(η^5-Pentamethylcyclopentadienyl)phosphinine Ruthenium(II) Complexes: η^1- vs η^6-Coordination

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4,5-Dimethyl-2-bromophosphinine reacts with [Ru(η^5-C_5Me_5)(η^4-C_6H_{10})Cl], in the presence of $AgBF_4$, to afford depending on the reaction conditions complexes resulting from the substitution of the chloride or the diene ligand. Under the same experimental conditions, reactions with the more sterically hindered 2,6-bis(trimethylsilyl)phosphinines yield the sandwich [Ru(η^5-C_5Me_5)(η^6-phosphinine)][BF_4] cationic complexes.

Introduction

Phosphinines are ambidentate ligands that may bind to metal centers either through the phosphorus atom lone pair or through their aromatic π-system.[1] Indeed, previous studies have shown that although they display higher π-acceptor properties than benzene derivatives, their π-donor strength is roughly similar. Over the past few years, many studies focused on the understanding of factors that govern the binding ability of the ring, and it is now clearly established that the electronic nature of the metal and the accessibility of the lone pair both play a predominant role.[2,3] Thus, whereas preference for η^6-coordination is clearly marked with early transition metals (group 4 and 5),[2] the *ortho*-H substitution plays a crucial role in the formation of η^6-complexes of group 6 zerovalent centers which have been thoroughly investigated.[4] Both types of complexes have also been characterized for groups 7[5] and 8 metal centers.[6] However, most studies dealing with group 8 metals focused on zerovalent centers. Two illustrative examples have been provided by Elschenbroich[6a] and Zenneck and co-workers [6b−d] with the respective isolation of the homoleptic η^1-iron(0) complex of the parent phosphinine C_5H_5P and that of the (η^6-phosphinine)(cyclooctadiene) iron(0) complexes. On the other hand, only little attention has been paid to the synthesis of cationic group 8 d^6 derivatives, and only one complex of the 2,4,6-triphenylphosphinine ligand was partially characterized in our laboratories a few years ago because of its high reactivity (Chart 1).[7]As part of a program aimed at exploring the synthesis of new types of η^6-phosphinine complexes, we first focused our attention on derivatives of the very electron-rich [Ru(η^5-C_5Me_5)]$^+$ fragment, which has been widely employed in the coordination chemistry of arenes and heteroarenes.[8] Herein we report on this study.

Results and Discussion

Many synthetic routes toward the preparation of Ru(η^5-C_5Me_5) complexes of arenes and heteroarenes have been devised. For the purpose of this study, we found the [Ru(η^5-C_5Me_5)(η^4-C_6H_{10})Cl] complex **1**[9] to be the most appropriate starting material in that the labile diene ligand allows the study of the preference for η^1- vs η^6-coordination. Our first experiments were carried out with the readily available 2-bromo-4,5-dimethylphosphinine, **2**.[10] Reaction of ligand **2** in the presence of equimolar amounts of [Ru(η^5-C_5Me_5)(η^4-C_6H_{10})Cl] and $AgBF_4$ in THF at 60 °C yields complex **3**, resulting from the substitution of the chloride ligand by one molecule

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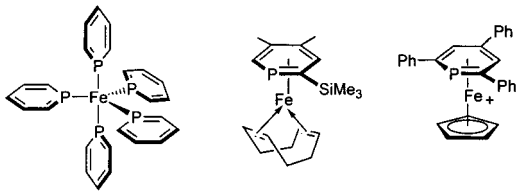
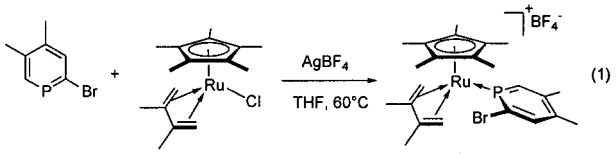
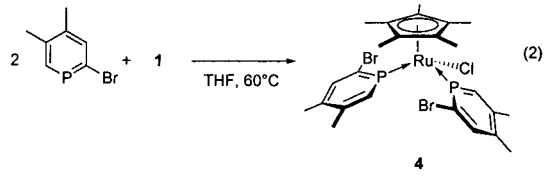
Chart 1

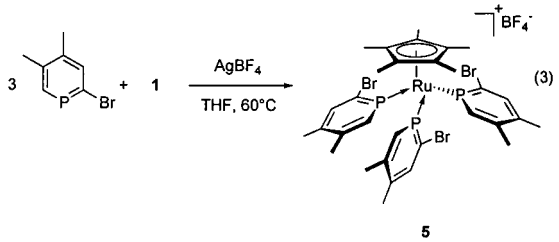


of **2** (eq 1). A monitoring of the reaction by ^{31}P NMR indicated that the formation of **3** is accompanied by two other side-products, **4** (<5%) (δ(THF) = 212.6 ppm) and **5** (<2%) (δ(THF) = 201.0 ppm). Fortunately, complex **3** could be easily separated from these two derivatives because of their difference in solubility by washings with hexanes. It must be noted that prolonged heating did not result in the formation of the expected η^6-phosphinine complex.

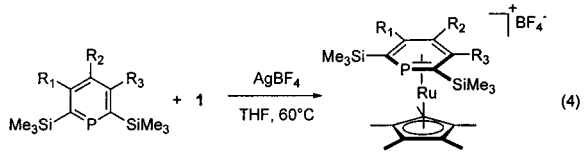


The formulation of **3** was unambiguously established on the basis of ^1H NMR data and elemental analyses. A particularly indicative piece of data is given by the presence of shielded signals corresponding to the terminal CH_2 units of the diene ($\delta(CDCl_3)$ = 3.43 ppm). Supposing that compounds **4** and **5** could result from the competitive displacement of the diene moiety by two and three phosphinine ligands, we turned our attention to the reaction of precursor **1** with 2 and 3 equiv of **2**. Substitution of the diene ligand by 2 equiv of **2** was easily achieved in THF at 60 °C (eq 2). As expected, its ^{31}P NMR data in THF compare with that recorded in our first experiment. Complex **4** was fully characterized by conventional NMR techniques and elemental analyses. Reaction of 3 equiv of ligand **2** with **1** exclusively yields complex **4**, and the presence of an equimolar amount of $AgBF_4$ is needed to ensure a complete conversion to **5** (eq 3).





All NMR data and elemental analyses support the formulation proposed. In the ^1H NMR spectrum the presence of 3 equiv of phosphinine nucleus coordinated at the Ru center is easily evidenced by the signals of the H_2 and H_6 protons, which appear as a characteristic AXX'_2 spin system. The preference for η^1-coordination does not result from electronic factors due to the presence of a bromine atom because similar results were obtained using the corresponding 2-chlorophosphinine ligand. The use of more hindered ligands such as 2,6-dibromophosphinines led to disappointing results, and only intractable mixture of complexes were obtained. Finally the use of bulky 2,6-bis(trimethylsilyl)phosphinines[11] such as **6**−**9** yielded more satisfactory results. Reactions of **6**−**9** with equimolar amounts of **1** and $AgBF_4$ in THF cleanly afford the expected (η^6-phosphinine) complexes **10**−**13**, respectively (eq 4).



6: R_1,R_2,R_3 = H
7: R_1,R_3 = Me, R_2 = H
8: R_1,R_2 = Me, R_3 = H
9: R_1,R_3 = $SiMe_3$, R_2 = H

10: R_1,R_2,R_3 = H
11: R_1,R_3 = Me, R_2 = H
12: R_1,R_2 = Me, R_3 = H
13: R_1,R_3 = $SiMe_3$, R_2 = H

Interestingly, a monitoring of the reaction by ^{31}P NMR indicated that no stable η^1-phosphinine complexes are formed prior to formation of the η^6-species. Cationic complexes **10**−**13** were recovered as stable yellow powders after precipitation with hexanes. All NMR data and elemental analyses support the proposed formulation. As usually observed, the η^6-coordination causes a dramatic upfield shift in ^{31}P NMR ($\Delta\delta$ = −220−230 ppm) as well as in the ^1H and ^{13}C NMR spectra for all nuclei directly attached to the ring (C_{ring}, H_{ring}). Thus, for complex **10**, we note an upfield shift of $\Delta\delta$ = 63 ppm for the signal of the two carbons adjacent to the P atom (C_2 and C_6), and the signal of the H_4 proton appears at $\delta(CDCl_3)$ = 6.28 ppm vs $\delta(CDCl_3)$ = 7.09 ppm in the free ligand. To gain more structural information on this new type of complex, an X-ray crystal structure study was carried out. Suitable crystals of **9** were obtained by diffusion of hexanes into a dichloromethane solution of the complex. An ORTEP view of one molecule of **9** is presented in Figure 1, and significant bond lengths and angles are listed below. The structure consists of a C_5Me_5 ligand and phosphinine **6** bound to ruthenium in a η^5- and η^6-fashion, respectively. The two rings are nearly parallel (θ = 4.99°) and planar, deviations out of the mean-planes being very weak in both cases (<1.5°) for C_{ring} and phosphorus atoms. Whereas the Ru−centroid bond distance for the C_5Me_5 ligand (1.825 Å) compares with that recorded in the [Ru(η^6-C_6Me_6)(η^5-C_5Me_5)][Otf] complex synthesized by Fagan and Ward et al. (1.753 Å) some years ago,[8g] the Ru−centroid (phosphinine) one appears to be shorter (1.676 Å). This deviation is in good agreement with the stronger π-accepting capability of phosphinine with respect to benzene derivatives. Inspection of internal bond distances within the phosphinine ring reveals that the aromaticity is not significantly disrupted and the most important deviation is given by the two P=C bond distances, which are slightly lengthened (average 1.772 Å) compared to values recorded in

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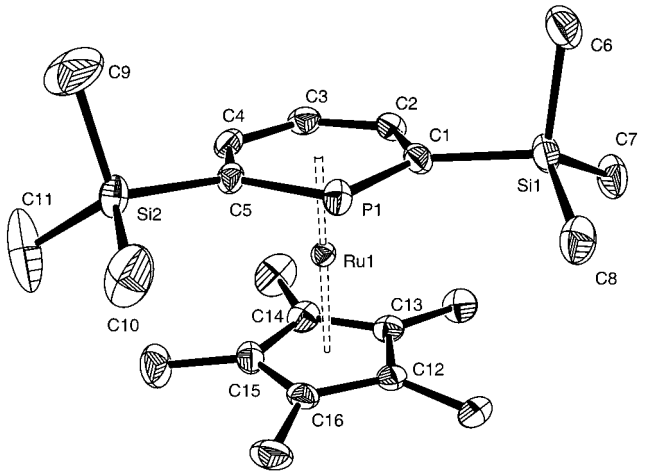

Figure 1. ORTEP drawing of complex **10**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. Labeling is arbitrary and different from that used in the assignment of NMR data. Selected bond distances (Å): P1−C1, 1.774(2); C1−C2, 1.411(3); C2−C3, 1.414(3); C3−C4, 1.422(3); C4−C5, 1.413(3);C5−P1, 1.772(2); C1−Si1, 1.904(2); C5−Si2, 1.899(2); P1−Ru1, 2.4391(5); C1−Ru1, 2.273(2); C2−Ru1, 2.216(2); C3−Ru1, 2.184(2); C4−Ru1, 2.220(2); C5−Ru1, 2.280(2); Ru1−centroid (phosphinine), 1.676; Ru1−centroid (Cp*), 1.825. Selected bond angles (deg): P1−C1−C2, 123.4(1); C1−C2−C3, 123.8(2); C2−C3−C4, 123.3(2); C3−C4−C5, 123.7(2); C4−C5−P1, 123.3(1); C5−P1−C1, 102.5(1); P1−C1−Si1, 116.2(1); P1−C5−Si2, 116.2(1).

free bis(silyl)phosphinines (1.73−1.74 Å).[12] This lengthening reflects the π-back-bonding in the π*-system of the ligand since the LUMO of phosphinines which presents an important coefficient at phosphorus is antibonding between P and the α-carbon atoms.[13] In view of the strong π-accepting ability of the phosphinine ligand, the electrochemical reduction of complexes **6**−**9** was attempted. Unfortunately, no reversible process leading to the corresponding stable 19 VE complexes could be observed. For example, the monoelectronic reduction of complex **12** occurs at $E_p = -1.46$ V vs SCE (E_p = peak potential) in THF at room temperature in the presence of *n*-Bu_4NBF_4 as electrolyte and remains irreversible even at high scan rates (up to 10 V s^{-1}). The presence of a second reduction peak at $E_p = -2.05$ V vs SCE was ascribed to the reduction of the released ligand by comparison with data of **8** recorded under the same conditions. In conclusion, we have developed an access to a series of [Ru(η^6-phosphinine)(η^5-C_5Me_5)] cationic complexes and reported the first structurally characterized derivative. Further work dealing with their electronic and coordinative properties as well as their reactivity are currently underway.

Experimental Section

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone, and dry $CDCl_3$ was obtained from P_2O_5. CD_2Cl_2 was dried and stored, like $CDCl_3$, on 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; v, virtual. IR data were collected on a Perkin-Elmer 297 spectrometer. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. Phosphinines **2**,[10] **8**,[11a] and **6**, **7**, **9**,[11b] and [Ru(η^5-C_5Me_5)(η^4-C_6H_{10})Cl][9] were prepared according to reported procedures.

Synthesis of [Ru(η^5-C_5Me_5)(η^4-C_8H_{10})(C_7H_8PBr)][BF_4] (3). [Ru(η^5-C_5Me_5)(η^4-C_8H_{10})Cl] (**1**, 65 mg, 0.185 mmol), 2-bromo-4,5-dimethylphosphinine (**2**, 37 mg, 0.185 mmol), and $AgBF_4$ (36 mg, 0.185 mmol) were weighed in air and then placed under nitrogen in a Schlenk flask. THF (5 mL) was syringed in, and the mixture was heated at 60 °C for 2 h. The solution was filtered on Celite and taken to dryness to afford the title compound as a green solid, which was then washed three times with hexanes (3 × 5 mL). Yield: 90 mg (80%). ^{31}P NMR ($CDCl_3$): δ 217.0 (s). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 2H, H vinyl), 1.75 (d, ^4J(H−P) = 2.3, 15H, CH_3 of C_5Me_5), 2.18 (s, 6H, CH_3), 2.34 (s, 3H, CH_3), 2.40 (d, ^2J(H−P) = 10.5, 3H, CH_3), 3.43 (s, 2H, =CH_2), 8.09 (d, ^2J(H−P) = 7.2, 1H, H_3) 8.19 (d, ^1J(H−P) = 10.0, 1H, H_6). ^{13}C NMR ($CDCl_3$): δ 10.0 (s, CH_3 of C_5Me_5), 18.1 (s, CH_3), 22.3 (d, J(C−P) = 4.5, CH_3), 23.4 (s, CH_3), 23.6 (s, CH_3), 46.2 (d, ^2J(C−P) = 65.0, CH_2), 99.2 (s, C of C_5Me_5), 99.5 (d, ^2J(C−P) = 65. 0, C of dmb), 139.8 (d, ^2J(C−P) = 26.0, $C_{3\ or\ 5}$), 141.5 (d, ^2J(C−P) = 26.1, $C_{3\ or\ 5}$), 145.2 (d, ^3J(C−P) = 10.7, C_4), 149.8 (d, ^1J(C−P) = 18.5, $C_{2\ or\ 6}$), 151.5 (d, ^1J(C−P) = 27.0, $C_{2\ or\ 6}$). Anal. Calcd for $C_{23}H_{33}BBrF_4PRu$: C, 45.42; H, 5.47. Found: C, 45.20; H, 5.59.

Synthesis of [Ru(η^5-C_5Me_5)(C_7H_8PBr)$_2$Cl] (4). [Ru(η^5-C_5Me_5)(η^4-C_8H_{10})Cl] (**1**, 38 mg, 0.11 mmol) and 2-bromo-4,5-dimethylphosphinine (**2**, 44 mg, 0.22 mmol) were weighed in air and then placed under nitrogen in a Schlenk flask. THF (5 mL) was syringed in, and the mixture was heated at 60 °C for 15 min. The solution was taken to dryness and the orange solid washed with hexanes (2 × 2 mL) to remove traces of dimethylbutadiene. The title compound was then dried under vacuum. Yield: 69 mg (95%). ^{31}P NMR ($CDCl_3$): δ 211.0 (s). ^{1}H NMR ($CDCl_3$): δ 1.79 (t, ^4J(H−P) = 2.6, 15H, CH_3 of C_5Me_5), 2.25 (s, 12H, CH_3), 7.90 (vdd, AXX′, $\sum J$(H−P) = 13.8, 1H, H_3) 8.27 (vt, AXX′, $\sum J$(H−P) = 21.0, 1H, H_6). ^{13}C NMR ($CDCl_3$): δ 10.8 (s, CH_3 of C_5Me_5), 22.0 (s, CH_3), 23.5 (vt, AXX′, $\sum J$(C−P) = 9.8, CH_3), 92.9 (s, C of C_5Me_5), 135.3 (vt, AXX′, $\sum J$(C−P) = 22.8, C_4), 142.1 (vt, AXX′, $\sum J$(C−P) = 13.3, $C_{3\ or\ 5}$), 143.8 (vt, AXX′, $\sum J$(C−P) = 12.3, $C_{3\ or\ 5}$), 145.5 (vt, AXX′, $\sum J$(C−P) = 18.0, $C_{2\ or\ 6}$), 148.5 (vt, AXX′, $\sum J$(C−P) = 16.5, $C_{2\ or\ 6}$). Anal. Calcd for $C_{24}H_{31}Br_2ClP_2Ru$: C, 42.53; H, 4.61. Found: C, 42.63; H, 4.71.

Synthesis of [Ru(η^5-C_5Me_5)(C_7H_8PBr)$_3$][BF_4] (5). Complex **4** (62 mg, 0.09 mmol) and 2-bromo-4,5-dimethylphosphinine (**2**, 18 mg, 0.09 mmol) were weighed in air and then placed under nitrogen in a Schlenk flask. THF (5 mL) was syringed in, and $AgBF_4$ (18 mg, 0.09 mmol) was then added to the mixture. A greenish yellow tinge developed, and ^{31}P NMR showed the reaction to be complete within 1 h. The solution was filtered over Celite and the volume reduced under vacuum until yellow crystals started to form. The mixture was then left unmoved for 2 days, and the crystals were collected on a fine frit. The title compound was then dried under vacuum. Yield: 77 mg (91%). ^{31}P NMR ($CDCl_3$): δ 199.0 (s). ^{1}H NMR ($CDCl_3$): δ 1.92 (vd, J(H−P) = 0.5, 15H, CH_3 of C_5Me_5), 2.31 (bs, 9H, CH_3), 2.46 (bs, 9H, CH_3), 7.85 (m, AXX′$_2$, $\sum J$(H−P) = 16.8, 1H, H_3), 8.16 (m, AXX′$_2$, $\sum J$(H−P) = 29.0, 1H, H_6). ^{13}C

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NMR (C_2D_6O): δ 10.9 (s, CH_3 of C_5Me_5), 21.9 (s, CH_3), 23.7 (bs, CH_3), 100.0 (s, C of C_5Me_5), 139.6 (m, C_4), 142.2 (m, $C_{3\text{ or }5}$), 145.2 (bs, $C_{3\text{ or }5}$), 147.6 (m, $C_{2\text{ or }6}$), 149.4 (m, $C_{2\text{ or }6}$). Anal. Calcd for $C_{31}H_{39}BBr_3F_4P_3Ru$: C, 39.94; H, 4.22. Found: C, 39.75; H, 4.01.

Synthesis of [Ru(η^5-C_5Me_5)(η^6-$C_{11}H_{21}PSi_2$)][BF_4] (10). Complex **1** (69 mg, 0.195 mmol) and 2,6-bis(trimethylsilyl)-phosphinine (**6**, 47 mg, 0.195 mmol) were weighed in air and then placed under nitrogen in a Schlenk flask. THF (5 mL) was syringed in, $AgBF_4$ (38 mg, 0.195 mmol) was added, and the mixture was heated at 60 °C for 3 h. The solution was filtered through Celite, and the volume reduced under vacuum until the title compound started to precipitate. The mixture was then allowed to crystallize, and the crystals were collected by filtration. Yield: 77 mg (70%). ^{31}P NMR ($CDCl_3$): δ 26.5 (s). ^{1}H NMR ($CDCl_3$): δ 0.33 (s, 18H, $SiMe_3$), 1.99 (s, 15H, CH_3 of C_5Me_5), 6.16 (dd, J(H−P) = 6.6, J(H−H) = 8.0, 2H, $H_{3,5}$), 6.44 (pt, J(H−P) = J(H−H) = 6.5, 1H, H_6). ^{13}C NMR ($CDCl_3$): δ 0.7 (d, ^3J(C−P) = 5.7, $SiMe_3$), 12.2 (s, CH_3 of C_5Me_5), 84.0 (d, ^3J(C−P) = 14.8, C_4), 94.5 (d, ^2J(C−P) = 6.1, $C_{3,5}$), 99.4 (s, C of C_5Me_5), 108.4 (d, ^1J(C−P) = 96.7, $C_{2,6}$). Anal. Calcd for $C_{21}H_{36}BF_4PRuSi_2$: C, 44.76; H, 6.44. Found: C, 44.69; H, 6.50.

Synthesis of [Ru(η^5-C_5Me_5)(η^6-$C_{13}H_{25}PSi_2$)][BF_4] (11). Complex **1** (60 mg, 0.17 mmol) and 3,5-dimethyl-2,6-bis-(trimethylsilyl)phosphinine (45 mg, 0.17 mmol) were weighed in air and then placed under nitrogen in a Schlenk flask. THF (10 mL) was syringed in, $AgBF_4$ (33 mg, 0.17 mmol) was added, and the mixture was heated at 60 °C for 3 h. The solution was filtered through Celite, the volume was reduced under vacuum, and hexanes were added to induce precipitation. The complex was then isolated by filtration and dried under vacuo. Yield: 78 mg (75%). ^{31}P NMR ($CDCl_3$): δ 39.6 (s). ^{1}H NMR ($CDCl_3$): δ 0.40 (d, ^4J(H−P) = 1.5, 18H, $SiMe_3$), 1.92 (s, 15H, CH_3 of Cp*), 2.35 (s, 6H, CH_3), 6.28 (m, 1H, H_4). ^{13}C NMR ($CDCl_3$): δ 2.7 (d, ^3J(C−P) = 10.5, $SiMe_3$), 11.6 (s, CH_3 of Cp*), 22.5 (s, CH_3), 84.0 (d, ^3J(C−P) = 12.0, C_4), 98.1 (s, C of Cp*), 105.8 (d, ^1J(C−P) = 99.2, $C_{2,6}$), 109.5 (d, ^2J(C−P) = 6.6, $C_{3,5}$). Anal. Calcd for $C_{23}H_{40}BF_4PRuSi_2$: C, 46.70; H, 6.82. Found: C, 46.52; H, 6.68.

Synthesis of [Ru(η^5-C_5Me_5)(η^6-$C_{13}H_{25}PSi_2$)][BF_4] (12). Complex **1** (60 mg, 0.17 mmol) and 3,4-dimethyl-2,6-bis-(trimethylsilyl)phosphinine (45 mg, 0.17 mmol) were weighed in air and then placed under nitrogen in a Schlenk flask. THF (10 mL) was syringed in, $AgBF_4$ (33 mg, 0.17 mmol) was added, and the mixture was heated at 60 °C for 3 h. The solution was filtered through Celite, the volume was reduced under vacuum, and hexanes were added to induce precipitation. The complex was then isolated by filtration and dried under vacuo. Yield: 85 mg (84%). ^{31}P NMR (CD_2Cl_2): δ 32.2 (s). ^{1}H NMR ($CDCl_3$): δ 0.40 (m, 18H, 2× $SiMe_3$), 1.90 (s, 15H, CH_3 of Cp*), 2.35 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.08 (m, 1H, H_5). ^{13}C NMR (CD_2Cl_2): δ 2.7 (d, ^4J(C−P) = 10.5, $SiMe_3$), 11.5 (s, CH_3 of Cp*), 22.5 (s, CH_3), 84.0 (d, ^3J(C−P) = 12.0, C_4), 98.0 (s, C of Cp*), 105.8 (d, ^1J(C−P) = 99.2, $C_{2,6}$), 109.5 (d, ^2J(C−P) = 6.6, $C_{3,5}$). Anal. Calcd for $C_{23}H_{40}BF_4PRuSi_2$: C, 46.70; H, 6.82. Found: C, 46.78; H, 6.89.

Synthesis of [Ru(η^5-C_5Me_5)(η^6-$C_{17}H_{37}PSi_4$)][BF_4] (13). Complex **1** [Cp*RuCl(dmb)] (60 mg, 0.17 mmol) and 2,3,5,6-tetra(trimethylsilyl)phosphinine (65 mg, 0.17 mmol) were weighed in air and then placed under nitrogen in a Schlenk flask. THF (10 mL) was syringed in, $AgBF_4$ (33 mg, 0.17 mmol) was added, and the mixture was heated at 60 °C for 3 h. The solution was filtered through Celite, the volume was reduced under vacuum, and hexanes were added to induce precipitation. The complex was then isolated by filtration and dried under vacuo. Yield: 96 mg (79%). ^{31}P NMR ($CDCl_3$): δ 41.1 (s). ^{1}H NMR ($CDCl_3$): δ 0.44 (s, 18H, $SiMe_3$), 0.47 (d, ^4J(H−P) = 1.5, 18H, $SiMe_3$), 1.94 (s, 15H, CH_3 of Cp*), 6.13 (s, 1H, H_4). ^{13}C NMR ($CDCl_3$): δ 3.3 (s, $SiMe_3$), 4.6 (d, ^4J(C−P) = 13.7, $SiMe_3$), 12.7 (s, CH_3 of Cp*), 87.7 (d, ^3J(C−P) = 18.9, C_4), 99.4 (s, C of Cp*), 106.4 (d, ^2J(C−P) = 3.3, $C_{3,5}$), 112.73 (d, ^1J(C−P) = 105.9, $C_{2,6}$). Anal. Calcd for $C_{27}H_{52}BF_4PRuSi_4$: C, 45.81; H, 7.40. Found: C, 45.72; H, 7.58.

Table 1. Crystallographic Data and Experimental Parameters for the Structure of Complex 10

mol formula	$C_{21}H_{36}BF_4PRuSi_2$
mol wt	563.53
cryst descripn	pale yellow plate
(habit/size (mm))	0.20 × 0.20 × 0.16
cryst syst	monoclinic
space group	$P2_1$
a (Å)	9.6581(3)
b (Å)	11.5315(4)
c (Å)	11.7881(3)
β (deg)	93.184(2)
V (Å^3)	1310.84(7)
Z	2
D (g/cm^3)	1.428
F(000)	580
μ (cm^{-1})	0.785
T (K)	150.0(1)
max θ (deg)	30.05
hkl ranges	−11 13; −16 15; −16 12
no. of rflns measd	9730
no. of indep rflns	7375
no. of rflns used	7234
R_{int}	0.0423
refinement type	F^2
hydrogen atoms	mixed
no. of params refined	282
Flack parameter	−0.018(17)
rfln/param ratio	25
wR2	0.0604
R1	0.0230
criterion	$>2\sigma(I)$
GOF	1.086
diff peak/hole (e Å^3)	0.736(0.060)/−0.469(0.060)

X-ray Crystallographic Studies of 10. Crystals suitable for X-ray diffraction were grown in a sealed tube by slow diffusion of hexanes into a dichloromethane solution of the complex. The tube was broken in the glovebox, and crystals were protected with paratone oil for handling and then submitted to X-ray diffraction analysis. Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved using SIR 97[14] and SHELXL-97.[15] ORTEP drawings were made using ORTEP III for Windows.[16]

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Supporting Information Available: Listings of atomic coordinates, including H atoms and equivalent isotropic displacement parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010215X

(14) SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single-crystal data: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.

(15) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.

(16) ORTEP-3 program created by Louis J. Farrugia (Department of Chemistry, University of Glasgow).