Reversible Activation of Water by an Air and Moisture Stable Frustrated Rhodium Nitrogen Lewis Pair

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Abstract: *$[Cp^*Rh(\kappa^3N,N',P\text{-}\mathbf{L})][SbF_6]$ ($Cp^* = C_5Me_5$), bearing a guanidine-derived phosphano ligand* **L**, *behaves as a "dormant" frustrated Lewis pair and activates H_2 and H_2O in a reversible manner. When D_2O is employed, a facile H/D exchange at the Cp* ring takes place through sequential $C(sp^3)-H$ bond activation.*

Activation of the O−H bond of water constitutes an important step in addressing the challenge of the catalytic functionalization of water and generation of renewable energy.[1] Activation of water includes strategies such as oxidative addition to transition-metal complexes[2] or to main group species,[3] metal-ligand cooperative chemistry,[4] O−H bond weakening either via water coordination to a metal center[5] or through the second coordination sphere interaction[6] and σ-bond metathesis.[7]

On the other hand, the last decade has witnessed the development of a new class of intra- or inter-molecular systems in which a Lewis acid and a Lewis base do not yield the classical Lewis acid/base adduct because of steric and/or electronic factors. In such systems, termed "frustrated Lewis pairs" (FLPs), the coexisting Lewis acid/Lewis base pairs exhibit cooperative behavior rendering excellent results in fields as relevant as those of small molecules activation or catalysis.[8] In the first reported examples, the roles of Lewis acid and Lewis base were played by main group elements, mostly boron (acid) and nitrogen or phosphorus (base). Of growing interest is the development of FLPs in which transition-metal species appear as one of the components[8d,f,9] with the aim of combining the powerful cooperative main group FLP reactivity with the rich transition-metal chemistry. For some FLP systems, the equilibrium between the dissociated acid and base and the classical Lewis acid/base adduct was detected. Interes-

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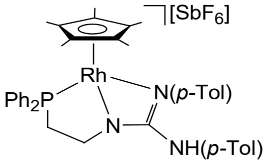
tingly, FLP reactivity has been observed even when the equilibrium was almost completely shifted toward the classical Lewis acid-base adduct, provided that the dissociated state was thermally accessible.[10] For this reactivity the concept of "thermally induced frustration" was introduced[11] and the terms "masked"[12] and "dormant"[13] have been used to describe the involved FLPs.

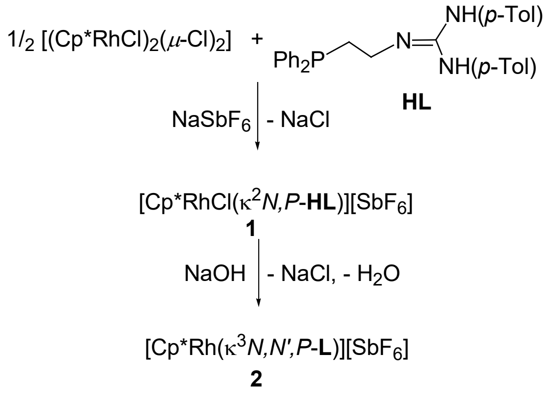
Although water activation by FLPs is known[14] and, recently, a few water-tolerant FLP systems have been reported,[15] moisture sensitivity is one of the limiting factors for the application of this type of systems in many catalytic transformations. Due to their high acidity, FLPs form water adducts that can be easily deprotonated by soft bases (for example, donor solvents) yielding species inactive for FLP chemistry.[14a,f,16]

Here we report on compound **2** (Chart 1), an air and moisture stable complex featuring a strong but constrained Rh−N(*p*-Tol) Lewis acid–base interaction, that is able to activate H_2O (and D_2O) in a reversible manner following an FLP reactivity pattern. Notably, the water activation process results in a facile H/D exchange of the Cp* protons. Complex **2** also activates heterolytically dihydrogen.

Chart 1. The Complex [Cp*Rh(κ^3*N,N',P*-L)][SbF$_6$] (2)



Reaction of the dimer [(Cp*RhCl)$_2$(μ-Cl)$_2$] with the phosphano-guanidine compound **HL** −prepared in situ from 2-(1-diphenylphosphano)ethylamine and 1,3-di-*p*-tolylcarbodiimide− in the presence of NaSbF$_6$ affords [Cp*RhCl(κ^2*N,P*-**HL**)][SbF$_6$]



Eq. 1

(**1**). Base induced HCl elimination from **1** renders [Cp*Rh(κ^3*N,N',P*-**L**)][SbF$_6$] (**2**) (Eq. 1, see SI). The molecular structure of complex **2** (Figure 1, SI)[17] reveals that the ligand **L** presents a *fac* κ^3*N,N',P* coordination mode that probably forces the central N(1) atom to adopt a pyramidal geometry (Σ°N(1) = 327.40(7)°). Accordingly, the small N(1)−Rh−N(2) and N(1)−C(25)−N(2) angles, 62.78(6) and 110.60(15)°, respectively, far from the ideal hybridization values, reflect the strain of the four-membered metalacycle Rh−N(1)−C(25)−N(2).

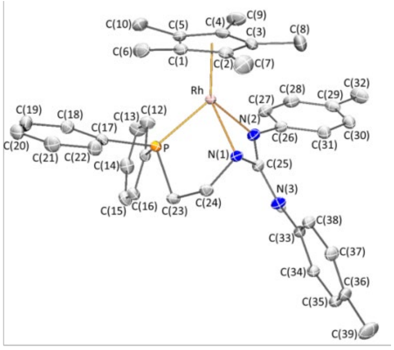


Figure 1. Molecular structure of the cation of complex **2**. For clarity, hydrogen atoms (except the NH proton) have been omitted. Selected bond lengths (Å) and angles (°): Rh−P 2.3146(5), Rh−N(1) 2.1054(14), Rh−Ct 1.8211(1), Rh−N(2) 2.1274(15), N(1)-C(25) 1.358(2), N(2)-C(25) 1.324(2), N(3)-C(25) 1.368(2); P−Rh−N(1) 80.48(4), P−Rh−Ct 133.42(1), P−Rh−N(2) 91.75(5), N(1)−Rh−Ct 131.65(1), N(1)−Rh−N(2) 62.78(6), Ct−Rh−N(2) 130.60(1). Ct represents the centroid of the C_5Me_5 ring.

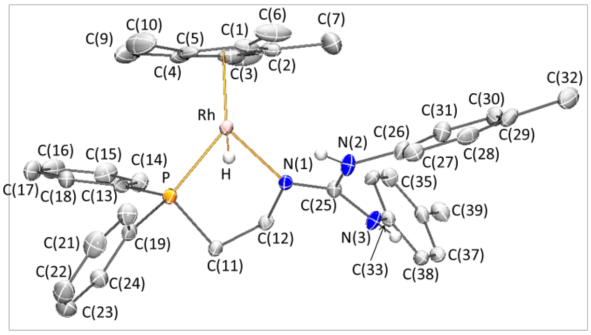


Figure 2. Molecular structure of the cation of complex **3**.

These crystal data gave us reasonable grounds for believing that this compound could show an FLP behavior. In fact, complex **2** reacts with H_2 affording [Cp*RhH(κ^2*N*,*P*-**HL**)][SbF$_6$] (**3**), a rhodium hydrido complex bearing a new N−H bond as shown by its crystal structure (Figure 2)[17]. The observed RhH···HN(2) separation, 2.20(7) Å, is shorter than twice the hydrogen Van der Waals radius, 2.4 Å, indicating a significant H···H interaction between the protic NH and hydridic RhH functionalities. Notably, heating **3** at 393 K for 30 min, about 30 % of clean conversion to **2** was measured by $^{31}P\{^1H\}$ NMR spectroscopy, thus indicating that **2** is a system capable of affording reversible uptake and release of H_2.[8,9]

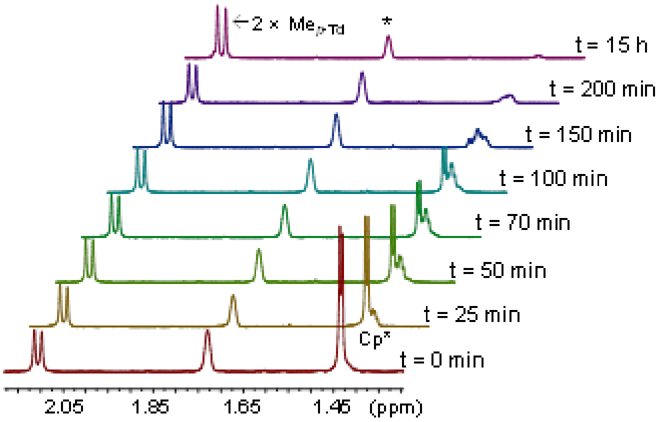


Figure 3. Monitoring of the sequential deuteration of complex **2** by NMR. Evolution of the ^1H NMR spectra of complex **2** in 78 % THF-d_8/22 % D_2O at 213 K. Asterisk denotes residual not fully deuterated THF.

Complex **2** also activates the polar O−H bond of water. Notably, addition of excess of water to THF solutions of complex **2** does not produce significant changes in its ^1H and ^{31}P NMR spectra. However, NMR and MS measurements clearly indicate that complex **2** reacts with deuterated water in a reversible fashion resulting in the deuteration of the Cp* group. The ^{31}P {^1H} NMR spectrum of THF-d_8/D_2O (78 % / 22 %, v/v) solutions does not change over time but the ^1H NMR spectrum was found to be time-dependent. In particular, a gradual decreasing of the doublet attributed to the Cp* protons together with the concurrent appearance of a broad signal at almost the same chemical shift was observed (Figure 3). The variation over time of the mass spectra of these solutions is shown in Figure 4. This whole set of data evidences the progressive deuteration of the methyl groups of the Cp* ring and, due to the low rotation barriers about the Cp*−Rh and C^{ring}−CH_3 axes, a sequential deuteration up to the $C_5(CD_3)_5$ isotopomer (**2**-d_{15}) occurred (Figure 4).

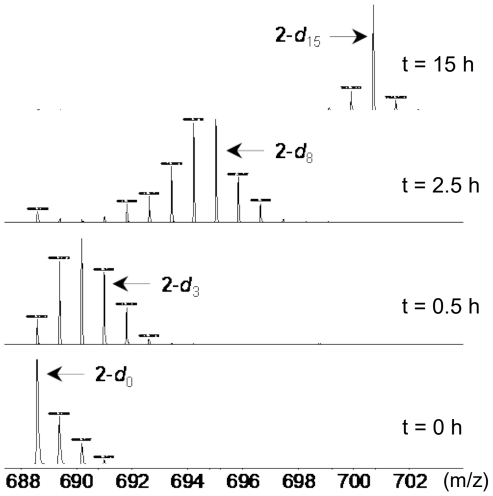


Figure 4. Monitoring of the sequential deuteration of complex **2** by MS. Evolution of the mass spectra of complex **2** in 78 % THF-d_8/22 % D_2O at 313 K.

It is interesting to point out that, although hydrogen isotope exchange reactions are well known,[18] examples of H/D exchange involving the methyl groups of the Cp* ligand are very scarce.[19] For this process, mechanisms in which a coordinated OH ligand deprotonates the Cp* ring followed by formation of a Rh(I)-fulvene species were proposed.[19] However, none of these deuterated complexes has been structurally characterized. To unambiguously determine the deuterated positions, a neutron diffraction experiment has been performed (see SI).[17] Structural analysis evidenced the complete deuteration of the methyl groups of the Cp* ligand and the partial deuteration of the N(3)−H proton in which a substitutional disorder has been found, with 0.68/0.32 H/D ratio. The structural model of **2**-d_{15} is depicted in Figure 5.

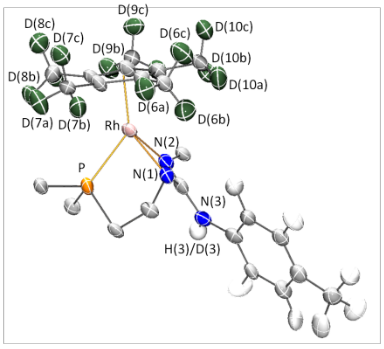


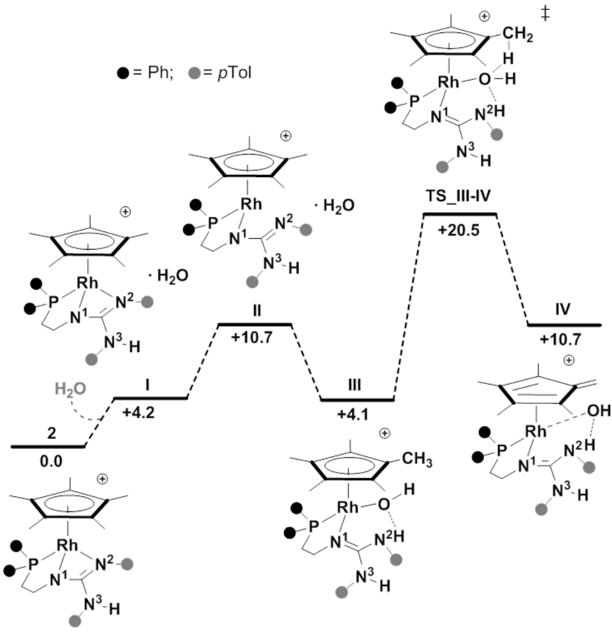
Figure 5. Molecular structure of the cation of complex **2-d_{15}** with a 30 % occupancy level. For clarity, the two phenyl groups of the PPh_2 fragment and the *p*-tolyl group bonded to the N(2) have been omitted.

Kinetic measurements indicate that the deuteration process obeys a pseudo-first-order rate law with k_{obs} values from 7.35 × 10^{-3} to 1.07 × 10^{-1} s^{-1}, in the 298-333 K temperature range. The linear fitting of ln(k_{obs}/T) *vs*. 1/T gives a $\Delta G^{\ddagger}$ value of 20(1) kcal·mol^{-1}. Notably, addition of NaOH does not change significantly the deuteration rate: at 313 K, the k_{obs} is 2.15 × 10^{-2} s^{-1}, in the absence of NaOH, and 2.12 × 10^{-2} s^{-1}, in the presence of 1 equiv. of NaOH (SI). This observation indicates that the mechanism operating in the deuteration of **2** should be different from those previously reported.[19]

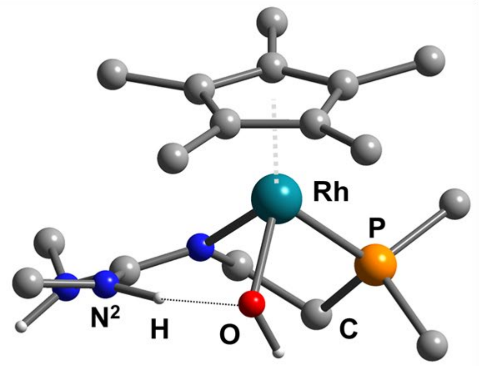
The formation of **2**-d_{15} from **2** is reversible. At 313 K, a 78 % THF-d_8/22 % H_2O solution of **2**-d_{15} evolves to **2** with an observed pseudo-first-order rate constant of 1.81 × 10^{-3} s^{-1}. The high measured ratio, k_H/k_D = 11.9, indicates that the rate-determining step for the exchange process is the C−H(D) bond cleavage.

It is relevant that throughout the studied H/D exchange process for **2**, the only detectable (^{1}H and ^{31}P NMR) species is complex **2** with different deuteration degrees. Complex **2** is an 18 electron complex that can be easily isolated and that it is stable enough to be handled under air at RT, in both solid state and solution, without apparent decomposition.

In order to gain insight into the reversible H/D exchange, DFT calculations (see SI) were performed concluding that the exchange should take place as a consequence of the activation of a H_2O (D_2O) molecule by the “dormant” FLP **2**.[20] Figure 6 shows the Gibbs free energy profile along with some selected data. The formation of the key intermediate **III** should take place stepwise: the Rh–N^2 bond of **I** breaks affording the coordinatively unsaturated complex **II**;[21] on its turn, **II** –the truly active FLP– reacts with H_2O rendering **III**. Notably, as an evidence of the activation of the H_2O molecule promoted by the FLP, **III** formally contains an OH ligand (Rh−O 2.075 Å) exhibiting an unusually short N^2–H···O hydrogen bond (N^2–H 1.069 Å, O···H 1.570 Å, N^2···O 2.605 Å, N–H–O 161.3°, Figure 6). The transition state for **II→III** could not be located on the potential energy surface. Nevertheless, a relaxed PES scan of the Rh···O distance of **III** indicates that the step **II→III** should be barrierless and that, as the water molecule approaches the Rh/N^2 FLP species **II**, an OH···N^2 interaction forms in the first place, followed by the coordination of the oxygen atom to the rhodium center and the final splitting of the O–H bond (see SI). Finally, **III** evolves to the fulvene rhodium(I) derivative **IV** through the transition state **TS_III-IV**. It is worth mentioning that the newly formed H_2O molecule of **IV** is weakly interacting with the metal center (Rh–O 2.505 Å) and an N^2–H···O hydrogen bond is still present (N^2–H 1.027 Å, O···H 1.786 Å, N^2···O 2.797 Å, N^2–H–O 167.2°), although weaker than that described for **III**. In view of the Gibbs free energy profile shown in Figure 6, the formation of **IV** should be reversible and operative under the experimental conditions of the observed deuteration of the Cp* ligand of **2**. Thus, as an essential concluding step of the deuteration process under discussion, a fast H_2O/D_2O exchange on **IV** should take place, eventually resulting in the progressive H/D exchange at the Cp* ligand of **2**.[22]



	2 (calc.)	I	II	III	TS_III-IV	IV
C-N^1 (Å)	1.354	1.354	1.389	1.317	1.312	1.310
C-N^2 (Å)	1.320	1.325	1.298	1.348	1.353	1.356
C-N^3 (Å)	1.359	1.357	1.383	1.368	1.370	1.370



N^2-H	1.069 Å
O···H	1.570 Å
N^2···O	2.605 Å
O-H-N^2	161.3°

Figure 6. (*top*) Gibbs free energy profile (B3PW91-GD3/def2-SVP//M06/def2-TZVP, kcal·mol^{-1}, 298 K, THF) for the hydrogen exchange at the Cp* ligand of **2** along with selected interatomic distances. (*bottom*) View of **III** with the selected data for the N^2–H···O hydrogen bond. All phenyl and tolyl groups and most hydrogen atoms are omitted for clarity.

Finally, regarding the role of the guanidine site in the exchange process, it is remarkable that a substantial electronic rearrangement takes place in the course of the hydrogen abstraction from the Cp* ligand. Indeed, as suggested by the C–N bond lengths shown in Figure 6, the C–N^3 bond remains basically single throughout the process **2** + H_2O $\leftrightarrows$ **IV**. On the other hand, the bonds C–N^1 and C–N^2 change from single to double and from double to single, respectively, as a consequence of the H–OH activation and the N^2–H bond formation.

In summary, the *fac* κ^3*N,N',P* coordination mode of **L** by the Cp*Rh(III) fragment generates the "dormant" FLP **2**. Complex **2** belongs to the class of thermally induced FLPs and presents the advantage of being air and moisture stable. The existence of a strong ring strain within the Rh−N−C−N four-membered cycle most probably facilitates the reversible cleavage of the Rh−N(sp^2) bond and makes accessible frustrated Lewis pair sites available for the reversible activation of both polar, H−O−H, and non-polar, H_2, bonds. When D_2O was employed, the generated Rh−OD intermediate is responsible for an unusual H/D exchange of the Cp* methyl protons. Further studies aimed at developing related complexes containing M−donor atom strained bonds and their application to new FLP activation processes are currently in progress in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: coordination modes · frustrated Lewis pairs · H/D exchange · HO−H bond activation · reaction mechanisms

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[20] Alternative pathways were also considered and studied by DFT calculations. In a stepwise and reversible way, either N^1 or N^2 (once dissociated from the metal center) could abstract one hydrogen atom from the Cp* ligand, thus rendering a coordinated fulvene and an N−H group prone to undergo H/D exchange by

reaction with D_2O. Although plausible, DFT calculations rule out that these pathways are operative under the experimental conditions for the Cp* deuteration in **2** (see SI).

[21] It is worth mentioning that the N^1 atom of **II** displays an almost planar geometry ($\Sigma^o N^1 = 359.3^o$).

[22] Alternatively, H/D exchange involving D_2O and acidic protons of either **III** (O−H, N^2−H) or **IV** (N^2−H) can provide deuterium atoms for the Cp* deuteration in **2**.

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And the beast wakes up: The dormant FLP complex of the Scheme can be isolated as an air and moisture stable solid. But, in solution, the dissociated active FLP state is easily accessible and the complex activates H_2O and H_2, under soft conditions, in a reversible manner. Concurrently, a facile H/D exchange at the Cp* ligand, associated with the water activation, was observed.