Ruthenium Half-Sandwich Complexes with Sterically Demanding Cyclopentadienyl Ligands

Barnali Dutta, Euro Solari, Sébastien Gauthier, Rosario Scopelliti, and Kay Severin*

Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

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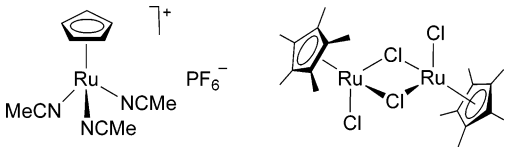
A chloro-bridged Ru^{III} complex of formula $[Cp^{\wedge}RuCl_2]_2$ ($Cp^{\wedge}$ = η^5-1-methoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl) (**1**) was obtained in a single step by reaction of $[RuCl_3(solv)_n]$ with *tert*-butylacetylene in methanol. Complex **1** showed polymorphism and crystallized in two distinct forms: an isomer, **1a**, with no significant metal−metal interactions (Ru···Ru = 3.684(1) or 3.743(1) Å) and an isomer, **1b**, in which the Ru atoms are 2.960(2) Å apart from each other. In solution, a temperature-dependent equilibrium between the two isomers is established. When the reaction of $[RuCl_3(solv)_n]$ with *tert*-butylacetylene was carried out in ethanol, the chloro-bridged dimer **2**, with an ethoxy instead of a methoxy group attached to the cyclopentadienyl ligand, was formed. Complex **1** was found to be a versatile starting material for the synthesis of mononuclear half-sandwich complexes. With phosphine ligands or norbornadiene (nbd), the 16 e^- complexes $[Cp^{\wedge}RuCl(PCy_3)]$ (**3**), $[Cp^{\wedge}RuCl(PPh_3)]$ (**4**), and $[Cp^{\wedge}RuCl(PnBu_3)]$ (**5**), the 17 e^- complex $[Cp^{\wedge}RuCl_2(PPh_3)]$ (**7**), and the 18 e^- complexes $[Cp^{\wedge}RuX(PPh_2RPPh_2)]$ (X = H, Cl; R = CH_2, C_2H_4; **8**−**11**) and $[Cp^{\wedge}RuCl(nbd)]$ (**12**) were obtained. Crystallographic analyses show that the Ru−P bond lengths in these complexes are longer than in corresponding pentamethylcyclopentadienyl complexes.

Introduction

Ruthenium half-sandwich complexes with cyclopentadienyl ligands represent a very important class of catalysts.[1] The organic reactions catalyzed by these complexes include allylic[2] and propargylic[3] substitutions, cycloadditions,[4] isomerizations,[5] hydrogenations,[6] alkane borylations,[7] and atom-transfer radical addition[8] and polymerization[9] reactions. For many of these the success of the catalytic process has been attributed to the electron richness of the ruthenium center or the steric hindrance of the cyclopentadienyl ligand.[1] To tune the reactivity, numerous co-ligands have been employed such as phosphines, olefins, halides, nitriles, and thiolates.[1−9] Structural modifications of the cyclopentadienyl ligand, however, are not very common, and many investigations have focused on Cp and Cp* complexes. The dominance of Cp and Cp* ligands can be explained by the fact that easily accessible starting materials are available. The cationic acetonitrile complex $[CpRu(CH_3CN)_3](PF_6)$ and the chloro-bridged dimer $[Cp^*RuCl_2]_2$ turned out to be particularly useful. The latter can be obtained in a one-step procedure from $[RuCl_3(H_2O)_n]$ by refluxing with C_5Me_5H in methanol.[10] For the former, the conventional route involves photolysis of $[CpRu(benzene)]^+$ in CH_3CN.[11] More recently, an efficient synthesis has been developed where the final step does not require photolysis.[12] Both complexes are commercially available as well.



In a recent communication we have reported the synthesis of the Ru^{III} half-sandwich complexes **1** and **2**, which have an overall structure analogous to $[Cp^*RuCl_2]_2$ but possess very distinct 1-alkoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl ligands (alkoxy = MeO or EtO).[13] These complexes are easily accessible in a one-step reaction of $[RuCl_3(solv)_n]$ with *tert*-

* Corresponding author. E-mail: kay.severin@epfl.ch.

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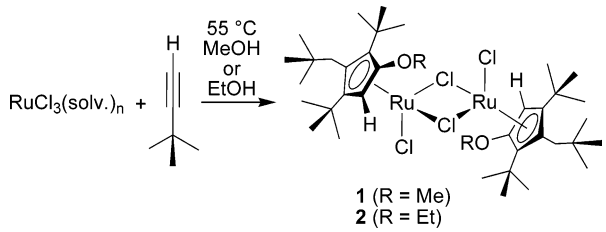
Scheme 1



butylacetylene (Scheme 1). First investigations had shown that the dimeric Ru^{III} complexes **1** and **2** can be transformed into mononuclear Ru^{II} complexes.[13] In the following, we describe detailed investigations about this new class of compounds. It is shown that the structure and the reactivity of **1** and **2** parallel to some extent that of $[Cp^*RuCl_2]_2$ but that the sterically demanding 1-alkoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl ligands favor the formation of electronically unsaturated 16 e^- complexes. The latter characteristic could be of importance for future catalytic applications.

Results and Discussion

Complex **1** was obtained in the form of a brown precipitate when a solution of commercial $[RuCl_3(H_2O)_n]$ in methanol and *tert*-butylacetylene was heated at 55 °C. The yield of this reaction did not exceed 35%, regardless of the absolute or the relative concentrations. Further investigations revealed that the presence of water was detrimental for the yield. We therefore thought to reduce the water content of the starting material $[RuCl_3(H_2O)_n]$. This was achieved by dissolving $[RuCl_3(H_2O)_n]$ in THF and distilling off the solvent. With the resulting $[RuCl_3(solv)_n]$ it was possible to prepare complex **1** in 51% yield (Scheme 1). When the reaction was performed in ethanol instead of methanol, the ethoxy complex **2** was obtained in 40% yield.

We had reported that complex **1** crystallizes as a chloro-bridged dimer.[13] Two crystallographically independent but structurally very similar complexes were observed in the crystal. The Ru···Ru distances of these dimers were 3.684(1) and 3.743(1) Å, indicating no significant metal−metal interaction (isomer **1a**, Figure 1). Interestingly, we were able to obtain a second type of crystal for complex **1** (isomer **1b**). A crystallographic analysis revealed a chloro-bridged dimer, in which the Ru atoms are 2.960(2) Å apart from each other (Figure 1). This value is in agreement with a metal−metal bond.

A related phenomenon has been observed for $[Cp^*RuCl_2]_2$. This complex was initially believed to be an oligomer,[10] but a crystallographic study by Kölle and co-workers showed that it is a dimer with two μ-Cl bridges.[14] Within the same crystal, they observed two distinct complexes with Ru···Ru distances of 2.930(1) and 3.752(1) Å. Further experimental investigations showed that in CD_2Cl_2 solution there is an equilibrium between a paramagnetic species and diamagnetic dimer with antiferromagnetically coupled Ru(III) centers.[14,15] A recent theoretical study concluded that $[Cp^*RuCl_2]_2$ is a rare system that fulfills the criteria of bond-stretch isomerism.[16] It is interesting to note that for the structurally related complexes $[(C_5Me_4Et)RuCl_2]_2$ and $[Cp^*RuBr_2]_2$ only the isomer with short Ru···Ru distances

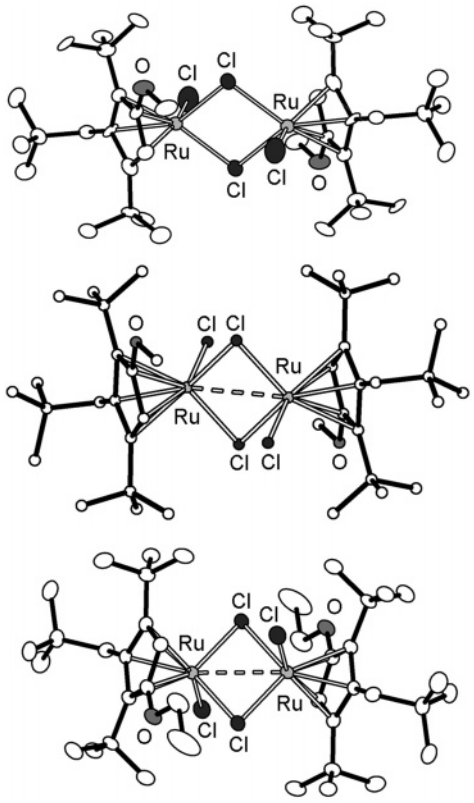
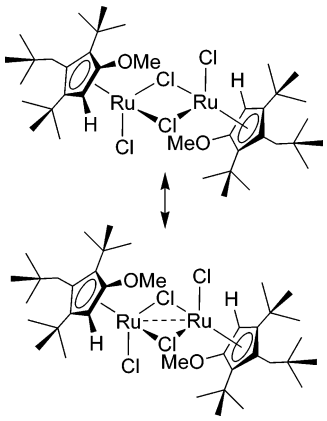


Figure 1. Graphic representation of the molecular structures of complex **1a** (top) (ref 13), **1b** (middle), and **2** (bottom) in the crystal. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are not shown for clarity.

has been observed in the solid state.[14] The complex $[CpRuCl_2]_2$ likewise shows a metal−metal bond with a length of 2.7748(6) Å, although the cyclopentadienyl ligands adopt a *cis* and not a *trans* configuration.[17] The observation of both isomers of complex **1** by crystallography is thus rather exceptional. Since the two different crystals were obtained from the same solvent methanol, it appeared likely that in solution the isomers **1a** and **1b** are in a dynamic equilibrium, similar to what had been observed for $[Cp^*RuCl_2]_2$. This was substantiated by ^1H NMR studies of complex **1** at variable temperatures (CD_2Cl_2), which showed a strong temperature dependence of the chemical shifts and a sharpening of some signals at − 50 °C.



Complex **2** was likewise investigated by X-ray crystallography. Its structure is analogous to that of isomer **1b**, with

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Table 1. Selected Distances (Å) and Angles (deg) for Complexes 1a, 1b, and 2

	1a[a]	1b	2
Ru···Ru	3.6840, 3.7431	2.960(2)	2.9768(5)
Ru−Cl_t	2.358, 2.354	2.408(3)	2.4151(9)
Ru−Cl_b	2.437, 2.446	2.370(3)	2.3721(8)
Ru−Cl_b'	2.443, 2.447	2.381(3)	2.3829(9)
Cl_b−$RuCl_b'$	81.99(9), 80.20(9)	102.92(9)	102.49(3)
Ru−Cl_b−Ru′	98.01(9), 99.80(9)	77.08(9)	77.51(3)

[a] Data from ref 13.

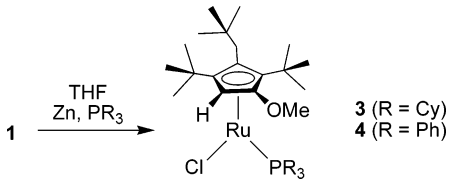
a short Ru···Ru distance of 2.9768(5) Å (Figure 1). As observed for both **1a** and **1b**, the dimer **2** has a crystallographic inversion center. A summary of the key structural data of complexes **1a**, **1b**, and **2** is given in Table 1.

The formation of complexes **1** and **2** requires the coupling of three *tert*-butylacetylenes with methanol or ethanol under elimination of HCl. There are examples of transition metal-mediated [2+2+1] cyclotrimerizations of alkynes,[18,19] but they are very rare compared to the more common [2+2+2] cyclotrimerizations.[1,4] The coupling of three alkynes and an alcohol giving a cyclopentadienyl ligand with an alkoxy substituent directly attached to the ring is—to the best of our knowledge—unprecedented. A plausible mechanism for this reaction could involve an intramolecular reaction of a metallacyclopentadiene with a vinylidene ligand.[18a] The formation of a fulvene π-complex, which was suggested for other [2+2+1] cyclotrimerizations of alkynes, appears unlikely in our case since the nucleophilic attack of the alcohol would occur at the exocyclic carbon atom.[19]

Attempts to substitute *tert*-butylacetylene with other alkynes such as phenylacetylene, cyclohexylacetylene, or trimethylsilylacetylene were not successful. When reacted with [$RuCl_3$(solv)$_n$], a mixture of unidentified products was obtained. This was not entirely unexpected. A complicated multicomponent reaction of this kind is likely to depend strongly on the size and the reactivity of the alkyne. Furthermore, it was known that (cyclopentadienyl)Ru half-sandwich complexes (including [Cp*$RuCl_2$]$_2$)[20] can react further with alkynes to give cycloaddition products or polymers.[1,4] It is conceivable, however, that complexes with a structure analogous to **1** and **2** can be obtained for other alkyne/alcohol combinations, given that a careful optimization of the reaction conditions is carried out.

The structural similarity of complexes **1** and **2** with [Cp*$RuCl_2$]$_2$ suggested that they should be suitable starting materials for the synthesis of mononuclear Ru^{II} complexes. This proved to be indeed the case. In a first series of experiments, we investigated the reaction of complex **1** with various phosphines. When **1** was reacted with PCy_3 in THF in the presence of Zn, deep violet solutions were obtained, from which the highly air-sensitive complex [Cp^RuCl(PCy_3)] (Cp^ = η^5-1-methoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl) (**3**) was isolated (Scheme 2). The ^{1}H NMR spectrum of **3** (CD_2Cl_2) showed three strong singlets between 1.1 and 1.5 ppm, which can be attributed to the *tert*-butyl groups. As a consequence of the planar chirality of **3**, the methylene CH protons of the neopentyl side chain are diastereotopic and appear as two doublets at 2.75 and 3.23 ppm. The $^{31}P\{^1H\}$ NMR displayed a single signal indicating the coordination of only one phosphine ligand. Further characterization by elemental analysis and single-crystal X-ray analysis (see below) confirmed the formation of the 16 e$^-$ complex **3**. The structurally related complex [Cp^RuCl(PPh_3)] (**4**) was obtained when PPh_3 was used instead of PCy_3 (Scheme 2). The reaction can be performed at room temperature, but slightly better yields were obtained at elevated temperatures. Crystallization from concentrated hexane solutions gave violet crystals of complex **4**, which are well soluble in nonpolar solvents and very air sensitive. Structurally related complexes of formula [Cp*RuCl(PR_3)] are known with sterically demanding phosphine ligands such as PCy_3 and P*i*Pr_3.[21] However, the attempted preparation of mononuclear [Cp*RuCl(PPh_3)] failed and resulted in the formation of an insoluble polymer.[22] The successful preparation of complex **4** is thus direct evidence that the sterically demanding Cp^ ligand is able to stabilize electronically unsaturated complexes, which are not accessible with the widely used Cp* ligand. In this context it is interesting to note that for the 18 e$^-$ complex [Cp*RuCl(PPh_3)$_2$], a frequently used catalyst, the dissociation of a phosphine ligand is often regarded as the key step to generate the catalytically active species.[1,23] In situ ^{31}P NMR experiments showed that the saturated complex [Cp^RuCl(PPh_3)$_2$] is not formed, even if an excess of PPh_3 was added to a solution of complex **4** in THF.

Scheme 2



The molecular structure of complex **3** shows the expected two-legged piano stool geometry (Figure 2). Both, the Ru−P bond (2.4188(9) Å) and the Ru−Cl bond (2.3936(9) Å) are slightly longer than what has been observed for the related complex [Cp*RuCl(PCy_3)] (Ru−P = 2.3834(4) Å; Ru−Cl =

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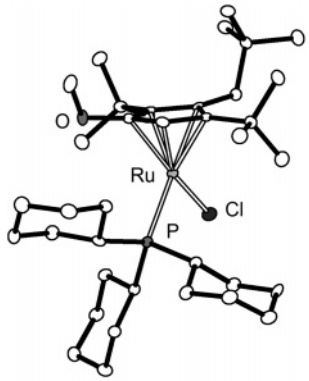


Figure 2. Graphic representation of the molecular structure of complex **3** in the crystal. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru−P 2.4188(9), Ru−Cl 2.3936(9); P−Ru−Cl 91.40(3).

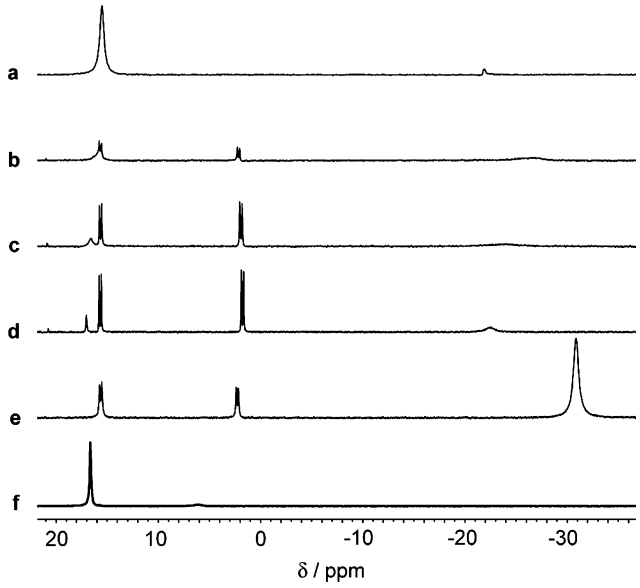
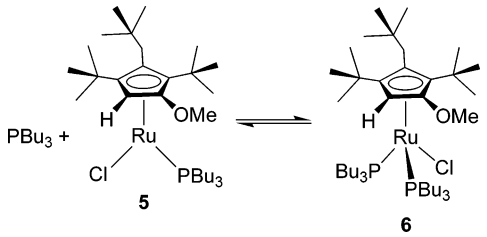


Figure 3. $^{31}P\{^1H\}$ NMR spectra of a THF solution obtained from the reaction of **1** with 4 equiv of P*n*Bu$_3$ recorded at 25 °C (a), 10 °C (b), −10 °C (c), and −30 °C (d). Spectrum "e" was obtained at 25 °C from a reaction with an excess of P*n*Bu$_3$, and spectrum "f" was obtained at −30 °C from a reaction with 2 equiv of P*n*Bu$_3$ with respect to **1**.

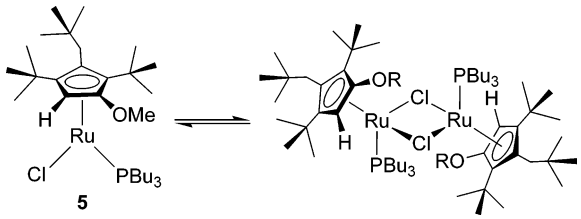
2.3776(5) Å).[21a] The PCy$_3$ ligand is oriented toward the sterically less crowded side of the Cp^ ligand.

When complex **1** was reacted with the less bulky phosphine P*n*Bu$_3$, a more complicated situation was encountered. With the aim to prepare a complex analogous to the known [Cp*RuCl(P*n*Bu$_3$)$_2$], we have reacted a THF solution of complex **1** with 4 equiv of P*n*Bu$_3$ in the presence of Zn. After workup, the $^{31}P\{^1H\}$ NMR spectrum (THF) showed a broad singlet at 15.30 ppm (Figure 3a). Upon cooling, the singlet transformed into a pair of doublets at 15.66 and 1.73 ppm ($^2J_{PP}$ = 35 Hz) along with a small singlet at 17.00 pm and a broad singlet at ca. −22.00 ppm (Figure 3b−d). The two doublets in the low-temperature spectra can be attributed to complex [Cp^RuCl(P*n*Bu$_3$)$_2$] (**6**), having two diastereotopic P atoms due to the planer chirality of the cyclopentadienyl ligand. The singlet at 17.00 ppm is proposed to belong to the 16 e$^-$ complex [Cp^RuCl(P*n*Bu$_3$)] (**5**), which is in a dynamic equilibrium with complex **6** and free P*n*Bu$_3$. This interpretation is supported by a $^{31}P\{^1H\}-^{31}P\{^1H\}$ exchange spectrum, performed at 10 °C with a mixing time (τ_m) of 20 ms, which showed cross-peaks at 1.5 and 14.9 ppm, demonstrating that two P*n*Bu$_3$ ligands of complex **6** undergo exchange reactions. Furthermore, when an excess of P*n*Bu$_3$ was employed in the reaction with **1**, the two doublets of complex **6** were already resolved at room temperature (Figure 3e). This is in agreement with Le Chatelier's principle according to which a higher concentration of the phosphine will shift the equilibrium to the right. When only 2 equiv of P*n*Bu$_3$ were used with respect to the dimer **1**, the $^{31}P\{^1H\}$ NMR spectrum showed the peak of [Cp^RuCl(P*n*Bu$_3$)] (**5**) at 16.85 ppm (Figure 3f). These data demonstrate that the P*n*Bu$_3$ ligand allows accessing both the electronically unsaturated monophosphine complex **5** and the saturated bisphosphine complex **6**. For Cp*Ru complexes, an analogous situation was found for the PMe*i*Pr$_2$ ligand. It was observed that [Cp*RuCl(PMe*i*Pr$_2$)] *and* [Cp*RuCl(PMe*i*Pr$_2$)$_2$] are accessible depending on the phosphine to [Cp*RuCl]$_4$ ratio.[24] Thereafter, the size of PMe*i*Pr$_2$ can be regarded as the lower limit, which allows the stabilization of [Cp*RuCl(PR$_3$)] species. For the Cp^ ligand it is possible to access a 16 e$^-$ complex with the significantly smaller phosphine P*n*Bu$_3$.



The THF solution of complex **5** showed the typical blue-violet color, which is characteristic for electronically unsaturated [(cyclopentadienyl)RuCl(PR$_3$)] complexes.[21,24] When the THF was removed under vacuum, a red solid was obtained. Redissolving this complex in THF or toluene gave again the blue-violet color. Solutions in hexane, however, were red and showed a $^{31}P\{^1H\}$ NMR spectrum that was clearly different from that in THF (hexane: δ = 10.30 ppm; THF: δ = 15.30 ppm). These observations can be explained by assuming that in the solid state and in hexane complex **5** exists in the form of a chloro-bridged dimer (Scheme 3). An equilibrium between the monomer and a chloro-bridged dimer has also been observed for [Cp*RuCl(PMe*i*Pr$_2$)].[24]

Scheme 3



Recently, we had reported that the Ru^{III} complex [Cp*RuCl$_2$(PPh$_3$)] can be used as a catalyst precursor for highly efficient atom-transfer radical addition reactions.[25] We were therefore interested to see whether we could prepare the analogous Cp^ complex. Paramagnetic [Cp*RuCl$_2$(PR$_3$)] complexes are generally obtained by reaction of [Cp*RuCl$_2$]$_2$ with 2 equiv of PR$_3$ at ambient temperature.[21d,26] However, a similar reaction of

(24) Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2000**, *609*, 161−168.

(25) (a) Thommes, K.; Içli, B.; Scopelliti, R.; Severin, K. *Chem.−Eur. J.* **2007**, DOI: 10.1002/chem.200700442. (b) Quebatte, L.; Thommes, K.; Severin, K. *J. Am. Chem. Soc.* **2006**, *128*, 7440−7441.

(26) Arliguie, T.; Chaudret, B. *Chem. Commun.* **1986**, *13*, 985−986.

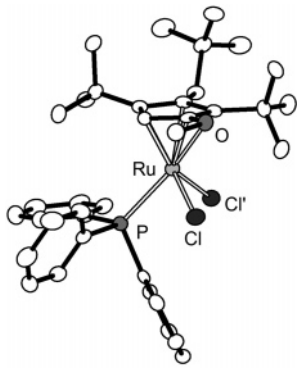
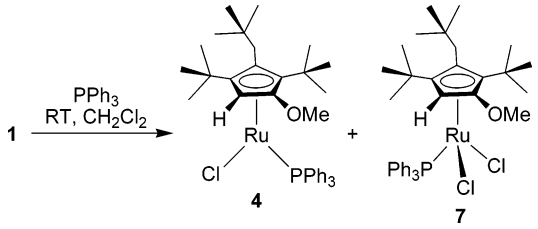


Figure 4. Graphic representation of the molecular structure of complex **7** in the crystal. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru−P 2.3819(12), Ru−Cl 2.3888(10), Ru−Cl′ 2.3722(11); P−Ru−Cl 82.22(4), P−Ru−Cl′ 87.15(4), Cl−Ru−Cl1 98.69(4).

Scheme 4



complex **1** with PPh_3 in CH_2Cl_2 resulted in the formation of a mixture of [Cp^RuCl(PPh_3)] (**4**) and [Cp^RuCl$_2$(PPh_3)] (**7**) (Scheme 4). The complexes could be separated by extraction of the diamagnetic Ru^{II} complex **4** with hexane. Complex **7** was then obtained in 64% yield.

A crystallographic analysis of complex **7** confirmed the formation of a mononuclear complex with one PPh_3 and two chloro ligands opposite the Cp^ ligand (Figure 4). At 2.3819(12) Å, the Ru−P bond length of **7** is longer than what has been found for [Cp*RuCl$_2$(PPh_3)] (Ru−P = 2.3506(2) Å).[25a] Most likely as a result of the increased steric demand of the Cp^ ligand, the Cl−Ru−Cl′ and Cl−Ru−P angles found for **7** (98.69(4)°, 82.22(4)°, and 87.15(4)°) are smaller than those of [Cp*RuCl$_2$(PPh_3)] (101.335(4)°, 86.509(4)°, and 91.156(4)°).

Next we have investigated the reaction of **1** with the chelating phosphine ligands bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)ethane (dppe). In view of the observation that the triphenylphosphine complex [Cp^RuCl(PPh_3)] (**4**) did not show any tendency to add another PPh_3 ligand, it was interesting to see whether electronically saturated chelate complexes or 16 e^- complexes with one noncoordinated phosphine group would form. An additional incentive to study the reactions with dppm and dppe was the fact that the Cp*Ru complexes with these ligands have found numerous applications in organometallic synthesis[27] and catalysis.[28]

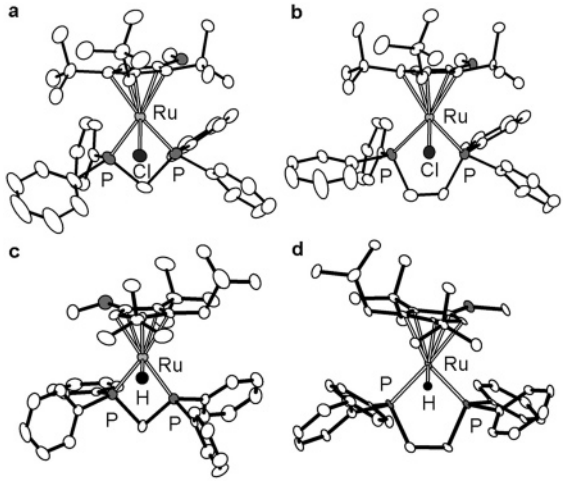
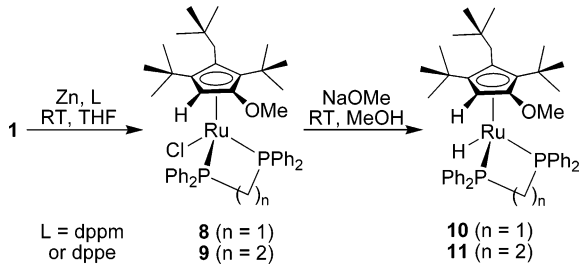


Figure 5. Graphic representation of the molecular structures of complexes **8** (a), **9** (b), **10** (c), and **11** (d) in the crystal. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are not shown for clarity.

Scheme 5



When complex **1** was reacted with dppm or dppe in THF at room temperature in the presence of Zn, the 18 e^- complexes **8** and **9** were obtained (Scheme 5). The coordination of two P atoms to one metal center was clearly evidenced by the $^{31}P\{^1H\}$ NMR spectra, which showed a pair of doublets for the two diastereotopic P atoms. Apparently, the energetic advantage of the five- or four-membered chelate is sufficient to overcome the steric protection provided by the bulky Cp^ ligand. Following a synthetic procedure developed for Cp*Ru complexes,[27j] the chloro compounds **8** and **9** were converted into the hydride complexes **10** and **11** by reaction with NaOMe in MeOH (Scheme 4). The hydride ligands give rise to distinct $\{^1H\}$ NMR signals at −7.0 and −14.0 ppm, respectively.

In addition to NMR studies, the complexes **8**−**11** were characterized by single-crystal X-ray analysis (Figure 5). Tables 2 and 3 give some key structural data along with the values of the related Cp*Ru complexes [Cp*RuCl(dppm)],[27e] [Cp*RuCl(dppe)],[27e] and [Cp*RuH(dppe)].[28a] The comparison shows that the Ru−P bond lengths found for the Cp^ complexes are consistently longer than those of the Cp* complexes. Yet again, this can be explained by the increased steric demand of the Cp^ ligand.

Reaction of **1** with norbornadiene (nbd) in ethanol at 55 °C gave complex [Cp^RuCl(nbd)] (**12**) in 60% yield (Scheme 5). Complex **12** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography (Figure 6). The accessibility of **12** is of interest in view of the fact that the Cp* complexes [Cp*RuCl(nbd)] and [Cp*RuCl(cod)] (cod = 1,5-cyclooctadiene) have been used extensively as catalysts for various organic

(27) (a) Belkova, N. V.; Dub, P. A.; Baya, M.; Houghton, J. *Inorg. Chim. Acta* **2007**, *360*, 149−162. (b) Singh, K. S.; Thoene, C.; Kollipara, M. R. *J. Organomet. Chem.* **2005**, *690*, 4222−4231. (c) Morandini, F; Munari, I.; Panese, M.; Ravazzolo, A.; Consiglio, G. *Inorg. Chim. Acta.* **2005**, *358*, 2697−2700. (d) Aneetha, H.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P.; Mereiter, K. *Organometallics* **2003**, *22*, 1779−1782. (e) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184−3198. (f) Law, J. K.; Mellows, H.; Heinekey, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 1024−1030. (g) Sato, M.; Kawata, Y.; Shintate, H.; Habata, Y.; Akabori, S.; Unoura, K. *Organometallics* **1997**, *16*, 1693−1701. (h) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161−171. (i) Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *Chem. Commun.* **1993**, 892−894. (j) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.

(28) (a) Guan, H.; Limura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805−7814. (b) Guan, H.; Saddoughi, S. A.; Shaw, A. P.; Norton, J. R. *Organometallics* **2005**, *24*, 6358−6364. (c) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778−1779.

Table 2. Selected Distances (Å) and Angles (deg) for the Chloro Complexes 8 and 9, in Comparison with [Cp*RuCl(dppm)] and [Cp*RuCl(dppe)]

	8	[Cp*RuCl(dppm)][a]	**9**	[Cp*RuCl(dppe)][a]
Ru−Cl	2.4567(15)	2.434(2)	2.452(2)	2.4532(5)
Ru−P	2.3289(16)	2.282(2)	2.353(3)	2.2882(5)
Ru−P′	2.3459(16)	2.294(2)	2.360(3)	2.2812(5)
P−Ru−P′	71.32(6)	71.53(6)	82.22(9)	82.15(2)

[a] Data from ref 27e.

Table 3. Selected Distances (Å) and Angles (deg) for the Hydrido Complexes 10 and 11 in Comparison with [Cp*RuH(dppe)]

	10	**11**	[Cp*RuH(dppe)][a]
Ru−H	1.57(3)	1.574(19)	1.59(2)
Ru−P	2.2531(11)	2.2433(14)	2.2363(6)
Ru−P′	2.2652(11)	2.2601(13)	2.2291(6)
P−Ru−P′	72.18(4)	84.19(5)	83.73

[a] Data from ref 28a.

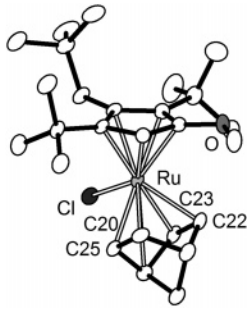
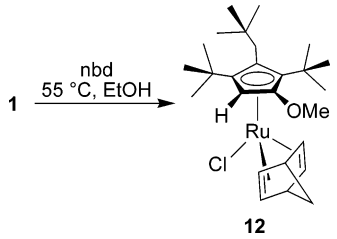


Figure 6. Graphic representation of the molecular structure of complex **12** in the crystal. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru−Cl 2.4738(10), Ru−C20 2.265(3), Ru−C22 2.259(4), Ru−C23 2.226(3), Ru−C25 2.234(4); Cl−Ru−C25 78.28(9), Cl−Ru−C23 77.46(9).

Scheme 6



transformations.[1,29] However, we did not succeed in preparing the analogous cyclooctadiene complex [Cp^RuCl(cod)]. The difficulty in synthesizing this complex could be related to the fact that the larger cod ligand is blocked by the bulky Cp^ ligand. A comparison of the structural data of complex **12** with that of [Cp*RuCl(nbd)][30] shows that the Ru−Cl bond and the average distance of the Ru to the olefinic carbons atoms are longer for complex **12** (**12**: Ru−Cl = 2.4738(10) Å, Ru−C_{nbd} = 2.246 Å; [Cp*RuCl(nbd)]: Ru−Cl = 2.443(2) Å, Ru−C_{nbd} = 2.18 Å). This reinforces the assumption that the cod could not be coordinated due to steric hindrance from the Cp^.

(29) For recent examples see: (a) Yamamoto, Y.; Kinpara, K.; Ogawa, R.; Nishiyama, H.; Itoh, K. *Chem.−Eur. J.* **2006**, *12*, 5618−5631. (b) Villeneuve, K.; Tam, W. *Organometallics* **2006**, *25*, 843−848. (c) Villeneuve, K.; Tam, W. *Eur. J. Org. Chem.* **2006**, 5449−5453. (d) Jordan, R. W.; Villeneuve, K.; Tam, W. *J. Org. Chem.* **2006**, *71*, 5830−5833. (e) Liu, P.; Jordan, R. W.; Kibbee, S. P.; Goddard, J. D.; Tam, W. *J. Org. Chem.* **2006**, *71*, 3793−3803.

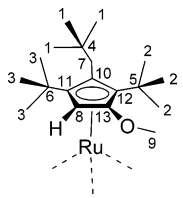
(30) Lubián, R. T.; Paz-Sandoval, M. A. *J. Organomet. Chem.* **1997**, *532*, 17−29.

Conclusion

The chloro-bridged Ru^{III} complexes **1** and **2** with η^5-1-methoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl (Cp^) and η^5-1-ethoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl ligands can be easily obtained in a one-pot reaction from $[RuCl_3(solv)_n]$ and *tert*-butylacetylene in methanol or ethanol, respectively. The methoxy complex $[Cp^{\wedge}RuCl_2]_2$ (**1**) shows an unusual type of polymorphism: in one crystalline form, the two Ru atoms are bonded, whereas in the other form, they are not. The facile accessibility of **1** and **2** makes them highly interesting starting materials for the synthesis of novel Ru half-sandwich complexes. Reactions of **1** with phosphine ligands and with nbd demonstrate that mononuclear complexes are rapidly obtained. For potential applications in the field of catalysis it is of special interest that the Cp^ ligand is sterically more demanding than the classical Cp* ligand. Consequently, it is easier to stabilize electronically unsaturated 16 e^- complexes.

Experimental Section

General Procedures. All experiments were performed inside a glovebox under an atmosphere of dinitrogen containing less than 1 ppm of oxygen and water. Thoroughly dried and deoxygenated solvents were used. PPh_3, P*n*Bu_3, nbd, cod, and NaOMe were purchased from Fluka. Metallic Zn and dppm were commercial products from Aldrich. *tert*-Butylacetylene was purchased from Alfa Aesar and dppe from Acros Organics. PCy_3 was obtained from Strem Chemicals and $RuCl_3(H_2O)_n$ from Precious Metals Online. All chemicals were used as received, unless otherwise stated. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker spectrometer at 400 MHz. The deuterated solvents CD_2Cl_2, $C_6D_5CD_3$, and C_6D_6 (from Aldrich) for NMR experiments were degassed by three freeze−pump−thaw cycles and then purified by vacuum transfer at room temperature. The following numbering scheme was used for the assignment of the ^{13}C NMR data:



$[Cp^{\wedge}RuCl_2]_2$ (1). $[RuCl_3(H_2O)_n]$ (500 mg, 1.90 mmol) was dissolved in 25 mL of THF with heating, and then the solvent was distilled off at 72 °C, normal pressure, using a Rotavapor. Complete removal of the solvent at this temperature led to a green, insoluble material. Hence, the last portion (5 mL) of the solvent was removed under high vacuum. The procedure was repeated, and then the resulting solid (reddish-brown in color) was dissolved in 10 mL of dry MeOH under nitrogen followed by the addition of *tert*-butylacetylene (1.0 mL, 8.0 mmol). The closed flask was heated at 55 °C for 24 h and then kept at −20 °C for 24 h to ensure complete precipitation. The solid brown precipitate was isolated, washed with MeOH (3.0 mL) followed by hexane (3.0 mL), and dried under vacuum. Yield: 434 mg (51%). Anal. Calcd for $C_{38}H_{66}Cl_4O_2Ru_2$: C, 50.78; H, 7.40. Found: C, 50.47; H, 7.36. Single crystals were

Table 4. Crystallographic Data for Complexes 1b, 2, and 3

	1b	2	3·THF
empirical formula	$C_{38}H_{66}Cl_4O_2Ru_2$	$C_{40}H_{70}Cl_4O_2Ru_2$	$C_{41}H_{74}ClO_2PRu$
mol weight/g mol^{-1}	898.85	926.90	766.49
cryst size/mm^3	0.30 × 0.18 × 0.16	0.28 × 0.20 × 0.08	0.53 × 0.17 × 0.12
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a/Å	8.1010(12)	27.5514(19)	10.9422(17)
b/Å	9.105(3)	8.0923(6)	22.462(4)
c/Å	15.473(4)	20.1765(14)	16.763(2)
α/deg	102.44(3)	90	90
β/deg	101.329(18)	95.420(6)	102.942(12)
γ/deg	100.876(19)	90	90
volume/Å^3	1060.5(5)	4478.4 (5)	4015.5(11)
Z	1	4	4
density/g cm^{-3}	1.407	1.375	1.268
temperature/K	140(2)	140(2)	100(2)
absorp coeff/mm^{-1}	0.993	0.943	0.529
θ range/deg	3.04 to 25.02	3.27 to 25.02	3.32 to 25.03
index ranges	−9 → 9, −10 → 10, −18 → 18	−32 → 32, −9 → 9, −21 → 22	−13 → 13, −26 → 26, −19 → 19
no. of reflns collected	6898	12 085	43 157
no. of indep reflns	3508 (R_{int} = 0.0774)	3823 (R_{int} = 0.0384)	7043 (R_{int} = 0.0815)
absorp corr	semiempirical	semiempirical	semiempirical
max. & min. transmn	1.0078 and 0.7995	0.9664 and 0.7047	1.0000 and 0.7203
no. of data/restraints/params	3508/0/210	3823/0/217	7043/0/415
goodness-of-fit on F^2	1.081	1.072	1.138
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0923, wR_2 = 0.2385	R_1 = 0.0366, wR_2 = 0.0840	R_1 = 0.0443, wR_2 = 0.0635
R indices (all data)	R_1 = 0.1043, wR_2 = 0.2537	R_1 = 0.0448, wR_2 = 0.0882	R_1 = 0.0744, wR_2 = 0.0719
larg diff peak and hole/e Å^{-3}	4.916 and −1.643	0.921 and −0.935	0.478 and −0.434

obtained from cold methanol.**[(η^5-1-Ethoxy-2,4-*tert*-butyl-3-neopentylcyclopentadienyl)RuCl$_2$]$_2$ (2).** The synthesis was performed analogously to that of complex **3** using ethanol (20 mL) instead of methanol. Yield: 365 mg (40%). Anal. Calcd for $C_{40}H_{70}Cl_4O_2Ru_2$: C, 51.83; H, 7.61. Found: C, 51.30; H, 7.31.

[Cp^RuCl(PCy$_3$)] (3). PCy_3 (62.3 mg, 222 μmol) and excess Zn dust were added to a solution of complex **1** (100 mg, 111 μmol) in THF (5 mL) and stirred at ambient temperature for 12 h. The color of the solution changed from brown to violet. The solution was filtered followed by complete removal of the solvent under high vacuum. Hexane was added and removed under vacuum to ensure complete removal of the THF. The product was then extracted with hexane (5 mL), while the $ZnCl_2$ formed during reaction remained as a white solid. The product was obtained by removing the hexane under vacuum. Yield: 153 mg (99%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ (ppm) 4.15 (s, 1 H, Cp-H), 3.55 (s, 3 H, OCH_3), 3.23, (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 2.75 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 1.47 (s, 9 H, *t*-Bu), 1.34 (s, 9 H, *t*-Bu), 1.15 (s, 9 H, *t*-Bu), 1.16−2.20 (m, 30 H, PCy_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ (ppm) 35.39 (s, 1 P, PCy_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ (ppm) 121.25 (C13), 83.72, 81.92, 81.10 (C10, C11, C12), 61.10 (C9), 54.14 (C8), 39.31 (C7), 34.60, 34.52, 33.43 (C4, C5, C6), 35.14, 34.27, 33.92 (C1, C2, C3), 29.0−38.0 (PCy_3). Anal. Calcd for $C_{37}H_{66}ClOPRu$: C, 64.00; H, 9.58. Found: C, 63.97; H, 9.44. Single crystals were obtained by slow evaporation from a solution of complex **3** in CH_2Cl_2/hexane.

[Cp^RuCl(PPh$_3$)] (4). Excess metallic Zn was added to a solution of complex **1** (100 mg, 111 μmol) in THF (5 mL) and stirred for 5 min at ambient temperature followed by the addition of PPh_3 (58.3 mg, 222 μmol). The reaction mixture was then stirred at 55 °C until the color of the solution became violet and no excess PPh_3 was detected in the ^{31}P NMR (after nearly 45 min). The Zn was filtered off, and the solvent was removed under vacuum. Hexane (2 mL) was added, and the mixture was stirred for 5 min and evaporated to ensure complete removal of the THF. The product was then extracted with several portions of hexane, while the $ZnCl_2$ formed during reaction remained as a white solid. The product was obtained by removing the hexane under vacuum. Yield: 72 mg (48%). The NMR spectra of the complex were recorded at −20 °C because broad peaks were observed at RT (25 °C), possibly due to hindered rotation of the π-ligand. ^{1}H NMR (CD_2Cl_2, −20 °C): δ (ppm) 7.32−7.52 (m, 15 H, PPh_3), 3.59 (s, 1 H, Cp-H), 3.22 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 2.75 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 2.63 (s, 3 H, OCH_3), 1.46 (s, 9 H, *t*-Bu), 1.22 (s, 9 H, *t*-Bu), 1.10 (s, 9 H, *t*-Bu). ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ (ppm) 35.08 (s, 1 P, PPh_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ (ppm) 129−136 (Ph), 120.04 (C13), 88.11, 83.43, 80.24 (C10, C11, C12), 57.73 (C9), 56.88 (C8), 37.02 (C7), 34.88, 32.97, 32.19 (C4, C5, C6), 33.30, 32.39, 31.98 (C1, C2, C3). Anal. Calcd for $C_{37}H_{48}ClOPRu$: C, 65.71; H, 7.15. Found: C, 65.88; H, 7.05. Single crystals were obtained from a solution of complex **4** in hexane.

[Cp^RuCl(P*n*Bu$_3$)] (5). P*n*Bu_3 (55 μL, 222 μmol) and excess Zn dust were added to a solution of complex **1** (100 mg, 111 μmol) in THF (10 mL), and the mixture was stirred at 65 °C for 12 h. The color of the solution changed from brown to blue-violet. The solution was filtered followed by complete removal of the solvent under high vacuum. Hexane was added and removed under vacuum to ensure complete removal of the THF. The product was then extracted with toluene (5 mL), while the $ZnCl_2$ formed during reaction remained as a white solid. The product was obtained by removing the toluene under high vacuum. Yield: 64 mg (94%). ^{1}H NMR ($C_6D_5CD_3$, 25 °C): δ (ppm) 4.21 (s, 1 H, Cp-H), 4.19 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 3.53 (s, 3 H, OCH_3), 3.06 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 2.06 (m, 6 H, P$CH_2$$CH_2CH_2CH_3$), 1.89 (s, 9 H, *t*-Bu), 1.65 (m, 6 H, $PCH_2CH_2CH_2CH_3$), 1.60 (s, 9 H, *t*-Bu), 1.53 (m, 6 H, $PCH_2CH_2CH_2CH_3$), 1.33 (s, 9 H, *t*-Bu), 1.12 (t, 9 H, $PCH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7 Hz). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, 25 °C): δ (ppm) 15.58 (s, 1 P, P*n*Bu_3). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 25 °C): δ (ppm) 82.48, 79.65, 79.53 (C10, C11, C12), 57.83 (C9), 52.73 (C8), 38.37 (C7), 34.85, 33.17, 32.57 (C4, C5, C6), 33.32, 32.66, 32.27 (C1, C2, C3), 27.80, 26.10, 25.98, 14.83 (P*n*Bu_3). Anal. Calcd for $C_{37}H_{48}ClOPRu$: C, 60.41; H, 9.81. Found: C, 60.09; H, 10.20.

[Cp^RuCl$_2$(PPh$_3$)] (7). PPh_3 (29.2 mg, 111 μmol) was added to a solution of complex **1** (100 mg, 111 μmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at ambient temperature for 24 h. The color of the solution turned purple-red. The solvent CH_2Cl_2 was completely removed under vacuum, and the solid was thoroughly washed with hexane until the washings were no longer violet. Complex **7** was obtained as a red solid and dried under high vacuum. Yield: 100 mg (64%). Anal. Calcd for $C_{37}H_{48}Cl_2OPRu$:

Table 5. Crystallographic Data for Complexes 7, 8, and 9

	7	**8**	**9**·0.5 THF
empirical formula	$C_{37}H_{48}Cl_2OPRu$	$C_{44}H_{55}ClOP_2Ru$	$C_{47}H_{61}ClO_{1.5}P_2Ru$
mol weight/g mol^{-1}	711.69	798.34	848.42
cryst size/mm^3	0.23 × 0.15 × 0.10	0.35 × 0.19 × 0.17	0.30 × 0.22 × 0.16
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	10.254(3)	25.177(3)	25.021(4)
b/Å	22.984(4)	12.1663(11)	12.680(3)
c/Å	14.983(2)	27.959(4)	27.431(5)
α/deg	90	90	90
β/deg	98.176(17)	107.204(8)	105.612(16)
γ/deg	90	90	90
volume/Å^3	3495.1(12)	8181.3(16)	8382(3)
Z	4	8	8
density/g cm^{-3}	1.353	1.296	1.345
temperature/K	140(2)	100(2)	100(2)
absorp coeff./mm^{-1}	0.675	0.558	0.550
θ range/deg	2.88 to 25.03	3.32 to 25.00	3.30 to 25.01
index ranges	−12 → 12, −27 → 27, −17 → 17	−29 → 29, −14 → 14, −33 → 33	−29 → 29, −11 → 15, −32 → 32
no. of reflns collected	22 058	86 845	53 204
no. of indep reflns	5988 (R_{int} = 0.0807)	14 323 (R_{int} = 0.1191)	14 406 (R_{int} = 0.1381)
absorp corrr	semiempirical	semiempirical	semiempirical
max. & min. transmn	0.7807 and 0.7673	1.0000 and 0.7089	1.0000 and 0.9297
no. of data/restraints/params	5988/0/379	14 323/0/883	14 406/35/946
goodness-of-fit on F^2	0.859	1.134	1.071
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0367, wR_2 = 0.0495	R_1 = 0.0609, wR_2 = 0.1021	R_1 = 0.0838, wR_2 = 0.1553
R indices (all data)	R_1 = 0.0804, wR_2 = 0.0606	R_1 = 0.1249, wR_2 = 0.1283	R_1 = 0.1780, wR_2 = 0.2001
larg diff peak and hole/e Å^{-3}	0.637 and −0.602	1.058 and −0.928	1.333 and −0.862

C, 62.44; H, 6.80. Found: C, 62.50; H, 6.82. Crystals of the complex **7** were obtained from a solution of CH_2Cl_2.

[Cp^RuCl(dppm)] (8). dppm (85.5 mg, 222 μmol) and excess metallic zinc were added to a solution of complex **1** (100 mg, 111 μmol) in THF (5 mL), and the mixture was stirred at ambient temperature for 24 h. The color of the solution changed from brown to bright orange. The solution was then filtered followed by the removal of THF under reduced pressure. Methanol (4 mL) was added to dissolve the $ZnCl_2$ formed during reduction. An orange powder was collected by filtration, which was washed thoroughly with methanol. Yield: 145 mg (82%). ^{1}H NMR (C_6D_6, 25 °C): δ (ppm) 6.85−8.30 (m, 20 H, 4Ph), 4.71 (ddd, 1 H, P-CH_2-P, $^2J_{HH}$ = 22, $^2J_{PH}$ = 11, $^2J_{PH}$ = 11 Hz), 4.58 (s, 1 H, Cp-H), 4.33 (ddd, 1 H, P-CH_2-P, $^2J_{HH}$ = 19, $^2J_{PH}$ = 9, $^2J_{PH}$ = 9 Hz), 3.36 (d, 1 H, CH_2, $^1J_{HH}$ = 17 Hz), 2.96 (d, 1 H, CH_2, $^1J_{HH}$ = 17 Hz), 2.76 (s, 3 H, OCH_3), 1.93 (s, 9 H, *t*-Bu), 1.43 (s, 9 H, *t*-Bu), 1.39 (s, 9 H, *t*-Bu). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ (ppm) 5.20 (d, 1 P, dppm, $^2J_{PP}$ = 41), −1.50 (d, 1 P, dppm, $^2J_{PP}$ = 41). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ (ppm) 130.0−142.0 (4 Ph), 132.53 (C13), 106.32, 98.37, 92.17 (C10, C11, C12), 58.32 (C9), 56.11 (C8), 41.19 (C7), 36.73, 36.16, 35.67 (C4, C5, C6), 36.35, 35.95 (C1, C2, C3), 33.72 (dppm). Anal. Calcd for $C_{44}H_{55}ClOP_2Ru$: C, 66.19; H, 6.94. Found: C, 66.36; H, 7.07. Orange crystals of complex **8** were obtained by slow evaporation of a hexane solution.

[Cp^RuCl(dppe)] (9). dppe (88.7 mg, 222 μmol) and excess metallic zinc were added to a solution of complex **1** (100 mg, 111 μmol) in THF (5 mL), and the mixture was stirred at ambient temperature for 24 h. The color of the solution changed from brown to orange-yellow. The solution was then filtered followed by removal of THF under reduced pressure. Methanol (4 mL) was added to dissolve the $ZnCl_2$ formed during reduction. The solution was filtered to obtain an orange-yellow powder, which was washed with methanol. Yield: 144 mg (80%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ (ppm) 7.2−8.0 (m, 20 H, 4 Ph), 4.43 (s, 1 H, Cp-H), 3.18 (s, 3 H, OCH_3), 2.85 (m, 2 H, CH_2), 2.27 (m, 2 H, PCH_2CH_2P), 2.71 (m, 2 H, PCH_2CH_2P), 1.26 (s, 9 H, *t*-Bu), 1.19 (s, 9 H, *t*-Bu), 1.03 (s, 9 H, *t*-Bu). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ (ppm) 63.79 (d, 1 P, dppe, $^2J_{PP}$ = 8 Hz), 63.25 (d, 1 P, dppe, $^2J_{PP}$ = 8 Hz). ^{13}C{^{1}H} (CD_2Cl_2, 25 °C): δ (ppm) 128−143 (4 Ph), 132.88 (C13), 106.23, 94.00, 93.35 (C10, C11, C12), 58.00 (C9), 56.13 (C8), 39.76 (C7), 34.88, 34.57, 32.85 (C4, C5, C6), 33.98, 33.01, 32.62 (C1, C2, C3), 30.47, 30.42 (dppe). [NMR data obtained from ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{1}H(F2)−^{13}C(F1) HSQC experiments]. Anal. Calcd for $C_{45}H_{57}ClOP_2Ru$: C, 66.53; H, 7.07. Found: C, 66.45; H, 7.08. Orange-yellow crystals of complex **9** were obtained by slow evaporation of a hexane/THF solution.

[Cp^RuH(dppm)] (10). Complex **8** (75.0 mg, 94 μmol) was taken in 10 mL of methanol, and an excess of NaOMe (20 mg) was added. The resulting mixture was stirred at room temperature for 1 h. The yellow solid formed during the reaction was collected by filtration, washed thoroughly with methanol, and dried under high vacuum. Yield: 65 mg (90%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ (ppm) 7.2−7.8 (m, 20 H, 4 Ph), 4.86 (s, 1 H, Cp-H), 4.72, 3.89 (m, 2 H, dppm), 3.41 (s, 3 H, OCH_3), 3.13 (d, 1H, CH_2, $^2J_{HH}$ = 16 Hz), 2.93 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 1.16 (s, 9 H, *t*-Bu), 1.15 (s, 9 H, *t*-Bu), 1.13 (s, 9 H, *t*-Bu), −11.38 (dd, 1 H, Ru-*H*, $^2J_{PH}$ = 32, $^2J_{PH}$ = 32 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ (ppm) 14.90 (d, 1 P, dppe, $^2J_{PP}$ = 68 Hz), 14.37 (d, 1 P, dppe, $^2J_{PP}$ = 68 Hz). ^{13}C{^{1}H} (CD_2Cl_2, 25 °C): δ (ppm) 128−141 (4 Ph), 136.05 (C13), 104.88, 96.48, 91.83 (C10, C11, C12), 60.64 (C9), 57.68 (C8), 40.94 (C7), 34.17, 33.85, 33.67 (C4, C5, C6), 34.09, 33.81, 33.53 (C1, C2, C3), 28.74 (dppm). Anal. Calcd for $C_{45}H_{58}OP_2Ru$: C, 69.18; H, 7.39. Found: C, 68.69; H, 6.69. Orange-yellow crystals of complex **10** were obtained by slow evaporation of a MeOH solution.

[Cp^RuH(dppe)] (11). Complex **9** (75.0 mg, 92 μmol) was taken in 10 mL of methanol, and excess (20 mg) sodium methoxide was added. The resulting mixture was stirred at room temperature for 1 h. The yellow solid formed during the reaction was collected by filtration, washed thoroughly with methanol, and dried under high vacuum. Yield: 66 mg (89%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ (ppm) 7.2−8.0 (m, 20 H, 4 Ph), 4.63 (s, 1 H, Cp-H), 3.20 (s, 3 H, OCH_3), 2.0−2.4 (m, 6 H, dppe, CH_2), 1.25 (s, 9 H, *t*-Bu), 0.89 (s, 9 H, *t*-Bu), 0.88 (s, 9 H, *t*-Bu), −13.87 (dd, 1 H, Ru-*H*, $^2J_{PH}$ = 35, $^2J_{PH}$ = 35 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ (ppm) 84.19 (d, 1 P, dppe, $^2J_{PP}$ = 11 Hz), 83.45 (d, 1 P, dppe, $^2J_{PP}$ = 11 Hz). ^{13}C{^{1}H} (CD_2Cl_2, 25 °C): δ (ppm) 128−146 (4 Ph), 136.05 (C13), 105.19, 96.66, 93.28 (C10, C11, C12), 62.10 (C9), 57.22 (C8), 39.37 (C7), 33.99, 33.95 (C4, C5, C6), 34.16, 33.62, 33.36 (C1, C2, C3), 36.27, 36.13 (dppe). Anal. Calcd for $C_{45}H_{58}OP_2Ru$: C, 69.47; H, 7.51. Found: C, 69.67; H, 7.34. Orange-yellow crystals of complex **11** were obtained by slow evaporation of a MeOH solution.

Table 6. Crystallographic Data for Complexes 10, 11, and 12

	10	**11**	**12**·hexane
empirical formula	$C_{44}H_{56}OP_2Ru$	$C_{45}H_{58}OP_2Ru$	$C_{32}H_{55}ClORu$
mol weight/g mol^{-1}	763.90	777.92	592.28
cryst size/mm^3	0.48 × 0.30 × 0.25	0.56 × 0.31 × 0.31	0.36 × 0.30 × 0.23
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$
a/Å	10.8194(9)	16.2705(19)	28.378(6)
b/Å	24.2560(18)	12.6160(10)	15.705(3)
c/Å	14.9797(5)	19.209(3)	14.595(3)
α/deg	90	90	90
β/deg	95.803(6)	97.415(10)	113.41 (3)
γ/deg	90	90	90
volume/Å^3	3911.0(5)	3910.0(8)	5970(2)
Z	4	4	8
density/g cm^{-3}	1.297	1.322	1.318
temperature/K	140(2)	100(2)	100(2)
absorp coeff/mm^{-1}	0.515	0.516	0.637
θ range/deg	2.86 to 25.03	3.40 to 25.03	3.39 to 25.03
index ranges	−12 → 12, −28 → 27, −17 → 17	−19 → 19, −15 → 15, −22 → 22	−33 → 33, −18 → 18, −17 → 17
no. of reflns collected	23 164	64 646	58 560
no. of indep reflns	6886 (R_{int} = 0.0785)	6877 (R_{int} = 0.1194)	5268 (R_{int} = 0.0888)
absorp corr	semiempirical	semiempirical	semiempirical
max. & min. transmn	1.0059 and 0.8315	1.0000 and 0.5970	1.0000 and 0.8712
no. of data/restraints/params	6886/0/436	6877/19/445	5268/42/325
goodness-of-fit on F^2	0.779	1.142	1.113
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0413, wR_2 = 0.0550	R_1 = 0.0630, wR_2 = 0.1530	R_1 = 0.0412, wR_2 = 0.0748
R indices (all data)	R_1 = 0.0978, wR_2 = 0.0646	R_1 = 0.0824, wR_2 = 0.1663	R_1 = 0.0607, wR_2 = 0.0819
larg diff peak and hole/e Å^{-3}	0.800 and −0.776	2.325 and −1.947	0.683 and −0.601

[Cp^RuCl(nbd)] (12). Norbornadiene (50 μL, 445 mmol) was added to a solution of complex **1** (100 mg, 111 μmol) in ethanol (5 mL) and stirred at 55 °C. The color of the solution changed from brown to light orange. After 3 h, some faint white precipitate appeared. After 6 h, the solution was filtered to remove the precipitate. The EtOH solution was concentrated under reduced pressure to give the product in the form of an orange, microcrystalline material. The product was washed with ethanol and dried under vacuum. Yield: 67 mg (60%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ (ppm) 5.19 (m, 1 H, CH═CH, nbd), 4.83 (s, 1 H, Cp-H), 4.67 (m, 1 H, CH═CH, nbd), 4.47 (m, 1 H, CH═CH, nbd), 3.72 (s, 3 H, OCH_3), 3.55−3.70 (m, 3 H, CH═CH, nbd, CH bridge, nbd), 2.56 (d, 1 H, CH_2, J = 16), 2.36 (d, 1 H, CH_2, J = 16), 1.36 (m, 2 H, CH_2, nbd), 1.19 (s, 9 H, *t*-Bu), 1.17 (s, 9 H, *t*-Bu), 1.15 (s, 9 H, *t*-Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ (ppm) 117.95, (C13), 87.67, 81.35, 80.76 (C10, C11, C12), 65.59, 62.53 (CH═CH, nbd), 59.23 (C9), 57.86 (bridging C, nbd), 53.09 (C8), 51.15 (CH_2, nbd), 40.59 (C7), 37.35, 36.29, 33.77 (C4, C5, C6), 35.55, 35.08, 33.61 (C1, C2, C3). Anal. Calcd for $C_{26}H_{41}ClORu$: C, 61.70; H, 8.17. Found: C, 61.58; H, 8.19. Single crystals were obtained from a solution of complex **12** in hexane.

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement can be found in the Supporting Information (cif file). Diffraction data were collected using Mo Kα radiation on different equipment and at different temperatures: a four-circle kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD (**2** and **10**) a Bruker APEX II CCD (**3**, **8**, **9**, **11**, and **12**), or a Marresearch mar345 IPDS (**1b** and **7**). Data were reduced by CrysAlis RED 1.7.1[31] (**1b**, **2**, **7**, and **10**) and EvalCCD (**3**, **8**, **9**, **11**, and **12**).[32] Absorption correction was applied to all sets using a semiempirical method.[33] All structures were refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others). Structure refinement and geometrical calculations were carried out on all structures with SHELXTL.[34] Disorder problems have been found for compound **9** and **12**, and these were treated by applying some restraints and constraints.

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Supporting Information Available: X-ray crystallographic file in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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