Solution and Solid-State Dynamics of Metal-Coordinated White Phosphorus

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Abstract: The dynamic behavior in solution of eight mono-hapto tetraphosphorus transition metal-complexes, *trans*-[Ru(dppm)₂(H)(η^1 -P₄)]BF₄ $([1]BF_4),$ *trans*-[Ru(dppe)₂(H)(η^{1} - $([2]BF_4),$ P_4)]BF₄ $[CpRu(PPh_3)_2(\eta^1 P_4$)]PF₆ $([3]PF_6),$ $[CpOs(PPh_3)_2(\eta^{1} [Cp*Ru(PPh_3)_2(\eta^1 P_4$)]PF₆ $([4]PF_6),$ P_4)]PF₆ $([5]PF_6),$ $[Cp*Ru(dppe)(\eta^{1} P_4$)] PF_6 [Cp*Fe(dppe)(n¹- $([6]PF_6),$ P_4)]PF₆ ([7]PF₆), [(triphos)Re(CO)₂(η^{1} -P₄)]OTf ([8]OTf), and of three bimetal-Ru(μ , $\eta^{1:2}$ -P₄)Pt species [{Rulic $(dppm)_2(H)$ $(\mu, \eta^{1:2} - P_4)$ $\{Pt(PPh_3)_2\}$ BF_4 $[{Ru(dppe)_2(H)}(\mu,\eta^{1:2}-$ ([**1-Pt**]BF₄), P_4 {Pt(PPh₃)₂]BF₄ ([**2-Pt**]BF₄), [{Cp- $Ru(PPh_3)_2$ ($\mu,\eta^{1:2}$ - P_4) { $Pt(PPh_3)_2$] BF₄

 $([3-Pt]BF_4)$, [dppm=bis(diphenylphosphanyl)methane; dppe=1,2-bis(diphenylphosphanyl)ethane; triphos = 1, 1, 1tris(diphenylphosphanylmethyl)ethane;

$Cp = \eta^{5} - C_{5}H_{5}; \quad Cp^{*} = \eta^{5} - C_{5}Me_{5}$ was studied by variable-temperature (VT) NMR and ³¹P{¹H} exchange spectroscopy (EXSY). For most of the mononuclear species, NMR spectroscopy allowed to ascertain that the metal-coordinated P₄ molecule experiences a dynamic process consisting, apart from the free rotation about the $M-P_4$ axis, in a tumbling movement of the P₄ cage while remaining chemically coordinated to the central metal. EXSY and VT ³¹P NMR experiments showed that also the binuclear complex cations [1-Pt]+ -[3-Pt]⁺ are subjected to molecular

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Introduction

The first neutral coordination complexes of white phospho- $[(NP_3)M(\eta^1-P_4)]$ $[M=Ni,^{[1]} Pd;^{[2]} NP_3=N(CH_2$ rus. CH₂PPh₂)₃], were described by Sacconi and co-workers

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motions featured by the shift of each metal from one P to an adjacent one of the P_4 moiety. The relative mobility of the metal fragments (Ru vs. Pt) was found to depend on the co-ligands of the binuclear complexes. For complexes $[2]BF_4$ and $[3]PF_6$, MAS, ³¹P NMR experiments revealed that the dynamic processes observed in solution (i.e., rotation and tumbling) may take place also in the solid state. The activation parameters for the dynamic processes of complexes 1⁺, 2⁺, 3⁺, 4⁺, 6⁺, 8^+ in solution, as well as the X-ray structures of 2^+ , 3^+ , 5^+ , 6^+ are also reported. The data collected suggest that metal-coordinated P4 should not be considered as a static ligand in solution and in the solid state.

more than 30 years ago and since then considered for a long time queer curiosities in the fast growing area of transition metal complexes incorporating naked phosphorus atoms and fragments. Currently, transition metal η^1 -tetrahedro-P₄ complexes, deriving from both neutral and cationic suitable transition-metal synthons,^[3] are a well-defined class of compounds whose potential reactivity is well known.^[4] Typical ³¹P NMR features for this class of complexes are two high field multiplets that appear, in the absence of additional coupling to other NMR active nuclei, as an MQ₃ spin system consisting of a doublet and a quartet with ${}^{1}J_{PP}$ values of about 200 Hz.^[5-7] The doublet is straightforwardly ascribed to the three uncoordinated phosphorus atoms, while the quartet, always shifted to low-field, is assigned to the single metalated P atom. Although some broadness of the ³¹P{¹H} NMR signals could anticipate the existence of fluxional processes involving metal bonded and metal free P atoms in some of the η^1 -coordinated tetrahedro-P₄ complexes, the dynamics in solution of coordinated P4 has not yet addressed in detail.^[6]

Recently,^[7] our research group has demonstrated by a combined NMR and DFT study that the P₄ cage of the mononuclear complex *trans*-[Ru(dppm)₂(H)(η^1 -P₄)]⁺ (1^+) dppm = bis(diphenylphosphanyl)methane) and of its bimetallic derivative *trans*-[{Ru(dppm)₂(H)}(μ , $\eta^{1:2}$ -P₄){Pt(PPh₃)₂]⁺ [**1-Pt**]⁺ participates in dynamic processes involving the Rubonded and the free P atoms of the tetrahedron. In particular, the dynamic process occurring in **1**⁺ consists of a free rotation of the P₄ cage upon itself in three dimensions while remaining chemically connected to the [Ru(dppm)₂(H)]⁺ fragment (Figure 1 a), while the main motion occurring in [**1-Pt**]⁺ can be regarded as a sort of oscillation of the [Ru-(dppm)₂(H)]⁺ fragment between P^I and P^{II}, as depicted in Figure 1 b. The activation parameters determined by line shape analyses for the scrambling of all P atoms of the tetra-



Figure 1. Molecular motions^[7] of the P_4 ligand in complexes a) 1^+ and b) $[1-Pt]^+$.

hedron in **1**⁺ were $\Delta G^{+}_{298\mathrm{K}} = 14.6 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta H^{+} = 9.6 \pm 0.5 \text{ kcal mol}^{-1}$, and $\Delta S^{+} = -17 \pm 1 \text{ cal mol}^{-1} \mathrm{K}^{-1}$.^[7]

Intrigued by these results, we started an in-depth study aimed at: 1) ascertaining whether fluxional processes of the coordinated P_4 occurred also in solutions of other tetraphosphorus complexes, 2) verifying whether the peculiar motion experienced by the coordinated P_4 molecule could still be present in the solid state, 3) finding a rational explanation of the possible scrambling processes.

Herein we report on the results of a detailed NMR studies which reveals the dynamics occurring for a variety of $[(L)_n M(\eta^1-P_4)]$ complexes [M=Fe, Ru, Os; L=dppm (n= 2), dppe (n=1 or 2), CP (n=1), Cp* (n=1), PPh₃ (n=2); dppe=1,2-bis(diphenylphosphanyl)ethane], as well as for the bimetallic species [{Ru(dppm)₂(H)}(μ , η ^{1:2}-P₄){Pt(PPh₃)₂}] $[1-Pt]^+$, $[{Ru(dppe)_2(H)}(\mu,\eta^{1/2}-P_4){Pt(PPh_3)_2}]$ $[2-Pt]^+$ and $[{CpRu(PPh_3)_2}(\mu,\eta^{1:2}-P_4){Pt(PPh_3)_2}]^+$ [3-Pt]⁺. We decided to investigate the known mononuclear complexes [CpRu- $(PPh_3)_2(\eta^1-P_4)]^+$ (3⁺), $[CpOs(PPh_3)_2(\eta^1-P_4)]^+$ (4⁺), $[Cp^*Ru (dppe)(\eta^{1}-P_{4})]^{+}$ $(dppe=Ph_{2}PCH_{2}PPh_{2})$ (6⁺), [Cp*Fe(dppe)- (η^1-P_4)]⁺ (7⁺), [(triphos)Re(CO)₂(P₄)]⁺ (8⁺) (triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane) as well as the new ones trans-[Ru(dppe)₂(H)(η^1 -P₄)]⁺, (2⁺) and [Cp*Ru- $(PPh_3)_2(\eta^1 - P_4)$]⁺ (5⁺). The sketches of all studied complexes are depicted in Scheme 1. All studied complexes, except 5⁺, showed a dynamic behavior in solution and, in the case of [2]BF₄ and [3]PF₆, even in the solid state.

Results and Discussion

Nuclear magnetic resonance is the technique of election for studying dynamic processes in solution by means of classic line-shape analysis at variable temperatures or by magnetization-transfer methods.^[8] In principle, magnetization-transfer experiments can provide qualitative and quantitative information on molecular motions in solution in terms of kinetic constants and, consequently, activation parameters. In



Scheme 1.

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the case of molecules containing coordinated P_4 , 2D-EXSY experiments can provide information about the sites involved in the possible exchange processes but cannot be used for extracting the relevant kinetic constants, due to the presence of COSY artifacts,^[9] and, more importantly, to the cross-peak multiplicity for the $P_{\rm M}$ and $P_{\rm Q}$ exchanging nuclei, which are strongly scalar coupled.^[10] These drawbacks are further aggravated by the non optimal hard pulse length for ³¹P imposed by the very wide spectral window.^[11] Thus, ³¹P{¹H} EXSY experiments were carried out to obtain qualitative information on dynamic motions, while lineshape analysis was performed to determine the kinetic constants. The processes considered in the computer simulations of the variable temperature ${}^{31}P{}^{1}H$ NMR spectra were the exchange between apical and basal P atoms of P4 and the rotation of the coordinated P_4 about the P_M -metal bond.

Synthesis and characterization: The synthetic protocols used for the preparation of all the new mononuclear and dinuclear P_4 metal complexes are summarized in Scheme 2.

The mononuclear complexes [1]BF₄ and [2]BF₄ were prepared by treating a 1:1 mixture of $[Ru(L)_2(H)_2]$ and HBF₄·Et₂O in CH₂Cl₂ with P₄ in THF (L=dppm or dppe). Complex [5]PF₆ was obtained following the protocol reported in the literature^[12] by reacting $[Cp*Ru(PPh_3)_2Cl]$ in a cold THF/CH₂Cl₂ mixture (-50 °C) with TIPF₆ and white phosphorus. The cognate complexes $[Cp*Ru(dppe)(\eta^1-P_4)]PF_6$ ([6]PF₆), and $[Cp*Fe(dppe)(\eta^1-P_4)]^+$ ([7]PF₆) were also prepared by reacting the [Cp*M(dppe)Cl] (M=Ru or Fe) precursors at room temperature with $TlPF_6$ and NH_4PF_6 , respectively.

The ³¹P{¹H} NMR spectra of complexes 1⁺ and 2⁺ in dichloromethane at room temperature consist of a first order A₄MQ₃ spin system (see Scheme 1 for P labeling). The four diphosphane P_A-phosphorus atoms gave broad doublets (²J_{P_AP_M} of ca. 20 Hz) at $\delta = -2.5$ for 1⁺ and at $\delta = 60.6$ for 2⁺. The Ru-bonded P_M resonances were found as broad quartets (¹J_{P_MP₀</sup> of ca. 220 Hz) at $\delta = -373.4$ for 1⁺ and at $\delta =$ -380.4 for 2⁺ while the basal, unmetalated P₀ atoms gave doublets at $\delta = -492.5$ for both 1⁺ and 2⁺. The ³¹P{¹H} NMR spectrum of complex 5⁺ exhibited the expected A₂MQ₃ spin system with signals at $\delta = -37.6$ (P_A), $\delta =$ -330.8 (P_M) and $\delta = -492.5$ (P₀). The main ³¹P{¹H} NMR features of the mononuclear complexes 1⁺-8⁺ are collected in Table 1.}

Table 1. ³¹P¹H} NMR features of mononuclear η^1 -P₄ complexes in dichloromethane at 298 K [δ are in ppm; coupling constants are in Hz].

Complex	δP_A	δP_M	δP_Q	$^{2}J(\mathbf{P}_{\mathrm{A}},\mathbf{P}_{\mathrm{M}})$	$^{1}J(\mathbf{P}_{\mathrm{M}},\mathbf{P}_{\mathrm{Q}})$	Ref.
1+	-2.5	-373.4	-492.5	23	224	[7]
2+	60.6	-380.4	-492.5	20	221	this work
3+	36.6	-343.4	-487.8	64	233	[20]
4+	-6.9	-381.5	-480.2	38	235	[21]
5+	37.6	-330.8	-492.5	57	227	this work
6+	71.0	-305.5	-489.0	45	233	[12]
7+	83.0	-303.3	-486.4	38	226	[12]
8 +[a]	-9.7	-398.6	-489.2	204	232	[6]

[a] AB₂MQ₃ spin system: $\delta P_B = -18.1$; ² $J_{P_AP_B} = 24$ Hz.



Scheme 2.

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All the bimetallic Ru/Pt species $[1-Pt]^+$, $[2-Pt]^+$ and $[3-Pt]^+$ were prepared by treating the appropriate Ru- (η^1-P_4) precursor with $[Pt(C_2H_4)(PPh_3)_2]$ in CH₂Cl₂. The high-field part of the ³¹P{¹H} NMR spectra of $[1-Pt]^+$, $[2-Pt]^+$, and $[3-Pt]^+$ recorded at the slow exchange regime temperature showed separated signals for the coordinated P₄ and are reported in Figure 2, while the relevant features are collected in Table 2. Whilst for $[1-Pt]^+$ and $[2-Pt]^+$ the Ru-bonded P_M



Figure 2. ³¹P NMR signals of coordinated P_4 in the slow exchange regime for complexes $[1-Pt]^+$, $[2-Pt]^+$, and $[3-Pt]^+$ in dichloromethane.

Table 2. NMR features of heterodinuclear $Ru/Pt(\mu,\eta^{1:2}-P_4)$ complexes $[1-Pt]^{+[a]}$ (180 K), $[2-Pt]^+$ (298 K), and $[3-Pt]^+$ (273 K) [δ values are in ppm; coupling constants are in Hz].

Complex	δP_A	δP_M	δP_Q	$\delta P_{\rm S}$	δP_Z	${}^{1}J(P_{M}P_{Q})$	$^{1}J(_{P_{M}P_{S}})$	${}^{1}J(P_{Q}P_{S})$	$^{2}J(_{P_{A}P_{M}})$
[1-Pt] ^{+[a]}	-2.3	-213.2	-346.0	-259.9	23.9	201	201	96	21
[2-Pt]+	62.1	-232.5	-336.4	-267.1	24.5	212	200	84	21
[3-Pt]+	41.0	-173.0	-329.8	-242.3	26.7	207	217	59	51

[a] Taken from reference [7].

appears as a broad pseudoquartet ($\Delta v_{1/2} = ca. 90 \text{ Hz}$), owing to three direct couplings of similar magnitude (200-212 Hz), in the case of [3-Pt]⁺ the P_M resonance is sharper ($\Delta v_{1/2} =$ ca. 25 Hz), appearing as a pseudoquartet (207-217 Hz) of triplets (51 Hz) owing to the resolved coupling with the two triphenylphosphane ligands (the corresponding coupling between P_M and the diphosphane P atoms in $[1-Pt]^+$ or [2-Pt]⁺, determined from the dppe signals is 21 Hz). On the contrary, the P_0 and P_s signals of the P_4 moiety are slightly broader for [3-Pt]⁺ than for [1-Pt]⁺ or [2-Pt]⁺. The lowfield part of the ³¹P{¹H} NMR spectra at 298 K of [1-Pt]⁺, $[2-Pt]^+$, and $[3-Pt]^+$ shows the P_A signals of the ancillary P ligands on Ru and the P_Z signals of the PPh₃ bonded to Pt. For all three dinuclear complexes the P_A signal is a doublet because of the geminal coupling with P_M while the Ptbonded Pz is a broad singlet. On cooling the solution to 200 K, the P_Z signal remains broad and only a pseudotriplet structure with an apparent J value of approximately 14 Hz becomes visible. The Pz pattern was observed also for the analogous complexes [$\{Co(\mu, \eta^{1:2:1}-P=P-PPh_2CH_2PPh_2)_2\}$ {Pt- $(PPh_3)_2$ ^[13] and *trans*-[PtCl(PMe_3)P_6C_4tBu_4Cl].^[14] Moreover, for all of the considered Ru-P₄-Pt species, the coupling constant between P_s and ¹⁹⁵Pt is about 600 Hz, as expected for a



Figure 3. ³¹P NMR signals of coordinated P_4 in the fast exchange regime for complexes $[1-Pt]^+$, $[2-Pt]^+$, and $[3-Pt]^+$ in dichloromethane.

direct ³¹P-¹⁹⁵Pt coupling involving naked P atoms (Figures 2 and 3).^[13,14]

X-ray crystal structure determinations: Crystals suitable for X-ray diffraction were obtained for 2^+ , 3^+ , 5^+ , and 6^+ . Figure 4 and Figure 5 show the complex cations 2^+ and 5^+ . The two structures are representative of the two classes of complexes, the octahedral and the piano-stool ones.

In the case of 3^+ , a crystal structure was known,^[17] but we found a new stable solvate form with formula [3]-[PF₆]·CH₂Cl₂, where two cations of 3^+ are present in the asymmetric unit. We also found two independent units of the cation in the crystal structure of 1^+ .^[7] The structures of $4^{+[30]}$ and $7^{+[12]}$ were already reported. It was not possible to obtain good quality crystals for 8^+ . For all complexes, we used a



Figure 4. Drawing of cation of 2^+ . Hydrogen atoms have been omitted for clarity.



Figure 5. Drawing of cation of 5⁺. The hydrogen atoms are omitted.

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consistent labeling scheme. The phosphorus atom of the P_4 unit bonded to the metal is P1 and corresponds to P_M of Scheme 1. The other three uncoordinated phosphorus atoms (P_Q in Scheme 1) are P2, P3, and P4. The P5, P6, and P7, P8 labels identify the phosphorus atoms of the biphosphanes. In Table 3 are collected the main geometrical features of cations 1^+-7^+ .

In the case of the octahedral complexes 1^+ and 2^+ , the P₄ unit is η^1 -bonded *trans* to the hydride ligand. The Ru–P1 distances are about 2.33 Å in 1^+ and 2^+ , while for the other ruthenium complexes, such distance is by almost 0.07 Å shorter. For piano-stool complexes 3^+ – 7^+ , the basal P_Q–P_Q distances of the coordinated P₄ unit are up to 0.07 Å longer than the P_M–P_Q ones, while for the octahe-

dral complexes the difference is much smaller. It is also interesting to evaluate the conformational differences between the basal plane of the P₄ unit with respect to the other part of the metal complex. The most convenient parameter to measure is the smallest P_M - P_O -M- P_A and P_M - P_O -M- C_t (where C_t is the Cp or Cp* centroid) dihedral angle in 1⁺ and 2⁺ and in 3^+ - 7^+ respectively. The values are widespread between the expected range of values $(-60 \text{ to } 60^\circ)$, and this is consistent with the fact that the P₄ unit has no preferential conformation and it is free to rotate around the M-P1 axis. As a consequence, in the solid state even weak interactions could have large influence in both the orientation of the P₄ basal plane and in the possible P₄ scrambling motion (see below). In keeping with this hypothesis, we noticed for the structure of $[3][PF_6] \cdot CH_2Cl_2$ that one phosphorus atom of the P₄ ligand in one of the two crystallographically independent molecules exhibits contacts with two fluorine atoms of the PF₆ anion as shown in Figure 6. The P2b…F2a and P2b…F5a distances are 3.339(2) Å and 3.468(2) Å, respectively. These values are only 2% and 6% longer than the sum of Van der Waals radii. Similar interactions were found also between the 3⁺ cation and the PF₆ anion [d(P - F) =3.249(14) Å] in the known structure^[17] without the chlathrated solvent molecule, as well as between one of the basal phosphorus and the oxygen atoms of the triflate anion $[d(P \cdots O) = 3.666(5) \text{ Å}]$ in the structure of 4⁺.

Dynamics of mononuclear complexes: To gain insights into the molecular dynamics in solution, ³¹P{¹H} EXSY experiments were recorded for all of the eight mononuclear complexes depicted in Scheme 1. The experiments were carried out, as specified below, at various mixing times and temperatures.

The octahedral Ru^{II} complexes 1^+ and 2^+ were found to be highly fluxional in solution, as intense cross peaks due to $P_M \leftrightarrow P_Q$ exchange were detected even at 260 K. Figure 7 shows the high field part of the room temperature ${}^{31}P{}^{1}H{}$ EXSY spectrum of 2^+ . The dynamic process responsible for the cross peaks in the ${}^{31}P{}^{1}H{}$ EXSY experiments may be safely assigned to the free tumbling of the P_4 ligand around the metal center encompassing therefore a sort of

Table 3. Selected bond lengths [Å] and dihedral angles [°] (see above) for the studied η^1 -P₄ metal complexes. The P_M-P_Q and P_Q-P_Q values are averaged on the three equivalent bonds.

	M-P _M	$P_M - P_Q$	$P_Q - P_Q$	P_Q - P_M - M - P_A	P_Q - P_M - M - C_t *	Ref.
1+	2.3215(17)	2.15(2)	2.15(3)	-2.9(2)		7
1	2.3270(16)	2.152(9)	2.17(2)	16.0(9)		,
2+	2.3449(12)	2.152(9)	2.18(2)	25.7(2)		this work
3+	2.2693(13)	2.147(6)	2.189(10)		8.34(13)	17
2+	2.2626(8)	2.159(11)	2.199(13)		-29.71(8)	this mont
3	2.2575(8)	2.159(3)	2.212(10)		12.50(8)	this work
4+	2.2632(9)	2.153(8)	2.209(10)		11.93(8)	29
5+	2.2614(17)	2.1623(11)	2.191(11)		18.9(2)	this work
6+	2.2582(8)	2.1541(10)	2.21(2)		-56.4(7)	this work
7+	2.1622(8)	2.162(4)	2.22(2)		56.5(5)	12

* Ct indicates the centroid of the cyclopentadienyl ring.



Figure 6. Drawing of one cation of $[3][PF_6]\cdot CH_2Cl_2$ and its contacts with the PF₆ anion [P2b…F2a 3.339(2) Å; P2b…F5a 3.468(2) Å]. Hydrogen atoms have been omitted for clarity.



Figure 7. Portion of the ${}^{31}P{}^{1}H$ EXSY spectrum of **2**⁺ (C₂D₂Cl₄, 298 K, $\tau_m = 0.1$ s).

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 $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ "walk" down an edge of P_4 moiety similar to what Eichhorn and co-workers proposed for the [PtH-(PPh₃)]⁺ fragment moving along the heptaphosphanortricyclene- P_7^{3-} moiety in the complex [η^2 - P_7 [PtH(PPh₃)]] [K(2,2,2-crypt)]₂.^[15]

The activation parameters calculated by analyzing a set of VT ${}^{31}P{}^{1}H{}$ NMR spectra for 2^+ are: $\Delta G^+_{298K} = 14.6 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta H^+ = 11.8 \pm 0.5 \text{ kcal mol}^{-1}$, and $\Delta S^+ = -9.5 \pm 1 \text{ cal mol}^{-1} \text{K}^{-1}$, values similar to those found for 1^+ .^[7] In agreement with the occurrence of a scrambling process, the variable temperature ${}^{31}P{}^{1}H{}$ NMR spectra of complex 2^+ (Figure 8) showed the broadening of both P_M and P_Q resonances with increasing temperatures. The fast exchange regime spectrum, which should result in coalescence of the high field resonances to a single signal, could, however, not be recorded due to extensive decomposition of 2^+ at temperatures above 360 K.



Figure 8. VT ${}^{31}P{}^{1}H$ NMR spectra of complex 2⁺ (C₂D₂Cl₄).

Complexes 3^+ , 4^+ , and 6^+ share the same piano-stool geometry. Although both $[CpRu(PPh_3)_2(\eta^1-P_4)]^+$ (3^+) and the homologous osmium species $[CpOs(PPh_3)_2(\eta^1-P_4)]^+$ (4^+) exhibit similar fluxional behavior of the coordinated P_4 ligand in solution, they feature slightly different activation parameters reflecting the higher fluxionality of 3^+ with respect to 4^+ ($\Delta G^+_3^+=15.4$ kcalmol⁻¹, $\Delta G^+_4^+=15.9$ kcalmol⁻¹). In keeping with the ΔG^+ values, the ³¹P{¹H} EXSY spectrum of 3^+ (298 K, $\tau_m=0.100$ s) showed neat exchange cross peaks between P_M and P_Q , while the Os complex 4^+ showed only COSY artifacts in the same experimental conditions, and clear exchange cross peaks between P_M and P_Q could be observed only at 348 K with a τ_m of 0.400 s.

A perusal of the activation parameters listed in Table 4 clearly indicates that the octahedral Ru^{II} complexes 1⁺ and 2⁺ are more fluxional than the Ru^{II} or Os^{II} Cp-based pianostool species. Similarly, for the octahedral rhenium(I) derivative 8⁺ ΔG^{\pm} value closer to that of the two diphosphane species was obtained. The higher fluxionality of 1⁺ and 2⁺ with respect to 3⁺ and 4⁺ is devoid of any simple explanation and likely results from the combination of a higher en-

Table 4. Activation parameters for the dynamic process of the investigated η^1 -P₄ metal complexes: ΔG^+_{298K} and ΔH^+ [kcalmol⁻¹] and ΔS^+ [calmol⁻¹K⁻¹]. The error on ΔG^+ and ΔH^+ is ± 0.5 kcalmol⁻¹, while that on ΔS^+ is ± 1 calmol⁻¹K⁻¹.

Complex ^[a]	$\Delta G^{*}_{_{298\mathrm{K}}}$	ΔH^{+}	ΔS^{+}
1 ^{+[b]}	14.6	9.6	-17
2+	14.6	11.8	-10
3+	15.4	5.3	-34
4+	15.9	5.0	-38
6+	16.0	7.8	-28
8+	14.8	7.5	-25

[a] The iron complex **7**⁺ is not reported (see text). [b] Taken from reference [7].

thalpic contribution with a significantly less negative entropic term.

To shed some light on the role played by steric and electronic factors on the dynamics of the η^1 -P₄ complexes, we prepared the new complex $[Cp^*Ru(PPh_3)_2(\eta^1-P_4)]^+$ (5⁺), which differs from 3^+ only in the formal replacement of Cp by Cp*. The ${}^{31}P{}^{1}H$ EXSY spectrum of a CD₂Cl₂ solution of 5^+ recorded at mixing times ranging from 0.100 s to 0.500 s at 298 K did not show any exchange cross peaks,^[16] which excludes any observable dynamic process of the coordinated P_4 for 5⁺ at room temperature. Recording ³¹P{¹H} EXSY spectra at temperature higher than 298 K resulted in decomposition of 5^+ . Again, the apparent lack of a fluxional process affecting the tetrahedro- P_4 in 5⁺ at room temperature cannot be simply interpreted, although the higher basicity of the pentamethylcyclopentadienyl ligand could be invoked as a possible explanation. In this regard, it is worth mentioning that complexes 5^+ and 3^+ exhibit a markedly different reactivity which stresses how even subtle differences in both steric and electronic requirements may strongly affect the solution chemistry of related species. For example, while the Cp derivative 3^+ easily undergoes stepwise hydrolysis to eventually afford [CpRu(PPh₃)₂(PH₃)]⁺,^[17] the Cp* derivative 5⁺ is reluctant to react with water even at high temperature.

As replacing the two PPh₃ with a 1,2-bis(diphenylphosphanyl)ethane (dppe) may result in more robust species, we completed the analysis of the Ru/P₄ complexes by recording ³¹P{¹H} EXSY and VT ³¹P{¹H} NMR spectra of [Cp*Ru- $(dppe)(\eta^1-P_4)$]⁺ (6⁺). With a mixing time of 0.100 s the ${}^{31}P{}^{1}H{}$ EXSY spectra of 6^+ in 1,1,2,2-tetrachloroethane (TCE) did not show any exchange cross peak at either 298 or 338 K. However, increasing the mixing time up to 0.400 s at 338 K revealed clear exchange cross peaks between P_M and P_{Ω} . The $P_{M}-P_{\Omega}$ exchange was evidenced also at 348 K with a mixing time of 0.100 s. These findings strongly suggest that the P₄ tumbling is always detectable, provided that the P₄ complex does not decompose on rising the temperature. From VT ${}^{31}P{}^{1}H$ NMR experiments, a ΔG^{+} value of 16.0 kcalmol⁻¹ was calculated, which represents the highest value among the studied $Ru_{(\eta^1-P_4)}$ complexes.

Complex 7^+ is the Fe analogue of 6^+ and showed, as major dynamic process, the dissociation of the P₄ ligand,

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which appears to be a peculiar process of the iron species not observed for Ru and Os congeners. In fact, dissolving isolated [7]PF₆ in [D₆]acetone, weak peaks attributable to free P₄ (δ =-520) and to [Cp*Fe(dppe)L]⁺ (δ =89.7, L= [D₆]acetone,) were detected, indicating around 10% dissociation at room temperature. The existence of a dissociation equilibrium was clearly indicated in the ³¹P{¹H} EXSY spectra of [7]PF₆ in [D₆]acetone recorded at 298 K or at 318 K by the appearance of exchange cross peaks between free and coordinated P₄ (Figure 9). The ³¹P{¹H} EXSY spectra at 318 K showed additional weak exchange peaks that can be due to thermal activation of the tumbling motion of the coordinated P₄ molecule, and/or multiple P₄ dissociation/coordination during the mixing time.



Figure 9. Portion of the ³¹P{¹H} EXSY spectrum of **7**⁺ in [D₆]acetone at 318 K ($\tau_m = 0.600$ s).

The occurrence of the independent dissociation equilibrium affected the reliability of the kinetic constants values calculated by DNMR and, together with the thermal instability of 7^+ (which decomposed at T > 318 K), eventually hampered the calculation of the activation parameters for 7^+ . The easy dissociation of the P₄ ligand in the iron complex suggests that the Fe–P_{ligand} bond is kinetically more labile than both Ru–P_{ligand} and Os–P_{ligand}. This finding is intriguing and contrasts with the general observation that down any series of homologous complexes of the iron triad, ruthenium forms the most substitution labile adducts.^[18]

Finally, reaction of $[(triphos)Re(CO)_2(OTf)]$ [triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane; OTf = MeO-SO_2CF_3] with a slight excess of white phosphorus in TCE straightforwardly afforded a solution containing [(triphos)Re(CO)_2(\eta^1-P_4)]OTf ([**8**]OTf), with a small amount of the known dinuclear compound [{(triphos)Re(CO)_2}_2(\mu,\eta^{1:1}-P_4)](OTf)_2 [**8-Re**](OTf)_2 (Scheme 3).^[6]

The ${}^{31}P{}^{1}H$ EXSY spectrum recorded at 298 K (Figure 10) showed intramolecular exchange cross-peaks between P_M and P_Q of the P_4 moiety both for the mononuclear



Figure 10. ³¹P{¹H} EXSY spectrum of a solution containing **8**⁺, [**8-Re**]²⁺, and free P₄ (CD₂Cl₂, 298 K, τ_m =0.100 s).

8⁺ and its dimer [**8**-**Re**]²⁺. For **8**⁺, the calculated activation free energy ($\Delta G^{+}_{298K} = 14.8 \pm 0.5 \text{ kcal mol}^{-1}$) was of the same order of that calculated for the octahedral Ru^{II} complexes **1**⁺ and **2**⁺. It is interesting to note that no intermolecular exchange between **8**⁺, excess P₄ and [**8**-**Re**]²⁺ was detected in the ³¹P{¹H} EXSY spectrum, nor was the solution dynamics slowed down by the presence of excess white phosphorus as it would be expected if ligand dissociation was involved in the fluxional process. These findings give not only indirect evidence for the lack of dissociative equilibria in the rheni-



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Scheme 3.

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um complexes, but also corroborate a high stability of the $Re-P_{P4}$ bond and allow to rule out a dissociative mechanism as a general explanation for the tumbling motion of the coordinated tetraphosphorus molecule.

Dynamics in the solid state: Intrigued by the discovery that the fluxional isomerization of coordinated tetraphosphorus moieties proceeds via an unexpected non-dissociative tumbling of the P₄ cage, which thus remains chemically connected to the metal center at all times, we wondered whether a similar dynamic process might be observed also in the solid state. Examples of a similar fluxional rearrangement in the solid state had previously been obtained for the weakly coordinated P₄ ligands in the homoleptic complex salts $[Ag(\eta^2 - P_4)_2][Al(OR_t)_4]$.^[19]

To establish the solid-state dynamics in the family of $[(L)_nM(\eta^1-P_4)]$ [Mu=Ru, L=dppe (*n*=2), Cp (*n*=1), Cp* (*n*=1) PPh₃ (*n*=2)] complexes investigated here, we decided to study [**2**]BF₄ and the solvate of [**3**]PF₆ as representative examples, by solid-state MAS ³¹P MMR spectroscopy.^[20] Figure 11 shows the one-dimensional ³¹P MAS NMR spectra of [**2**]BF₄ and [**3**]PF₆ at 296 K. The spectrum of [**2**]BF₄ con-



Figure 11. a) ³¹P MAS NMR spectrum of [2]BF₄ (MAS spinning rate 13000 Hz, relaxation delay 5 s); b) CP-MAS NMR spectrum of [3]PF₆ (MAS spinning rate 11500 Hz, relaxation delay 5 s). The isotropic lines of spinning sideband manifolds representing different types of phosphorus atoms are labeled (P_A, P_M, P_Q, and so on); unlabeled lines are spinning sidebands. The spectral regions containing the isotropic lines of the P_M and P_Q phosphorus atoms of [3]PF₆ are expanded in order to show the doubling of these signals due to the presence of two crystallographically independent molecules.

sists of four spinning sideband manifolds which are attributable to two sets of crystallographically inequivalent phosphorus atoms in the dppe ligands, and the metal coordinated (P_M) and basal (P_Q) phosphorus atoms of the P_4 unit. The spectrum of [**3**]PF₆ shows single resonances for the phosphorus atoms in the PPh₃ ligands and the PF₆ anion, and two sets of equally intense spinning sideband manifolds attributable to the P_M and P_Q atoms of the P_4 ligands of crystallographically independent molecules. The signals of metalbound and basal phosphorus atoms in the same molecule were readily identified from a 2D-³¹P-CP-INADEQUATE spectrum (see the Supporting Information).

The failure to observe separate resonances for the crystallographically distinguishable basal phosphorus atoms in [2]BF₄ and [3]PF₆ suggests that the P₄ ligands undergo rapid molecular jumps about the local threefold axis parallel to the P–Ru bond. Such dynamic behavior is quite common for molecular frameworks derived from P₄ tetrahedra and has been observed for P₄ itself^[21] and phosphorus chalcogenides such as P₄S₃,^[22] or P₄O₆S and P₄O₇.^[23] The effect of these motions adds up to a rotational reorientation of the P₄ unit and induces a collapse of the individual chemical shielding tensors to a single, axially symmetrical, averaged tensor which then gives rise to a single spinning sideband manifold in the ³¹P MAS spectrum.^[23]

Further insight into the dynamic behavior of the P_4 ligands was obtained from rotor synchronized, two-dimensional ³¹P MAS EXSY experiments^[24] (Figure 12,



Figure 12. a) Section of the rotor synchronized ³¹P CP-MAS EXSY spectrum^[24] of [3]PF₆ (MAS spinning rate 11.5 kHz, mixing time 2000 rotor cycles (174 ms), relaxation delay 8 s, spectral window 64725 Hz in both dimensions, 2k data points in t_2 and 128 t_1 increments, 8 transients per t_1 increment, acquisition time 31.7 ms in t_2 and 1 ms in t_1) at 296 K showing spinning sideband manifolds of P_{M1,2} and P_{Q1,2} phosphorus atoms in the P_4 ligands. Arrows indicate cross peaks that connect resonance lines in different spinning sideband manifolds and prove thus the presence of chemical exchange between P_M and P_O sites. b) Analysis of cross-peak profiles reveals that correlation signals connecting different spinning sidebands of the PQ (or PM) signal consist of two components, thus indicating that the P₄ ligand in both crystallographically independent molecules undergo rotational reorientation. c) Profiles of cross-peaks connecting spinning sidebands of P_M and P_O signals reveal that a tumbling motion of the P4 unit is only observable for one of the two crystallographically distinguishable molecules.

Figure 13). The spectra show, in addition to the diagonal peaks, two types of off-diagonal peaks. Cross peaks of the first type connect different spinning sidebands within the same manifold (Figure 12b) and can again be related to rotational reorientation of the P_4 unit during the mixing time.^[24] Cross peaks of the second type connect individual sidebands of the P_M and P_Q resonances (Figure 12c) and provide evidence that also the tumbling motion of the





Figure 13. a) Expanded section of the rotor synchronized ³¹P MAS EXSY spectrum of [2]BF₄ (MAS 13 kHz, mixing time 2000 rotor cycles (154 ms), relaxation delay 8 s, spectral window 80625 Hz in both dimensions, 1k data points in t_2 and 64 t_1 increments, 8 transients per t_1 increment, acquisition time 6.4 ms in t_2 and 0.4 ms in t_1) at 296 K with ¹H-decoupled ³¹P MAS NMR spectrum as projections. Diagonal peaks arising from the isotropic lines of the two phosphorus sites in the P₄ ligands are labeled as P_M and P_O, and correlation signals connecting different spinning sidebands within the P_O manifold or between the P_M and P_O mass for through ³¹P 2D EXSY spectra recorded with mixing times of 154 ms (top trace), 77 ms (1000 rotor cycles, middle trace), and 20 ms (260 rotor cycles, bottom trace), showing the increase of the intensity of A type stiton of the dashed line in the 2D representation.

P4 tetrahedra persists in the solid state. Comparison of crosssections of 2D³¹P EXSY spectra of [2]BF₄ recorded with different mixing times reveals that the relative intensities of the rotational cross peaks are independent from the mixing time whereas those of cross peaks associated with the tumbling process grow with increasing mixing time (Figure 13). These findings confirm that the rotational motion is a fast process and occurs on a timescale that is short compared to the mixing time, whereas the tumbling process is slower and proceeds on a timescale which by far exceeds the longest mixing time applied. Careful inspection of cross peak profiles in ³¹P MAS EXSY spectra of $[3]PF_6$ reveals, quite interestingly, that the effects of the tumbling motion are only detectable for one of the two crystallographically independent molecules (Figure 12c; this differentiation allows also to rule out that the correlation signal is produced by spin diffusion processes^[25] as in this case the effect should be observable for both molecules). This finding emphasizes that the solid state dynamics is apparently controlled by subtle influ-

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ences of the molecular environment which can in principle be of either intramolecular or intermolecular origin. Although we currently cannot provide an ultimate explanation, the observation that only one of the two crystallographically independent cations of $[3][PF_6][CH_2Cl_2]$ exhibits short contacts between one basal P atom of the coordinated P₄ ligand and two PF₆ fluorine atoms (see above) could be reasonably invoked to account for the different solid-state dynamic behavior of both entities.

The occurrence of tumbling motion in the solid state definitely rules out that the scrambling of the four P_4 atoms proceeds via a dissociative mechanism, and further supports the conclusion obtained from the solution dynamics of 8^+ (see above) that no fast dissociative/reassociative pathways, too short to be detected on the NMR timescale, have to be invoked to explain the observed fluxional behavior in solution.

Dynamics of dinuclear complexes: In dinuclear adducts like $[1-Pt]^+$ and $[2-Pt]^+$, beside the integral rotation about the Ru–P_M bond, two possible dynamic processes may in principle involve the coordinated P₄: one in which the Ru fragment passes from P_M to P_Q and acts as a sort of pendulum moving between two extreme positions (in the following Ru motion), and another one in which the Pt center passes from P_S to P_Q via a pathway involving all the P atoms of the original P₄ tethrahedron but the Ru-bonded one (in the following Pt motion), as shown in Scheme 4 below. For $[1-Pt]^+$ we



Scheme 4. For each step of the motion, Ru-coordinated P atoms correspond to P_M ; Pt-coordinated P atoms correspond to P_S ; uncoordinated P atoms correspond to P_Q in the labeling of the NMR experiments.

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have demonstrated that the molecule experiences both motions in solution, with different rates. In particular, a fast Ru motion (calculations gave $\Delta G^{+}_{298\mathrm{K}} = 13.2 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta H^{+} = 5.0 \pm 0.5 \text{ kcal}$ mol⁻¹, $\Delta S^{+} = -28 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$), was accompanied by a slow Pt motion that was evidenced by recording ³¹P{¹H} EXSY experiments at 305 K.^[7]

The ${}^{31}P{}^{1}H$ EXSY spectrum of $[2-Pt]^+$ at 298 K (Figure 14) showed intense cross peaks indicating



Figure 14. ³¹P{¹H} EXSY spectrum of [2-Pt]⁺ (CD₂Cl₂, 298 K, $\tau_m = 0.100$ s). The sequence of Ru and Pt motions during mixing time results in the complete P_M-P_S exchange.

that P_M , P_Q , and P_s undergo fast exchange with each other. Since relative cross-peak intensities suggest that Ru and Pt motions occur with comparable frequencies, we considered both Ru motion (i.e., the P_M-P_Q exchange) and Pt motion (i.e., the P_S-P_Q exchange) in the simulation of the VT ³¹P{¹H} spectra. Therefore, the line shape analysis provided two series of kinetic constants that were used to calculate the activation parameters for both dynamic processes. The calculated free activation energy for the Ru motion was $14.7 \pm 0.5 \text{ kcal mol}^{-1}$, while ΔG^{\pm}_{298K} for the Pt motion was slightly higher ($\Delta G^{\pm}_{Pt \text{ motion}} = 15.3 \pm 0.5 \text{ kcal mol}^{-1}$).

If one considers the propensity of the Pt(PPh₃)₂ fragment to move around the tetraphosphorus unit together with the less pronounced fluxionality of the piano-stool Ru complexes compared to octahedral ones, it is conceivable that the Pt motion in the bimetallic complex [**3-Pt**]⁺ could be faster than the Ru motion. This was demonstrated by recording the ³¹P{¹H} EXSY spectra of [**3-Pt**]⁺ which showed only intense exchange cross peaks between P_s and P_Q (Figure S11 in the Supporting Information). For this exchange, a ΔG^{+}_{298K} of 14.4 ± 0.5 kcalmol⁻¹ was calculated (Table 5). The combination of the Ru and Pt motions in the dinuclear complexes [**1-Pt**]⁺ and [**2-Pt**]⁺ is responsible for the complete scrambling of the phosphorus atoms in the {Ru(η^{1} -P₄)Pt} complex and suggests that complicated dynamic pro-

Table 5. Activation parameters for the dynamic processes of the dinuclear Ru/Pt complexes [1-Pt]⁺, [2-Pt]⁺, and [3-Pt]⁺ calculated at 298 K. ΔG^{+} and ΔH^{+} values are in kcal mol⁻¹, ΔS^{+} values are in cal K⁻¹mol⁻¹ The error on ΔG^{+} and ΔH^{+} is ± 0.5 kcal mol⁻¹ while that on ΔS^{+} is ± 1 cal mol⁻¹K⁻¹.

Complex	$\Delta G^{*}{}_{\rm Rumotion}$	$\Delta G^{*}{}_{\rm Ptmotion}$	$\Delta H^{*}_{\rm Rumotion}$	$\Delta H^{*}{}_{\rm Ptmotion}$	$\Delta S^{\dagger}_{Ru motion}$	$\Delta S^{+}_{ m Pt\ motion}$
[1-Pt] ^{+[a]}	13.2		5.0		-28	
[2-Pt]+	14.7	15.3	6.3	8.9	-28	-21
[3-Pt]+		14.4		9.8		-15

[a] Taken from reference [7].

cesses may also be active in many of the known polynuclear polyphosphorus compounds providing that the fluxional processes occur with comparable kinetic rates.

Conclusion

A combination of solution and solid-state NMR methods was applied to study the dynamic behavior of a series of transition-metal complexes incorporating white phosphorus as a ligand, either in the form of terminal η^1 -monohapto ligand or as dimetalated ($\eta^{1:1}$ or $\eta^{1:2}$) moiety. From the data obtained, it could be established that metal-coordinated P_4 does not behave as a static ligand both in solution and in the solid state.

Apart from the rotational motion of the tetrahedro- P_4 unit around the M– P_{P4} axis, the mononuclear M(η^1 - P_4) complexes (M=Fe, Ru, Os, Re) undergo a fluxional process in solution which scrambles all of the P_4 phosphorus atoms via a non-dissociative pathway. This additional dynamics may be described as involving a tumbling motion of the tetraphosphorus moiety which does not lose its connectivity to the metal. Line-shape analysis and 2D-EXSY spectra allowed us to figure out the relevant thermodynamic parameters of the dynamic process, and showed further that also the dinuclear species [{(triphos)Re(CO)_2}_2(\mu,\eta^{1:1}-P_4)]^{2+} experiences a similar fluxional behavior in solution.

Solid-state MAS ³¹P NMR spectroscopy carried out on [2]BF₄ and [3]PF₆ confirmed that the rotational and the tumbling processes leading to scrambling of all the tetraphosphorus P atoms are also operating in the crystal lattice. Remarkably, the solid state NMR analysis of [3]PF₆ demonstrates that only one of two crystallographically independent cations experiences the P₄ tumbling motion and points out that solid-state constraints, possibly dictated in the case at hand by weak interactions of one P_{P4} atom with the counteranion, may easily block the P₄ ligand in a definite orientation and eventually halt the whole fluxional process.

Dinuclear ruthenium-platinum tetraphosphorus complexes of formula $[L_nRu(\mu,\eta^{1:2}-P_4){Pt(PPh_3)_2}]^+$ $[L_n = {(dppm)_2(H)}, {(dppe)_2(H)}$ and ${Cp(PPh_3)_2}]$ were also synthesized and their dynamic behavior in solution analyzed by ${}^{31}P{}^{1}H$ EXSY experiments. This study revealed that a combination of two independent motions is responsible for the observed fluxionality which eventually results in the complete scrambling of all the phosphorus atoms. The first motion, identified as ruthenium motion, recalls a pendulum motion oscillating from the Ru-bonded P atom to the unmetalated one, while the second process, indicated as platinum motion, accounts for the $\{Pt(PPh_3)_2\}$ ride along the three P atoms not coordinated to ruthenium.

Currently we are investigating the reactivity of these mononuclear and dinuclear tetraphosphorus derivatives towards different reagents and expanding the class of co-ligands at both ruthenium and platinum to provide a rationale to the observed dynamic behavior.

Experimental Section

General details: All reactions and manipulations were carried out under nitrogen using standard Schlenk glassware and techniques. Dichloromethane was purified by distillation over CaH₂. THF was purified by distillation over sodium wire and benzophenone. Diethyl ether and *n*-pentane were purified by passing them over two columns filled with molecular sieves (4 Å) (LabMaster MBRAUN MD SPS). *n*-Hexane was used as purchased. Deuterated solvents (Aldrich) were pre-treated with three freeze-thaw pump cycles before use and kept under an inert atmosphere. Literature methods were used for the preparation of [Pt(C₂H₄)-(PPh₃)₂],^[26] [Ru(dppm)₂(H)₂],^[27] [Ru(dppm)₂(H)(\eta²-H₂)]BF₄,^[28] [Ru-(dppe)₂(H)₂],^[29] [CpRu(PPh₃)₂(η¹-P₄)]PF₆,^[17] [CpOs(PPh₃)₂(η¹-P₄)]PF₆,^[30] and [(triphos)Re(CO)₂(η¹-P₄)]PF₆,^[12] were carried out according to the literature with only slight modifications as explained below.

Solution multinuclear NMR spectra were recorded on a Bruker Avance 400 spectrometer, equipped with a variable temperature control unit. ³¹P{¹H} EXSY spectra were recorded by using the library pulse program "noesyph" modified for ¹H decoupling. Line-shape analysis was performed by DNMR module of TopSpin BRUKER. ΔG^{*} values were calculated at 298 K. ¹H chemical shifts are referenced to tetramethylsilane (TMS), ³¹P chemical shifts are referenced to 85% H₃PO₄ (161.92 MHz), and ¹⁹⁵Pt chemical shifts are referenced to H₂PtCl₆ (85.98 MHz). Solid-state NMR spectra at 9.4 T ($v_0 = 161.9$ MHz) were recorded at ambient temperature (296 K) on a BRUKER AVANCE 400 spectrometer equipped with a 4 mm MAS probe. All spectra were acquired using magic angle spinning (MAS) at spinning speeds between 9 and 14 kHz, and high power ¹H decoupling was applied during acquisition. All experiments were recorded with pulse sequences from the standard BRUKER pulse program library. Two-dimensional EXSY spectra were recorded using rotor synchronized mixing times^[24] and 90° pulses of 3.9 µs duration. Cross polarization with a ramp-shaped contact pulse and mixing times of 5 ms was used for signal enhancement in measurements of CP MAS spectra of [3]PF6. The presence of solvent in the used sample of $[3]PF_6$ was verified by solution ¹H NMR spectroscopy. IR spectra were recorded with a Spectrum BX II Perkin-Elmer spectrometer; ESI-MS analyses were performed using a Finnigan Analytic LTQ instrument. High resolution mass spectrometry (HRMS) analyses were performed using a time-of-flight mass spectrometer equipped with an electro-spray ion source (Bruker micrOTOF-Q II). The analyses were carried out in positive ion mode. The sample solutions were introduced by continuous infusion with the aid of a syringe pump at a flow-rate of 180 µL h⁻¹. The instrument was operated at end plate offset -500 V and capillary 4500 V. Nebulizer pressure was 0.3 bar (N2) and the drying gas (N₂) flow 4 L min⁻¹. Drying gas temperature was set at 180 °C. The software used for the simulation is Bruker Daltonics DataAnalysis (version 4.0).

Synthesis of *trans*-[Ru(dppm)₂(H)(η^1 -P₄)]BF₄ ([1]BF₄): A solution of white phosphorus in THF (0.1 M, 2.29 mL, 0.229 mmol) was syringed into a solution of *trans*-[Ru(dppm)₂(H)(η^2 -H₂)]BF₄ (200 mg, 0.229 mmol) in CH₂Cl₂ (10 mL). After 15 min the resulting dark brown solution was concentrated under vacuum. Addition of 20 mL of diethyl ether gave an ivory colored solid which was filtered off and washed with toluene (25 mL). Yield: 84%, 209 mg. Crystals suitable for X-ray analysis were

obtained from a diluted CH_2Cl_2/n -hexane (1:1) solution by slow concentration under nitrogen. The crystals were filtered off and dried in the air.

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tration under nitrogen. The crystals were filtered off and dried in the air. ¹H NMR (400 MHz, CD₂Cl₂, 295 K): δ =7.91–6.86 (m, 40H; Ph), 4.88 (br s, 2H; CH₂), 4.56 (bs, 2H; CH₂), -3.69 ppm (brd, 1H, ²*J*_{H,Pnum} = 162 Hz; Ru-H); ³¹P{¹H} NMR (400 MHz, CD₂Cl₂, 295 K): δ =-2.5 (d, ¹*J*_{P_AP_M}=23 Hz; P_A, 4P), -373.4 (q, ¹*J*_{P_AP₀}=224 Hz; P_M, 1P), -492.5 ppm (d, ¹*J*_{P_AP₀}=224 Hz; P_Q, 3P); IR (CH₂Cl₂): $\tilde{\nu}_{(Ru-H)}$ =1975 cm⁻¹; MS (ESI): *m*/*z*: 995.07 (1⁺); elemental analysis calcd (%) for C₅₀H₄₅BF₄P₈Ru (1081.56): C 55.53, H 4.19; found: C 55.71, H 4.25.

Synthesis of *trans*-[**Ru**(**dppe**)₂(**H**)(**η**¹-**P**₄)]**BF**₄ ([**2**]**B**F₄): A solution of white phosphorus in THF (0.1 M, 2.22 mL, 0.229 mmol) was syringed into a solution of *trans*-[**Ru**(dppe)₂(H)₂] (200 mg, 0.229 mmol) and HBF₄.EtO₂ (31 µL, 1 equiv) in a mixture of THF (10 mL) and CH₂Cl₂ (6 mL). After 30 min the resulting brown solution was concentrated under vacuum. Addition of 20 mL of diethyl ether gave an ivory colored solid which was filtered off and washed with toluene (25 mL). Yield: 89%, 222 mg. Crystals suitable for X-ray analysis were obtained from a diluted CH₂Cl₂/*n*-hexane (1:1) solution by slow concentration under nitrogen. The crystals were filtered off and dried in the air. ¹H NMR (400 MHz, CD₂Cl₂, 295 K): δ = 7.69–6.39 (m, 40H; Ph), 2.43 (m, 4H; C₂H₄), 2.11 (m, 4H; C₂H₄), -5.68 ppm (brd, 1H; Ru-H, ²J_{HPmm} = 175 Hz); ³¹P[¹H] NMR (400 MHz, CD₂Cl₂, 295 K): δ = 6.66.6 (d, ¹J_{PAPM} = 20 Hz; 4P, P_A), -380.4 (q, ¹J_{PMP} = 221 Hz; P_M, 1P), -492.5 ppm (d, ¹J_{PMP} = 221 Hz; P_O, 3P); IR (CH₂Cl₂): $\tilde{r}_{(Ru-H)}$ = 1975 cm⁻¹; MS (ESI): *m*/*z*: 933.36 (**2**⁺); elemental analysis calcd (%) for C₅₂H₄₉BF₄P₈Ru (1109.24): C 56.25, H 4.45; found: C 56.41, H 4.72.

Improved synthesis of [Cp*Ru(PPh_3)_2Cl]_{[31]} A suspension of $[Cp*RuCl_2]_2$ (0.5 g, 1.64 mmol), PPh₃ (1.73 g, 6.6 mmol) and an excess of zinc dust in THF (65 mL) was stirred for 2 h. The solution was filtered and transferred to another flask containing *n*-pentane (200 mL). Upon 15 min formation of orange crystals was observed. After precipitation was complete (1 h), the crystals were filtered off and dried under nitrogen. Yield: 90%, 0.58 g.

Synthesis of [Cp*Ru(PPh₃)₂(η¹-P₄)]PF₆ ([5]PF₆): A THF solution of white phosphorus (0.1 м, 1.94 mL, 0.194 mmol) was added to a solution of [Cp*Ru(PPh₃)₂Cl] (200 mg, 0.194 mmol) and TIPF₆ (101 mg, 0.289 mmol) in a mixture of CH₂Cl₂ (5 mL) and THF (4 mL). The resulting slurry was stirred at -50 °C for 2 h; the TICl which separated out was filtered off and [CpRu(PPh₃)₂(η¹-P₄)]PF₆ was obtained as orange microcrystals by evaporating the solvent under reduced pressure. Yield: 90%, 231 mg. Crystals suitable for X-ray analysis were obtained by layering Et₂O (50 mL) over the CH₂Cl₂/THF solution. ¹H NMR (400 MHz, CD₂Cl₂, 295 K): \delta=7.50–6.94 (m, 30 H; Ph), 1.30–1.25 ppm (m, 15 H; Cs-(CH₃)₅); ³¹Pl⁺H] NMR (400 MHz, CD₂Cl₂, 295 K): \delta=37.6 (d, ¹J_{PAPM} = 57 Hz; 4P, P_A), -330.8 (qt, ¹J_{PMP0} =227 Hz, ²J_{PAPM} =57 Hz; 1P, P_M), -492.5 ppm (d, ¹J_{PMP0} =227 Hz; 3P, P_O), MS (ESI): *m***/***z***: 885.1 (5⁺); elemental analysis calcd (%) for C₄₆H₄₅P₇RuF₆ (1029.72): C 53.65, H 4.40; found: C 53.76, H 4.63.**

Improved synthesis of [Cp*Ru(dppe)(η^1 -P₄)]PF₆ ([6]PF₆):^[12] A THF solution of white phosphorus (0.1 m, 2.49 mL, 0.249 mmol) was added to a solution of [Cp*Ru(dppe)Cl] (200 mg, 0.249 mmol) and TIPF₆ (87 mg, 0.249 mmol) in a mixture of CH₂Cl₂ (5 mL) and THF (4 mL). The resulting slurry was stirred at room temperature for 2 h; the precipitated TICI was filtered off and [CpRu(dppe)(η^1 -P₄)]PF₆ was obtained as orange crystals by layering Et₂O (50 mL) over the CH₂Cl₂/THF solution. Yield: 90%, 243 mg.

Improved synthesis of [Cp*Fe(dppe)(η^{1} -P₄)**]**PF₆ (**[7]**PF₆)^{:[12]} A THF solution of white phosphorus (0.1 M, 3.19 mL, 0.319 mmol) was added to a solution of [Cp*Fe(dppe)Cl] (200 mg, 0.319 mmol) and NH₄PF₆ (80 mg, 0.480 mmol) in a mixture of CH₂Cl₂ (12 mL) and THF (8 mL). The resulting slurry was stirred at room temperature overnight; the precipitated NH₄Cl was filtered off and [Cp*Fe(dppe)(η^{1} -P₄)]PF₆ was obtained as purple microcrystals by evaporating the solvent under reduced pressure. Yield: 80%, 219 mg.

Synthesis of trans-[{Ru(dppm)₂(H)}(μ , η ^{1:2}-P₄){Pt(PPh₃)₂]]BF₄ ([1-Pt]BF₄): Solid [Pt(C₂H₄)(PPh₃)₂] (140 mg, 0.183 mmol) was added portion-wise to a solution of [1]BF₄ (200 mg, 0.183 mmol) in 10 mL of CH₂Cl₂ under nitrogen at room temperature. After stirring for 5 min, the

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Table 6.	Crystallographic	data for compounds	containing cations 2	+, 3+	⁺, 5⁺	⁺ , and 6 ⁺ .
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	$[2][BF_4] \cdot 2C_6H_{14}$	$[3][PF_6] \cdot CH_2Cl_2$	$[5][\mathbf{PF}_6] \cdot 2 \operatorname{CH}_2\operatorname{Cl}_2$	$[6][\mathrm{PF}_6]\cdot\mathrm{C}_4\mathrm{H}_{10}\mathrm{O}$
empirical formula	$C_{64}H_{72}BF_4P_8Ru$	$C_{42}H_{37}Cl_2F_6P_7Ru$	$C_{48}H_{49}Cl_4F_6P_7Ru$	C_{40} H ₄₉ F ₆ OP ₇ Ru
formula weight	1276.86	1044.48	1199.53	977.65
temperature [K]	293(2)	100(2)	150(2)	150(2)
wavelength [Å]	0.71069	0.71069	0.71069	0.71069
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_{1}/c$	$P2_1/n$	$P2_1/n$
unit cell dimensions				
a [Å]	13.3004(7)	18.4709(11)	10.6313(3)	11.6882(2)
b [Å]	13.7148(7)	29.2905(18)	17.3818(5)	18.3613(4)
c [Å]	18.9937(9)	16.0236(11)	27.8900(6)	19.5351(3)
α [°]	97.255(4)	90	90	90
β[°]	104.751(4)	99.708(2)	98.898(2)	91.0107(15)
γ[°]	113.811(5)	90	90	90
V [Å ³]	2960.8(3)	8545.0(9)	5091.8(2)	4191.79(13)
Z, calculated density $[Mgm^{-3}]$	2, 1.432	8, 1.624	4, 1.565	4, 1.549
absorption coefficient [mm ⁻¹]	0.535	0.813	0.794	0.7
F(000)	1322	4208	2432	2000
data/restraints/parameters	13230/0/581	26124/0/1045	11300/0/595	11267/0/484
goodness-of-fit on F^2	0.917	1.045	1.031	1.042
$[I > 2\sigma(I)]$	0.0567	0.0530	0.0782	0.0448
wR_2	0.1635	0.0865	0.1906	0.1054
R_1 (all data)	0.0932	0.1106	0.1287	0.0617
wR_2 (all data)	0.1737	0.0960	0.2248	0.1175

solution was concentrated under vacuum to leave a ivory colored solid. After stirring for 5 min, the solution was concentrated under vacuum and the product was isolated as pale brown solid by addition of diethyl ether (10 mL). Yield 220 mg (66%). ¹H NMR (400 MHz, CD₂Cl₂, 180 K): δ = 7.61–6.72 (m, 70 H; Ph), 5.01 (brs, 2H; CH₂), 4.53 (brs, 2H; CH₂), -5.48 (brd, 1H, ²J_{H,P_{max}}=107 Hz; Ru-H); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 180 K): δ = 23.9 (br, ¹J_{P₂Pt}=2270 Hz; 2P, P₂), -2.3 (d, ²J_{P_APa}=21 Hz; 4P, P_A), -213.2 (pq, ¹J_{P_APs}=1J_{P_MPs}=201 Hz; 1P, P_M), -259.9 (m; 2P, Ps), -346.0 ppm (m, ¹J_{P₃Pt}=96 Hz; 1P, P_Q); ¹⁹⁵Pt{¹H} NMR (86.01 MHz, CD₂Cl₂, 180 K): δ =-3987 (m, ¹J_{P₂Pt}=2270 Hz, ¹J_{P₃Pt}=820 Hz; Pt,); IR (CH₂Cl₂): v_(Ru-H) $\tilde{\nu}$ =1966 cm⁻¹; MS (ESI): *m*/*z*: 1713.45 (**1-Pt**⁺); elemental analysis calcd (%) for C₈₆H₇₅BF₄P₁₀RuPt (1801.21): C 57.35, H 4.20; found: C 57.04, H 4.24.}}

Synthesis of *trans*-[**Ru(dppe)**₂(**H**)}(µ,η^{1:2}-**P**₄)**{Pt(PPh**₃)₂]**BF**₄ ([2-**Pt**]**BF**₄). Solid [Pt(C₂H₄)(PPh₃)₂] (135 mg, 0.180 mmol) was added portion-wise to a solution of [2]**BF**₄ (200 mg, 0.180 mmol) in 10 mL of CH₂Cl₂ under nitrogen at room temperature to give a deep brown solution. The product could not be isolated in the solid state due to extensive decomposition to unknown species. It was therefore characterized by in situ NMR, IR, and ESI-MS techniques. ¹H NMR (400 MHz, CD₂Cl₂, 245 K): δ =8.00–6.41 (m, 70 H; Ph), 3.69 (brs, 4H; CH₂), 1.83 (brs, 4H; CH₂), -9.15 ppm (brd, 1H, ²J_{H,P_{nem}}=122 Hz; Ru-H); ³¹P[¹H] NMR (162 MHz, CD₂Cl₂, 145 K): δ =62.1 (d, ²J_{P_AP_M}=21 Hz; 4P, P_A), 24.5 (br, ¹J_{P_AP_I=2286 Hz; 2P, P_Z), -213.2 (pq, ¹J_{P_AP_M</sup>=200 Hz, ¹J_{P_AP₀=212 Hz; 1P, P_M), -267.1 (m; 2P, P_S), -340.1 ppm (dt, ¹J_{P_AP₀=84 Hz; 1P, P_Q); ¹⁹⁵Pt[¹H] NMR (86.01 MHz, CD₂Cl₂, 298 K): δ =-3962 ppm (m, ¹J_{P_AP_I=2286 Hz, ¹J_{P_AP₀=610 Hz; Pt); IR (CH₂Cl₂): ν_{(Ru-Hi}=1965 cm⁻¹; MS (ESI): *m*/z: 897.20 (**2-Pt⁺**).}}}}}}

Synthesis of [CpRu(PPh₃)₂(µ,η^{1:2}-P₄){Pt(PPh₃)₂]}PF₆ ([3-Pt]BF₄): Solid [Pt(C₂H₄)(PPh₃)₂] (160 mg, 0.210 mmol) was added portion-wise to a solution of [3]BF₄ (200 mg, 210 mmol) in 10 mL of CH₂Cl₂ under nitrogen at room temperature to give a dark orange solution. The product could not be isolated in the solid state due to extensive decomposition to an oily sticky material. It was therefore characterized by in situ NMR and ESI-MS techniques. ¹H NMR (400 MHz, CD₂Cl₂, 273 K): δ =7.08–6.60 (m, 60H; Ph), 4.41 (s, 5H; C₅H₅); ³¹P{¹H</sup> NMR (162 MHz, CD₂Cl₂, 273 K): δ =41.0 (d, ²J_{PAPM}=51 Hz; 2P, P_A), 26.7 (br, ¹J_{PAPI}=2259 Hz; 2P, P_Z), -173.0 (pq, ¹J_{PAPM}=51 Hz; 1P, P_A), 26.7 (br, ¹J_{PAPI}=2259 Hz; 2P, P_S), -329.8 ppm (dt, ¹J_{PAPI}=59 Hz; 1P, P_Q); ¹⁹⁵Pt NMR (86.01 MHz, CD₂Cl₂, 298 K): δ =-3989 ppm (m, ¹J_{PAPI}=2259 Hz, ¹J_{PAPI}=607 Hz; Pt); MS (ESI): *m*/z: 1333.60 (**3-Pt**⁺).

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XRD analyses: A summary of the crystallographic data and structure refinement results for the structure containing cations 2+, 3+, 5+, and 6+ is given in Table 6. The X-ray data of 2⁺, 5⁺, and 6⁺ were collected using an Oxford Diffraction Excalibur 3 diffractometer equipped with MoKa radiation ($\lambda = 0.71069$ Å) and CCD area detector using the program CrysAlis CCD^[32] Data reductions were carried out with the program CrysAlis RED^[33] and adsorption correction was applied through the program AB-SPACK.^[34] The data of **3⁺** were collected on Bruker-Nonius Kappa CCD diffractometer at 100(2) K using Mo_{Ka} radiation ($\lambda = 0.71069$ Å). These complexes had some difficulties to crystallize due to the presence of disordered anion and solvent molecules even at low temperature. As consequence, the refinement of the crystal structures was problematic. The structures were solved by direct methods (SIR97,^[34] SHELXS-97^[35]) and refined by full-matrix F² refinement (SHELXL-97).^[36] Generally all the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. In the structure of cation 2^+ , the hydride atom was located on the Fourier map, the disordered BF4 anion was modeled splitting over five positions three of the four fluorine atoms. On the other site, two nhexane solvent molecules present in the asymmetric unit were removed using the SQUEEZE procedure,[35] after unsuccessful attempts to model them. In the structure of cation 6⁺, Et₂O solvent molecules were disordered and modeled using isotropic displacement parameters.

CCDC-874683 (2⁺), CCDC-874684 (3⁺), CCDC-874685 (5⁺), CCDC-874686 (6⁺), 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.

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V. Mirabello, M. Caporali, V. Gallo, L. Gonsalvi, D. Gudat, W. Frey, A. Ienco, M. Latronico, P. Mastrorilli, M. Peruzzini*.....

Solution and Solid-State Dynamics of Metal-Coordinated White Phosphorus



A detailed solution and solid-state NMR dynamics study on mono- and bimetallic transition metal complexes, coordinating white phosphorus in η^1 -P₄ fashion, has revealed that this ligand is endowed of motions which depend on the nature of co-ligands and geometries around the metals. Activation parameters of the processes and X-ray crystal structures were also obtained (see figure).

Coordinated P₄...

...showed a high fluxionality in η^{1-} P₄ metal complexes, in solution and in the solid state, investigated by NMR techniques. For more details ssee the paper by M. Peruzzini et al. on page \blacksquare ff. The background shows part of the ancient painting "The Alchemist in Search of the Philosopher's Stone Discovers Phosphorus." by Joseph Wright.



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