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Half-Sandwich Ruthenium-Phosphine Complexes with Pentadienyl and Oxo- and Azapentadienyl Ligands

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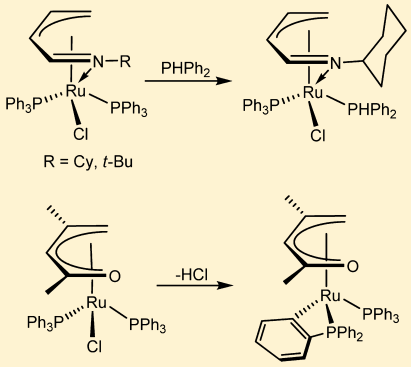
Supporting Information

ABSTRACT: Treatment of $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ with the tin compound $CH_2C(Me)CHC(Me)CH_2SnMe_3$ gives the corresponding acyclic pentadienyl half-sandwich (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuX(PPh_3)_2$ [X = Cl, (**2**); H, (**3**)]. The steric congestion in **2** is most effectively relieved by formation of the cyclometalated complex (η^5-$CH_2C(Me)CHC(Me)CH_2$)$Ru(C_6H_4PPh_2)(PPh_3)$ (**4**). Addition of 1 equiv of $PHPh_2$ to (η^5-$CH_2CHCHCHCH_2$)$RuCl(PPh_3)_2$ (**1**) affords the chiral complex (η^5-$CH_2CHCHCHCH_2$)$RuCl(PPh_3)(PHPh_2)$ (**5**), while compound (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuCl(PPh_3)(PHPh_2)$] (**6**) is directly obtained from the reaction of $RuCl_2(PPh_3)_3$ with $CH_2C(Me)CHC(Me)CH_2Sn(Me)_3$ and $PHPh_2$. Treatment of $RuCl_2(PPh_3)_3$ with the corresponding $Me_3SnCH_2CH{=}CHCH{=}NR$ (R = Cy, *t*-Bu) affords (1-3,5-η-$CH_2CHCHCHNCy$)$RuCl(PPh_3)_2$ (**7**) and [1-3,5-η-$CH_2CHCHCHN(t\text{-}Bu)$]$RuCl(PPh_3)_2$ (**8**). The hydrolysis of **7**, on a silica gel chromatography column, allows the isolation of $RuCl(\eta^5\text{-}CH_2CHCHCHO)(PPh_3)_2$ (**9**). The azapentadienyl complex **7** reacts with 1 equiv of $PHPh_2$ to afford [1-3,5-η-$CH_2CHCHCHN(Cy)$]$RuCl(PPh_3)(PHPh_2)$ (**10**), while the corresponding product [1-3,5-η-$CH_2CHCHCHN(t\text{-}Bu)$]$RuCl(PPh_3)(PHPh_2)$ (**11**) from **8** is only observed through ^1H and ^{31}P NMR spectroscopy as a mixture of isomers. Two equivalents of $PHPh_2$ gives spectroscopic evidence of [η^3-$CH_2CHCHCHN(t\text{-}Bu)$]$RuCl(PHPh_2)_3$. A mixture of products [η^5-$CH_2C(Me)CHC(Me)O$]$RuCl(PPh_3)_2$ (**12**) and [η^5-$CH_2C(Me)CHC(Me)O$]$RuH(PPh_3)_2$ (**13**) is obtained from reaction of $RuCl_2(PPh_3)_3$ with $Li[CH_2C(Me)CHC(Me)O]$. In contrast, the oxopentadienyl compound **13** is cleanly formed from $RuHCl(PPh_3)_3$ and $Li[CH_2C(Me)CHC(Me)O]$. An attempt to separate compounds **12** and **13** by crystallization gives an orthometalated product [η^5-$CH_2C(Me)CHC(Me)O$]$Ru(C_6H_4PPh_2)(PPh_3)$ (**14**), which is the oxopentadienyl analogue to **4**. The bulky [1-3,5-η-$CH_2C(t\text{-}Bu)CHC(t\text{-}Bu)O$]$RuH(PPh_3)_2$ (**15**) analogue to **13** has also been prepared from $RuHCl(PPh_3)_3$ and $Li[CH_2C(t\text{-}Bu)CHC(t\text{-}Bu)O]$. Compounds **3**, **5**, **6**, **7**, and **12**–**15** have been structurally characterized. The preferred heteropentadienyl orientations and the relative positions of the H, Cl, PPh_3, and $PHPh_2$ ligands have been established in the piano-stool structures for all compounds, and it can be definitively surmised that the chemistry involved in the heteropentadienyl half-sandwich compounds studied is dominated by steric effects.



INTRODUCTION

In efforts to gain a better understanding of acyclic versus cyclic pentadienyl ligands, many "half-open ruthenocenes" have been prepared and comparisons between complexes having both types of coordinated ligands have been carried out, including CpRu(2,4-Me_2-η^5-pentadienyl),[1a] Cp*Ru(η^5-pentadienyl),[1b] Cp*Ru(2,4-Me_2-η^5-pentadienyl),[1b] and [Cp*RuH(2,4-Me_2-η^5-pentadienyl)]$[BF_4]$.[1c] The chemistry of pentadienyl ligands has shown interesting and new possibilities of reactivity compared to the chemistry of the well-known cyclopentadienyl ligand, due to the former's unique properties, such as the ability to adopt a variety of bonding modes and to shift easily among them.[2] The incorporation of heteroatoms such as sulfur, oxygen, and nitrogen into the pentadienyl fragment has led to a wider scope in the chemistry of the Cp′Ru(heteropentadienyl) (Cp′ = Cp, Cp*) complexes, and the coordinated heteropentadienyl ligands display a much wider range of ligand substitutions and additions, oxidative additions, and coupling reactions, among others.[3] The interesting reaction chemistry displayed by their simple pentadienyl analogues follows from their differences in electronic structure. It was then of considerable interest to continue the study and development of

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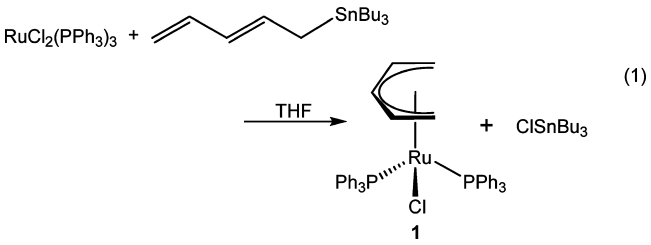
"acyclic half-sandwich" complexes, through which the modulation of the steric and electronic properties of the complementary ligands will be reflected in the chemistry of the acyclic heteropentadienyl complexes. In fact, the acyclic (η^5-$CH_2CHCHCHCH_2$)$RuCl(PPh_3)_2$ (**1**)[4] analogue (eq 1) to the classical



(1)

$Cp'RuCl(PPh_3)_2$ (Cp′ = Cp,[5] Cp*[6]) complexes has been shown to be a convenient starting material for the synthesis of a large family of new pentadienyl−ruthenium−phosphine complexes.[4]

The chemistry of the $Cp'RuCl(PPh_3)_2$ complexes (Cp′ = Cp, Cp*) has been explored extensively, with a key observation being that the steric strain between the two bulkytriphenylphosphine ligands, together with the high electron density localized at the ruthenium atom, results in the ready dissociation of one triphenylphosphine, with a consequent result being that a wide variety of two-electron donor derivatives $Cp'RuCl(PPh_3)L$ may be isolated.[7−9] In particular, reactions of $Cp'RuCl(PPh_3)_2$ with the secondary phosphine $PHPh_2$ have yielded the mono- and disubstituted complexes $Cp'RuCl(PPh_3)(PHPh_2)$[8,9] and $Cp'RuCl(PHPh_2)_2$,[8] respectively. Related half-sandwich η^5-dienyl compounds have been synthesized directly from $RuH_2(PPh_3)_4$ and cyclohexa-1,3-diene or through the reaction of bis(styrene)bis(triphenylphosphine)ruthenium(0) with cyclohexene, to afford (η^5-cyclohexadienyl)$RuH(PPh_3)_2$.[10] Likewise, the reactions of $RuHCl(PPh_3)_3$ with unsaturated olefins such as 1,3- or 1,5-cyclooctadiene,[11a] 1,4-pentadiene, 1,3-cycloheptadiene, cycloheptatriene, and cyclooctatetraene have been reported to afford η^5-dienyl complexes with the $RuCl(PPh_3)_2$ moiety.[11b−d]

Some examples of crystalline structures of ruthenium complexes incorporating oxodiene, oxopentadienyl, or oxocyclohexadienyl ligands, with a three-legged piano stool arrangement, have been published, including (η^4-$CH_2C(Me)CHO$)$Ru(CO)(PPh_3)_2$,[12a] (η^4-CH(Ph)C(Me)CO)$Ru(CO)_2(PPh_3)$,[12b] (η^5-$CH_2C(Ph)CHC(Ph)O$)$RuH(R$-binap),[13] and (η^5-C_5H_5CO)$RuCl(PPh_3)_2$.[14] As far as we know, there are no reported examples of ruthenium half-sandwiches with azapentadienyl ligands.

In this paper, as an extension of our investigations of half-open ruthenocene chemistry, we describe some examples of acyclic half-sandwich (heteropentadienyl)$RuX(PPh_3)_2$ (X = H, Cl) complexes with pentadienyl and oxo- and azapentadienyl ligands, and their reactivities with $PHPh_2$. Special attention is paid to the influences of geometric and steric constraints on the reactivities of these ruthenium compounds.

RESULTS

Pentadienyl Compounds. Reactions of $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ with the tin compounds $CH_2CHCHCHCH_2SnBu_3$ and $CH_2C(Me)CHC(Me)CH_2SnMe_3$ give the corresponding acyclic pentadienyl half-sandwich (η^5-$CH_2CHCHCHCH_2$)$RuCl(PPh_3)_2$ (**1**)[4] (eq 1) and (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuX(PPh_3)_2$ [X = Cl (**2**); H (**3**)] (Scheme 1). Compound **1** has been shown to exhibit dynamic behavior in solution[4] and, as incorporation of methyl substituents in the pentadienyl ligands enhances the barriers to the ligand oscillation processes[2a] as well as the favorability of the η^5-U coordination and the stabilities of the complexes, compound **2** was prepared in order to compare the effects of the differing methyl substitution patterns in compounds **1** and **2**. Additionally, we studied the behavior of the hydrido ligand in compound **3**, which was isolated as a beige solid in moderate yield (31%), and its crystalline structure has been obtained (*vide infra*).

Attempts to synthesize (η^5-$CH_2CHCHCHCH_2$)$RuH(PPh_3)_2$ by the reaction of $RuHCl(PPh_3)_3$ with 1 and 2 equiv of $CH_2CHCHCHCH_2SnBu_3$ resulted in the formation of **1**, without evidence of the hydrido analogue. However, the $RuHCl(PPh_3)_3$ is not as useful a precursor, in the synthesis of **1**, compared to $RuCl_2(PPh_3)_3$.[15]

A 2-fold excess of the tin compound is required in the reaction of $RuHCl(PPh_3)_3$ with $CH_2C(Me)CHC(Me)CH_2SnMe_3$ due to the low solubility of $RuHCl(PPh_3)_3$, which increases in the presence of an excess of the tin compound, with consequently shorter periods of time required and less decomposition of **3**.

The reaction of $RuCl_2(PPh_3)_3$ with 3 equiv of $CH_2C(Me)CHC(Me)CH_2SnMe_3$ results initially in the formation of (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuCl(PPh_3)_2$ (**2**)[16] (Scheme 1).

Several attempts to isolate **2** pure were unsuccessful, due to its transformation to (η^5-$CH_2C(Me)CHC(Me)CH_2$)$Ru(C_6H_4PPh_2)(PPh_3)$ (**4**) (Scheme 1). The congestion in **2** is most effectively

Scheme 1

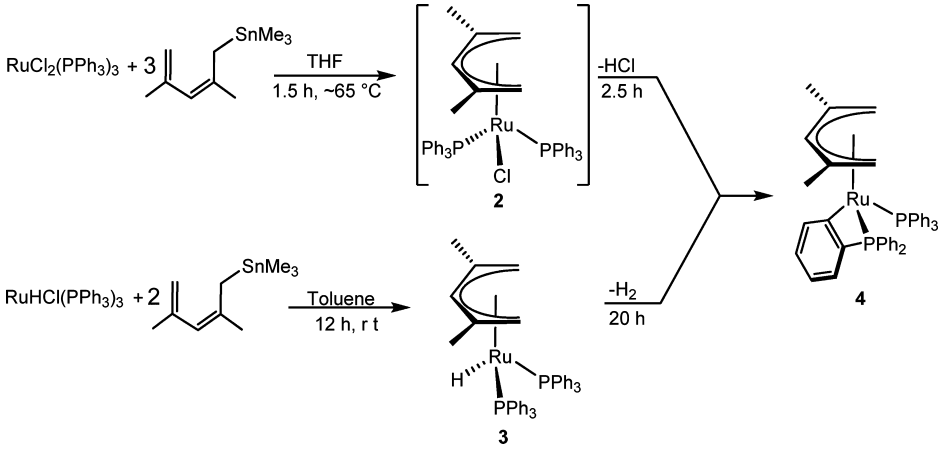


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Chart 1

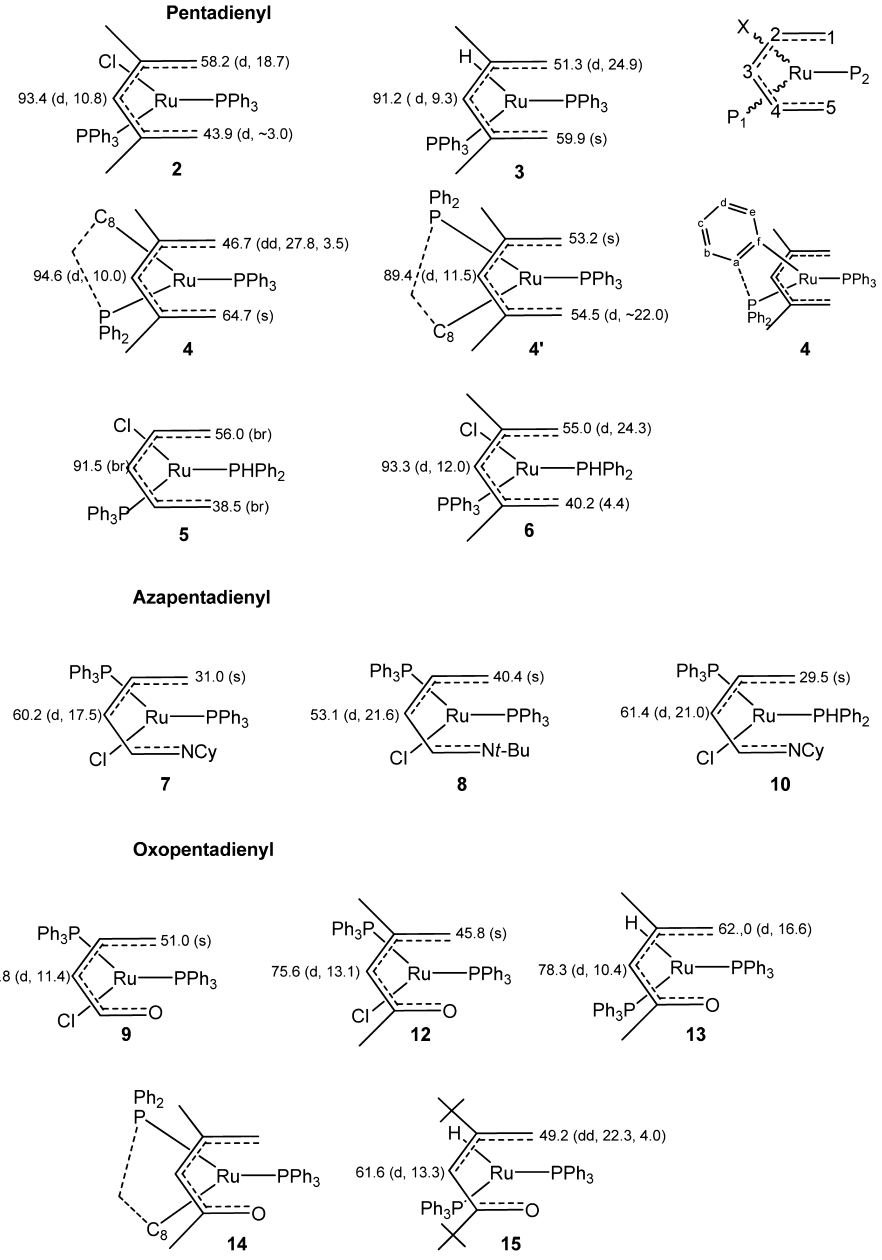

Chart 1

relieved by formation of the cyclometalated complex **4**.[14,17,18] This was supported by the isolation, and complete characterization, of the less sterically crowded compound (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuH(PPh_3)_2$ (**3**), which was found to be a static molecule in solution and only under thermolysis in toluene (20 h) gave compound **4**, through the loss of hydrogen, along with a mixture of unidentified products. Complex **4** is more conveniently obtained from the precursor $RuCl_2(PPh_3)_3$ in mildly refluxing THF (2.5 h). However, pure **4** was obtained in very low yield (10%) due to the purification process, which required several chromatography columns in order to remove PPh_3 and $OPPh_3$. It seems likely that the elimination of HCl or H_2 in compounds **2** and **3** is a concerted process occurring through a four-center transition state, as previously described in the literature.[17,18] Compound **1** does not give evidence of conversion to the corresponding orthometalated derivative, which seems to confirm the importance of the steric congestion needed for activation of phenyl C−H and Ru−X (X = H, Cl) bonds. The sterically bulky phosphine P(*t*-Bu)$_3$ does not react with **1**. The NMR spectroscopic data of **2**−**4** are assigned according to Chart 1, and the crystal structure of **3** is described in Figure 1.

The ^{1}H, ^{13}C, and ^{31}P NMR data described in Tables 1 and 2 give evidence of the unsymmetrical ground-state structures of **2**−**4**, as was observed previously in **1**.[4]

In the ^{31}P NMR spectra, two phosphorus signals are observed, as doublets, for compounds **3** (δ = 52.2, 68.2; J_{PP} = 18.7 Hz) and **4** (δ = 56.6, −36.3; J_{PP} = 19.8 Hz), while **2** shows different patterns depending on the solvent used. Compound **2** in $CDCl_3$ shows an A_2 spectrum at δ = 36.5 at room temperature, while better resolution as an AB quartet was found in CD_2Cl_2 (δ = 36.8, 37.1, J_{AB} = 25.0 Hz) and signals of an AB quartet were observed when aromatic solvents

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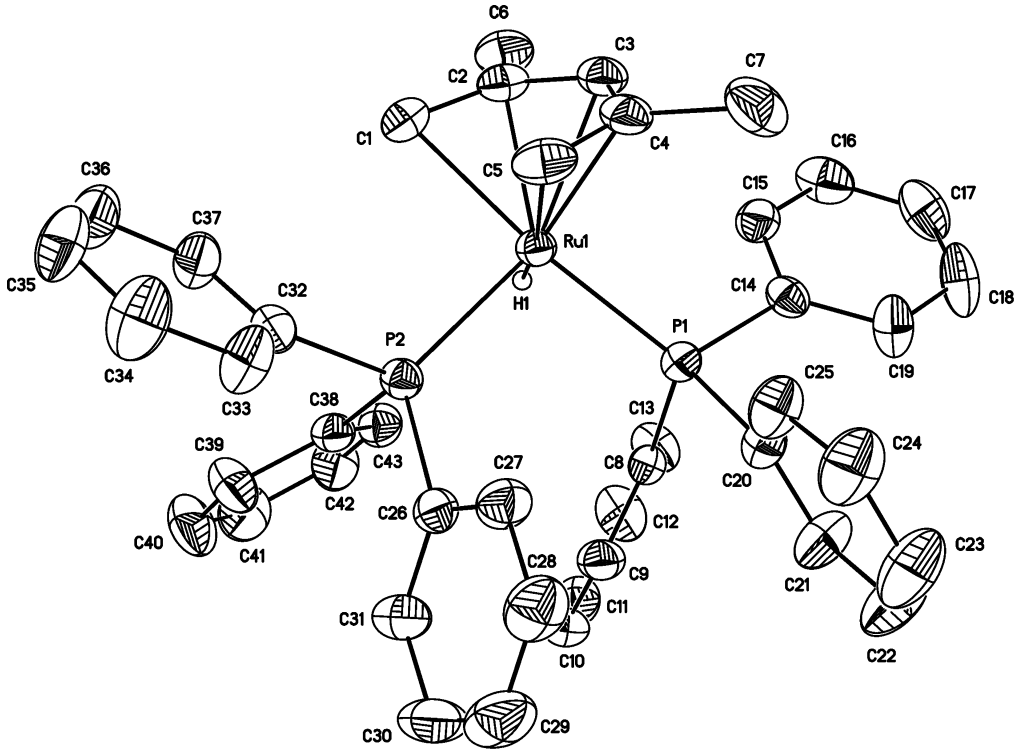

Figure 1. Perspective view of compound **3** drawn at the 45% probability level. Hydrogen atoms have been omitted for the sake of clarity, except the hydride.

such as C_6D_6 (δ = 36.4, 37.0, J_{AB} = 26.0 Hz) or toluene-d_8 (δ = 36.2, 37.0, J_{AB} = 24.8 Hz) were used; see the Supporting Information.

In the ^{31}P NMR spectrum of **2**, along with the signal at δ = 36.5, there is always evidence of free PPh_3 (δ = −4.1), and two doublets appearing at δ = 56.6 (J_{PP} = 19.8 Hz) and δ = −36.3 (J_{PP} = 19.8 Hz) can be assigned to **4**, for the unmetalated and orthometalated phosphines, respectively. The upfield signal is assigned to the orthometalated phosphine, in agreement with the incorporation of the phosphorus atom into a four-membered ring.[17a,19] It should be mentioned that a second pair of doublets was found at ^{31}P δ = 53.9 and δ = −14.2 with J_{PP} = 13.5 Hz, in a very small amount, during the monitoring of the formation of **2**. This minor isomer is observed in the ^{31}P NMR spectrum in a 1:9 ratio, but in our hands this species could not be isolated. The minor compound is tentatively assigned as the diastereomer **4′** described in Chart 1. This proposal was supported through the crystallographic study, in which both isomers **4** and **4′** were detected in the asymmetric unit, *vide infra*. From the monitoring of the reaction through ^{31}P NMR spectroscopy, there was no evidence of any change in the ratio of these two compounds **4** and **4′**, regardless of whether they came from the orthometalation of **2** or instead from **3**. A rapid equilibrium is evident from the ^{31}P NMR spectra of crystals or powder of **4**; see the Supporting Information. The orthometalated compound **4** gives evidence of the increased complexity of the phenyl region as compared to that of **3**. The ^{1}H NMR spectrum of the phenyl region of **4** contains four signals at 6.65 (dd, 7.0 Hz), 6.86−6.92, (m), 6.92−7.10, (m), and 7.91 (dd, 8.3 Hz), of which the well resolved doublet of doublets at 6.65 was found to collapse to a doublet (J = 7.4 Hz) and likewise the 7.91 signal collapsed to a triplet (J = 6.5 Hz), when the phosphorus resonance at −36.6 was irradiated, confirming that these signals are due to protons on the metalated phosphine. Also, no evident change for the above-mentioned signals occurred upon irradiation of the ^{31}P signal at 56 ppm. Similar ^{1}H NMR spectroscopic behavior has been reported for orthometalated ruthenium[20] and dinuclear iridium−ruthenium[21] complexes. The pentadienyl ligand signals at −0.4 (br), 2.05 (doublet to singlet), and 2.19 (doublet to singlet) ppm were shown also to be coupled to the orthometalated phosphine, allowing for the assignment of the preferred orientation of the pentadienyl ligand in the chiral compound **4**.

The ^{13}C NMR spectrum of **4** shows in the aromatic region the presence of a low-intensity carbon resonance which confirms the inequivalence among the rings arising from the orthometalation of one of the triphenylphosphine ligands. A triplet found for the highest downfield peak [170.0 ppm (J = 16.6 Hz)] indicates coupling to more than one phosphorus atom. On the basis of the extreme downfield chemical shift of this signal, as well as the presence of coupling to more than one phosphorus atom, this signal is assigned to a carbon atom that has undergone orthometalation. The full assignment of all orthometalated aromatic carbon atoms is described in Table 2. Similar behavior has been reported, with a detailed spectroscopic assignment, for a ruthenium−iridium polyhydride which underwent orthometalation.[21]

The ^{13}C NMR chemical shifts and coupling constants J_{PC} of carbon atoms C1, C3, and C5 are particularly useful in supporting the assignment of the preferred pentadienyl orientation and the relative orientations of the H, Cl, PPh_3, and $PHPh_2$ ligands in the piano stool structure, as described in Chart 1, which contains overhead views of the series of heteropentadienyl compounds reported in this study.

In agreement with the presence of a hydride ligand in compound **3**, the ^{1}H NMR spectrum in C_6D_6 shows a doublet at −11.89 (dd, J_{PH} = 28.0 Hz). The hydride ligand gives rise to a ν(RuH) IR band at 1933 cm^{-1}; the complex is soluble in aromatic hydrocarbons and chlorinated solvents. However, **3** in the presence of $CDCl_3$ affords compound **2** as well as $OPPh_3$ and traces of $RuHCl(PPh_3)_3$, and it appears completely consumed after 3 h.

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Table 1. ^{1}H NMR Data of Compounds 1−10, 12, 13, and 15[a]

	H1 *anti*	H1 *syn*	H2/Me2	H3	H4/Me4	H5a	H5s	*H*, *R*, or Ph_2PH	Ph
1[b]	−0.30	2.90	5.15	5.63	4.22	−1.24	0.91		7.10−7.80
2[b]	−0.51	2.55	2.08	5.61	0.98	−0.82	1.03		6.90−8.00
2[c]	−0.24 (s, br)	2.80 (s, br)	2.29 (s)	5.54 (s)	1.01 (s)	−0.68 (s, br)	0.56 (s, br)		6.90−7.10; 7.63−7.67; 7.80−7.97
3[d]	0.57	3.43	2.40 (s)	4.50 (s)	1.74 (s)	−0.89	2.54	−11.89 (dd, 27.7, 28.0)	6.82−7.12; 7.27−7.52; 7.70−7.90
4[e]	0.67 (s)	3.11 (s)	1.92 (s)	4.88 (s)	2.05 (d, 3.2)	−0.40 (s, br)	2.19 (d, 3.4)		6.63 (dd, 7.3, H_e, *m*); 6.80−6.90, H_c, *m*); 6.90−7.10 (H_d, *p*); 7.30−7.68 (H_b, *o*)
5[b]	0.37	3.02	5.11	6.25	3.66	−1.06	1.61		7.18−7.55; 7.82 (m, br, *o*)
5[e,b]	0.15	3.50	5.10	6.60	3.50	−1.60	0.30	6.20 (d, 12.6)	6.90−8.00
5[f]	0.40 (d, 8.5)	2.70 (d, 8.6)	5.15 (d, 8.5)	6.00	3.80	−0.55 (d, 8.0)	0.90 (d, 8.6)	6.3 (d, 12.0)	6.90−7.40; 7.60−7.80; 7.90−8.10
6[g,b]	0.11	2.69	2.07	6.17	0.73	−0.99	0.85	6.30 (d, 9.7)	6.74 (t, 7.8); 7.00 (t, 6.9); 7.20−7.80 (m)
7[d]	1.84 (d, 10.1)	2.21 (d, 7.1)	4.87 (m)	3.80 (m)	7.85[h]			0.40−1.54 (m); 2.49 (m, HCy)	6.85−7.27; 7.75−7.94
8[d]	1.82 (d, 10.5)	2.11 (d, 6.6)	4.60 (m)	3.77 (m)	7.10[h]			1.03 (s)	6.80−7.10 (m); 7.44 (m, br); 7.70−7.80 (m); 8.02 (m)
9[d]	2.09 (dd, 2.9, 7.9)	2.23 (d, 11.0)	4.22 (m)	4.79 (m)	8.13 (s, br)				6.80−7.10; 7.20−7.40; 7.65−8.05
10	1.06 (d, br, ∼9.2)	1.48 (d, br, ∼10.0)	4.10 (m)	4.44 (m)	8.23 (d, 3.1)			5.90 (d, 7.7, P*H*); 0.50−2.0 (m, Cy); 2.59 (m, *H*NCy)	7.00−7.96
10[c]	1.13 (d, 7.2)	1.92 (d, 9.7)	4.25 (m)	4.45 (m)	7.90 (d, 4.0)			6.17 (d, 7.4, P*H*); 0.45−2.10 (m, Cy); 2.66 (m, *H*NCy)	6.86−8.40
12[d]	2.11 (s, br)	2.38 (s, br)	1.03 (d, 0.7)	4.63 (s, br)	2.19 (d, 1.0)				6.52 (s, br, *o*, A); 6.74 (s, br, *m*); 6.99 (m, *m*, *p*); 7.49 (s, br, *o*, A); 8.04 (t, 8.5, *o*, B); 8.28 (s, br, *o*, A)
12[c]	2.05 (s)	2.28 (s)	1.03 (s)	4.58 (s, br)	2.16 (s)				6.47 (s, br, *o*, A); 6.71 (s, br, *m*); 6.97 (m, *m*, *p*); 7.38 (m, *o*, A); 7.95 (m, *o*, B); 8.20 (s, br, *o*, A); 8.20 (m, *o*, A)
12[b,i]	2.02	2.54	0.96	4.46	2.30				6.35 (t); 6.61 (t); 6.72 (t); 6.83 (m); 6.91 (d); 6.96 (m); 7.00 (s); 7.09 (s); 7.53 (m); 8.05 (t); 8.35 (t)
13[d]	2.63 (d, 4.4)	2.83 (d, 4.4)	1.42 (s)	4.15 (s)	2.08 (s)			−20.65 (dd, 29.7)	6.92−7.03 (m, *m*, *p*, A, B); 7.61 (m, *o*, A); 7.76 (m, *o*, B)
15[d]	2.11 (d, 5.1)	2.81 (d, 5.1)	1.15 (s)	4.16 (s)	0.86 (s)			−23.3 (t, 29.8)	6.93−7.30 (m); 7.66−7.69 (m)

[a]For numbering see Chart 1 and the corresponding figures. In $CDCl_3$. [b]Broad signals. [c]In toluene-d_8 at 25 °C. [d]In C_6D_6. [e]In CD_2Cl_2 at −90 °C. [f]In toluene-d_8 at 100 °C. [g]In $CDCl_3$ at −40 °C. [h]Overlapped. [i]In toluene at −80 °C.

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Table 2. ^{13}C and ^{31}P NMR Data of Compounds 1−10, 12, 13, and 15[a]

	heteropentadienyl ligand					aromatic carbons				^{31}P NMR	
	C1	C2/Me2	C3	C4/Me4	C5	C *ipso*	C *ortho*	C *meta*	C *para*	PPh_3	$PHPh_2$
1[b,c,d]	55.2 (d, 22.0)	109.5	93.8 (d, 12.0)	87.6	42.0	138.2 (d, 39.0)	133.4 (d, 10.0)	127.2 (d, 9.0)	128.7 (s)	27.4 (d, 30.0, P2)	
							134.0 (d, 10.0)	127.8 (d, 9.0)	129.1 (s)	38.0 (d, 30.0, P1)	
2[e,f]	58.2 (d, 18.7)	117.1	93.4 (d, 10.8)	103.2	43.9 (d, ~3.0)	140.0 (d, 36.9)	134.5 (d, 9.2)	127.0 (d, 7.7)	128.1[g]	36.2, 37.0 (AB quartet, 24.8)	
		24.4		23.8							
3[h]	51.3 (d, 24.9)	111.7	91.2 (d, 9.3)	106.7	59.9	142.0 (d, 32.7)	134.3 (d, 10.9)	127.0 (d, 8.8)	128.1[g]	52.2 (d, 18.7, P2)	
		29.0		27.1		141.0 (d, 37.9)	134.1 (d, 11.4)			68.2 (d, 18.7, P1)	
4[h]	46.7 (dd, 27.8, 3.5)	109.7	94.6 (d, 10.0)	106.2	64.7	139.0 (d, 39.2, PPh_3)	134.0 (d, 10.0, PPh_3)	127.1 (d, 8.5, PPh_3)	127.4−128.7 (m, PPh_3, PPh_2)	56.6 (d, 19.8, P2)	
		23.4		27.4 (d, 6.9)		141.7 (d, 24.6, PPh_2)	131.9 (d, 10.8, PPh_2)	127.4−128.7 (m, PPh_2)	129.8 (d, 2.3, C_d, PPh_2)	−36.3 (d, 19.8, P1)	
							132.7 (d, 10.7, PPh_2)				
						153.4 (d, 46.2, C_a, PPh_2)	134.4 (m, C_b, PPh_2)	121.8 (d, 8.5, C_c, PPh_2)			
							169.9 (t, 16.6, Ru−C_β, PPh_2)	125.2 (s, C_e, PPh_2)			
4′[h]	53.2	n.o.[i]	89.4	108.9	54.5	n.o.[i]	n.o.[i]	n.o.[i]	n.o.[i]	54.3	
		25.9 (d, 3.8)	(d, 11.5)	20.6	(d, ~25.0)					(d, 13.5, P2)	
										−14.1	
										(d, 13.5, P1)	
5[j,k,l]	53.0	110.0	91.5	88.5	38.5	n.o.[i]	133.8 (br)	127.9 (d, 8.8)	129.4 (s, PPh_3)	38.7 (s, P2)	
							131.6 (d, 9.9)	128.1 (d, 4.4)	128.7 (s, br)	J_{PH} = 356.0	
								128.3 (d, 5.5)		45.0 (s, P1)	
6[j,l]	56.6 (d, 22.2)	118.9	93.3 (d, 12.3)	102.8	39.9	n.o.[i]	127.5−130.2	127.5−130.2	127.5−130.2	42.9 (d, 30.3, P2)	
		26.0		24.0 (d, 1.5)			131.3−138.0	131.3−138.0	131.3−138.0	J_{PH} = 346.0	
										47.7 (d, 32.3, P1)	
7[h,m]	31.0	92.3	60.2 (d, 17.5)	163.4		139.3 (d, 34.9)	134.8 (d, 10.0)	127.7[g]	127.1 (s)	41.9 (d, 32.1, P2)	
							132.2 d, 10.0)		127.3 (s)	49.1 (d, 32.1, P1)	
									128.8 (d, 7.7)		
									134.3 (br)		
									131.3 (d, br, 0.3)		
8[h]	40.4	93.3	53.1 (d, 21.6)	173.0		137.0 (d, 43.6)	134.9 (d, 10.4)	127.5 (d, ~8.3)	128.4 (s)	38.8 (d, 32.7, P2)	
						138.4 (d, 35.3)	134.3 (d, 10.4)		128.8 (s)	61.1 (d, 38.2, P1)	
9[h]	51.0	89.0	80.8 (d, 11.4)	161.5		135.9 (d, 44.6)	134.2 (d, 9.3)	127.4[g]	129.0 (s, br)	34.9 (d, 32.1, P2)	
						137.5 (d, 39.4)	134.8 (d, 10.4)	127.7[g]	129.3 (d, br, 2.1)	48.6 (d, 32.1, P1)	
10[h,n]	29.5	94.5	61.4 (d, 21.0)	160.7		135.2 (d, 42.0) 136.9 (d, 43.6)	133.4 (d, 9.3) 134.2 (d, 9.4)	127.6[g]	128.0[g]	34.6 (d, 37.5, P2), J_{PH} = 390.0	
										57.6 (d, 37.5, P1)	
10[j,o]	28.4	94.6	62.2 (d, 19.2)	161.3		136.7 (d, 44.1)	126.0−130.0 (s, br)	126.0−130.0 (s, br)	126.0−130.0 (s, br)	33.9 (d, 37.6, P2)	
							132.0−136.0 (m, br)	132.0−136.0 (m, br)	132.0−136.0 (m, br)	56.4 (d, 37.6, P1)	
12[h]	45.8	107.3	75.6 (d, 13.1)	181.9		134.0 (d, 10.8, A)	134.8 (d, 10.0, A, B)	127.4 (d, 10.0, B)	128.6 (s, B)	38.6 (d, 32.3, P2)	
		22.4		27.2		134.3 (d, 11.5, A)					
						134.5 (d, ~11.0, A)	135.0 (br, A)	127.0 (br, A)	129.2 (br, A)	55.7 (d, 32.3, P1)	
						137.8 (d, 39.2, B)	135.6 (br, A)				
12[p]	45.1	107.5	75.5 (d, 13.5)	182.5		132.0 (d, 50.0, A)	134.3 (d, 9.2, B)	127.0 (d, 8.5, A)	129.3 (m, B)		

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Table 2. continued

	heteropentadienyl ligand					aromatic carbons				^{31}P NMR	
	C1	C2/Me2	C3	C4/Me4	C5	C *ipso*	C *ortho*	C *meta*	C *para*	PPh_3	$PHPh_2$
		22.5		27.4		136.3 (d, 44.6, A)	134.6–134.9 (m, 3A)	127.4–127.9 (m, 2A, B)	129.4 (s, A)		
						137.0 (d, 53.0, A)			129.5 (s, A)		
						137.5 (d, 40.0, B)			129.8 (s, A)		
13[h]	62.0 (d, 16.6)	112.5	78.3 (d, 10.4)	169.5		139.8 (d, 35.3)	134.0 (d, 12.5)	127.1[g]	128.4 (s)	51.2 (d, 24.1, P2)	
		25.6		28.6		140.3 (d, 39.4)	134.4 (d, 12.5)	127.5 (d, 10.4)	128.6 (s)	62.7 (d, 24.1, P1)	
15[h,q]	49.2 (dd, 4.0, 22.3)	n. o.[i]	61.6 (d, 13.3)	206.6		141.3 (d, 36.7)	134.9 (d, 12.0)	127.6 (d, 12.5)	128.4 (d, 1.6)	50.8 (d, 18.0, P2)	
				43.0							
		36.5		31.0		141.6 (d, 33.3)	134.2 (d, 10.7)	127.7 (d, 12.8)	128.6 (d, ~1.5)	60.0 (d, 18.0, P1)	
		27.4									
15[h,r]	49.2 (t, 154.0)	n. o.[i]	61.6 (d, 163.1)	206.4 (s)		141.6 (d, 37.0)	134.5 (dd, 153.0, 37.0)	127.7 (m, ~153.0)	128.4 (m, ~153.0)		
		36.5 (s, br)		43.0 (m)							
		27.4 (d, 126.7)		31.0 (d, 125.6)							

[a] In ppm and *J* in Hertz. For numbering see Chart 1 and corresponding figures. [b] In CD_2Cl_2 at −40 °C. Reference 4. [c] ^{31}P δ = 27.2 (s, br) in toluene-d_8 at 100 °C, ref 4. [d] ^{31}P δ = 29.0 (s, br), 36.8 (s, br) in $CDCl_3$ at 25 °C. [e] In toluene-d_8. [f] ^{31}P δ = 36.5 (A_2, see text) in $CDCl_3$; ^{31}P δ = 36.8, 37.1 (AB quartet, J_{AB} = 25.0 Hz) in CD_2Cl_2. [g] Overlapped signal. [h] In C_6D_6. [i] Not observed. [j] In $CDCl_3$ at −40 °C. [k] ^{31}P{1H} δ = 46.3 (d, 34.2 Hz, PPh_3), δ = 41.9 (d, 34.2 Hz, $PHPh_2$) in CD_2Cl_2 at −40 °C; ^{31}P δ = 46.0 (s, br, PPh_3), 39.8 (d, $J_{PH} \approx$ 350.0 Hz, $PHPh_2$) in toluene at 100 °C. [l] Broad signals. [m] Cyclohexyl carbon atoms at 25.5, 25.8, 26.5, 34.3, 35.5, and 62.3 ppm. [n] Cyclohexyl carbon atoms at 25.4, 25.6, 25.8, 32.0, 35.8, and 62.3 ppm. [o] Cyclohexyl carbon atoms at 25.4, 25.4, 25.8, 32.6, 35.7, and 62.9 ppm. [p] In CD_2Cl_2 at −90 °C. [q] In ^{31}P NMR two minor species were detected at 48.6 (d, 22.3, P2), 59.4 (d, 22.3, P1) and 50.7 (d, 18.0, P2), 62.0 (d, 18.0, P1) in a 0.13:0.10 ratio. [r] ^{13}C NMR coupled spectrum.

Compound **3** has been structurally characterized, showing a *pseudo*-octahedral geometry about the metal center with the pentadienyl ligand occupying three coordination sites, with the other three sites occupied by one hydride and two triphenylphosphine ligands (Figure 1). Crystallographic data and selected bond lengths and angles are described in Tables 3 and 4, respectively.

The bond angles of this piano stool fragment give evidence of the influence of the small hydride ligand compared to the bulky triphenylphosphines [P(2)−Ru(1)−P(1) 99.46(4), P(1)−Ru(1)−H(1) 76.3(12), and P(2)−Ru(1)−H(1) 86.1(12)°]. Comparatively, the $CpRuH(PPh_3)_2$ complex shows coordination angles of 101.4(1), 73.2(15), and 92.7 (15)° for the P(2)−Ru(1)−P(1), P(1)−Ru(1)−H(1), and P(2)−Ru(1)−H(1) units, respectively.[22] The larger size of the chlorine atom in $Cp'RuCl(PPh_3)_2$ is reflected by the greater bond angles, P(1)−Ru(1)−Cl(1) and P(2)−Ru(1)−Cl(1), of the corresponding complexes, with the Cp and Cp* ligands being 89.05(3), 90.41(4)[7c] and 87.72(2), 93.42(2)°,[23] respectively.

The two bond distances Ru1−P1 [2.3111(11) Å] and Ru1−P2 [2.3029(10) Å] are essentially equivalent, but they are significantly longer than the Ru−P distances found in the complex $CpRuH(PPh_3)_2$ [Ru−P1, 2.256(1) and Ru−P2, 2.265 (1) Å].[22] The Ru−H bond lengths are similar, with that for compound **3** being 1.53(3) Å and that for $CpRuH(PPh_3)_2$ being 1.51(4) Å.[22] The crystal structure of the cationic complex $[(\eta^6\text{-CHCHC(OH)CHCHCH})RuH(PPh_3)_2]Cl$ showed a similar Ru−H distance of 1.53(3) Å but longer bond Ru−P lengths [2.3289(8) and 2.3319(8) Å][14] compared to **3**. The dihedral angle between C1−C2−C3−C4 and C2−C3−C4−C5 in **3** [0.88(31)°] gives evidence of the planarity of the pentadienyl ligand, contrasting with the heteropentadienyl derivatives **7** and **12**−**15** (*vide infra*).

Compound **4** shows a disordered crystalline structure with three independent molecules in the asymmetric unit, with C_6D_6 present as a cocrystallized solvent. In spite of the disorder, these molecules are unquestionably isostructural to **14**. Interestingly, one of these three molecules shows the chemical structure described as **4** in Chart 1, where the orthometalated carbon atom is nearly opposite to C5 in the pentadienyl ligand [C25−Ru1−C5, 169.7(2)°]. The other two correspond to **4′** (see Chart 1), being both slightly different, with the orthometalated carbon atom nearly opposite to C1 in the pentadienyl ligand [C20A−Ru1A−C1A, 172.0(3) and C20B−Ru1B−C1B, 171.4(2)°]. Crystallographic data, bond lengths, and angles of **4** and **4′** are included in the Supporting Information.

*Reactivity of Compounds **1**, **2**, and **3** with $PHPh_2$.* Addition of 1 equiv of $PHPh_2$ to **1** in THF at room temperature affords the monosubstituted phosphine complex $(\eta^5\text{-}CH_2CHCHCHCH_2)RuCl(PPh_3)(PHPh_2)$ (**5**) in 75% yield, while compound $(\eta^5\text{-}CH_2C(Me)CHC(Me)CH_2)RuCl(PPh_3)(PHPh_2)$ (**6**) was directly obtained from the reaction of $RuCl_2(PPh_3)_3$ with $CH_2C(Me)CHC(Me)CH_2SnMe_3$ and $PHPh_2$ in 10.6% yield. ^{1}H, ^{13}C {^{1}H} and ^{31}P {^{1}H} NMR spectra show broad signals for compounds **5** and **6**. The monosubstituted chiral compounds **5** and **6**, with stereogenic centers at ruthenium, show in solution only one isomer (Chart 1). The spectroscopic data are included in Tables 1 and 2. Line-shape simulations of the variable-temperature ^{31}P{^{1}H} NMR spectra for the rotational processes suggest that the barriers to pentadienyl ligand rotation are quite high for neutral mixed-phosphine derivatives, such as $(\eta^5\text{-}CH_2CHCHCHCH_2)RuCl(PPh_3)(L)$ [L = PMe_2Ph, PEt_3, PEt_2Ph, $PEtPh_2$],[4] as well as for the cationic $[(\eta^5\text{-}CH_2CHCHCHCH_2)Ru(PPh_3)(PMe_3)_2]BF_4$.[4]

Table 3. Crystal Data and Experimental Parameters for Compounds 3, 5, 6, and 7

compd	3	5	6	7
formula	$C_{43}H_{42}P_2Ru$	$C_{35}H_{33}ClP_2Ru$	$C_{37}H_{37}ClP_2Ru$	$C_{50}H_{56}ClNOP_2Ru$
fw	721.78	652.07	680.13	885.42
crystal syst	tetragonal	triclinic	triclinic	orthorhombic
space group	$P42/n$	$P\bar{1}$	$P\bar{1}$	$Pna21$
a (Å)	27.150(4)	10.3273(5)	9.8512(2)	26.420(5)
b (Å)	27.150(4)	10.9844(4)	9.9517(3)	15.661(3)
c (Å)	9.967(2)	13.2916(7)	17.5270(5)	10.368(2)
β (deg)	90	80.670(3)	101.132(2)	90
		80.643(2)	94.1290(10)	
		88.944(3)	109.474(2)	
V (Å^3)	7347(2)	1468.00(12)	1572.14(7)	4289.7(15)
Z	8	2	2	4
D_{calc} (g/cm^3)	1.305	1.475	1.437	1.371
radiation, wavelength	Mo Kα, λ = 0.71073 Å	Mo Kα, λ = 0.71073 Å	Mo Kα, λ = 0.71073 Å	Mo Kα, λ = 0.71073 Å
size (mm)	0.12 × 0.10 × 0.08	0.15 × 0.10 × 0.03	0.18 × 0.10 × 0.03	0.20 × 0.10 × 0.05
index range	$-20 \le h \le 35$	$-13 \le h \le 13$	$-12 \le h \le 12$	$-28 \le h \le 34$
	$-24 \le k \le 34$	$-14 \le k \le 14$	$-12 \le k \le 12$	$-19 \le k \le 20$
	$-12 \le l \le 11$	$-17 \le l \le 17$	$-22 \le l \le 22$	$-13 \le l \le 13$
F(000)	2992	668	700	1848
2θ range (deg)	6.36−54.96	8.38−55.06	6.00−54.90	6.60−55.00
no. reflns, collected	25190	22228	27665	32878
no. unique reflns	8255 (R_{int} = 0.0637)	6580 (R_{int} = 0.0706)	7128 (R_{int} = 0.0457)	8855 (R_{int} = 0.0646)
no. obsd reflns	5054 ($F > 4\sigma(F)$)	4771 ($F > 4\sigma(F)$)	5783 ($F > 4\sigma(F)$)	7281 ($F > 4\sigma(F)$)
abs corr (T_{max}, Tmin)	0.9579, 0.9378	0.9813, 0.8948	0.9790, 0.8827	0.9735, 0.8995
R	0.0533	0.0475	0.0359	0.0518
R_w	0.1169	0.0822	0.0782	0.1015
wR_2 (all data)	0.1372	0.0923	0.0851	0.1099
gof	1.014	1.004	1.023	1.079

The substitution of one triphenylphosphine in **1** by $PHPh_2$ in order to afford compound **5** was found to occur exclusively on the ruthenium atom, contrasting to the addition on the pentadienyl ligand when (η^5-$CH_2CHCHCHCH_2$)$Mn(CO)_3$ reacts with $PHPh_2$.[24] This is consistent with the presence of greater positive charge on the dienyl ligand in a complex having strong π-acid ligands. Addition of nitrogen ligands, such as piperidine, to compound **1**, in a ratio 20:1 under reflux for 8 h, showed no reaction, and the starting material could be recovered.

Attempts to synthesize the analoguous hydrido derivative (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuH(PPh_3)(PHPh_2)$ from the reaction of **3** with 1 equiv of $PHPh_2$ resulted, according to ^{31}P $\{^1H\}$ NMR spectroscopy, in a mixture of products. Similar results were obtained even under different experimental conditions.

Treatment of **1** with 2 equiv of $PHPh_2$, or addition of 1 equiv to **5**, resulted in complex mixtures of products without isolation of the expected disubstituted compound (η^5-$CH_2CHCHCHCH_2$)$RuCl(PHPh_2)_2$. The complexes *cis*-$RuCl_2(PHPh_2)_4$ and *trans*-$RuCl_2(PHPh_2)_4$ were found through the ^{31}P NMR spectra to be the predominant products. The dissociation of the PPh_3 in **5** and **6** compared to **1** and **2** is significantly less favored to occur, due to the fact that **5** and **6** are less crowded, and as a consequence, stronger conditions are required if the disubstituted diphenylphosphine pentadienyl complexes are expected to be obtained. However, it appears at least for acyclic pentadienyl ligands that there is a relatively weak binding to the ruthenium atom compared to that achieved by the combination of ligands PPh_3 and $PHPh_2$ in **5** and **6**. While electronic factors may be significant, it is worth noting that the higher cone angle of the acyclic pentadienyl ligand (180−182°)[25] relative to the cyclic Cp (136°)[25] or Cp* (167°)[25] is sufficient to rationalize the different behavior observed. In fact, the compounds Cp′$RuCl(PHPh_2)_2$ (Cp′ = Cp, Cp*) have been isolated in 74%[26] and 90%[8a] yield, respectively, while the bulky Tp (180°)[27] shows similar behavior to the acyclic ligands, for which the disubstituted $TpRuCl(PHPh_2)_2$ was just observed spectroscopically (^{31}P δ = 45.1) and only *trans*-$RuCl_2(PHPh_2)_4$ was isolated.[28]

The crystalline structures of compounds **5** and **6** are described in Figures 2 and 3, while selected crystallographic data and bond lengths and angles are included in Tables 3 and 4.

Both compounds show a *pseudo*-octahedral coordination geometry with the smaller $PHPh_2$ ligand under the open side of the pentadienyl ligand, and the bulky PPh_3 and the chloro ligand lying under the pentadienyl edges, essentially as observed in the large family of pentadienyl−ruthenium−phosphine complexes reported by Bleeke.[4]

The three-legged piano stool geometries in **5** and **6** show P(2)−Ru(1)−P(1) bond angles of 97.80(3)° and 92.45(2)°, respectively, which reflect a relief from steric congestion as compared to the bulky triphenylphosphine derivatives $CpRuCl(PPh_3)_2$ [P(2)−Ru(1)−P(1), 103.99(4)°[7c] and $TpRuCl(PPh_3)_2$, 101.9(1)°].[29] However, similar bond angles are detected for $Cp^*RuCl(PPh_3)_2$ [P(2)−Ru(1)−P(1), 96.430(2)°][23a] and Cp′$RuCl(PPh_3)(PHPh_2)$ [P(2)−Ru(1)−P(1), Cp, 92.3(5)° and Cp*, 91.33(8)°].[8a] The Ru−P and Ru−Cl bond lengths are in the expected range of typical mixed half-sandwich compounds, such as Cp′$RuCl(PPh_3)(PHPh_2)$ [Cp′ = Cp, Cp*].[8a,9a] The dihedral angles of **5** [1.39(4)°] and **6** [1.04(2)°] show the near planarity of both pentadienyl ligands.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 3, 5, 6, and 7

bond lengths (Å)						bond angles (deg)					
	3	5	6		7		3	5	6		7
C1−C2	1.404(6)	1.407(6)	1.410(4)		1.411(9)	C1−C2−C3	121.9(4)	125.3(4)	123.5(3)		122.3(5)
C2−C3	1.413(6)	1.413(5)	1.430(4)		1.409(8)	C2−C3−C4	127.1(4)	124.1(4)	126.6(3)		124.8(6)
C3−C4	1.431(6)	1.415(5)	1.415(4)		1.448(8)	C3−C4−C5	125.6(4)	125.9(4)	122.1(3)	C3−C4−N1	115.3(4)
C4−C5	1.391(6)	1.400(5)	1.427(4)	C4−N1	1.294(7)	C1−C2−C6	119.6(4)		119.2(3)	C4−C3−Ru1	84.8(3)
Ru1−C1	2.234(4)	2.262(3)	2.245(3)		2.146(5)	C1−C2−Ru1	72.6(2)	73.9(2)	72.05(15)		70.1(3)
Ru1−C2	2.207(4)	2.204(3)	2.234(3)		2.167(5)	C2−C3−Ru1	70.7(2)	71.1(2)	71.06(15)		66.5(3)
Ru1−C3	2.224(4)	2.210(4)	2.243(3)		2.303(5)	C3−C4−Ru1	69.5(2)	73.5(2)	72.45(15)	N1−C5−C6	111.5(4)
Ru1−C4	2.276(4)	2.147(4)	2.218(3)		2.608(5)	C4−C5−Ru1	69.7(2)	70.0(2)	72.42(16)	C4−N1−Ru1	95.3(3)
Ru1−C5	2.348(4)	2.175(4)	2.183(3)	Ru1−N1	2.147(4)	C5−Ru1−P1	111.97(12)	96.85(11)	100.27(9)	N1−Ru1−P1	167.12(13)
Ru1−P1	2.3111(11)	2.3194(8)	2.3484(7)		2.3132(14)	C3−Ru1−P2	152.92(11)	150.88(11)	154.52(8)		152.73(16)
Ru1−P2	2.3029(10)	2.2890(9)	2.3020(7)		2.3408(15)	C1−Ru1−P1	164.97(11)	172.52(11)	178.18(7)		98.25(15)
Ru1−X	1.53(3)	2.4601(9)	2.4568(7)		2.4914(13)	C5−Ru1−P2	97.09(11)	89.26(11)	97.84(8)	C1−Ru1−P2	95.74(17)
P1−C8	1.834(4)			C5−N1	1.486(6)	P1−Ru1−P2	99.47(4)	97.80(3)	92.45(2)		97.31(5)
				P1−C21	1.841(5)	C1−Ru1−X	92.2(12)	92.97(11)	93.75(8)	N1−Ru1−Cl1	85.28(12)
						C5−Ru1−X	170.3(12)	172.71(11)	172.64(8)	C1−Ru1−Cl1	158.15(16)
						P1−Ru1−X	76.4(12)	88.68(3)	85.81(2)		89.10(5)
						P2−Ru1−X	86.0(12)	94.72(3)	85.97(2)		103.74(5)
										C4−N1−C5	121.4(4)
							0.88 (0.31)[a]	1.39 (0.40)[a]	1.04 (0.19)[a]		23.66 (0.30)[a]

[a]Dihedral angles formed by LSQ-planes.

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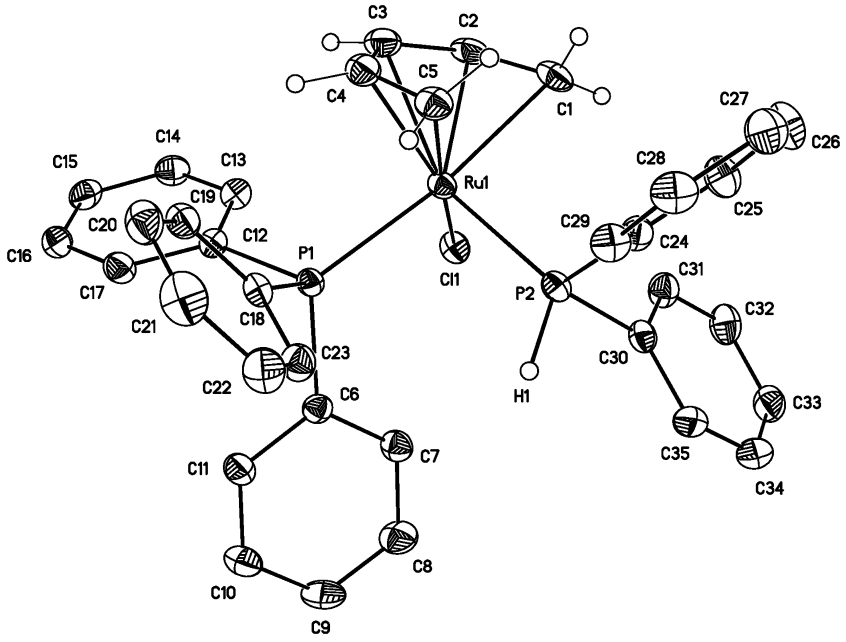

Figure 2. Perspective view of compound **5** drawn at the 45% probability level. Most hydrogen atoms have been omitted for clarity.

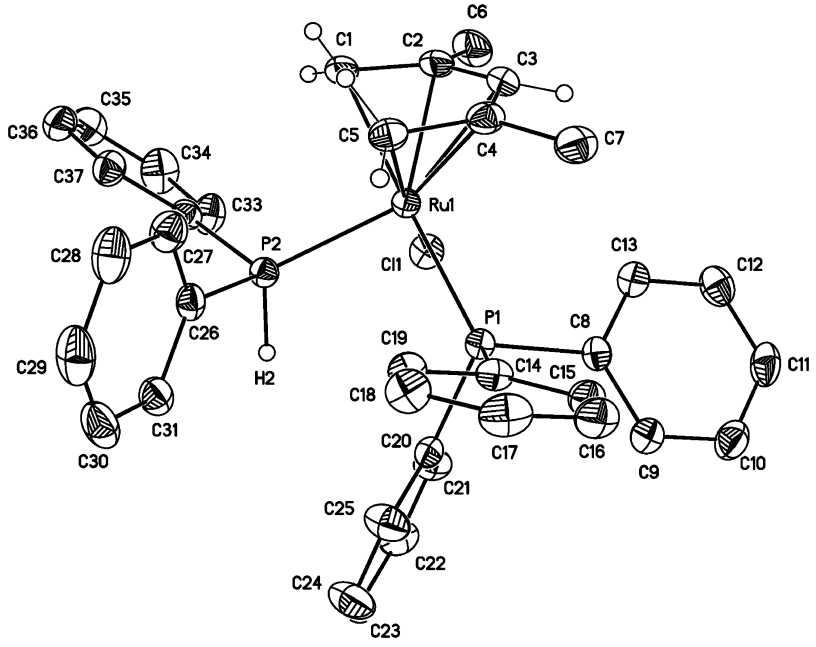

Figure 3. Perspective view of compound **6** drawn at the 45% probability level. Most hydrogen atoms have been omitted for clarity.

From the results of this study it can be concluded that the steric bulkiness of the PPh_3 ligands plays an important role, as observed in the chemistry of many related complexes.

Azapentadienyl Compounds. The analogous ruthenium heteropentadienyl complexes were prepared in a straightforward fashion, as described for the pentadienyls, though it was a more difficult task to work with the azapentadienyl derivatives, compared to pentadienyl and oxopentadienyl complexes (*vide infra*).

The azapentadienyl compounds are synthesized as indicated in Scheme 2, by first treating the appropriate $RuClX(PPh_3)_3$ complex (X = Cl, H) with $Me_3SnCH_2CH{=}CHCH{=}N(t\text{-}Bu)$ to afford the bright-yellow [1-3,5-η-$CH_2CHCHCHN(t\text{-}Bu)$]-$RuCl(PPh_3)_2$ (**8**) in 30% yield (X = Cl), while only traces are obtained when X = H. The reaction of $RuCl_2(PPh_3)_3$ with $Me_3SnCH_2CH{=}CHCH{=}N(Cy)$ allows the isolation of the brick-red (1-3,5-η-$CH_2CHCHCHNCy)RuCl(PPh_3)_2$ (**7**) in 37% yield while the analogous hydride derivative of **7** was never observed. The synthesis of **7** needs to be carried out under mild conditions, leading to the isolation of a more reactive and sensitive compound compared to **8**, which is conveniently obtained under refluxing conditions. It is interesting to mention that if the reaction of $RuCl_2(PPh_3)_3$ is carried out with 2 equiv of $Me_3SnCH_2CH{=}CHCH{=}N(t\text{-}Bu)$, the ^{31}P NMR spectroscopic data reveal as small signals a pair of doublets at δ = 54.6 and −33.5, J = 20.4 Hz, with a $\Delta\delta$ = 88.1 ppm, which suggest the presence of a small amount of ortho-metalated azapentadienyl complex (analogous to the situation for

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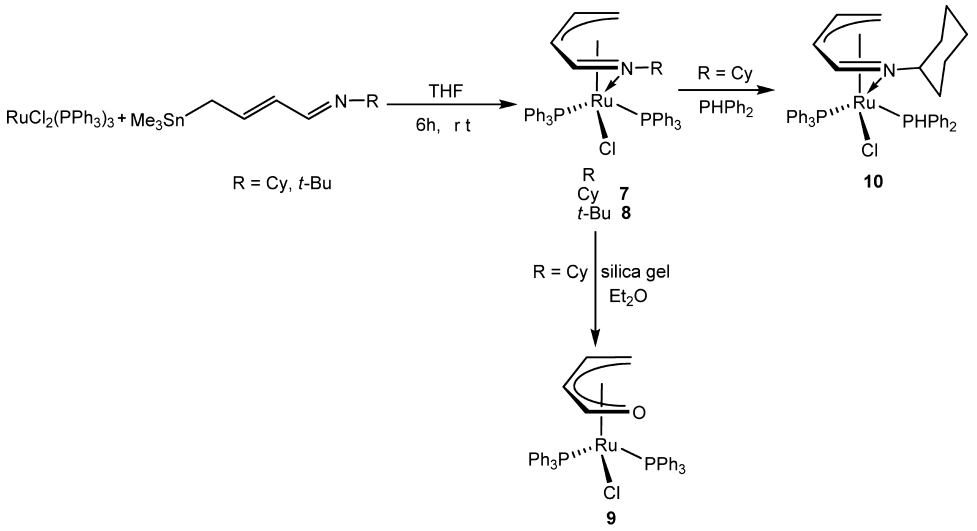
Scheme 2



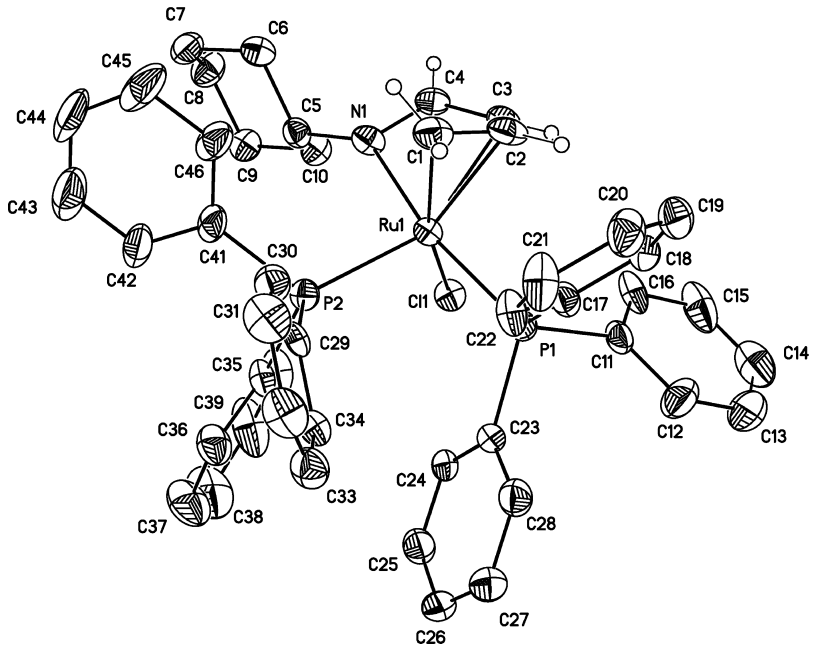


Figure 4. Perspective view of compound **7** drawn at the 45% probability level. Most hydrogen atoms have been omitted for clarity.

the corresponding pentadienyl complexes **4**, **4′** (*vide supra*), and oxopentadienyl **14** (^{31}P NMR at δ = 55.0 and −18.6, J = 24.8 Hz) (*vide infra*).

Square red crystals of **7** can be obtained by recrystallization in diethyl ether at −5 °C. The absence of planarity in the azapentadienyl ligand is clearly demonstrated from the crystallographic study of this, the first example of a half-sandwich azapentadienyl ruthenium complex, as illustrated in Figure 4. The crystal data and bond lengths and angles are described in Tables 3 and 4, respectively.

The dihedral angles formed by the least-squares planes (C1−C2−C3−C4) and (C2−C3−C4−N1) are 23.66(30)° and 156.34(30)°. The absence of planarity, as well as the short C4−N1 bond length of 1.294(7) Å and the long Ru1−C4 distance measured for (2.608 Å) confirm the preference of the azapentadienyl ligand to engage in lone pair coordination by the nitrogen atom, in tandem with η^3-allyl coordination.

A similar but not fully delocalized system has been observed in manganese derivatives, such as $CH_2C(Me)CHCHN(Cy)$-$Mn(CO)_3$, in which the short distance of 1.275(3) Å reflects the C4−N1 double bond, and the Mn−C4 bond shows a long distance of 2.550(2) Å, accompanied by a dihedral angle of 20.7(2)°.[3b] The chlorine atom in **7** (Chart 1) resides on the same side of the nitrogen atom, in a similar arrangement to those observed in oxopentadienyl compounds **9** and **12** (*vide infra*, Chart 1).

The ^{1}H and ^{13}C{^{1}H} chemical shifts for compounds **7** and **8** are assigned according to the structures shown in Figure 4 and Chart 1, and they are given in Tables 1 and 2. The chemical shifts of H4 (>7.0 ppm) and C4 (>160.0 ppm) in the ^{1}H and ^{13}C NMR spectra do contain a potentially valuable hint with respect to the bonding mode, which suggests that there is no interaction between the imine hydrogen and the carbon with the ruthenium center, as was confirmed in the solid state of **7** (*vide supra*). The assignment of the PPh_3 ligands in **7** and **8** was

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carried out through decoupled ^{1}H NMR by selective irradiation of the corresponding ^{31}P signals (see Supporting Information). The ^{31}P NMR spectra show two doublets for **7** with $\Delta\delta$ = 7.2, and for **8** with $\Delta\delta$ = 22.3; the significant difference between them is attributed to the bulkiness of the *t*-Bu group of the azapentadienyl ligand, which modifies the corresponding P1−Ru1−P2 angles.

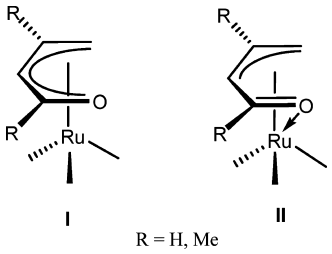
The syntheses of half-open sandwich compounds with the moiety Ru(η^5-$CH_2CHCHCHR$) [R = O, N(*t*-Bu)] which have only hydrogen atoms substituted in the azapentadienyl and oxopentadienyl ligands, generally involved unselective reactions,[30−32] and sometimes it was necessary to isolate them through indirect routes, such as dismutation,[33] or through hydrolysis.[34] In the chemistry of the half-sandwich compound **7**, we found similar behavior. The hydrolysis of **7**, on a silica gel chromatographic column, allowed the isolation of (η^5-$CH_2CHCHCHO$)$RuCl(PPh_3)_2$ (**9**) in 49% yield. Attempts to isolate **9** directly from $RuCl_2(PPh_3)_3$ with the lithium oxopentadienide derivatives, prepared from crotonaldehyde and LDA or CH_2=CHCH=$CHOSiMe_3$[35] and *n*-BuLi, were unsuccessful. Only in the last reaction was there evidence of the formation of **9** through ^{1}H and ^{31}P NMR spectroscopy, but competitive formation of the dimeric compound $[RuCl_2(PPh_3)_2]_2$[36,37] (δ = 48.0, 52.3; J_{AB} = 37.2 Hz, $CDCl_3$) made this approach not synthetically useful. The ^{31}P NMR spectrum of **9** showed a pair of doublets at δ = 34.9 and 48.6 with J_{PP} = 32.1 Hz. The ^{1}H and $^{13}C\{^{1}H\}$ NMR data (Tables 1 and 2) showed chemical shifts for H4 at δ = 8.13 and C4 at δ = 161.5 pointing to a contribution from resonance hybrid II, (Chart 2) as observed for the oxopentadienyl ligands in **12** and **13**, *vide infra*.

The azapentadienyl complexes **7** and **8** react in the presence of 1 equiv of $PHPh_2$ to afford the corresponding complexes (1-3,5-η-$CH_2CHCHCHNCy$)$RuCl(PPh_3)(PHPh_2)$ (**10**) in 62% yield and [1-3,5-η-$CH_2CHCHCHN(t\text{-Bu})$]$RuCl(PPh_3)(PHPh_2)$ (**11**). However, **11** was only observed through the ^{1}H and ^{31}P NMR spectra, as a mixture of isomers **11a** and **11b** (Scheme 3).

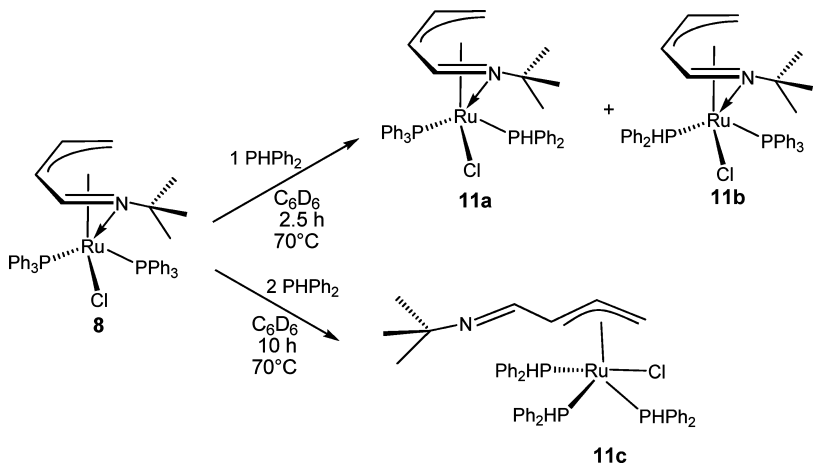
Compounds **11a** and **11b** showed through ^{31}P NMR spectroscopy two pairs of doublets, at δ = [67.0 (PPh_3), 42.2 ($PHPh_2$)] and [54.4 ($PHPh_2$), 41.2 (PPh_3)] with the corresponding J_{PP} = 38 Hz in each case. The ^{31}P NMR coupled spectrum showed J_{PH} values of ∼350 and 327 Hz for signals at 42.2 and 54.4 ppm, respectively. The ^{1}H NMR spectra confirm the presence of both coordinated azapentadienyl ligands.[38a] The ^{31}P NMR spectrum of compound **10** shows also the corresponding doublets at δ = 56.4 and 33.9 with J_{PP} = 37.6 Hz. According to the $\Delta\delta$ value of 22.5 ppm found in **10**, and those of the isomers **11a** ($\Delta\delta$ = 24.8 ppm) and **11b** ($\Delta\delta$ = 13.2 ppm), we tentatively propose that **11a** should have the same arrangement of its piano stool structure as **10**, in which the $PHPh_2$ ligand is under the open edge of the azapentadienyl complex.

While compound **7** reacts selectively with 1 equiv of $PHPh_2$ to afford **10**, in the presence of a second equivalent of $PHPh_2$, **7** is totally transformed to complexes *cis*-$RuCl_2(PHPh_2)_4$ and *trans*-$RuCl_2(PHPh_2)_4$. This fact gives evidence of the preference for the $PHPh_2$-Ru bonds compared to the heteropentadienyl-ruthenium bond. A similar trend has been observed in unsuccessful attempts to prepare analogous compounds, such as (η^5-pentadienyl)$RuCl(PHPh_2)_2$, (2,4-Me_2-η^5-pentadienyl)-$RuCl(PHPh_2)_2$, (2,4-Me_2-η^5-oxopentadienyl)$RuCl(PHPh_2)_2$, and (Tp)$RuCl(PHPh_2)_2$.[28] The double substitution by $PHPh_2$ occurs only when cyclic ligands Cp and Cp* are involved.[8,9a] This behavior is explained in terms of the small steric interaction between the cyclic ligands and the secondary phosphine bonds to the ruthenium atom. Interestingly, an NMR tube reaction of the more robust compound **8**, in C_6D_6, with 2 equiv of $PHPh_2$ shows, after 10 h under an oil bath (70 °C), spectroscopic evidence of a new azapentadienyl complex [η^3-$CH_2CHCHCHN(t\text{-Bu})$]$RuCl(PHPh_2)_3$ (**11c**)[38b] (Scheme 3). The ^{31}P NMR spectrum shows a triplet at δ = 49.0 with J_{PP} = 33.7 Hz, and two doublets of doublets at δ = 32.1 and δ = 30.6 ppm with J_{PP} = 33.7 and 8.5 Hz, respectively, along with other products (Supporting Information). Related compounds with tertiary phosphines (η^3-pentadienyl)$RuCl(PR_3)_3$ (R = Me, Me_2Ph),[4] (η^3-azapentadienyl)$Ir(PMe_3)_3$,[39]

Chart 2



Scheme 3



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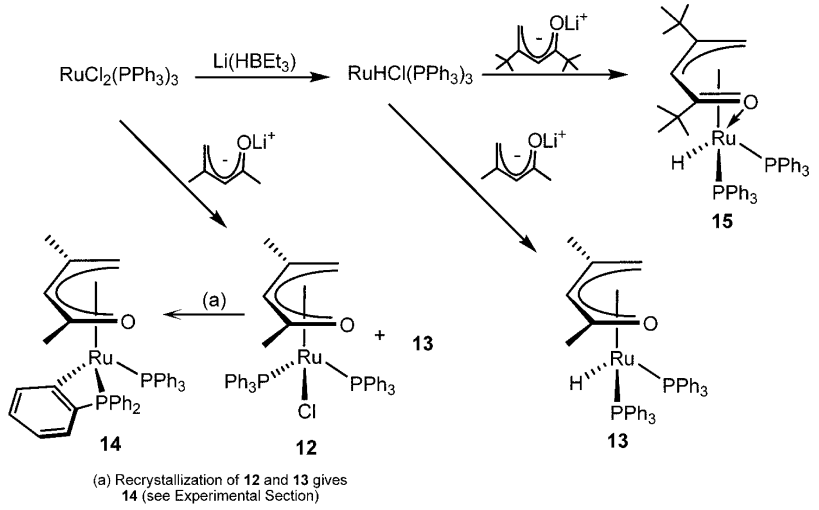
Scheme 4



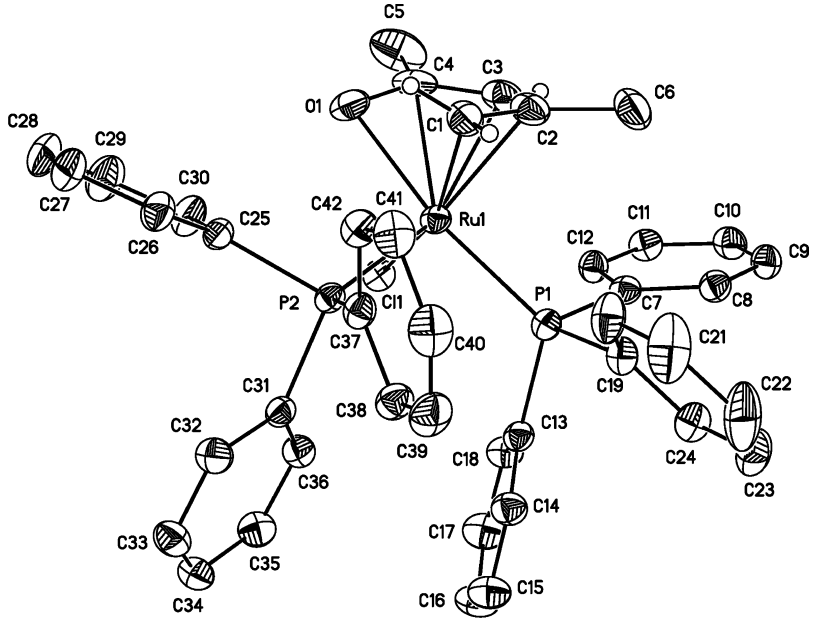


Figure 5. Perspective view of compound **12** drawn at the 45% probability level. Most hydrogen atoms have been omitted for clarity.

(η^3-azapentadienyl)$Co(PMe_3)_3$,[40] and $Cp^*Ru(\eta^3$-azapentadienyl)$(Cl)_2$[30] have been reported.

As already mentioned, in general terms, the isolation of the azapentadienyl derivatives is more difficult than that of the corresponding pentadienyl compounds and the influence of the sustituent R is relevant in the chemistry involved.

Oxopentadienyl Compounds. The oxopentadienyl compounds $[\eta^5$-$CH_2C(Me)CHC(Me)O]RuCl(PPh_3)_2$ (**12**)[3b] and $[\eta^5$-$CH_2C(Me)CHC(Me)O]RuH(PPh_3)_2$ (**13**)[3b] were formed, in THF, from $RuCl_2(PPh_3)_3$ and $Li[CH_2C(Me)CHC(Me)O]$ in 14% and 15% yields, respectively (Scheme 4). Monitoring the reaction through ^{31}P NMR spectroscopy showed immediate formation of **12** and **13**, in a 0.45:0.55 ratio, along with $[RuCl_2(PPh_3)_2]_2$[36] (sharp AB pattern observed at δ = 49.6, 52.6, J_{AB} = 36.5 Hz, C_6D_6) and free PPh_3. No further improvement in either selectivity or yield of **12** was achieved, even though several attempts were made.

In order to clarify why **13** had been formed and in order to prepare compound **12** selectively, the reactions of $RuCl_2(PPh_3)_3$ with mesityl oxide and either K_2CO_3, Li_2CO_3, or NEt_3 in THF were carried out. In fact, the formation of **12** was observed, but not selectively. When NEt_3 or Li_2CO_3 was used for the reaction, the formation of $RuHCl(PPh_3)_3$ was confirmed by ^{31}P NMR spectroscopy. Previously, it has been established in several reports that $RuHCl(PPh_3)_3$ is readily formed when $RuCl_2(PPh_3)_3$ in THF is exposed to the presence of a reducing agent. It has also been proposed that the source of the hydride ligand is the solvent.[18b] According to these observations, we could conclude that the formation of **13** is due to the presence *in situ* of $RuHCl(PPh_3)_3$, which has been consequently formed by the lithium oxopentadienide.

Conversion of **13** back to **12** is achieved from simple dissolution in $CDCl_3$. It should be mentioned that **12** decomposes easily in solution, while the hydride derivative **13**, in a sealed NMR tube, is stable at least for three months in C_6D_6.

In contrast to the mixture of products (**12** and **13**) obtained by using $RuCl_2(PPh_3)_3$, compound **13** could easily be obtained in 65% yield, from the reaction of $RuHCl(PPh_3)_3$ with

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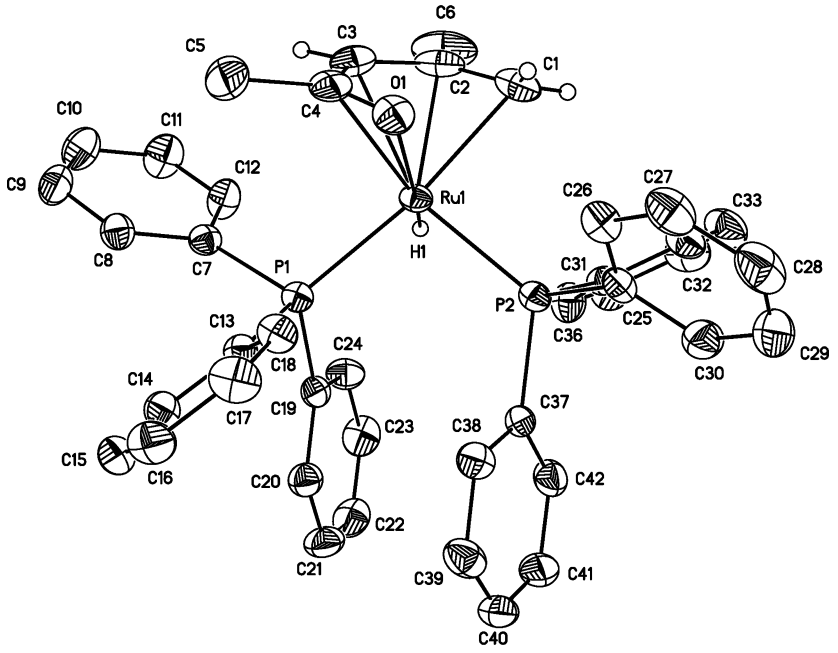

Figure 6. Perspective view of compound **13** drawn at the 45% probability level. Most hydrogen atoms have been omitted for clarity.

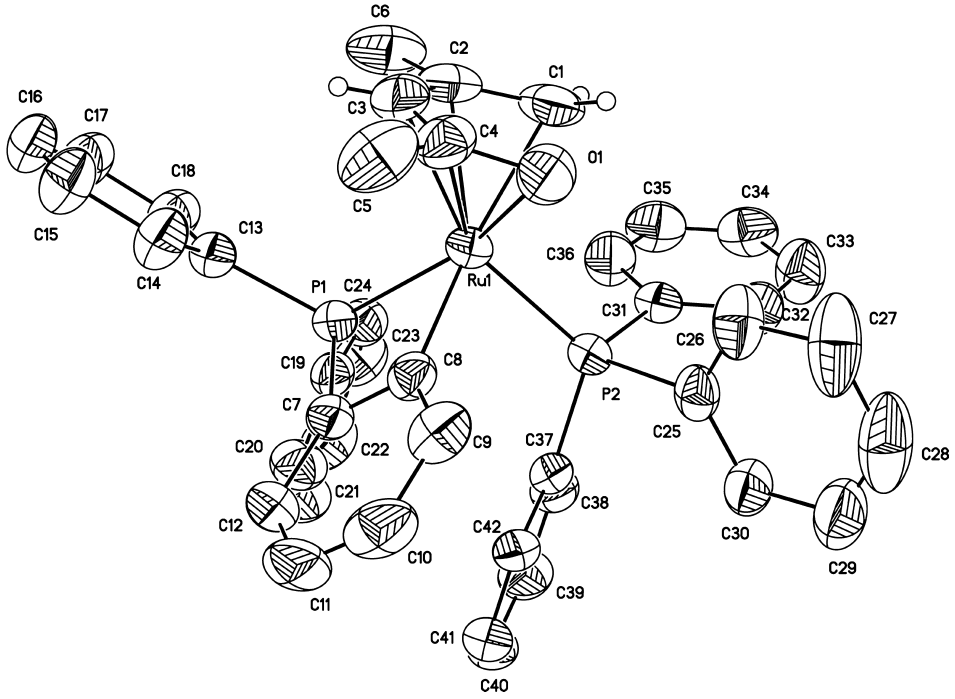

Figure 7. Perspective view of compound **14** drawn at the 45% probability level. Most hydrogen atoms have been omitted for clarity.

$Li[CH_2C(Me)CHC(Me)O]$ in THF. There was no evidence of **12**, which suggests that the preference of formation of LiCl vs LiH induces a more selective reaction. This result contrasts with what was found in the related azapentadienyl chemistry, *vide supra*. The presence of the ν(Ru−H) stretch was observed, as a medium intensity band at 2051 cm^{-1} in the IR spectrum.

During an attempt to separate compounds **12** and **13** by column chromatography, through elution with diethyl ether, an oily residue was obtained and subsequently dissolved in C_6D_6. According to the ^1H NMR spectrum, a mixture was still present, and pentane was then added to the NMR sample, which led to formation of a few single crystals after several days at −5 °C.[41] The X-ray diffraction study of the single crystal showed the formation of the orthometalated product (η^5-$CH_2C(Me)$-$CHC(Me)O)Ru(C_6H_4PPh_2)(PPh_3)$ (**14**), which is the oxopentadienyl complex analogue to **4′**. It should have been formed as a consequence of the elimination of HCl or H_2 from **12** or **13**, respectively. According to the chemistry discussed for the pentadienyl derivatives **2** and **3** and the azapentadienyl derivative **8** (*vide supra*), we propose that C−H activation of **12** is more likely. The solid state structures of the acyclic half-sandwich compounds **12**, **13**, and **14** may be seen in Figures 5, 6, and 7, respectively, while pertinent bonding parameters are contained in Tables 5 and 6 and will be discussed below. The basic

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Table 5. Crystal Data and Experimental Parameters for Compounds 12−15

	12	13	14	15
formula	$C_{42}H_{39}OP_2ClRu$	$C_{42}H_{40}OP_2Ru$	$C_{94}H_{92}O_3P_4Ru_2$	$C_{48}H_{52}OP_2Ru$
fw	758.19	723.75	1595.70	807.91
crystal syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*21/*n*	*P*21/*c*	*P*21/*n*	*P*21/*n*
a (Å)	10.5927(2)	14.6304(2)	10.86590(10)	19.6864(3)
b (Å)	17.9038(4)	10.2836(2)	23.4861(4)	20.2907(4)
c (Å)	19.2645(4)	23.7864(5)	15.9331(2)	21.8553(5)
β (deg)	105.0960(1)	102.8860(1)	94.5690(10)	107.2420(1)
V (Å^3)	3527.42(13)	3488.61(11)	4053.17(9)	8337.8(3)
Z	4	4	2	8
D_{calc} (g/cm^3)	1.428	1.378	1.307	1.287
radiation, wavelength	Mo K*α*, *λ* = 0.71073 Å	Mo K*α*, *λ* = 0.71073 Å	Mo K*α*, *λ* = 0.71073 Å	Mo K*α*, *λ* = 0.71073 Å
size (mm)	0.50 × 0.25 × 0.20	0.25 × 0.25 × 0.12	0.40 × 0.20 × 0.15	0.15 × 0.1 × 0.05
index range	$-13 \le h \le 13$	$-18 \le h \le 18$	$-14 \le h \le 14$	$-24 \le h \le 24$
	$-23 \le k \le 22$	$-13 \le k \le 13$	$-30 \le k \le 30$	$-24 \le k \le 24$
	$-25 \le l \le 21$	$-30 \le l \le 27$	$-20 \le l \le 20$	$-26 \le l \le 26$
F(000)	1560	1496	1656	3376
2*θ* range (deg)	6.84−54.98	6.86−54.98	5.02−54.98	6.80−51.98
no. reflns, collected	27462	24205	64110	58347
no. unique reflns	7976 (R_{int} = 0.0444)	7946 (R_{int} = 0.0507)	9260 (R_{int} = 0.0926)	16302 (R_{int} = 0.1335)
no. obsd reflns	6099 ($F > 4\sigma(F)$)	5726 ($F > 4\sigma(F)$)	5472 ($F > 4\sigma(F)$)	9450 ($F > 4\sigma(F)$)
abs corr (T_{max}, T_{min})	0.8820, 0.7390	0.9344, 0.8699	0.9286, 0.8247	0.9529, 0.8676
R	0.0394	0.0402	0.0647	0.0706
R_w	0.0785	0.0670	0.1263	0.1495
wR_2 (all data)	0.0879	0.0759	0.1478	0.1818
gof	1.075	1.012	1.037	1.012

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compounds 12−15

bond lengths (Å)					bond angles (deg)				
	12	13	14	15[a]		12	13	14	15[a]
C1−C2	1.405(4)	1.399(5)	1.393(8)	1.399(9)	C1−C2−C3	121.7(3)	121.7(3)	121.4(6)	118.8(6)
C2−C3	1.419(5)	1.423(4)	1.426(8)	1.426(9)	C2−C3−C4	124.5(3)	125.2(3)	127.6(6)	125.4(6)
C3−C4	1.421(5)	1.430(4)	1.401(8)	1.441(10)	C3−C4−O1	119.6(3)	122.8(3)	119.9(5)	118.4(7)
C4−O1	1.278(4)	1.275(3)	1.296(6)	1.259(8)	C1−C2−C6	120.1(3)	119.9(3)	120.5(6)	123.8(6)
C2−C6	1.511(5)	1.511(4)	1.506(7)	1.534(9)	C1−C2−Ru1	71.10(18)	73.81(17)	74.5(3)	71.8(4)
C4−C5	1.485(5)	1.514(4)	1.494(8)	1.518(10)	C2−C3−Ru1	69.65(18)	69.38(17)	72.5(3)	69.0(4)
Ru1−C1	2.200(3)	2.240(3)	2.298(5)	2.192(7)	C3−C4−Ru1	65.94(19)	67.99(16)	69.3(3)	59.6(4)
Ru1−C2	2.208(3)	2.182(3)	2.237(5)	2.178(7)	O1−C4−Ru1	64.45(16)	73.47(15)	71.2(3)	62.8(4)
Ru1−C3	2.256(3)	2.229(3)	2.206(5)	2.234(7)	O1−Ru1−P1	163.93(6)	104.64(5)	149.82(11)	103.83(14)
Ru1−O1	2.200(2)	2.3148(16)	2.220(3)	2.302(5)	C3−Ru1−P2	152.20(9)	154.33(9)	157.66(18)	155.07(17)
Ru1−P1	2.2865(8)	2.2913(7)	2.2837(12)	2.2932(17)	C1−Ru1−P1	109.15(10)	171.13(10)	125.3(2)	164.94(17)
Ru1−P2	2.3341(7)	2.2728(8)	2.3193(12)	2.2749(17)	C1−Ru1−P2	90.41(9)	87.41(10)	92.76(16)	91.94(18)
C7−P1	1.857(3)	1.854(3)	1.815(4)	1.848(6)[b]	P1−Ru1−P2	98.88(3)	100.95(3)	96.46(4)	102.59(6)
C25−P2	1.846(3)	1.846(3)	1.832(5)	1.858(7)[c]	O1−Ru1−X	83.91(6)	166.7(10)	92.59(16)	165.2(19)
Ru1−X	2.4544(7)	1.53(2)	2.060(4)	1.61(5)	C1−Ru1−X	159.20(11)	100.4(9)	167.2(2)	97.5(19)
					P1−Ru1−X	89.76(3)	78.3(9)	67.33(13)	78.5(19)
Ru1−C4	2.425(3)	2.329(3)	2.270(5)	2.587(7)	P2−Ru1−X	95.24(3)	80.7(10)	87.47(12)	91.2(19)
					O1−Ru1−P2	96.41(6)	111.06(5)	105.25(10)	102.40(13)

[a]Crystal structure of molecule A described in Figure 8. [b]C19A−Ru1A. [c]C31A−P2A.

geometry of the piano stool structure in **13** is the same as that of **12**, with some distortion resulting from the small hydride ligand.

The oxopentadienyl complexes **12** and **14** show shorter Ru−P1 bond lengths compared to those of Ru−P2, while for **13** both distances are not significantly different. The Ru−Cl distance [2.4544(7) Å] in **12**, the Ru−H distance [1.53(2) Å] in **13**, and the Ru−C distance [2.060(4) Å] in **14** can be compared with the values of similar complexes, such as Cp′RuCl(PPh_3)$_2$ [Cp, 2.453(2),[7c] Cp*, 2.4575(5) Å];[23a] (η^5-C_8H_9)RuCl(PPh_3)$_2$ [2.4462(4) Å];[11a] CpRuH(PPh_3)$_2$ [1.51(4) Å];[22] K[RuH_2(*o*-$C_6H_4PPh_2$)(PPh_3)$_2$] [2.098(11) Å];[42] CpRu(*o*-$C_6H_4PPh_2$)(PPh_3) [2.07(2) Å];[43] and (η^5-CHCHC(R)CHCHCO)(Ru(*o*-$C_6H_4PPh_2$)(PPh_3))·[HOC(CH)$_2$C(R)(CH)$_2$] [R = *t*-Bu, 2.074(4); R = H, 2.083(4) Å].[14]

The oxopentadienyl ligands show, on one hand, the following Ru−O bond lengths and long Ru−C4 distances for compounds **12**, [2.200(2), 2.425(3) Å], **13** [2.315(2), 2.329(3) Å], and **14** [2.220(3), 2.269(5) Å], which are longer than those of

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the half-open sandwich compounds, such as Cp*Ru(2,4-Me_2-η^5-oxopentadienyl) [2.167(5), 2.170(7) Å];[44] (η^5-C_5Me_4CHO)-Ru(2,4-Me_2-η^5-oxopentadienyl) [2.152(5), 2.196(7) Å];[44] and [Cp*Ru(2,4-Me_2-η^5-oxopentadienyl)]$_2$(μ^2-$ZnCl_2$) [2.169(3), 2.165(3); 2.178(5) and 2.172(5) Å].[31] On the other hand, comparison of the C4−O1 bond lengths between the acyclic half-sandwich compounds [1.278(4) Å, **12**; 1.275(3) Å, **13**] and those of half-open sandwich compounds [Cp*Ru(2,4-Me_2-η^5-oxopentadienyl) [1.348(11) Å][44] and [Cp*Ru(2,4-Me_2-η^5-oxopentadienyl)]$_2$(μ^2-$ZnCl_2$) [1.392(6) and 1.332(6) Å][31]] reveals shorter values for the piano stool compounds, except for (η^5-C_5Me_4CHO)Ru(2,4-Me_2-η^5-oxopentadienyl) [1.294(8) Å].[44]

The crystal structure result of the oxocyclohexadienyl complex (η^5-CHCHCHCHCHCO)$RuCl(PPh_3)_2$[14] is presented as an overhead view with the chloro ligand preferentially residing on the same side as the more electronegative oxygen atom (as in compounds **9** and **12**; see Chart 1), whereas, for the cyclic ligand complex, this position corresponds to the "open" side of the oxocyclohexadienyl ligand, having both PPh_3 ligands underneath the cyclohexadienyl "edges", which contrasts with all the acyclic compounds described in Chart 1. The oxocyclohexadienyl complex has the most symmetric Ru−PPh_3 bond lengths [Ru−P1, 2.355(3) and Ru−P2, 2.353(3) Å] compared to **12** [2.2865(8), 2.3341(7) Å], while the P1−Ru−P2 bond angles are quite similar. This should be a consequence of the more symmetric hydrocarbon skeleton of the oxocyclohexadienyl ligand, compared to the asymmetric and substituted oxopentadienyl ligand in **12**. Compound **13** confirmed the position of the hydride being *trans* to the oxygen center, as suggested by the crystal structure of [η^5-CH_2C(Ph)CHCO-(Ph)]RuH(*R*-binap), in which the hydride was not located.[13]

The formation of the four-membered ring in **14** distorts the geometry at Ru, C8, C7, and P1, but not as significantly as was found in the orthometalated compound $CpRu(C_6H_4PPh_2)$-(PPh_3).[43]

On the basis of the X-ray diffraction studies of **12**−**14**, there is a similar interaction of the oxopentadienyl ligands as described in the resonance hybrid **I** in Chart 2, while the study in solution for **12** and **13** is more consistent with a contribution from resonance hybrid **II** (Chart 2) as observed from ^{1}H and ^{13}C NMR spectroscopy, in which there is an allylic bond with ruthenium, along with donation of one electron pair from the oxygen center. This result is in agreement with the planarity differences found for the heterodienyl ligands (*vide infra*).

The ^{1}H NMR spectrum of **13** features a metal-hydride signal at δ −20.65 ppm. The characteristic doublet of doublets pattern arises from coupling to the phosphine ligands (J_{PH} = 29.7 Hz). Hydrogen atoms $H1_{anti}$ and $H1_{syn}$ are coupled to the hydride with J = 4.4 Hz, indicating that they are on the same side of the molecule, and the hydride resides *trans* to the oxygen atom. The aromatic region shows two sets of *ortho*-hydrogen atoms (assigned as A and B in Tables 1 and 2, for which B is at higher frequency than A because of its proximity to the oxygen atom), which reflects the asymmetry of the molecule. However, the *meta*- and *para*-hydrogen signals also overlap considerably. In contrast, the aromatic region in compound **12** reflects lower symmetry, as revealed by four nonequivalent sets of aromatic resonances. Three rigid phenyl groups were assigned as A and one dynamic system as B. The assignment was carried out by 2D NMR experiments, as well as through variable temperature spectroscopic studies (−90 to 80 °C). ^{31}P NMR irradiation of the doublets at 55.7 and 38.6 revealed correlation with the A and B phenyl groups, respectively.

The ^{13}C NMR spectra of **12** and **13** showed the characteristic carbonyl resonances for C4 at δ 181.9 and 169.5 ppm, whereas the chemical shifts of C4 in fully delocalized coordinated ligands, such as (2,4-dimethyl-η^5-oxopentadienyl), are found at δ = 135.0−140.0, while those with (2,4-dimethyl-η^3-oxodienyl) are higher than 200 ppm.[44] The typical chemical shift ranges for C1−C3 are observed for the corresponding allylic carbons.[31,32] Thus, we could propose that the oxopentadienyl ligand in these half-sandwich complexes, especially for **12**, invokes a contribution of the resonance hybrid **II** (Chart 2), which coordinates through the lone pair of the oxygen atom and with the η^3 allyl fragment C1−C3. This type of bonding has been previously observed for several cationic oxodienylrhodium complexes,[45] as well as in the azapentadienyl complexes previously discussed.

The bulky [1-3,5-η-CH_2C(*t*-Bu)CHC(*t*-Bu)O]$RuH(PPh_3)_2$ (**15**) analogue to **13** can be prepared in reasonable yield (64%) using a similar procedure involving $RuHCl(PPh_3)_3$ and Li[CH_2C(*t*-Bu)CHC(*t*-Bu)O], although a considerably longer reaction time is required (∼12 h) (Scheme 4). The NMR spectra are consistent with the formulation of **15** as an η^3-allyl-η^1-O complex, similar to the descriptions for the azapentadienyl complexes, and to some extent the oxopentadienyl derivatives **12** and **13**. The carbonyl atom C4 (δ = 206.6 ppm) is observed at higher frequency compared to **12** (δ = 181.9 ppm) and **13** (δ = 169.5 ppm), suggesting that there is no relevant interaction with the ruthenium atom. The ^{31}P NMR spectrum shows two doublets for **15** (δ = 50.8, 60.0 ppm with J = 18.0 Hz), along with two minor signals detected as two pairs of doublets (δ = 48.6, 59.4 ppm with J = 22.3 Hz. and δ = 50.7, 62.0 ppm with J = 18.0 Hz) in a 1.0:0.13:0.10 ratio, respectively. According to the similar chemical shifts of both minor species, we propose similar distributions and arrangements of the H and PPh_3 ligands in the three-legged piano stool structure, as a result of the congestion by the presence of the *t*-Bu groups in the oxopentadienyl ligand. Unsuccessful attempts were made to synthesize the chloro derivative [1-3,5-η-CH_2C(*t*-Bu)CHC-(*t*-Bu)O]$RuCl(PPh_3)_2$ from $RuCl_2(PPh_3)_3$, and the synthetic failure is attributed to the great steric bulk of both *t*-butyl substituents in the oxopentadienyl ligand and two triphenylphosphine ligands in the coordination sphere. This result is consistent with our observations related to compounds **2**, **8**, and **12**, which are within the limits of steric tolerances and undergo facile orthometalation reactions.

While **13** could be transformed to **12** (*vide supra*), compound **15** reacts differently in $CHCl_3$. In the proton NMR spectrum, two pairs of doublets were observed, with similar intensities, as was observed in the solution chemistry of **13** (*vide supra*), but without evidence of the formation of the chloro derivative [1-3,5-η-CH_2C(*t*-Bu)CHC(*t*-Bu)O]$RuCl(PPh_3)_2$. After one day, compound **15** in $CHCl_3$ or CCl_4 had decomposed, and the oxopentadienyl ligand decoordinated. There is no evidence of orthometalation, and this fact is attributed to the labile bond between the bulky oxopentadienyl ligand and the ruthenium atom.

Compound **15** shows two independent molecules in the asymmetric unit, which are isostructural with **12**−**14**. Molecule **15**A is described in Figure 8 and Tables 5 and 6. The long distances observed for Ru−C4 [2.587(7) Å], RuA−C4A [2.623(8) Å], and Ru−C4 confirm that the predominant structural feature in the oxopentadienyl ligand in **15** involves the 1-3,5-η bonding mode with the metal atom, as described in Scheme 4. The Ru1−O1 bond length [2.302(5) Å] is similar to that in the hydride derivative **13** [2.315(2) Å] and longer than the chloro or the orthometalated complexes **12** [2.200(2) Å] and **14** [2.220(3) Å], respectively.

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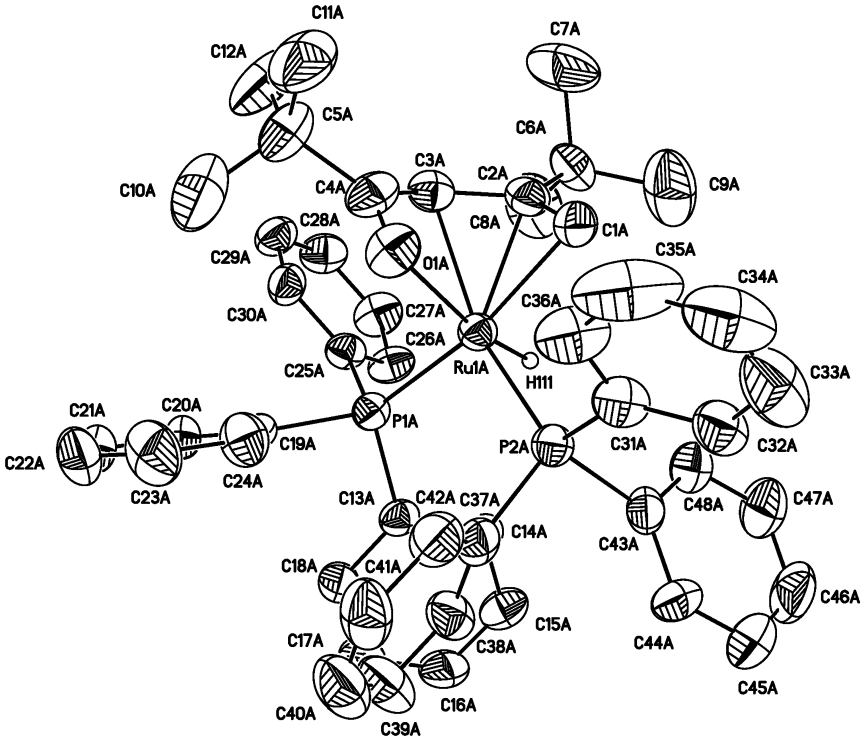

Figure 8. Perspective view of compound **15** drawn at the 45% probability level. Hydrogen atoms have been omitted for clarity, except the hydride.

CONCLUSIONS

In accordance with structural results, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic studies at variable temperatures showed that the ground states of the half-sandwich complex were all asymmetric in solution. Electronic factors have been implicated as being most responsible for leading to a preference for one isomeric form over another. The presence of the open edge for the acyclic pentadienyl ligands leads to unused metal orbital density in that area, leading to an upward tilt of the proximate ligand toward that open edge.[46] The magnitude of the tilts may be readily gauged by a comparison of the idealized *trans* P−Ru−X angles for the two phosphine (or other) ligands. For the edge-located phosphines, these angles fall in a relatively narrow range of 150.88(11)°−155.07(17)°, as compared to values ranging from 163.93(6)° to 178.18(7)° for the other phosphines, in complexes **3**, **5**, **6**, **12**, **13**, and **15**. The smaller values in the former range indicate that their phosphine ligands have been electronically directed upward toward the heteropentadienyl ligand into a sterically crowded region, thus resulting in a rather narrow range of values. In contrast, the alternative location maintains the phosphine ligands further from the hetero-pentadienyl ligand, and there is thus more flexibility in the phosphine positions, and a corresponding greater range in angles. Previous studies have indicated the following relative preferences for ligands to be positioned under the open dienyl edge:[46] R_3P > CO > I, CH_3. This trend is consistent with the observations herein, considering H and Cl to be relatively similar to CH_3 and I, respectively. It has also been previously observed that a smaller phosphine will have a greater tendency than a larger phosphine to be located under the open edge,[4] which is consistent with the structures of complexes **5** and **6**.

Investigations through ^{31}P NMR spectroscoscopy were particularly informative, indicating that the J_{PP} values for all compounds with Ru−Cl bonds were found to vary from ∼30 to 38 Hz, while those compounds with a hydride ligand or orthometalation showed J values of ∼18−24 Hz. In particular, the J_{PC} values found by ^{13}C NMR spectroscopy of the terminal and central carbon atoms allow us to assign a preferred orientation of the substituents in the piano stool structure relative to the heteropentadienyl ligand (Chart 1).

The steric influences of the Me, Ph, and *t*-Bu substituents on the 2,4-substituted-oxopentadienyl hydride derivatives **13**, $[\eta^5\text{-}CH_2C(Ph)CHC(Ph)O]RuH(PPh_3)_2$,[13] and **15** are reflected through diminished J_{PP} values of 24.8, 22.0, and 18.0 Hz, respectively. In contrast, the ^{31}P NMR chemical shifts did not follow any trend for these hydride complexes. The orthometalated carbon atom or the H or Cl substituents in the three-legged piano stool oxopentadienyl complex showed greatly modified values of $\Delta\delta$ (80.5, 17.1, and 11.5 for **14**, **12**, and **13**, respectively).

The study of the reactivity of pentadienyl compounds **1** and **2**, as well as azapentadienyl **7**, has given spectroscopic NMR evidence of a different behavior compared to the pentadienyl complex **3** and the oxopentadienyl-derivatives **13** and **15**. While the substitution reactions of one PPh_3 in the chloro complexes **1**, **2**, and **7** proceeded readily, to afford the corresponding chiral complexes **5**, **6**, and **10**, apparently resulting from the high degree of steric interaction between the two PPh_3 ligands, compounds **3**, **13**, and **15**, with much smaller hydride ligands, lessened the interaction between these two PPh_3 ligands, and thus substitution did not occur.

The chloro-ruthenium pentadienyl and azapentadienyl complexes **1**, **2**, **5**−**8**, and **10** do not undergo a second substitution for the remaining bulky triphenylphosphine ligand. This behavior differs from those of the cyclic derivatives $Cp'RuCl(PPh_3)_2$ (Cp′ = Cp, Cp*), which can afford the corresponding disubstituted $Cp'RuCl(PHPh_2)_2$. These results seem to emphasize the importance of steric strain, and that the dissociation of the second PPh_3 is at least less favorable. If forcing conditions are employed, such as higher temperatures or an increase in the equivalents of $PHPh_2$ in the reaction mixture, one observes preferential loss of the heteropentadienyl ligand, rather than the loss of a PPh_3 ligand.

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It is well-known that steric crowding is significantly greater for 2,4-Me_2-pentadienyl ligands compared to Cp and even Cp*. Evidence of this is also provided by the easier orthometalation of these acyclic ligands compared to their cyclic analogues.

According to the crystalline structures, the range of dihedral angles between the C1−C2−C3−C4 and C2−C3−C4−X planes (X = C5, N, O) of the complexes illustrated that the nonplanarity increases in the following order: **3** [0.9(3)°] ∼ **6** [1.0(2)°] ∼ **5** [1.4(4)°] < **14** [2.3(4)°] ∼ **4** [2.4(5)°] ∼ **13** [2.5(2)°] < **12** [7.8(3)°] ≪ **15** [15.4(7)°, 19.6(6)°] ≪ **7** [23.66°(30)]. Two extreme examples in the trend described here are provided by the homoleptic complex (2,4-dimethyl-η^5-oxopentadienyl)$_2$Ru (0.045°)[47] and the half-open sandwich Cp*Ru(O_2)(2,4-dimethyl-η^3-oxopentadienyl) (∼90°).[44] Concerning the ordering of relative ligand planarities in the oxodienyl complexes, as they are located between the pentadienyl and azapentadienyl complexes, there seems to be a combination of two resonance forms as described in Chart 2. It is also relevant to mention that for the oxodienyl **15** there is a much greater degree of nonplanarity than in the other oxodienyls. This is explained due to the steric repulsion between the *t*-Bu groups and the ligands below them, which destabilized the resonance contribution involving the η^5 coordination, thereby favoring the nonplanar alternative with more oxygen lone pair donation, which leads to a greater separation between the *t*-Bu groups and proximate ligands.

Perhaps the most important future developments in the chemistry of these acyclic half-sandwich ruthenium-heteropentadienyl complexes will involve gaining an understanding of their reactivity trends, which differ significantly from those of their cyclic analogues.

EXPERIMENTAL SECTION

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were dried by standard methods (hexane and pentane with CaH_2, diethyl ether and THF with Na/benzophenone, CH_2Cl_2 and $CHCl_3$ with $CaCl_2$, benzene and toluene with Na) and distilled under nitrogen prior to use. The compounds **1**,[4] $Me_3SnCH_2CH{=}CHCH{=}N(t\text{-}Bu)$,[30] Li[$CH_2C(Me)CHC(Me)O$],[44] $CH_2CHCHCHCH_2SnBu_3$,[48] $CH_2C(Me)CHC(Me)CH_2SnMe_3$,[32] $RuCl_2(PPh_3)_3$,[49] and $RuHCl(PPh_3)_3$[50] were prepared according to literature procedures. $Me_3SnCH_2CH{=}CHCH{=}N(Cy)$ and Li[$CH_2C(t\text{-}Bu)CHC(t\text{-}Bu)O$] were prepared in the same manner as $Me_3SnCH_2CH{=}CHCH{=}N(t\text{-}Bu)$ and Li[$CH_2C(Me)CHC(Me)O$], respectively. All other chemicals were used as purchased from Sigma-Aldrich, Strem Chemicals, Merck, and J. T. Baker. Elemental analyses were performed with a Thermo-Finnigan Mod. Flash 1112 combustion analyzer, at the Chemistry Department at Cinvestav and Desert Analytics, Tucson, Arizona, USA. Infrared spectra were recorded on FT-IR Perkin-Elmer16F and 1600 spectrometers using KBr pellets or methylene chloride. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Jeol GSX-270 and Eclipse 400 MHz or Bruker 300 MHz spectrometers in deoxygenated, deuterated solvents. NMR chemical shifts are reported relative to their residual protium resonances in the solvent, and ^{31}P NMR chemical shifts relative to 85% H_3PO_4. Mass spectra were recorded on a Hewlett-Packard HP-5990A spectrometer, while high resolution mass spectra were obtained by LC/MSD TOF spectroscopy on an Agilent Technologies instrument with APCI as the ionization source and FAB or ESI at the University of Washington, St. Louis, Missouri; *m*/*z* values are given relative to the ^{102}Ru, ^{35}Cl, and ^{119}Sn isotopes. Melting points were determined in a Melt-Temp Gallenkamp (digital) instrument and are uncorrected.

Synthesis of (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuCl(PPh_3)_2$ (2). A THF solution (200 mL) of $RuCl_2(PPh_3)_3$ (945.0 mg, 0.99 mmol) was filtered, and 2,4-dimethyl-1-trimethyltin-2,4-pentadiene (760.0 mg, 2.96 mmol) added. The mixture was stirred for 1.5 h, in an oil bath at ∼65 °C. After that, the brown solution turned amber, the mixture was filtered, and the solvent was removed under vacuum. The foamy amber residue was washed with pentane (20 mL × 3), giving an orange solid which was dried under vacuum. The ^{31}P NMR spectrum in $CDCl_3$ showed an A_2 pattern with δ = 36.5 (*vide supra*), along with resonances for **4**, PPh_3, and traces of **4′**. MS: 755 (0.8) [M^+], 751 (1.5), 720 (2.7), 625 (0.5), 557 (2.2), 538 (3.1), 524 (2.5), 262 (100.0), 183 (23.0).

Synthesis of (η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuH(PPh_3)_2$ (3). In a Schlenk flask equipped with a stir bar, $RuHCl(PPh_3)_3$ (1.09 g, 1.20 mmol) was kept under vacuum for 15 min, and toluene (200 mL) was added. The 2,4-dimethyl-1-trimethyltin-2,4-pentadiene (1.0 g, 3.8 mmol), previously dissolved in toluene (1.0 mL), was added to the purple solution and the mixture was stirred at room temperature overnight. The resulting amber-yellow solution was filtered, the solvent was totally evaporated, and the remaining oily solid was washed several times with pentane (∼200 mL) and filtered, and the volume was reduced until ∼50 mL remained and a pink salmon solid precipitated. After filtration, the solid was washed again with pentane (3 × 10 mL) and dried under vacuum, giving a beige powder with 31% yield (0.21 g, 3.0 mmol). Single crystals were obtained from pentane at −5 °C. Mp: 171−172 °C. IR (KBr, cm^{-1}): 1933 (m, br), 1589 (s, br), 1491 (s), 1443 (vs), 1189 (vs), 1116 (vs), 1085 (w), 1047 (w), 1027 (w), 1000 (w), 871 (w), 825 (m), 750 (w), 719 (m), 696 (vs), 541 (vs). ESI + TOF: *m*/*z* 721.1726; error ppm 0.6207; DBE 24.5. Anal. Calcd for $C_{43}H_{41}P_2Ru$: C, 71.54; H, 5.86. Found: C, 71.25; H, 6.58.

Synthesis of (η^5-$CH_2C(Me)CHC(Me)CH_2$)$Ru(C_6H_4PPh_2)(PPh_3)$ (4). A THF solution (100 mL) of $RuCl_2(PPh_3)_3$ (777.0 mg, 0.81 mmol) was filtered, and 2,4-dimethyl-1-trimethyltin-2,4-pentadiene (630.0 mg, 2.43 mmol) previously dissolved in THF (3 mL) was added. The mixture was kept under reflux for 2.5 h. After that, the brown solution turned amber. The mixture was filtered, and the solvent was removed under vacuum. The remaining oily yellow-brown residue was purified on an alumina column (25.0 cm × 1.5 cm) through elution with toluene. A lemon-yellow fraction was obtained after a second chromatographic elution with diethyl ether. The solvent was removed under reduced pressure; this gave compound **4** as a yellow powder in 10.5% yield (65.0 mg, 0.090 mmol). Single crystals were obtained from C_6D_6 and EtOH at room temperature. Mp: 155−157 °C. IR (KBr, cm^{-1}): 3035 (s, br), 2913 (s, br), 2380 (vw), 2274 (w, br), 1951 (dw, br), 1894 (w, br), 1810 (w, br), 1663 (w, br), 1584 (m), 1552 (m), 1478 (s), 1432 (vs), 1371 (m), 1307 (w), 1265 (m), 1182 (m), 1155 (w), 1089 (vs), 1027 (s), 904 (w), 857 (m), 803 (m), 741 (vs), 695 (vs) 515 (vs), 462 (m), 432 (w). ESI + TOF: *m*/*z* 720.1645; error ppm 0.2397; DBE 25.0. Anal. Calcd for $C_{43}H_{40}P_2Ru$: C, 71.65; H, 5.73. Found: C, 71.91; H, 6.11.

Synthesis of (η^5-$CH_2CHCHCHCH_2$)$RuCl(PPh_3)(PHPh_2)$ (5). To a toluene solution (50 mL) containing 1.00 g of compound **1** (1.37 mmol) was added 0.26 g (0.24 mL, 1.37 mmol) of $PHPh_2$ with continuous stirring for 12 h at room temperature, which led to a change in color from pale-yellow to a yellow-orange solution. The solvent was removed under vacuum, and the oily yellow product was dissolved in the minimum amount of diethyl ether and then chromatographed on a silica gel column (1.5 cm × 30 cm) with a mixture of hexane−diethyl ether (1:1). After the volume was reduced, a yellow solid precipitated and **5** was obtained in 75% yield (672.0 mg, 1.03 mmol; mp: 178−181 °C, without decomposition). Single crystals were obtained by recrystallization from methylene dichloride/hexane (1:4). IR (KBr, cm^{-1}): 3054 (s), 3018 (w), 2963 (s), 2866 (w), 2725 (m), 2346 (w), 2308 (m), 1952 (br), 1810 (vw), 1744 (vw), 1663 (vw), 1621 (vw), 1572 (m), 1480 (s), 1434 (vs), 1310 (w), 1261 (vs), 1185 (m), 1091 (vs), 1025 (vs), 925 (m), 882 (s), 802 (vs), 742 (vs), 695 (vs), 512 (vs), 457 (vw), 424 (m). MS (FAB, *m*-nitrobenzyl alcohol/toluene matrix): $RuC_{35}H_{34}ClP_2$: 653.0868 (calculated), *m*/*z* 653.0855. Anal. Calcd for $C_{35}H_{33}ClP_2Ru$: C, 64.46, H, 5.06. Found: C, 64.50, H, 5.18.

Synthesis of [(η^5-$CH_2C(Me)CHC(Me)CH_2$)$RuCl(PPh_3)(PHPh_2)$] (6). A THF solution (100 mL) of $RuCl_2(PPh_3)_3$ (935.0 mg, 0.98 mmol) was filtered, and 2,4-dimethyl-1-trimethyltin-2,4-pentadiene (757.0 mg, 2.92 mmol), previously dissolved in THF (3 mL), was added.

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The mixture was maintained under mild reflux (oil bath ~65 °C) for 1.5 h. By that time, the brown solution had turned amber. The mixture was filtered and the solvent was removed under vacuum. The remaining oily amber residue of **2** was dissolved in toluene (50 mL) and $PHPh_2$ in hexane (10%) (1.2 mL, 1.24 g, 0.66 mmol). The reaction mixture was heated in an oil bath to ~60 °C for 15 min, and evaporation of the toluene under vacuum afforded an oily, amber residue, which was chromatographed on deactivated alumina[51] via elution with hexane, followed by diethyl ether, to afford compound **4** along with PPh_3 and **6** along with $OPPh_3$, respectively. The solvent was removed under reduced pressure; this gave compound **7** as an orange-yellow powder in 10.6% yield (75.0 mg, 0.11 mmol). Decomposition occurred at 160 °C without melting. Recrystallization in CH_2Cl_2/pentane (1:3) at −5 °C afforded single crystals. IR (KBr, cm^{-1}): 3053 (s), 3002 (w), 2910 (m), 2853 (w), 2346 (w), 1964 (w, br), 1899 (w, br), 1816 (w, br), 1664 (vw), 1620 (w), 1586 (m), 1483 (s), 1435 (vs), 1370 (m), 1313 (m), 1281 (m), 1186 (m), 1091 (s), 1027 (s), 1000 (m), 904 (s), 866 (s), 742 (vs), 696 (vs), 527 (vs), 508 (vs), 479 (w), 461 (w), 422 (m). MS: 680 (31.3) [M^+], 645 (34.4), 585 (3.7), 548 (14.0), 495 (23.4), 460 (20.2), 418 (11.0), 391 (7.0), 380 (12.4), 363 (14.1), 307 (22.0), 289 (14.6), 262 (13.3), 183 (15.2), 154 (100.0), 136 (71.2). Anal. Calcd for $C_{37}H_{37}ClP_2Ru$: C, 65.34, H, 5.48. Found: C, 65.47, H, 5.71.

Synthesis of [1-3,5-η-$CH_2CHCHCHN(Cy)$]$RuCl(PPh_3)_2$ (7). A THF solution (20 mL) of $RuCl_2(PPh_3)_3$ (631.0 mg, 0.59 mmol) was filtered, and $Me_3SnCH_2CHCHCHN(Cy)$ (206.7 mg, 0.66 mmol), previously dissolved in THF (1 mL), was added. The mixture was stirred at room temperature for 6 h. The red-brown coloration of the solution remained after all this time. The mixture was filtered, and the solvent was removed under vacuum. The foamy red-brown residue was washed with hexane (300 mL), giving an orange solution. The volume was reduced to ~150 mL and cooled overnight at −4 °C, to afford a microcrystalline brick-red precipitate, which after filtration and drying under vacuum gave 181.2 mg (0.22 mmol) (37% yield). Single crystals were obtained from recrystallization with diethyl ether at −5 °C. Mp: 157−158 °C. IR (KBr, cm^{-1}): 2672 (w, br), 2352 (m, br), 2270 (w, br), 2160 (w, br), 1969 (m, br), 1896 (w, br), 1818 (m, br), 1734 (w), 1679 (w), 1589 (m), 1571 (w), 1481 (vs), 1433 (vs), 1393 (m), 1362 (w), 1336 (w), 1301 (m), 1260 (m), 1185 (s), 1153 (m), 1121 (m), 1089 (vs), 1029 (s), 988 (s, br), 929 (m), 905 (w), 845 (m), 744 (vs), 697 (vs). ESI + TOF: m/z 817.2411 error 0.064 ppm; DBE 25.5. Anal. Calcd for $C_{46}H_{46}NClP_2Ru$: C, 68.09; H, 5.71. Found: C, 67.94; H, 5.90.

Synthesis of [1-3,5-η-$CH_2CHCHCHN(t\text{-}Bu)$]$RuCl(PPh_3)_2$ (8). A THF solution (30 mL) of $RuCl_2(PPh_3)_3$ (880.0 mg, 0.91 mmol) was filtered, and $Me_3SnCH_2CHCHCHN(t\text{-}Bu)$ (290.0 mg, 1.01 mmol) previously dissolved in THF (1 mL) was added. The reaction mixture was kept under reflux for 2.5 h. The red-brown solution turned wine-red after this time. The mixture was filtered, and the solvent was removed under vacuum. The foamy wine-red residue was dissolved in the minimum amount of THF, and thin-layer chromatography was carried out with alumina plates and a mixture of hexane/diethyl ether (1:1), leading to separation of pink and pale orange bands. The latter was extracted with THF, and a second round of thin layer chromatography on alumina, with elution by the same ratio of solvents, led to two bands, pale-pink and yellow. Extraction of the yellow band with THF and removal of the solvent afforded a bright lemon-yellow solid, which was washed with a small amount of pentane (2 mL). Compound **8** was obtained in 30% yield (260.0 mg, 0.33 mmol; mp: 149−151 °C). IR (KBr, cm^{-1}): 3048 (w), 2964 (w), 2341 (w), 1569 (vs), 1530 (w), 1429 (vs), 1371 (w), 1270 (m), 1214 (m), 1183 (m), 1155 (vw), 1091 (s), 1024 (w), 993 (vw), 912 (vw), 800 (w), 741 (s), 691 (vs), 537 (s), 515 (vs). Anal. Calcd for $C_{44}H_{44}NClP_2Ru$: C, 67.29; H, 5.64. Found: C, 66.55; H, 5.99.

Synthesis of $RuCl(\eta^5\text{-}CH_2CHCHCHO)(PPh_3)_2$ (9). Compound **7** (91.0 mg, 0.11 mmol) was dissolved in the minimum amount of THF and passed down a silica gel column (50.0 cm × 1.5 cm) by elution with diethyl ether. A yellow fraction was collected, and the solvent removed under reduced pressure; this gave compound **9** (40.0 mg, 0.06 mmol) as a bright yellow powder in 49% yield, mp: 119−121 °C). IR (KBr, cm^{-1}): 2387 (w), 1923 (w, br), 1564 (w, br), 1502 (vw), 1482 (vs), 1434 (vs), 1385 (vw), 1308 (m), 1264 (vw), 1231 (vw), 1189 (m), 1152 (w), 1119 (w), 1090 (vs), 1066 (w), 1028 (w), 999 (w), 919 (m, br), 847 (vw), 806 (m, br), 745 (vs), 696 (vs), 521 (vs), 459 (m). ESI + TOF: m/z 695.1190 (-HCl); error ppm −1.60; RDB 24.5.

Synthesis of [1-3,5-η-$CH_2CHCHCHN(Cy)$]$RuCl(PPh_3)(PHPh_2)$ (10). Compound **7** (90.0 mg, 0.11 mmol) was dissolved in THF (15 mL), and $PHPh_2$ (20.5 mg, 171.0 μL, 0.11 mmol) was added. The reaction mixture was stirred for 45 min at room temperature. Filtration of the yellow-orange solution and evaporation of the solvent under vacuum afforded an ochre-yellow powder. This powder was treated with pentane (2 × 10 mL) and then evaporated until dry, giving a yellow-brown solid in 62% yield (50.0 mg, 0.07 mmol). Mp: 177−179 °C. IR (KBr, cm^{-1}): 3049 (s), 2925 (vs), 2853 (m), 2610 (m, br), 2367 (m, br), 2258 (w, br), 2155 (w, br), 1956 (m, br), 1814 (w, br), 1744 (w, br), 1597 (s, br), 1434 (vs), 1370 (w, br), 1308 (w, br), 1256 (w), 1186 (m), 1155 (w), 1119 (w), 1110 (s), 1070 (w), 1026 (m), 930 (w), 897 (m, br), 882 (w, br), 822 (vw), 801 (w), 698 (vs), 623 (vw). ESI + TOF: m/z 700.1829; error ppm 0.0693; DBE 21.5. Anal. Calcd for $C_{40}H_{42}NClP_2Ru$: C, 65.34; H, 5.76. Found: C, 65.00; H, 5.84.

Identification of Isomers [1-3,5-η-$CH_2CHCHCHN(t\text{-}Bu)$]$RuCl(PPh_3)(PHPh_2)$ (11a and 11b) and Compound [η^3-$CH_2CHCHCHN(t\text{-}Bu)$]$RuCl(PHPh_2)_3$ (11c). An NMR tube containing compound **8** (40.0 mg, 0.05 mmol) and 0.6 mL of C_6D_6 was prepared. One equivalent of $PHPh_2$ (11.4 μL, 0.05 mmol) was added into the NMR tube, followed by heating for 2.5 h in an oil bath (70 °C), affording a mixture of isomers **11a** and **11b**. Addition of 2 equiv of $PHPh_2$ (3.0 μL, 0.016 mmol) to an NMR tube with **8** (6.3 mg, 0.008 mmol) in C_6D_6, followed by heating for 10 h in an oil bath (70 °C), led to the formation of the tentatively assigned compound [η^3-$CH_2CHCHCHN(t\text{-}Bu)$]$RuCl(PHPh_2)_3$ (**11c**), along with *trans*-$RuCl_2(PHPh_2)_4$, $OPPh_3$, $OPHPh_2$, and unknown species having chemical shifts at 27.04 (br) and 47.80 (s). Characterization of **11a**, **11b**, and **11c** was carried out exclusively through ^1H and ^{31}P NMR spectroscopy.

Synthesis of [η^5-$CH_2C(Me)CHC(Me)O$]$RuCl(PPh_3)_2$ (12) and [η^5-$CH_2C(Me)CHC(Me)O$]$RuH(PPh_3)_2$ (13). The freshly prepared *in situ* lemon-yellow solution of the lithium oxopentadienide salt (0.34 mmol) was slowly added dropwise to a cold (−110 °C), previously filtered, THF solution (20 mL) of $RuCl_2(PPh_3)_3$ (300.0 mg, 0.31 mmol). After the solution was warmed to room temperature and stirred for 2 h, the volatiles were removed under vacuum. The oily residue was extracted with hexane and filtered, and the solution was evaporated. After chromatography (5 cm × 15 cm) using deactivated alumina (5%)[51] and elution with hexane/toluene (9:1), toluene/CH_2Cl_2 (7:3), and CH_2Cl_2, free PPh_3 and compounds **13** and **12** were obtained, respectively. The orange solid **12** was obtained in 14% yield (31.7 mg, 0.042 mmol), and the yellow solid **13** in 15% yield (35.5 mg, 0.049 mmol). Single crystals of **12** were obtained by recrystallization through diffusion in THF/hexane at −5 °C (mp: 190−195 °C with decomposition). IR (KBr, cm^{-1}): 3053 (s), 2904 (w), 2863 (w), 2582 (w), 2347 (w, br), 1967 (w, br), 1905 (w, br), 1827 (w, br), 1583 (w, sh), 1572 (w), 1482 (s), 1434 (vs), 1384 (m), 1350 (w), 1313 (w), 1277 (s), 1188 (s), 1155 (w), 1117 (s), 1088 (vs), 1029 (s), 1002 (w), 925 (s), 866 (s), 795 (w), 744 (vs), 696 (vs), 620 (s), 583 (m), 520 (vs, br), 466 (m), 424 (s). Anal. Calcd for $C_{42}H_{39}OP_2ClRu$: C, 66.53; H, 5.18. Found: C, 66.67; H, 5.39.

Synthesis of [η^5-$CH_2C(Me)CHC(Me)O$]$RuH(PPh_3)_2$ (13). The freshly prepared *in situ* lemon-yellow solution of the lithium oxopentadienide salt (0.58 mmol) was slowly added dropwise to a cold (−110 °C), purple suspension of $RuHCl(PPh_3)_3$ (270 mg, 0.29 mmol) in 50 mL of THF. After the solution was warmed to room temperature and stirred for 12 h, a bright yellow solution was observed. The volatiles were removed under vacuum and the crude, oily, amber-colored product was washed five times with hexane (15 mL), affording a fine yellow precipitate. The solid was recrystallized from methylene chloride−hexane at room temperature to give 141.0 mg (0.19 mmol, 67%) of **13**, which melts at 205−209 °C, with decomposition.

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Slow evaporation of a diethyl ether solution at −5 °C afforded single crystals of **13**. IR (KBr, cm^{-1}): 3056 (s), 2998 (w), 2959 (w), 2914 (w), 2852 (w), 2530 (w, br), 2345 (w, br), 2051 (m), 1903 (w, br), 1716 (w, br), 1640 (m, br), 1579 (s), 1522 (m), 1481 (s), 1433 (vs), 1356 (m), 1313 (w), 1267 (m), 1186 (s), 1121 (s), 1090 (vs), 999 (vs, br), 859 (vs), 797 (w), 748 (s), 695 (vs), 632 (s), 537 (s), 522 (s, sh), 458 (m), 408 (m). MS (EI, 20 eV): 724 (0.3) [M^+], 626 (6.0), 547 (1.0), 486 (0.2), 458 (1.0), 441 (3.0), 392 (1.0), 363 (4.0), 262 (100.0), 183 (65.0), 108 (31.0), 43 (12.0). LRESI: 723, 625, 547, 461, 363. Anal. Calcd for $C_{42}H_{40}OP_2Ru$: C, 69.70; H, 5.57. Found: C, 69.68; H, 5.33.

Synthesis of [η^5-$CH_2C(Me)CHC(Me)O$]Ru($C_6H_4PPh_2$)(PPh_3) (14). From an attempt to separate compounds **12** and **13** by column chromatography, through elution with diethyl ether, an oily residue was obtained and dissolved in C_6D_6. Subsequently, pentane was added to the NMR sample, and after some time at −5 °C, a few single crystals were obtained.

Synthesis of [1-3,5-η-$CH_2C(t\text{-}Bu)CHC(t\text{-}Bu)O$]RuH($PPh_3$)$_2$ (15). The compound Li[$CH_2C(t\text{-}Bu)CHC(t\text{-}Bu)O$] (1.02 mmol) was slowly added dropwise to a cold (−78 °C) solution of $RuHCl(PPh_3)_3$ (470.0 mg, 0.51 mmol) in 60 mL of THF. Afterward, the solution was warmed to room temperature and stirred overnight. The volatiles of the amber solution were removed under vacuum, and compound **15** was then extracted from the remaining residue with hexane. After the volume of the solvent was reduced and the solution was cooled to −78 °C, a mustard-yellow solid precipitated. Filtration afforded 263.0 mg (0.33 mmol) in 64% yield. Mp: 165−172 °C. Single crystals were obtained by recrystallization from CH_2Cl_2/hexane (1:3). Anal. Calcd for $C_{48}H_{52}OP_2Ru$: C, 71.36; H, 6.49. Found: C, 71.43; H, 6.65.

Crystal Structure Determinations. X-ray diffraction measurements were made at 293(2) K (**3**); 173(2) K (**5**, **6**, **7**); 198(2) K (**12**, **13**, **14**); and 223(2) K (**15**) on an Enraf Nonius-Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A summary of crystal data collection and refinement (SHELX-97) parameters for compounds **3** and **5**−**7** is given in Tables 3 and 4, and for compounds **12**−**15** in Tables 5 and 6. The structures of **3**, **5**−**7**, **12**, and **14** were solved by direct methods, and **13** and **15** by the heavy-atom-method, using SHELX-97[52] included in WinGX[53] and refined by a full-matrix least-squares method based on F^2. Absorption corrections were performed by Multi-Scan. All non-hydrogen atoms were refined with anisotropic thermal displacement coefficients unless specified otherwise.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic and refinement details for compounds **3** (CCDC-879286), **4** (CCDC-885312), **5** (CCDC-879290), **6** (CCDC-879291), **7** (CCDC-879293), **12** (CCDC-879287), **13** (CCDC-879288), **14** (CCDC-879289), and **15** (CCDC-882692). Additional information of ^{31}P NMR spectra of **2**, **4**, **4′**, and **14** and $^1H\{^{31}P\}$ decoupling experiments of **7** and **8** are included, as well as ^1H and ^{31}P NMR evidence of the mixture of **11a** and **11b** and compound **11c**. Supplementary crystallographic data can be obtained, free of charge, from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) The reaction of the pentadienyltributyltin with the carbonyl complex $RuCl_2(CO)_2(PPh_3)_2$ affords a mixture of compound **1**, $RuCl_2(PPh_3)_3$, and $RuCl_2(CO)_2(PPh_3)_2$, which establishes, once again, the superiority of $RuCl_2(PPh_3)_3$ as a reactant in the formation of **1**.

(16) If potassium 2,4-dimethylpentadienide is used instead of the 2,4-dimethyl-pentadienyltrimethyltin, the reaction with $RuCl_2(PPh_3)_3$ is less selective, affording a mixture of compounds **2**, **3**, **4**, **4′**, $OPPh_3$, and PPh_3, plus specie(s) having an unassigned doublet at ^{31}P δ = 58.2, a triplet at ^{31}P δ = 46.0 with J = 17.7 Hz, and a singlet at ^{31}P δ = 61.7 in a ratio of 1.0:2.4:2.2:0.7:6.3:3.0:2.0:1.8, respectively.

(17) Orthometalation is commonly observed in products of a number of reactions with precursors such as $RuHCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$, as well as in η^5-Cp′$RuXL_2$ complexes. The half-sandwich compounds

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