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Preparation and Reactivity of Organometallic Complexes Bearing the Fragment “$Cp^*Ru(CO)(PR_3)$” ($PR_3 = PMe^iPr_2, PEt_3$): Dinuclear Complexes $[\{Cp^*Ru(CO)(PR_3)\}_2(\mu\text{-}Cl)]^+$ Containing Two Chiral Centers, η^2-Alkene, and Other Mononuclear Complexes

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The reactions of $[Cp^*RuCl(CO)(PMe^iPr_2)]$ (**1**) and $[Cp^*RuCl(CO)(PEt_3)]$ (**2**) with $NaBAr'_4$ in fluorobenzene both under argon and under dinitrogen generate the binuclear compounds $[\{Cp^*Ru(CO)(PMe^iPr_2)\}_2(\mu\text{-}Cl)][BAr'_4]$ (**3**) and $[\{Cp^*Ru(CO)(PEt_3)\}_2(\mu\text{-}Cl)][BAr'_4]$ (**4**), respectively, which were fully characterized. The crystal structure of compound **4** is reported, showing for the first time two chiral “Cp*Ru” fragments bonded through only one bridging chloride ligand. No dinitrogen complexes or 16-electron species could be isolated. Halide abstraction from **1** using dry acetone as solvent yields the compound $[Cp^*Ru(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PMe^iPr_2)][BAr'_4]$ (**5**). A range of olefins react with $[Cp^*RuCl(CO)(PMe^iPr_2)]$ and $NaBAr'_4$ furnishing the corresponding cationic η^2-alkene complexes $[Cp^*Ru(CO)(L)(PMe^iPr_2)][BAr'_4]$ ($L = C_2H_4$, **6**; $H_2C{=}CHPh$, **7**; and $H_2C{=}CHCOOCH_3$, **8**), which are stable under argon atmosphere in solution. The crystal structure of compound **6** is also reported. Both **1** and **2** react with $SnCl_2$ in CH_2Cl_2 to yield the insertion derivatives $[Cp^*Ru(CO)(SnCl_3)(PR_3)]$ ($PR_3 = PMe^iPr_2$, **9**; PEt_3, **10**), which have also been characterized.

Introduction

Half-sandwich compounds $[Cp^*RuCl(PP)]$ (PP = two monodentate or one bidentate phosphine ligand) have been well studied over the past years.[1] However, there is only a small group of well-known related compounds $[Cp^*RuCl(CO)P]$ in which a carbonyl ligand substitutes one phosphine.[2] This change modifies properties and reactivity of the metal center. They should also be obtained by different synthetic methods.

On the other hand, the introduction of the noncoordinating anion $[BAr'_4]^-$ (BAr'_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) as halide scavenger has recently allowed the isolation of coordinatively unsaturated cationic complexes $[Cp^*Ru(PP)][BAr'_4]$ (PP = 1,2-bis(diisopropylphosphino)ethane (dippe), $(PMe^iPr_2)_2$, $(PEt_3)_2$, $(PPh^iPr_2)_2$, $(PPh_3)_2$),[3,4] as well as some others containing hard nitrogen donor ligands.[5−7] However, the reaction of $[Cp^*RuCl(dppm)]$ (dppm = bis(diphenylphosphino)methane) with $NaBAr'_4$ in fluorobenzene under argon generates the binuclear complex $[\{Cp^*Ru\}_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][BAr'_4]$.[8] No complex was isolated from a similar reaction using $[Cp^*RuCl(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) under argon, although halide abstraction from $[Cp^*RuCl(PP)]$ (PP = dppm, dppe) under dinitrogen yielded the corresponding cationic terminal dinitrogen complexes $[Cp^*Ru(N_2)(PP)][BAr'_4]$.[8] Attempts to isolate species $[Cp^*Ru(PP)]^+$, analogous to those containing other phosphine ligands such as P^iPr_3, PCy_3, or PMe_3, led to the sandwich derivative $[Cp^*Ru(\eta^6\text{-}FPh)][BAr'_4]$. Both $[Cp^*Ru(PPh_3)_2][BAr'_4]$ and $[Cp^*Ru(PPh^iPr_2)_2][BAr'_4]$ are unstable and rearrange to the 18-electron sandwich species $[Cp^*Ru(\eta^6\text{-}C_6H_5PR_2)][BAr'_4]$, and $[Cp^*Ru(\eta^6\text{-}C_6H_5\text{-}POR_2)][BAr'_4]$ (R = Ph, ^iPr) in the presence of trace amounts of oxygen.[4]

The 16-electron species can provide binding sites for a range of molecules such as dihydrogen, dinitrogen, and

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alkenes. Dihapto-alkene complexes have been used as intermediates in a large number of organic processes such as hydrogenation, isomerization, and hydroformylation.[9] After the first described ruthenium-η^2-alkene complex $[RuCl_2(CO)(H_2C{=}CH_2)(PMePh)_2]$,[10] other cationic half-sandwich complexes $[CpRu(L)(PMe_3)_2]^+$ (L = ethylene, styrene, propylene, and COD)[11,12] have been reported. We have carried out the syntheses of $[(C_5R_5)Ru(H_2C{=}CH_2)(dippe)]^+$ (R = H, Me)[13] and $[(C_5R_5)Ru(H_2C{=}CH_2)(PP')]^+$ (R = H, Me, P = P′ = PEt_3; R = H, P = PPh_3, P′ = PMe^iPr_2). Similarly, some other complexes with styrene, $[CpRu(H_2C{=}CHPh)(PEt_3)_2]^+$, and methyl-acrylate, $[(C_5R_5)Ru(H_2C{=}CHCOOMe)(PEt_3)_2]^+$ (R = H, Me), have been obtained.[14] Our synthetic method was the abstraction of chloride ligand from the starting compound $[Cp^*RuCl(PMe^iPr_2)]$ in the presence of the corresponding alkene.

The insertion of SnX_2 in a M−X bond yielding $M{-}SnX_3$ is a well-known process. This reaction is stereospecific, and when carried out with compounds with catalytical activity, it produces a better selectivity of the catalyst.[15,16] Some products derived from these reactions are very interesting to industry and pharmacology. The ruthenium chemistry involving $SnCl_3^-$ as a ligand is poorly developed, despite being promising; for example, $[Ru(SnCl_3)_5(PPh_3)]^{3-}$ catalyzes the formation of acetic acid from methanol.[17] In this way, we have previously reported the reactions of [CpRuCl(dippe)] and [Cp*RuCl(dippe)] with $SnCl_2$ in CH_2Cl_2, which give insertion derivatives of $SnCl_2$ in the Ru−Cl bond, namely, the orange compounds $[CpRu(SnCl_3)(dippe)]$ and $[Cp^*Ru(SnCl_3)(dippe)]$.[18] The formation of these derivatives is consistent with the lability of the chloride ligand in the starting complexes. However, it has been found that the dissociation of either chloride or phosphines is not really necessary for the formation of insertion derivatives. The fact that the reaction of the chiral complex [CpRuCl(dppp)] with $SnCl_2$ proceeds with net retention of configuration at the metal center is consistent with the associative mechanism for this reaction.[19]

In this work we describe the synthesis of $[Cp^*RuCl(CO)(PR_3)]$ ($PR_3 = PMe^iPr_2$, PEt_3) and halide abstraction reactions with $Na[BAr'_4]$ in fluorobenzene and dry acetone as solvents. The results are compared with those systems containing the "Cp*RuCl(PP)" fragment which we have previously reported. Related reactions with alkenes, and $SnCl_2$ insertion reactions into the Ru−Cl bond, complete our work on this subject.

Results and Discussion

The reduction of $\{Cp^*RuCl_2\}_2$[20] with Zn in thf in the presence of 1 equiv of diisopropylmethylphosphine produces the 16-electron complex $[Cp^*RuCl(PMe^iPr_2)]$, in dynamic equilibrium in solution with the corresponding compound containing two phosphine ligands.[21] The treatment of these solutions with CO affords the complex $[Cp^*RuCl(CO)(PMe^iPr_2)]$ (**1**). The presence of the carbonyl ligand is confirmed by the IR spectrum of **1** showing the characteristic ν(CO) band as a sharp peak at 1940 cm^{-1}. In the $^{31}P\{^1H\}$ NMR spectrum **1** exhibits a singlet at 42 ppm, and its ^1H NMR spectrum displays a characteristic doublet at 1.74, which corresponds to Cp* hydrogens coupled to one phosphorus. A doublet in the $^{13}C\{^1H\}$ NMR spectrum corresponds to the carbonyl ligand carbon atom coupled with one phosphorus (J = 20 Hz).

However, the same method was unsuccessful for the synthesis of $[Cp^*RuCl(CO)(PEt_3)]$ (**2**), which was alternatively prepared by displacement of one phosphine in the direct reaction of $[Cp^*RuCl(PEt_3)_2]$[22] with CO. This method has been already used to obtain analogous complexes,[23] although it often affords mixtures with other undesirable products, consequently lowering the yields. The spectral data for complexes **1** and **2** are very similar. **2** also shows in the IR spectrum an intense ν(CO) peak at 1940 cm^{-1} as well as the doublet signal corresponding to a Cp* proton resonance in the ^1H NMR spectrum and the doublet for the carbonylic carbon in the $^{13}C\{^1H\}$ NMR spectrum.

Complexes **1** and **2** do not undergo chloride ion dissociation in alcohol solution, this behavior being different from that exhibited by the analogous $[Cp^*RuCl(P)_2]$ systems. The carbonyl ligand is a stronger π-acceptor ligand compared to phosphines, and, therefore, the ruthenium center is less electron rich in complexes **1** and **2**. This accounts for their comparatively lower tendency to dissociate chloride ions. The salt $NaBAr'_4$ in fluorobenzene was used for chloride abstraction in the same way as it was already used to isolate the 16-electron complex $[Cp^*Ru(dippe)]^+$.[3] Fluorobenzene was chosen as solvent for its high polarity and weak coordinative character in order to favor dissociation of the sodium salt and the ruthenium complex. The anion $[BAr'_4]^-$ shows very weak or no tendency to coordinate, contributing to the formation of unsaturated species. When complex **1** reacts with $NaBAr'_4$ in fluorobenzene, the color changes from yellow-orange to red, characteristic of the compound $[\{Cp^*Ru(CO)(PMe^iPr_2)\}_2(\mu\text{-}Cl)][BAr'_4]$ (**3**). In a similar way $[\{Cp^*Ru(CO)(PEt_3)\}_2(\mu\text{-}Cl)][BAr'_4]$ (**4**) has also been obtained. The half-sandwich

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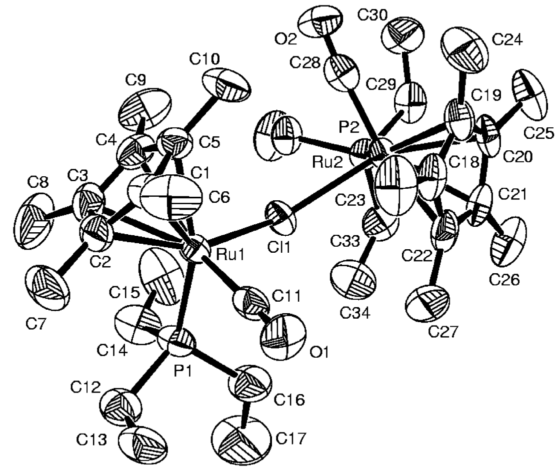
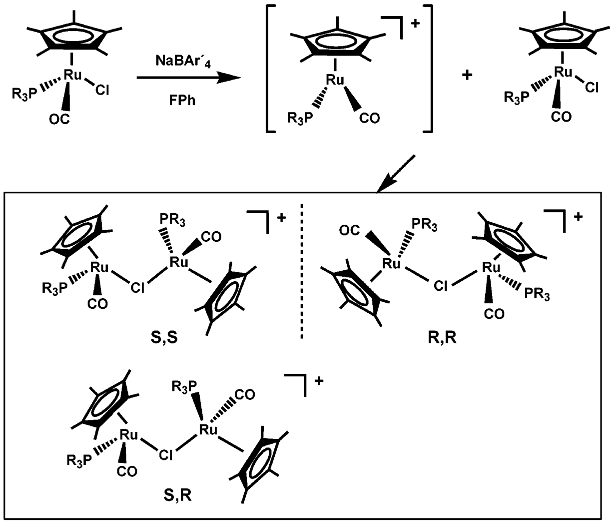


Figure 1. ORTEP diagram of cation $[\{Cp^*Ru(CO)(PEt_3)\}_2(\mu\text{-}Cl)]^+$ in compound **4** showing the non-hydrogen atom-numbering scheme. Selected bond distances (Å) and angles (deg) for compound **4**: Ru(1)−Cl 2.4952(19); Ru(2)−Cl 2.4976(19); Ru(1)−P(1) 2.328(2); Ru(2)−P(2) 2.340(2); Ru(1)−C(11) 1.854(9); Ru(2)−C(28) 1.860(10); Ru(1)−Cl−Ru(2) 137.33(8); P(1)−Ru(1)−Cl 86.66(7); C(11)−Ru(1)−P(1) 86.6(3); C(11)−Ru(1)−Cl 97.0(2); Cl−Ru(2)−P(2) 88.21(7); P(2)−Ru(2)−C(28) 88.0(2); Cl−Ru(2)−C(28) 95.4(3).

Scheme 1. Proposed Reaction Sequence for the Formation of 3 and 4



ruthenium 16-electron complexes already described in the literature are characteristically blue or deep violet, whereas in the processes described above these colors were not observed during reaction. It is likely that in this case the 16-electron species are extremely reactive and they rapidly react with the starting complex to generate dimer derivatives **3** and **4** (Scheme 1).

Recrystallization of **4** from diethyl ether/petroleum ether afforded crystals suitable for single-crystal X-ray diffraction. An ORTEP view of the dinuclear complex cation $[\{Cp^*Ru(CO)(PEt_3)\}_2(\mu\text{-}Cl)]^+$ is presented in Figure 1 including a selection of bond lengths and angles in the footnote. The structure can be described as a three-legged piano stool around each metal center. The geometry of each ruthenium center can be described as formally octahedral with the Cp* ligand occupying three coordination positions and the others occupied by CO, the phosphine ligand, and the bridging Cl. The distances between the Cp* ring plane and the metal are 1.886(4) Å for Ru(1) and 1.877(3) Å for Ru(2), respectively. Both ruthenium atoms are chiral centers. The priority order in the first coordination sphere is Cp* > Cl > P > C. Consequently, the chirality in the represented complex is *SS*. Since the space group is the centrosymmetric $P2_1/c$, its enantiomer *RR* is also contained in the unit cell. The other possible diastereomer, *RS*, was identified in solution and will be discussed below. This is the first reported structure of a binuclear ruthenium complex with two Cp*Ru fragments linked only by one single atom bridging ligand. Bond distances Ru(1)−Cl(1) and Ru(2)−Cl(1) are very similar, 2.4952(19) and 2.4976(19) Å, as expected. They are comparable with, although slightly longer than, those observed in binuclear complexes with two bridging ligands $[\{Cp^*Ru(C_2F_4)(\mu\text{-}Cl)\}_2]$, 2.462(1) and 2.448(1) Å,[24] and $[\{Cp^*Ru(py)\ (\mu\text{-}Cl)\}_2]^+$, 2.427(1) and 2.442(1) Å,[25] and even closer to 2.4750(8) and 2.4788(8) Å found in $[\{(C_5Me_4Et)Ru(C_2H_4)(\mu\text{-}Cl)\}_2]$.[26]

The IR spectra of **3** and **4** show intense ν(CO) peaks at 1942 and 1944 cm^{-1}, respectively. In the ^{1}H NMR spectrum of **3** the methyl hydrogens of C_5Me_5 were observed as one broad singlet at 1.59 ppm, which probably consists of two close signals. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 38.2 and 39.5 ppm, with approximately equal intensities, indicating two non-equivalent phosphorus atoms. The ^{1}H NMR spectrum of compound **4** shows two close signals for Cp* protons at 1.68 and 1.69 ppm; the coupling constants with phosphorus could be measured, giving similar values (1.61 and 1.65 Hz, respectively). In the $^{31}P\{^1H\}$ NMR spectrum two singlets appear at 33.95 and 34.72 ppm corresponding, as in the case of **3**, to the diastereomers (*RR* or *SS*) and *RS*. The $^{13}C\{^1H\}$ NMR spectra are very similar in both cases, and they can be compared with that of **1** except by the fact that for complexes **3** and **4** phosphine carbons produce broader, although yet unresolved signals due to the presence of the two diastereomers. In addition, the integrals for the different NMR spectra give a ratio of approximately 1:1 for the two diastereomers, in agreement with a pseudostatistical distribution of *RR*, *RS*, *SR* (identical to *RS*), and *SS*.

The isolation or even the unequivocal identification of coordinatively unsaturated complexes is not an easy task. The 16-electron species $[Cp^*Ru(PR_3)_2]^+$ ($PR_3 = PMe^iPr_2$, PEt_3) have already been characterized,[27] whereas the complex $[Cp^*Ru(dippe)]^{+3}$ shows an agostic interaction with one isopropylic proton. In other cases, binuclear complexes such as $[\{CpRu(P_2)\}_2(\mu\text{-}N_2)][BAr'_4]$ (P_2 = dippe or 2 PMe^iPr_2)[4] or $[\{Cp^*Ru\}_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][BAr'_4]$ (dppm = 1,1-bis(diphenylphosphino)methane)[8] are obtained. Cp produces less electron richness at the Ru center than Cp*, and hence coordinatively unsaturated species containing the fragment {CpRu} are much more reactive and difficult to isolate than those contain-

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ing {Cp*Ru}. In addition, the stability of the moiety {Cp*Ru(PP)} depends also on the phosphine ligands. For instance, the five-membered chelate ring makes $[Cp^*Ru(dippe)]^+$ more stable than the complex $[Cp^*Ru(dppm)]^+$, with a four-membered chelate ring, which has not been isolated. On the other hand, $[Cp^*Ru(CO)(PR_3)]^+$ should be more electrophilic than $[Cp^*Ru(PR_3)_2]^+$ because of the strong π-acceptor character of carbonyl ligand.

The reaction of **1** with a solution of NaBAr′$_4$ in a 1:1 acetone/fluorobenzene mixture leads to the yellow compound $[Cp^*Ru\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PMe^iPr_2)][BAr'_4]$ (**5**). The presence of the CO ligand is indicated by a sharp ν(CO) band at 1951 cm^{-1}, and the band corresponding to coordinated acetone appears at 1660 cm^{-1} in the IR spectrum. Its ^1H NMR spectrum shows the signals corresponding to proton resonances of Cp* and phosphine ligands and also one singlet at 2.23 ppm corresponding to the six hydrogen atoms of coordinated acetone. A singlet at 39.56 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum as expected. The $^{13}C\{^1H\}$ NMR spectrum displays one singlet at 213.5 ppm for the carbonyl carbon atom and another resonance at 32.2 for methyl carbon atoms in coordinated acetone. In addition, the CO resonance appears as a doublet at 205 ppm with $J_{C-P} = 19.53$ Hz. These spectral data are in agreement with those reported by Esteruelas[2a] for the complex $[CpRu(CO)\{\eta^1\text{-}OC(CH_3)_2\}(P^iPr_3)]^+$, which was prepared by protonation of the monohydride complex $[CpRu(CO)(P^iPr_3)H]$ with HBF_4 in acetone and subsequent displacement of the dihydrogen ligand.

As indicated above, the coordinatively unsaturated species $[Cp^*Ru(CO)(PMe^iPr_2)]^+$ was not isolated but can be generated in situ by reaction of compound **1** and NaBAr′$_4$ in fluorobenzene. This species reacts with alkenes yielding η^2-alkene complexes. In this way, complexes **6**, **7**, and **8** were isolated as crystalline $[BAr'_4]^-$ salts. These compounds are air-stable both in solution and in the solid state.

The identity of compound **6** was established by X-ray crystallography. The ORTEP diagram of the cation is depicted in Figure 2. Its structure can be described as an overall three-legged piano stool geometry. All Ru−C distances of the pentamethylcyclopentadiene moiety are rather uniform, ranging from 2.219(5) to 2.280(5) Å, the distance Ru(1)−Cp* ring being 1.893(2) Å, which is comparable with values found for compound **4**. The C(11)−C(12) bond length of 1.416(13) Å compares well with the values found for other ruthenium η^2-ethylene complexes, i.e., 1.43(2) Å for $[Cp^*Ru(C_2H_4)(dippe)]^+$ [13] and 1.439 Å for $[Ru(C_2H_4)(PMe_3)_4]$.[28] Free ethylene ligand has a C−C bond distance of 1.337 Å, only slightly shorter than in coordinated ethylene. It shows the slight activation of C_2H_4 by coordination to the Ru center. The angle C(11)−Ru(1)−C(12) is 37.5(3)°. Bond lengths Ru−C(11) and Ru−C(12) are very similar (2.197(8) and 2.204(7) Å), showing a symmetric coordination of the ethylene ligand to the metal.

The crystalline compounds **6**, **7**, and **8** display in their IR spectra the characteristic strong band corresponding to ν(CO). In addition, bands attributed to the coordinated alkene were observed at 1611, 1620, and 1707 cm^{-1} for **6**, **7**, and **8**, respectively. These compounds are stable in solution under argon atmosphere, making their characterization possible. Whereas the coordination of ethylene in **6** is irreversible, the analogous $[Cp^*Ru(\eta^2\text{-}C_2H_4)(dippe)]^+$ [13] is *labile* and loses C_2H_4, so its characterization in solution was made under ethylene atmosphere. The instability of ethylene-Cp*Ru adducts was also observed for $[Cp^*Ru(\eta^2\text{-}C_2H_4)(P{\sim}O)][BPh_4]$ (P∼O = (1,2-dioxan-2-ylmethyl)(diphenylphosphine)),[29] which is stable only under an atmosphere of ethylene, whereas other cyclopentadienylruthenium complexes such as $[CpRu(\eta^2\text{-}C_2H_4)(PPh_3)_2]^+$ [30] and $[CpRu(\eta^2\text{-}C_2H_4)(PMe_3)_2]^+$ [31] are stable species. It seems that the effects of fragments $[Cp^*Ru(CO)(P)]^+$ and $[CpRu(PP)]^+$ on the lability of bound ethylene are similar. Whereas compound **7** is stable in solution, $[CpRu(CH_2{=}CHPh)(PEt_3)_2][BPh_4]$ was characterized in acetone only in the presence of styrene.[14] The protons of the C_2H_4 ligand appear in the ^1H NMR spectrum of **6** as two multiplets at 2.42 and 2.52 ppm. The ethylene carbon atoms appear as one singlet at 47.32 ppm in the $^{13}C\{^1H\}$ NMR spectrum. This signal was observed for the complexes $[CpRu(\eta^2\text{-}C_2H_4)(PEt_3)_2]^+$ and $[Cp^*Ru(\eta^2\text{-}C_2H_4)(dippe)]^+$ at 39.9 and 33.3 ppm, respectively.[13] A similar chemical shift was observed for complex $[Cp^*Ru(\eta^2\text{-}C_2H_4)(P{\sim}O)]^+$ ($\delta = 46.9$ ppm).

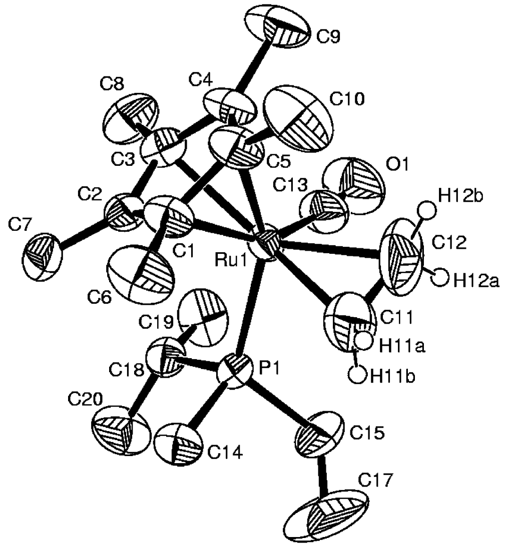

Figure 2. ORTEP diagram of cation $[Cp^*Ru(\eta^2\text{-}H_2C{=}CH_2)(CO)(PMe^iPr_2)]^+$ in compound **6** showing the non-hydrogen atom-numbering scheme. Selected bond distances (Å) and angles (deg) for compound **6**: Ru−C(11) 2.197(8); Ru−C(12) 2.204(7); C(11)−C(12) 1.416(13); C(11)−H(11A) 0.94(8); C(11)−H(11B) 0.87(9); C(12)−H(12A) 0.97; C(12)−H(12B) 0.97; C(11)−Ru−C(12) 37.5(3); C(12)−C(11)−Ru 71.5(5); C(11)−C(12)−Ru 71.0(5); C(12)−Ru−P(1) 104.0(3).

Three multiplets at 2.19, 3.23, and 4.65 ppm are observed in the ^1H NMR spectrum of compound **7** corresponding to the styrene ligand, and similarly at 2.32, 3.02, and 3.19 ppm for the methyl acrylate derivative **8**. In the $^{13}C\{^1H\}$ NMR spectra two singlets at 41.77 and 74.18 ppm for compound **7** and similarly at

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52.43 and 46.33 ppm for compound **8** are observed, corresponding to the primary and secondary C atoms of the alkene ligand. This is the difference that was found in relation to compound **6**, where the two double-bonded carbon atoms are equivalent.

In the $^{31}P\{^1H\}$ NMR spectra only one signal is observed in all cases, showing that they are not a mixture of products. Of the two possible *endo* and *exo* isomers, only one is obtained, and probably it is the *exo* because of steric features.

Compounds **1** and **2** react with anhydrous $SnCl_2$ in CH_2Cl_2, yielding the neutral trichlorostannyl complexes [Cp*Ru(CO)(PMe^{i}Pr$_2$)(SnCl$_3$)] (**9**) and [Cp*Ru(CO)(PEt$_3$)(SnCl$_3$)] (**10**), yellow and orange, respectively. These compounds are generated by insertion of $SnCl_2$ into the Ru−Cl bond, a process that is well-known and has been thoroughly studied[15] due to the ability of the trichlorostannyl ligand to promote or modify the catalytic activity of transition metal complexes.[16] The $^{31}P\{^1H\}$ NMR spectra of both compounds consist of one singlet at 26.13 and 37.62 ppm, respectively, showing small satellites due to coupling of the phosphorus atom to the NMR active ^{117}Sn and ^{119}Sn nuclei. The coupling constants are $J(P,^{117}Sn) = 347$ Hz and $J(P,^{119}Sn) = 322$ Hz for compound **9**. For compound **10**, these coupling constants are 355.4 and 340.49 Hz. Consistent with this, the ^{119}Sn NMR spectra of **9** and **10** display one doublet in both cases, at $\delta = 44.19$ ppm ($J_{P-Sn} = 346$ Hz) for **9** and $\delta = 36.77$ ppm ($J_{P-Sn} = 354.36$ Hz) for **10**, respectively, due to coupling of the ^{119}Sn nucleus with the phosphorus atom.

Experimental Section

All synthetic operations were performed under a dry argon atmosphere, using conventional Schlenck techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40−60 °C) were distilled from the appropiate drying agents. Fluorobenzene was purchased from Aldrich and acetone (0.01% water max.) from SDS. All solvents were deoxygenated inmediately before use. The complexes {Cp*RuCl$_2$}$_2$[20] and Na[BAr′$_4$][32] were prepared according to reported procedures. Tetrahydrofuran solutions of [Cp*RuCl(PMe^{i}Pr$_2$)][21] and [Cp*RuCl(PEt$_3$)$_2$][22] were generated in situ and used straightforwardly. IR spectra were recorded in Nujol mulls on a Perkin-Elmer Spectrum 1000 spectrophotometer. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 300 MHz equipment using the appropriate deuterated solvent. Chemical shifts are given in ppm from $SiMe_4$ (^{1}H and $^{13}C\{^1H\}$), 85% H_3PO_4 ($^{31}P\{^1H\}$), or $SnBu_4$ ($^{119}Sn\{^1H\}$). Microanalyses were performed by the Serveis Científico-Tècnics, Universitat of Barcelona.

[Cp*RuCl(CO)(PMe^{i}Pr$_2$)] (1). To a solution of {Cp*RuCl$_2$}$_2$ (0.800 g, 2.94 mmol) in tetrahydrofuran (20 mL) were added diisopropylmethylphosphine (0.50 mL, 3.30 mmol) and Zn powder (ca. 1 g). The mixture was stirred for 45 min at room temperature and then filtered through Celite. CO was bubbled through this solution for 2 min. The solvent was removed under vacuum, and the residue extracted with diethyl ether. The solution was concentrated to the point of incipient crystallization, and then it was stored at −30 °C. After 24 h a microcrystalline yellow solid was formed, which was filtered and dried in vacuo. Yield: 0.72 mg, 90%. Anal. Calcd for $C_{18}H_{32}ClOPRu$: C, 49.9; H, 7.46. Found: C, 49.8; H, 7.49. IR (Nujol): ν(CO) 1940(s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.11 (m, 12 H, PCH(C*H*$_3$)$_2$, 1.32 (d, 3 H, $^2J_{HP} = 8.4$ Hz, PC*H*$_3$), 2.11 (m, 1 H, PC*H*(CH$_3$)$_2$), 2.24 (m, 1 H, PC*H*(CH$_3$)$_2$), 1.74 (d, 15 H, $^4J_{HP} = 1.6$ Hz, C$_5$(CH$_3$)$_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 41.82 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 7.8 (d, $^1J_{CP} = 25.9$ Hz, P*C*H$_3$), 10.48 (s, C$_5$(*C*H$_3$)$_5$), 17.7 (d, $^2J_{CP} = 14.7$ Hz, PCH(*C*H$_3$)$_2$), 18.4 (d, $^2J_{CP} = 18.0$ Hz, PCH(*C*H$_3$)$_2$), 27.0 (d, $^1J_{CP} = 26.8$ Hz, P*C*H(CH$_3$)$_2$), 28.2 (d, $^1J_{CP} = 22.9$ Hz, P*C*H(CH$_3$)$_2$), 99.63 (d, $^2J_{CP} = 1.8$ Hz, *C*$_5$(CH$_3$)$_5$), 207.4 (d, $^2J_{CP} = 20.4$ Hz, *C*O).

[Cp*RuCl(CO)(PEt$_3$)] (2). To a solution of {Cp*RuCl$_2$}$_2$ (0.80 g, 2.94 mmol) in tetrahydrofuran (25 mL) were added triethylphosphine (0.9 mL, 6.0 mmol) and Zn powder (ca. 1.0 g). The mixture was stirred for 45 min at room temperature and then filtered through Celite. CO was bubbled through the orange solution, then it was stirred for 30 min. The solvent was removed in vacuo, and the resulting sticky residue was washed with petroleum ether several times in order to remove the released phosphine. A yellow solid was obtained, which was dried in vacuo. Yield: 0.480 g, 60%. Anal. Calcd for $C_{17}H_{30}ClOPRu$: C, 48.8; H, 7.24. Found: C, 48.7; H, 7.27. IR (Nujol): ν(CO) 1931(s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.06 (m, 9 H, PCH$_2$C*H*$_3$), 1.82 (m, 6 H, PC*H*$_2$CH$_3$), 1.78 (d, 15 H, $^4J_{HP} = 1.5$ Hz, C$_5$(C*H*$_3$)$_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 36 (s). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 7.95 (s, PCH$_2$*C*H$_3$), 10.12 (s, C$_5$(*C*H$_3$)$_5$), 18.70 (m, P*C*H$_2$CH$_3$), 95.80 (d, $^2J_{CP} = 1.4$ Hz, *C*$_5$(CH$_3$)$_5$), 207.86 (d, $^2J_{CP} = 18.5$ Hz, *C*O).

[{Cp*Ru(CO)(PMe^{i}Pr$_2$)}$_2$(μ-Cl)][BAr′4] (3). To a solution of **1** (0.170 g, 0.39 mmol) in fluorobenzene (10 mL) was added solid NaBAr′$_4$ (0.34 g, 0.39 mmol). The reaction mixture was stirred at room temperature for 30 min. A color change from yellow-orange to dark red was observed. Sodium chloride was removed by filtration through Celite. The filtrate was concentrated under reduced pressure to a volume of ca. 1 mL, then layered with petroleum ether and left undisturbed at room temperature. Red crystals were obtained by slow diffusion of petroleum ether into the fluorobenzene. The crystals were separated from the supernatant liquor, washed with petroleum ether, and dried in an argon stream. Yield: 0.46 g, 70%. Anal. Calcd for $C_{68}H_{76}BClF_{24}O_2P_2Ru_2$: C, 48.3; H, 4.53. Found: C, 47.9; H, 4.58. IR (Nujol): ν(CO) 1942(s) cm^{-1}, ν(Ar′) 1609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.12 (m, 30 H, PCH(C*H*$_3$)$_2$ and PC*H*$_3$) 1.59 (s, 30 H, C$_5$(C*H*$_3$)$_5$), 2.07 (m, 4 H, PC*H*(CH$_3$)$_2$). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 38.2 (s), 39.5 (s). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 7.70 (m, P*C*H$_3$), 10.19 (m, C$_5$(*C*H$_3$)$_5$), 18.50 (m, PCH(*C*H$_3$)$_2$), 26.84 (m, P*C*H(CH$_3$)$_2$), 96.12 (s, *C*$_5$(CH$_3$)$_5$), 207.33 (d, $^2J_{CP} = 19.5$ Hz, *C*O).

[{Cp*Ru(CO)(PEt$_3$)}$_2$(μ-Cl)][BAr′$_4$] (4). This compound was obtained in a fashion analogous to that for **3**, starting from **2** (0.130 g, 0.3 mmol) and NaBAr′$_4$ (0.3 g, 0.33 mmol) in fluorobenzene (10 mL). Yield: 0.45 g, 70%. Anal. Calcd for $C_{66}H_{72}BClF_{24}O_2P_2Ru_2$: C, 47.6; H, 4.36. Found: C, 47.5; H, 4.40. IR (Nujol): ν(CO) 1944(s) cm^{-1}, ν(Ar′) 1609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.04 (m, 18 H, PCH$_2$C*H*$_3$), 1.78 (m, 12 H, PC*H*$_2$CH$_3$), 1.68 (d, 15H, $^4J_{HP} = 1.61$ Hz, C$_5$(C*H*$_3$)$_5$). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 33.95 (s), 34.72 (s). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 7.82 (m, PCH$_2$*C*H$_3$), 10.02 (s, C$_5$(*C*H$_3$)$_5$), 17.80 (m, P*C*H$_2$CH$_3$), 95.62 (s, *C*$_5$(CH$_3$)$_5$), 206.90 (d, $^2J_{CP} = 18.2$ Hz).

[Cp*Ru{η^1-OC(CH$_3$)$_2$}(CO)(PMe^{i}Pr$_2$)][BAr′$_4$] (5). To a solution of **1** (0.1 g, 0.23 mmol) in 6 mL of fluorobenzene were added NaBAr′$_4$ (0.2 g, 0.23 mmol) and 6 mL of dry acetone. The mixture reaction was stirred for 15 min. Sodium chloride was removed by filtration through Celite. After concentration of the resulting solution to a volume of ca. 1 mL, petroleum ether was added and the resulting solution was left undisturbed at room temperature. A microcrystalline orange solid was formed, which was separated from the supernatant liquor, washed with petroleum ether, and dried in an argon stream. Yield: 0.16 g, 70%. Anal. Calcd for $C_{53}H_{50}BF_{24}O_2PRu$: C, 48.31;

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[32] Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

H, 3.82. Found: C, 48.1; H, 3.79. IR (Nujol): ν(CO) 1951(s) cm^{-1}, ν($O{=}C(CH_3)_2$) 1660 cm^{-1}, ν(Ar′) 1609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.05 (m, 12 H, $PCH(CH_3)_2$), 1.12 (d, 3 H, $^2J_{HP} = 8.75$ Hz, PCH_3), 2.06 (m, 2 H, $PCH(CH_3)_2$), 1.62 (d, 15 H, $^4J_{HP} = 1.53$ Hz, $C_5(CH_3)_5$), 2.23 (s, 6 H, $OC(CH_3)_2$). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 39.56 (s). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 6.80 (d, $^1J_{CP} = 26.2$ Hz, PCH_3), 10.09 (s, $C_5(CH_3)_5$,), 17.1 (s, $PCH(CH_3)_2$), 17.82 (s, $PCH(CH_3)_2$) 26.5 (d, $^1J_{CP} = 25.3$ Hz, $PCH(CH_3)_2$), 32.2 (s, $(CH_3)_2CO$), 96.3 (s, $C_5(CH_3)_5$), 205.4 (d, CO, $^2J_{CP} = 19.5$ Hz), 213.5 (s, $(CH_3)_2CO$).

[Cp*Ru(η^2-H$_2$C=CH$_2$)(CO)(PMe^{i}Pr$_2$)][BAr′$_4$] (6). Ethylene was bubbled through a solution of **1** (0.1 g, 0.23 mmol) in fluorobenzene (8 mL) for 1 min. Then NaBAr′$_4$ (0.2 g, 0.23 mmol) was added, and ethylene was bubbled through the solution for a further 1 min. The mixture was stirred at room temperature for 30 min. The color turned from yellow-orange to colorless. Sodium chloride was removed by filtration through Celite. The filtrate was concentrated under reduced pressure to a volume of ca. 1 mL, then layered with petroleum ether and left undisturbed at room temperature. White crystals were obtained by slow diffusion of petroleum ether. These were separated from the supernatant liquor and dried in an argon stream. Yield: 0.215 g, 60%. Anal. Calcd for $C_{52}H_{48}PBOF_{24}Ru$: C, 48.5; H, 3.76. Found: C, 48.7; H, 3.70. IR (Nujol): ν(CO) 1995(s) cm^{-1}, ν(C=C) 1611 cm^{-1}, ν(Ar′) 1609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.09 (m, 12 H, $PCH(CH_3)_2$), 1.23 (d, 3 H, $^2J_{HP} = 8.44$ Hz, PCH_3), 2.07 (m, 2 H, $PCH(CH_3)_2$), 1.63 (s, 15 H, $C_5(CH_3)_5$), 2.42 and 2.52 (m, 2 H, C_2H_2). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 42.13 (s). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 8.90 (s, PCH_3), 9.19 (d, $^3J_{CP} = 3.6$ Hz, $C_5(CH_3)_5$), 18.10, 18.57, 18.85, 19.17 (s, $PCH(CH_3)_2$), 28.21 (d, $^1J_{CP} = 27.41$ Hz, $PCH(CH_3)_2$), 28.58 (d, $^1J_{CP} = 27.5$ Hz, $PCH(CH_3)_2$), 47.32 (s, C_2H_2), 101.6 (s, $C_5(CH_3)_5$), 206.8 (d, $^2J_{CP} = 18.5$ Hz, CO).

[Cp*Ru(η^2-H$_2$C=CHPh)(CO)(PMe^{i}Pr$_2$)][BAr′$_4$] (7). An excess of styrene (28 μL, 0.3 mmol) and NaBAr′$_4$ (0.2 g, 0.23 mmol) were added to a solution of **1** (0.1 g, 0.23 mmol) in 5 mL of fluorobenzene. The mixture was stirred for 30 min at room temperature. Sodium chloride was removed by filtration through Celite. The filtrate was concentrated under reduced pressure to a volume of ca. 1 mL, then layered with petroleum ether and left undisturbed at room temperature. A white solid was obtained, which was filtered off, washed, and dried. Yield: 0.2 g, 60%. Anal. Calcd for $C_{58}H_{52}PBOF_{24}Ru$: C, 51.1; H, 3.84. Found: C, 51.5; H, 3.88. IR (Nujol): ν(CO) 2002(s) cm^{-1}, ν(C=C) 1620 cm^{-1}, ν(Ar′) 1609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.11 (m, 12 H, $PCH(CH_3)_2$), 1.26 (d, 3 H, $^2J_{HP} = 8.39$ Hz, PCH_3), 2.20 (m, 2 H, $PCH(CH_3)_2$), 1.76 (s, 15 H, $^4J_{HP} = 1.22$ Hz, $C_5(CH_3)_5$), 2.19 (m, 1 H, $H_2C{=}CHPh$), 3.23 (m, 1 H, $H_2C{=}CHPh$), 4.65 (m, 1 H, $H_2C{=}CHPh$), 7.1−7.4 (m, 5 H, Ph). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 42.48 (s). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 9.35 (s, PCH_3), 9.83 (s, $C_5(CH_3)_5$), 18.15, 18.93, 19.69, 19.82 (s, $PCH(CH_3)_2$), 29.09 (d, $^1J_{CP} = 26.1$ Hz, $PCH(CH_3)_2$), 29.54 (d, $^1J_{CP} = 26.10$ Hz, $PCH(CH_3)_2$), 41.77 (s, $H_2C{=}CHPh$), 74.18 (s, $H_2C{=}CHPh$), 101.5 (s, $C_5(CH_3)_5$), 205.7 (d, $^2J_{CP} = 19.6$ Hz, CO).

[Cp*Ru(η^2-H$_2$C=CHCOOCH$_3$)(CO)(PMe^{i}Pr$_2$)][BAr′$_4$] (8). This complex, isolated as a white solid, was prepared as described for **7** starting from **1** (0.1 g, 0.23 mmol), methyl acrylate (28 μL, 0.3 mmol), and NaBAr′$_4$ (0.2 g, 0.23 mmol). Yield: 0.19 g, 63%. Anal. Calcd for $C_{54}H_{50}PBOF_{24}Ru$: C, 49.8; H, 3.84. Found: C, 49.1; H, 3.79. IR (Nujol): ν(CO) 1995(s) cm^{-1}, ν(C=O) 1707 cm^{-1}, ν(Ar′) 1609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.18 (m, 12 H, $PCH(CH_3)_2$), 1.42 (d, 3 H, $^2J_{HP} = 8.92$ Hz, PCH_3), 1.81 (m, 2 H, $PCH(CH_3)_2$), 1.72 (d, 15 H, $^4J_{HP} = 1.34$ Hz, $C_5(CH_3)_5$), 2.32 (m, 1 H, $H_2C{=}CHCOOCH_3$), 3.02 (m, 1 H, $H_2C{=}CHCOOCH_3$), 3.19 (m, 1 H, $H_2C{=}CHCOOCH_3$), 3.72 (s, 3 H, $COOCH_3$). ^{31}P{^{1}H} NMR (161.89 MHz, $CDCl_3$, 298 K): δ 41.20 (s). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 8.59 (d, $^1J_{CP} = 31.4$ Hz, PCH_3), 9.34 (s, $C_5(CH_3)_5$), 18.15, 18.67, 19.32, 19.50 (s, $PCH(CH_3)_2$), 27.42 (d, $^1J_{CP} = 27.6$ Hz, $PCH(CH_3)_2$), 30.25 (d, $^1J_{CP} = 26.3$ Hz, $PCH(CH_3)_2$), 46.33 (s, $CH_2{=}CHCOOMe$), 52.43 (s, $={CHCOOCH_3}$) 102.9 (s, $C_5(CH_3)_5$), 72.02 (s, $COOCH_3$), 204.6 (d, $^2J_{CP} = 19.3$ Hz, CO).

[Cp*Ru(CO)(PMe^{i}Pr$_2$)(SnCl$_3$)] (9). To a solution of **1** (0.06 g, 0.14 mmol) in 5 mL of dichloromethane was added an excess of $SnCl_2$ (0.04 g, 0.22 mmol). The reaction mixture was stirred for 6 h at room temperature. A color change from yellow-orange to pale yellow was observed. This solution was filtered through Celite, and the filtrate was concentrated under reduced pressure to a volume of ca. 1 mL. Then it was layered with petroleum ether and left undisturbed at room temperature. A microcrystalline pale yellow solid was formed, which was filtered off and dried in vacuo. Yield: 0.100 g, 85%. Anal. Calcd for $C_{18}H_{32}POCl_3SnRu$: C, 32.9; H, 4.91. Found: C, 33.2; H, 4.85. IR (Nujol): ν(CO) 1935(s) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.12 (m, 12 H, $PCH(CH_3)_2$), 1.47 (d, 3 H, $^2J_{HP} = 7.9$ Hz, PCH_3) 2.08 (m, 2 H, $PCH(CH_3)_2$), 1.98 (d, 15 H, $^4J_{HP} =1.51$ Hz). ^{31}P{^{1}H} NMR (161.89 MHz, CD_2Cl_2, 298 K): δ 26.13 (t, $^2J_{P^{119}Sn} = 347$ Hz, $^2J_{P^{117}Sn} = 332.8$ Hz). ^{119}Sn{^{1}H} NMR (149.158 MHz, CD_2Cl_2, 298 K): δ 44.19 (d, $^2J_{PSn} =346.6$ Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ 10.43 (d, $^1J_{CP} = 29.6$ Hz, PCH_3), 11.18 (s, $C_5(CH_3)_5$), 16.69 (d, $^2J_{CP} = 5.8$ Hz, $PCH(CH_3)_2$), 18.91 (d, $^2J_{CP} = 16.7$ Hz, $PCH(CH_3)_2$), 18.95 (d, $^2J_{CP} = 17.6$ Hz, $PCH(CH_3)_2$), 97.98 (s, $C_5(CH_3)_5$), 204.65 (d, $^2J_{CP} = 16.2$ Hz, CO).

[Cp*Ru(CO)(PEt$_3$)(SnCl$_3$)] (10). This compound, isolated as a microcrystalline orange solid, was prepared as described for **9**, starting from [Cp*RuCl(CO)(PEt$_3$)] (**2**) (0.06 g, 0.14 mmol) and $SnCl_2$ (0.04 g, 0.22 mmol) in 5 mL of CH_2Cl_2. Yield: 0.125 g, 85%. Anal. Calcd for $C_{17}H_{30}POCl_3SnRu$: C, 31.7; H, 4.70. Found: C, 31.9; H, 4.80. IR (Nujol): ν(CO) 1930(s) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.02 (m, 9 H, PCH_2CH_3), 1.96 (m, 6 H, PCH_2CH_3), 1.91 (d, 15 H, $^4J_{HP} = 1.60$, $C_5(CH_3)_5$). ^{31}P{^{1}H} NMR (161.89 MHz, CD_2Cl_2, 298 K): δ 37.62 (t, $^2J_{P\,^{119}Sn} = 355.40$ Hz, $^2J_{P^{117}Sn} = 340.49$ Hz). ^{119}Sn{^{1}H} NMR (149.158 MHz, CD_2Cl_2, 298 K): δ 36.77 (d, $^2J_{PSn} = 354.36$ Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K): δ 8.28 (d, $^2J_{CP} = 2.9$ Hz, PCH_2CH_3), 10.84 (s, $C_5(CH_3)_5$), 20.92 (m, PCH_2CH_3), 95.80 (d, $^2J_{CP} = 1.4$ Hz, $C_5(CH_3)_5$), 207.86 (d, $^2J_{CP} = 18.5$ Hz, CO).

X-ray Structure Determinations. Crystals of **4** and **6** were obtained by recrystallization from ethyl ether/petroleum ether and fluorobenzene/petroleum ether, respectively. Crystal data and experimental details are given in Table 1. X-ray diffraction data were collected on a Bruker SMART APEX 3-circle diffractometer with CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by omega scan frames with δ(ω) 0.30°. Correction for absorption and crystal decay (insignificant) were applied by a semiempirical method from equivalents using the program SADABS.[33] The structures were solved by direct methods, completed by subsequent difference Fourier synthesis, and refined on F^2 by full matrix least-squares procedures using the program SHELXTL.[34] All non-hydrogen atoms were refined with anisotropic displacement coefficients. CF_3 groups of the $[BAr'_4]^-$ anion showed orientation disorder in both cases. All CF_3 groups for compound **4** and six of eight for compound **6** were refined as pairs of CF_3 with complementary orientations. The remaining two orientation disordered CF_3 groups were approximated with two split F atoms in each one. For compound **6** the four hydrogen atoms in the ethylene ligand were localized in

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(33) Sheldrick G. M. *SADABS*, version of 2001; University of Goettingen: Germany.

(34) *SHELXTL*, version 6.10, Crystal Structure Analysis Package; Bruker AXS: Madison, WI, 2000.

Table 1. Crystal Data and Details of the Structure Determination for Compounds 4 and 6

	4	**6**
formula	$C_{34}H_{59}ClO_2P_2Ru_2$ 1+, $C_{32}H_{12}BF_{24}$ 1−	$C_{20}H_{36}NOPRu$ 1+, $C_{32}H_{12}BF_{24}$ 1−
fw	1662.57	1286.75
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
unit cell params a, b, c (Å)	$a = 21.267(4)$	$a = 13.5449(10)$
	$b = 18.870(3)$	$b = 13.7047(10)$
	$c = 19.103(3)$	$c = 17.4456(13)$
α, β, γ (deg)	$\alpha = 90$	$\alpha = 103.465(2)$
	$\beta = 102.186(4)$	$\beta = 111.8560(10)$
	$\gamma = 90$	$\gamma = 97.466(2)$
V (Å^3)	7493(2)	2837.6(4)
Z	4	2
δ(calc) (g/cm^3)	1.474	1.507
μ(Mo Kα) (mm^{-1})	0.581	0.420
F(000)	3356	1296
cryst size (mm)	0.13 × 0.32 × 0.34	0.22 × 0.27 × 0.42
T (K)	293	293
λ (Å)	Mo Kα 0.71073	Mo Kα 0.71073
$\theta_{min}-\theta_{max}$ (deg)	1.7, 23.3	1.6, 25.6
dataset (h,k,l limits)	−23:23; −20:20; −20:21	−15:16; −16:16; −21:21
no. of total, unique data, R(int)	49 964, 10 692, 0.055	25 473, 10 484, 0.038
no. of obsd data ($I > 2\sigma_I$)	9350	8636
no. of reflns, no. of params	10 692, 1107	10 484, 943
R, wR_2, GOF	0.0803, 0.1724, 1.09	0.0751, 0.1686, 1.08
w	$1/[\sigma^2(F_o^2) + (0.0638P)^2 + 27.1900P]$ where $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0701P)^2 + 2.7532P]$ where $P = (F_o^2 + 2F_c^2)/3$
max. and av shift/error	0.23, 0.02	0.16, 0.02
min. and max. resd dens (e/Å^3)	−0.92, 1.94	−0.62, 0.80

regular difference Fourier maps. Hydrogen atoms bonded to C(11) were allowed to refine with thermal parameters related to U_{iso} for C(11). All the remaining hydrogen atoms in both compounds were refined using the SHELX riding model. The program ORTEP-3[35] was used for plotting.

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Supporting Information Available: Crystallographic tables and ORTEP diagrams for compounds **4** and **6**. Data are also given as crystallographic information files (CIF). This material is avalaible free of charge via the Internet at http://pubs.acs.org.

OM034186X

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(35) Faruggia, L. J. ORTEP-3 for Windows version 1.076. *J. Appl. Crystallogr.* **1997**, *30*, 565.