

Supporting Information for:

**Stereoselective Formation and Catalytic Activity of
Hydrido(acylphosphane)(chlorido)(pyrazole}rhodium(III) complexes.
Experimental and DFT Studies.**

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Table SI-1. PCM corrected (benzene) relative free energy values (ΔG , kcal/mol) calculated at M062X/6-311++G(2d,2p)/B3LYP/6-31G(d,p)&LANL2DZ level of theory, for the different isomers/rotamers of compounds 1-Hpz, 1-Hmpz and 1-Hdmpz, respectively, “uns.” refers to unstable, meaning that the indicated structure converged to a different rotamer upon DFT optimization. “—” sign: the indicated rotamer is not plausible. For clarity, most stable structures were named following the same nomenclature as in the main text.

^acis or trans disposition of chlorido with respect to hydrido. ^bNature of R and R' in pyrazole trans to phosphorus. ^cNature of R and R' in pyrazole cis to phosphorus. ^dAcceptor group of the hydrogen bond established by the pyrazole trans to the phosphorus atom.

^eAcceptor group of the hydrogen bond established by the pyrazole *cis* to the phosphorus atom.

Compound	ΔG_{solv}		H-bond	
	cis ^a	trans ^a	OH/CHO ^b	pyrazole ^d
3-Hdmpz	3a-Hdmpz 0.60	3b-Hdmpz 0.00		chlorido
4-Hdmpz	4-Hdmpz 0.00		2.99	O-acyl chlorido
	3.91		5.93	chlorido chlorido
	-		-	hydrido chlorido
5-Hdmpz		uns	5b-Hdmpz 0.82	O-acyl ^c chlorido ^c
		uns	uns	chlorido ^c hydrido ^c
	5a-Hdmpz 0.00		uns	chlorido

Table SI-2. PCM corrected (benzene) relative free energy values (ΔG , kcal/mol) calculated at M062X/6-311++G(2d,2p)//B3LYP/6-31G(d,p)&LANL2DZ level of theory, for the different isomers/rotamers of compounds 3-Hdmpz, 4-dmHpz and 5-dmHpz, respectively. “uns.” refers to unstable, meaning that the indicated structure converged to a different rotamer upon DFT optimization. “-“ sign: the indicated rotamer is not plausible. For clarity, most stable structures were named following the same nomenclature as in the main text.

^acis or trans disposition of chlorido with respect to hydrido. ^bAcceptor group of the hydrogen bond established by OH in **4-Hdmpz** or H in CHO of **5-Hdmpz**. ^cConsidering the moderate polarity of the C-H bond in aldehydes, the quantitative significance of the indicated hydrogen bonds may be modest. Still they could be identified based on the directionality of the groups involved. Oxygen atom in CHO of **5-Hdmpz** was not found to be able to establish hydrogen bonds. ^dAcceptor group of the hydrogen bond established by the pyrazole.

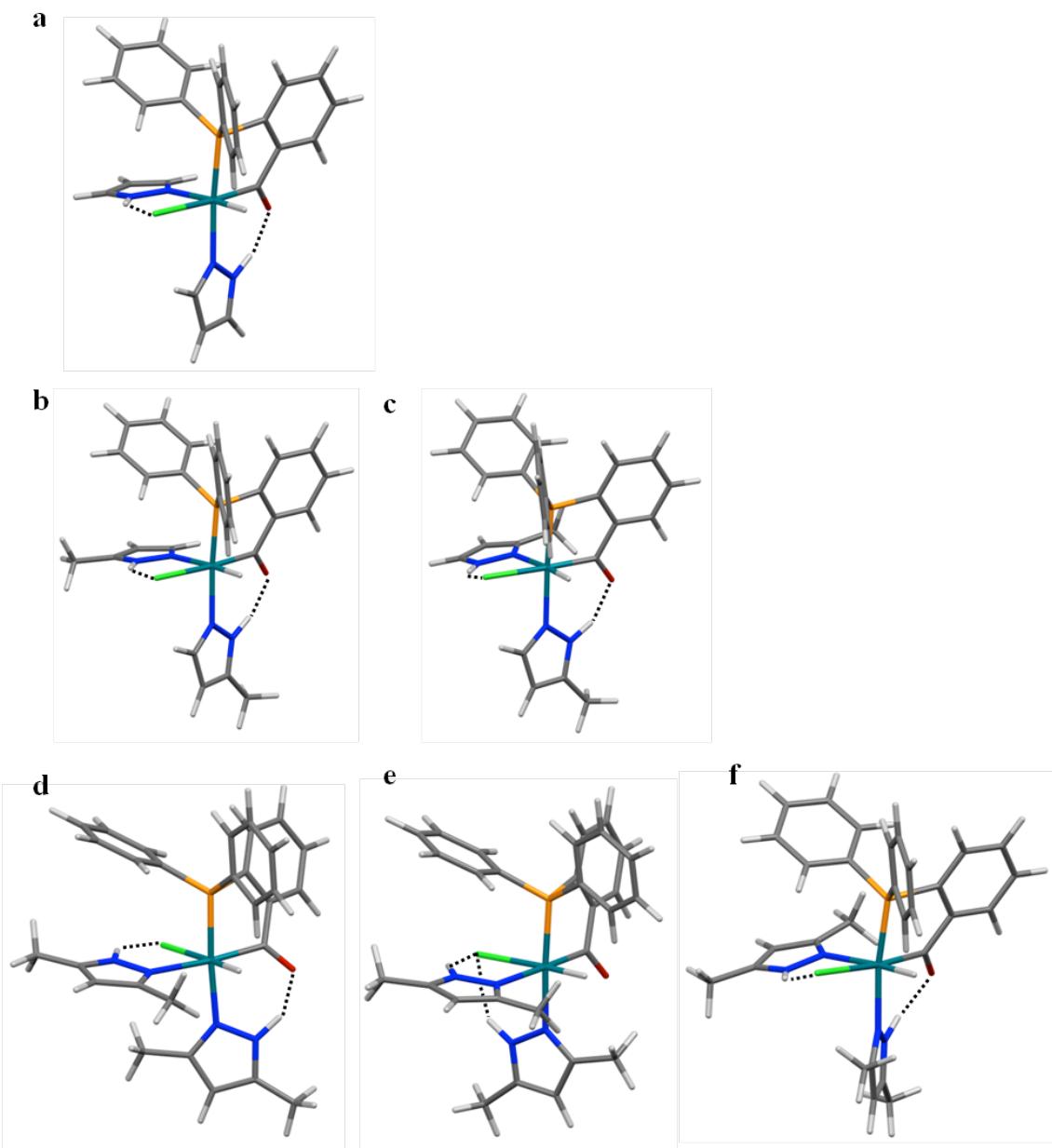


Figure SI-1. Stick representation of the gas phase optimized structures. a) 1-Hpz; b) 1a-Hmpz; c) 1a'-Hmpz; d) 1b-Hdmpz; e) 1b'-Hdmpz; f) 1a-Hdmpz. Atom coloring: rhodium: dark green; chlorine: light green; phosphorus: orange; oxygen:red; nitrogen: blue; carbon: grey; hydrogen: white. Hydrogen bonds are indicated as dashed lines.

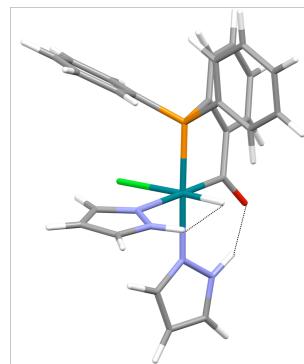


Figure SI-2. Stick representation of an unstable rotamer ($\Delta G = 7.43\text{kcal/mol}$) of a trans (H/Cl) isomer of 1-Hpz, where the O-acyl and the hydrido group act as hydrogen bond acceptors.

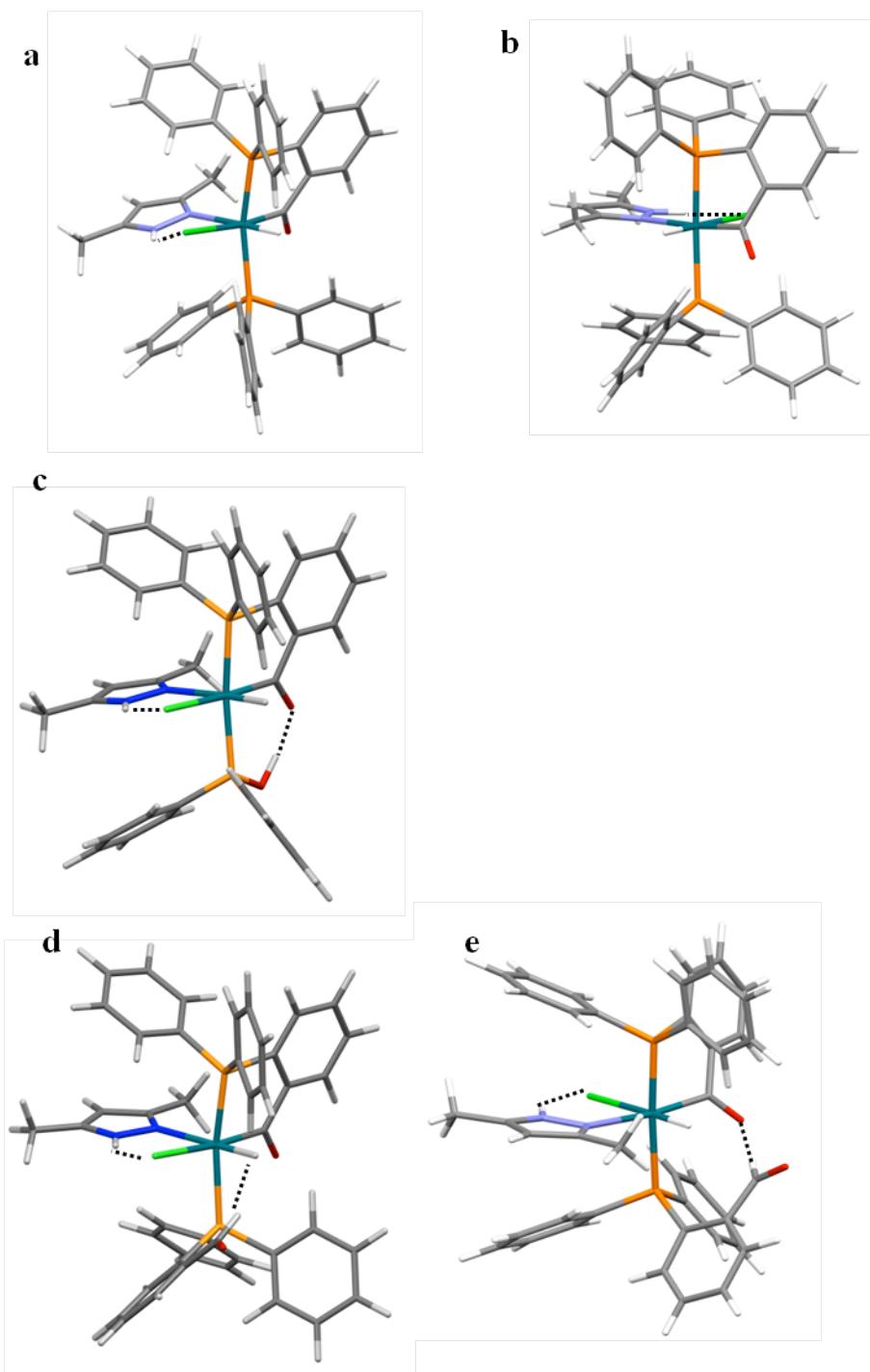


Figure SI-3. Stick representation of the gas phase optimized structures. a) 3a-Hdmpz; b) 3b-Hdmpz; c) 4-Hdmpz; d) 5a-Hdmpz; e) 5b-Hdmpz. Atom coloring: rhodium: dark green; chlorine: light green; phosphorus: orange; oxygen:red; nitrogen: blue; carbon: grey; hydrogen: white. Hydrogen bonds are indicated as dashed lines.

Table SI-3. Crystal data and structure refinement for compounds **2-Hpz**, **3a-Hdmpz** and **7-Hpz**.

Compound	2-Hpz	3a-Hdmpz	7-Hpz
Formula	C ₂₆ H ₂₄ N ₄ OCl ₄ PRh	C ₄₃ H ₃₉ N ₂ OCl ₄ P ₂ Rh	C ₄₁ H ₃₂ N ₂ O ₂ CIP ₂ Rh
M _r	684.17	906.41	784.99
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P-1 (2)	P21/n
a (Å)	17.0245(2)	12.0092(6)	12.142(4)
b (Å)	11.2585(2)	14.0790(9)	15.103(5)
c (Å)	28.3044(4)	14.3161(9)	18.918(6)
α (°)	90.00	104.680(5)	90.00
β (°)	94.3310(10)	105.492(5)	104.432(5)
γ (°)	90.00	111.777(5)	90.00
V (Å ³)	5409.62(14)	1991.0(2)	3359.7(19)
Z	8	2	4
D _c (g cm ⁻³)	1.603	1.512	1.552
μ (MoK _α) (mm ⁻¹)	1.017	6.988	0.724
T (K)	100(2)	100(2)	100(2)
Observed reflections	5849 (5165)	7267 (7850)	12068 (10635)
R _{int}	0.0353	0.0256	0.01814
Parameters	307	484	442
GOF	1.040	1.062	0.943
R ₁ ^{a,b}	0.0338 (0.0284)	0.0372 (0.0342)	0.0878 (0.1999)
wR ₂ ^c	0.0687 (0.0660)	0.0920 (0.0888)	0.1837 (0.1394)
Largest difference in peak and hole (e Å ⁻³)	0.484 and -0.376	1.092 and -0.544	1.408 and -0.948

^a R₁ = $\sum |F_o| - |F_c| / \sum |F_o|$.

^b Values in parentheses for reflections with $I > 2\sigma(I)$.

^c wR₂ = $\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

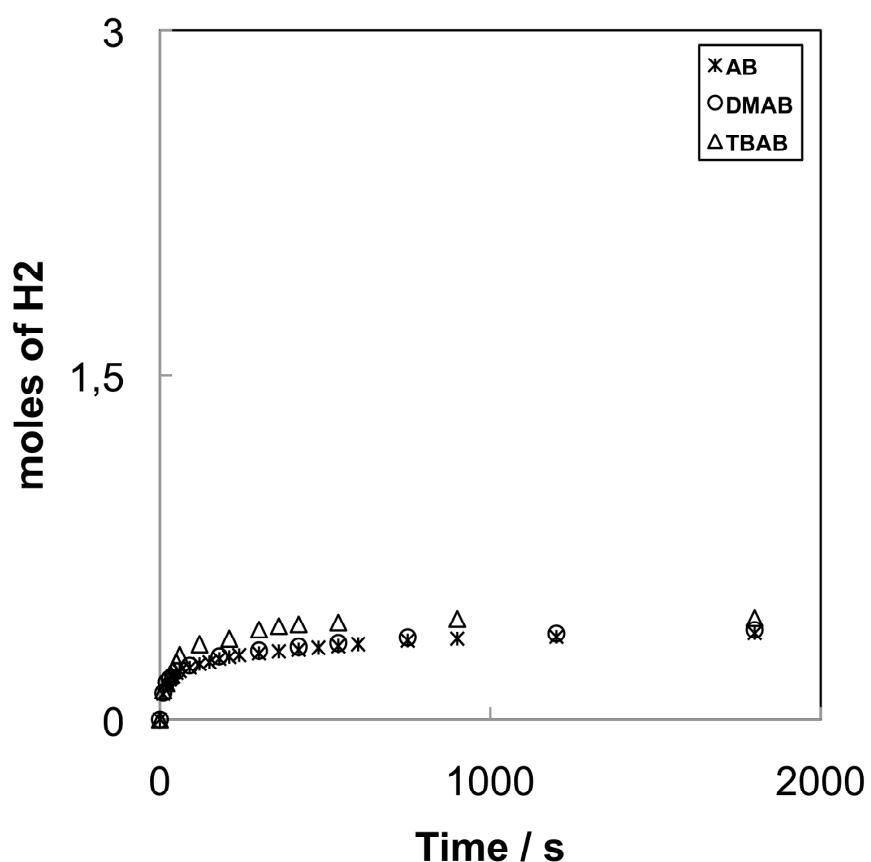


Figure SI-4. Blank tests for the hydrogen release from AB (x), TBAB (Δ), or DMAB (\circ) as substrates, in the absence of catalyst in THF/H₂O = 1:1 mixtures. T, 298 K.