Reactivity of The P_4 Molecule with Cobalt(I) and Rhodium(I) Polyphosphane Fragments

Massimo Di Vaira,[a] Markus P. Ehses,[a] Maurizio Peruzzini,[b] and Piero Stoppioni*[a]

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The reaction of white phosphorus with the electronically and coordinatively unsaturated systems $[(PP_3)M]^+$ [PP_3 = tris(2-diphenylphosphanylethyl)phosphane; M = Co, Rh] and $[(NP_3)Rh]^+$ [NP_3 = tris(2-diphenylphosphanylethyl)amine] in tetrahydrofuran affords new tetraphosphorus complexes. The PP_3 metal fragments yield the trigonal bipyramidal $[(PP_3)M(\eta^1\text{-}P_4)]^+$ complex cations [M = Co^I **(1)**, Rh^I **(2)**] containing the intact P_4 molecule bonded end-on to the metal. In contrast, the $[(NP_3)Rh]^+$ system yields an octahedral rhodium(III) complex of formula $[(NP_3)Rh(\eta^2\text{-}P_4)]BPh_4$ **(3)** which contains a bicyclotetraphosphane ligand (P_4^{2-}) coordinated to the metal through the wing-tip P atoms. Compound **3** forms through the oxidative addition of the P_4 molecule to the metal fragment. These new tetraphosphorus derivatives, which are very reactive, have been characterized in solution at low temperature by ^{31}P NMR spectroscopy.

Introduction

White phosphorus, P_4, is highly reactive towards a variety of organometallic and transition metal fragments. Very often the reactions proceed through complicated multistep thermal or photochemical degradation and aggregation to form metal complexes containing P_n groups for which the original tetrahedral tetraphosphorus topology is no longer evident.[1] Although specific steps of the progressive disruption of the tetrahedral molecule have been documented only in some instances,[2] among the numerous compounds described there are many complexes containing P_n units which may be formally considered as resulting from the initial interaction of the metal fragment with the intact P_4 molecule, followed by stepwise disruption of P−P bonds. The P_n units which have been found to form through the metal-mediated degradation of P_4 are shown in Scheme 1 according to the number of bond(s) which have been cleaved. Coordination of the intact P_4 molecule has been achieved through the end-on[3] and side-on[4] coordination modes, the formally possible face coordination mode having only been postulated on spectroscopic grounds.[4a] The insertion of a metal fragment into a P−P bond to form a bicyclotetraphosphane (**A** in Scheme 1) is generally considered to be the first step in the degradation of the tetrahedral molecule.[5] A second bond of the original P_4 may be cleaved either next to the first one or opposite to it, yielding three-, **C**,[5a,6] or four-membered, **B**, cyclic P_4 ligands; planar and bent topologies of the latter are known.[5d,7] Starting from **C**, the cleavage of another bond may furnish tetraphosphorus ligands, with either tripodal, **D**,[8] or chain arrangements, **E**,[5f,9] or it may produce two separated units, **F**, i.e. one *cyclo*-P_3 ring and a single P atom.[10] Open P_3 structures are less common,[11] whereas numerous examples exist where P_4 is cleaved into two P_2 units, **G**.[12]

Up to now the course of the reaction of P_4 with a metal fragment has been difficult to predict. This is due in part to the small number of stable complexes containing the intact P_4 molecule. Furthermore, these complexes are either poorly soluble or too reactive to be isolated and characterized by standard techniques. Hence, systematic studies on the factors favouring specific activation modes and on the reactivity of such complexes are sparse.

We have investigated the reactivity of white phosphorus toward group 9 coordinatively and electronically unsaturated fragments stabilized by tripodal tetradentate ligands, which are known to be excellent precursors for the activation of H−H and C−H bonds.[13] The $[(PP_3)M]^+$ species [PP_3 = tris(2-diphenylphosphanylethyl)phosphane; M = Co, Rh] react with white phosphorus yielding adducts of formula $[(PP_3)M(\eta^1\text{-}P_4)]^+$ in which the intact P_4 molecule is η^1 bound to the metal. In contrast, the related $[(NP_3)Rh]^+$ [NP_3 = tris(2-diphenylphosphanylethyl)amine] fragment yields a compound of formula $[(NP_3)Rh(\eta^2\text{-}P_4)]BPh_4$, which contains a bicyclotetraphosphane ligand (P_4^{2-}) coordinated to the metal through the wing-tip P atoms. The complex forms through the oxidative addition of the P_4 molecule to the metal fragment. The compounds are extremely reactive and have been characterized in solution at low temperature.

Results and Discussion

The reaction at room temperature of $[(PP_3)CoH]$, dissolved in THF under argon, with CF_3SO_3Me, under nitrogen, yields the dinitrogen complex cation $[(PP_3)CoN_2]^+$ [14]

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[a] Dipartimento di Chimica, Università di Firenze,
via Maragliano 77, 50144, Firenze, Italy
E-mail: stopmora@chim1.unifi.it
[b] I.S.S.E.C.C., C.N.R.,
via J. Nardi 39, 50132 Firenze, Italy
E-mail: peruz@fi.cnr.it

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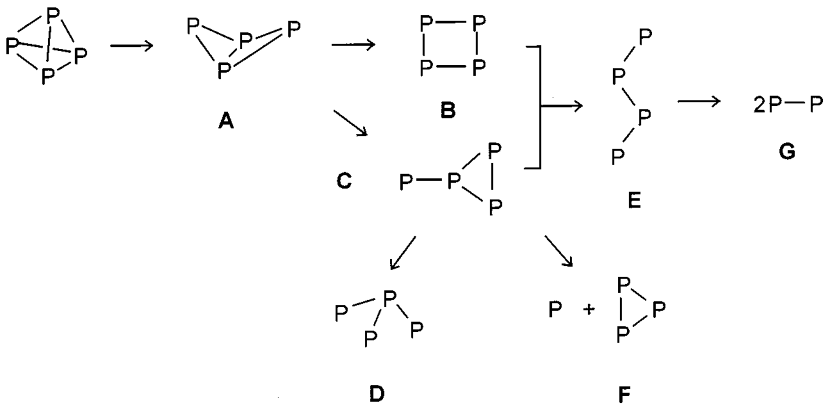
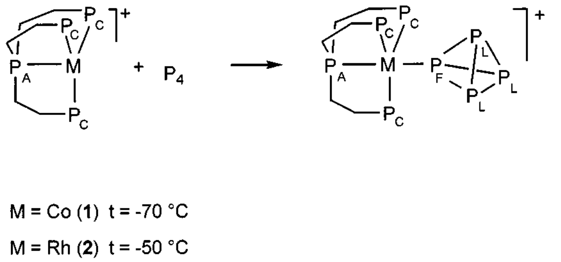


Scheme 1. Phosphorus units from formal stepwise cleavage of P−P bonds in the P_4 tetrahedron

and two species, denoted *a* and *b* in ref.[15], where their NMR spectroscopic data are reported. They exhibit an AC_3 $^{31}P\{^1H\}$ spin system suggestive of a trigonal geometry. Such species are likely to consist of the $[(PP_3)Co]^+$ cation and/or the complexes resulting from the interaction of the unsaturated $16e^-$ fragment with the solvent or with the weakly coordinating $CF_3SO_3^-$ anion. These species react immediately with P_4 at temperatures as low as −70 °C to form a P_4 complex **(1)** (Scheme 2) which is stable up to −40 °C and decomposes unspecifically at higher temperature. Interestingly, the dinitrogen complex cation does not react with P_4 in the range of temperatures within which the P_4 adduct is stable.



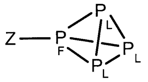
Scheme 2. Reaction of $[(PP_3)M]^+$ species with white phosphorus

Monitoring the electrophilic attack on the rhodium complex $[(PP_3)RhH]$ at −20 °C with CF_3SO_3Me by ^{31}P NMR spectroscopy provides evidence for three species (*a*′, *b*′ and *c*′; NMR in ref.[16]) each exhibiting an AC_3X spin system, characteristic of rhodium(I) complex cations with trigonal geometry; such species are likely to consist of the $[(PP_3)Rh]^+$ cation and of the complexes resulting from its interaction with the solvent or with the weakly coordinating $CF_3SO_3^-$ anion. Interestingly, such electrophilic attack, carried out at low temperature, does not yield the square pyramidal cations which have been observed by performing the reaction at room temperature.[13] The three $[(PP_3)Rh]^+$ synthons react at −50 °C with an equimolar amount of P_4 yielding the complex cation $[(PP_3)Rh(\eta^1\text{-}P_4)]^+$ **(2)**, Scheme 2, which is stable up to −20 °C and decomposes unspecifically at higher temperature. The high reactivity of the cations **1** and **2** prevented their isolation as pure solids, and accordingly they have been characterized in solution by $^{31}P\{^1H\}$ NMR spectroscopy.

The $^{31}P\{^1H\}$ NMR spectra of the complexes **1** and **2** do not change in the temperature ranges investigated (from −70 to −40 °C for **1** and from −50 to −20 °C for **2**), which allows us to exclude dynamic behaviour. They exhibit four resonances (see the Experimental Section) with intensity ratios 1:3:1:3, the most significant difference between the spectra of the cobalt and of the rhodium derivative being due to the coupling with ^{103}Rh in compound **2**. Thus the cobalt derivative exhibits an AC_3FL_3 spin system and the rhodium derivative gives an AC_3FL_3X spin system, which are both consistent with a trigonal bipyramidal geometry around the metal. The metal should therefore be bound to the four donors of the tripodal PP_3 ligand and to one phosphorus atom of the intact P_4 molecule. The shifts and the coupling constants of the polyphosphane P atoms are typical for cobalt(I)[14] and rhodium(I)[13] complexes with trigonal bipyramidal geometry. The phosphorus atom (P_F) of the P_4 molecule which is bound to the metal is deshielded with respect to those of the "distal" P_3 face; the latter are only slightly affected by the nature of the metal fragment and have chemical shifts close to that of free P_4. These data are in accordance with those found for the few other complexes containing an intact P_4 molecule end-on bound to a metal fragment (Table 1). The values of the direct coupling constants $^1J_{P_FP_L}$ for all compounds, ranging from 185 to 235 Hz, are relatively close to each other. The bridgehead phosphorus of the PP_3 ligand in the two compounds is highly deshielded with respect to the value found for PP_3 in cobalt(I)[17] and rhodium(I)[13] complexes with coligands such as CO, PPh_3, CH_3, Ph, Cl^- and H^- in the fifth position.

In an attempt to rationalize some aspects of the bonding in these compounds both extended-Hückel[18] (EH) and ab initio[19] Hartree−Fock (HF) calculations were undertaken on model systems where the presence of the polyphosphane ligand was simulated by four properly arranged PH_3 groups and the coligand was the η^1-coordinated P_4 cage or, for comparison, the CO or Cl^- moiety. The HF calculations were of the single-point energy type, except for a preliminary set in which the metal−phosphorus distances were optimized: the ratios between distances at the energy minimum (individual values being unreliable at the level of the

Table 1. $^{31}P\{^1H\}$ NMR spectroscopic data of the P_4 molecule bound end-on to a metal fragment (Z)

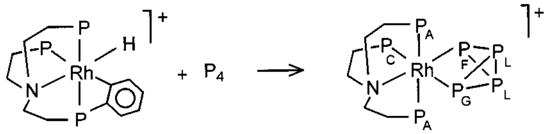


Z	δP_F	δP_L	$^1J(P_F\text{-}P_L)$	$\Delta\delta(P_L\text{-}P_L)$	Ref.
$[(PP_3)Co]^+$	-333.5	-472.3	219.0	138.8	[a]
$[(PP_3)Rh]^+$	-372.5	-493.8	226.5	121.3	[a]
$[(triphos)Re(CO)_2]^+$	-390.5	-488.9	235.7	98.4	[3a]
$[(CO)_3(PPh_3)MoP_4]$	-400.2	-480.0	185.0	79.8	[3b]
$[(CO)_3(PPh_3)WP_4]$	-422.0	-473.0	204.0	51.0	[3b]

[a] Data of the present work.

model) showed that the P_4 cage is competitive with the PH_3 groups as a ligand. The basis set in the HF calculations was either the LANL2DZ,[20] or it ranged from the 6−31G(d)[21] to the 6−311+G(d,p)[22] if the Rh metal was replaced by Co in the model. The pattern of atomic charges yielded by the EH calculations run with standard parameters[18] agrees with the trend expected in view of the NMR results, with the phosphorus atom in the bridgehead position of the phosphane ligand bearing a higher positive charge than the peripheral P atoms and with positive/negative charges for the coordinating/distal P_4 atoms. The HF calculations yield a similar pattern if polarization functions are included in the basis set. Although with differences in detail, both types of calculations give the same picture for bonding of the cage molecule to the metal, through an analysis of the changes in the atomic-orbital occupancies as the P_4 molecule is allowed to approach the metal centre from a distance. A synergic mechanism is in action, with σ-donation from the apical P_4 atom to the metal and back-donation from metal π orbitals. The latter shift of electron density reaches the distal P atoms of the cage through its peripheral MO′s. As expected, there are substantial analogies with the picture obtained for the model with the CO coligand and notable differences with respect to the Cl^- model. The values of the isotropic shielding tensor for atoms of the P_4 model compound agree with the expected trend, but the calculations do not provide a clue to the significantly higher deshielding of the bridgehead polyphosphane P atom in a P_4 than in a (for example) CO derivative.

The *ortho*-metallated product[13] which forms by electrophilic attack of CF_3SO_3Me on $[(NP_3)RhH]$ reacts in a short time at −20 °C (see Scheme 3) with a stoichiometric amount of P_4 in THF yielding, after addition of $NaBPh_4$, a pale-red compound of formula $[(NP_3)Rh(\eta^2\text{-}P_4)]BPh_4$ **(3)**. The solid, which has been isolated at low temperature, may be stored under inert atmosphere at room temperature but it decomposes in solution above 10 °C. Compound **3** exhibits at 0 °C a $^{31}P\{^1H\}$ NMR spectrum (see the Experimental Section) which presents five resonances with intensity ratios 2:1:1:1:2; it has been successfully simulated as an A_2CFGL_2X spin system. The two low-field resonances at $\delta = 29.8$ and -12.5 are due to the phosphorus atoms of the NP_3 ligand and are consistent with an octahedral rhodium(III)[13] complex having two chemically and magnetically equivalent phosphorus atoms (P_A) *trans* to each other and the third one (P_C) in the *cis* position (Scheme 3). The three high-field resonances are due to the four phosphorus atoms of the P_4 unit. Those at comparatively low field are assigned to atoms, P_F ($\delta = -224.3$) and P_G ($\delta = -194.5$) occupying the coordination sites, hereafter "equatorial", lying opposite the P_C and the NP_3 nitrogen positions. Finally, the resonance ($\delta = -237.8$) occurring at higher field is attributed to the two phosphorus atoms of the bicyclotetraphosphane (P_L) which are not bound to the metal. The P_F and P_G signals, in view of their different multiplicities, have been assigned considering that the one with higher multiplicity should be due to the phosphorus atom (P_G) lying *trans* to the P_C phosphorus atom of NP_3. The equivalence of the P_L sites suggests that the bond joining them should be normal to the equatorial plane and parallel to the line connecting the P_A positions. The weak coupling (40 Hz; see Experimental Section) between the inequivalent wing-tip atoms (P_F and P_G) in compound **3**, points to an open P_4 frame, which accounts for the presence of "through-metal" geminal coupling of the coordinating P atoms.



Scheme 3. Reaction of $[(NP_3)Rh]^+$ species with white phosphorus

On lowering the temperature below −40 °C the P_L and P_A signals become more complex and the positions of the sites are no longer equivalent. On the other hand, the chemical shifts of all absorptions, and the shapes of the remaining three signals, are substantially unchanged. The reversibility of this diversification points to the presence of a dynamic behaviour. The low activation barrier and the small deviations in the NMR parameters for the P_A and P_L sets suggest limited changes in stereochemistry for the two pairs of phosphorus atoms on the NMR time-scale at low temperature.

The NMR spectroscopic data for coordinating bicyclotetraphosphane in complexes of this type reported up to now appear in Table 2; they refer to compounds which contain insertion products of one metal fragment into a P−P bond (*endo-endo*) or two metal fragments bound to the wing-tip P atoms of the butterfly skeleton (*exo-exo*). As might be expected, the chemical shift of the wing-tip atoms depends heavily on the electronic and steric properties of the metal fragment. These resonances are shifted to lower field with respect to the P_2 backbone phosphorus atoms, which exhibit absorptions between $\delta = -377$ and -214, in the high-field region typical for phosphorus atoms participating in small cycles.[23] Interestingly, the chemical shift difference ($\Delta\delta = \delta P_F - \delta P_L$) within the P_4 ligand is smaller for the heavier group-9 complexes.

Table 2. $^{31}P\{^1H\}$ NMR spectroscopic data of the bicyclotetraphosphane unit bound to metal fragment(s) (Z′, Z")

Z′	δP_F	δP_G	δP_L	$^1J(P_F\text{-}P_L)$	$^1J(P_G\text{-}P_L)$	$\Delta\delta(P_L\text{-}P_L)$	Ref.
$[(NP_3)Rh]^+$	-224.3	-194.5	-237.8	160.0	166.0	13.5	[a]
$[Cp''_2Hf]$	117.5	117.5	-219.3	193.9	193.9	336.8	[5f]
$[Cp^*_2Zr]$	93.3	93.3	-214.0	201.1	201.1	307.3	[5f]
$[Cp^*CoCO]$	-258.2	-258.2	-335.9, -376.9	156	156	77.7	[5d]
$[Cp''RhCO]$	-310.0	-310.0	-325.6, -341.9	160	160	15.6	[5g]
[(triphos)IrH]	-235.0	-251.3	-272.7	133.0	141.3	37.7	[5a]
Z"							
$[Cp'''Fe(CO)_2]$	-81.4	-81.4	-237.8	183.0	183.0	156.4	[5e]

[a] Data of the present work.

The remarkable difference in reactivity between $[(PP_3)Rh]^+$ and $[(NP_3)Rh]^+$ toward white phosphorus is in line with other results reported for the organometallic chemistry of the two systems.[13,14] The attainment of a pseudo-octahedral coordination geometry, as proposed for **3**, involves a considerable increase for one of the P−Rh−P angles formed by the peripheral P atoms of the ligand. It was pointed out on the basis of EH calculations on model systems for the tripod ligand and the four-coordinate metal[24] that such deformation should be easier for $[(NP_3)Rh]^+$ than for $[(PP_3)Rh]^+$ as a consequence of the early occurrence of a HOMO−LUMO avoided crossing in the former case. By similar (EH) calculational procedures we expect the $[(NP_3)Rh]^+$ system to be more prone to distortion than the $[(NP_3)Co]^+$ one because of a smaller HOMO−LUMO gap for the former, in the undistorted geometry over a range of reasonable metal−donor atom distances. These conclusions (easier angle opening in presence of the NP_3 ligand and of the Rh metal) are supported by trends in single-point energy values calculated by the HF method with LANL2DZ basis functions at various points of the deformation path and for various sets of metal−donor atom distances (one NH_3 group being used in addition to the PH_3 groups to mimic the NP_3 donors). However, the angle opening is definitely disfavoured in all cases if a fifth ligand, such as η^1-P_4, is allowed to approach the metal from the direction opposite the bridgehead atom position, since this has a dramatic effect on the HOMO−LUMO gap, reducing the extent of the intended crossing and the effects on the rehybridization at the metal, which are essential for a process of oxidative addition. On the other hand, it appears that suitable conditions for the oxidative addition may consist of a concerted P−Rh−P angle opening and side-on P_4 approach to the two prospective pseudo-octahedral sites. As shown in Figure 1, produced by the EH calculations, even in the early stages of such a path the metal atom develops a suitable hybrid HOMO to interact with the LUMO of the P_4 fragment. As a consequence of this, even at a distance of ca. 2.8 Å between the metal centre and each of the two P_4 atoms, set at 2.4 Å from each other, a 70% decrease in the value of the overlap population of the approaching P−P bond has already occurred, while the values for the incipient Rh−P(P_4) bonds are already half as large as those for the bonds formed by rhodium with the phosphane P atoms.

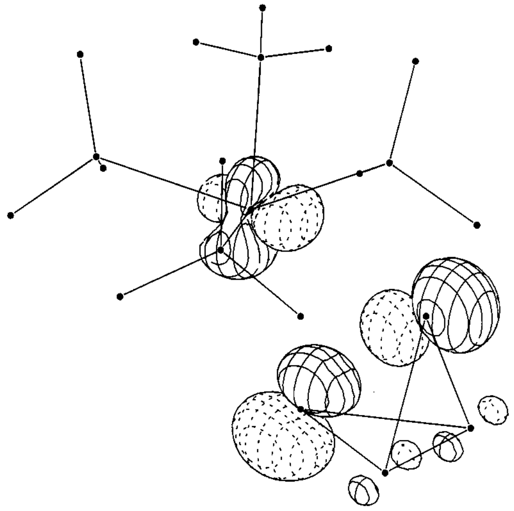


Figure 1. Drawing, from EH calculations, of significant parts of the HOMO for the model of $[(NP_3)Rh]^+$ interacting with partially cleaved P_4; according to a fragment orbital analysis, the main contributions are from the fragment cation HOMO and the P_4 LUMO; the bonding Rh···P(P_4) and antibonding P···P interactions may be appreciated

Experimental Section

General: All reactions and manipulations were performed under an atmosphere of dry oxygen-free argon, unless otherwise stated. THF was freshly distilled from potassium; toluene and diethyl ether were freshly distilled from sodium. – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra were measured in [D_8]THF on a Bruker AC 200 spectrometer at 81.02 MHz. Chemical shifts are relative to 85% H_3PO_4 as external standard at 0.00 ppm. – Analytical data for carbon, hydrogen, nitrogen and phosphorus were obtained from the Microanalytical Laboratory of the Department of Chemistry of the University of Florence. – The hydride complexes [(PP_3)CoH],[14] [(PP_3)RhH] and [(NP_3)RhH][13] were prepared according to the literature methods; CF_3SO_3Me (Aldrich) was used as purchased and stored at 0 °C.

Synthesis of [(PP_3)Co(P_4)]CF_3SO_3 (1): Neat CF_3SO_3Me (0.05 mmol) stored under nitrogen was added at room temperature to [(PP_3)CoH] (36 mg, 0.05 mmol) dissolved in [D_8]THF (0.8 mL). The resulting solution was stirred for 10 min and then cooled to −70 °C. P_4 (0.055 mmol) dissolved in THF (0.7 mL) was added and the resulting solution was immediately investigated at this temperature by NMR spectroscopy. – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ ([D_8]THF, 233 K, 81.02 MHz): δ = 194.8 (dm, $^{2}J_{\mathrm{P_AP_C}} = 35.0$ Hz, $^{2}J_{\mathrm{P_AP_F}} = 178.0$ Hz, $^{3}J_{\mathrm{P_AP_L}} = 5.0$ Hz, 1 P, P_A), 73.6 (ddm, $^{2}J_{\mathrm{P_CP_F}} = 71.0$ Hz, $^{3}J_{\mathrm{P_CP_L}} = 1.7$ Hz, 3 P, P_C), −333.5 (m, $^{1}J_{\mathrm{P_FP_L}} = 219.0$ Hz, 1 P, P_F), −472.3 (dm, 3 P, P_L).

Synthesis of [(PP_3)Rh(P_4)]CF_3SO_3 (2): The rhodium derivative was prepared following the same procedure as described for **1** by adding P_4 (0.05 mmol) dissolved in THF (0.5 mL) to the clear solution obtained by adding CF_3SO_3Me (0.04 mmol) to [(PP_3)RhH] (31 mg, 0.04 mmol) in [D_8]THF (0.5 mL). – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ ([D_8]THF, 223 K, 81.02 MHz): δ = 175.3 (ddm, $^{1}J_{\mathrm{P_ARh}} = 111.9$ Hz, $^{2}J_{\mathrm{P_AP_C}} = 15.3$ Hz, $^{2}J_{\mathrm{P_AP_F}} = 399.3$ Hz, $^{3}J_{\mathrm{P_AP_L}} = 12.7$ Hz, 1 P, P_A), 59.8 (ddd, $^{1}J_{\mathrm{P_FRh}} = 134.8$ Hz, $^{2}J_{\mathrm{P_CP_F}} = 61.0$ Hz, 3 P, P_C), −372.5 (m, $^{1}J_{\mathrm{P_FRh}} = 111.0$ Hz, $^{1}J_{\mathrm{P_FP_L}} = 226.5$ Hz, 1 P, P_F), −493.8 (dd, 3 P, P_L).

Synthesis of [(NP_3)Rh(P_4)]BPh_4 (3): CF_3SO_3Me (0.16 mmol) was added to a suspension of [(NP_3)RhH] (114 mg, 0.15 mmol) in THF (20 mL) at room temperature in a Schlenk tube and stirred for 30 min. The resulting clear yellow solution was cooled to −10 °C and P_4 (20 mg, 0.16 mmol) dissolved in THF (5 mL) was added. The solution turned dark red within 3 h. Solid $NaBPh_4$ (103 mg, 0.3 mmol) was then added. Concentration of the resulting solution at −30 °C yielded orange red microcrystals within 7 days, which were separated from the solvent, washed with toluene, diethyl ether and dried (120 mg, yield *ca* 67%). – $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ ([D_8]THF, 253 K, 81.02 MHz): δ = 29.8 (dd, $^{1}J_{\mathrm{P_ARh}} = 110.6$ Hz, $^{2}J_{\mathrm{P_AP_C}} = 24.8$ Hz, 2 P, P_A), −12.5 (ddt, $^{1}J_{\mathrm{P_CRh}} = 86.0$ Hz, $^{2}J_{\mathrm{P_CP_G}} = 40.0$ Hz, 1 P, P_C), −194.5 (tq, $^{1}J_{\mathrm{P_GRh}} = 40$ Hz, $^{2}J_{\mathrm{P_GP_L}} = 166.0$, $^{2}J_{\mathrm{P_GP_F}} = 40$ Hz, 1 P, P_G), −224.3 (tt, $^{1}J_{\mathrm{P_FRh}}{}^{1}J_{\mathrm{PFRh}} = 40$ Hz, $^{1}J_{\mathrm{P_FP_L}} = 160$ Hz, 1 P, P_F), −237.8 (tm, 2 P, P_L). – $C_{66}H_{62}BNP_7Rh$ (1199.7): calcd. C 66.07, H 5.21, N 1.17, P 18.07; found C 66.02, H 5.26, N 1.09, P 17.85.

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[15] $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ {[D_8]THF, δ (ppm); J (Hz)]}: 253 K. *a*: 147.5 (q, $^{2}J_{\mathrm{P_AP_C}} = 23.0$ Hz, 1 P, P_A), 50.0 (d, 3 P, P_C); *b*: 143.5 ($^{2}J_{\mathrm{P_AP_C}} = 32.0$ Hz, 1 P, q, P_A), 48.5 (d, 3 P, P_C).

[16] $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ {[D_8]THF, δ (ppm); J (Hz)]}: 253 K. *a′*: 141.2 (dq, $^{1}J_{\mathrm{P_ARh}} = 141.7$ Hz, $^{2}J_{\mathrm{P_AP_C}} = 15.4$ Hz, 1 P, P_A), 45.0 (dd, $^{1}J_{\mathrm{P_CRh}} = 128.7$ Hz, 3 P, P_C); *b′*: 137.8 (dq, $^{1}J_{\mathrm{P_ARh}} = 132.2$ Hz, $^{2}J_{\mathrm{P_AP_C}}{}^{2}J_{\mathrm{P_AP_C}} = 15.3$ Hz, 1 P, P_A), 46.9 (dd, $^{1}J_{\mathrm{P_CRh}} = 128.6$ Hz, 3 P, P_C); *c′*: 136.0 (dq, $^{1}J_{\mathrm{P_ARh}} = 130.8$ Hz, $^{2}J_{\mathrm{P_AP_C}} = 13.1$ Hz, 1 P, P_A), 47.9 (dd, $^{1}J_{\mathrm{P_CRh}} = 130.8$ Hz, 3 P, P_C).

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