Electronic Supplementary Material (ESI) for Dalton Transactions
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Dynamic Behaviour of Ru and Ru-Pt complexes containing tetrahedron-P4 Ligand

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Supporting information

Experimental Details

General details. All reactions and manipulations were carried out under nitrogen using standard Schlenk glassware and techniques. Dichloromethane was purified by distillation over CaH_2. Literature methods were used for the preparation of $[Ru(dppm)_2(H)_2]$,[S1] $[Ru(dppm)_2(H)(\eta^2\text{-}H_2)]BF_4$,[S2] and $[Pt(C_2H_4)(PPh_3)_2]$[S3].Deuterated solvents (Aldrich) were pre-treated with three freeze-thaw pump cycles before use, and kept under an inert atmosphere.

Solution multinuclear NMR spectra were recorded on a BRUKER AVANCE 400 spectrometer, equipped with a variable temperature control unit. ^1H chemical shifts are referenced to tetramethylsilane (TMS), ^{31}P chemical shifts are referenced to 85% H_3PO_4, ^{195}Pt chemical shifts are referenced to H_2PtCl_6.

Experimental Section

Synthesis of *trans*-$[Ru(dppm)_2(H)(\eta^1\text{-}P_4)]BF_4$ ([**2**]BF_4). A solution of white phosphorus in THF (0.10 M, 2.29 mL, 0.229 mmol) was syringed into a solution of *trans*-$[Ru(dppm)_2(H)(\eta^2\text{-}H_2)]BF_4$ (200 mg, 0.229 mmol) in CH_2Cl_2 (10 mL). After 15 minutes 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. El. Anal. (%) for $C_{50}H_{45}BF_4P_8Ru$ (1081.56), calcd: C, 55.53; H, 4.19; found: C, 55.71; H, 4.25. ESI-MS m/z (%): 995.07 (35.69). ^1H NMR (400 MHz, CD_2Cl_2, 295 K): δ = 7.91-6.86 (m, 40H, Ph), 4.88 (br s, 2H, CH_2), 4.56 (bs, 2H, CH_2), -3.69 ppm (br d, 1H, Ru-H, $^2J_{H,Ptrans}$ = 162 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 295 K): δ = - 2.5 (d, 4P, P_A, $^1J_{PAPM}$ = 23 Hz), -373.4 (q, 1P, P_M $^1J_{PMPQ}$ = 224 Hz), -492.5 ppm (d, 3P, P_Q $^1J_{PMPQ}$ = 224 Hz). IR (CH_2Cl_2): ν(Ru-H) 1975 cm^{-1}.

Synthesis of *trans*-[{Ru(dppm)$_2$(H)}(μ,η$^{1:2}$-P$_4$){Pt(PPh$_3$)$_2$}]BF$_4$ ([**3**]BF$_4$). Solid [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (140 mg, 0.183 mmol) was added portion-wise to a solution of [**2**]BF$_4$ (200 mg, 0.183 mmol) in 10 mL of CH_2Cl_2 under nitrogen at room temperature. 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%). El. Anal. (%) for $C_{86}H_{75}BF_4P_{10}RuPt$ (1801.21), calcd: C,57.35; H, 4.20; found: C, 57.04; H, 4.24. ESI-MS m/z (%): 1713.45 (86) [{Ru(dppm)$_2$(H)}(μ,η$^{1:2}$-P$_4$){Pt(PPh$_3$)$_2$}]$^+$. ^{1}H NMR (400 MHz, CD_2Cl_2, 180 K): δ = 7.61–6.72 (m, 40H, Ph), 5.01 (br s, 2H, CH_2), 4.53 (bs, 2H, CH_2), -5.48 (br d, 1H, Ru-H, $^2J_{H,Ptrans}$ = 107 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 180 K): δ = 23.9 (br, 2P, P_Z, $^1J_{PZPt}$ = 2270 Hz); -2.3 (d, 4P, P_A, $^2J_{PAPM}$ = 21 Hz); -213.2 (pq, 1P, P_M, $^1J_{PMPS}$ = $^1J_{PM\text{-}PQ}$ = 201 Hz); -259.9 (m, 2P, P_S), -346.0 (dt,1P, P_Q, $^1J_{PSPQ}$ = 96 Hz). ^{195}Pt NMR (86.01MHz, CD_2Cl_2, 180 K): δ = -3987 (tt, Pt, $^1J_{PZPt}$ = 2270 Hz, $^1J_{PSPt}$ = 820 Hz). IR (CH_2Cl_2): ν(Ru-H) 1966 cm^{-1}.

VT-NMR monitoring of [**3**]BF$_4$. Complex [**2**]BF$_4$ (35 mg, 0.032 mmol) and [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (24,5 mg, 0.032 mmol) were placed into a 5 mm NMR tube under an inert atmosphere. CD_2Cl_2 (0.5 mL) was transferred into the tube using a Hamilton® microsyringe. The resulting solution (complex [**3**]BF$_4$) was brought to 180 K using a liquid nitrogen-acetone bath and the tube was then inserted into the NMR probe head pre-cooled at the same temperature. Subsequently, the probe was warmed slowly to room temperature in steps of 10 K each, and sets of multinuclear NMR data were collected at each step (Fig. S1-S2).

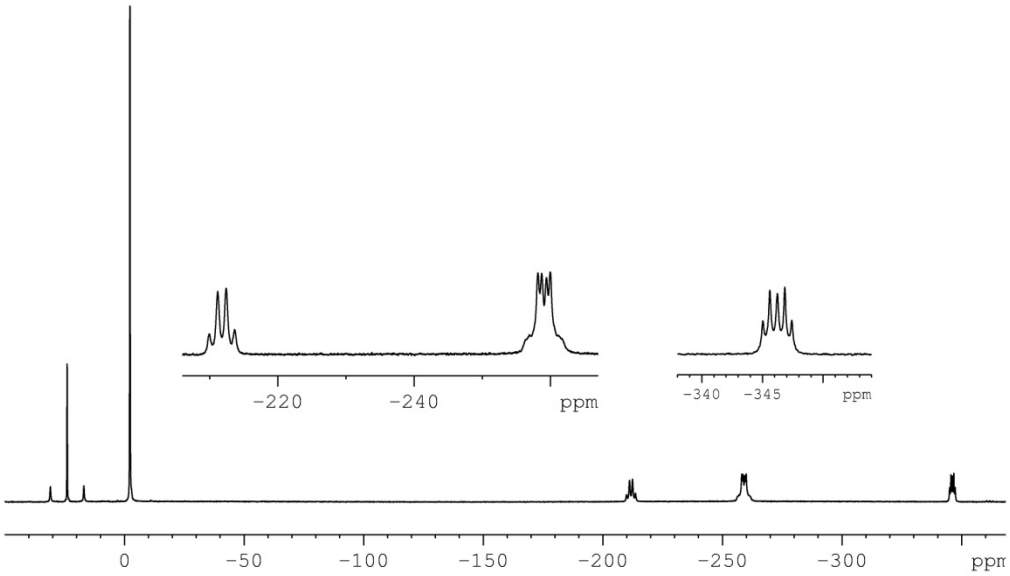

Figure S1. $^{31}P\{^1H\}$ NMR of complex [**3**]BF$_4$ (CD_2Cl_2, 180 K)

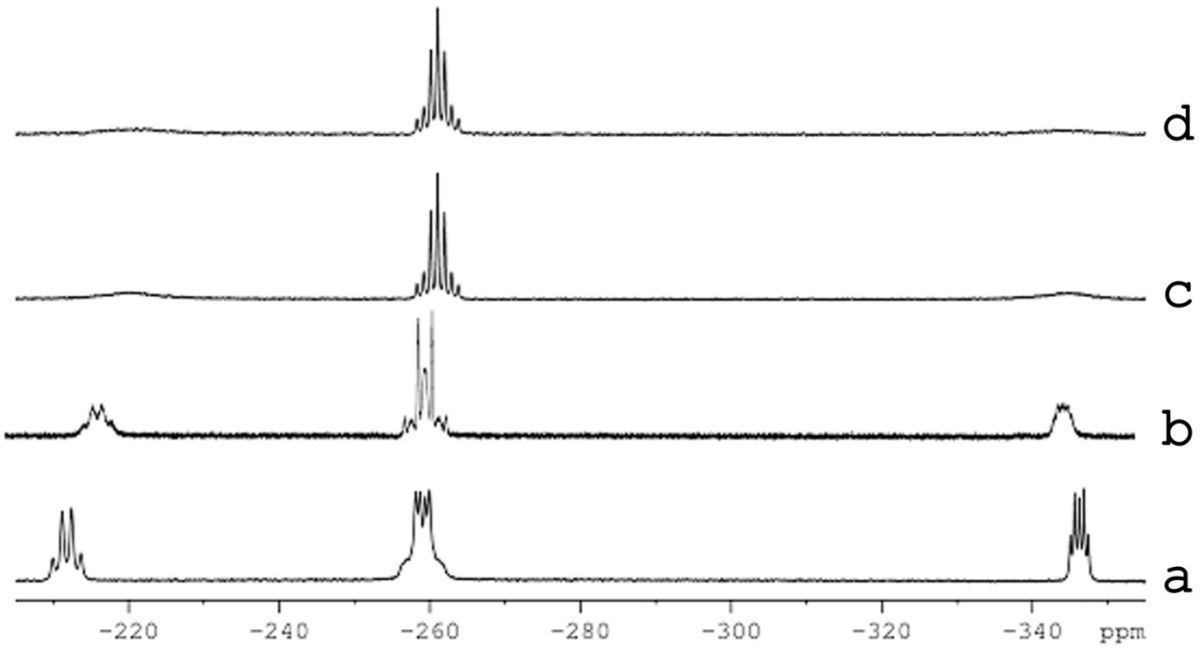

Figure S2. Portion of the $^{31}P\{^{1}H\}$ NMR spectra of complex [**3**]BF_4 (in CD_2Cl_2) recorded at 180 K (a), 258 K (b), 298 K (c), 308 K (d).

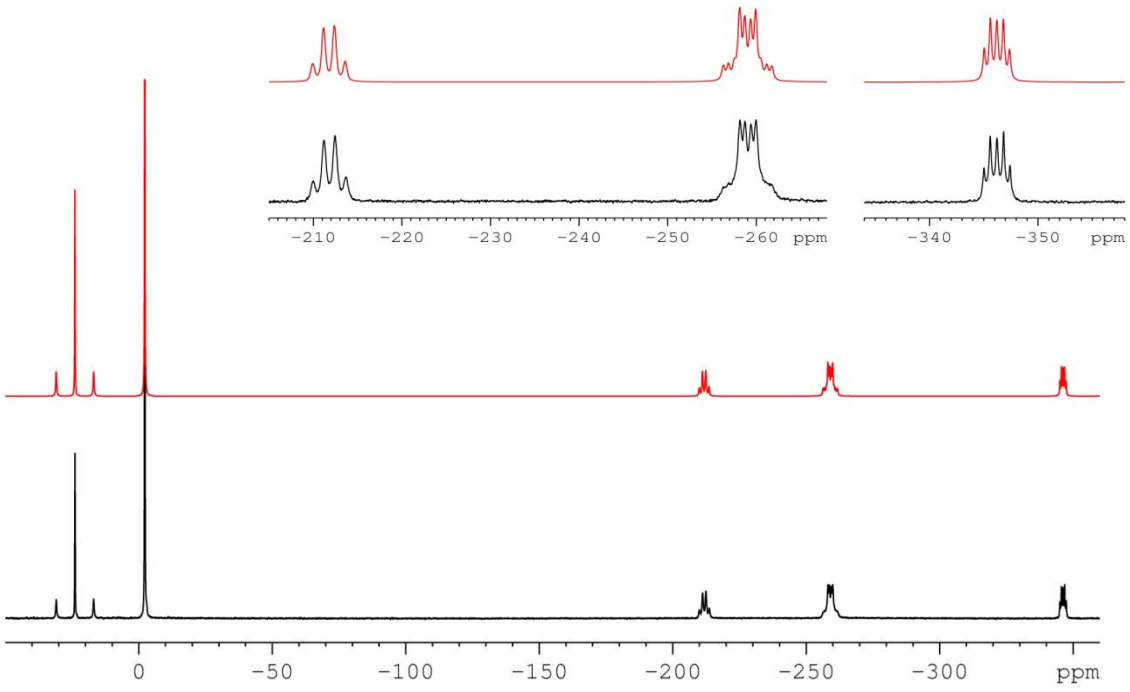

Figure S3. Experimental (black) and calculated (red) $^{31}P\{^{1}H\}$ NMR of complex [**3**]BF_4 (200 K). Calculated spectrum was obtained by DAISY package in TOPSPIN 2.1 PL4 software.

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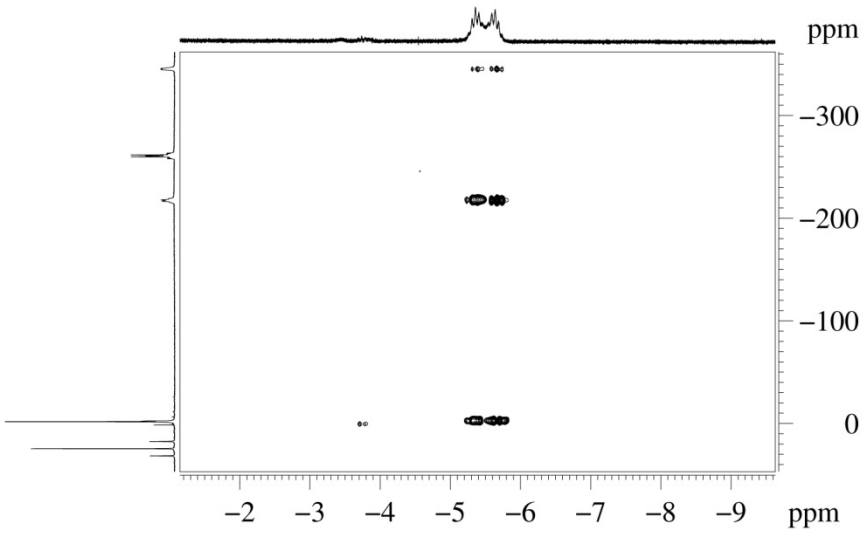

Figure S4. Portion (^{1}H hydride region) of the ^{1}H-^{31}P HMQC spectrum of [**3**]BF_4 (CD_2Cl_2, 258 K)

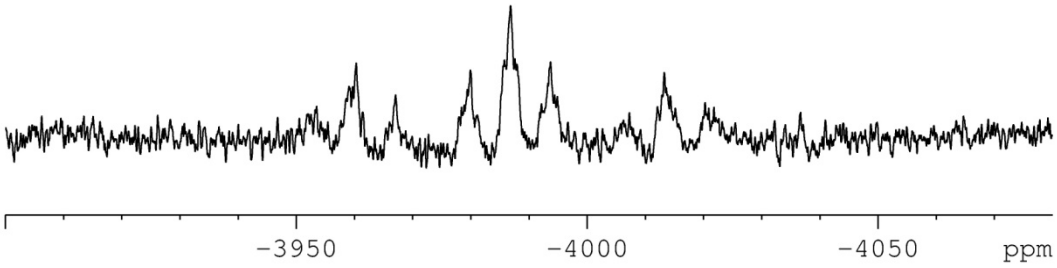

Figure S5. ^{195}Pt{^{1}H} NMR spectrum of complex [**3**]BF_4 (298 K, CD_2Cl_2)

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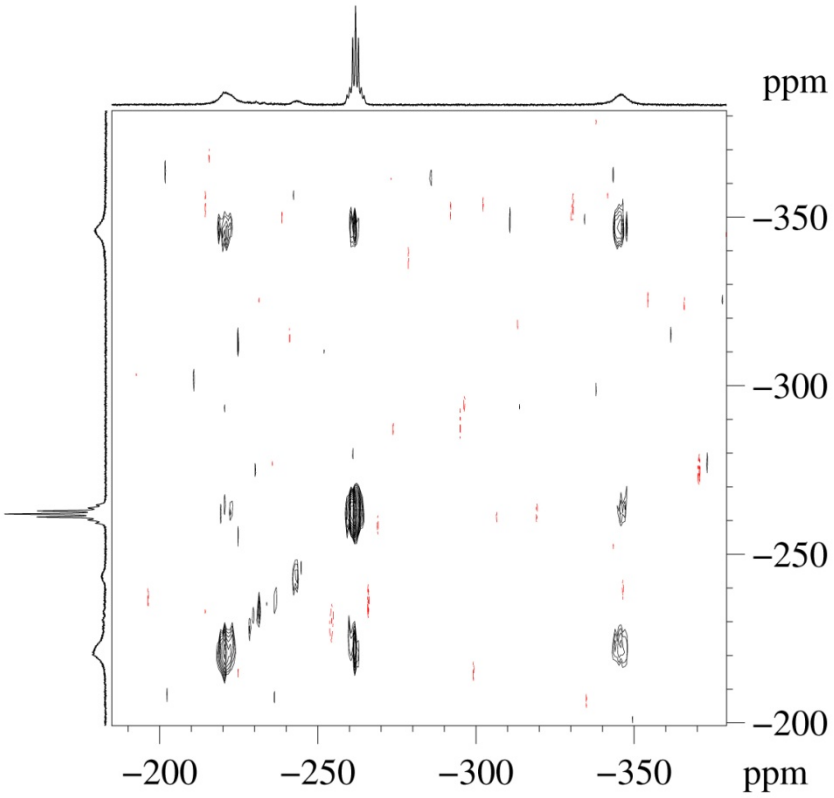


Figure S6. High-field part of the ^{31}P EXSY 2D-NMR spectrum of [**3**]BF_4 ($CHCl_2CHCl_2$, T = 32 °C, τ_m = 50 ms, 162 MHz).

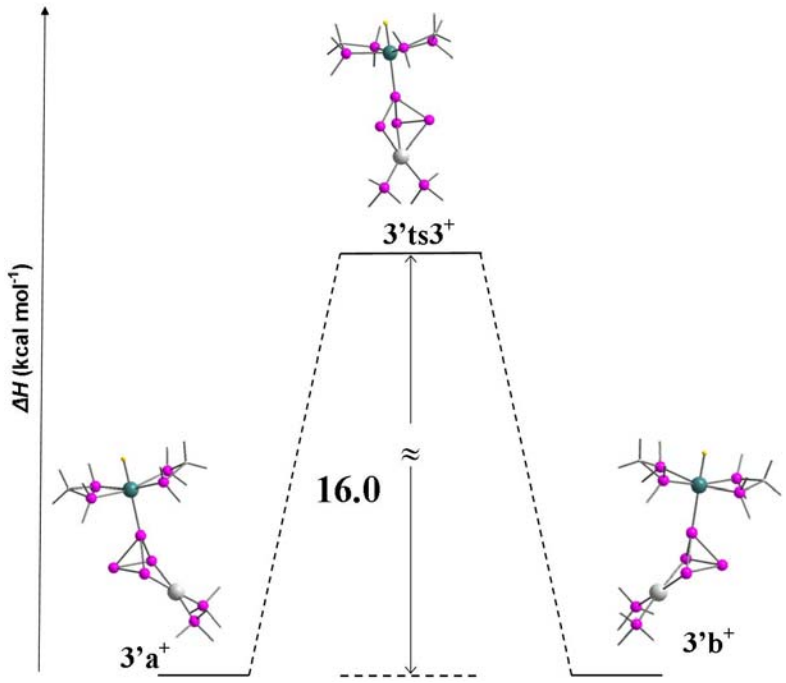


Figure S7. Enthalpy profiles for the additional motion, of platinum η^2-η^1 coordinated to three phosphorus atoms in complex **3**'.

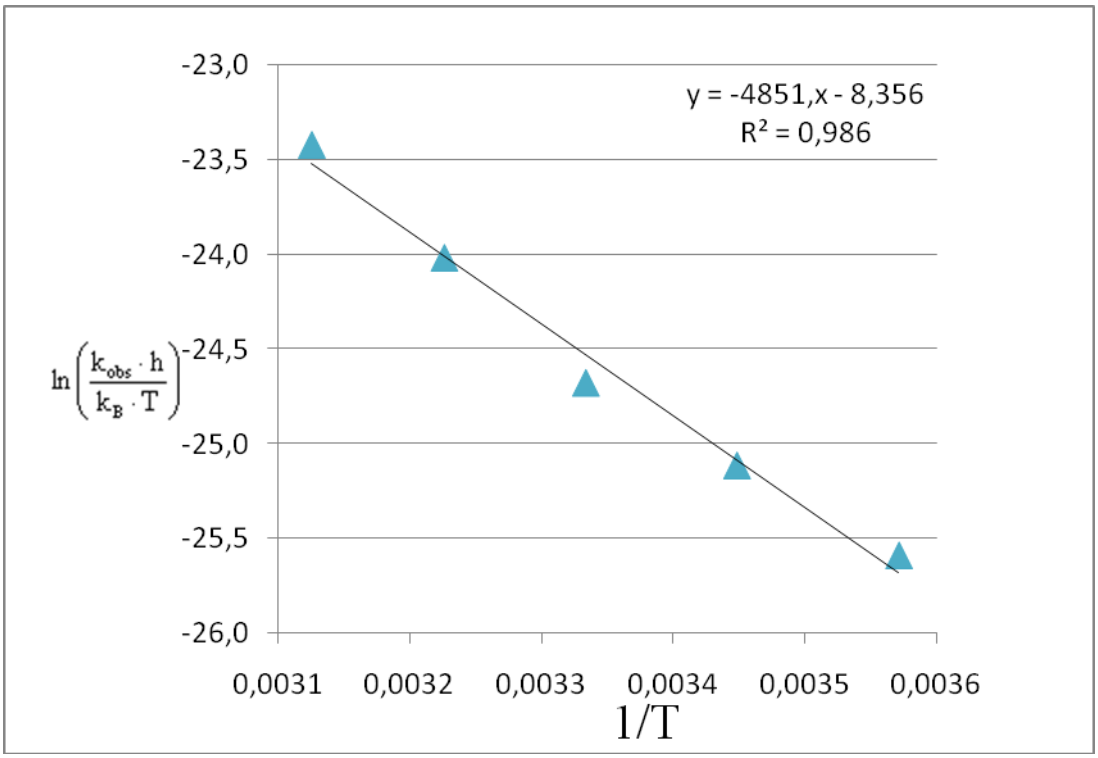
Activation parameters for the exchange processes. Exchange constants (K_{obs}) were determined by a line shape analysis performed with Dynamic NMR package in TOPSPIN 2.1 PL4 software.

Activation parameters were extracted by $\ln\left(\frac{k_{obs}\cdot h}{k_B\cdot T}\right)$ *vs* 1/T plot according to equation 1.

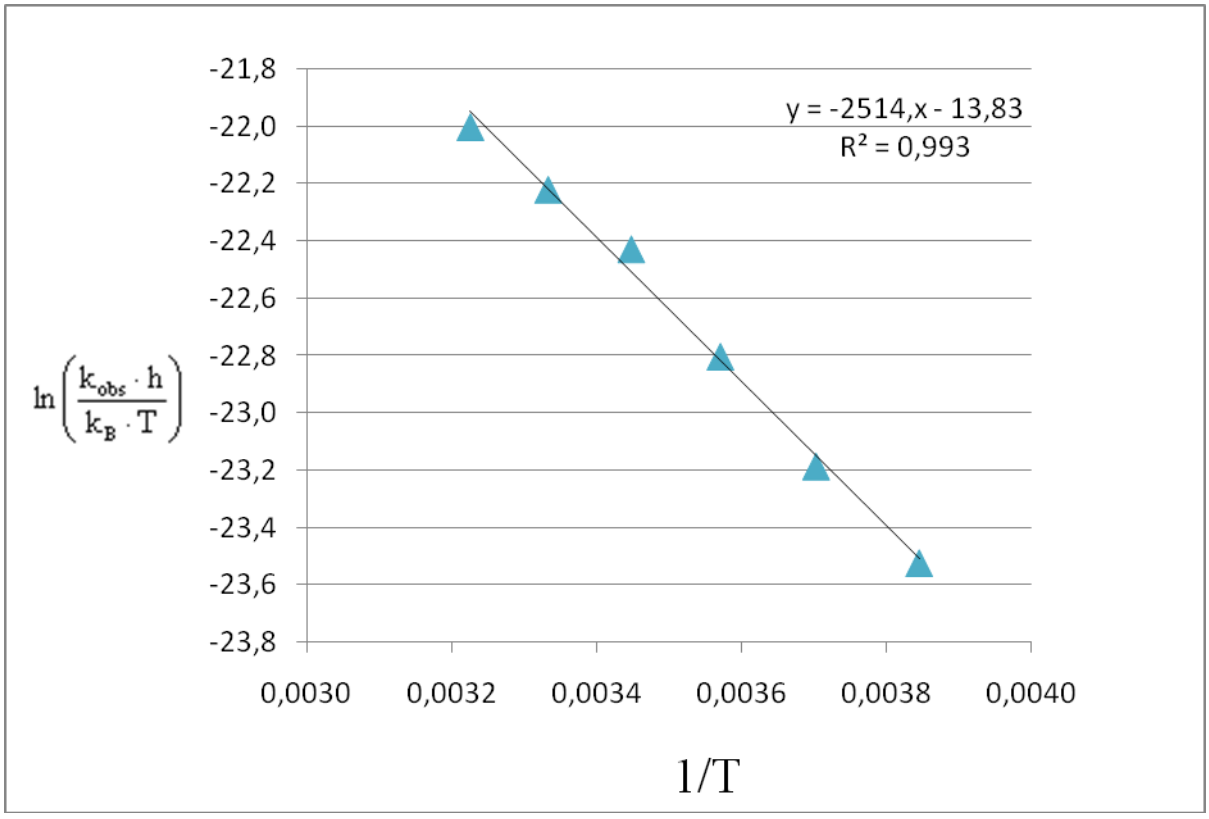
$$\ln\left(\frac{k_{obs}\cdot h}{k_B\cdot T}\right)=-\frac{\Delta H^{\neq}}{R\cdot T}+\frac{\Delta S^{\neq}}{R}$$

Equation 1

Complex 2^+



Complex 3^+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R² = 0,993
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-22,0
-22,2
-22,4
-22,6
-22,8
-23,0
-23,2
-23,4
-23,6
-23,8
0,0030
0,0032
0,0034
0,0036
0,0038
0,0040
1/T

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Computational details

DFT Calculations. Structural optimizations were carried out at the hybrid density functional theory (DFT) using the Gaussian03 suite of programs.[S4] The method used was the Becke's three-parameter hybrid exchange-correlation functional[S5] containing the nonlocal gradient correction of Lee, Yang and Parr (B3LYP).[S6] Calculations of the frequencies were performed to validate the nature of the optimized stationary points. The Stuttgart/Dresden effective core potential was used for metals.[S7] The basis set used for the remaining atomic species was the 6-31G(d, p).[S8]

Table S1: Free Gibbs energies, enthalpies and internal energies differences in kcal/mol for the calculated models in gas phase. The effect of the zero-point vibrations was considered in the reported values.

	ΔG	ΔH	ΔE
2'a$^+$ **- 2'c**$^+$	9.0	8.3	8.2
2'a$^+$ **- 2'ts**$^+$	10.6	9.1	9.4
2'c$^+$ **- 2'ts**$^+$	1.5	0.7	1.1
3'a$^+$ **- 3'c**$^+$	10.7	9.4	9.7
3'a$^+$ **- 3'ts1**$^+$	11.7	9.6	9.9
3'c$^+$ **- 3'ts1**$^+$	1.0	0.2	0.2
3'c$^+$ **- 3'ts3**$^+$	19.5	16.0	16.7

2'a$^+$ and **2'b**$^+$
Energy =-2909.6626088
Zero-point vibrational energy 394840.5 (Joules/Mol)
Zero-point correction= 0.150387 (Hartree/Particle)
Thermal correction to Energy= 0.168211
Thermal correction to Enthalpy= 0.169155
Thermal correction to Gibbs Free Energy= 0.101091
Sum of electronic and zero-point Energies= -2909.512222
Sum of electronic and thermal Energies= -2909.494398
Sum of electronic and thermal Enthalpies= -2909.493454
Sum of electronic and thermal Free Energies= -2909.561518

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P,-0.1335403613,-0.1306796364,-2.5628646592
P,1.0932404851,-0.0397214383,-4.3831484154
P,-0.9543582511,0.857070966,-4.345356971

P,-0.708117376,-1.3702386733,-4.2795155411
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P,-2.2959864513,-0.4921588877,0.2748916429
P,1.1505081627,-2.0058548465,0.2113320863
P,2.2621802293,0.5312803499,0.0069132071
C,-2.7819758597,1.2733265498,0.6827770188
H,-2.8791161537,1.4026201446,1.7638542581
H,-3.6940730965,1.6333974878,0.2021651465
C,2.7906716007,-1.1741303276,0.5820829908
H,2.9824493426,-1.1718110613,1.6582424629
H,3.658791707,-1.5956997485,0.0710109437
H,-0.8653071327,3.0464057762,1.0119637175
H,-1.5898823503,2.8702508885,-1.0049327881
H,-2.7406797962,-1.2673766987,1.3666246111
H,-3.2478194213,-0.9015077547,-0.6867667278
H,1.4642862206,-2.9694602051,-0.7742327094
H,0.9136127986,-2.8736752217,1.2982448134
H,2.8109429532,1.4325303849,0.9436600209
H,3.1090425646,0.8051154917,-1.0914047973

2'c^{+}

Energy =-2909.6489318
Zero-point vibrational energy 393399.0 (Joules/Mol)
Zero-point correction= 0.149838 (Hartree/Particle)
Thermal correction to Energy= 0.167839
Thermal correction to Enthalpy= 0.168784
Thermal correction to Gibbs Free Energy= 0.101823
Sum of electronic and zero-point Energies= -2909.499094
Sum of electronic and thermal Energies= -2909.481092
Sum of electronic and thermal Enthalpies= -2909.480148
Sum of electronic and thermal Free Energies= -2909.547109

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P,-1.0738975897,0.5615243279,-4.2945638089
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P,-1.1563060158,2.1137939488,0.1480579918
P,-2.271193303,-0.4243584985,0.148447486
P,1.1792987208,-1.9397300833,0.0855987687
P,2.2938588055,0.5985267818,0.0846196958
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H,-2.8521508209,1.3449929098,1.7866802429
H,-3.6617128452,1.7003629738,0.2454122059

C,2.7915565812,-1.1336595922,0.5978098266
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H,1.5513941341,-2.855516363,-0.9263318815
H,0.8737723433,-2.8583969616,1.1125314069
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2'ts^{+}

Energy =-2909.6467673
****** 1 imaginary frequencies (negative Signs) ******
Zero-point vibrational energy 392517.9 (Joules/Mol)
Zero-point correction= 0.149502 (Hartree/Particle)
Thermal correction to Energy= 0.166816
Thermal correction to Enthalpy= 0.167760
Thermal correction to Gibbs Free Energy= 0.102102
Sum of electronic and zero-point Energies= -2909.497265
Sum of electronic and thermal Energies= -2909.479952
Sum of electronic and thermal Enthalpies= -2909.479007
Sum of electronic and thermal Free Energies= -2909.544665

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P,-1.041227291,0.6627604259,-4.4291600823
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P,-1.1788661764,2.0661344265,0.1223141418
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P,1.1583413028,-1.9885349026,0.1740350737
P,2.2738812217,0.5485852739,0.0557607498
C,-2.7664341331,1.2730365979,0.7306216399
H,-2.8417638202,1.3554042688,1.81805682
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3'a^{+} and **3'b**$^{+}$

Energy =-3715.4588596
Zero-point vibrational energy 540813.8 (Joules/Mol)
Zero-point correction= 0.205985 (Hartree/Particle)
Thermal correction to Energy= 0.232665
Thermal correction to Enthalpy= 0.233610
Thermal correction to Gibbs Free Energy= 0.141831
Sum of electronic and zero-point Energies= -3715.252874
Sum of electronic and thermal Energies= -3715.226194
Sum of electronic and thermal Enthalpies= -3715.225250
Sum of electronic and thermal Free Energies= -3715.317029

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P,-0.3279160008,2.1330136623,1.1290417609
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P,2.3260139542,-0.5118343761,0.832656441
C,-2.1869496191,1.9157014826,1.2705222533
H,-2.4726140309,1.7478224747,2.312096838
H,-2.7910541666,2.7302781237,0.8652153535
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H,-1.5197457921,3.0333866758,-7.6710142104

H,-2.7522197382,2.0592979051,-6.2147880125

3'c^{+}
Energy =-3715.4428504
Zero-point vibrational energy 539651.3 (Joules/Mol)
Zero-point correction= 0.205542 (Hartree/Particle)
Thermal correction to Energy= 0.232507
Thermal correction to Enthalpy= 0.233451
Thermal correction to Gibbs Free Energy= 0.142880
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Sum of electronic and thermal Enthalpies= -3715.2102100
Sum of electronic and thermal Free Energies= -3715.299971

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H,4.2212645388,1.9546464463,2.3589354282
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H,-5.842833026,-1.5615502242,-0.1089059402
H,-4.4576051448,2.6185250305,1.1506213652
H,-5.8552790491,1.5298110284,-0.0549776894
H,-4.3551431888,2.7462430552,-0.9851032371

3'ts1^{+} and **3'ts2**$^{+}$

Energy =-3715.4424832
****** 1 imaginary frequencies (negative Signs) ******
Zero-point vibrational energy 539291.4 (Joules/Mol)
Zero-point correction= 0.205405 (Hartree/Particle)
Thermal correction to Energy= 0.231559
Thermal correction to Enthalpy= 0.232503
Thermal correction to Gibbs Free Energy= 0.144046
Sum of electronic and zero-point Energies= -3715.237078
Sum of electronic and thermal Energies= -3715.210924
Sum of electronic and thermal Enthalpies= -3715.209980
Sum of electronic and thermal Free Energies= -3715.298437

Ru,2.9128246322,0.017008711,0.0599778792
H,4.5025644715,0.0273604205,-0.1675591192
P,0.0414613091,0.0226423472,-0.9655780614
P,-0.9930188218,-1.4873509908,0.3488480746
P,-1.0050364407,1.4790104299,0.3989166382
P,0.4871486735,-0.0129533835,1.2514351781
P,3.4463353906,-1.8831623776,1.3507744205
P,3.040255695,-1.8395069704,-1.3910117215
P,3.0247017027,1.9233863825,-1.3261808734
P,3.4312144417,1.8758539162,1.4155007428
C,3.7436511575,-3.0188743308,-0.1120742679
H,4.8138912756,-3.1725450407,-0.2716473477
H,3.25109763,-3.9918663015,-0.0550515924
C,3.7185557501,3.0637939762,-0.0073183228
H,4.7874095625,3.2319380134,-0.161500704
H,3.2178103043,4.0300371527,0.0832453842
H,4.607421776,-1.9962732718,2.1473147361
H,2.5527054354,-2.6082947315,2.1741368299
H,3.9270412801,-1.9137766875,-2.4880039912
H,1.9546651437,-2.5534253227,-1.9519131643
H,1.9331074742,2.6471545854,-1.8622481308
H,3.9106260198,2.0427633841,-2.4198837963
H,4.5917223529,1.9709072658,2.2152336085
H,2.5320751532,2.5647621681,2.2636026602
Pt,-2.8296109081,-0.0176530226,0.7338449799
P,-4.396835462,1.7482878194,1.0554764435
P,-4.3822409268,-1.8062019579,0.9958583271
H,-4.244022289,-2.6155223393,2.145028115
H,-4.3636523603,-2.8221481541,0.01581636
H,-5.7789713818,-1.591147475,1.0562610394
H,-4.2665627562,2.5183788076,2.2322099061
H,-5.7918404404,1.5199923797,1.1063714824
H,-4.3853288446,2.7977155981,0.1112662871

3'ts3^{+}
Energy =-3715.4325158

****** 1 imaginary frequencies (negative Signs) ******
Zero-point vibrational energy 541477.3 (Joules/Mol)
Zero-point correction= 0.206238 (Hartree/Particle)
Thermal correction to Energy= 0.231828
Thermal correction to Enthalpy= 0.232772
Thermal correction to Gibbs Free Energy= 0.146571
Sum of electronic and zero-point Energies= -3715.226278
Sum of electronic and thermal Energies= -3715.200688
Sum of electronic and thermal Enthalpies= -3715.199743
Sum of electronic and thermal Free Energies= -3715.285945

Ru,-2.8724079572,-0.0054791743,0.035865962
H,-4.5082598995,-0.0138551716,0.1242038438
P,-0.488377282,-0.0018175278,-0.0022212412
P,0.9416205991,1.265563286,-1.1612518171
P,0.9449746757,-0.901917091,-1.461694225
P,0.977381865,-0.2227147461,1.607669563
P,-3.2265665265,-1.7421199145,-1.5065787217
P,-3.0885008324,-2.0077270515,1.2500913077
P,-3.0868795713,1.7279239452,1.6109628868
P,-3.2366214609,1.9933086631,-1.1443556795
C,-3.632345737,-3.0434848702,-0.2169965982
H,-4.7096164916,-3.2240130608,-0.1802804348
H,-3.1170477191,-3.9992128789,-0.334440333
C,-3.6506371095,3.018797287,0.3715251969
H,-4.7302535543,3.1720914849,0.4452327082
H,-3.1497641748,3.9870012022,0.4379266655
H,-4.2902250162,-1.7940316246,-2.4336123974
H,-2.2212598591,-2.347160242,-2.2966929216
H,-4.0613042468,-2.2344670237,2.2477396453
H,-2.0239999683,-2.7465982413,1.8163771491
H,-2.0186610677,2.3539643106,2.2940273441
H,-4.0487339957,1.7569006848,2.643917729
H,-4.3006894931,2.2147228238,-2.0456333487
H,-2.2364710648,2.7479187943,-1.8012063869
Pt,2.7099513208,-0.0060665953,0.0756387362
P,4.264314191,-0.2505288056,1.8431623618
P,4.3861311418,0.2404520167,-1.6568486698
H,5.302296494,1.3170496126,-1.6266527947
H,3.8805044909,0.4231174266,-2.9615403657
H,5.3075483509,-0.7981371173,-1.9246202311
H,5.1782470341,0.7939669035,2.1083965597
H,5.1781319581,-1.3279356289,1.81638689
H,3.714195427,-0.4273827095,3.1283024362

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Crystallographic studies: Data collection for complex *trans*-[Ru(dppm)$_2$(H)(η^1-P$_4$)]BF$_4$ was carried out on a Oxford Diffraction Xcalibur3 diffractometer equipped with Mo K$_\alpha$ radiation (0.71073 Å). Data were collected at 150 K. Data collection was performed with the program CrysAlis CCD[S9] and data reduction was carried out with the program CrysAlis RED [S10]. Absorption correction was applied through the program ABSPACK [S10]. Crystal data and structure refinement details are given in Table S1. The structure was solved with direct method implemented in the program Sir97 [S11] and the refinement was completed by full-matrix least squares against F^2 using all data implemented in SHELXL [S12]. All the non-hydrogen atoms were refined anisotropically. Basal phosphorus atoms of the P$_4$ units show large anisotropic displacement parameters caused by the rotation of the P$_4$ units around the metal-coordinated phosphorus axes. Attempts to refine the disorder did not improve the overall refinement. The hydrogen atoms were set in calculated position and all refined isotropically with thermal factors depending on the ones of the atom to which they are bound. Molecular plots were produced by the program ORTEP3 [S13]. All the calculations were performed using the package WINGX [S14]. Crystallographic data (excluding structure factors) for the compound reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 793923. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

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Table S2. Crystal data and structure refinement for *trans*-[Ru(dppm)$_2$(H)(η^1-P$_4$)]BF$_4$.

Empirical formula	C50 H45 B1 F4 P8 Ru1
Formula weight	1081.5
Temperature	150(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	*P* $2_{1/}$c
Unit cell dimensions	a = 17.5322(2) Å
	b = 23.5016(3) Å
	c = 23.7195(4) Å
	b= 94.9185(13)°.
Volume	9737.3(2) Å^3
Z	8
Density (calculated)	1.476 Mg/m^3
Absorption coefficient	5.513 mm^{-1}
F(000)	4400
Crystal size	.30 x .20 x .20 mm^3
Theta range for data collection	3.76 to 62.03°.
Index ranges	-9<=h<=19, -25<=k<=26, -26<=l<=26
Reflections collected	39029
Independent reflections	14901 [$R_{(int)}$ = 0.0539]
Completeness to theta = 62.03°	97.2 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.332 and 0.139
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14901 / 0 / 967
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	$R_1 = 0.0574$, $wR_2 = 0.1292$
R indices (all data)	$R_1 = 0.0962$, $wR_2 = 0.1479$
Largest diff. peak and hole	1.221 and -0.825 e.Å^{-3}

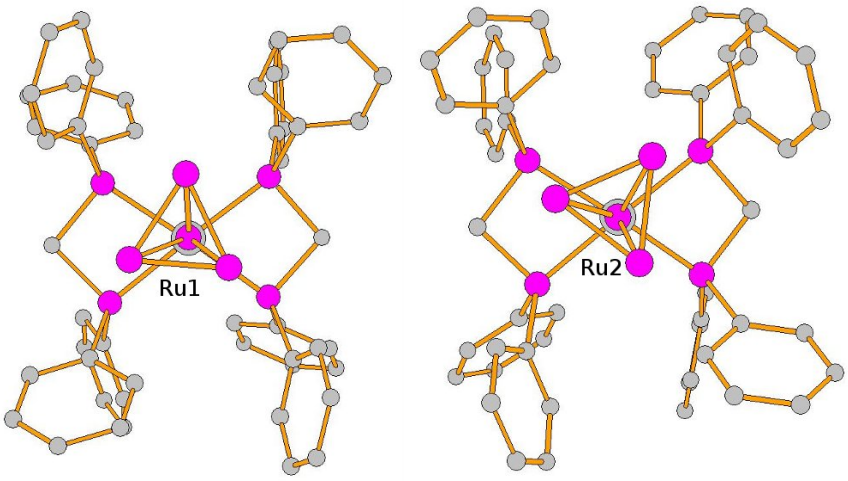

Figure S8. Ball and stick views of the two units of the cations *trans*-$[(dppm)_2Ru(H)(\eta^1\text{-}P_4)]^+$, **2**$^+$, emphasizing the different orientations of the P_4 ligand respect to the metal fragment.

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