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

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The unsaturated trihydrido complex $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ reacts with diaryl- or dialkylphosphines PR_2H to give the dinuclear cations $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ (R= Ph, **1**; R = *t*-Bu, **2**). Surprisingly, complexes of the type $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ with R = Ph (**1**), *n*-Bu (**3**), *n*-Oct (**4**) are also accessible in high yield from the reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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, $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (**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 η^1-μ_2 fashion to the diruthenium backbone. With the mixed phosphine PMe_2Ph, $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ reacts to give $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PMe_2)(\mu_2\text{-}H)_2]^+$ (**6**) and the corresponding intermediate $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PMe_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (**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 studied[6] because of their

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(1) (a) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741. (b) Tolman, C. A.; Faller, J. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 13−109. (c) Forster, D. *Adv. Organomet. Chem.* **1979**, *17*, 255. (d) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133. (e) Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1965**, 7, 131. (f) Cannel, L. G.; Slaugh, L. H.; Mullineaux, R. D. *Chem. Abstr.* **1965**, *62*, 16054.

(2) (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171. (b) Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Adams, R. D., Kaesz, H. D., Eds.; VCH: New York, 1990. (c) Kong, K. C.; Cheng, C. H. *J. Am. Chem. Soc.* **1991**, *113*, 6313. (d) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576. (e) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441.

(3) (a) Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2589. (b) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *J. Organomet. Chem.* **2002**, *651*, 124. (c) Deeming, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (d) Deeming, A. J.; Kimber, R. E.; Underhill, M. J. *J. Chem. Soc., Dalton Trans.* **1973**, 2727.

(4) (a) Alvarez, M. A.; Garcia, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1997**, *16*, 354. (b) Garcia, G.; Garcia, M. E.; Melon, S.; Riera, V.; Ruiz, M. A.; Villafane, F. *Organometallics* **1997**, *16*, 624. (c) Alvarez, C.; Garcia, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1997**, *16*, 1378. (d) Quesada, R.; Ruiz, J.; Riera, V.; Garcia-Granda, S.; Rosario-Diaz, M. *Chem. Commun.* **2003**, 1942. (e) Alvarez, C. M.; Garcia, M. E.; Ruiz, M. A.; Connelly, N. G. *Organometallics* **2004**, *23*, 4750.

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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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$, 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 clusters[11] and as a building block for conjugated organometallic polymers.[12] In this paper we report (i) the synthesis of the phosphido derivatives $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ from $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ and PR_2H, (ii) a surprisingly facile P−C bond cleavage occurring in the trisubstituted phosphines PPh_3 and PMe_2Ph and even in the trialkylphosphines $P(n\text{-}Bu)_3$ and $P(n\text{-}Oct)_3$ by reaction with the dinuclear complex $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$, and (iii) the characterization of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$, containing a bridging phenyl ligand, as a possible intermediate in the reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with PPh_3.

Results and Discussion

Recently we found $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ to react with thiophenols RSH to give complexes of the type $[(C_6Me_6)_2Ru_2(\mu_2\text{-}SR)_2(\mu_2\text{-}H)]^+$.[12] In an effort to extend our reactivity study of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ to phosphorus derivatives, we reacted $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with dialkyl- and diarylphosphines R_2PH. In contrast to the reaction with RSH, giving thiolato or dithiolato hydrido derivatives, the reaction of R_2PH leads only to the monophosphido dihydrido derivatives $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ (R = Ph, **1**; R = *t*-Bu, **2**) (see Scheme 1).

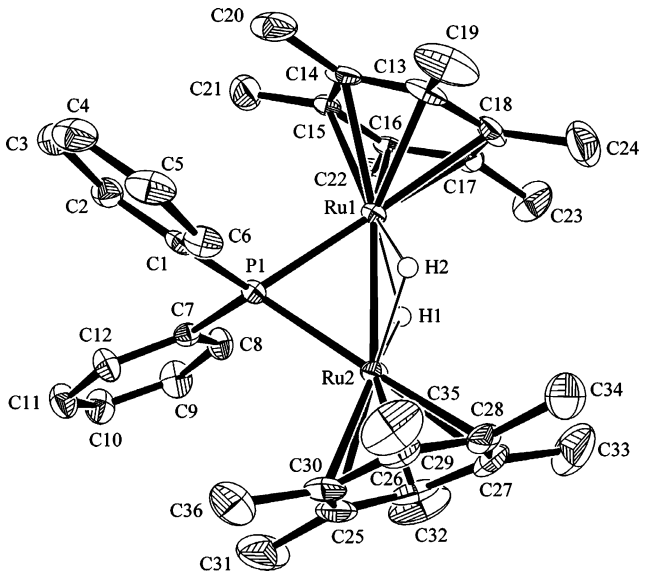
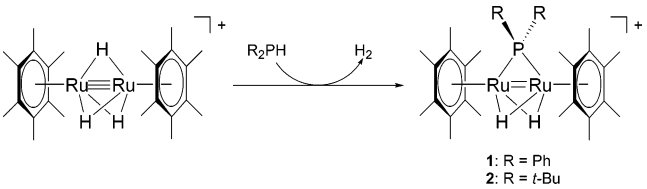


Figure 1. Molecular structure of **1**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the two hydrido ligands, are omitted for clarity.

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



The reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 $[\mathbf{1}]BF_4$ 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-C_6Me_6 ligand. The molecular structure of **1** is shown in Figure 1.

The skeleton of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$ (**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 C_6Me_6 ligand planes is 34.81°. In the case of the thiolato and dithiolato complexes $[(C_6Me_6)_2Ru_2(\mu_2\text{-}SR)(\mu_2\text{-}H)_2]^+$ and $[(C_6Me_6)_2Ru_2(\mu_2\text{-}SR)_2(\mu_2\text{-}H)]^+$ (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

(5) (a) Briard, P.; Cabeza, J. A.; Llamazares, A.; Ouahab, L.; Reira, V. *Organometallics* **1993**, *12*, 1006. (b) Cabeza, J. A.; Franco, R. J.; Llamazares, A.; Reira, V.; Pérez-Carreno, E.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 55. (c) Cabeza, J. A.; del Rio, I.; Reira, V.; Garcia-Granda, S.; Bamidele Sanni, S. *Organometallics* **1997**, *16*, 3914.

(6) (a) Bennett, M. A. *Coord. Chem. Rev.* **1997**, *166*, 225. (b) Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc., Dalton Trans.* **1994**, 3215. (c) Chérioux, F.; Thomas, C. M.; Therrien, B.; Süss-Fink, G. *Chem. Eur. J.* **2002**, *8*, 4377. (d) Chérioux, F.; Therrien, B.; Süss-Fink, G. *Chem. Commun.* **2004**, 204. (e) Pinto, P.; Marconi, G.; Heinemann, F. W.; Zenneck, U. *Organometallics* **2004**, *23*, 374. (f) Stodt, R.; Gencaslan, S.; Muller, I. M.; Shledrick, W. S. *Eur. J. Inorg. Chem.* **2003**, 1873. (g) Kraemer, R. *Angew. Chem., Int. Ed.* **1996**, *35*, 1197. (h) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809. (i) Crabtree, R. H.; Pearman, A. J. *J. Organomet. Chem*. **1977**, *141*, 325.

(7) (a) Bennett, M. A.; Ennett, J. P. *Inorg. Chim. Acta* **1992**, *198−200*, 583. (b) Daguenet, C.; Scopelliti, R.; Dyson, P. J. *Organometallics* **2004**, *23*, 4849. (c) Pertici, P.; Vitulli, G.; Bigelli, C.; Lazzaroni, R. *J. Organomet. Chem.* **1984**, *275*, 113. (d) Bennett, M. A.; Huang, T. N.; Smith, A. K.; Turney, T. W. *J. Chem. Soc., Chem. Commun*. **1978**, 582.

(8) (a) Brandt, P.; Roth, P.; Andersson P. G. *J. Org. Chem*. **2004**, *69*, 4885. (b) Soleimannejad, J.; Sisson, A.; White, C. *Inorg. Chim. Acta* **2003**, *352*, 121. (c) Ghebreyessus, K. Y.; Nelson, J. H. *J. Organomet. Chem*. **2003**, *669*, 48. (d) Yamakawa, M.; Yamada, I.; Noyori, R. *Angew. Chem., Int. Ed*. **2001**, *40*, 2818. (e) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res*. **1997**, *30*, 97.

(9) (a) Süss-Fink, G. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 2001; Vol. 10. (b) Süss-Fink, G.; Faure, M.; Ward, T. R. *Angew. Chem., Int. Ed.* **2001**, *41*, 89. (c) Dyson, P. J.; Ellis, D. J.; Hemdreson, W.; Laurenczy, G. *Adv. Synth. Catal.* **2003**, *345*, 216. (d) Dyson, P. J.; Ellis, D. J.; Laurenczy, G. *Adv. Synth. Catal.* **2003**, *345*, 211.

(10) (a) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74. (b) Jahncke, M.; Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Organometallics* **1997**, *16*, 1137. (c) Bennett, M. A.; Ennett, P. J. *Inorg. Chim. Acta* **1992**, *198−200*, 583.

(11) (a) Vieille-Petit, L.; Therrien, B.; Süss-Fink, G. *Eur. J. Inorg. Chem*. **2003**, 3707. (b) Vieille-Petit, L.; Therrien, B.; Süss-Fink, G.; Ward, T. *J. Organomet. Chem*. **2003**, *684*, 117. (c) Vieille-Petit, L.; Karmazin-Brelot, L.; Labat, G.; Süss-Fink, G. *Eur. J. Inorg. Chem*. **2004**, *3907*.

(12) Tschan, M. J.-L.; Chérioux, F.; Therrien, B.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2004**, 2405.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in [1][BF_4]

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)

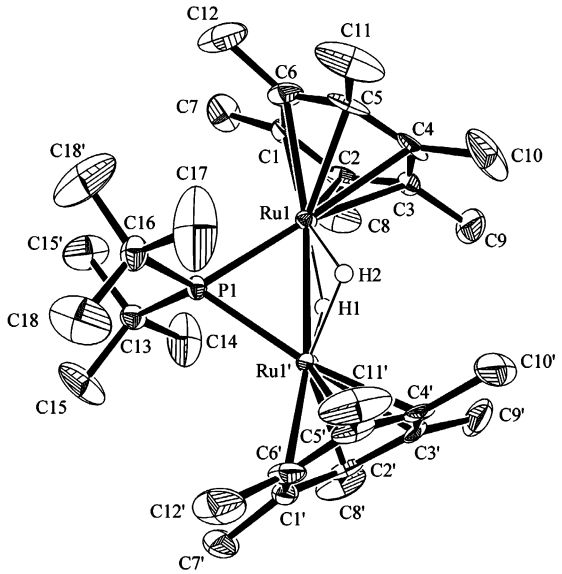


Figure 2. Molecular structure of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}P(t\text{-}Bu)_2)(\mu_2\text{-}H)_2]^+$ (**2**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the two hydrido ligands, are omitted for clarity.

μ_2-PPh_2 ligand is similar to that of two μ_2-SR ligands. This explains why the reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with Ph_2PH 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**]BF_4 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 BF_4^- anion. The single-crystal X-ray structure analysis reveals for the cation **2** a triangular Ru_2P core, each ruthenium atom being coordinated to a η^6-C_6Me_6 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}P(t\text{-}Bu)_2)(\mu_2\text{-}H)_2]^+$ (**2**) consists of a triangle constituted by two ruthenium atoms and one phosphorus atom. Significant bond lengths and 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 C_6Me_6 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 C_6Me_6 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.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in [2][BF_4]

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.

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 $[(C_5Me_5)_2Ru_2(\mu_2\text{-}\eta^2\text{-}C_2Ph_2)(\mu_2\text{-}H)_2]$.[13]

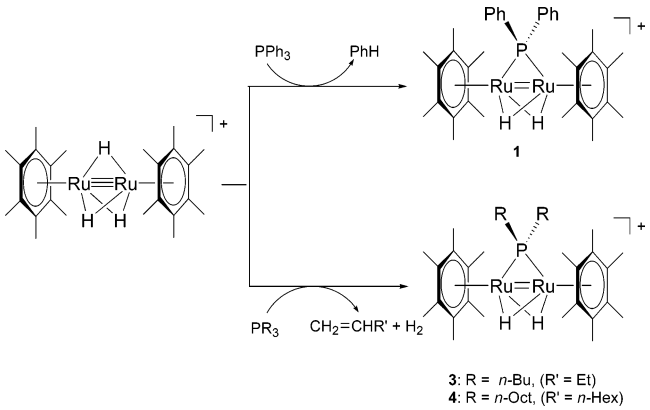
To our surprise, $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$ (**1**) is equally well accessible from $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with triphenylphosphine, implying the cleavage of a phosphorus−carbon bond in PPh_3. This P−C cleavage is very facile, since the almost quantitative reaction proceeds at room temperature in dichloromethane solution. Even with trialkylphosphines, the P−C bond cleavage occurs under mild conditions: Thus, $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ reacts with P(*n*-Bu)$_3$ or with P(*n*-Oct)$_3$ in refluxing ethanol to give $[(C_6Me_6)_2Ru_2(\mu_2\text{-}P(n\text{-}Bu)_2)(\mu_2\text{-}H)_2]^+$ (**3**) and $[(C_6Me_6)_2Ru_2(\mu_2\text{-}P(n\text{-}Oct)_2)(\mu_2\text{-}H)_2]^+$ (**4**) in good yields (Scheme 2)

Cations **1**−**4** have all been unambiguously characterized by their MS and ^1H, ^{13}C, and ^{31}P NMR data, as well as by satisfactory elemental analysis data of the tetrafluoroborate salts; in none of the cases has ^{31}P−^{13}C coupling been observed in the ^{13}C 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 hydrido ligands and the phosphorus atom, in accordance with the value found for $[Cp_2Fe_2(CO)_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)]$.[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

(13) Omori, H.; Suzuki, H.; Kakigano, T.; Moro-Oka, Y. *Organometallics* **1992**, *11*, 989.

Scheme 2. Synthesis of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ to the reaction of PR_3 with the isoelectronic neutral complex $[(C_5Me_5)_2Ru_2(\mu_2\text{-}H)_4]$, 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ involves a β-hydrogen elimination.

To understand the P−C activation process in the triaryl-substituted phosphines, we studied in detail the reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (**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).

(14) Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2994.

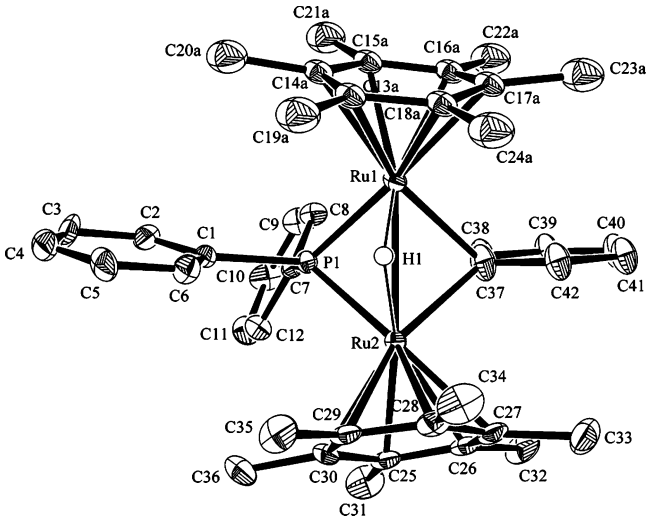


Figure 3. Molecular structure of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (**5**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the hydrido ligand, are omitted for clarity.

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 η^6-C_6Me_6 ligand, a bridging phosphorus atom, and the bridging ipso carbon atom of a phenyl ligand. The η^1-μ_2-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)°, and the C(7)−P(1)−Ru(2)−Ru(1) torsion angle is 122.42(19)°. 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 $[(CO)_6Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}Ph)(\mu_3\text{-}L)]$ (L = 2-amino-6-methylpyridinate, 2-mercaptobenzimidazolate, *N*,*N*-dimethylurea) containing a bridging η^1-μ_2-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.

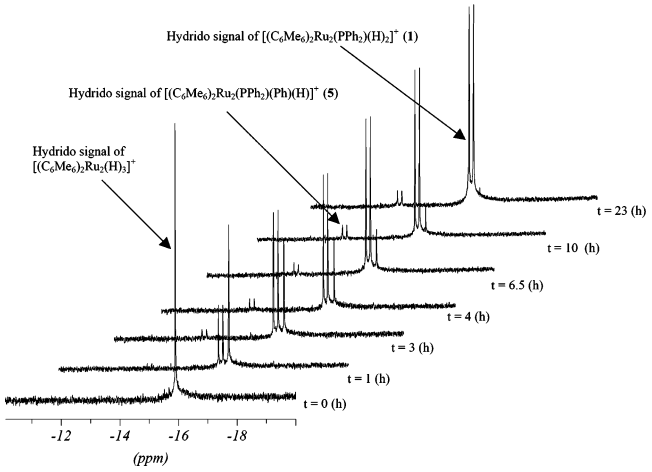
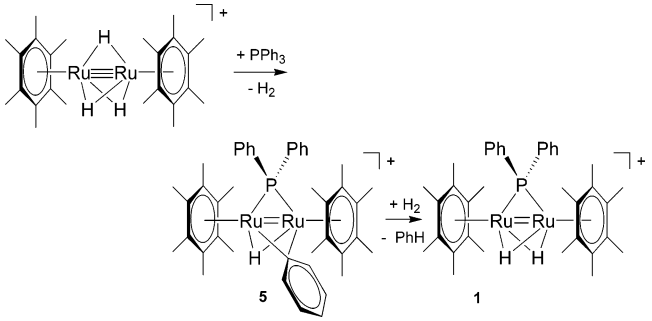


Figure 4. Reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with triphenylphosphine followed by ^1H NMR in the hydrido range recorded in acetone-d_6.

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



To address the question of the intermediacy of the phenyl complex **5** in the formation of **1** from $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with PPh_3 (Scheme 3).

In the beginning, only the hydride signal of the starting complex $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (**5**) and $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$ (**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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ is balanced by the formation of the two complexes $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$ (**1**) and $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (**5**). However, while the hexamethylbenzene signal of **1** increases steadily with the decrease of the corresponding $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 quantatively **1** within 4 days. In addition, no trace of **5** is detected, if the reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with PPh_3 to give **1**.

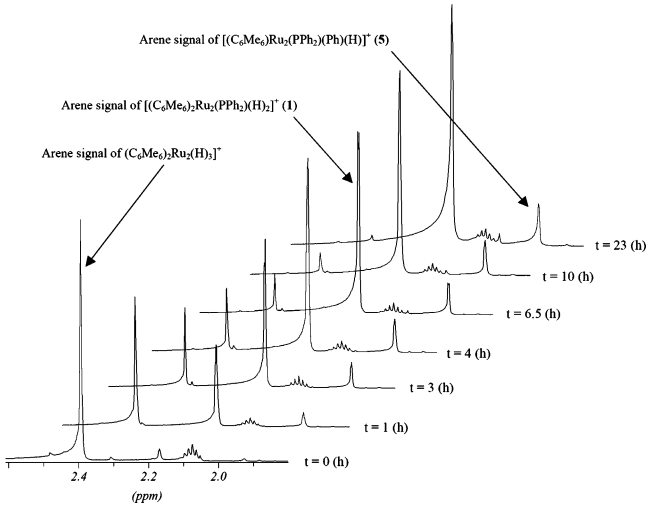
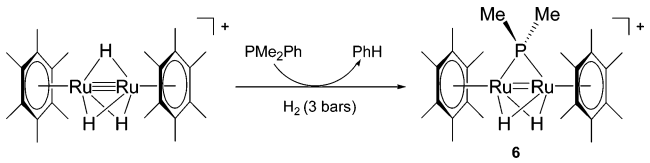


Figure 5. Reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with triphenylphosphine followed by ^1H NMR in the hexamethylbenzene range recorded in acetone-d_6.

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



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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ to give the dimethylphosphido derivative $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PMe_2)(\mu_2\text{-}H)_2]^+$ (**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 tetrafloroborate salt (Scheme 4).

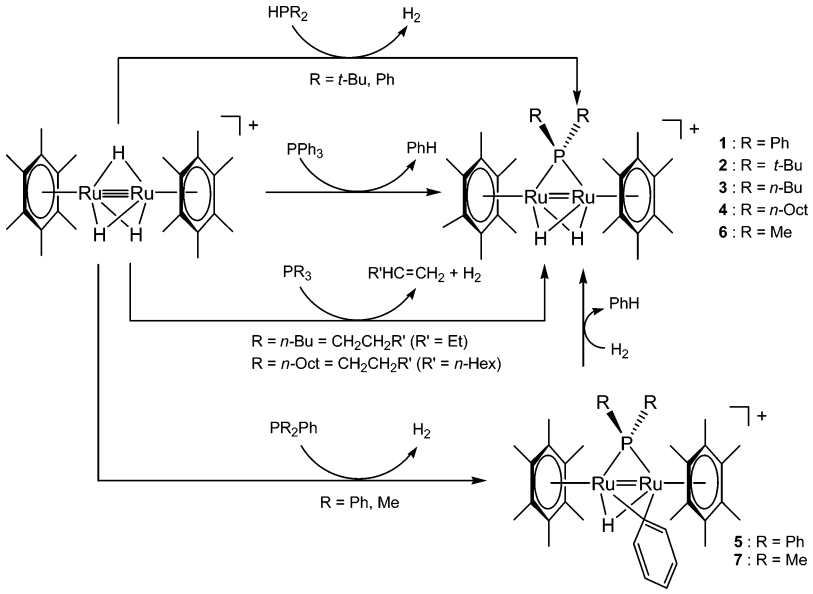
If the reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with PMe_2Ph is carried out in dichloromethane at 55 °C (pressure Schlenk tube) without hydrogen being present, a mixture of **6** and the expected intermediary phenyl complex $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PMe_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (**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 $[\mathbf{7}][BF_4]$ is always contaminated by $[\mathbf{6}][BF_4]$ (∼20%).

Conclusion

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

(15) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

Scheme 5. Reactivity of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (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 Sclenk 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ was synthezised 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2][BF_4]$ ([1][BF$_4$]). (a) By Reaction of $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ and $HPPh_2$. $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ (100 mg, 0.16 mmol) and diphenylphosphine (35 mg, 0.19 mmol, 33 μL) 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ and PPh_3. $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ (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).

^{1}H 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; C*H* of phenyl), 7.40 (6H, m, C*H* of phenyl). ^{13}C{^{1}H} NMR (CD_3COCD_3, 100 MHz): δ 17.25 (Ru−CCH_3), 97.22 (Ru−*C*CH_3), 128.19, 128.30, 129.35, 129.38, 133.03, 133.16, 137.64, 137.99 (P−*Ph*). ^{31}P{^{1}H} 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}P(t\text{-}Bu)_2)(\mu_2\text{-}H)_2][BF_4]$ ([2][BF$_4$]). $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ (100 mg, 0.16 mmol) and di-*tert*-butylphosphine (28.5 mg, 0.19 mmol, 36 μL) 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). ^{1}H 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{^{1}H} NMR (CD_3COCD_3, 100 MHz): δ 18.07 (Ru−CCH_3), 33.43 (C(*C*H_3) of *t*-Bu), 33.49 (C(*C*H_3) of *t*-Bu), 38.04 (*C*(CH$_3$) of *t*-Bu), 38.10 (*C*(CH$_3$) of *t*-Bu), 96.51 (Ru−*C*CH$_3$). ^{31}P{^{1}H} 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 $[(C_6Me_6)_2Ru_2(\mu_2\text{-}P(n\text{-}Bu)_2)(\mu_2\text{-}H)_2][BF_4]$ ([3][BF$_4$]). $[(C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ (100 mg, 0.16 mmol) and tri-*n*-butylphosphine (64 mg, 0.32 mmol, 80 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 53%, 0.08 mmol, 64 mg). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ −16.48 (2H, d,

Table 4. Crystallographic Data for the Structures of Complexes [1][BF$_4$], [2][BF$_4$], and [5][BF$_4$]

	[**1**][BF$_4$]	[**2**][BF$_4$]	[**5**][BF$_4$]
chem formula	$C_{36}H_{48}BF_4PRu_2$	$C_{32}H_{56}BF_4PRu_2$	$C_{42}H_{52}BF_4PRu_2$
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	$P2_1/c$	$Pnma$	$P2_1/n$
a (Å)	10.3464(9)	22.5729(13)	11.2717(7)
b (Å)	18.4596(12)	16.3209(8)	17.0632(14)
c (Å)	18.1656(14)	8.7729(6)	19.4068(12)
β (deg)	96.111(10)	90	92.226(7)
V (Å^3)	3449.7(5)	3232.0(3)	3729.7(4)
Z	4	4	4
D_{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)
F(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 ($I > 2\sigma(I)$)	5277	1394	4647
R_{int}	0.0306	0.1421	0.0927
final R indices ($I > 2\sigma(I)$)	R1 = 0.0293, wR2[a] = 0.0748	R1 = 0.0389, wR2[a] = 0.0814	R1 = 0.0431, wR2[a] = 0.0973
R indices (all data)	R1 = 0.0383, wR2[a] = 0.0774	R1 = 0.1093, wR2[a] = 0.0925	R1 = 0.0722, wR2[a] = 0.1057
goodness of fit	1.019	0.749	0.900
residual density: max, min $\Delta\rho$ (e Å^{-3})	1.554, −0.849	1.282, −1.282	1.022, −1.343

[a] The structure was refined on F_o^2: wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

$^2J_{H,P}$ = 30 Hz, hydride), 0.89 (6H, t, $^3J_{H,H}$ = 13 Hz, CH_2CH_3), 0.95 (4H, hept, $^3J_{H,H}$ = 13 Hz, $CH_2CH_2CH_3$), 1,31 (4H, q, $^3J_{H,H}$ = 13 Hz, $CH_2CH_2CH_2CH_3$), 1.87 (4H, td, $^2J_{H,P}$ = 4.4 Hz, $^3J_{H,H}$ = 13 Hz, P−CH_2CH_2), 2.26 (36H, s, $C_6(CH_3)_6$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 14.36 (CH_3), 18.42 (Ru−CCH_3), 24.09 (CH_2), 24.26 (CH_2), 28.97 (CH_2), 29.15 (CH_2), 30.47 (P−CH_2), 96.61 (Ru−CCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz): δ 115.91 (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, 50.71; H, 7.49.

Synthesis of [(C_6Me_6)$_2$Ru$_2$(μ_2-P(*n*-Oct)$_2$)(μ_2-H)$_2$][BF$_4$] ([4][BF$_4$]). [(C_6Me_6)$_2$Ru$_2$(μ_2-H)$_3$][BF$_4$] (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 (CD_3COCD_3, 400 MHz): δ −16.34 (2H, d, $^2J_{H,P}$ = 30 Hz, hydride), 0.88 (6H, t, $^3J_{H,H}$ = 7 Hz, CH_2CH_3), 1.25−1.37 (24H, broad, $CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.02 (4H, m, P−$CH_2$), 2.33 (36H, s, $C_6(CH_3)_6$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz): δ 14.25 (CH_3), 18.22 (Ru−CCH_3), 23.04 (CH_3CH_2), 28.37 (CH_2), 28.40 (CH_2), 29.18 (CH_2), 29.35 (CH_2), 29.48 (CH_2), 29.59 (CH_2), 29.87 (CH_2), 30.08 (CH_2), 31.02 (CH_2), 31.19 (CH_2), 32.16 (P−CH_2), 32.21 (P−CH_2), 96.59 (Ru−CCH_3). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 161 MHz): δ 118.05 (t, $^2J_{H,P}$ = 30 Hz). MS (ESI, *m/z*): 786 $[M + H]^+$. Anal. Calcd for $C_{40}H_{72}BF_4PRu_2$: C, 57.06; H, 8.62. Found: C, 57.07; H, 8.89.

Isolation and Characterization of [(C_6Me_6)$_2$Ru$_2$(μ_2-PPh$_2$)(μ_2-H)(μ_2-Ph)][BF$_4$] ([5][BF$_4$]). [(C_6Me_6)$_2$Ru$_2$(μ_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 nitrogen (instead of hydrogen), and the mixture was stirred for 2 days at room temperature (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 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**][BF$_4$]) on the preparative thin-layer chromatography plate, which was extracted from silica with acetone. The evaporation of the solvent gave the impure product [**5**][BF$_4$], contaminated by [**1**][BF$_4$] (~40%). The product [**5**][BF$_4$] crystallizes from slow diffusion of hexane in a dichloromethane solution of the mixture of [**5**][BF$_4$] and [**1**][BF$_4$]. ^1H NMR (CD_3COCD_3, 200 MHz): δ −13.12 (1H, d, $^2J_{H,P}$ = 30 Hz, hydride), 1.92 (36H, s, $C_6(CH_3)_6$), 6.40−8.0 (14H, m, C*H* of phenyl), 8.60 (1H, d, $^3J_{H,H}$ = 7.6 Hz, C*H* of phenyl). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 80 MHz): δ 117 (s). MS (ESI, *m/z*): 791 $[M + H]^+$.

Synthesis of [(C_6Me_6)$_2$Ru$_2$(μ_2-PMe$_2$)(μ_2-H)$_2$][BF$_4$] ([6][BF$_4$]). [(C_6Me_6)$_2$Ru$_2$(μ_2-H)$_3$][BF$_4$] (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 (CD_2Cl_2, 400 MHz): δ −16.19 (2H, d, $^2J_{H,P}$ = 32 Hz, hydride), 1.42 (6H, d, $^2J_{H,P}$ = 13 Hz, P−CH_3), 2.28 (36H, s, $C_6(CH_3)_6$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz): δ 18.14 (Ru−CCH_3), 30.07 (P−CH_3), 96.82 (Ru−CCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161 MHz): δ 67.90 (t, $^2J_{H,P}$ = 32 Hz). MS (ESI, *m/z*): 590 $[M + H]^+$. Anal. Calcd for $C_{27.5}H_{45}BF_4O_{0.5}PRu_2$ ([**6**][BF$_4$]·$^1/_2$-CH_3COCH_3): C, 46.95; H, 6.45. Found: C, 46.94; H, 6.31.

Isolation and Characterization of [(C_6Me_6)$_2$Ru$_2$(μ_2-PMe$_2$)(μ_2-H)(μ_2-Ph)][BF$_4$] ([7][BF$_4$]). [(C_6Me_6)$_2$Ru$_2$(μ_2-H)$_3$][BF$_4$] (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**][BF$_4$]) 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**][BF_4], contaminated by [**6**][BF_4] (~20%). ^{1}H NMR (CD_3COCD_3, 400 MHz): δ −16.79 to −16.69 (1H, m, hydride), 1.56 (6H, d, $^2J_{H,P}$ = 10 Hz, C*H*$_3$ of P(CH_3)$_2$), 2.176 (12H, s, $C_6(CH_3)_6$), 2.117 (12H, s, $C_6(CH_3)_6$), 2.19 (12H, s, $C_6(CH_3)_6$), 7.19−7.24 (2H, m. C*H* of phenyl), 7.41−7.44 (3H, m, C*H* of phenyl), ^{31}P{^{1}H} NMR (CD_3COCD_3, 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−Kα radiation, λ = 0.710 73 Å). Totals of 192 exposures for [**1**][BF_4] and 200 exposures for [**2**][BF_4] and [**5**][BF_4] (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 192°$ for [**1**][BF_4] and $0 < \varphi < 200°$ for [**2**][BF_4] and [**5**][BF_4], 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-97[16] 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_{iso}(H) = 0.05 Å^2; 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**][BF_4], one *tert*-butyl group and the BF_4^- 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**][BF_4], the BF_4^- 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**][BF_4], Table 2 for [**2**][BF_4], and Table 3 for [**5**][BF_4]. 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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(16) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(17) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(18) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.