SUPPORTING INFO

Ruthenium mediated halogenation of white phosphorus: synthesis and reactivity of the unprecedented P_4Cl_2 moiety.

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VT-NMR Study

A total line shape analysis of the spectra acquired at different temperatures was carried out using the DNMR tool of TopSpin.[1] The rate constants of the chemical exchange process k were determined by a simplex iteration, fitting the simulated to the experimental spectra. A plot of the linearized Eyring allowed calculating enthalpy ΔH and entropy ΔS of activation from the linear fit of the data.

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H}{R}\cdot\frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R}$$

$$\text{Slope} = -\frac{\Delta H}{R} \qquad \text{Intercept} = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R}$$

k_B = Boltzmann constant; h = Planck constant

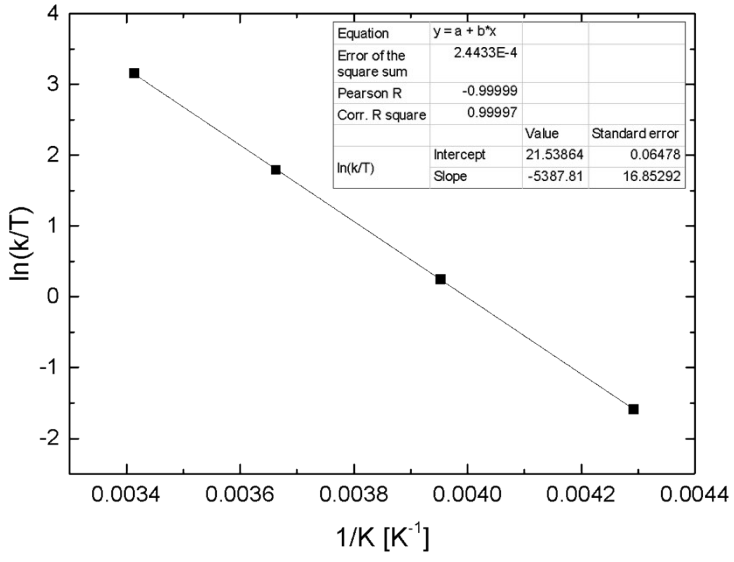

Fig. S1 Eyring plot of the rate constants of the chemical exchange process taking place in **1**.

The bromide derivative **1-Br** is endowed with dynamic behavior at room temperature as the chloride analogue **1**, showing a broad doublet around 261 ppm (w½ = 255 Hz, ^{1}J = 387 Hz), attributed to the two bromine-substituted phosphorus atoms and a very broad singlet around -58 ppm (w½ = 1300 Hz) whose resonance concurs with the other two phosphorus atoms, see Figure S2. Besides, a triplet at 40 ppm ($^{2}J_{PP}$ = 37.0 Hz) corresponds to PCy_3**.** At −40 ºC, the fine structure of the spectrum is well resolved into an ABMXY spin system. At 0 ºC P1 and P4 go through coalescence, whereas P2 and P3 coalesce into a broad bump at about 20 °C. Unfortunately, both signals disappear at higher temperature, showing only an uninformative singlet at 32 ppm, indicating the decomposition of **1-Br**. The latter is more air and moisture sensitive than **1** and its synthesis and manipulation requested strictly anhydrous and oxygen-free conditions, thus the less stability prevented us to obtain suitable crystals for X-ray diffraction.

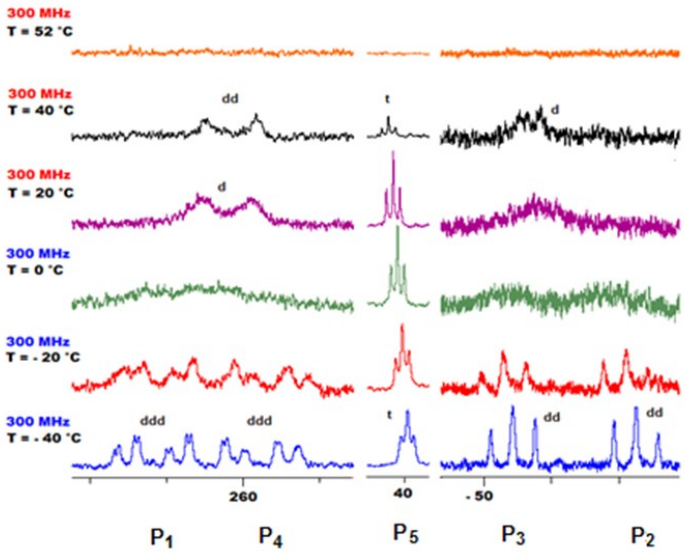

Fig. S2 $^{31}P\{^{1}H\}$VT NMR spectra of **1-Br** (121 MHz, THF-d_8)

X-ray diffraction studies

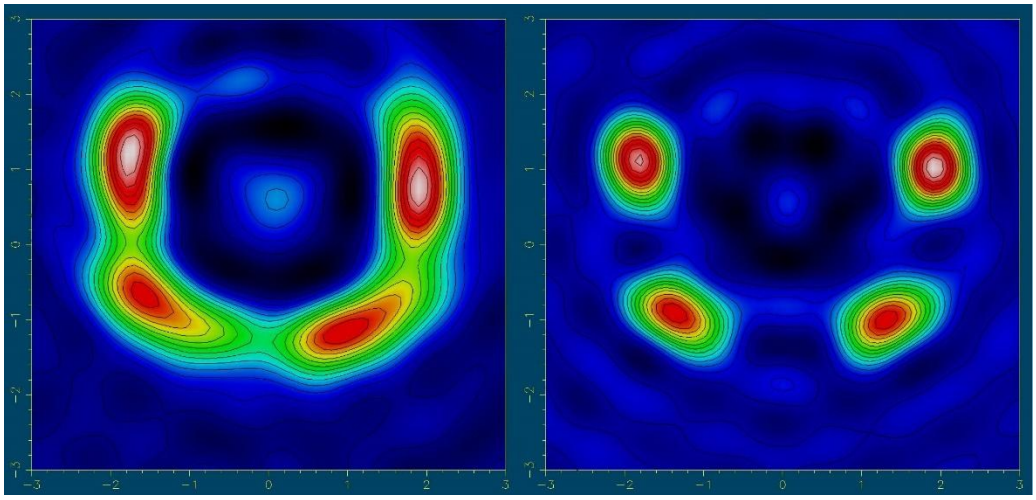

Fig. S3 XRD electron density plot of **3** in the P_4 plane at 100 K (left) and 300 K (right). Each plot displays 15 contour lines displayed from 0 to max. distance 1 e (100 K), 0.75 e (300 K).

Table S1 Crystal data and structure refinement details.

Compound	**1**	**2**
Empirical formula	$C_{42}H_{72}Cl_2O_2P_5Ru_2$	$C_{42}H_{73}Cl_5GaO_2P_5Ru_2$
Formula weight	1036.88	1213.96
Temperature/K	296.15	106.5(6)
Crystal system	triclinic	Monoclinic
Space group	P-1	$P2_1/n$
a/Å	12.7474(2)	9.5596(3)
b/Å	13.3991(2)	32.7266(13)
c/Å	14.5781(3)	16.3335(5)
α/°	70.6590(10)	90
β/°	79.0950(10)	94.033(3)
γ/°	88.9330(10)	90
Volume/Å^3	2304.44(7)	5097.3(3)
Z	2	4
ρ_{calc}g/cm^3	1.494	1.582
μ/mm^{-1}	0.979	1.563
F(000)	1074.0	2480.0
Crystal size/mm^3	0.15 × 0.08 × 0.08	0.07 × 0.03 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.018 to 61.012	5.572 to 52.744
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 19, -20 ≤ l ≤ 20	-11 ≤ h ≤ 11, -40 ≤ k ≤ 40, -19 ≤ l ≤ 20
Reflections collected	60966	24113
Independent reflections	14013 [R_{int} = 0.0237, R_{sigma} = 0.0227]	10407 [R_{int} = 0.0651, R_{sigma} = 0.1060]
Data/restraints/parameters	14013/30/586	10407/0/526
Goodness-of-fit on F^2	1.055	0.991
Final R indexes [I>=2σ (I)]	R_1 = 0.0268, wR_2 = 0.0665	R_1 = 0.0519, wR_2 = 0.0900
Final R indexes [all data]	R_1 = 0.0332, wR_2 = 0.0710	R_1 = 0.0974, wR_2 = 0.1054
Largest diff. peak/hole / e Å^{-3}	1.59/-0.69	0.90/-0.62

Compound	3	4
Empirical formula	$C_{20}H_{30}P_4Ru_2$	$C_{64}H_{112}O_2P_8Ru_4$
Formula weight	596.46	1565.57
Temperature/K	105(1)	104(2)
Crystal system	tetragonal	Triclinic
Space group	$P4_2bc$	P-1
a/Å	22.8500(5)	11.9212(3)
b/Å	22.8500(5)	12.4576(3)
c/Å	8.9379(3)	13.0288(3)
α/°	90	112.290(2)
β/°	90	107.073(2)
γ/°	90	90.803(2)
Volume/Å^3	4666.7(3)	1694.14(8)
Z	8	1
ρ_{calc}g/cm^3	1.698	1.535
μ/mm^{-1}	1.572	1.104
F(000)	2384.0	808.0
Crystal size/mm^3	0.22 × 0.06 × 0.04	0.1 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.638 to 61.008	5.744 to 56.564
Index ranges	$-32 \le h \le 32$, $-26 \le k \le 32$, $-12 \le l \le 12$	$-15 \le h \le 15$, $-16 \le k \le 16$, $-17 \le l \le 17$
Reflections collected	36044	22671
Independent reflections	7101 [R_{int} = 0.0671, R_{sigma} = 0.0534]	8394 [R_{int} = 0.0338, R_{sigma} = 0.0440]
Data/restraints/parameters	7101/1/245	8394/0/364
Goodness-of-fit on F^2	1.031	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0354, wR_2 = 0.0599	R_1 = 0.0339, wR_2 = 0.0719
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.0640	R_1 = 0.0465, wR_2 = 0.0766
Largest diff. peak/hole / e Å^{-3}	0.78/-0.69	1.89/-1.19
Flack parameter	-0.05(2)	

The Cp* ring on ruthenium 2 in compound **1** shows a positional disorder distributed on 3 sites. Refinement was achieved by splitting the ring into 3 parts, constraining the isotropic or anisotropic displacement of the carbon atoms belonging to the Cp* and restraining the distances between the carbon atoms in Cp* to be equal.

BADER ANALYSIS, NPA Calculations

All calculations were performed with the Gaussian09 [2] package at the BP86/cc-pVDZ(-PP) level. All the structures have been fully optimized and then the second derivative matrices have been calculated to prove the nature of the stationary point found. The NPA charges and Wiberg bond indices were obtained with NBO 3.10 [3] implemented in Gaussian09. For the Bader analysis [4] the code AIM2000 [5] has been used on wave-functions obtained with second order DKH correction [6] implemented in Gaussian09. For these calculations, the BP86 functional and the following basis set was used: cc-pVDZ for lighter atoms and a contracted double zeta all electron basis for Ru see https://bse.pnl.gov/bse/portal.

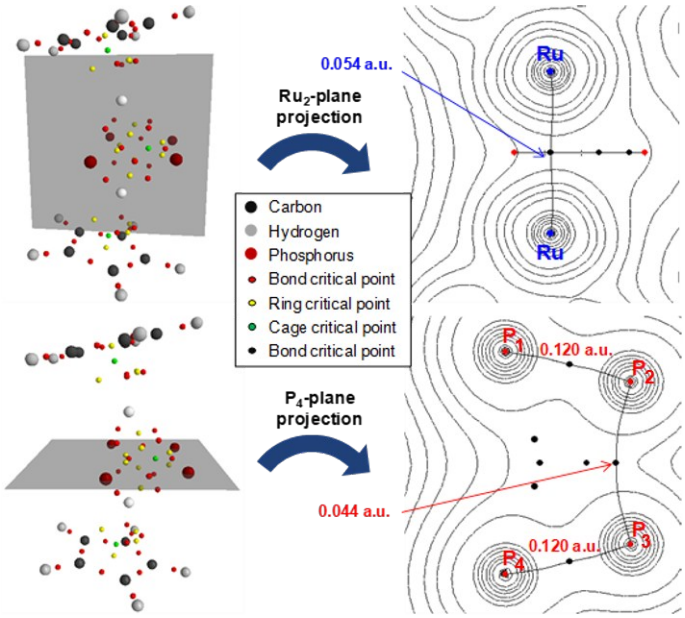

Fig. S4. Bader analysis of the Ru–P4 adduct **3** using a simplified geometry with Cp instead of Cp* ligands.

XYZ coordinates

Compound **1**

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bp86 genecp pop=Nboread\\L_SnPSiH32\\0,1\C\C,1,1.441549\C,2,1.44998,1

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Compound **2**

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Compound **3**

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Compound **4**

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