

Reactivity of the Unsaturated Complex
 $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ toward Phosphines: Synthesis and
Molecular Structure of the Dinuclear Cations
 $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)_2]^+$ and Characterization of the
P–C Bond Activation Intermediate
 $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)(\mu_2-Ph)]^{+\dagger}$

Mathieu J.-L. Tschan,[‡] Frédéric Chérioux,[§] Lydia Karmazin-Brelot,[‡] and
 Georg Süss-Fink^{*,‡}

*Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2007 Neuchâtel,
 Suisse, Laboratoire FEMTO-ST/LPMO, CNRS UMR 6174, 32 Avenue de l'Observatoire,
 F-25044 Besançon, France*

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The unsaturated trihydrido complex $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ reacts with diaryl- or dialkylphosphines PR_2H to give the dinuclear cations $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)_2]^+$ ($R = Ph$, **1**; $R = t\text{-Bu}$, **2**). Surprisingly, complexes of the type $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)_2]^+$ with $R = Ph$ (**1**), $n\text{-Bu}$ (**3**), $n\text{-Oct}$ (**4**) are also accessible in high yield from the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with the corresponding triaryl- or trialkylphosphine PPh_3 , $P(n\text{-Bu})_3$, or $P(n\text{-Oct})_3$ by carbon–phosphorus bond cleavage. A possible intermediate of the reaction with PPh_3 , $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)(\mu_2-Ph)]^{+\dagger}$ (**5**), could be isolated from the reaction mixture as the tetrafluoroborate salt, the single-crystal X-ray structure analysis of which reveals a bridging phenyl ligand coordinated in an $\eta^1\text{-}\mu_2$ fashion to the diruthenium backbone. With the mixed phosphine PMe_2Ph , $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ reacts to give $[(C_6Me_6)_2Ru_2(\mu_2-PMe_2)(\mu_2-H)_2]^+$ (**6**) and the corresponding intermediate $[(C_6Me_6)_2Ru_2(\mu_2-PMe_2)(\mu_2-H)(\mu_2-Ph)]^{+\dagger}$ (**7**). All dinuclear cations are isolated as the tetrafluoroborate salts.

Introduction

Tertiary phosphines are without any doubt among the most important ligand systems used in organometallic chemistry and in molecular catalysis.¹ It is almost impossible to quote all the applications of phosphines in coordination chemistry and catalysis in the face of the plethora of complexes and reactions even of the most frequently used phosphines such as PPh_3 ^{1d,f} and $P(n\text{-Bu})_3$.^{1e} The cleavage of carbon–phosphorus bonds has been observed in numerous cases, essentially by pyrolyzing metal carbonyl complexes with aromatic phosphines; these reactions are referenced in several extensive reviews.² In most of these cases, the triarylphosphine ligand PR_3 , previously coordinated to a metal center in di- or oligonuclear complexes, undergoes P–C bond cleavage to give a phosphido-bridged derivative, the loss of an aryl substituent R being accompanied by the loss

of a ligand at the second metal center. However, to the best of our knowledge, P–C cleavage in tertiary phosphines is known only for triarylphosphines and has never been observed for trialkylphosphines, because of competition between C–H activation and C–P activation in these compounds.³ However, the cleavage of carbon–phosphorus bonds has been observed in the case of alkyl-substituted diphosphines such as bis(dimethylphosphino)methane and bis(diphenylphosphino)methane.⁴ In ruthenium chemistry, C–P bond cleavage has been almost exclusively observed with arylphosphines in the case of carbonyl clusters, leading to aryl-bridged ruthenium clusters.⁵

Over the three past decades, arene ruthenium complexes have been extensively studied⁶ because of their

* To whom correspondence should be addressed. E-mail: georg.suess-fink@unine.ch. Fax: 413 2718 2511. Tel: 413 2718 2405.

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[‡] Université de Neuchâtel.

[§] Laboratoire FEMTO-ST/LPMO, CNRS UMR 6174.

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potential to develop hydrogenation catalysts for unsaturated substrates such as olefins,⁷ ketones,⁸ and aromatic derivatives.⁹ The electron-deficient dinuclear complex $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$, isolated as the tetrafluoroborate salt,¹⁰ is soluble in both water and organic solvents and has turned out to be a versatile starting material for organometallic synthesis: thus, it has been used as a precursor for the assembly of trinuclear arene ruthenium clusters¹¹ and as a building block for conjugated organometallic polymers.¹² In this paper we report (i) the synthesis of the phosphido derivatives $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)_2]^+$ from $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ and PR_2H , (ii) a surprisingly facile P–C bond cleavage occurring in the trisubstituted phosphines PPh_3 and PM_ePh and even in the trialkylphosphines $P(n-Bu)_3$ and $P(n-Oct)_3$ by reaction with the dinuclear complex $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$, and (iii) the characterization of $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)(\mu_2-Ph)]^+$, containing a bridging phenyl ligand, as a possible intermediate in the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PPh_3 .

Results and Discussion

Recently we found $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ to react with thiophenols RSH to give complexes of the type $[(C_6Me_6)_2Ru_2(\mu_2-SR)_2(\mu_2-H)]^+$.¹² In an effort to extend our reactivity study of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ to phosphorus derivatives, we reacted $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with dialkyl- and diarylphosphines R_2PH . In contrast to the reaction with RSH, giving thiolato or dithiolato hydrido derivatives,

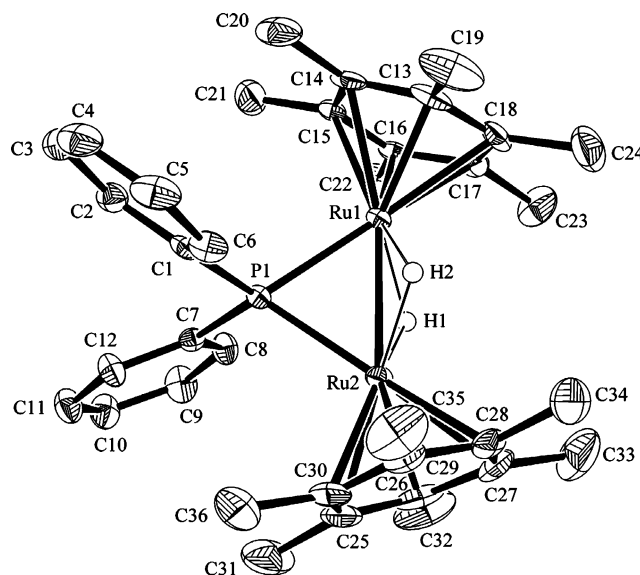
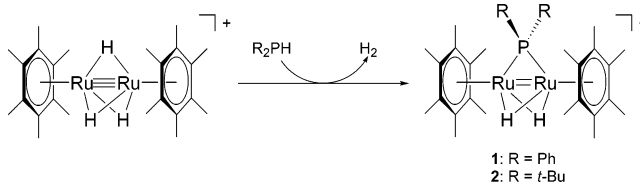


Figure 1. Molecular structure of **1**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the two hydride ligands, are omitted for clarity.

Scheme 1. Synthesis of $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)_2]^+$ by P–H Bond Cleavage in R_2PH



the reaction of R_2PH leads only to the monophosphido dihydride derivatives $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)_2]^+$ ($R = Ph$, **1**; $R = t-Bu$, **2**) (see Scheme 1).

The reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with Ph_2PH or with $t-Bu_2PH$, carried out in a dichloromethane solution at 50 °C (pressurized Schlenk tube), yields the products **1** and **2** quantitatively. Both cations are easily isolated as the tetrafluoroborate salts, giving air-stable black crystals.

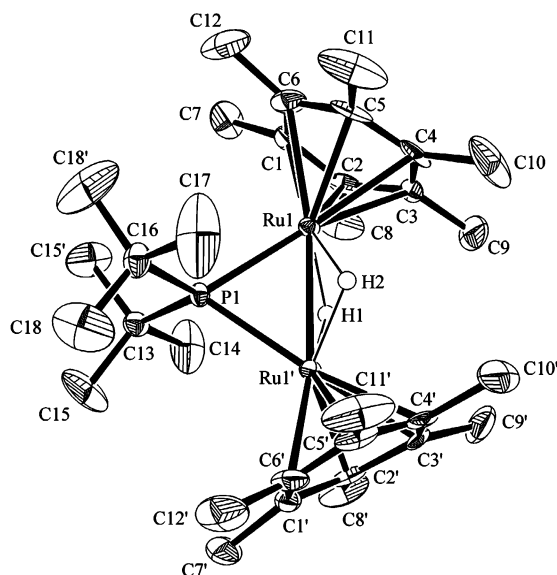
Black crystals of **1**·BF₄ suitable for X-ray analysis were obtained by diffusion of hexane in a dichloromethane solution of the complex. The single-crystal X-ray structure analysis reveals for the cation **1** a triangular Ru_2P core, each ruthenium atom being coordinated to a η^6 -C₆Me₆ ligand. The molecular structure of **1** is shown in Figure 1.

The skeleton of $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)_2]^+$ (**1**) consists of a triangle constituted of two ruthenium atoms and one phosphorus atom. Significant bond lengths and bond angles are listed in Table 1. The Ru–Ru distance (2.6425(4) Å) is in accordance with a metal–metal double bond. The presence of two phenyl groups at the phosphorus atom forces the arene–Ru–Ru–arene moieties to adopt a distorted geometry. The angle between the two C₆Me₆ ligand planes is 34.81°. In the case of the thiolato and dithiolato complexes $[(C_6Me_6)_2Ru_2(\mu_2-SR)(\mu_2-H)_2]^+$ and $[(C_6Me_6)_2Ru_2(\mu_2-SR)_2(\mu_2-H)]^+$ ($R = p-C_6H_4Br$), these angles are 21 and 37°, respectively.¹² This comparison shows that the distortion of the arene–Ru–Ru–arene moiety due to the steric bulk of only one

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Table 1. Selected Bond Lengths (Å) and Angles (deg) in [1][BF₄]

Interatomic Distances			
Ru(1)–Ru(2)	2.6425(4)	Ru(1)–H(2)	1.80(4)
Ru(1)–P(1)	2.2913(7)	Ru(2)–H(2)	1.77(4)
Ru(2)–P(1)	2.2806(8)	P(1)–C(1)	1.819(3)
Ru(1)–H(1)	1.75(4)	P(1)–C(7)	1.818(3)
Ru(2)–H(1)	1.69(4)		
Bond Angles			
P(1)–Ru(1)–Ru(2)	54.50(2)	Ru(1)–H(1)–Ru(2)	100.27
P(1)–Ru(2)–Ru(1)	54.88(2)	Ru(1)–H(2)–Ru(2)	95.67
Ru(1)–P(1)–Ru(2)	70.62(2)	C(1)–P(1)–C(7)	106.08(13)

**Figure 2.** Molecular structure of [(C₆Me₆)₂Ru₂(μ₂-P(*t*-Bu)₂)(μ₂-H)₂]⁺ (**2**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the two hydride ligands, are omitted for clarity.

μ₂-PPh₂ ligand is similar to that of two μ₂-SR ligands. This explains why the reaction of [(C₆Me₆)₂Ru₂(μ₂-H)₃]⁺ with Ph₂PH gives only monophosphido derivatives, while the reaction with RSH leads also to dithiolato derivatives, the steric hindrance not allowing the formation of diphosphido (just as of trithiolato) derivatives. The C(1)–P(1)–Ru(1)–Ru(2) torsion angle is 119.03(11)°, and the C(7)–P(1)–Ru(1)–Ru(2) torsion angle is –108.89(12)°. The distances between the metal and the associated ring centroid are very similar for both ruthenium atoms (1.7025 Å for Ru(1) and 1.7022 Å for Ru(2)). The Ru–C distances fall in the range 2.168(4)–2.257(3) Å, with an average Ru–C distance of 2.22(3) Å for each ruthenium atom.

Black crystals of [2]BF₄ suitable for X-ray analysis were obtained by slow diffusion of hexane in an acetone solution of the complex. The asymmetric unit comprises half a molecule of **2** with a disordered *tert*-butyl group and half a disordered BF₄[–] anion. The single-crystal X-ray structure analysis reveals for the cation **2** a triangular Ru₂P core, each ruthenium atom being coordinated to a η⁶-C₆Me₆ ligand. The molecular structure of **2** is shown in Figure 2.

The complex possesses a crystallographically imposed mirror plane (atoms P(1), H(1), H(2), C(13), C(14), H(14a), C(16), B(1), and F(1) lie on this plane). The skeleton of [(C₆Me₆)₂Ru₂(μ₂-P(*t*-Bu)₂)(μ₂-H)₂]⁺ (**2**) consists of a triangle constituted by two ruthenium atoms and one phosphorus atom. Significant bond lengths and

Table 2. Selected Bond Lengths (Å) and Angles (deg) in [2][BF₄]

Interatomic Distances			
Ru(1)–Ru(1') ^a	2.6400(8)	Ru(1)–H(2)	1.67(7)
Ru(1)–P(1)	2.3210(18)	Ru(1')–H(2)	1.67(7)
Ru(1')–P(1)	2.3210(18)	P(1)–C(13)	1.901(9)
Ru(1)–H(1)	1.60(7)	P(1)–C(16)	1.894(9)
Ru(1')–H(1)	1.60(7)		
Bond Angles			
P(1)–Ru(1)–Ru(1')	55.34(3)	Ru(1)–H(1)–Ru(1')	111.29
P(1)–Ru(1')–Ru(1)	55.34(3)	Ru(1)–H(2)–Ru(1')	104.02
Ru(1)–P(1)–Ru(1')	69.32(6)	C(13)–P(1)–C(16)	110.8(4)

^a Symmetry transformations used to generate equivalent atoms: (') *x*, –*y* + 1/2, *z*.

bond angles are listed in Table 2. The Ru–Ru distance (2.6400(8) Å) is in accordance with a metal–metal double bond. The presence of two *tert*-butyl groups on the phosphorus bridging ligand causes the arene–Ru–Ru–arene moieties to adopt a distorted geometry. The angle between the two C₆Me₆ arene ligands is 50.80°. This is due to the more important steric hindrance of the *tert*-butyl groups with regard to the phenyl groups. The C(16)–P(1)–Ru(1)–Ru(1') torsion angle is 111.9(2)°, and the C(13)–P(1)–Ru(1)–Ru(1') torsion angle is –111.0(2)°. The distance between the metal and the C₆Me₆ ring centroid is 1.7296 Å. The Ru–C distances fall in the range 2.197(7)–2.269(7) Å, with an average Ru–C distance of 2.24(3) Å.

The ruthenium–hydrogen distances in both cations **1** and **2** are within the range 1.60(7)–1.80(4) Å, which compares well to the corresponding values (1.57(8) and 1.83(7) Å) in the isoelectronic neutral complex [(C₅Me₅)₂Ru₂(μ₂-η²-C₂Ph₂)(μ₂-H)₂].¹³

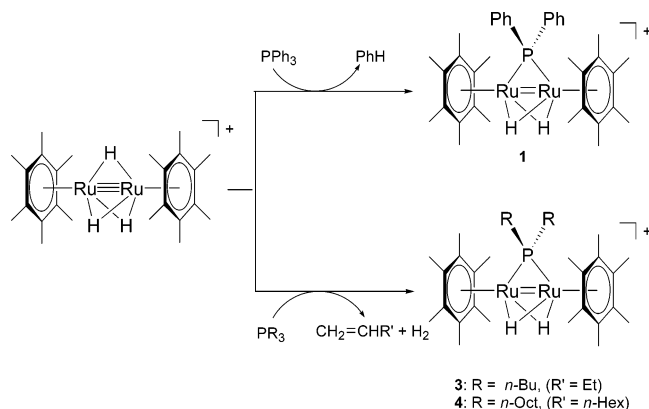
To our surprise, [(C₆Me₆)₂Ru₂(μ₂-PPh₂)(μ₂-H)₂]⁺ (**1**) is equally well accessible from [(C₆Me₆)₂Ru₂(μ₂-H)₃]⁺ with triphenylphosphine, implying the cleavage of a phosphorus–carbon bond in PPh₃. This P–C cleavage is very facile, since the almost quantitative reaction proceeds at room temperature in dichloromethane solution. Even with trialkylphosphines, the P–C bond cleavage occurs under mild conditions: Thus, [(C₆Me₆)₂Ru₂(μ₂-H)₃]⁺ reacts with P(*n*-Bu)₃ or with P(*n*-Oct)₃ in refluxing ethanol to give [(C₆Me₆)₂Ru₂(μ₂-P(*n*-Bu)₂)(μ₂-H)₂]⁺ (**3**) and [(C₆Me₆)₂Ru₂(μ₂-P(*n*-Oct)₂)(μ₂-H)₂]⁺ (**4**) in good yields (Scheme 2).

Cations **1**–**4** have all been unambiguously characterized by their MS and ¹H, ¹³C, and ³¹P NMR data, as well as by satisfactory elemental analysis data of the tetrafluoroborate salts; in none of the cases has ³¹P–¹³C coupling been observed in the ¹³C NMR spectra. These compounds are air-stable and soluble in polar organic solvents such as methanol, ethanol, dichloromethane, acetone, and acetonitrile. All these compounds are brown, except **2**, which is violet. ¹H NMR spectra of **1**–**4** show a strong coupling constant (30 Hz) between hydride ligands and the phosphorus atom, in accordance with the value found for [Cp₂Fe₂(CO)₂(μ₂-PPh₂)(μ₂-H)].^{5e}

The P–C activation process in the trialkylphosphines requires temperatures (refluxing ethanol) higher than those for triarylphosphines but can be carried out without hydrogen pressure. In addition, steric factors

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Scheme 2. Synthesis of $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)_2]^+$ by C–P Bond Cleavage in PR_3



play an important role for trialkylphosphines: thus, the reaction works with $P(n\text{-Bu})_3$ but not with the bulky phosphines $P(t\text{-Bu})_3$ and PCy_3 . It is interesting to compare the reaction of trisubstituted phosphines PR_3 with $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ to the reaction of PR_3 with the isoelectronic neutral complex $[(C_5Me_5)_2Ru_2(\mu_2-H)_4]$, recently reported by Suzuki et al.,¹⁴ which did not result in a P–C cleavage of the phosphine but in the fluxional migration of the PR_3 from one Ru atom to the other one.

To understand the P–C activation process of trialkylphosphines, we studied the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with tri-*n*-octylphosphine, $P(n\text{-Oct})_3$, because the organic byproducts should be liquid at room temperature and thus more easily detectable as the corresponding side products of $P(n\text{-Bu})_3$. GC analysis of the reaction solution reveals that the byproduct of the formation of **4** is the olefin (*n*-octene) and not the alkane (*n*-octane), which means that the P–C activation in trialkylphosphines with $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ involves a β -hydrogen elimination.

To understand the P–C activation process in the triaryl-substituted phosphines, we studied in detail the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PPh_3 to give **1**. The elimination of benzene as a reaction product during this reaction was proven by gas chromatography. It turned out that we could obtain a yield of **1** and PhH of greater than 90% by carrying out the reaction under a pressure of hydrogen (3 bar). Without hydrogen pressure, the yield of **1** drops to 85%, giving also a violet minor product in low yield, which can be separated from **1** by preparative thin-layer chromatography. This violet complex, isolated as the tetrafluoroborate salt, turned out to be the cation $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)(\mu_2-Ph)]^+$ (**5**).

Dark purple crystals of $[5]BF_4$ suitable for single-crystal X-ray structure analysis were obtained by diffusion of hexane in a dichloromethane solution of the complex. The asymmetric unit comprises a molecule of the cationic diruthenium complex with a C_6Me_6 ligand disordered over two positions (moiety a and moiety b) and a disordered BF_4^- anion. The molecular structure of **5** is shown in Figure 3; only one position of the disordered hexamethylbenzene ring is shown (moiety a).

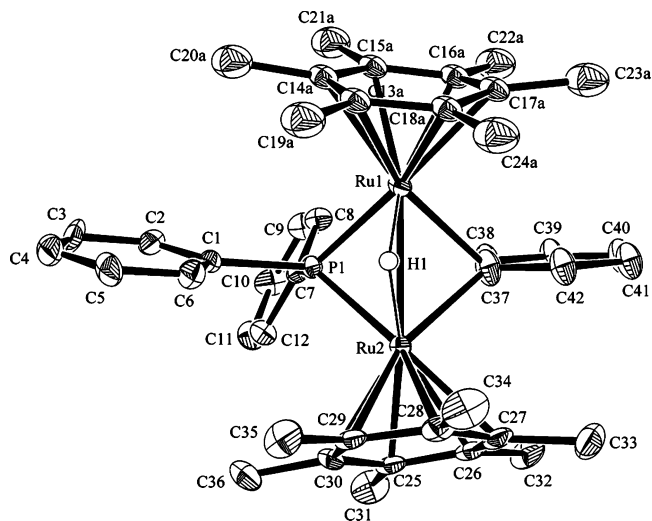


Figure 3. Molecular structure of $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)(\mu_2-Ph)]^+$ (**5**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the hydrido ligand, are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[5][BF_4]$

Interatomic Distances			
Ru(1)–Ru(2)	2.7307(4)	Ru(1)–C(37)	2.264(5)
Ru(1)–P(1)	2.2881(13)	Ru(2)–C(37)	2.236(5)
Ru(2)–P(1)	2.2917(13)	P(1)–C(1)	1.837(5)
Ru(1)–H(1)	1.47(6)	P(1)–C(7)	1.819(5)
Ru(2)–H(1)	1.59(6)		
Bond Angles			
P(1)–Ru(1)–Ru(2)	53.46(3)	Ru(1)–H(1)–Ru(2)	126.35
P(1)–Ru(2)–Ru(1)	53.34(3)	Ru(1)–C(37)–Ru(2)	74.71(14)
Ru(1)–P(1)–Ru(2)	73.20(4)	C(1)–P(1)–C(7)	101.4(2)

In cation **5**, each ruthenium atom is coordinated to a $\eta^6\text{-}C_6Me_6$ ligand, a bridging phosphorus atom, and the bridging ipso carbon atom of a phenyl ligand. The $\eta^1\text{-}\mu_2\text{-}C_6H_5$ ring is orthogonal to the Ru–Ru vector. Significant bond lengths and bond angles are given in Table 3. The Ru–Ru distance (2.7307(4) Å) is longer than in complex **1** (2.6425(4) Å) but is in accordance with a metal–metal double bond. The presence of two phenyl groups at the bridging phosphorus atom forces the arene–Ru–Ru–arene moieties to adopt a distorted geometry. The angle between the nondisordered C_6Me_6 arene ligand and the disordered C_6Me_6 arene ligand is 36.00° (for moiety a) and 37.60° (for moiety b). The C(1)–P(1)–Ru(2)–Ru(1) torsion angle is $-109.57(18)^\circ$, and the C(7)–P(1)–Ru(2)–Ru(1) torsion angle is $122.42(19)^\circ$. The distances between the metal and the associated ring centroid are similar for both ruthenium atoms (1.7319 Å for Ru(1) and moiety a, 1.7360 Å for Ru(1) and moiety b, and 1.7599 Å for Ru(2)). The Ru–C distances fall in the range 2.183(12)–2.339(5) Å for the C_6Me_6 arene ligands, with an average Ru–C distance of 2.25(4) Å. The average Ru–C_{ipso} distance for the bridging phenyl ligand (2.25(2) Å) is similar to the other average Ru–C distance. The Ru–C_{ipso} distances are shorter than in the trinuclear complexes $[(CO)_6Ru_3(\mu_2-PPh_2)_2(\mu_2-Ph)(\mu_3-L)]$ (L = 2-amino-6-methylpyridinate, 2-mercaptobenzimidazole, *N,N*-dimethylurea) containing a bridging $\eta^1\text{-}\mu_2\text{-phenyl}$ group, described by Cabeza et al.⁵ (2.29(2)–2.35(2) Å), but these complexes are different inasmuch as the Ru_3 skeleton contains only single Ru–Ru bonds.

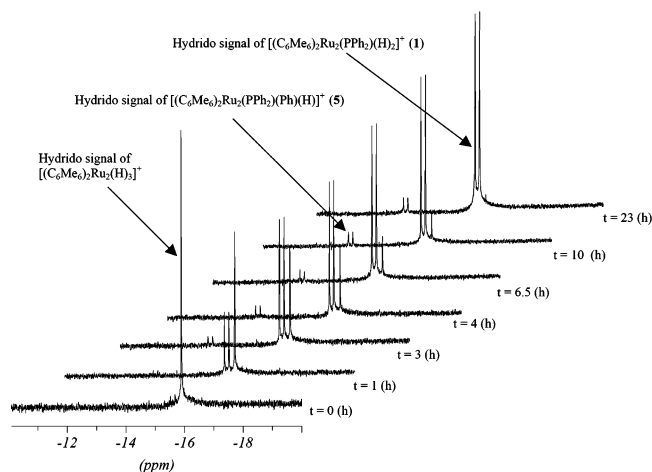
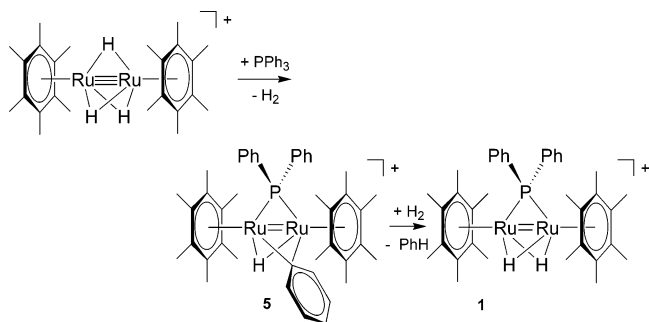


Figure 4. Reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with triphenylphosphine followed by 1H NMR in the hydrido range recorded in acetone- d_6 .

Scheme 3. Mechanistic Hypothesis of the Reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PPh_3 to Give 1



To address the question of the intermediacy of the phenyl complex **5** in the formation of **1** from $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PPh_3 , we followed the reaction at room temperature in acetone- d_6 by 1H NMR spectroscopy, which should allow us to decide if **5** and **1** are consecutive or parallel products of the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PPh_3 (Scheme 3).

In the beginning, only the hydride signal of the starting complex $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ at -15.89 ppm is detected (Figure 4). After 3 h, this singlet has considerably decreased, while two doublet signals had appeared at -13.12 and -16.60 ppm, which can be assigned to the hydrido ligands of $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)(\mu_2-Ph)]^+$ (**5**) and $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)_2]^+$ (**1**), respectively. The signals of the hexamethylbenzene ligands show the same trend (Figure 5).

When the integrals of the C_6Me_6 signals of the three complexes in the sequence $t = 3$ h to $t = 23$ h are compared, it becomes clear that the disappearance of the starting complex $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ is balanced by the formation of the two complexes $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)_2]^+$ (**1**) and $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)(\mu_2-Ph)]^+$ (**5**). However, while the hexamethylbenzene signal of **1** increases steadily with the decrease of the corresponding $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ signal, the hexamethylbenzene signal of **5** stays almost constant.

As this result is ambiguous, we checked the reaction of **5** with hydrogen: indeed, complex **5** is found to react with H_2 (3 bar) in dichloromethane at room temperature to give quantitatively **1** within 4 days. In addition, no

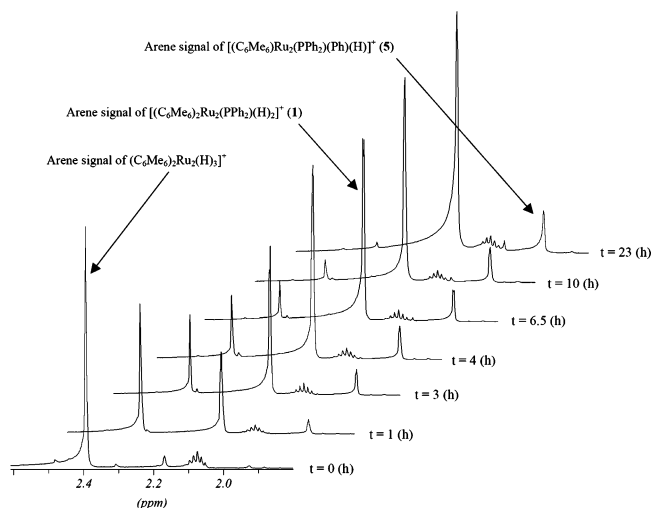
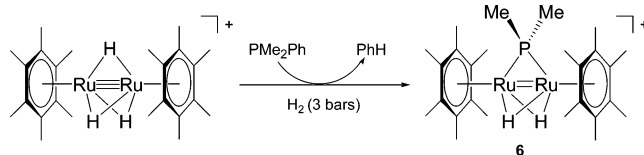


Figure 5. Reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with triphenylphosphine followed by 1H NMR in the hexamethylbenzene range recorded in acetone- d_6 .

Scheme 4. Reactivity of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ toward Mixed Tertiary Phosphines



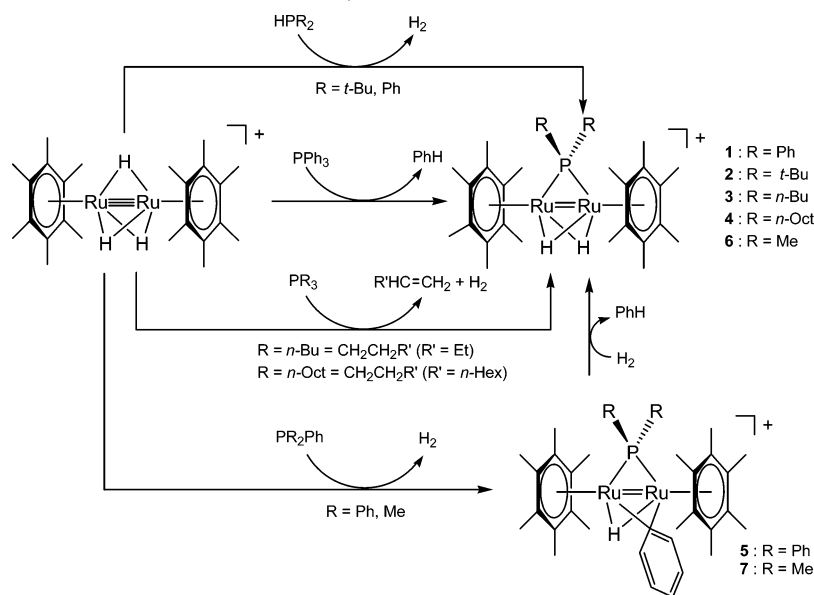
trace of **5** is detected, if the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PPh_3 to give **1** is carried out under a hydrogen atmosphere (3 bar) at room temperature over a period of 5 days. These findings strongly support the hypothesis of the phenyl complex **5** being an intermediate in the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PPh_3 to give **1**.

In the case of mixed alkylarylphosphines, the P–C bond of the aryl substituent is cleaved preferentially with respect to the P–C bond of the alkyl substituent: thus, dimethylphenylphosphine reacts with $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ to give the dimethylphosphido derivative $[(C_6Me_6)_2Ru_2(\mu_2-PMe_2)(\mu_2-H)_2]^+$ (**6**), in line with the observation of Carty et al., according to which the P–C bond cleavage in phosphines follows the order $P-C(sp) > P-C(sp^2) > P-C(sp^3)$.¹⁵ Also in this reaction, the presence of hydrogen is beneficial for the yield of **6**, isolated as the tetrafluoroborate salt (Scheme 4).

If the reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ with PMe_2Ph is carried out in dichloromethane at $55^\circ C$ (pressure Schlenk tube) without hydrogen being present, a mixture of **6** and the expected intermediary phenyl complex $[(C_6Me_6)_2Ru_2(\mu_2-PMe_2)(\mu_2-H)(\mu_2-Ph)]^+$ (**7**) is obtained. The two complexes can be separated by preparative thin-layer chromatography and characterized by their 1H and ^{31}P NMR as well as MS data. However, only **6** can be isolated in a pure form as the tetrafluoroborate salt; the isolated product **[7][BF₄]** is always contaminated by **[6][BF₄]** (~20%).

Conclusion

In conclusion, we have studied the reactivity of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ toward di- and trisubstituted phosphines. The results are summarized in Scheme 5.

Scheme 5. Reactivity of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ toward Di- or Trisubstituted Phosphines

In the case of tertiary phosphines, facile cleavage of a phosphorus–carbon bond is observed; even trialkylphosphines undergo this process, so far considered to be restricted to aromatic phosphines. With PPh_3 and PMe_2Ph , the phenyl complexes $[(C_6Me_6)_2Ru_2(\mu_2-PR_2)(\mu_2-H)(\mu_2-Ph)]^+$ ($R = Ph, Me$) have been identified as P–C bond activation intermediates and unambiguously characterized.

Experimental Section

All manipulations were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques. All solvents were degassed with nitrogen prior to use. Silica gel (type G) used for preparative thin-layer chromatography was purchased from Macherey Nagel GmbH. All phosphines were purchased from Fluka, Aldrich, or Strem Chemicals and used as received. The dinuclear trihydrido complex $[(C_6Me_6)_2Ru_2(\mu_2-H)_3]^+$ was synthesized by previously described methods.¹⁰ Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded using a Bruker 400 MHz and a Varian-Gemini 200 MHz spectrometer, and ESI mass spectra were recorded at the University of Fribourg by Prof. Titus Jenny. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva.

Synthesis of $[(C_6Me_6)_2Ru_2(\mu_2-PPh_2)(\mu_2-H)_2][BF_4]$ ([1]- $[BF_4]$). (a) By Reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3][BF_4]$ and $HPPH_2$. $[(C_6Me_6)_2Ru_2(\mu_2-H)_3][BF_4]$ (100 mg, 0.16 mmol) and diphenylphosphine (35 mg, 0.19 mmol, 33 μ L) were dissolved in degassed technical grade dichloromethane (25 mL) in a pressurized Schlenk tube, and the mixture was stirred for 16 h at 50 °C. Then the solvent was evaporated to dryness and the brown product obtained was purified by preparative thin-layer chromatography on silica (eluant acetone/dichloromethane 1/10). The fraction containing the product was extracted from the brown band with acetone; evaporation of the solvent gave the pure product in quantitative yield.

(b) By Reaction of $[(C_6Me_6)_2Ru_2(\mu_2-H)_3][BF_4]$ and PPh_3 . $[(C_6Me_6)_2Ru_2(\mu_2-H)_3][BF_4]$ (100 mg, 0.16 mmol) and triphenylphosphine (93 mg, 0.32 mmol) were dissolved in technical grade dichloromethane (25 mL) degassed with hydrogen, and the mixture was stirred for 2 days at room temperature under 3 bar of hydrogen by using a pressurized Schlenk tube (the disappearance of the green starting compound $[H_3Ru_2(C_6Me_6)_2][BF_4]$ was monitored by TLC). Then the solvent was evaporated

to dryness and the brown product obtained was purified by preparative thin-layer chromatography on silica (eluant acetone/dichloromethane 1/10). The fraction containing the product was extracted from the brown band with acetone; evaporation of the solvent gave the pure brown product (yield 93%, 0.15 mmol, 119 mg).

1H NMR (CD_3COCD_3 , 400 MHz): δ –15.60 (2H, d, $^2J_{H,P}$ = 30 Hz, hydride), 2.16 (36H, s, $C_6(CH_3)_6$), 7.14 (4H, ddd, $^4J_{H,H}$ = 1.7 Hz, $^3J_{H,H}$ = 8 Hz, $^3J_{H,P}$ = 12.5 Hz; CH of phenyl), 7.40 (6H, m, CH of phenyl). $^{13}C\{^1H\}$ NMR (CD_3COCD_3 , 100 MHz): δ 17.25 (Ru–CCH₃), 97.22 (Ru–CCH₃), 128.19, 128.30, 129.35, 129.38, 133.03, 133.16, 137.64, 137.99 (P–Ph). $^{31}P\{^1H\}$ NMR (CD_3COCD_3 , 161 MHz): 98.7 (s). MS (ESI, m/z): 715 [$M + H$]⁺. Anal. Calcd for $C_{36}H_{48}BF_4PRu_2$: C, 53.85; H, 6.03. Found: C, 54.15; H, 6.15.

Synthesis of $[(C_6Me_6)_2Ru_2(\mu_2-P(t-Bu)_2)(\mu_2-H)_2][BF_4]$ ([2]- $[BF_4]$). $[(C_6Me_6)_2Ru_2(\mu_2-H)_3][BF_4]$ (100 mg, 0.16 mmol) and di-*tert*-butylphosphine (28.5 mg, 0.19 mmol, 36 μ L) were dissolved in degassed technical grade dichloromethane (25 mL) in a pressurized Schlenk tube, and the mixture was stirred for 16 h at 50 °C. Then the solvent was evaporated to dryness and the violet product obtained was purified by preparative thin-layer chromatography on silica (eluant acetone/dichloromethane 1/10). The fraction containing the product was extracted from the violet band with acetone; evaporation of the solvent gave the pure violet product in quantitative yield (100%, 0.16 mmol, 122 mg). 1H NMR (CD_3COCD_3 , 400 MHz): δ –17.13 (2H, d, $^2J_{H,P}$ = 30 Hz, hydride), 1.02 (18H, d, $^3J_{H,P}$ = 14 Hz, CH_3 of *t*-Bu), 2.36 (36H, s, $C_6(CH_3)_6$). $^{13}C\{^1H\}$ NMR (CD_3COCD_3 , 100 MHz): δ 18.07 (Ru–CCH₃), 33.43 (C(CH₃) of *t*-Bu), 33.49 (C(CH₃) of *t*-Bu), 38.04 (C(CH₃) of *t*-Bu), 38.10 (C(CH₃) of *t*-Bu), 96.51 (Ru–CCH₃). $^{31}P\{^1H\}$ NMR (CD_3COCD_3 , 161 MHz): δ 180.80 (t, $^2J_{H,P}$ = 30 Hz). MS (ESI, m/z): 674 [$M + H$]⁺. Anal. Calcd for $C_{32}H_{56}BF_4PRu_2$: C, 50.52; H, 7.42. Found: C, 50.70; H, 7.47.

Synthesis of $[(C_6Me_6)_2Ru_2(\mu_2-P(n-Bu)_2)(\mu_2-H)_2][BF_4]$ ([3]- $[BF_4]$). $[(C_6Me_6)_2Ru_2(\mu_2-H)_3][BF_4]$ (100 mg, 0.16 mmol) and tri-*n*-butylphosphine (64 mg, 0.32 mmol, 80 μ L) were dissolved in degassed purissimum ethanol (100 mL) and heated under reflux for 18 h. Then the solvent was evaporated to dryness and the brown mixture obtained was purified by preparative thin-layer chromatography on silica (eluant acetone/dichloromethane 1/10). The fraction containing the product was extracted from the main brown band with acetone; evaporation of the solvent gave the pure brown product (yield 53%, 0.08 mmol, 64 mg). 1H NMR (CD_2Cl_2 , 400 MHz): δ –16.48 (2H, d,

Table 4. Crystallographic Data for the Structures of Complexes [1][BF₄], [2][BF₄], and [5][BF₄]

	[1][BF ₄]	[2][BF ₄]	[5][BF ₄]
chem formula	C ₃₆ H ₄₈ BF ₄ PRu ₂	C ₃₂ H ₅₆ BF ₄ PRu ₂	C ₄₂ H ₅₂ BF ₄ PRu ₂
formula wt	800.66	760.69	876.76
cryst color and shape	black block	black block	dark purple block
cryst size	0.30 × 0.30 × 0.30	0.30 × 0.10 × 0.10	0.30 × 0.20 × 0.10
cryst syst	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.3464(9)	22.5729(13)	11.2717(7)
<i>b</i> (Å)	18.4596(12)	16.3209(8)	17.0632(14)
<i>c</i> (Å)	18.1656(14)	8.7729(6)	19.4068(12)
β (deg)	96.111(10)	90	92.226(7)
<i>V</i> (Å ³)	3449.7(5)	3232.0(3)	3729.7(4)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.542	1.563	1.561
μ(Mo Kα) (mm ⁻¹)	0.968	1.028	0.903
temp (K)	153(2)	153(2)	153(2)
<i>F</i> (000)	1632	1568	1792
scan range (deg)	2.28 < θ < 25.90	2.28 < θ < 25.90	2.28 < θ < 25.90
cell refinement params rflns	8000	7347	8000
no. of rflns measd	25 771	24 403	29 114
no. of indep rflns	6476	3264	6886
no. of rflns obsd (<i>I</i> > 2σ(<i>I</i>))	5277	1394	4647
<i>R</i> _{int}	0.0306	0.1421	0.0927
final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.0293, <i>wR</i> 2 ^a = 0.0748	<i>R</i> 1 = 0.0389, <i>wR</i> 2 ^a = 0.0814	<i>R</i> 1 = 0.0431, <i>wR</i> 2 ^a = 0.0973
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0383, <i>wR</i> 2 ^a = 0.0774	<i>R</i> 1 = 0.1093, <i>wR</i> 2 ^a = 0.0925	<i>R</i> 1 = 0.0722, <i>wR</i> 2 ^a = 0.1057
goodness of fit	1.019	0.749	0.900
residual density: max, min Δρ (e Å ⁻³)	1.554, -0.849	1.282, -1.282	1.022, -1.343

^a The structure was refined on *F*_o²: *wR*2 = [Σ(*wF*_o² - *F*_c²)/Σ*wF*_o²]^{1/2}, where *w*⁻¹ = [Σ(*F*_o²) + (*aP*)² + *bP*] and *P* = [max(*F*_o², 0) + 2*F*_c²]/3.

²*J*_{H,P} = 30 Hz, hydride), 0.89 (6H, t, ³*J*_{H,H} = 13 Hz, CH₂CH₃), 0.95 (4H, hept, ³*J*_{H,H} = 13 Hz, CH₂CH₂CH₃), 1.31 (4H, q, ³*J*_{H,H} = 13 Hz, CH₂CH₂CH₂), 1.87 (4H, td, ²*J*_{H,P} = 4.4 Hz, ³*J*_{H,H} = 13 Hz, P-CH₂CH₂), 2.26 (36H, s, C₆(CH₃)₆). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 14.36 (CH₃), 18.42 (Ru-CCH₃), 24.09 (CH₂), 24.26 (CH₂), 28.97 (CH₂), 29.15 (CH₂), 30.47 (P-CH₂), 96.61 (Ru-CCH₃). ³¹P{¹H} NMR (CDCl₃, 161 MHz): δ 115.91 (t, ²*J*_{H,P} = 30 Hz). MS (ESI, *m/z*): 674 [M + H]⁺. Anal. Calcd for C₃₂H₅₆BF₄PRu₂: C, 50.52; H, 7.42. Found: C, 50.71; H, 7.49.

Synthesis of [(C₆Me₆)₂Ru₂(μ₂-P(*n*-Oct)₂)(μ₂-H)₂][BF₄] ([4][BF₄]). [(C₆Me₆)₂Ru₂(μ₂-H)₃][BF₄] (200 mg, 0.32 mmol) and tri-*n*-octylphosphine (240 mg, 0.65 mmol, 288 μL) were dissolved in degassed purissimum ethanol (100 mL) and heated under reflux for 18 h. Then the solvent was evaporated to dryness and the brown mixture obtained was purified by preparative thin-layer chromatography on silica (eluant acetone/dichloromethane 1/10). The fraction containing the product was extracted from the main brown band with acetone; evaporation of the solvent gave the pure brown product (yield 45%, 0.14 mmol, 125 mg). ¹H NMR (CD₃COCD₃, 400 MHz): δ -16.34 (2H, d, ²*J*_{H,P} = 30 Hz, hydride), 0.88 (6H, t, ³*J*_{H,H} = 7 Hz, CH₂CH₃), 1.25–1.37 (24H, broad, CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 2.02 (4H, m, P-CH₂), 2.33 (36H, s, C₆(CH₃)₆). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ 14.25 (CH₃), 18.22 (Ru-CCH₃), 23.04 (CH₃CH₂), 28.37 (CH₂), 28.40 (CH₂), 29.18 (CH₂), 29.35 (CH₂), 29.48 (CH₂), 29.59 (CH₂), 29.87 (CH₂), 30.08 (CH₂), 31.02 (CH₂), 31.19 (CH₂), 32.16 (P-CH₂), 32.21 (P-CH₂), 96.59 (Ru-CCH₃). ³¹P{¹H} NMR (CD₃COCD₃, 161 MHz): δ 118.05 (t, ²*J*_{H,P} = 30 Hz). MS (ESI, *m/z*): 786 [M + H]⁺. Anal. Calcd for C₄₀H₇₂BF₄PRu₂: C, 57.06; H, 8.62. Found: C, 57.07; H, 8.89.

Isolation and Characterization of [(C₆Me₆)₂Ru₂(μ₂-PPh₂)(μ₂-H)(μ₂-Ph)][BF₄] ([5][BF₄]). [(C₆Me₆)₂Ru₂(μ₂-H)₃][BF₄] (100 mg, 0.16 mmol) and triphenylphosphine (93 mg, 0.32 mmol) were dissolved in technical grade dichloromethane (25 mL) degassed with nitrogen (instead of hydrogen), and the mixture was stirred for 2 days at room temperature (the disappearance of the green starting compound [H₃Ru₂(C₆Me₆)₂][BF₄]) was monitored by TLC. Then the solvent was evaporated to dryness and the brown mixture obtained was purified by preparative thin-layer chromatography on silica (eluant

acetone/dichloromethane 1/10). A violet fraction could be observed, above the brown one ([1][BF₄]) on the preparative thin-layer chromatography plate, which was extracted from silica with acetone. The evaporation of the solvent gave the impure product [5][BF₄], contaminated by [1][BF₄] (~40%). The product [5][BF₄] crystallizes from slow diffusion of hexane in a dichloromethane solution of the mixture of [5][BF₄] and [1][BF₄]. ¹H NMR (CD₃COCD₃, 200 MHz): δ -13.12 (1H, d, ²*J*_{H,P} = 30 Hz, hydride), 1.92 (36H, s, C₆(CH₃)₆), 6.40–8.0 (14H, m, CH of phenyl), 8.60 (1H, d, ³*J*_{H,H} = 7.6 Hz, CH of phenyl). ³¹P{¹H} NMR (CD₃COCD₃, 80 MHz): δ 117 (s). MS (ESI, *m/z*): 791 [M + H]⁺.

Synthesis of [(C₆Me₆)₂Ru₂(μ₂-PMe₂)(μ₂-H)₂][BF₄] ([6][BF₄]). [(C₆Me₆)₂Ru₂(μ₂-H)₃][BF₄] (100 mg, 0.16 mmol) and dimethylphenylphosphine (33 mg, 0.24 mmol, 36 μL) were dissolved in technical grade dichloromethane (100 mL) degassed with hydrogen and heated to 55 °C for 16 h under 3 atm of hydrogen by using a pressurized Schlenk tube. Then the solvent was evaporated to dryness and the brown mixture obtained was purified by preparative thin-layer chromatography on silica (eluant acetone/dichloromethane 1/10). The fraction containing the product was extracted from the brown band with acetone; evaporation of the solvent gave the pure brown product (yield 27%, 4.3 mmol, 29 mg).

¹H NMR (CD₂Cl₂, 400 MHz): δ -16.19 (2H, d, ²*J*_{H,P} = 32 Hz, hydride), 1.42 (6H, d, ²*J*_{H,P} = 13 Hz, P-CH₃), 2.28 (36H, s, C₆(CH₃)₆). ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ 18.14 (Ru-CCH₃), 30.07 (P-CH₃), 96.82 (Ru-CCH₃). ³¹P{¹H} NMR (CD₂Cl₂, 161 MHz): δ 67.90 (t, ²*J*_{H,P} = 32 Hz). MS (ESI, *m/z*): 590 [M + H]⁺. Anal. Calcd for C_{27.5}H₄₅BF₄O_{0.5}PRu₂ ([6][BF₄])^{1/2}·CH₃COCH₃: C, 46.95; H, 6.45. Found: C, 46.94; H, 6.31.

Isolation and Characterization of [(C₆Me₆)₂Ru₂(μ₂-PMe₂)(μ₂-H)(μ₂-Ph)][BF₄] ([7][BF₄]). [(C₆Me₆)₂Ru₂(μ₂-H)₃][BF₄] (100 mg, 0.16 mmol) and dimethylphenylphosphine (33 mg, 0.24 mmol, 36 μL) were dissolved in technical grade dichloromethane (100 mL) degassed with nitrogen (instead of hydrogen) and heated under reflux for 20 h. Then the solvent was evaporated to dryness and the brown mixture obtained was purified by preparative thin-layer chromatography on silica (eluant acetone/dichloromethane 1/10). A violet fraction could be observed, above the brown one ([1][BF₄]) on the preparative thin-layer chromatography plate, which was ex-

tracted from silica with acetone. The evaporation of the solvent gave the impure product **[7]**[BF₄], contaminated by **[6]**[BF₄] (~20%). ¹H NMR (CD₃COCD₃, 400 MHz): δ -16.79 to -16.69 (1H, m, hydride), 1.56 (6H, d, ²J_{H,P} = 10 Hz, CH₃ of P(CH₃)₂), 2.176 (12H, s, C₆(CH₃)₆), 2.117 (12H, s, C₆(CH₃)₆), 2.19 (12H, s, C₆(CH₃)₆), 7.19–7.24 (2H, m, CH of phenyl), 7.41–7.44 (3H, m, CH of phenyl), ³¹P{¹H} NMR (CD₃COCD₃, 161 MHz): δ 31 (t, ²J_{H,P} = 24 Hz). MS (ESI, *m/z*): 666 [M + H]⁺.

X-ray Crystallographic Study. Data were collected using a Stoe imaging plate diffractometer system (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite monochromator (Mo–K α radiation, λ = 0.710 73 Å). Totals of 192 exposures for **[1]**[BF₄] and 200 exposures for **[2]**[BF₄] and **[5]**[BF₄] (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 192^\circ$ for **[1]**[BF₄] and $0 < \varphi < 200^\circ$ for **[2]**[BF₄] and **[5]**[BF₄], and with the crystal oscillating through 1° in φ . The resolution was $D_{\min} - D_{\max} = 12.45 - 0.81$ Å.

The structures were solved by direct methods using the program SHELXS-97¹⁶ and refined by full-matrix least squares on F^2 with SHELXL-97.¹⁶ The hydrido ligands were located from Fourier difference maps, and during the least-squares refinement they were held fixed with $U_{\text{iso}}(\text{H}) = 0.05$ Å²; the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. In the structure of **[2]**[BF₄], one *tert*-butyl group and the BF₄[−] counteranion are disordered over two positions, and a

semiempirical absorption correction was applied using MULABS (PLATON03):¹⁷ $T_{\min} = 0.7474$, $T_{\max} = 0.8297$. In the structure of **[5]**[BF₄], the BF₄[−] counteranion and one hexamethylbenzene ring are disordered over two positions; a semiempirical absorption correction was applied using MULABS (PLATON03):¹⁸ $T_{\min} = 0.66327$, $T_{\max} = 0.86390$.

Crystallographic details are given in Table 4, and significant bond lengths and bond angles are listed in Table 1 for **[1]**[BF₄], Table 2 for **[2]**[BF₄], and Table 3 for **[5]**[BF₄]. The figures were drawn with ORTEP.¹⁹

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Supporting Information Available: Complete tables of crystal and structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compounds **1**, **2**, and **5** as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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