure), giving rise to two ^{103}Rh NMR signals at $\delta = -205.27$ and -471.87 ppm.[15]

The distances between the metal centers and their corresponding η^6-bound arene rings are very similar, being measured as 1.85 and 1.82 Å for Rh1 and Rh2, respectively. These values are comparable to those reported by Dixon and co-workers for a cationic, mononuclear η^6-arene pianostool Rh^{II} complex.[16] The two aromatic rings of complex **5** are slanted towards each other around the Rh–Rh bond axis, such that the dihedral angle defined by the centroid of each ring and the two Rh atoms (arene-Rh-Rh-arene) is 134°. This geometrical arrangement is probably imposed by the existence of the methylene bridge (Ar-CH_2-Rh), without which the angle would have been closer to 180° due to steric repulsions. The bond length between Rh1 and the benzylic carbon (C30) is 2.141(6) Å, which is longer than the analogous bond (2.087(7) Å) in the mononuclear Rh^{III} complex of ligand **1** discussed below (complex **7**).[17] The Rh–P bonds of complex **5** (Rh1–P1 2.2746(15) Å, Rh2–P2 2.2657(18) Å) are slightly longer than the analogous bond of the mononuclear Rh^{III} complex (2.242(2) Å), yet shorter than those of the aforementioned Rh^{II} complex reported by Dixon and co-workers (2.3381(7) Å, 2.3463(8) Å).[16] Further data regarding bond lengths and angles in complex **5** are given in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] for complex **5** (from THF).

Rh1–Rh2	2.6708(9)	Rh1–P1	2.2746(15)
Rh2–P2	2.2657(18)	Rh1–C30	2.141(6)
Rh2–H	1.50(7)	Rh1–C15	2.342(6)
Rh1–C16	2.263(5)	Rh1–C17	2.281(5)
Rh1–C18	2.343(6)	Rh1–C19	2.322(6)
Rh1–C20	2.410(6)	Rh1–arene	1.85
Rh2–C21	2.243(6)	Rh2–C22	2.210(6)
Rh2–C23	2.334(6)	Rh2–C24	2.401(6)
Rh2–C25	2.340(6)	Rh2–C26	2.339(6)
Rh2–arene	1.83	F6–H23	2.48(5)
O1–H25	2.53(6)		
P1-Rh1-Rh2	85.11(5)	P2-Rh2-Rh1	96.85(4)
P1-Rh1-C30	83.80(14)		
P1-Rh1-Rh2-P2	131.86(6)	P2-Rh2-Rh1-C30	143.54(14)

When one examines a space-filling model of **5** it becomes clearly evident that the structure of this complex is sterically congested, as the arene and isopropyl moieties of the two phosphine ligands are in very close proximity. Had ligand **1** been replaced by **3**, the extra methyl group added to each isopropyl group would probably cause the structure to collapse, either by reductive elimination of the methylene bridge (Ar-CH_2-Rh) to relieve the strain, or by complete decomposition into monomeric complex **4**. This may account for the fact that no dimerization is observed for **4** after several days in acetone at room temperature.

Another interesting observation regarding the crystal structure of complex **5** was made when the crystal isolated from THF was compared with another crystal isolated from acetone (grown at −25 °C). It was found that although the cocrystallized solvent is different (acetone versus THF) the two crystal structures are virtually identical in every other term, including the unit-cell dimensions (see Table 1) and the relative positions of counterions and solvent molecules. In particular, both the acetone and THF molecules are located close to the methylene-bridged arene moiety (ring C21–C26), such that the oxygen atoms of both solvents point towards that ring (Figure 1b). In fact, the distance between the oxygen atom and H25 (hydrogen bound to C25) of ring C21–C26 is practically identical in both cases, at 2.50 Å, which is well within the sum of van der Waals radii of hydrogen and oxygen atoms ($r_H + r_O = 1.20 + 1.52$ Å = 2.72 Å). This implies the existence of a hydrogen bond between the complex (donor) and the solvent molecule (acceptor). The existence of such interactions may account for the low-field shift of the aromatic protons in the ^1H NMR spectrum of complex **5** in [D_6]acetone ($\delta = 7.61$–6.42 ppm) relative to those measured in CD_2Cl_2 ($\delta = 7.27$–6.25 ppm). Furthermore, one BF_4^- counterion is positioned near ring C21–C26, such that the distance between one of its fluorine atoms (F6) and H23 (hydrogen bonded to C23) is about 2.49 Å, regardless of the solvent from which the crystal was isolated (Figure 1b). This distance is also within the sum of van der Waals radii of hydrogen and fluorine atoms ($r_H + r_F = 1.20 + 1.47$ Å = 2.67 Å), again implying hydrogen bonding.

Effect of solvent on the dimerization of 2 and its reversibility: As mentioned above, when complex **2** was prepared and kept in methanol it was found to be highly stable, even when warmed to 80 °C. In acetone, on the other hand, complex **2** underwent conversion to dimer **5** even at room temperature, but this reaction was nonquantitative and eventually reached a state of equilibrium (e.g., within 11 h for $[\mathbf{2}]_0 \approx 40$ mM,[18,19] at which point the molar ratio was **2**:**5** ≈ 1:1). Nonetheless, when the weakly coordinating dichloromethane was used as solvent quantitative formation of **5** was observed. Thus, when ligand **1** was reacted with one equivalent of $[Rh(coe)_2(acetone)_2]BF_4$ (80 mM of each, after mixing) in dichloromethane complex **5** was observed within only a few minutes at room temperature (evidenced by the rapid color change from orange-yellow to brown and then dark blue-violet) and virtually quantitative yield was obtained within six hours. In fact, we utilized this method for the synthesis of pure samples of complex **5** (see Experimental Section). Lastly, it is interesting to note that the important role of solvent in the formation of complex **5** was also highlighted by the observation that the absence of solvent can also promote this reaction. This was seen during attempts to isolate pure samples of complexes **2a** and **2b** by evaporating their respective solutions under vacuum. For example, when a freshly prepared solution of complex **2b** in acetone, containing no complex **5**, was evaporated to dry-

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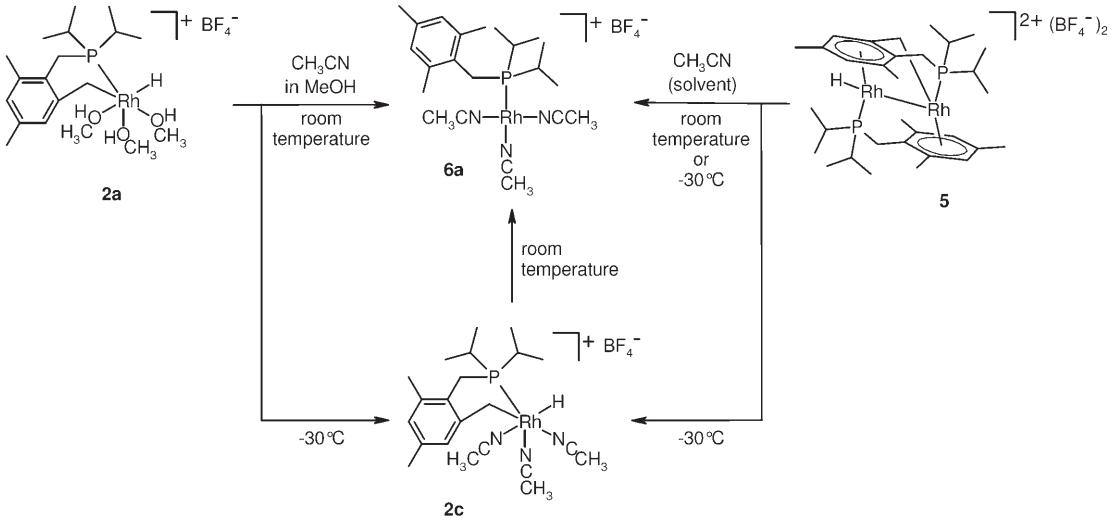
ness for a few minutes and then kept under vacuum at room temperature for 2.5 h, it was found that nearly 90% of **2** had been converted to **5** in the absence of any solvent (a similar observation was also made in the case of **2a**).

The dimerization of complex **2** into **5** was also found to be highly reversible, as demonstrated by the reactions of **5** with various solvents. When a sample of pure complex **5** was dissolved in either methanol or acetone, at room temperature, it underwent conversion to complex **2a** or **2b**, respectively. The extent of conversion was highly dependent on the solvent, such that in methanol complex **5** was completely converted into **2a** (within 19 h for initial concentration $[\mathbf{5}]_0 = 10$ mM), whereas in acetone the system was found to reach a state of equilibrium (within 6 h, for the same initial concentration of **5**), at which point the molar ratio was **2**:**5** $\approx$1:1 (equivalent to $\approx$30% conversion). However, when acetonitrile was used to dissolve complex **5** a very different result was obtained. When this solvent, which is more strongly coordinating than either acetone or methanol, was added to a sample of pure **5** at room temperature an immediate color change from blue-violet to yellow took place. This was also accompanied by the complete disappearance of **5** and formation of two new complexes: a major product, which was different from **2**, and a minor product ($\approx$16 mol%),[20] which was identified as the acetonitrile adduct of **2** (**2c**; see Experimental Section for characterization). NMR analysis of the major product revealed it to be complex **6a**, a noncyclometalated monophosphine Rh^I species (see Scheme 2), which was also obtained in high yield by addition of excess acetonitrile to a methanol solution of **2a**. The $^{31}P\{^1H\}$ NMR spectrum of complex **6a** in CD_2Cl_2 exhibits a doublet at $\delta = 53.05$ ppm ($^1J(Rh,P) = 175.0$ Hz) and its ^1H NMR spectrum is generally characteristic of a freely rotating monodentate ligand (for example, the aromatic protons are magnetically equivalent, as are the methylene protons; see the Experimental Section for further details).

In an attempt to probe the relationship between complexes **2c** and **6a**, we carried out the above experiments at low temperatures. When a sample of pure **5** was dissolved in cold (−35°C) acetonitrile, and was then examined at −30°C, complexes **2c** and **6a** were found at nearly equimolar amounts, in contrast to the abovementioned case at room temperature. Then, as the sample was warmed to room temperature, the amount of complex **2c** quickly decreased, as the amount of **6a** increased, until the system reached a state of equilibrium, within 30 minutes, for which the molar ratio was **2c**:**6a**$\approx$1:15. Direct evidence for this equilibrium was obtained from spin saturation transfer (SST) experiments which showed that **2c** undergoes facile, reversible C–H reductive elimination of the methylene bridge (Ar-CH_2-Rh). Because **6a** is the fully opened product of C–H reductive elimination from **2c**,[21] it is reasonable to assume that complexes **2c** and **6a** are in mutual equilibrium. These observations clearly indicate that complex **2c** is not merely a byproduct of the reaction of **5** with acetonitrile, but is in fact intimately related to the formation of **6a**.[22] This conclusion was further supported by the observation that adding excess acetonitrile ($\approx$50 equivalents) to a cold (−35°C) methanol solution of complex **2a** ($[\mathbf{2a}]_0 = 44$ mM) resulted in **2c** as the *major* product, with a molar ratio of **2c**:**6a**$\approx$3:1 (as observed at −30°C). In this case, complex **2c** most probably originated directly from **2a** by simple solvent substitution, which explains the initially high ratio of **2c**:**6a** (i.e., solvent substitution is faster than C–H reductive elimination). As the sample was then warmed to room temperature, complex **6a** became the predominant species, as described above for the acetonitrile solution (with a very similar product ratio).

Effect of chelation on the dimerization of 2: Further evidence to the importance of solvent dissociation in the dimerization reaction was obtained when the chelating ligand tetramethylethylenediamine (TMEDA) was added to complex



Scheme 2. Reactions of complexes **2a** and **5** with acetonitrile.

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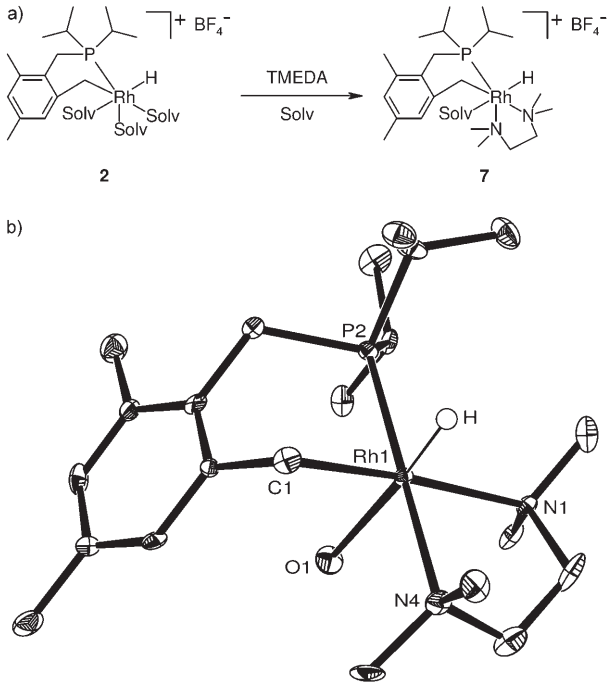
2. When one equivalent of this ligand was added to complex **2** the conversion to dimer **5** was completely prevented, even in weakly coordinating solvents and/or elevated temperatures (e.g., over one hour at 80 °C in dioxane). The TMEDA adduct of **2**, complex **7** (Scheme 3), was isolated from either



Scheme 3. a) Reaction of complex **2** (**2b**: Solv = acetone; **2d**: Solv = THF) with TMEDA to afford complex **7** (**7a**: Solv = acetone; **7b**: Solv = THF). b) Crystal structure of complex **7** (H_2O adduct). All hydrogen atoms (except for the hydride) and the BF_4^- counterion were omitted for clarity.

acetone (**7a**) or THF (**7b**) and fully characterized by solution NMR techniques and X-ray crystallography (Scheme 3b; see the Experimental Section for more details). A solution of complex **7** in acetone exhibits a doublet at $\delta =$ 92.32 ppm (^1J(Rh,P) = 165.5 Hz) in the $^{31}P\{^1H\}$ NMR spectrum, which is markedly different from the signal attributed to complex **2** ($\delta = 111.81$ ppm, doublet, ^1J(Rh,P) = 190.6 Hz). Furthermore, the ^1H NMR spectrum shows a high-field hydride signal at $\delta = -26.65$ ppm, which is characteristic of a hydride *trans* to a vacant coordination site or to a loosely coordinated ligand, such as acetone. However, the most intriguing attribute of **7** is related to the chelating TMEDA ligand itself. At room temperature, all protons associated with this ligand give rise to very broad, overlapping signals at $\delta = 2.50$–3.00 ppm in the ^1H NMR spectrum, indicating that a facile dynamic process takes place. The individual signals become resolved only at low temperatures, for example, −73 °C. Similar fluxionality is also observed for the parts of ligand **1** which are close to the first coordination sphere, that is, some of the isopropyl protons and all of the methylene protons (Ar-CH_2-P, Ar-CH_2-Rh), the latter being practically unobserved at room temperature. Further evidence for the nature of this fluxionality came from H/D exchange and SST experiments. When a solution of complex **7** in CD_3OD was warmed to 50 °C facile H/D exchange took place between the solvent, the hydride ligand, and the arene methyl group which is situated *ortho* to the phosphine "arm", as indicated by the disappearance of the corresponding signals in the ^1H NMR spectrum. Moreover, room-temperature SST experiments (also in methanol) clearly demonstrated direct chemical exchange between the hydride ligand and the arene methyl group mentioned above. It is noteworthy that in both exchange experiments the signals associated with the bridging methylene (Ar-CH_2-Rh) could not be observed due to overlap with the TMEDA protons and it is therefore unclear whether this group participates in any exchange.[23] Nonetheless, the above observations indicate that complex **7** undergoes facile C–H reductive elimination, even at room temperature.[24] It was shown that ligand dissociation is a prerequisite for C–H reductive elimination from octahedral alkyl hydride Rh^{III} complexes,[25] and hence it is reasonable to assume that dissociation of either the solvent molecule or one of the amine groups of the TMEDA ligand (probably *trans* to the methylene bridge, due to its strong *trans* influence) contributes to the dynamic process of complex **7.**

Crystal structure of 7: Crystals of complex **7** suitable for X-ray diffraction structural analysis were obtained from a concentrated acetone solution cooled to −30 °C. The crystal structure (Scheme 3b) was found to contain a coordinated water molecule, which probably originated from trace amounts of water in the acetone. It exhibits a rhodium center situated in a slightly distorted octahedral environment, with the hydride ligand located *trans* to the water molecule, in accordance with the NMR data (hydride *trans* to a labile solvent molecule). The Rh–N1 (*trans* to methylene bridge) bond length (2.260(6) Å) is longer than the Rh–N4 (*trans* to phosphine) bond (2.220(6) Å), the difference being due to the higher *trans* influence of the methylene as compared with the phosphine donor. The other metal-to-ligand bond lengths (see Table 3) are similar to those observed for the ketol adduct of complex **4**, which closely resembles complex **7** and was previously reported by our group.[8]

Table 3. Selected bond lengths [Å] and angles [°] for complex **7** (H_2O adduct).

Rh1–C1	2.087(7)	Rh1–P2	2.242(2)
Rh1–N1	2.260(6)	Rh1–N4	2.220(6)
Rh1–O1	2.315(6)	Rh1–H	1.47(8)
C1-Rh1-P2	83.6(2)	P2-Rh1-N1	103.3(2)
N1-Rh1-N4	81.6(2)	N4-Rh1-C1	91.2(3)
C1-Rh1-O1	89.0(3)	C1-Rh1-H	85(3)
O1-Rh1-H	174(3)		
N1-C17-C18-N4	60.3(9)		

Side reactions and mechanistic insights related to the formation of complex 5: When ligand **1** was reacted with one

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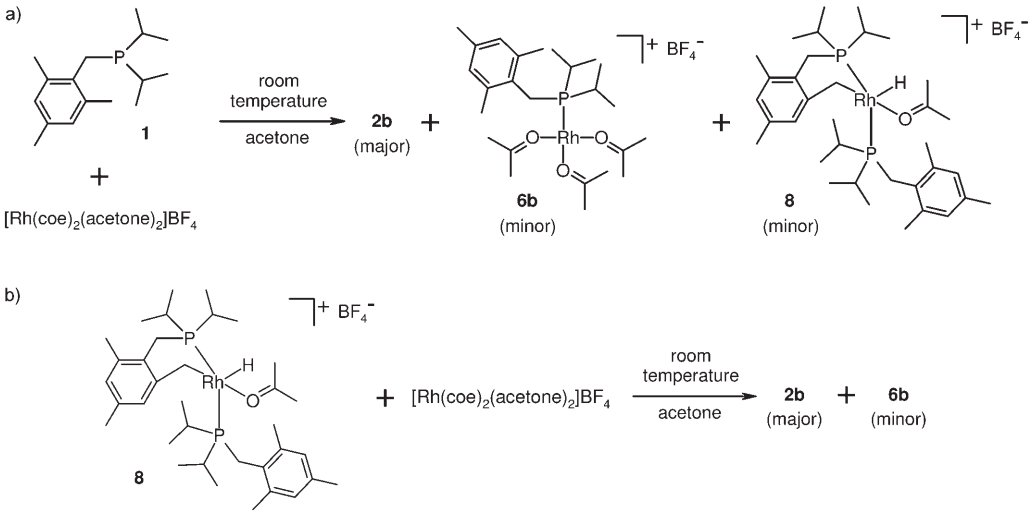

Scheme 4. a) Reaction of **1** with $[Rh(coe)_2(acetone)_2]BF_4$ in acetone, leading to complex **2b** and side products. (b) Reaction of complex **8** with $[Rh(coe)_2(acetone)_2]BF_4$.

equivalent of $[Rh(coe)_2(acetone)_2]BF_4$ in acetone the formation of complex **2b** was accompanied by the appearance of two side products (see Scheme 4a). The first side product gives rise to a doublet at $\delta = 55.50$ ppm ($^1J(Rh,P) = 189.2$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum and was identified as the acetone analogue of complex **6a**. This acetone adduct (**6b**) could not be isolated, due to its facile cyclometalation reaction to afford complex **2b**, but its acetonitrile analogue was fully characterized, as described above. The second side product gives rise to two signals in the $^{31}P\{^1H\}$ NMR spectrum: a double doublet at $\delta = 80.48$ ppm ($^2J(P,P) = 332.9$ Hz, $^1J(Rh,P) = 128.9$ Hz) and another double doublet at $\delta = 47.67$ ppm ($^2J(P,P) = 332.8$ Hz, $^1J(Rh,P) = 118.6$ Hz). Furthermore, the ^1H NMR spectrum of this complex exhibits a broad singlet at $\delta = -23.11$ ppm, characteristic of a hydride ligand *trans* to a vacant coordination site or to a loosely coordinated solvent molecule (acetone). Full NMR analysis of this complex revealed it to be the new complex **8**, an adduct of complex **2** with ligand **1**. This complex was synthesized independently as a pure substance and fully characterized (see Experimental Section).[26] It is important to note that under the reaction conditions discussed here the existence of complex **8** means that the solution must also contain an equivalent amount of the unreacted precursor $[Rh(coe)_2(acetone)_2]BF_4$. Furthermore, it should be noted that the fact that two molecules of ligand **1** can bind to the Rh^I center is in marked contrast to the behavior of the bulkier ligand **3**, only one molecule of which can bind to the metal center.[8] This further demonstrates the effect of ligand bulkiness on its reactivity, as was evident in the dimerization reaction (see above).

As the mixture of complexes **2b**, **6b**, and **8** (40, 20, and 5 mM, respectively)[19] in acetone was allowed to stand at room temperature complex **5** slowly formed, whereas the amounts of the former complexes decreased. However, as the system approached equilibrium only complex **8** disappeared completely, whereas complexes **2b** and **6b** remained in the solution (with a molar ratio of **5**:**2b**:**6b** ≈ 2:2:1, after 11 h). In an attempt to clarify this observation we reacted a pure sample of **8** in acetone with one equivalent of $[Rh(coe)_2(acetone)_2]BF_4$ (simulating the free precursor found in the above reaction mixture; see Scheme 4b). The two complexes fully reacted at room temperature within less than 15 minutes to generate complexes **2b** and **6b** (in a molar ratio of roughly 6:1, respectively).[27] When the resulting solution, which was practically void of complex **8**, was then warmed to 60 °C complex **5** was generated. It may therefore be concluded that complex **8** probably has no significant role in the formation of dimer **5**.

On the other hand, complex **6b** was found to be persistent in the acetone solution, along with complex **2b**. Complex **2b** was found by SST experiments to undergo facile, reversible C–H reductive elimination of the methylene bridge (Ar-CH_2-Rh), in a manner similar to its bulkier analogue, complex **4**.[8] It is therefore reasonable to assume that, like complexes **2c** and **6a** discussed above, complexes **2b** and **6b** are also in mutual equilibrium, since **6b** is the fully opened product of C–H reductive elimination from **2b**.[21] This equilibrium is strongly influenced by the solvent, as demonstrated above, such that in methanol only **2a** is observed, in acetonitrile **6a** is the predominant species, and in acetone **2b** is the predominant species.

Both the existence of the above equilibrium (**2**⇔**6**) and the solvent effect can be rationalized on the basis of density functional theory (DFT) calculations previously reported by our group regarding complex **4a**.[28] These calculations were based on a simplified model system which had methyl instead of *tert*-butyl substituents on the phosphine moiety, and hence they are also relevant to the current case. The DFT study identified three pathways that may be involved in the reversible C–H reductive elimination from the cyclometalated complex (**2a** or **4a**), all of which include the dissociation of one solvent molecule from the parent complex as a prerequisite for C–H elimination. Furthermore, all pathways in-

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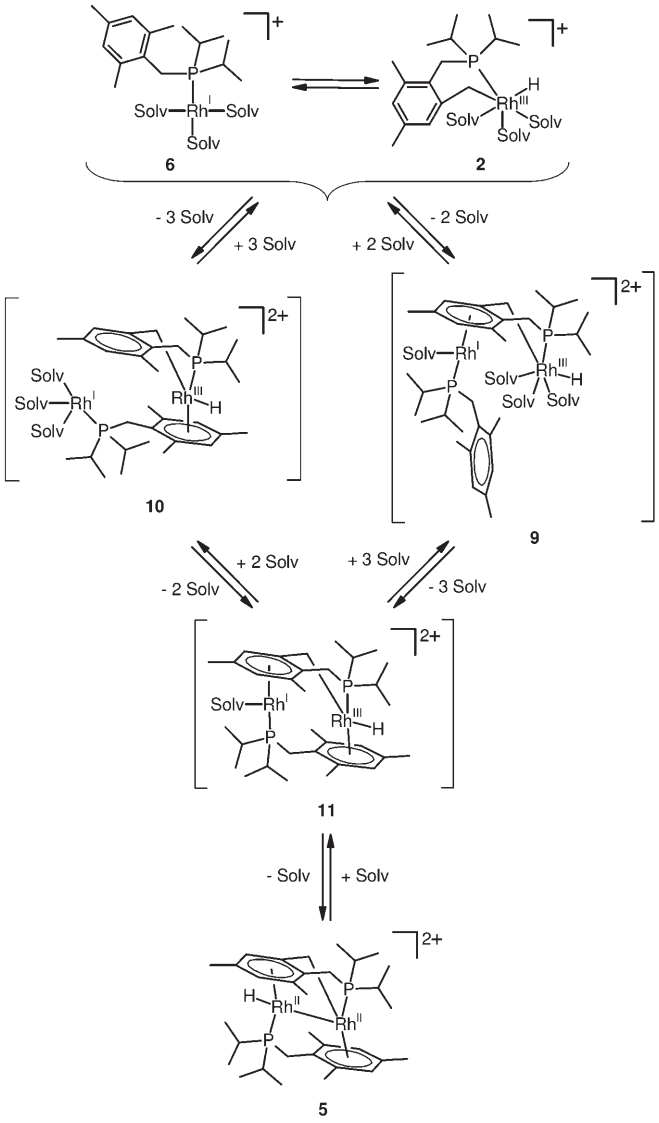
volve C–H agostic intermediates, which are crucial for the stability of the alkyl-hydride complexes by serving as a barrier to decomposition. Nonetheless, one of the pathways does lead to a noncyclometalated product analogous to complex **6** (with methanol instead of acetonitrile or acetone ligands), which was calculated to be about 9 kcal mol^{-1} less stable than the cyclometalated complex. This result accounts for the fact that the noncyclometalated complexes of either ligands **1** or **3** have not been observed in methanol.

When methanol is replaced with either acetone or acetonitrile, the relative stabilities of the cyclometalated (**2**) and noncyclometalated (**6**) complexes change. Acetone, which is a "softer" σ donor than methanol, is bound more weakly to the Rh^{III} center of **2** (as shown experimentally in our previous work[28]), but is expected to bind more strongly to the "softer" Rh^{I} center of **6**. Therefore, the energy gap between **2b** and **6b** is expected to diminish relative to the methanol case, as was indeed observed experimentally, since both complexes were found to coexist in acetone. As for the effect of acetonitrile, it is a "softer" donor than either methanol or acetone, and therefore the changes in relative stabilities should be even more pronounced than in the case of acetone. Moreover, acetonitrile can also function as a π acid, receiving backdonation from the rhodium center, especially if it is relatively electron-rich, as in the case of Rh^{I} relative to Rh^{III}. Consequently, **6a** becomes more stable than **2c**, such that the former is the predominant species observed when excess acetonitrile is present. It is also important to note the effect of solvent on the formation and stability of the C–H agostic intermediates mentioned above. In general, the more labile the solvent is with respect to Rh^{III}, the more facile is the C–H reductive elimination and formation of the appropriate agostic intermediate. Furthermore, because all of the agostic intermediates are Rh^{I} species they should also be stabilized by acetone and acetonitrile relative to methanol.

The above observations regarding complexes **2** and **6**, together with the very structure of complex **5** (which is essentially an interlocking combination of complexes **2** and **6**), point to a plausible mechanism that can lead to the formation of the Rh^{II} dimer. The general outline of this mechanism is shown in Scheme 5. The initial stage would be a bimolecular reaction of Rh^{III} complex **2** with Rh^{I} complex **6** to give a mixed-valence Rh^{I}/Rh^{III} species in which the rhodium center of one complex is coordinated to the arene moiety of the second complex.[29,30] We have identified two such possible species, namely **9** and **10**, neither of which have been experimentally observed. We believe that the pathway involving intermediate **9** is more likely, because the formation of this species requires the dissociation of only two solvent molecules from complex **6** (at least from the electronic point of view), whereas the formation of intermediate **10** requires three solvent molecules to be released. Nevertheless, both pathways should then lead to the same mixed-valence Rh^{I}/Rh^{III} species **11** (not observed), which has the two rhodium centers closely positioned, but still lacks a true Rh–Rh bond. This complex would then undergo intramolecular



Scheme 5. Putative mechanisms for the formation of complex **5**.

comproportionation to yield the dirhodium(II) complex **5**, in a process that might involve hydride-bridged electron transfer.[31]

The putative mechanism described herein accounts for the strong solvent effect observed for the formation (and decomposition) of complex **5**. Virtually all of the mechanistic stages leading to **5** involve solvent dissociation and hence rely heavily on the coordinating ability of the solvent. In particular, the very first stage is strongly hindered by solvents such as methanol or acetonitrile that strongly stabilize either species **2** or **6**, respectively, as was shown above. On the other hand, more weakly coordinating solvents, such as acetone and dichloromethane, would allow both monomeric species to coexist, as well as allow the dissociation of solvent molecules necessary for the coordination of the arene moieties to the rhodium centers.

Regarding the reversibility of the overall mechanism (e.g., reaction of **5** with acetonitrile to yield **6**), our findings are

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strongly supported by previous works that have shown that both solvent and arene coordination to cationic rhodium centers can be highly reversible. For example, Bittersmann and co-workers showed that complexes of the form $[Rh(\eta^6\text{-arene})L_2]ClO_4$ (arene = mesitylene, toluene, benzene; L = P(OPh)$_3$) undergo reversible displacement of the arene ligands by solvent (acetone) molecules, as well as other arene ligands.[32] Similar reactivity was observed by Singewald and co-workers in a cationic rhodium complex containing two monophosphine ligands with flexible arene-containing arms, which are reminiscent of ligand **1**.[33]

Conclusion

The reaction of ligand **1** with one equivalent of the Rh^I precursor $[Rh(coe)_2(acetone)_2]BF_4$ yielded several products, depending on the solvent used. In methanol, a hard coordinating solvent, the aryl-hydride Rh^{III} complex **2a** was obtained, which is analogous to the previously reported complex **4a**. However, in acetone and dichloromethane, which are softer and more weakly coordinating solvents than methanol, the reaction yielded a dimeric, dinuclear Rh^{II} structure, complex **5**. A third product, the noncyclometalated Rh^I complex **6a**, was obtained when the soft, strongly-coordinating acetonitrile was added to either **2** or **5**. Thus, the choice of solvent could be used to dictate the outcome of the reaction, both in terms of complex structure and formal oxidation state. The critical role of solvent coordination was further demonstrated by showing that the addition of a chelating ligand (TMEDA) to complex **2** completely prevented its transformation to complex **5**, even when the solvent used was acetone and high temperatures were employed. On the basis of these observations, as well as previous theoretical work done by our group, we discussed the behavior of the monophosphine–rhodium system in terms of relative stabilities and suggested a putative mechanism for the formation of the unique dirhodium(II) complex **5**.

In summary, this work clearly demonstrates the remarkable role of the solvent in the coordination chemistry of rhodium. Thus, the complex structure and the metal oxidation state can be determined simply by the choice of solvent. This behavior of the cationic monophosphine–rhodium system described here stems from stabilization of the metal center by solvent molecules and from the versatile nature of ligand **1**, which can serve as a σ donor (via the phosphine), π donor (via the arene moiety), and substrate for C–H activation.[7] We believe that these findings should be kept in mind in the design and mechanistic evaluations of reactions promoted and catalyzed by rhodium complexes.

Experimental Section

All experiments with metal complexes and the phosphine ligand were carried out under an atmosphere of purified nitrogen in an MBraun MB 150B-G glove-box. The complex $[Rh(coe)_2(acetone)_2]BF_4$ was prepared according to a literature procedure, with appropriate modifications.[34] All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon or nitrogen and kept in the glove-box over 3 Å or 4 Å molecular sieves (except for acetone, which was dried with Drierite). Commercially available reagents were used as received.

Analysis: NMR spectra (^{1}H, ^{13}C, ^{19}F, and ^{31}P) were recorded by using Brüker Avance-400 or Brüker Avance-500 NMR spectrometers. ^{103}Rh–^{1}H and ^{103}Rh–^{31}P correlation spectroscopies were carried out on the Brüker Avance-500 NMR spectrometer, by using a TXI probe (with a dedicated ^{31}P channel). All measurements were performed at 20 °C, unless noted otherwise. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to tetramethylsilane. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvents, and the ^{13}C NMR chemical shifts are referenced to the ^{13}C signal(s) of the deuterated solvents. ^{19}F NMR chemical shifts are reported in ppm relative to $CFCl_3$ and referenced to an external solution of C_6F_6 in $CDCl_3$. ^{31}P NMR chemical shifts are reported in ppm relative to H_3PO_4 and referenced to an external 85 % solution of phosphoric acid in D_2O. Abbreviations used in the description of NMR data are as follows: Ar, aryl; br, broad; v, virtual; s, singlet; d, doublet; m, multiplet.

Electrospray (ES) mass spectrometry was performed at the Chemical Analysis Laboratory (Chemical Research Support Unit), Weizmann Institute of Science, by using a Micromass Platform LCZ 4000 spectrometer (Micromass, Manchester, UK) with cone voltage of 43 V, extractor voltage of 4 V, and desolvation temperature of 150 °C. Elemental analysis was performed at the H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Synthesis of α^2-(diisopropylphosphino)-isodurene (1): The synthesis of this ligand has been already reported by our group,[35] but the following procedure was found to provide a better yield. A pressure vessel equipped with a magnetic stirring bar was loaded, in the glove-box, with a solution of 2-bromomethyl-1,3,5-trimethylbenzene[36] (12.78 g, 60.0 mmol) in methanol (50 mL). To this was added a solution of diisopropylphosphine (8.5 g, 71.9 mmol) in methanol (25 mL). The vessel was then tightly closed, removed from the glove-box and heated at 50 °C, with stirring, for 48 h. At this stage the vessel was cooled to room temperature, reintroduced into the glove-box and triethylamine (20 mL, 143 mmol) was added. The solution was stirred at room temperature for 30 min and the solvent was then removed under vacuum. The resulting residue was extracted with ether, filtered and the solvent was removed again under vacuum. The crude residue was distilled under high vacuum to afford the pure product as a colorless oil (12.6 g, 50.3 mmol, 84 % yield). B.p. 105 °C, 0.01 mm Hg; ^{1}H NMR ([D$_6$]acetone): $\delta = 6.77$ (s, 2H; Ar-*H*), 2.81 (d, ^2J(P,H) = 2.4 Hz, 2H; Ar-C*H*$_2$-P), 2.34 (s, 6H; Ar-C*H*$_3$), 2.17 (s, 3H; Ar-C*H*$_3$), 1.80 (m, ^3J(H,H) = 7.1 Hz, ^2J(P,H) = 2.0 Hz, 2H; PC*H*(CH$_3$)$_2$), 1.10 (dd, ^3J(P,H) = 11.9 Hz, ^3J(H,H) = 7.1 Hz, 6H; PCH(C*H*$_3$)$_2$), 0.99 ppm (dd, ^3J(P,H) = 12.3 Hz, ^3J(H,H) = 7.0 Hz, 6H; PCH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR ([D$_6$]acetone): $\delta = 136.82$ (d, ^3J(P,C) = 3.0 Hz, Ar), 134.99 (d, ^5J(P,C) = 2.4 Hz, Ar), 134.12 (d, ^2J(P,C) = 5.4 Hz, Ar), 129.80 (d, ^4J(P,C) = 1.5 Hz, *C*$_{Ar}$-H), 24.26 (d, ^1J(P,C) = 16.4 Hz, P*C*H(CH$_3$)$_2$), 23.95 (d, ^1J(P,C) = 22.9 Hz, Ar-*C*H$_2$-P), 21.21 (d, ^2J(P,C) = 6.5 Hz, P*C*H(CH$_3$)$_2$), 19.91 (d, ^3J(P,C) = 3.6 Hz, PCH(*C*H$_3$)$_2$), 19.78 ppm (d, ^3J(P,C) = 5.9 Hz, PCH(*C*H$_3$)$_2$). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135; ^{31}P{^{1}H} NMR ([D$_6$]acetone): $\delta = 5.45$ ppm (s).

Reaction of $[Rh(coe)_2(acetone)_2]BF_4$ with ligand 1 in CD_3OD and [D$_6$]acetone—formation of complex 2: The following procedure pertains to CD_3OD, but was also used with [D$_6$]acetone as solvent. To a solution of $[Rh(coe)_2(acetone)_2]BF_4$ (17.0 mg, 0.032 mmol) in CD_3OD (0.25 mL) was added ligand **1** (8.1 mg, 0.032 mmol) dissolved in CD_3OD (0.55 mL). The color of the solution immediately changed from orange to yellow and then rapidly to pale yellow. The product could not be isolated in dry solid form due to its instability under vacuum and the characterization was therefore accomplished in situ. The yield of the product in methanol was quantitative, based on ^{1}H and ^{31}P{^{1}H} NMR spectra. In acetone the

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product underwent slow conversion into complex **5**, as described in the main text.

2a: ^{1}H NMR (CD_3OD): $\delta = 6.91$ (s, 1H; Ar-*H*), 6.71 (s, 1H; Ar-*H*), 2.87 (m, $^2J(H,H) = 14.1$ Hz, $^2J(P,H) = 11.3$ Hz, 1H; Ar-CH_2-P), 2.73 (dd, $^2J(H,H) = 8.8$ Hz, $^2J(Rh,H) = 3.0$ Hz, 1H; Ar-CH_2-Rh), 2.56 (m, 2H; Ar-CH_2-P and Ar-CH_2-Rh), 2.27 (s, 3H; Ar-CH_3), 2.27 (m, 1H; PC*H*(CH_3)$_2$), 2.20 (s, 3H; Ar-CH_3), 2.08 (m, 1H; PC*H*(CH_3)$_2$), 1.34 (m, $^3J(H,H) = 13.8$ Hz, $^3J(P,H) = 13.7$ Hz, 6H; PCH(CH_3)$_2$), 1.01 (m, 6H; PCH(CH_3)$_2$), −24.72 ppm (dd, $^1J(Rh,H) = 29.4$ Hz, $^2J(P,H) = 21.9$ Hz, 1H; Rh-*H*); ^{13}C{^{1}H} NMR (CD_3OD): $\delta = 150.95$ (d, $J(P,C) = 6.7$ Hz, Ar), 136.05 (s, Ar), 135.65 (d, $J(P,C) = 5.3$ Hz, Ar), 131.16 (s, Ar), 127.75 (s, C_{Ar}-H), 125.67 (s, C_{Ar}-H), 27.73 (dd, $^1J(P,C) = 32.4$ Hz, $J = 1.5$ Hz, PC*H*(CH_3)$_2$), 26.78 (d, $^1J(P,C) = 22.5$ Hz, PC*H*(CH_3)$_2$), 21.07 (d, $^1J(P,C) = 31.7$ Hz, Ar-CH_2-P), 21.01 (s, Ar-CH_3), 20.34 (s, Ar-CH_3), 18.79 (PCH(CH_3)$_2$), 18.52 (PCH(CH_3)$_2$), 18.35 (PCH(CH_3)$_2$), 18.23 (PCH(CH_3)$_2$), 13.65 ppm (dd, $^1J(Rh,C) = 25.4$ Hz, $^2J(P,C) = 7.4$ Hz, Ar-CH_2-Rh). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135; ^{31}P{^{1}H} NMR (CD_3OD): $\delta = 111.85$ ppm (d, $^1J(Rh,P) = 193.0$ Hz).

2b: Selected ^{1}H NMR ([D$_6$]acetone): $\delta = 6.82$ (s, 1H; Ar-*H*), 6.75 (s, 1H; Ar-*H*), 2.92 (m, 1H; Ar-CH_2-P), 2.82 (m, 1H; Ar-CH_2-Rh), 2.75–2.67 (m, 2H; Ar-CH_2-P and Ar-CH_2-Rh), 2.30 (s, 3H; Ar-CH_3), 2.18 (s, 3H; Ar-CH_3), −23.99 ppm (dd, $^1J(Rh,H) = 31.0$ Hz, $^2J(P,H) = 20.1$ Hz, 1H; Rh-*H*); ^{31}P{^{1}H} NMR ([D$_6$]acetone): $\delta = 111.81$ ppm (dd, $^1J(Rh,P) = 189.2$ Hz, $^2J(P,H) = 15.2$ Hz).

Reaction of [Rh(coe)$_2$(acetone)$_2$]BF$_4$ with ligand 1 in CH_2Cl_2—synthesis of complex 5: To a solution of [Rh(coe)$_2$(acetone)$_2$]BF$_4$ (95.3 mg, 0.181 mmol) in CH_2Cl_2 (1.5 mL) was added ligand **1** (46.1 mg, 0.184 mmol) dissolved in CH_2Cl_2 (1.1 mL). The solution was stirred at room temperature for 16 h during which its color changed from light orange to dark blue-violet. The solvent was removed under vacuum and the resulting solid was redissolved in CH_2Cl_2 (1.0 mL) and added to pentane (17 mL), with stirring, to precipitate the product. The liquid phase was then decanted and the product was washed with pentane and dried under vacuum to afford the product as a blue-violet powder (79.5 mg, 0.090 mmol, quantitative yield).

^{1}H NMR (CD_2Cl_2): $\delta = 7.27$ (s, 1H; Ar-*H*), 7.03 (s, 1H; Ar-*H*), 6.77 (s, 1H; Ar-*H*), 6.25 (s, 1H; Ar-*H*), 3.92 (dd, $^2J(H,H) = 15.6$ Hz, $^2J(P,H) = 9.1$ Hz, 1H; Ar-CH_2-P, left part of ABX-system), 3.87 (m, $^2J(H,H) = 7.3$ Hz, $^2J(Rh,H) = 3.5$ Hz, 1H; Ar-CH_2-Rh, left part of ABX-system), 3.84 (dd, $^2J(H,H) = 15.6$ Hz, $^2J(P,H) = 10.8$ Hz, 1H; Ar-CH_2-P, right part of ABX-system), 3.06 (m, $^2J(H,H) = 6.9$ Hz, $^2J(Rh,H) = 3.2$ Hz, 1H; Ar-CH_2-Rh, right part of ABX-system), 2.60 (dd, $^2J(H,H) = 15.1$ Hz, $^2J(P,H) = 10.7$ Hz, 1H; Ar-CH_2-P, left part of ABX-system), 2.49 (s, 3H; Ar-CH_3), 2.47 (s, 3H; Ar-CH_3), 2.45 (dd, $^2J(H,H) = 13.7$ Hz, $^2J(P,H) = 7.8$ Hz, 1H; Ar-CH_2-P, right part of ABX-system, overlaps with methyl signals), 2.44 (m, 2H; PC*H*(CH_3)$_2$, overlaps with methyl signals), 2.42 (s, 3H; Ar-CH_3), 2.36 (s, 3H; Ar-CH_3), 2.34 (d, $J(P,H) = 2.9$ Hz, 3H; Ar-CH_3), 2.30 (m, 1H; PC*H*(CH_3)$_2$), 2.11 (m, 1H; PC*H*(CH_3)$_2$), 1.50–1.25 (m, 24H; overlapping signals of PCH(CH_3)$_2$), −12.88 ppm (vtd, $^2J(P,H) = 26.1$ Hz, $^1J(Rh,H) = 24.8$ Hz, $^3J(P,H) = 7.9$ Hz, 1H; Rh-*H*). Assignment of the ^{1}H NMR signals was confirmed by ^{13}C–^{1}H heteronuclear correlation; ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 133.79$ (s, Ar), 123.61 (d, $J(P,C) = 4.3$ Hz, Ar), 118.35 (s, C_{Ar}-H), 118.11 (s, Ar), 115.33 (d, $J(P,C) = 3.6$ Hz, Ar), 113.98 (s, Ar), 110.71 (s, Ar), 108.17 (d, $J(P,C) = 11.0$ Hz, Ar), 107.83 (s, C_{Ar}-H), 101.95 (s, C_{Ar}-H), 100.42 (s, C_{Ar}-H), 98.70 (d, $J(P,C) = 11.3$ Hz, Ar), 37.98 (d, $^1J(P,C) = 30.2$ Hz, PC*H*(CH_3)$_2$), 33.57 (d, $^1J(P,C) = 25.4$ Hz, PC*H*(CH_3)$_2$), 31.77 (d, $^1J(P,C) = 17.3$ Hz, PC*H*(CH_3)$_2$), 30.96 (d, $^1J(P,C) = 24.9$ Hz, Ar-CH_2-P), 29.92 (d, $^1J(P,C) = 21.7$ Hz, PC*H*(CH_3)$_2$), 21.99 (d, $^2J(P,C) = 2.8$ Hz, PCH(CH_3)$_2$), 21.35 (s, Ar-CH_3), 20.71 (s, Ar-CH_3), 20.52 (s, Ar-CH_3), 20.17 (s, PCH(CH_3)$_2$), 20.12 (s, PCH(CH_3)$_2$), 20.07 (s, PCH(CH_3)$_2$), 19.73 (s, Ar-CH_3), 19.59 (d, $^2J(P,C) = 4.5$ Hz, PCH(CH_3)$_2$), 19.43 (d, $^1J(P,C) = 26.3$ Hz, Ar-CH_2-P), 19.29 (d, $^2J(P,C) = 4.5$ Hz, PCH(CH_3)$_2$), 18.90 (s, Ar-CH_3), 18.74 (d, $^2J(P,C) = 4.5$ Hz, PCH(CH_3)$_2$), 18.48 (d, $^2J(P,C) = 4.1$ Hz, PCH(CH_3)$_2$), 6.62 ppm (dd, $^1J(Rh,C) = 18.3$ Hz, $^2J(P,C) = 7.7$ Hz, Ar-CH_2-Rh). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135 and ^{13}C–^{1}H heteronuclear correlation; ^{19}F{^{1}H} NMR (CD_2Cl_2): $\delta = -151.28$ ppm (s, free BF_4); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta = 86.74$ (dd, $^1J(Rh,P) = 151.6$ Hz, $^2J(Rh,P) = 21.2$ Hz, *P*-Rh-CH_2Ar), 56.94 ppm (dvt, $^1J(Rh,P) = 161.7$ Hz, $^2J(Rh,P) \approx {}^2J(P,H) = 22.5$ Hz, *P*-Rh-H); ^{103}Rh NMR (CD_2Cl_2): $\delta = -205.27$ (*Rh*-H), −471.87 ppm (*Rh*-CH_2Ar); ESI MS (MeOH): m^+/z (%): 353 (100) [cationic dimer, $z = 2$], 705 (47) [cationic dimer−H$^+$, $z = 1$]; m^-/z (%): 87 (100) [BF_4]; elemental analysis calcd (%) for $C_{32}H_{54}B_2F_8P_2Rh_2$: C 43.67, H 6.18, F 17.27; found: C 43.45, H 6.25, F 17.37.

X-ray structural analysis of complex 5 that was grown from tetrahydrofuran: Complex **5** was crystallized from a tetrahydrofuran solution at room temperature.

Crystal data: $C_{32}H_{54}P_2Rh_2 + 2BF_4 + C_4H_8O$, brown prism, $0.5 \times 0.3 \times 0.05$ mm^3, monoclinic, $P2_1/n$ (no. 14), $a = 10.174(2)$, $b = 31.348(6)$, $c = 12.688(3)$ Å, $\beta = 92.70(3)°$, from 20 degrees of data, $T = 120(2)$ K, $V = 4042(1)$ Å^3, $Z = 4$, $F_w = 959.24$ g mol^{-1}, $\rho_{calcd} = 1.565$ g cm^{-3}, $\mu = 0.961$ mm^{-1}.

Data collection and processing: Nonius Kappa CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), graphite monochromator, 45774 reflections collected, $-12 \le h \le 12$, $0 \le k \le 37$, $0 \le l \le 15$, frame scan width = 1.0°, scan speed 0.6° min^{-1}, typical peak mosaicity 0.467°, 9315 independent reflections ($R_{int} = 0.153$). The data were processed with Denzo-Scalepack.

Solution and refinement: The structure was solved by direct methods with SHELXS-97. Full-matrix least-squares refinement based on F^2 with SHELXL-97. 483 parameters with no restraints, final $R_1 = 0.0564$ (based on F^2) for data with $I > 2\sigma(I)$ and $R_1 = 0.1260$ for 7282 reflections, goodness-of-fit on $F^2 = 1.016$, largest electron density peak = 1.421 Å^{-3}.

X-ray structural analysis of complex 5 that was grown from acetone: Complex **5** was crystallized from an acetone solution at −25 °C.

Crystal data: $C_{32}H_{54}P_2Rh_2 + 2BF_4 + C_3H_6O$, orange prism, $0.3 \times 0.3 \times 0.2$ mm^3, monoclinic, $P2_1/n$ (no. 14), $a = 10.217(2)$, $b = 31.049(6)$, $c = 12.679(3)$ Å, $\beta = 92.16(3)°$, from 20 degrees of data, $T = 120(2)$ K, $V = 4019(1)$ Å^3, $Z = 4$, $F_w = 938.21$ g mol^{-1}, $\rho_{calcd} = 1.550$ g cm^{-3}, $\mu = 0.965$ mm^{-1}.

Data collection and processing: Nonius Kappa CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), graphite monochromator, 40579 reflections collected, $-12 \le h \le 0$, $-37 \le k \le 37$, $-15 \le l \le 15$, frame scan width = 0.9°, scan speed 0.43° min^{-1}, typical peak mosaicity 0.36°, 15660 independent reflections ($R_{int} = 0.057$). The data were processed with Denzo-Scalepack.

Solution and refinement: The structure was solved by direct methods with SHELXS-97. Full-matrix least-squares refinement based on F^2 with SHELXL-97. 438 parameters with no restraints, final $R_1 = 0.0392$ (based on F^2) for data with $I > 2\sigma(I)$ and $R_1 = 0.0571$ for 8200 reflections, goodness-of-fit on $F^2 = 1.038$, largest electron density peak = 0.903 Å^{-3}.

Reaction of complex 5 with acetonitrile at low temperature—in situ formation of complex 2c: Complex **2c** rapidly converts to complex **6a**, as described in the main text, and therefore the following low-temperature technique was employed in order to facilitate the measurement of NMR spectra for **2c**. Complex **5** (16.7 mg, 0.019 mmol) was dissolved in CD_3CN (0.62 mL), which was pre-cooled to −35 °C. The resulting orange-yellow solution was immediately transferred to the NMR spectrometer and the sample was rapidly cooled to −30 °C before measurement was commenced. Some of the NMR signals of **2c** were obscured by those of **6a**, because both complexes coexist in solution (molar ratio of ≈1:1 under the conditions described here; see below for full characterization of **6a**).

^{1}H NMR (CD_3CN, −30 °C): $\delta = 6.84$ (s, 1H; Ar-*H*), 6.70 (s, 1H; Ar-*H*), 2.90 (m, $^2J(H,H) = 14.2$ Hz, $^2J(P,H) = 11.5$ Hz, $^3J(Rh,H) = 2.1$ Hz, 1H; Ar-CH_2-P), 2.48 (dd, $^2J(H,H) = 14.2$ Hz, $^2J(P,H) = 8.9$ Hz, 1H; Ar-CH_2-P), 2.42 (m, 2H; Ar-CH_2-Rh), 2.22 (s, 3H; Ar-CH_3), 2.19 (s, 3H; Ar-CH_3), 2.18 (m, 1H; PC*H*(CH_3)$_2$, overlaps with Ar-CH_3 signals), 1.72 (m, $^3J(H,H) = 7.2$ Hz, 1H; PC*H*(CH_3)$_2$), 1.23–1.17 (m, 6H; PCH(CH_3)$_2$, overlaps with signals from **6a**), 1.14 (dd, $^3J(P,H) = 15.4$ Hz, $^3J(H,H) = 6.7$ Hz, 3H; PCH(CH_3)$_2$), 1.02 (dd, $^3J(P,H) = 15.8$ Hz, $^3J(H,H) = 7.0$ Hz, 3H; PCH(CH_3)$_2$), −19.21 ppm (t, $^1J(Rh,H) = 18.5$ Hz, $^2J(P,H) = 18.2$ Hz, 1H; Rh-*H*); selected ^{13}C{^{1}H} NMR (CD_3CN, −30 °C): $\delta = 150.76$ (dd, $J(P,C) = 7.2$ Hz, $J = 1.5$ Hz, Ar), 135.81 (d, $J(P,C) = 5.1$ Hz, Ar), 127.10 (s, C_{Ar}-H), 126.37 (s, C_{Ar}-H), 20.95 (s, Ar-CH_3), 20.74 (d, $^1J(P,C) = 30.4$ Hz, Ar-CH_2-P), 20.36 (s, Ar-CH_3), 11.20 ppm (dd, $^1J(Rh,C) = 20.7$ Hz, $^2J(P,C) = 6.4$ Hz, Ar-CH_2-Rh). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135 and ^{13}C–^{1}H heteronuclear correlation; ^{31}P{^{1}H} NMR (CD_3CN, −30 °C): $\delta = 108.26$ ppm (d, $^1J(Rh,P) = 166.7$ Hz).

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Reaction of complex 2a with acetonitrile—synthesis of complex 6a: To a solution of $[Rh(coe)_2(acetone)_2]BF_4$ (40.3 mg, 0.077 mmol) in CH_3OH (0.53 mL) was added ligand **1** (19.3 mg, 0.077 mmol) dissolved in CH_3OH (0.56 mL). The solution was stirred at room temperature for 10 min and then CH_3CN (0.55 mL, 10.5 mmol) was added. Stirring was continued for 20 min and the solution was then added to pentane (18 mL), with stirring, to precipitate the product. The mixture was allowed to stand at −35 °C overnight to facilitate the precipitation. The liquid phase was then decanted and the product was washed with diethyl ether and dried under vacuum to afford the product (36.0 mg, 0.064 mmol, 83.5 % yield) as a yellow powder.

^{1}H NMR (CD_2Cl_2): δ = 6.83 (s, 2H; Ar), 3.01 (d, ^2J(P,H) = 11.6 Hz, 2H; Ar-CH_2-P), 2.73 (s, 6H; Ar-CH_3), 2.28 (s br, 3H; NCCH_3), 2.20 (s, 3H; Ar-CH_3), 1.98 (m, 2H; PCH(CH$_3$)$_2$), 1.92 (s, 6H; NCCH_3), 1.31 (dd, ^3J(P,H) = 14.4 Hz, ^3J(H,H) = 7.0 Hz, 6H; PCH(CH_3)$_2$), 1.26 ppm (dd, ^3J(P,H) = 14.4 Hz, ^3J(H,H) = 7.1 Hz, 6H; PCH(CH_3)$_2$). Assignment of the ^{1}H NMR signals was confirmed by ^{13}C–^{1}H heteronuclear correlation; ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 137.98 (d, J(P,C) = 3.7 Hz, Ar), 135.88 (d, J(P,C) = 2.8 Hz, Ar), 130.95 (d, J(P,C) = 3.6 Hz, Ar), 129.52 (d, ^4J(P,C) = 2.3 Hz, C_{Ar}-H), 122.48 (d, ^2J(Rh,C) = 12.2 Hz, CN), 118.46 (s br, CN), 26.27 (d, ^1J(P,C) = 25.3 Hz, PCH(CH$_3$)$_2$), 24.78 (d, ^1J(P,C) = 19.7 Hz, Ar-CH$_2$-P), 22.54 (s, Ar-CH$_3$), 20.75 (d, J = 0.6 Hz, Ar-CH$_3$), 19.26 (s, PCH-(CH_3)$_2$), 18.83 (s, PCH(CH_3)$_2$), 3.84 (s, NCCH_3), 3.40 ppm (s br, NCCH_3). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135 and ^{13}C–^{1}H heteronuclear correlation; ^{19}F{^{1}H} NMR (CD_2Cl_2): δ = −153.07 ppm (s, free BF_4); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 53.05 ppm (d, ^1J(Rh,P) = 175.0 Hz); elemental analysis calcd (%) for $C_{22}H_{36}BF_4N_3PRh$: C 46.92, H 6.44; found: C 46.98, H 6.55.

In situ formation of complex 6b: To a solution of $[Rh(coe)_2(acetone)_2]BF_4$ (48.8 mg, 0.093 mmol) in [D$_6$]acetone (0.45 mL) was added ligand **1** (23.2 mg, 0.093 mmol) dissolved in [D$_6$]acetone (0.39 mL). The primary product of this reaction was complex **2b**, as described above. Complex **6b** was identified as a by-product of this reaction.

Selected ^{1}H NMR ([D$_6$]acetone): δ = 6.92 (s, 2H; Ar), 3.05 (d, ^2J(P,H) = 11.0 Hz, 2H; Ar-CH_2-P), 2.71 (s, 6H; Ar-CH_3), 2.22 (s, 3H; Ar-CH_3), 1.32 ppm (m, 24H; PCH(CH_3)$_2$); ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 55.50 ppm (d, ^1J(Rh,P) = 189.2 Hz).

Synthesis of complex 7: To a solution of $[Rh(coe)_2(acetone)_2]BF_4$ (55.0 mg, 0.105 mmol) in THF (1.2 mL) was added tetramethylethylenediamine (12.2 mg, 0.105 mmol) dissolved in THF (0.8 mL). The solution was stirred at room temperature for 15 min, during which its color changed from orange to orange-yellow. Then a solution of ligand **1** (26.4 mg, 0.105 mmol) in THF (1.0 mL) was added and the resulting solution was stirred at room temperature for 50 min, during which the color changed to yellow. The solution was concentrated under vacuum (to 0.8 mL) and then pentane (13 mL) was added, with stirring, to precipitate the product. The liquid phase was decanted and the solids were washed with pentane and dried under vacuum to afford the product (60.3 mg, 0.096 mmol, 91.8 % yield) as a light-beige powder. It is important to note that while the solid product is **7b** (THF adduct; see elemental analysis), the NMR spectra were measured in acetone and are thus representative of complex **7a** (acetone adduct).

^{1}H NMR ([D$_6$]acetone, 20 °C): δ = 6.95 (s, 1H; Ar-H), 6.69 (s, 1H; Ar-H), 3.00–2.50 (very broad overlapping signals, 16H; NCH_2CH_2N and 2 N-(CH_3)$_2$), 2.37 (m, ^3J(H,H) = 6.7 Hz, 2H; PCH(CH$_3$)$_2$), 2.30 (s, 3H; Ar-CH_3), 2.17 (s, 3H; Ar-CH_3), 1.29 (dd, ^3J(P,H) = 12.7 Hz, ^3J(H,H) = 6.9 Hz, 6H; PCH(CH_3)$_2$), 1.14 (s br, 6H; PCH(CH_3)$_2$), −26.65 ppm (s br, 1H; Rh-H); Assignment of the ^{1}H NMR signals was confirmed by ^{13}C–^{1}H heteronuclear correlation; ^{13}C{^{1}H} NMR ([D$_6$]acetone, 20 °C): δ = 151.48 (d, J(P,C) = 6.0 Hz, Ar), 135.13 (d, J(P,C) = 1.4 Hz, Ar), 134.70 (d, J(P,C) = 5.8 Hz, Ar), 131.48 (s, Ar), 127.11 (s, C_{Ar}-H), 125.34 (s, C_{Ar}-H), 61.98 (s, NCH_2CH_2N), 52.34 (s br, 2N(CH_3)$_2$), 26.90 (d, ^1J(P,C) = 23.4 Hz, PCH-(CH$_3$)$_2$), 20.94 (s, Ar-CH$_3$), 20.28 (s, Ar-CH$_3$), 19.15 (d, ^1J(P,C) = 30.3 Hz, Ar-CH$_2$-P), 18.95 (s, PCH(CH_3)$_2$), 17.62 (s, PCH(CH_3)$_2$), 15.10 ppm (d br, ^1J(Rh,C) = 21.1 Hz, Ar-CH$_2$-Rh). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135 and ^{13}C–^{1}H heteronuclear correlation; ^{31}P{^{1}H} NMR ([D$_6$]acetone, 20 °C): δ = 92.32 ppm (d, ^1J(Rh,P) = 165.5 Hz); ^{19}F{^{1}H} NMR ([D$_6$]acetone, 20 °C): δ = −151.96 ppm (s, free BF_4).

^{1}H NMR ([D$_6$]acetone, −73 °C): δ = 6.97 (s, 1H; Ar-H), 6.64 (s, 1H; Ar-H), 3.26 (m br, 1H; NCH_2), 3.04 (m br, 1H; Ar-CH_2-P), 2.89 (s br, 3H; NCH_3), 2.74 (s br, 3H; NCH_3), 2.58 (m br, 1H; NCH_2), 2.55 (m br, 1H; Ar-CH_2-Rh), 2.49 (s br, 3H; NCH_3), 2.42 (s br, 3H; NCH_3), 2.34 (m br, 1H; PCH(CH$_3$)$_2$), 2.27 (m br, 1H; PCH(CH$_3$)$_2$), 2.25 (s, 3H; Ar-CH_3), 2.13 (s, 3H; Ar-CH_3), 1.30 (dd, ^3J(P,H) = 11.5 Hz, ^3J(H,H) = 6.3 Hz, 3H; PCH(CH_3)$_2$), 1.24 (m br, ^3J(H,H) = 6.4 Hz, 3H; PCH(CH_3)$_2$), 1.17 (m br, 3H; PCH(CH_3)$_2$), 0.90 (dd, ^3J(P,H) = 15.3 Hz, ^3J(H,H) = 6.7 Hz, 3H; PCH(CH_3)$_2$), −26.01 ppm (dd, ^1J(Rh,H) = 31.1 Hz, ^2J(P,H) = 18.1 Hz, 1H; Rh-H). Assignment of the ^{1}H NMR signals was confirmed by ^{13}C–^{1}H heteronuclear correlation; ^{13}C{^{1}H} NMR ([D$_6$]acetone, −73 °C): δ = 153.10 (s, Ar), 134.67 (d, J(P,C) = 14.8 Hz, Ar), 134.54 (s, Ar), 132.34 (s, Ar), 126.75 (s, C_{Ar}-H), 124.85 (s, C_{Ar}-H), 61.93 (s, NCH_2), 61.39 (s, NCH_2), 55.98 (s br, NCH_3), 52.77 (s br, NCH_3), 51.80 (s br, NCH_3), 47.56 (s br, NCH_3), 27.28 (d br, ^1J(P,C) = 21.3 Hz, PCH(CH$_3$)$_2$), 25.85 (d br, ^1J(P,C) = 25.8 Hz, PCH(CH$_3$)$_2$), 21.28 (s, Ar-CH$_3$), 20.91 (s, Ar-CH$_3$), 18.94 (s, PCH(CH_3)$_2$), 18.88 (s, PCH(CH_3)$_2$), 18.34 (d, ^1J(P,C) = 32.4 Hz, Ar-CH$_2$-P), 18.05 (s, PCH(CH_3)$_2$), 16.43 (s br, PCH(CH_3)$_2$), 14.20 ppm (d br, ^1J-(Rh,C) = 21.3 Hz, Ar-CH$_2$-Rh). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135 and ^{13}C–^{1}H heteronuclear correlation; ^{31}P{^{1}H} NMR ([D$_6$]acetone, −73 °C): δ = 94.28 ppm (d, ^1J(Rh,P) = 165.3 Hz); ^{19}F{^{1}H} NMR ([D$_6$]acetone, −73 °C): δ = −150.21 ppm (s, free BF_4); ESI MS (MeOH): m^+/z (%): 469 (52) [complex−THF]; m^-/z (%): 87 (100) [BF_4]; elemental analysis calcd (%) for $C_{26}H_{51}BF_4N_2OPRh$ (one THF molecule present): C 49.70, H 8.18; found: C 49.01, H 7.96.

X-ray structural analysis of complex 7 (H_2O adduct): Complex **7** was crystallized at −30 °C from a concentrated acetone solution (the coordinated water molecule probably originates from trace amounts of water in the acetone).

Crystal data: $C_{22}H_{45}N_2OP_2Rh + BF_4$, colorless plate, $0.1 \times 0.1 \times 0.03$ mm^3, monoclinic, $P2_1/c$ (no. 14), a = 11.645(2), b = 11.209(2), c = 20.688(4) Å, α = 90.0°, β = 102.95(3)°, γ = 90.0°, from 20 degrees of data, T = 120(2) K, V = 2631.7(9) Å^3, Z = 4, F_w = 574.29 g mol^{-1}, ρ_{calcd} = 1.449 g cm^{-3}, μ = 0.755 mm^{-1}.

Data collection and processing: Nonius Kappa CCD diffractometer, $Mo_{K\alpha}$ (λ = 0.71073 Å), graphite monochromator, 13284 reflections collected, $-11 \le h \le 11$, $0 \le k \le 11$, $0 \le l \le 21$, frame scan width = 1.5°, scan speed 0.17° min^{-1}, typical peak mosaicity 0.50°, 3881 independent reflections (R_{int} = 0.100). The data were processed with Denzo-Scalepack.

Solution and refinement: The structure was solved by direct methods with SHELXS. Full-matrix least-squares refinement based on F^2 with SHELXL-97. 308 parameters with no restraints, final R_1 = 0.0564 (based on F^2) for data with $I > 2\sigma(I)$ and R_1 = 0.0652 for 2960 reflections, goodness-of-fit on F^2 = 1.097, largest electron density peak = 1.097 Å^{-3}.

H/D exchange experiments for complex 7 in CD_3OD: Complex **7** (22.2 mg, 0.035 mmol) was dissolved in CD_3OD (0.66 mL). The ^{1}H and ^{31}P NMR spectra of this sample were recorded and the solution was warmed to 50 °C for 3.5 h. ^{1}H and ^{31}P NMR spectra of the sample were then recorded again and compared with the initial spectra. No significant changes were observed in the ^{31}P NMR spectrum, indicating that no appreciable decomposition of complex **7** had taken place. In the ^{1}H NMR spectrum, on the other hand, some of the signals had disappeared, which indicated exchange of the respective protons with deuterons from the solvent.

Synthesis of complex 8: A solution of $[Rh(coe)_2(acetone)_2]BF_4$ (69.7 mg, 0.132 mmol) in acetone (0.8 mL) was added dropwise to a solution of ligand **1** (66.3 mg, 0.265 mmol) in acetone (1.0 mL) and the resulting solution was stirred at room temperature for 40 min. The solution was then added to pentane (17 mL), with stirring, to precipitate the product. The liquid phase was decanted and the solids were washed with pentane and dried under vacuum to afford the product (94.2 mg, 0.126 mmol, 95.0 % yield) as a yellow powder. The product was found to exhibit fluxional behavior in solution at room temperature and therefore NMR spectra were recorded both at room temperature and at −20 °C.

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^{1}H NMR ([D$_6$]acetone, 20 °C): δ = 7.00 (s, 1H; Ar, cyclometalated ligand), 6.95 (s, 1H; Ar, cyclometalated ligand), 6.94 (s, 2H; Ar, monodentate ligand), 3.72 (sbr, 1H; Ar-CH_2-P), 3.58 (sbr, 1H; Ar-CH_2-Rh), 3.26 (sbr, 1H; Ar-CH_2-P), 3.20–2.93 (overlapping singlets, 3H; Ar-CH_2-P + PCH(CH$_3$)$_2$ + Ar-CH_2-Rh), 2.86 (sbr, 1H; Ar-CH_2-P), 2.52 (sbr, 1H; PCH(CH$_3$)$_2$), 2.34 (s, 3H; Ar-CH_3, cyclometalated ligand), 2.21 (s, 6H; Ar-CH_3, cyclometalated ligand + monodentate ligand), 1.93 (sbr, 1H; PCH(CH$_3$)$_2$), 1.80 (s, 6H; Ar-CH_3, monodentate ligand), 1.62–1.12 (mbr, 18H; PCH(CH_3)$_2$), 1.08 (sbr, 3H; PCH(CH_3)$_2$), 0.50 (sbr, 3H; PCH-(CH_3)$_2$), −23.11 ppm (sbr, 1H; Rh-H). Assignment of the ^{1}H NMR signals was confirmed by ^{13}C–^{1}H heteronuclear correlation; selected ^{13}C{^{1}H} NMR ([D$_6$]acetone, 20 °C): δ = 130.46 (s, C_{Ar}-H, monodentate ligand), 130.16 (s, C_{Ar}-H, cyclometalated ligand), 128.74 ppm (s, C_{Ar}-H, cyclometalated ligand). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135 and ^{13}C–^{1}H heteronuclear correlation; ^{31}P{^{1}H} NMR ([D$_6$]acetone, 20 °C): δ = 80.48 (dd, ^2J(P,P) = 332.9 Hz, ^1J(Rh,P) = 128.9 Hz), 47.67 ppm (dd, ^2J(P,P) = 332.8 Hz, ^1J(Rh,P) = 118.6 Hz); ^{19}F{^{1}H} NMR ([D$_6$]acetone, 20 °C): δ = −151.83 ppm (s, free BF_4).

^{1}H NMR ([D$_6$]acetone, −20 °C): δ = 6.98 (s, 1H; Ar, cyclometalated ligand), 6.95 (s, 3H; Ar, overlapping cyclometalated + monodentate ligands), 3.79 (m, ^2J(H,H) = 14.1 Hz, 1H; Ar-CH_2-P), 3.56 (m, ^2J(H,H) = 7.1 Hz, 1H; Ar-CH_2-Rh), 3.29 (m, ^2J(H,H) = 14.1 Hz, 1H; Ar-CH_2-P), 3.10 (m, ^2J(H,H) = 14.1 Hz, 1H; Ar-CH_2-P), 3.05 (m, 1H; PCH(CH$_3$)$_2$, overlaps with methylene signal), 2.97 (m, 1H; Ar-CH_2-Rh), 2.81 (m, ^2J-(H,H) = 14.4 Hz, 1H; Ar-CH_2-P), 2.54 (m, 1H; PCH(CH$_3$)$_2$), 2.32 (s, 3H; Ar-CH_3, cyclometalated ligand), 2.30 (m, 1H; PCH(CH$_3$)$_2$, overlaps with methyl signal), 2.22 (sbr, 3H; Ar-CH_3, cyclometalated ligand), 2.20 (sbr, 3H; Ar-CH_3, monodentate ligand), 1.82 (mbr, 1H; PCH(CH$_3$)$_2$), 1.75 (sbr, 6H; Ar-CH_3, monodentate ligand), 1.51 (dd, ^3J(P,H) = 10.6 Hz, ^3J-(H,H) = 6.8 Hz, 3H; PCH(CH_3)$_2$), 1.45 (dd, ^3J(P,H) = 10.8 Hz, ^3J(H,H) = 7.1 Hz, 3H; PCH(CH_3)$_2$), 1.33 (m, 6H; PCH(CH_3)$_2$), 1.24 (dd, ^3J(P,H) = 16.0 Hz, ^3J(H,H) = 7.0 Hz, 3H; PCH(CH_3)$_2$), 1.16 (m, 3H; PCH(CH_3)$_2$), 0.99 (dd, ^3J(P,H) = 15.4 Hz, ^3J(H,H) = 6.9 Hz, 3H; PCH(CH_3)$_2$), 0.34 (dd, ^3J(P,H) = 15.5 Hz, ^3J(H,H) = 6.5 Hz, 3H; PCH(CH_3)$_2$), −22.98 ppm (m, ^1J-(Rh,H) = 29.8 Hz, 1H; Rh-H). Assignment of the ^{1}H NMR signals was confirmed by ^{13}C–^{1}H heteronuclear correlation; ^{13}C{^{1}H} NMR ([D$_6$]acetone, −20 °C): δ = 146.05 (dd, J(P,C) = 9.3 Hz, J(P,C) = 2.8 Hz, Ar), 138.07 (d, J(P,C) = 4.1 Hz, Ar), 137.42 (d, J(P,C) = 4.9 Hz, Ar), 137.16 (d, J(P,C) = 2.6 Hz, Ar), 136.85 (d, J(P,C) = 1.8 Hz, Ar), 135.79 (d, J(P,C) = 2.5 Hz, Ar), 131.68 (s, Ar), 130.54 (s, C_{Ar}-H, monodentate ligand), 130.13 (s, C_{Ar}-H, cyclometalated ligand), 128.76 (s, C_{Ar}-H, cyclometalated ligand), 25.70 (d, ^1J(P,C) = 25.4 Hz, PCH(CH$_3$)$_2$), 25.27 (d, ^1J-(P,C) = 23.7 Hz, PCH(CH$_3$)$_2$), 22.65 (dd, ^1J(P,C) = 16.7 Hz, ^2J(Rh,C) = 2.1 Hz, PCH(CH$_3$)$_2$), 22.21 (sbr, Ar-CH$_3$, monodentate ligand), 21.21 (dd, ^1J(P,C) = 11.0 Hz, ^3J(Rh,H) = 1.3 Hz, Ar-CH$_2$-P), 20.95 (s, Ar-CH$_3$, monodentate ligand), 20.81 (s, Ar-CH$_3$, cyclometalated ligand), 20.75 (d, ^1J-(P,C) = 22.9 Hz, Ar-CH$_2$-P), 20.52 (d, ^2J(P,C) = 5.7 Hz, PCH(CH$_3$)$_2$), 20.34 (d, ^2J(P,C) = 4.0 Hz, PCH(CH$_3$)$_2$), 20.22 (s, Ar-CH$_3$, cyclometalated ligand), 19.49 (s, PCH(CH$_3$)$_2$), 19.39 (s, PCH(CH$_3$)$_2$), 18.84 (d, ^2J(P,C) = 2.0 Hz, PCH(CH$_3$)$_2$), 18.08 (d, ^2J(P,C) = 3.1 Hz, PCH(CH$_3$)$_2$), 17.85 (m, PCH(CH$_3$)$_2$), 16.13 (d, ^2J(P,C) = 3.4 Hz, PCH(CH$_3$)$_2$), 14.44 ppm (d, ^1J-(Rh,C) = 28.0 Hz, Ar-CH$_2$-Rh). Assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT 135 and ^{13}C–^{1}H heteronuclear correlation; ^{31}P{^{1}H} NMR ([D$_6$]acetone, −20 °C): δ = 80.84 (dd, ^2J(P,P) = 333.3 Hz, ^1J-(Rh,P) = 128.4 Hz), 48.13 ppm (dd, ^2J(P,P) = 333.3 Hz, ^1J(Rh,P) = 117.7 Hz); elemental analysis calcd (%) for $C_{35}H_{60}BF_4OP_2Rh$ (one acetone molecule present): C 56.16, H 8.08; found: C 56.05, H 8.02.

Spin saturation transfer experiments:[37] Saturation transfer experiments were performed for complexes **2** and **7** by selective saturation of the hydride resonance in the ^{1}H NMR spectrum. The response of the signals of the appropriate aromatic and aliphatic protons was detected by comparison (difference spectrum) with a control experiment in which a signal-free area was irradiated under the same conditions.

CCDC-648207 (**5** from acetone), CCDC-648208 (**7**), and CCDC-648209 (**5** from THF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This research was supported by the Israel Science Foundation, the DIP program for German–Israeli Cooperation, and the Helen and Martin Kimmel Center for Molecular Design. D.M. is the holder of the Israel Matz Professorial Chair. The authors would like to thank the referees of this manuscript for their valuable comments.

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[7] Ligands of this type have also been described by Werner and coworkers. For examples, see: a) H. Werner, *Dalton Trans.* **2003**, 3829–3837; b) G. Canepa, C. D. Brandt, K. Ilg, J. Wolf, H. Werner, *Chem. Eur. J.* **2003**, *9*, 2502–2515; c) G. Canepa, C. D. Brandt, H. Werner, *Organometallics* **2004**, *23*, 1140–1152.

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[9] Determination of the number of coordinated solvent molecules requires the removal of excess solvent. This can be accomplished by precipitation and/or removal of the solvent under vacuum. Unfortunately, attempts to isolate pure samples of **2a** by these methods were unsuccessful due to the instability of the complex in the absence of a stabilizing solvent (see the main text for further discussion).

[10] It was shown by NMR and IR spectroscopies, as well as X-ray crystallography, that complex **4b** contains three solvent molecules (see ref. [8]). This conclusion may also be applied to **4a**, because methanol is both smaller in size (less steric hindrance) and more strongly-coordinating than acetone. We may then further extend this conclusion to **2a**, because the metal center in this complex is less sterically hindered than in **4a** (ligand **1** is less bulky than **3**).

[11] Complex **4** may also undergo dimerization, as was observed for similar systems (unpublished results), but such a process has not been reported thus far.

[12] To the best of our knowledge, this is the only case reported thus far of a dinuclear Rh^{II} complex with an η^6-bound benzenoid ligand. For examples of dinuclear Rh^{II} complexes with benzenoid ligands in other binding modes, see: a) F. A. Cotton, E. V. Dikarev, S.-E. Stiriba, *Organometallics* **1999**, *18*, 2724–2726; b) H. Wadepohl, A. Metz, H. Pritzkow, *Chem. Eur. J.* **2002**, *8*, 1591–1602; c) M. A. Petrukhina, A. S. Filatov, Y. Sevryugina, K. W. Andreini, S. Takamizawa, *Organometallics* **2006**, *25*, 2135–2142.

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[15] It should be noted that ^{103}Rh chemical shifts do not correlate well with the oxidation state of the metal. They are, however, strongly influenced by ligand type and complex geometry. For a review of this topic see: J. M. Ernsting, S. Gaemers, C. J. Elsevier, *Magn. Reson. Chem.* **2004**, *42*, 721–736.

[16] a) F. M. Dixon, J. R. Farrell, P. E. Doan, A. Williamson, D. A. Weinberger, C. A. Mirkin, C. Stern, C. D. Incarvito, L. M. Liable-Sands, L. N. Zakharov, A. L. Rheingold, *Organometallics* **2002**, *21*, 3091–3093; b) F. M. Dixon, M. S. Masar III, P. E. Doan, J. R. Farrell, F. P. Arnold Jr., C. A. Mirkin, C. D. Incarvito, L. N. Zakharov, A. L. Rheingold, *Inorg. Chem.* **2003**, *42*, 3245–3255.

[17] To the best of our knowledge, no crystal structure of analogous Rh^{II}-benzyl complexes has been reported elsewhere.

[18] The reported initial concentration of complex **2** was obtained by reacting $[Rh(coe)_2(acetone)_2]BF_4$ and ligand **1**, each at 80 mM concentration (after mixing). The relatively low concentration of **2** obtained in this reaction is due to the formation of other products, as described in the main text.

[19] The concentration of complexes was estimated on the basis of $^{31}P\{^1H\}$ NMR spectra and the initial concentration of precursors ($[Rh(coe)_2(acetone)_2]BF_4$ and ligand **1**).

[20] The amount of minor product decreased even further as the system approached equilibrium at room temperature. See the main text for further information.

[21] As suggested in our previous publication (ref. [8]), the chemical exchange observed by SST is due to rapid C–H reductive elimination without complete detachment of the arene moiety from the metal center (a process which involves agostic intermediates).

[22] The fact that addition of acetonitrile to complex **5** leads to a product ratio of **2c**:**6a** ≈ 1:1 can be rationalized on the basis of the structure of complex **5** (Figure 1a). This is essentially made up of one unit of complex **2** and one unit of complex **6** (without the solvent molecules), and hence the solvent-promoted breakup of complex **5** should first lead to an equimolar mixture of **2c** and **6a**.

[23] We have previously shown that in complex **4** the bridging methylene protons are also involved in the exchange. For further details, see ref. [8].

[24] Similar observations were previously reported by our group for complex **4**, see ref. [8].

[25] a) D. Milstein, *J. Am. Chem. Soc.* **1982**, *104*, 5227–5228; b) D. Milstein, *Acc. Chem. Res.* **1984**, *17*, 221–226.

[26] Complex **8** was found to exhibit fluxional behavior in solution at room temperature. Therefore, characterization of this complex by NMR spectroscopy was done both at room temperature and −20 °C (see Experimental Section). The fluxionality of complex **8** and related issues will be discussed elsewhere.

[27] The mechanism of this reaction is unclear, but it is unlikely to involve predissociation of ligand **1** from **8**, since this complex was found to be stable in acetone, even at elevated temperatures (e.g., 90 min at 60 °C), with no free ligand being observed. Further observations related to complex **8** will be reported elsewhere.

[28] B. Rybtchinski, R. Cohen, Y. Ben-David, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **2003**, *125*, 11041–11050.

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[37] For previous examples to the use of spin saturation transfer in studies of chemical exchange in rhodium systems, see: A. Vigalok, H.-B. Kraatz, L. Konstantinovski, D. Milstein, *Chem. Eur. J.* **1997**, *3*, 253–260; and ref. [8].

Received: May 26, 2007
Revised: August 17, 2007
Published online: September 28, 2007

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