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Synthesis and Characterization of (Alkynyl)-, (Vinylidene)-, and (Carbene)ruthenium Indenyl Complexes: X-ray Crystal Structure of $[Ru(=C=CMe_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][CF_3SO_3]\cdot{}^1/_2CH_2Cl_2$ and EHMO Calculations[1]

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The σ-alkynyl complexes $[Ru(C{\equiv}CR^1)(\eta^5\text{-}C_9H_7)L_2]$ (L_2 = 2PPh$_3$, 1,2-bis(diphenylphosphino)ethane (dppe), R^1 = Ph, ^{t}Bu, ^{n}Pr; L_2 = bis(diphenylphosphino)methane (dppm), R^1 = Ph) have been prepared by reaction of the complex $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ with $HC{\equiv}CR^1$ and potassium hydroxide in refluxing methanol. Electrophilic additions of $HBF_4\cdot OEt_2$ and $MeOSO_2CF_3$ to the neutral σ-alkynyl complexes yield the cationic vinylidene complexes $[Ru(=C=CR^2R^1)(\eta^5\text{-}C_9H_7)L_2]^+$ (R^2 = H, Me), which have been isolated as tetrafluoroborate or triflate salts in good yields. Reaction in refluxing dichloromethane of $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ with NH_4PF_6 and $HC{\equiv}CSiMe_3$ gives the cationic unsubstituted vinylidene complexes $[Ru(=C=CH_2)(\eta^5\text{-}C_9H_7)L_2]^+$; deprotonation of these cationic unsubstituted vinylidene species with potassium *tert*-butoxide yields the neutral σ-ethynyl complexes $[Ru(C{\equiv}CH)(\eta^5\text{-}C_9H_7)L_2]$ (L_2 = 2PPh$_3$, dppe). Methylation of these compounds leads to a mixture of the symmetrical vinylidene complexes $[Ru(=C=CR_2)(\eta^5\text{-}C_9H_7)L_2]^+$ (R = H, Me). Reaction in refluxing methanol or ethanol of $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ with $HC{\equiv}CSiMe_3$ or $HC{\equiv}CPh$ and NH_4PF_6 yields the alkoxycarbene derivatives $[Ru\{=C(OR^2)R^1\}(\eta^5\text{-}C_9H_7)L_2][PF_6]$($L_2$ = 2PPh$_3$, dppe, R^1 = Me, R^2 = Me, Et; L_2 = dppm, R^1 = Me, R^2 = Me, Et; L_2 = dppm, R^1 = Bz, R^2 = Me). The synthesis of the alkoxycarbenes has also been achieved by treatment of the unsubstituted vinylidene complexes with methanol or ethanol. The aminocarbene derivative $[Ru\{=C(NH_2)Me\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ has been prepared by reaction of $[RuCl(\eta^5\text{-}C_9H_7)(dppm)]$ with $HC{\equiv}CSiMe_3$ and NH_4PF_6 in CH_2Cl_2. The crystal structure of $[Ru(=C=CMe_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][CF_3SO_3]\cdot{}^1/_2CH_2Cl_2$ (monoclinic, space group $P2_1/c$, $Z = 4$, a = 12.854(4) Å, b = 14.42(1) Å, c = 23.98(3) Å, β = 92.25(7)°, R = 0.066) has been determined by X-ray diffraction methods. In the structure of the cationic complex the dimethylvinylidene ligand is almost linearly bound to the Ru atom (Ru−C(1)−C(2) = 173.7(6)°) with an Ru−C(1) distance of 1.839(7) Å and the ruthenium−vinylidene chain Ru=C=C lying out of the mirror molecular plane (conformational angle (CA) = 22.2(4)°). The coordination around the Ru atom is completed by two P atoms from the triphenylphosphine ligand and a η^5-bonded indenyl ligand with the benzo ring orientated trans to the vinylidene group. The structure shows distortions of the five-carbon ring from planarity with hinge angle (HA) and fold angle (FA) values of 8.1(6) and 13.1(6)°, respectively, and a pronounced slip-fold value of 0.197(7) Å. Extended Hückel molecular orbital calculations were used to rationalize the preferred "trans" orientation of the indenyl ligand with respect to the vinylidene group. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra are discussed. ^{13}C{^{1}H} NMR data are used for the calculation of the indenyl distortion parameters, showing that the distortion of the η^5-indenyl coordination in the solid state is maintained in solution.

Introduction

Although experimental and theoretical studies on half-sandwich cyclopentadienyl complexes containing the moiety $[(\eta^5\text{-}C_5R_5)M]$ (M = Fe, Ru) have formed one of the cornerstones in the development of the organometallic chemistry, analogous derivatives containing the indenyl ligand (η^5-C_9H_7) have attracted comparatively less attention. However, during the last decade a wide number of indenyl complexes have been described for other transition metals.[2] This significant progress was primarily motivated by kinetic and mechanistic studies carried out after Basolo et al. proposed in 1983 the *kinetic indenyl ligand effect*,[3] and also by the interest raised by the enhanced reactivity of indenyl complexes

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[1] Unsaturated Carbene Transition-Metal Indenyl Complexes. 3. Parts 1 and 2: see refs 16 and 17. To the memory of Marisa Tiripicchio-Camellini.

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vs cyclopentadienyl derivatives, in a number of reactions such as ligand substitution and carbonyl migratory insertion reactions. These processes may proceed through both associative and dissociative mechanisms, but the former pathway—based on the formation of a η^3-indenyl intermediate complex to which the incoming ligand is coordinated—is predominant.[4] The special ability of the indenyl ring to undergo $\eta^5 \rightarrow \eta^3$ isomerizations, *ring slippage*,[5] has been attributed to the stabilization associated with the aromatization of the fused six-membered ring in the transition state.

Even though both bis(indenyl) sandwich compounds $[Fe(\eta^5\text{-}C_9H_7)_2]$[6] and $[Ru(\eta^5\text{-}C_9H_7)_2]$[7] were synthesized soon after ferrocene[8] and ruthenocene,[9] the chemistry of the corresponding half-sandwich derivatives $[M(\eta^5\text{-}C_9H_7)XL_2]$ (M = Fe, Ru) is still rather limited and is mostly devoted to the iron derivatives.[10] At present, as far as we are aware, only the following ruthenium half-sandwich complexes have been isolated: (i) the carbonyl dimer $[Ru(\eta^5\text{-}C_9H_7)(CO)_2]_2$,[11] (ii) dicarbonyl complexes $[Ru(\eta^5\text{-}C_9H_7)(EM_3)(CO)_2]$ (E = Si, Ge)[12] and $[Ru(\eta^5\text{-}C_9H_7)I(CO)_2]$,[13] (iii) monocarbonyl complexes $[Ru(\eta^5\text{-}C_9H_7)I(CO)L]$ (L = monodentate phosphines)[13] and $[Ru(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_3H_5)(CO)]$,[14] and (iv) a large series of neutral and cationic phosphine complexes, namely $[Ru(\eta^5\text{-}C_9H_7)XL_2]$ (L_2 = 2PPh$_3$, X = H, CH$_3$, I, Cl, SnCl$_3$, C$_2$R; L_2 = diphos, X = Cl, C$_2$Ph), $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2L]^+$ (L = CN^{t}Bu, CO, C$_2$H$_4$, C=C(H)Ph, N-donor ligands), and $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)(L{-}L)]^+$ (L–L = diolefin, bidentate N-donor ligands).[15a,b] Recently we have also reported[16] the synthesis of novel allenylidene, alkenylvinylidene, and enynyl complexes containing the moiety $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ as the metal auxiliary as well as the chemical behavior of the cationic diphenylallenylidene complex $[Ru(=C=C=CPh_2)(\eta^5\text{-}C_9H_7)L_2]^+$ (L_2 = 2PPh$_3$, dppe, dppm) toward nucleophiles which leads to the formation of novel functionalized alkynyl complexes.[17]

Cyclopentadienyl and arene half-sandwich ruthenium complexes containing the moieties [(η-ring)Ru] are typical metal auxiliaries widely used for the stabilization of carbene groups, in particular for those containing vinylidene ($=C=CR_2$) and other cumulene systems ($=C=(C)_x=CR_2$).[18] While the synthetic applications of conventional Fischer carbene complexes are well-known, the potential utility of unsaturated carbenes for chemical transformations has been comparatively much less studied.[19a] In this regard, the possibility of enhancing the reactivity of carbene complexes by using (indenyl)ruthenium moieties as metal auxiliaries is particularly interesting.[19b] Hence, the preparation of novel (indenyl)ruthenium derivatives would be desirable. In this paper, we report the synthesis and characterization of a series of vinylidene and alkoxy- or aminocarbene complexes of the type shown in Chart 1. Alkynyl derivatives, which are used as precursors for the preparation of the corresponding vinylidene complexes, are also described.[15c]

Furthermore, the structure of complex **12a** has been determined by X-ray diffraction. These structural data together with the indenyl ring resonances in the $^{13}C\{^1H\}$ NMR spectra have been used to get appropriate correlation parameters which are of interest in determining the indenyl ring distortion in solution and in the solid state.

Results and Discussion

Alkynyl Complexes. The alkynyl derivatives $[Ru(C\equiv CR^1)(\eta^5\text{-}C_9H_7)L_2]$ (L_2 = 2PPh$_3$, dppe, dppm; **1–3**) have been prepared by reaction of $[RuCl(\eta^5\text{-}C_9H_7)L_2]$

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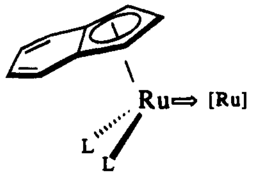
Chart 1



L_2= $2PPh_3$ (**a**), dppe (**b**), dppm (**c**)

[Ru]-C≡CR¹	(**1a-4a**; **1b-4b**; **1c**)
$[Ru]^+$=C=CR²R¹	(**5a-12a**; **5b-12b** ; **5c**, **9c**)
$[Ru]^+$=C(OR²)R¹	(**13a**,**14a**; **13b**,**14b**; **13c-15c**)
$[Ru]^+$=C(NH₂)Me	(**16c**)

[Ru]-C≡CR¹

	1	2	3	4
R¹=	Ph	ᵗBu	ⁿPr	H

$[Ru]^+$=C=CR²R¹

	5	6	7	8	9	10	11	12
R²=	H	H	H	H	Me	Me	Me	Me
R¹=	Ph	ᵗBu	ⁿPr	H	Ph	ᵗBu	ⁿPr	Me

$[Ru]^+$=C(OR²)R¹

	13	14	15
R²=	Me	Et	Me
R¹=	Me	Me	Bz

with HC≡CR¹ (R¹ = Ph, ᵗBu, ⁿPr) and potassium hydroxide in refluxing methanol. All attempts to prepare the (trimethylsilyl)ethynyl derivatives failed even when LiC≡CSiMe₃ was used. In contrast, this method proved to be efficient in the preparation of the analogous iron complex $[Fe(C{\equiv}CSiMe_3)(\eta^5\text{-}C_5H_5)(dppm)]$.[20] The complexes $[Ru(C{\equiv}CH)(\eta^5\text{-}C_9H_7)L_2]$ (L_2 = $2PPh_3$ (**4a**), dppe (**4b**)) have been obtained by deprotonation of the corresponding vinylidene derivatives $[Ru({=}C{=}CH_2)(\eta^5\text{-}C_9H_7)L_2][PF_6]$ (L_2 = $2PPh_3$ (**8a**), dppe (**8b**)) (see below) using KOᵗBu in THF.

The novel alkynyl complexes have been characterized by infrared spectroscopy, microanalysis, and NMR (^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$) spectroscopy (details are given in the Experimental Section). The infrared spectra exhibit the expected $\nu(C{\equiv}C)$ absorption band in the range 2075–2100 cm^{-1} for **1**–**3** (R¹ = Ph, ᵗBu, ⁿPr) and at 1936 and 1933 cm^{-1} for **4a** and **4b** (R¹ = H), respectively. These low energies are typical of bands for ethynyl transition-metal complexes,[21] which generally appear below 2000 cm^{-1}. The ^1H and $^{31}P\{^1H\}$ NMR spectra exhibit resonances for aromatic, indenyl, methylene ($(CH_2)_2P_2$ or CH_2P), and R groups in accordance with the proposed structures. In the ^1H NMR spectrum of **4a** the ethynyl proton resonates at δ 2.39 (t, $^4J_{HP}$ = 2.0 Hz) (this signal is overlapped in **4b** by the CH_2 resonances of dppe). The $^{31}P\{^1H\}$ NMR spectra show a single resonance consistent with the chemical equivalence of the phosphorus atoms.

The $^{13}C\{^1H\}$ NMR spectra exhibit the expected signals for the C_α and C_β atoms of the acetylide groups which have been assigned on the basis of the observed $J_{C_\alpha P}$ coupling constant. Significantly, the C_β resonance appears as a singlet (δ 117–123 ppm) at lower field than that of C_α (δ 87–115 ppm, triplet, J_{CP} = *ca.* 25 Hz), in accordance with those reported for $[Ru(C{\equiv}CCH_2CH_2C_2H)(\eta^5\text{-}C_5H_5)(PPh_3)_2]$[22] ($C_\alpha$, δ 95.3 ppm, t, J_{CP} = 25 Hz; C_β, 109.1 ppm) and for $[Ru(C{\equiv}CR^1)(\eta^5\text{-}C_5R_5)L_2]$[23] (R = H, Me) ($C_\alpha$, δ 87–103 ppm; C_β, 116–121 ppm).

Vinylidene Complexes. Addition of electrophiles to C_β of σ-alkynyl complexes $[M]{-}C{\equiv}CR^1$ has been described as the most versatile entry into vinylidene complexes for a wide variety of systems.[18a,24] Accordingly, we have used the complexes $[Ru(C{\equiv}CR^1)(\eta^5\text{-}C_9H_7)L_2]$ as precursors of novel vinylidene derivatives.

The treatment of a solution of **2a**, **3a**, **1b**, **2b** or **3b** in diethyl ether with an excess of $HBF_4{\cdot}OEt_2$, at room temperature, leads to the formation of the monosubstituted cationic vinylidene complexes $[Ru\{{=}C{=}C(H)R^1\}(\eta^5\text{-}C_9H_7)L_2]^+$ (L_2 = $2PPh_3$, R¹ = ᵗBu (**6a**), ⁿPr (**7a**); L_2 = dppe, R¹ = Ph (**5b**), ᵗBu (**6b**), ⁿPr (**7b**)) which have been isolated from the reaction mixture as insoluble tetrafluoroborate salts.

The analogous methyl-substituted vinylidene complexes $[Ru\{{=}C{=}C(Me)R^1\}(\eta^5\text{-}C_9H_7)L_2][CF_3SO_3]$ (L_2 = $2PPh_3$, R¹ = Ph (**9a**), ᵗBu (**10a**), ⁿPr (**11a**); L_2 = dppe, R¹ = Ph (**9b**), ᵗBu (**10b**), ⁿPr (**11b**); L_2 = dppm, R¹ = Ph (**9c**)) have been similarly prepared by reaction of the corresponding alkynyl derivatives with equimolar amounts of $MeOSO_2CF_3$ in dichloromethane, after addition of Et_2O to the concentrated solution. If this reaction is carried out in Et_2O, an excess of $MeOSO_2CF_3$ is required, but the desired vinylidene complexes are obtained along with additional unidentified species.

All attempts to obtain $[Ru\{{=}C{=}C(H)Me\}(\eta^5\text{-}C_9H_7)L_2][CF_3SO_3]$ or $[Ru({=}C{=}CMe_2)(\eta^5\text{-}C_9H_7)L_2][CF_3SO_3]$ (L_2 = $2PPh_3$, dppe) by methylation of the ethynyl complexes **4a** and **4b** led to a mixture containing $[Ru({=}C{=}CMe_2)(\eta^5\text{-}C_9H_7)L_2][CF_3SO_3]$ (**12a**, **12b**) and the unsubstituted vinylidene complexes **8a** and **8b**, as is evidenced from the ^1H and $^{31}P\{^1H\}$ NMR spectra. The

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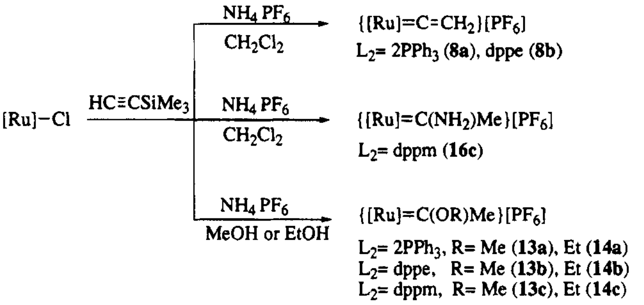
Scheme 1



complexes **12a** and **12b**[25] have been isolated from the crude mixture by column chromatography. We and others have reported[24] that a similar mixture is obtained from the ethynyliron complex [Fe(C≡CH)(η^5-C_5H_5)(L–L)] (L–L = dppm, dppe).

Alternatively, the vinylidene complexes [Ru{=C=C(H)R^1}(η^5-C_9H_7)L_2][PF$_6$] can be also obtained from [RuCl(η^5-C_9H_7)L_2] (L_2 = 2PPh$_3$, dppe) by reaction with HC≡CR^1 in refluxing methanol and in the presence of NaPF$_6$ (1:2:2 molar ratio) (see Experimental Section). However, the reaction with [RuCl(η^5-C_9H_7)(dppm)] produced a much more reactive vinylidene complex and the methoxycarbene derivative **15c** was directly isolated (see below). The vinylidene complex **5c** can be obtained by using ethanol as solvent.

The reaction of [RuCl(η^5-C_9H_7)L_2] (L_2 = 2PPh$_3$, dppe) with HC≡CSiMe$_3$ and NH$_4$PF$_6$ in dichloromethane results in the formation of the unsubstituted vinylidene complexes [Ru(=C=CH$_2$)(η^5-C_9H_7)L_2][PF$_6$] (L_2 = 2PPh$_3$ (**8a**), dppe (**8b**)) in *ca.* 75% yield (see Scheme 1). Complex **8a** is obtained in refluxing dichloromethane (40 °C, 4 h), while complex **8b** requires more severe reaction conditions (sealed tube, 90 °C, 7 h). The presence of the indenyl group decreases the reaction time with respect to the cyclopentadienyl group, since similar reactions involving [RuCl(η^5-C_5H_5)L_2] (L_2 = 2PPh$_3$, dppe) take place[26] at higher temperatures and/or longer reaction times (L_2 = 2PPh$_3$ (60 °C, 7 h); L_2 = dppe (90 °C, 48 h)). In contrast, the complex [RuCl(η^5-C_9H_7)(dppm)] reacts with HC≡CSiMe$_3$ and NH$_4$PF$_6$, under similar conditions (dichloromethane, sealed tube, 90 °C, 15 h), to give the aminocarbene complex **16c** (65% yield), which is formed by addition of NH$_3$ to the vinylidene intermediate (Scheme 1). All attempts to prepare the unsubstituted vinylidene complex by using a conventional Schlenk flask to facilitate the loss of NH$_3$ have failed. It is worth mentioning that we have prepared the unsubstituted iron vinylidene complex [Fe(=C=CH$_2$)(η^5-C_5H_5)(dppm)][BF$_4$] by protonation of [Fe(C≡CSiMe$_3$)(η^5-C_5H_5)(dppm)].[24] We cannot use this synthetic method for the preparation of the corresponding ruthenium indenyl derivative, since we were not able to prepare the (trimethylsilyl)ethynyl precursor complex (see above).

All vinylidene complexes are air stable in the solid state and soluble in chlorinated solvents and tetrahydrofuran. They have been characterized by elemental analysis, conductance measurements, mass spectra (FAB), and NMR (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}) spectroscopy. Selected NMR spectroscopic data are given in Tables 1 and 2. Conductivity data (in Me$_2$CO) show that the vinylidene complexes are 1:1 electrolytes, and the IR spectra (KBr) exhibit the expected absorptions for the anions (BF_4^-, PF_6^-, and $CF_3SO_3^-$) as well as those characteristic for the phosphines (see Experimental Section). Absorption bands which appear in the range of 1600–1700 cm^{-1} can be tentatively assigned to υ(C=C) of the vinylidene group, but they are in general overlapped by those of the phosphines, and consequently the assignment is uncertain.

In order to find the indenyl distortion parameters in the solid state and the orientation of the benzo ring with respect to the vinylidene group, the structure of the complex [Ru(=C=CMe$_2$)(η^5-C_9H_7)(PPh$_3$)$_2$][CF$_3$SO$_3$] (**12a**) has been determined by X-ray diffraction.

Molecular Structure of [Ru(=C=CMe$_2$)(η^5-C_9H_7)(PPh$_3$)$_2$][CF$_3$SO$_3$] (12a). The crystal structure consists of [Ru(=C=CMe$_2$)(η^5-C_9H_7)(PPh$_3$)$_2$]$^+$ cations, triflate anions, and CH$_2$Cl$_2$ molecules of crystallization ($^1/_2$ CH$_2$Cl$_2$ solvate). Selected bond distances, bond angles, indenyl distortion parameters, and crystallographic data are listed in Tables 3 and 4. Three views of the cationic complex together with the labeling scheme are presented in Figure 1. The molecule exhibits the usual allylene structure of the η^5-indenyl ligand in the pseudooctahedral three-legged piano-stool geometry. The values of the interligand angles P(1)–Ru–P(2), C(1)–Ru–P(1), and C(1)–Ru–P(2) are 102.34(9), 87.5(2), and 95.1(2)°, whereas those between the centroid and the legs are 122.0(3), 124.9(2), and 117.7(2)°, as expected for a pseudooctahedron. The dimethylvinylidene ligand is bound to Ru with an Ru–C(1) distance of 1.839(7) Å, a C(1)–C(2) distance of 1.30(1) Å, and a Ru–C(1)–C(2) angle of 173.7(6)°. This coordination is typical of a ruthenium(II) vinylidene complex showing values of the bonding parameters which can be compared with those reported for the analogous cyclopentadienyl complexes [Ru(=C=CR$_2$)(η^5-C_5H_5)(PR$_3$)$_2$]$^+$.[27] However, significant deviations of the angles at the C(2) atom expected for an sp^2 hybridization can be observed, i.e. 123.6(8), 122(1), 110(1)° (see Figure 1a). The vinylidene ligand also deviates significantly from the planarity with the C(1), C(2), C(3), and C(4) atoms deviating from the mean least-squares plane passing through them by 0.015(7), −0.045(8), 0.03(1), and 0.34(4)Å, respectively (the C(4) atom is disordered, and its position has been taken as an average). Figure 1b shows the orientation of the vinylidene group with respect to the [Ru(η^5-C_9H_7)(PPh$_3$)$_2$] moiety. The dihedral angle between the mean vinylidene plane and the pseudo mirror plane of the metallic moiety (containing the Ru atom, the C(1) atom, and the centroid of the five-carbon ring of the indenyl ligand) is 71.4(7)°, revealing a deviation from the orthogonal relationship as expected by theoretical studies.[28]

The indenyl group is η^5-bonded to ruthenium with a distance between the metal atom and the centroid (C*)

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[25] An alternative route for the synthesis of the compounds **12a** and **12b** in a selective manner will be published elsewhere: Gamasa, M. P.; Gimeno, J.; Godefroy, I.; Lastra, E.; Martín-Vaca, B. M. Manuscript in preparation.

[26] Bruce, M. I.; Koutsantonis, G. A. *Aust. J. Chem.* **1991**, *44*, 207.

[27] The bond lengths range from 1.824 to 1.864 Å for Ru–C and 1.253 to 1.339 Å for C(1)–C(2), and the angles Ru–C(1)–C(2) range from 165.8 to 179.9°: Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518.

[28] (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

Table 1. ^{31}P{^{1}H} and ^{1}H NMR Data for the Vinylidene Complexes[a]

		^{1}H					
		η^5-C$_9$H$_7$[m]					
complex	^{31}P{^{1}H}	H-1,3	H-2	J_{HH}	H-4,7, H-5,6	=CR^{2}R^1	others
[Ru{=C=C(H)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$][b] (**5a**)	38.93 s	5.60 d	5.74 t	2.5	6.07 m, 7.18 m	5.22 s, br (=CH), (=CPh)[d]	6.78−7.43 m (PPh$_3$, Ph)
[Ru{=C=C(H)^{t}Bu}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$][b] (**6a**)	38.15 s	5.45 d	5.52 t	2.6	5.94 m, 7.22 m	0.95 s (=C^{t}Bu), 3.9 s, br (=CH)	6.76−7.47 m (PPh$_3$)
[Ru{=C=C(H)^{n}Pr}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$][c] (**7a**)	41.26 s	5.38 d	5.54 t	2.7	6.07 m, *d*	0.82 t (CH$_3$),[e] 1.21 m (CH$_2$), 1.95m (=CCH$_2$), 4.25 t (=CH)[f]	6.79−7.48 m (PPh$_3$)
[Ru{=C=C(H)H}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$][b] (**8a**)	41.31 s	5.35 d	5.65 t	2.6	6.00 m, 7.17 m	3.89 t (=CH$_2$, $^4J_{HP}$ = 1.8)	6.79−7.46 m (PPh$_3$)
[Ru{=C=C(H)Ph}(η^5-C$_9$H$_7$)(dppe)][BF$_4$][c] (**5b**)	73.25 s	6.05 d	5.96 t	2.5	6.24 m, 7.16 m	4.32 s, br (=CH), (=CPh)[d]	2.53 m, 2.92 m (P(CH$_2$)$_2$P); 6.84−7.50 m (PPh$_2$, Ph)
[Ru{=C=C(H)^{t}Bu}(η^5-C$_9$H$_7$)(dppe)][BF$_4$][c] (**6b**)	74.75 s	5.87 d	5.82 t	2.5	*d*, 7.17 m	0.53 s (=C^{t}Bu), 3.03 s, br (=CH)	2.78 m (P(CH$_2$)$_2$P); 6.80−7.50 m (PPh$_2$)
[Ru{=C=C(H)^{n}Pr}(η^5-C$_9$H$_7$)(dppe)][BF$_4$][c] (**7b**)	76.95 s	5.88 d	5.71 t	2.7	6.76 m, 7.52 m	0.53 t (CH$_3$),[g] 0.79 m (CH$_2$), 1.11 m (=CCH$_2$), 3.36 t (=CH)[h]	2.68 m (P(CH$_2$)$_2$P); 6.76−7.52 m (PPh$_2$)
[Ru{=C=C(H)H}(η^5-C$_9$H$_7$)(dppe)][BF$_4$][c] (**8b**)	77.46 s	5.91 d	5.76 t	2.8	6.63 m, 7.00 m	2.93 s, br (=CH$_2$)	2.75 m (P(CH$_2$)$_2$P); 6.80−7.40 m (PPh$_2$)
[Ru{=C=C(H)Ph}(η^5-C$_9$H$_7$)(dppm)][PF$_6$][b] (**5c**)	3.49 s	6.15 d	5.76 t	2.7	6.20 m, 7.01 m	4.45 s, br (=CH), (=CPh)[d]	4.56 dt,[i] 4.96 dt (PCH$_a$H$_b$P);[j] 6.80−7.34m (PPh$_2$, Ph)
[Ru{=C=C(Me)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][CF$_3$SO$_3$][b] (**9a**)	38.75 s	5.27 m	6.18 m		5.64 m, 7.18 m	1.85 s (=CCH$_3$), (=CPh)[d]	6.59−7.53 m (PPh$_3$, Ph)
[Ru{=C=(Me)^{t}Bu}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][CF$_3$SO$_3$][c] (**10a**)	37.83 s	5.37 m	5.88 m		5.64 m, 7.15 m	0.98 s (=CC(CH$_3$)$_3$), 1.28 s (=CCH$_3$)	6.80−7.50 m (PPh$_3$)
[Ru{=C=C(Me)^{n}Pr}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][CF$_3$SO$_3$][b] (**11a**)	40.06 s	5.45 d	5.68 t	2.7	5.95 m, 7.19 m	0.86 t (CH$_3$),[k] 1.23 m (CH$_2$), 1.56 s (=CCH$_3$), 1.80 m (=CCH$_2$)	6.76−7.50 m (PPh$_3$)
[Ru{=C=C(Me)Me}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$][CF$_3$SO$_3$][c] (**12a**)	39.82 s	5.45 d	5.79 t	2.6	5.91 m, 7.18 m	1.54 (=C(CH$_3$)$_2$)	6.76−7.53 m (PPh$_3$)
[Ru{=C=C(Me)Ph}(η^5-C$_9$H$_7$)(dppe)][CF$_3$SO$_3$][c] (**9b**)	75.60 s	5.86 m	6.50 m		*d*	1.19 s (=CCH$_3$), (=CPh)[d]	2.75 m (P(CH$_2$)$_2$P); 6.87−7.53 m (PPh$_2$, Ph)
[Ru{=C=C(Me)^{t}Bu}(η^5-C$_9$H$_7$)(dppe)][CF$_3$SO$_3$][c] (**10b**)	76.74 s	5.55 d	5.96 t	2.6	7.04 m, *d*	0.59 s (= C^{t}Bu), 0.75 s (=CCH$_3$)	2.59 m, 2.67 m (P(CH$_a$H$_b$)$_2$P); 6.80−7.71 m (PPh$_2$)
[Ru{=C=C(Me)^{n}Pr}(η^5-C$_9$H$_7$)(dppe)][CF$_3$SO$_3$][c] (**11b**)	76.39 s	5.83 d	5.73 t	2.7	6.97 m, 7.16 m	0.55 t (CH$_3$),[l] 0.77 s (=CCH$_3$), 0.9 m (CH$_2$), 1.00 m (=CCH$_2$)	2.67 m (P(CH$_2$)$_2$P); 6.88−7.69 m (PPh$_2$)
[Ru{=C=C(Me)Me}(η^5-C$_9$H$_7$)(dppe)][CF$_3$SO$_3$][c] (**12b**)	76.42 s	5.75 d	5.68 t	2.6	7.11 m, *d*	0.78 (=C(CH$_3$)$_2$)	2.46 m (P(CH$_2$)$_2$P); 6.76−7.45 m (PPh$_2$)
[Ru{=C=C(Me)Ph}(η^5-C$_9$H$_7$)(dppm)][CF$_3$SO$_3$][c] (**9c**)	2.09 s	6.26 d	5.94 t	2.6	*d*	1.15 s (CH$_3$), (=CPh)[d]	4.63 m, 4.96 m (PCH$_a$H$_b$P); 6.43−7.83 m (PPh$_2$, Ph)

[a] δ in ppm, J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] Spectra recorded in CD$_2$Cl$_2$. [c] Spectra recorded in CDCl$_3$. [d] Overlapped by the PPh$_3$ or PPh$_2$ protons. [e] J_{HH} = 7.1 Hz. [f] t, J_{HH} = 8.1 Hz. [g] J_{HH} = 7.2 Hz. [h] t, J_{HH} = 8.2 Hz. [i] J_{HH} = 15.3 Hz, $^2J_{HP}$ = 12.7 Hz. [j] J_{HH} = 15.3 Hz, $^2J_{HP}$ = 10.3 Hz. [k] J_{HH} = 7.2 Hz. [l] J_{HH} = 7.1 Hz. [m] Legend for protons:

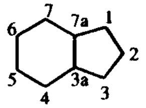

Table 2. $^{13}C\{^1H\}$ NMR Data for the Vinylidene Complexes[a]

	η^5-C_9H_7								
complex	C-1,3	C-2	C-3a,7a	$\Delta\delta$(C-3a,7a)[b]	C-4,5,6,7	Ru=C_α	$^2J_{CP}$	C_β	others
5a	82.81	97.86	114.37	−16.33	122.20, 129.44	350.32 t	16.4	117.16	125.97−132.63 (m, PPh_3 and Ph)
6a	82.35	98.96	115.13	−15.57	123.24, 129.81	347.66 t	16.3	124.65	32.04 (s, $3CH_3$), 32.70 (s, $C(CH_3)_3$), 128.35−133.89 (m, PPh_3)
7a[c]	84.07	99.49	115.41	−15.29	123.69, 130.43	345.90 t	16.5	113.28	14.50 (s, CH_3), 24.03 (s, CH_2), 25.20 (s, CH_2), 129.08−134.61 (m, PPh_3)
8a[c]	84.02[d]	99.05	115.42	−15.28	123.24, 130.45	344.34 t	16.5	97.71	128.81−134.13 (m, PPh_3)
5b[c]	79.36	98.23	113.34	−17.36	123.53, 128.76	353.10 t	16.9	116.80	26.30 (m, $P(CH_2)_2P$), 125.64−132.47 (m, PPh_2 and Ph)
6b	78.82	98.25	112.84	−17.86	123.80, 128.94	348.90 t	16.7	124.17	26.40 (m, $P(CH_2)_2P$), 31.59 (s, $3CH_3$), 32.16 (s, $C(CH_3)_3$), 129.23−132.83 (m, PPh_2)
7b[c]	79.55	97.91	112.85	−17.85	123.87, 129.12	345.50 t	17.0	112.33	13.82 (s, CH_3), 21.87 (s, CH_2), 25.31 (s, CH_2), 27.40 (m, $P(CH_2)_2P$), 129.27−135.12 (m, PPh_2)
8b	79.50[e]	98.30	112.99	−17.71	123.43, 129.21	342.50 t	17.1	96.01	27.60 (m, $P(CH_2)_2P$), 128.54−136.03 (m, PPh_2)
5c	79.46	95.49	111.57	−19.13	124.37, 128.57	357.00 t	15.2	118.66	46.00 (t, J_{CP} = 28.2, PCH_2P), 126.18−134.65 (m, PPh_2)
9a	81.40	100.00	116.92	−13.78	123.94, 130.71	348.30 t	17.5	123.44	13.07 (s, $=CCH_3$), 128.56−134.74 (m, PPh_2 and Ph)
10a	78.28	98.15	115.37	−15.33	122.33, 128.96	353.83 t	17.5	126.22	7.24 (s, $=CCH_3$), 28.82 (s, $3CH_3$), 31.07 (s, $C(CH_3)_3$), 127.37−132.88 (m, PPh_2)
11a	82.18	98.40	115.18	−15.28	123.53, 130.09	349.58 t	16.7	119.33	9.36 (s, $=CCH_3$), 14.14 (s, CH_3), 21.61 (s, CH_2), 28.35 (s, CH_2), 128.53−134.79 (m, PPh_2)
12a	81.26	98.27	*f*		123.04, 129.34	350.75 t	17.0	*f*	11.85 (s, $=C(CH_3)_2$), 128.23−134.38 (m, PPh_3)
9b	79.87	97.53	112.89	−17.81	123.97, 129.47	356.22 t	17.0	123.92	9.27 (s, CH_3), 27.61 (m, $P(CH_2)_2P$), 126.47−134.60 (m, PPh_2 and Ph)
10b	78.75	97.63	112.94	−17.76	124.14, 128.99	356.01 t	16.6	123.81	6.57 (s, CH_3), 27.47 (m, $P(CH_2)_2P$), 30.00 (s, $3CH_3$), 33.09 (s, $C(CH_3)_3$), 129.21−135.9 (m, PPh_2)
11b	78.83	96.43	112.19	−18.51	123.86, 128.69	350.60 t	16.8	120.22	7.27 (s, CH_3), 13.85 (s, CH_3), 21.84 (s, CH_2), 26.61 (s, CH_2), 27.10 (m, $P(CH_2)_2P$), 129.20−136.1 (m, PPh_2)
12b	79.06	96.73	112.42	−18.28	124.06, 129.00	352.32 t	17.4	116.60	10.36 (s, $=C(CH_3)_2$), 27.42 (m, $P(CH_2)_2P$), 129.49−136.11 (m, PPh_2)
9c	79.36	94.55	111.45	−19.25	124.65, 128.37	358.50 t	15.1	125.84	7.62 (s, $=CCH_3$), 44.90 (t, J_{CP} = 28.3, PCH_2P), 125.97−134.52 (m, PPh_2 and Ph)

[a] Spectra recorded in CD_2Cl_2. δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] $\Delta\delta$(C-3a, 7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)). δ(C-3a,7a) for sodium indenyl 130.70 ppm. [c] DEPT. [d] t, $^2J_{CP}$ = 2.8 Hz. [e] t, $^2J_{CP}$ = 2.5 Hz. [f] 114.94 and 115.40 (s, C_β, C-3a,7a).

of the five-membered ring of 1.97(9) Å (1.8216 Å in $[Ru(\eta^5\text{-}C_9H_7)_2]$).[7] The preferred conformation of the indenyl ligand is such that the benzo ring is orientated *trans* to the vinylidene group, although their C(1) and C(2) atoms are not contained in the mirror plane of the indenyl ring (Figure 1c). The conformational angle (CA), defined as the dihedral angle between the planes C** (centroid of the benzo ring of the indenyl ligand), C*, Ru and C*, Ru, C(1) (Table 3) is 22.2(4)°. On the other hand, the ligands seem to arrange themselves according to the largest *trans* influence, as was suggested by Crabtree et al. for a range of η^5-indenyl complexes.[29] In fact, according to EHMO calculations (see below) the "trans" orientation (benzo ring and vinylidene group mutually trans, CA = 0°) is energetically more favored than the "cis" orientation (CA = 180°) by *ca.* 7 kcal mol^{-1}.

The structure shows distortions of the five-carbon ring from planarity with the hinge angle (HA) and fold angle (FA) values of 8.1(6) and 13.1(6)°, respectively (Table 3). The characteristic displacement of the metal atom away from the C(70)−C(74) ring junction in the indenyl ligand is also observed with a slip-fold (Δ) value of 0.197(7) Å. This Δ value is the highest reported for three-legged piano-stool indenyl complexes (in the range 0.08−0.18 Å)[30] and is in contrast with those found in the other structurally characterized (indenyl)ruthenium complexes, namely $[Ru(\eta^5\text{-}C_9H_7)_2]$ (Δ = 0.03 Å),[7] $[Ru(\eta^5\text{-}C_9H_7)I(CO)\{P(CH_2Ph)_3\}]$ (Δ = 0.07 Å),[13] $[Ru(\eta^5\text{-}C_9H_7)(CO)(PPh_3)_2]^+$ (Δ = 0.10 Å),[15a] $[Ru(\eta^5\text{-}C_9H_7)(C{\equiv}CPh)(dppe)]$ (Δ = 0.09 Å),[15b] and $[Ru\{=C=C=C(C_{13}H_{20})\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (Δ = 0.082 Å).[16] The moderate distortions toward an η^3 binding mode in the solid state appear to be maintained in solution, according to the relatively downfield ^{13}C chemical shifts of the ring-junction carbon atoms (C(70), C(74)) (see below).

A further distortion is observed in the coordination of the indenyl ring arising from the differences between the distances Ru−C(73) (2.261(7) Å) and Ru−C(71),C(72) (2.222(8) Å average), giving a tilted indenyl coordination in which the C(71) and C(72) atoms are closer to ruthenium. The selective approach of these carbon atoms to the metal may be related to the preferential overlapping of the corresponding p_z ring orbitals and those of the metal atom (see below).

EHMO Calculations. We report here the results of the extended Hückel molecular orbital calculations on $[Ru(=C=CMe_2)(\eta\text{-}C_9H_7)(PH_3)_2]^+$ as a model of the complex **12a**. In our optimized geometry for the ground state, we keep the distortion parameters Δ, FA, DA, and HA as well as the Ru−indenyl distances determined by the X-ray diffraction study (see Table 3).

Figure 2 represents a Walsh diagram showing the relationship between the conformational angles (CA from 0 to ±180°) and the calculated energies for the five highest occupied orbitals and the LUMO. The results indicate that minimum energies are obtained for CA ≠ 0° (the chain Ru=C=C of the vinylidene group lying out of the C**, C*, Ru plane). The relative total minimum energy is found for CA = 10.7°. This position is predicted to be more stable than CA = 180° by about 7.5 kcal mol^{-1} but only by 1 kcal mol^{-1} from CA = 0°.

Figure 3 shows the two top filled MO's (45,46) and the LUMO for the conformational angle (CA = 10.7°).

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[29] (a) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929. However, this is not the case for a number of indenyl complexes which have been described in the last few years; see for instance: (b) Reference 2g. (c) Pannell, K. H.; Lin, S. H.; Kapoor, R. N.; Cervantes-Lee, F.; Pinon, M.; Parkanyi, L. *Organometallics* **1990**, *9*, 2454.

[30] See refs 2a,g, 10j,k, and 29a,c.

Table 3. Selected Bond Distances and Slip Parameter Δ[a] (Å) and Bond Angles and Dihedral Angles FA,[b] HA,[c] DA,[d] and CA[e] (deg) for Complex 12a

	Distances		
Ru—C*	1.97(9)	C(1)—C(2)	1.30(1)
Ru—P(1)	2.352(2)	C(2)—C(3)	1.50(1)
Ru—P(2)	2.367(3)	C(2)—C(4)	1.56(3)
Ru—C(1)	1.839(7)	C(70)—C(78)	1.39(1)
Ru—C(70)	2.436(7)	C(70)—C(74)	1.44(1)
Ru—C(71)	2.223(8)	C(70)—C(71)	1.44(1)
Ru—C(72)	2.221(8)	C(71)—C(72)	1.40(1)
Ru—C(73)	2.261(7)	C(72)—C(73)	1.41(1)
Ru—C(74)	2.443(7)	C(73)—C(74)	1.42(1)
P(1)—C(11)	1.818(7)	C(74)—C(75)	1.41(1)
P(1)—C(21)	1.834(7)	C(75)—C(76)	1.37(1)
P(1)—C(31)	1.833(7)	C(76)—C(77)	1.38(1)
P(2)—C(41)	1.839(7)	C(77)—C(78)	1.36(1)
P(2)—C(51)	1.833(7)	Δ	0.197(7)
P(2)—C(61)	1.824(7)		
	Angles		
C*—Ru—C(1)	122.0(3)	C(78)—C(70)—C(74)	120.3(7)
C*—Ru—P(1)	124.9(2)	C(78)—C(70)—C(71)	134.0(7)
C*—Ru—P(2)	117.7(2)	C(74)—C(70)—C(71)	105.6(7)
C(1)—Ru—P(1)	87.5(2)	C(72)—C(71)—C(70)	108.5(8)
C(1)—Ru—P(2)	95.1(2)	C(71)—C(72)—C(73)	108.9(8)
P(1)—Ru—P(2)	102.34(9)	C(72)—C(73)—C(74)	107.6(8)
C(2)—C(1)—Ru	173.7(6)	C(75)—C(74)—C(70)	119.3(8)
C(1)—C(2)—C(3)	123.6(8)	C(75)—C(74)—C(73)	131.8(8)
C(1)—C(2)—C(4)	122.(1)	C(73)—C(74)—C(70)	108.7(7)
C(3)—C(2)—C(4)	110.(1)	C(76)—C(75)—C(74)	117.6(9)
C(75)—C(76)—C(77)	122.3(9)	C(77)—C(78)—C(70)	118.6(8)
C(78)—C(77)—C(76)	121.9(9)		
FA	13.1(6)	HA	8.1(6)
DA	71.4(7)	CA	22.2(4)

[a] Δ = d(Ru—C(74),C(70)) − d(Ru—C(71),C(73)). [b] FA (fold angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(70), C(74), C(75), C(76), C(77), C(78). [c] HA (hinge angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(71), C(74), C(70), C(73). [d] DA (dihedral angle) = angle between normals to least-squares planes defined by C*, Ru, C(1) and C(1), C(2), C(3), C(4). [e] CA (conformational angle) = angle between normals to least-squares planes defined by C**, C*, Ru and C*, Ru, C(1) (C* = centroid (C(70), C(71), C(72), C(73), C(74); C** = centroid (C(70), C(74), C(75), C(76), C(77), C(78))).

The LUMO is a π-antibonding combination between the p_z orbital of C_α of the vinylidene group (30% of the contribution) and an hybrid orbital (25%) involving $d_{x^2-y^2}$, d_{z^2}, and d_{xz}. The HOMO is a combination of the orbitals p_y C_β (20%), p_y C_α (5%), d_{xy} (37%), and one p_z orbital of the five-membered ring of the indenyl group (3%). The following filled orbital (MO 46) is a bonding combination mainly of the $d_{x^2-y^2}$ (48%) and one p_z orbital of the indenyl ring (4%). As can be observed from Figure 2, the minimum energy mainly arises from the contribution of the HOMO and the second highest occupied orbital (MO 46) due to the most favored overlapping (Figure 3) between the orbitals $d_{x^2-y^2}$ (in the HOMO) and d_{xy} (in MO 46) with one of the p_z orbitals in the five-membered ring of the indenyl group. It is worth mentioning that the maximum destabilization of the LUMO is also reached for CA = 10.7°, leading to the maximum gap HOMO−LUMO.

The low barrier (*ca.* 3 kcal mol^{-1}) between the different conformers of the complex for the values of CA = ±10.7° allows the chemical equivalence of the phosphorus atoms in solution, as shown by the $^{31}P\{^1H\}$ NMR spectra at room temperature (see below and Scheme 2).

The difference found in the conformational angles between the X-ray structural determination and the theoretical calculations may be due to the use of idealized parameters for the indenyl ring and phosphine ligands and other effects in the crystal packing. We are extending this work to *ab initio* methods also involving other (indenyl)ruthenium complexes prepared in our laboratory.

Table 4. Crystallographic Data for Complex 12a

formula	$C_{50.5}H_{44}F_3O_3P_2RuSCl$
fw	985.37
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	12.854(4)
b, Å	14.42(1)
c, Å	23.98(3)
β, deg	92.25(7)
V, Å^3	4441(6)
Z	4
D_{calcd}, g cm^{-3}	1.47
$F(000)$	2016
wavelength, Å	0.710 73
temp, K	293
radiation	Mo Kα
monochromator	graphite cryst
cryst size, mm	0.26 × 0.16 × 0.16
μ, mm^{-1}	0.59
range of abs	0.73, 1.18
diffractometer	Enraf-Nonius CAD-4
diffraction geom	$\omega-2\theta$
θ range for data collection, deg	1.59−24.98°
index ranges for data collection	$-15 \le h \le 15, 0 \le k \le 17, 0 \le l \le 28$
no. of rflns measd	8346
no. of indep rflns	7795
no. of variables	507
agreement between equiv rflns	$R_{int} = \sum(I - \langle I \rangle)/\sum I = 0.038$
final R factors	
$R(I > 2\sigma(I))$ (4189 rflns)	$R1 = 0.066$, w$R2 = 0.173$
R(all data)	$R1 = 0.148$, w$R2 = 0.221$
goodness of fit on F^2	0.958

NMR Studies. The room-temperature $^{31}P\{^1H\}$ NMR spectra show a single resonance (δ 37.83−41.31, 73.25−77.46, and 2.09−3.49 ppm for the PPh_3, dppe, and dppm complexes, respectively, see Table 1) at higher fields than those shown by the corresponding alkynyl precursor complexes. The chemical equivalence of the phosphorus atoms in the unsymmetrically substituted vinylidene complexes ($R^1 \neq R^2$) is consistent with a rapid rotation of the vinylidene group around the Ru=C bond on the NMR time scale,[31] as well as with the theoretical calculations—the conversion of the conformers arising from CA values of ±10.7° is energetically favorable at room temperature (see above and Scheme 2).

Proton and $^{13}C\{^1H\}$ NMR spectra in CD_2Cl_2 at room temperature exhibit aromatic, indenyl, methylene ($(CH_2)_2P_2$ or CH_2P) and R vinylidene signals in accordance with the proposed structures (Tables 1 and 2). In the ^1H NMR spectra of the monosubstituted complexes **5a**, **5b**, **6a**, and **6b**, the vinylidene proton signal appears as a broad singlet in the range δ 3.03−5.22 ppm and as a triplet for **7a** and **7b** (J_{HH} = 8.1−8.2 Hz). The corresponding resonances in the unsubstituted vinylidene complexes **8a** and **8b** appear as a triplet signal at δ 3.89 ($^4J_{HP}$ = 1.8 Hz) and a broad singlet at δ 2.93 ppm, respectively. The H-1,3 and H-2 resonances of the indenyl ligand appear in the ranges δ 5.27−6.26 ppm (H-1,3) and δ 5.52−6.50 ppm (H-2) as a doublet and a triplet (J_{HH} = 2.5−2.8 Hz), respectively.

The $^{13}C\{^1H\}$ NMR spectra in CD_2Cl_2 show the typical low-field signal for the C_α atom, which appears as a

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(31) At lower temperatures the signal broadens, which is in agreement with the dynamic behavior found by us in the case of cyclopentadienyliron vinylidene complexes.[24] Further studies on the apparent fluxional behavior of these complexes are in progress: Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M. Unpublished work.

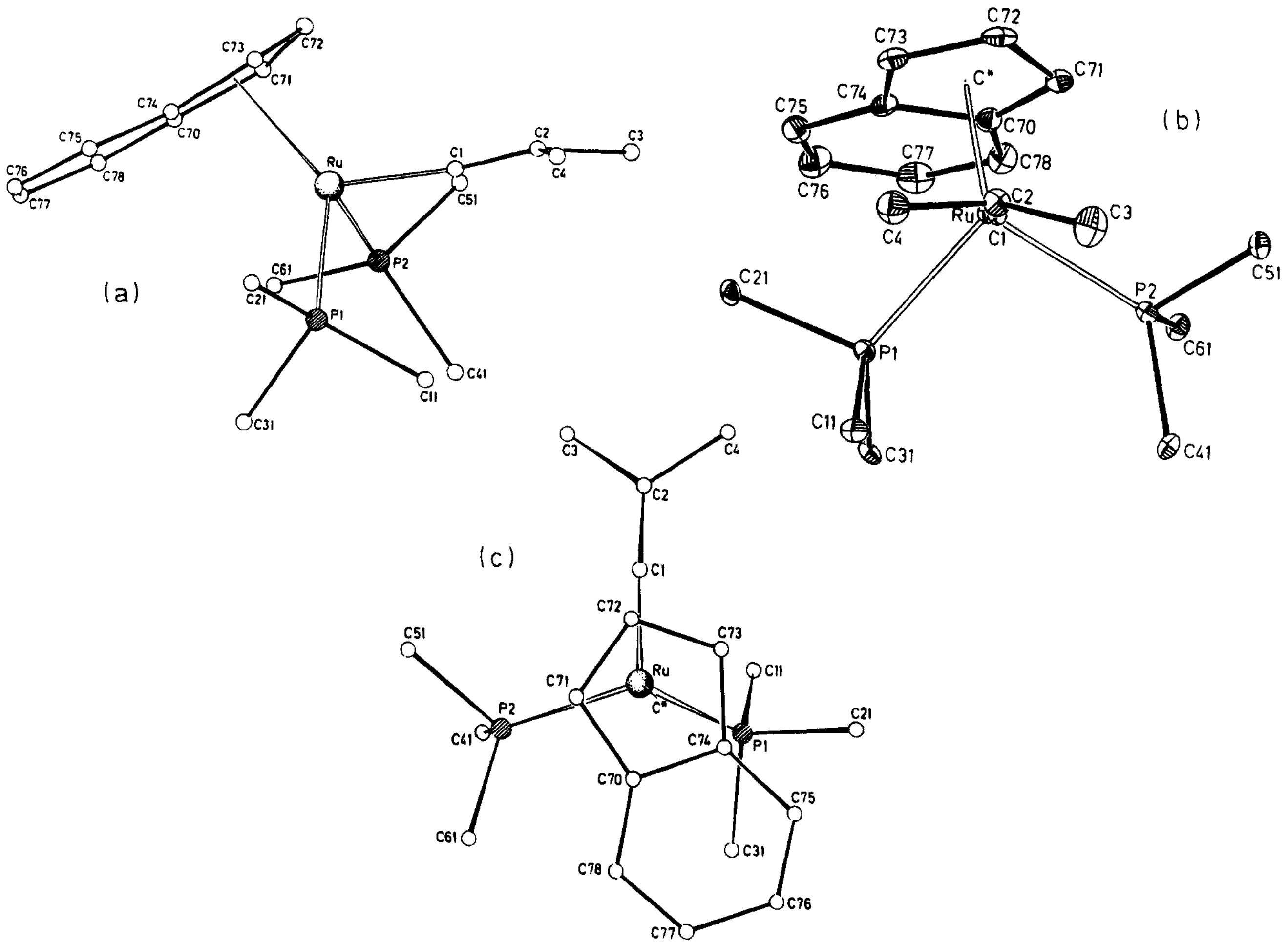

Figure 1. Views of the structure of the cationic complex [Ru(=C=CMe$_2$)(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ (**12a**) with the atom-numbering scheme (phenyl rings of the triphenylphosphine ligands have been omitted for clarity): (a) perspective view; (b) ORTEP view along the Ru—vinylidene axis; (c) top view.

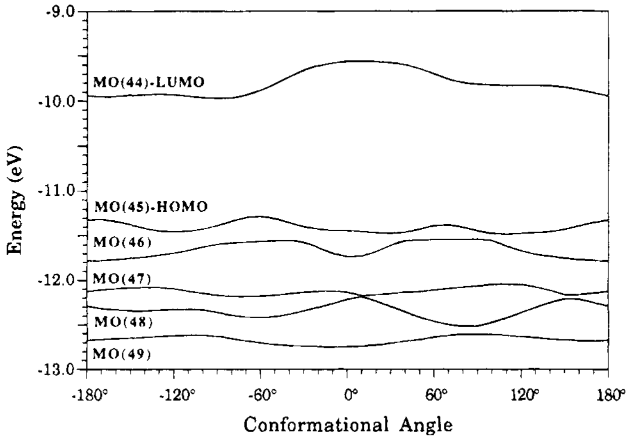

Figure 2. Walsh diagram for the conformation angle (CA) in [Ru(=C=CMe$_2$)(η^5-C$_9$H$_7$)(PH$_3$)$_2$]$^+$.

triplet due to coupling with the two equivalent phosphorus atoms (δ 342.50−358.50 ppm, $^2J_{CP}$ = 15.1−17.5 Hz). The C$_\beta$ atom resonates as a singlet in the range δ 112.33−126.22 ppm for the mono− and disubstituted vinylidene complexes (at higher field in the monosubstituted species: e.g. [Ru{=C=C(H)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ δ 117.16 ppm, [Ru{=C=C(Me)Ph}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]$^+$ δ 123.44 ppm). These signals appear at a considerably lower field than those found in the analogous unsubstituted vinylidene complexes (δ 97.71 (**8a**), 96.01 ppm (**8b**)), in agreement with previously reported data.[32]

Indenyl carbon resonances have been assigned (Table 2), and the chemical shifts can be compared with those reported for other transition-metal complexes.[33] Significantly, C-2 and C-3a,7a resonances appear as singlet signals while those of C-1,3 indicate effective P—C coupling, since broad or triplet signals ($^2J_{PC}$ = 2.5−2.8 Hz, **8a**, **8b**) are observed. Baker et al. have reported[34] (in agreement with Kohler analysis[35]) that the hapticity of the indenyl ligand can be assessed spectroscopically by comparing the NMR chemical shift of the ring-junction carbon atoms (C-3a,7a) in the metal complex with those of the sodium indenyl: larger distorations result in larger downfield shifts. The parameter $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a-(sodium indenyl)) has been proposed as an indication of the indenyl distortion, having values in the range −20 to −40 ppm for planar η^5-indenyl, −10 to −20 ppm for distorted η^5-indenyl, and +5 to +30 ppm for η^3-indenyl ligands.[34] The $\Delta\delta$(C-3a,7a) values for the vinylidene complexes, in the range from *ca.* −13 to −19 ppm (see Table 2), are consistent with a moderate distortion of the η^5-indenyl ligand. This seems to indicate that the observed distortion in the solid state (see above) is maintained in solution. The $\Delta\delta$(C-3a,7a) values for the

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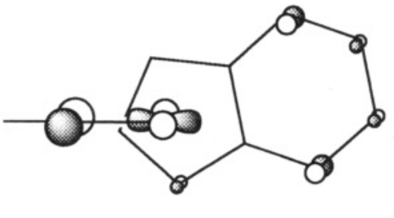
[32] Bruce, M. I.; Koutsantonis, G. A. *Aust. J. Chem.* **1991**, *44*, 2071.

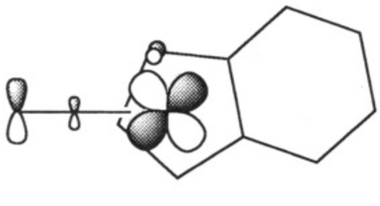
[33] (a) See ref 2a. (b) Ceccon, A.; Elsevier, C. J.; Ernsting, J. M.; Gambaro, A.; Santi, S.; Venzo, A. *Inorg. Chim. Acta* **1993**, *204*, 15.

[34] Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

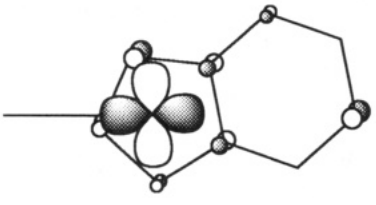
[35] Kohler, F. G. *Chem. Ber.* **1974**, *107*, 570.



MO(44)-LUMO



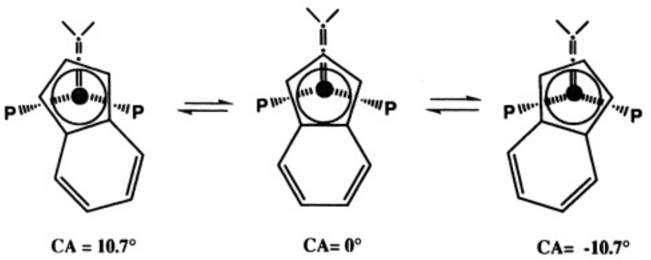
MO(45)-HOMO



MO(46)

Figure 3. The LUMO and the two top filled MO's (only the more important contributions are shown).

Scheme 2



alkynyl complexes (−20 to −23 ppm) seem to indicate a less distorted η^5-indenyl coordination.

Alkoxy- and Aminocarbene Complexes. The most significant reactions of vinylidene complexes are nucleophilic attacks at the C_α atom. Unsubstituted vinyldiene complexes **8a** and **8b** react with methanol or ethanol to give the alkoxycarbene derivatives [Ru{=C-(OR)Me}(η^5-C_9H_7)L_2][PF_6] (L_2 = 2PPh$_3$, R = Me (**13a**), Et (**14a**); L_2 = dppe, R = Me (**13b**), Et (**14b**)). The synthesis of the complexes **13a**, **13b**, **13c**, **14a**, **14b**, and **14c** has also been achieved, in comparable yields, by treatment of [RuCl(η^5-C_9H_7)L_2] (L_2 = 2PPh$_3$, dppe, dppm) with HC≡CSiMe$_3$ and NH$_4$PF$_6$ in methanol or ethanol (Scheme 1).

The influence of the substituents on the ability of the vinylidene group to undergo nucleophilic additions to the C_α atom is clearly shown by the behavior of the monosubstituted vinylidene complexes; thus, [Ru{=C=C-(H)Ph}(η^5-C_9H_7)L_2][BF_4] compounds (L_2 = 2PPh$_3$, dppe) are unreactive toward methanol or ethanol. On the other hand, the influence of the small-bite chelating dppm ligand is also evident, since the analogous complex [Ru{=C=C(H)Ph}(η^5-C_9H_7)(dppm)][BF_4] reacts quickly with methanol to give the methoxycarbene complex **15c**, although the reaction with ethanol requires a longer reaction time, giving the ethoxycarbene derivative along with decomposition products.

The aminocarbene derivative [Ru{=C(NH$_2$)Me}(η^5-C_9H_7)(dppm)][PF_6] (**16c**) is obtained by reaction of [RuCl(η^5-C_9H_7)(dppm)] with HC≡CSiMe$_3$ and NH$_4$PF$_6$ (dichloromethane, sealed tube, 90 °C, 15 h) (Scheme 1). A similar procedure involving "in situ" generation of NH$_3$ from NH$_4$PF$_6$ and NEt^{i}Pr$_2$ has been reported in the case of [Ru{=C(NH$_2$)CH$_2$(CH$_2$)$_2$CH$_2$Cl}(η^5-C_5H_5)-(dppe)]$^+$.[18b]

All carbene complexes are air stable in the solid state and soluble in chlorinated solvents and tetrahydrofuran. They have been characterized by elemental analysis, conductance measurements, mass spectra (FAB), and NMR (^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}) spectroscopy. Selected NMR spectroscopic data are given in Tables 5 and 6. Conductivity data (in Me$_2$CO) show that the complexes are 1:1 electrolytes, and the IR spectra (KBr) exhibit the expected absorptions for the anions (BF_4^-, PF_6^-) as well as those characteristic for the phosphines. All alkoxycarbene complexes also exhibit the absorption band v(COR) at *ca.* 1234−1253 cm^{-1}.

The ^{31}P{^{1}H} NMR spectra show a single resonance (δ 43.33−45.22, 93.99−94.52, and 13.50−15.79 ppm for the PPh$_3$, dppe, and dppm complexes, respectively; see Table 5), indicating a rapid rotation of the carbene group around the Ru=C bond on the NMR time scale. ^{1}H and ^{13}C{^{1}H} NMR spectra in CD$_2$Cl$_2$ at room temperature exhibit aromatic, indenyl, methylene ((CH$_2$)$_2$P$_2$ or CH$_2$P) alkoxy, and R signals in accordance with the proposed structures (Tables 5 and 6). The H-1,3 and H-2 signals of the indenyl ligand are found in the ranges δ 5.20−6.19 ppm (H-1,3) and δ 4.99-5.62 ppm (H-2) and appear, in most cases, as a doublet and a triplet (J_{HH} = 2.0−2.8 Hz), respectively. In the ^{13}C{^{1}H} NMR, the C_α atom signal appears as a triplet at the typical low field (δ 261.22−309.60 ppm, $^2J_{PC}$ = 11.2−13.0 Hz) expected for carbene complexes. The $\Delta\delta$(C-3a,7a) values range from −14.70 to −20.22 ppm and are also consistent with a moderate distortion of the η^5-indenyl ligand, as was similarly found for the vinylidene derivatives (see above).

Experimental Section

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complexes [RuCl(η^5-C_9H_7)L_2] (L_2 = 2PPh$_3$,[15a] dppe,[15a] dppm) were prepared by literature methods.[36] MeOSO$_2$CF$_3$, HBF$_4$·OEt$_2$, NaPF$_6$, NH$_4$PF$_6$, and all the alkynes were used as received from Aldrich Chemical Co.

Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. Mass spectra (FAB) were recorded using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer (uncompleted combustion was systematically observed for the dppe complexes **4b**, **5b**, and **10b**). NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using

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(36) Preparation of the dppm complex and improved methods for the other complexes will be published elsewhere: Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M. Manuscript in preparation.

Table 5. $^{31}P\{^1H\}$ and ^1H NMR Data for the Alkoxy- and Aminocarbene Complexes[a]

		^{1}H					
		η^5-C_9H_7					
complex	$^{31}P\{^1H\}$	H-1,3	H-2	J_{HH}	H-4,7, H-5,6	$=C(XR^2)R^1$	others
$[Ru\{=C(OMe)Me\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**13a**)	43.33 s	5.24 m	5.30 m		6.90 m, *b*	2.91 s ($=CCH_3$), 3.02 s ($=COCH_3$)	6.69−7.48 m (PPh_3)
$[Ru\{=C(OEt)Me\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**14a**)	45.22 s	5.20 d	5.39 t	2.0	7.00 m, *b*	0.67 t (J_{HH} = 7.1, CH_3), 2.80 s ($=CCH_3$), 3.42 q (J_{HH} = 7.1, $=COCH_2$)	6.71−7.52 m (PPh_3)
$[Ru\{=C(OMe)Me\}(\eta^5\text{-}C_9H_7)(dppe)][PF_6]$ (**13b**)	93.99 s	5.39 d	5.06 t	2.7	6.72 m, 6.99 m	2.26 s ($=CCH_3$), 2.62 s ($=COCH_3$)	2.62 m, 2.86 m ($P(CH_2)_2P$); 7.12−7.67 m (PPh_2)
$[Ru\{=C(OEt)Me\}(\eta^5\text{-}C_9H_7)(dppe)][PF_6]$ (**14b**)	94.52 s	5.37 d	4.99 t	2.8	6.69 m, 7.00 m	0.25 m ($-CH_3$), 2.27 s ($=CCH_3$), 2.88 m ($=COCH_2$)	2.80 m ($P(CH_2)_2P$); 7.22−7.50 m (PPh_2)
$[Ru\{=C(OMe)Me\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**13c**)	15.25 s	5.57 d	5.41 t	2.6	6.81 m, 6.94 m	2.45 s ($=CCH_3$), 2.65 s ($=COCH_3$)	4.95 m, (PCH_2P); 7.19−7.60 m (PPh_2)
$[Ru\{=C(OEt)Me\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**14c**)	15.79 s	5.65 d	5.45 t	2.8	6.87 m, 6.97 m	0.10 t (J_{HH} = 7.1, CH_3), 2.58 s ($=CCH_3$), 3.05 q (J_{HH} = 7.1, $=COCH_2$)	4.78 m, 5.20 m (PCH_2P); 7.25−8.33 m (PPh_2)
$[Ru\{=C(OMe)Bz\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**15c**)	13.50 s	6.19 d	5.62 t	2.7	6.77 m, 7.06 m	2.81 s ($=COCH_3$), 4.36 s ($=CCH_2Ph$)	5.40 t (PCH_2P);[c] 7.24−7.41 m (PPh_2)
$[Ru\{=C(NH_2)Me\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (**16c**)	14.96 s	5.29 d	5.14 t	2.7	*b*	1.67 s ($=CCH_3$), 9.40 br ($=CNH_2$)	4.30 dt,[d] 4.93 dt[e] (PCH_2P); 7.14−7.43 m (PPh_2)

[a] Spectra recorded in CD_2Cl_2. δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] Overlapped by the PPh_3 signals. [c] $^2J_{HP}$ = 11.5 Hz. [d] J_{HH} = 15.7 Hz, $^2J_{HP}$ = 11.0 Hz. [e] J_{HH} = 15.7 Hz, $^2J_{HP}$ = 10.4 Hz.

Table 6. $^{13}C\{^1H\}$ NMR Data for the Alkoxy- and Aminocarbene Complexes[a]

	η^5-C_9H_7							$=C(XR^2)R^1$		
complex	C-1,3	C-2	C-4,7 and C-5,6	C-3a,7a	$\Delta\delta$(C-3a,7a)[b]	$Ru=C_\alpha$	$^2J_{CP}$	XR^2	R^1	others
13a	78.85	101.08	123.46, 128.08	116.00	−14.70	302.90 t	12.7	61.73 (OCH_3)	43.93 ($=CCH_3$)	128.49−135.77 m (PPh_3)
14a	79.42	101.02	123.78, 128.53	116.58	−14.72	303.43 t	12.1	15.82 (CH_3), 66.38 (OCH_2)	44.79 ($=CCH_3$)	128.77−136.06 m (PPh_3)
13b	78.58	100.07	124.85, 127.29	111.97	−18.73	309.60 t	13.0	60.58 (OCH_3)	42.61 ($=CCH_3$)	29.84 m ($P(CH_2)_2P$); 127.58−139.23 m (PPh_2)
14b	77.82	99.25	123.87, 127.00	111.11	−19.59	290.30 t	12.6	12.86 (CH_3), 70.63 (OCH_2)	42.67 ($=CCH_3$)	28.57 m ($P(CH_2)_2P$); 128.15−138.59 m (PPh_2)
13c	77.20	96.78	123.87, 126.83	110.48	−20.22	308.35 t	11.7	59.70 (OCH_3)	42.55 ($=CCH_3$)	50.15 t (J_{CP} = 25.0, PCH_2P); 127.07−134.95 m (PPh_2)
14c	78.15	98.52	124.62, 127.34	111.48	−19.22	308.32 t	11.5	13.07 (CH_3), 71.22 (OCH_3)	44.00 ($=CCH_3$)	50.50 t (J_{CP} = 25.3, PCH_2P); 129.00−136.5 m (PPh_2)
15c	77.92	98.08	124.10, 128.72	111.96	−18.74	307.80 t	11.2	59.25 (OCH_3)	54.25 ($=CCH_2$)	48.10 t (J_{CP} = 26.2, PCH_2P); 125.12−135.82 m (PPh_2, Ph)
16c	71.16	93.23	124.26, 126.22	109.68	−18.98	261.22 t	12.1		41.81 ($=CCH_3$)	48.60 t (J_{CP} = 23.4, PCH_2P); 128.41 −136.47 (PPh_2, Ph)

[a] Spectra recorded in CD_2Cl_2. δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [b] $\Delta\delta$(C-3a,7a) = δ(C-3a,7a(η-indenyl complex)) − δ(C-3a,7a(sodium indenyl)). δ(C-3a,7a(sodium indenyl)) = 130.70 ppm.

$SiMe_4$ or 85% H_3PO_4 as standards. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic data for the vinylidene and carbene complexes are collected in Tables 1, 2, 5, and 6.

Preparation of Alkynyl Complexes. (a) [Ru(C≡CR^1)(η^5-C_9H_7)L_2] (L_2 = 2PPh$_3$, R^1 = Ph (1a), ^{t}Bu (2a), ^{n}Pr (3a); L_2 = dppe, R^1 = Ph (1b), ^{t}Bu (2b), ^{n}Pr (3b); L_2 = dppm, R^1 = Ph (1c)). General Procedure. A solution of potassium hydroxide (9.1 mL, 0.11 M in methanol, 1 mmol) was added to a solution prepared by gentle reflux of a mixture of [RuCl(η^5-C_9H_7)L_2] (1 mmol) and the corresponding alkyne (6 mmol) in methanol (60 mL). Immediately, a yellow-orange suspension was formed. The solvent was then decanted, and the solid residue was dissolved in dichloromethane (5 mL) and transferred to an Alox IV chromatography column. Elution with dichloromethane gave an orange band which was collected and evaporated to give the desired compounds. Yield (%), color, IR (KBr, *υ*(C≡C), cm^{-1}), and NMR spectroscopic and analytical data are as follows. **1a**: identified by comparison with reported data;[15a] further information, 70; yellow; ^{31}P{^{1}H}-($CDCl_3$) δ 52.27 ppm; ^{13}C{^{1}H}($CDCl_3$) δ 74.87 (s, C-1.3), 94.93 (s, C-2), 109.08 (s, C-3a,7a), 114.25 (m, Ru-C$_\alpha$), 122.40 (s, ≡C$_\beta$), 123.17 and 126.10 (s, C-4,7 and C-5,6), 127.49−138.83 (m, PPh$_3$, Ph) ppm. **2a**: 65; yellow-orange; 2095; ^{31}P{^{1}H} ($CDCl_3$) δ 53.29 ppm; ^{1}H ($CDCl_3$) δ 1.16 (s, 9H, C(CH_3)$_3$), 4.37 (d, 2H, J_{HH} = 2.6 Hz, H-1,3), 4.98 (t, 1H, J_{HH} = 2.6 Hz, H-2), 6.24 and 6.65 (m, 2H each, H-4,7 and H-5,6), 6.98-7.36 (m, 30H, PPh$_3$) ppm. Anal. Calcd for $RuC_{51}H_{46}P_2$: C, 74.54; H, 5.64. Found: C, 74.06; H, 5.53. **3a**: 75; yellow-orange; 2098; ^{31}P{^{1}H} ($CDCl_3$) δ 51.78 ppm; ^{1}H ($CDCl_3$) δ 0.92 (t, 3H, J_{HH} = 7.27 Hz, −CH_3), 1.41 (m, 2H, −CH_2), 2.37 (t, 2H, J_{HH} = 7.0 Hz, ≡CCH_2), 4.45 (d, 2H, J_{HH} = 2.3 Hz, H-1,3), 5.27 (t, J_{HH} = 2.3 Hz, 1H, H-2), 6.14 and 6.67 (m, 2H each, H-4,7 and H-5,6), 7.04-7.59 (m, 30H, PPh$_3$) ppm; ^{13}C{^{1}H}($CDCl_3$) δ 15.08 (s, CH_3), 25.69 (s, CH_2), 26.72 (s, =CCH_2), 75.29 (t, $^2J_{CP}$ = 3.5 Hz, C-1,3), 87.30 (t, $^2J_{CP}$ = 25.0 Hz, Ru−C$_\alpha$), 96.28 (s, C-2), 109.82 (s, C-3a,7a), 111.18 (s, ≡C$_\beta$), 123.78 and 126.24 (s, C-4,7 and C-5,6), 127.82-140.17 (m, PPh$_3$) ppm. Anal. Calcd for $RuC_{50}H_{44}P_2$: C, 74.33; H, 5.48. Found: C, 73.73; H, 5.48. **1b**: 75; yellow; 2079; ^{31}P{^{1}H} (CD_2Cl_2) δ 87.03 ppm; ^{1}H (CD_2Cl_2) δ 2.12 (m, 2H, P(C*H*$_a$H$_b$)$_2$P), 2.51 (m, 2H, P(CH$_a$*H*$_b$)$_2$P), 5.01 (d, 2H, J_{HH} = 2.5 Hz, H-1,3), 5.21 (t, 1H, J_{HH} = 2.5 Hz, H-2), 6.35−7.18 (m, 29H, PPh$_2$, Ph, H-4,7 and H-5,6) ppm. Anal. Calcd for $RuC_{43}H_{36}P_2$: C, 72.16; H, 5.07. Found: C, 71.66; H, 5.12. **2b**: 70; orange; 2097; ^{31}P{^{1}H} (CD_2Cl_2) δ 87.63 ppm; ^{1}H (CD_2Cl_2) δ 0.55 (s, 9H, C(CH_3)$_3$), 2.09 (m, 2H, P(C*H*$_a$H$_b$)$_2$P), 2.54 (m, 2H, p(CH$_a$*H*$_b$)$_2$P), 4.95 (d, 2H, J_{HH} = 2.5 Hz, H-1.3), 5.08 (t, 1H, J_{HH} = 2.5 Hz, H-2), 6.87 and 6.99 (m, 2H each, H-4,7 and H-5,6), 7.08−7.55 (m, 20H, PPh$_2$) ppm; ^{13}C{^{1}H} (CD_2Cl_2) δ 27.95 (m, P(CH_2)$_2$P), 29.50 (s, =C*C*(CH_3)$_3$), 32.45 (s, (CH_3)$_3$), 69.58 (t, $^2J_{CP}$ = 2.6 Hz, C-1,3), 89.01 (t, $^2J_{CP}$ = 25.4 Hz, Ru−C$_\alpha$), 92.11 (s, C-2), 107.72 (s, C-3a,7a), 117.99 (s, ≡C$_\beta$), 123.61 and 124.35 (s, C-4,7 and C-5,6), 127.34-142.36 (m, PPh$_2$) ppm. Anal. Calcd for $RuC_{41}H_{40}P_2$: C, 70.77; H, 5.79. Found: C, 70.39; H, 5.78. **3b**: 80; yellow; 2100; ^{31}P{^{1}H} ($CDCl_3$) δ 87.08 ppm; ^{1}H ($CDCl_3$) δ 0.74 (t, 3H, J_{HH} = 7.2 Hz, CH_3), 1.12 (m, 2H, CH_2), 1.92 (m, 2H, P(CH_2)$_2$P), 2.15 (t, 2H, J_{HH} = 6.7 Hz, ≡CCH_2), 2.51 (m, 2H, P(CH_2)$_2$P), 5.05 (d, 2H, J_{HH} = 2.4 Hz, H-1,3), 5.18 (t, 1H, J_{HH} = 2.4 Hz, H-2), 6.92 (m, 2H, Ind), 7.03−7.65 (m, 22H, PPh$_2$, Ind) ppm; ^{13}C{^{1}H} (CD_2Cl_2) δ 13.56 (s, CH_3), 24.37 (s, CH_2), 24.83 (s, =CCH_2), 27.80 (m, P(CH_2)$_2$P), 69.36 (s, C-1,3), 91.91 (s, C-2), 107.82 (s, C-3a,7a), 123.64 and 124.22 (s, C-4,7 and C-5,6), 127.58−137.86 (m, PPh$_2$) ppm. Anal. Calcd for $RuC_{40}H_{38}P_2$: C, 70.47; H, 5.62. Found: C, 70.66; H, 5.91. **1c**: 75; yellow; 2075; ^{31}P{^{1}H} ($CDCl_3$) δ 19.02 ppm; ^{1}H ($CDCl_3$) δ 4.05 (dt, 1H, J_{HH} = 14.0 Hz, $^2J_{HP}$ = 12.0 Hz, P(C*H*$_a$H$_b$)P), 4.74 (dt, 1H, J_{HH} = 14.0 Hz, $^2J_{HP}$ = 9.6 Hz, P(CH$_a$*H*$_b$)P), 5.19 (t, 1H, J_{HH} = 2.6 Hz, H-2), 5.24 (d, 2H, J_{HH} = 2.6 Hz, H-1,3), 6.05−7.57 (m, 29H, PPh$_2$, Ph, H-4,7 and H-5,6) ppm. Anal. Calcd for $RuC_{42}H_{34}P_2$: C, 71.88; H, 4.88. Found: C, 72.76; H, 4.83.

(b) [Ru(C≡CH)(η^5-C_9H_7)L_2] (L_2 = 2PPh$_3$ (4a), dppe (4b)). General Procedure. A solution of **8a** or **8b** (1 mmol) in THF (10 mL) was treated with KO^{t}Bu (0.123 g, 1.1 mmol) and the mixture stirred at room temperature for 0.5 h. The solution was then evaporated to dryness and the residue extracted with diethyl ether. The partial evaporation of the diethyl ether gave **4a** and **4b** as yellow solids. Yield (%), color, and IR (KBr, *υ*(C≡C), cm^{-1}), and NMR spectroscopic, and analytical data are as follows. **4a**: 80; yellow; 1936; ^{31}P{^{1}H} ($CDCl_3$) δ 51.36 ppm; ^{1}H ($CDCl_3$) δ 2.39 (t, 1H, $^4J_{HP}$ = 2.0 Hz, ≡CH), 4.73 (d, 2H, J_{HH} = 2.3 Hz, H-1,3), 5.66 (t, 1H, J_{HH} = 2.3 Hz, H-2), 6.34 and 6.68 (m, 2H each, H-4,7 and H-5,6), 6.92−7.52 (m, 30H, PPh$_3$) ppm; ^{13}C{^{1}H} (CD_2Cl_2) δ 74.34 (t, $^2J_{CP}$ = 3.7 Hz, C-1,3), 95.41 (s, C-2), 98,39 (s, ≡C$_\beta$), 104.88 (t, $^2J_{CP}$ = 23.0 Hz, Ru−C$_\alpha$), 109.32 (s, C-3a,7a), 123.19, 126.02 (s, C-4,7 and C-5,6), 127.28−139.13 (m, PPh$_3$) ppm. Anal. Calcd for $RuC_{47}H_{38}P_2$: C, 73.71; H, 5.00. Found: C, 72.39; H, 5.10. **4b**: 70; yellow; 1933; ^{31}P{^{1}H} ($CDCl_3$) δ 84.00 ppm; ^{1}H ($CHCl_3$) δ 2.13 (m, 2H, P(C*H*$_a$CH$_b$)P), 2.80 (m, 3H, P(CH$_a$C*H*$_b$)P, ≡CH), 5.26 (d, 2H, J_{HH} = 2.4 Hz, H-1,3), 5.42 (t, 1H, J_{HH} = 2.4 Hz, H-2), 6.99−7.93 (m, 24H, PPh$_2$, H-4,7 and H-5,6) ppm; ^{13}C{^{1}H} ($CDCl_3$) δ 27.75 (m, P(CH_2)$_2$P), 69.81 (s, C-1,3), 92.22 (s, C-2), 94.83 (s, ≡C$_\beta$), 108.03 (s, C-3a,7a), 108.89 (m, Ru−C$_\alpha$), 124.05 and 124.33 (s, C-4,7 and C-5,6), 127.66−141.64 (m, PPh$_2$) ppm. Anal. Calcd for $RuC_{37}H_{32}P_2$: C, 69.47; H, 5.04. Found: C, 68.17; H, 5.20.

Preparation of Vinylidene Complexes. (a) [Ru{=C=C(H)R^1}(η^5-C_9H_7)L_2][Y] (L_2 = 2PPh$_3$, R^1 = Ph (5a), ^{t}Bu (6a), ^{n}Pr (7a); L_2 = dppe, R^1 = Ph (5b), ^{t}Bu (6b), ^{n}Pr (7b); L_2 = dppm, R^1 = Ph (5c); [Y] = BF_4^-, PF_6^-). Procedure a. A stirred solution of the corresponding alkynyl complex [Ru(C≡CR^1)(η^5-C_9H_7)L_2] (1 mmol) in diethyl ether (100 mL), at room temperature, was treated dropwise with a dilute solution of HBF_4·OEt_2 in diethyl ether. Immediately, an insoluble solid precipitated but the addition was continued until no further solid was formed. The solution was decanted and the solid washed with diethyl ether (3 × 20 mL) and vacuum-dried.

Procedure b. A mixture of [RuCl(η^5-C_9H_7)L_2] (0.5 mmol), $NaPF_6$ (0.168 g, 1 mmol), and the corresponding alkyne (2.5 mmol) in methanol (30 mL), or ethanol in the case of the preparation of the complex **5c**, was heated under reflux (*ca.* 15 min) to give a yellow-orange solution. The resulting solution was evaporated to dryness and the solid residue was dissolved in dichloromethane (*ca.* 4 mL) and filtered into 100 mL of stirred diethyl ether to give a solid precipitate. The resulting solid was washed with diethyl ether (3 × 20 mL) and vacuum-dried.

The procedure used, yield (%), color, IR (KBr, cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m/e*), and analytical data (NMR spectroscopic data are collected in Tables 1 and 2) are as follows. **5a**: (b); 75; pink; 837 *υ*(PF_6^-); 116.2; [M$^+$] = 843, [M$^+$ − R] = 741 (R: =C=C(H)Ph), [M$^+$ − R − PPh$_3$] = 479, [M$^+$ − PPh$_3$] = 581, [M$^+$ − R − C_9H_7] = 625, [M$^+$ − R − C_9H_7 − PPh$_3$] = 363. Alternatively, procedure a can also be used. Anal. Calcd for $RuC_{53}H_{43}P_3F_6$: C, 64.44; H, 4.39. Found: C, 63.62; H, 4.28. **6a**: (a); 75; orange; 1084 *υ*(BF_4^-); 123.8; [M$^+$] = 823, [M$^+$ − R] = 741 (R: =C=C(H)^{t}Bu), [M$^+$ − R − PPh$_3$] = 479, [M$^+$ − PPh$_3$] = 560, [M$^+$ − R − C_9H_7] = 625, [M$^+$ − R − C_9H_7 − PPh$_3$] = 363. Anal. Calcd for $RuC_{51}H_{47}P_2BF_4$: C, 67.33; H, 5.21. Found: C, 67.13; H, 5.22. **7a**: (a); 90; orange; 1085 *υ*(BF_4^-); 125.9; [M$^+$] = 809, [M$^+$ − R] = 741 (R: =C=C(H)^{n}Pr), [M$^+$ − R − PPh$_3$] = 479, [M$^+$ − PPh$_3$] = 581, [M$^+$ − R − C_9H_7] = 625, [M$^+$ − R − C_9H_7 − PPh$_3$] = 363. Anal. Calcd for $RuC_{50}H_{45}P_2BF_4$: C, 67.05; H, 5.06. Found: C, 67.22; H, 5.02. **5b**: (a); 80; sand; 1084 *υ*(BF_4^-); 130; [M$^+$] = 717, [M$^+$ − R] = 615 (R: =C=C(H)Ph), [M$^+$ − R − C_9H_7] = 497. Anal. Calcd for $RuC_{43}H_{37}P_2BF_4$: C, 64.27; H, 4.64. Found: C, 63.11; H, 4.60. Alternatively procedure b can also be used. **6b**: (a); 80; sand; 1084 *υ*(BF_4^-); 149; [M$^+$] = 697, [M$^+$ − R] = 615 (R: =C=C(H)^{t}Bu), [M$^+$ − R − C_9H_7] = 497. Anal. Calcd for $RuC_{41}H_{41}P_2BF_4$; C, 62.84; H, 5.27. Found: C, 62.71; H, 4.98. **7b**: (a); 85; sand; 1084 *υ*(BF_4^-); 142; [M$^+$] = 683, [M$^+$ − R] = 615 (R: =C=C(H)^{n}Pr), [M$^+$ − R − C_9H_7] = 497. Anal. Calcd for $RuC_{40}H_{39}P_2BF_4$: C, 62.43; H, 5.11. Found: C, 61.70; H, 4.98. **5c**: (b); 75; orange;

837 $\nu(PF_6^-)$; 141; $[M^+] = 703$, $[M^+ - R] = 605$ (R: $=C=C(H)Ph$), $[M^+ - R - C_9H_7] = 485$. Anal. Calcd for $RuC_{42}H_{35}P_3F_6$: C, 59.43; H, 4.12. Found: C, 59.32; H, 4.14. Alternatively procedure a can also be used.

(b) $[Ru\{=C=C(Me)R^1\}(\eta^5\text{-}C_9H_7)L_2][CF_3SO_3]$ (L_2 = 2PPh$_3$, R^1 = Ph (9a), ^{t}Bu (10a), ^{n}Pr (11a); L_2 = dppe, R^1 = Ph (9b), ^{t}Bu (10b), ^{n}Pr (11b); L_2 = dppm, R^1 = Ph (9c)). General Procedure. A solution of the corresponding alkynyl complex $[Ru(C{\equiv}CR^1)(\eta^5\text{-}C_9H_7)L_2]$ (1 mmol) in dichloromethane (15 mL) was treated with $MeOSO_2CF_3$ (0.11 mL, 1 mmol) and stirred at room temperature until the complete disappearance of the $\nu(C{\equiv}C)$ band (the reaction was monitored by IR spectroscopy). The resulting solution was then partially concentrated and added into 100 mL of stirred diethyl ether. The resulting solid was washed with diethyl ether (2 × 30 mL) and vacuum-dried. Yield (%), color, IR (KBr, $\nu(CF_3SO_3^-)$, cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m/e*), and analytical data (NMR spectroscopic data are collected in Tables 1 and 2) are as follows. **9a**: 85; pink; 1262 s, br, 1222 s, 1145 s; 119.2; $[M^+] = 857$, $[M^+ - R] = 741$ (R: $=C=C(Me)Ph$), $[M^+ - PPh_3] = 595$, $[M^+ - R - PPh_3] = 479$. Anal. Calcd for $RuC_{55}H_{45}P_2O_3SF_3$: C, 65.66; H, 4.50. Found: C, 65.86; H, 4.50. **10a**: 60; orange; 1265 s, br, 1225 s, 1149 s; 120; $[M^+] = 837$, $[M^+ - R] = 741$ (R: $=C=C(Me)^tBu$), $[M^+ - PPh_3] = 575$, $[M^+ - R - PPh_3]$ 479, $[M^+ - R - PPh_3 - C_9H_7] = 363$. Anal. Calcd for $RuC_{53}H_{49}P_2O_3SF_3$: C, 64.55; H, 5.09. Found: C, 65.39; H, 5.29. **11a**: 70; orange; 1267 s, br, 1224 s, 1152 s; 107; $[M^+] = 823$, $[M^+ - PPh_3] = 561$, $[M^+ - R - PPh_3] = 479$ (R: $=C=C(Me)^nPr$), $[M^+ - PPh_3 - C_9H_7] = 443$. Anal. Calcd for $RuC_{52}H_{47}P_2O_3SF_3$: C, 64.30; H, 4.87. Found: C, 63.74; H, 4.78. **9b**: 75; pink; 1272 s, br, 1224 s, 1145 s; 125; $[M^+] = 731$, $[M^+ - R] = 615$ (R: $=C=C(Me)Ph$), $[M^+ - R - C_9H_7] = 499$. Anal. Calcd for $RuC_{45}H_{39}P_2O_3SF_3$: C, 61.95; H, 4.47. Found: C, 61.50; H, 4.50. **10b**: 70; pink; 1266 s, br, 1223 s, 1149 s; 144; $[M^+] = 711$, $[M^+ - R] = 615$ (R: $=C=C(Me)^tBu$), $[M^+ - R - C_9H_7] = 499$. Anal. Calcd for $RuC_{43}H_{43}P_2O_3SF_3$: C, 60.06; H, 5.04. Found: C, 58.94; H, 5.03. **11b**: 70; orange; 1262 s, br, 1224 s, 1152 s; 135. Anal. Calcd for $RuC_{42}H_{44}P_2O_3SF_3$: C, 59.42; H, 5.24. Found: C, 59.44; H, 5.55. **9c**: 80; pink; 1263 s, br, 1223 s, 1149 s; 128; $[M^+] = 717$, $[M^+ - R] = 605$ (R: $=C=C(Me)Ph$), $[M^+ - R - C_9H_7] = 485$. Anal. Calcd for $RuC_{44}H_{37}P_2O_3SF_3$: C, 61.04; H, 4.28. Found: C, 60.30; H, 4.32.

(c) $[Ru(=C=CMe_2)(\eta^5\text{-}C_9H_7)L_2][CF_3SO_3]$ (L_2 = 2PPh$_3$ (12a), dppe (12b)). $MeOSO_2CF_3$ (0.22 mL, 2 mmol) was added dropwise to a solution of $[Ru(C{\equiv}CH)(\eta^5\text{-}C_9H_7)L_2]$ (1 mmol) in dichloromethane. The solution was stirred for 10 min and evaporated to dryness. The resulting solid was then transferred into an Alox I chromatography column. Elution with a mixture of diethyl ether and methanol (10:1) gave a band which was collected and evaporated to give the desired compound as a brown solid. Yield (%), IR (KBr, $\nu(CF_3SO_3^-)$, cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m/e*), and analytical data are as follows (NMR spectroscopic data are collected in Tables 1 and 2). **12a**: 35; 1273 s, br, 1223 s, 1149 s; 148. Anal. Calcd for $RuC_{50}H_{43}P_2O_3SF_3$: C, 61.30; H, 4.55. Found: C, 61.59; H, 5.59. **12b**: 30; 1270 s, br, 1227 s, 1147 s; 135; $[M^+] = 669$, $[M^+ - R] = 615$ (R: $=C=CMe_2$), $[M^+ - C_9H_7] = 553$, $[M^+ - R - C_9H_7] = 499$. Anal. Calcd for $RuC_{40}H_{37}P_2O_3SF_3$: C, 58.75; H, 4.50. Found: C, 58.11; H, 4.19.

(d) $[Ru(=C=CH_2)(\eta^5\text{-}C_9H_7)L_2][PF_6]$ (L_2 = 2PPh$_3$ (8a), dppe (8b)). General Procedure. A mixture of $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ (1 mmol), $HC{\equiv}CSiMe_3$ (0.7 mL, 5 mmol), and NH_4PF_6 (0.326 g, 2 mmol) in dichloromethane (40 mL) was heated at a temperature and for a time that is indicated below. The resulting suspension was then partially concentrated and filtered into 100 mL of stirred diethyl ether. The resulting solid was washed with diethyl ether (3 × 20 mL) and vacuum-dried. Temperature (°C), reaction time, yield (%), color, IR (KBr, $\nu(PF_6^-)$, cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m/e*), and analytical data are as follows (NMR spectroscopic data are collected in Tables 1 and 2). **8a**: 40; 4 h; 75; yellow-sand; 836; 140.1; $[M^+] = 767$, $[M^+ - R - PPh_3] = 479$ (R: $=C=CH_2$), $[M^+ - PPh_3] = 503$, $[M^+ - PPh_3 - C_9H_7] = 395$, $[M^+ - R - C_9H_7 - PPh_3] = 363$. Anal. Calcd for $RuC_{47}H_{39}P_3F_6$: C, 61.91; H, 4.31. Found: C, 62.16; H, 4.45. **8b**: 90, in a sealed tube; 7 h; 75; yellow-sand; 838; 135; $[M^+] = 641$, $[M^+ - R] = 615$ (R: $=C=CH_2$), $[M^+ - R - C_9H_7] = 497$. Anal. Calcd for $RuC_{37}H_{33}P_3F_6$: C, 56.57; H, 4.23. Found: C, 56.72; H, 4.12.

Preparation of Carbene Complexes. (a) $[Ru\{=C(OR^2)R^1\}(\eta^5\text{-}C_9H_7)L_2][PF_6]$ (L_2 = 2PPh$_3$, R^1 = Me, R^2 = Me (13a), Et (14a); L_2 = dppe, R^1 = Me, R^2 = Me (13b), Et (14b); L_2 = dppm, R^1 = Me, R^2 = Me (13c), Et (14c), R^1 = Bz, R^2 = Me (15c)). Procedure a. A mixture of the complex $[RuCl(\eta^5\text{-}C_9H_7)L_2]$ (1 mmol), NH_4PF_6 (0.25 g, 1.5 mmol), and the alkyne (5 mmol) ($HC{\equiv}CSiMe_3$ for the complexes **13a**, **13b**, and **13c** or $HC{\equiv}CPh$ for the complex **15c**) in methanol was heated under reflux for approximately 3 h. The yellow solution was then evaporated to dryness; the solid residue was extracted with dichloromethane (ca. 3 mL), and the extracts were filtered into 100 mL of stirred diethyl ether, giving the desired complex as a light yellow precipitate.

Procedure b. A suspension of the vinylidene **8a** or **8b** (1 mmol) in methanol was heated under reflux for approximately 3 h. The yellow solution was then evaporated to dryness. The resulting solid was extracted with dichloromethane (*ca.* 3 mL), and the extracts were filtered into 100 mL of stirred diethyl ether, giving the desired complex as a light yellow precipitate. The complexes **14a**, **14b**, and **14c** were prepared using ethanol instead of methanol. Procedure employed, yield (%), IR (KBr, $\nu(PF_6^-, =COR^2)$, cm^{-1}), conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}), mass spectrum (FAB, *m/e*), and analytical data are as follows (NMR spectroscopic data are collected in Tables 5 and 6). **13a**: procedures a and b gave similar results; 85; 840, 1253; 121; $[M^+] = 799$, $[M^+ - PPh_3] = 537$, $[M^+ - PPh_3 - R] = 479$ (R: $=C(OMe)Me$). Anal. Calcd for $RuC_{48}H_{43}P_3F_6O$: C, 61.08; H, 4.59. Found: C, 60.50; H, 4.59. **14a**: procedures a and b gave similar results; 75; 840, 1234; 140.1; $[M^+] = 813$, $[M^+ - PPh_3] = 507$, $[M^+ - PPh_3 - R] = 479$ (R: $=C(OEt)Me$). Anal. Calcd for $RuC_{49}H_{45}P_3F_6O$: C, 61.44; H, 4.73. Found: C, 60.62; H, 4.63. **13b**: procedures a and b gave similar results; 85; 839, 1236; 150; $[M^+] = 673$, $[M^+ - R] = 615$ (R: $=C(OMe)Me$). Anal. Calcd for $RuC_{38}H_{37}P_3F_6O$: C, 55.82; H, 4.56. Found: C, 56.72; H, 4.52. **14b**: procedures a and b gave similar results; 85; 838, 1241; 110; $[M^+] = 687$, $[M^+ - R] = 615$ (R: $=C(OEt)Me$). Anal. Calcd for $RuC_{39}H_{39}P_3F_6O$: C, 56.32; H, 4.73. Found: C, 56.44; H, 4.59. **13c**: (a); 85; 838, 1240; 105.7; $[M^+] = 659$, $[M^+ - R] = 601$ (R: $=C(OMe)Me$), $[M^+ - R - C_9H_7] = 485$. Anal. Calcd for $RuC_{37}H_{35}P_3F_6O$: C, 55.30; H, 4.39. Found: C, 54.33; H, 4.37. **14c**: (a); 80; 838, 1235; 135. Anal. Calcd for $RuC_{38}H_{37}P_3F_6O$: C, 55.82; H, 4.56. Found: C, 55.95; H, 4.60. **15c**: procedures a and b gave similar results; 75; 837, 1236; 122.5; $[M^+] = 735$, $[M^+ - R] = 601$ (R: $=C(OMe)Bz$). Anal. Calcd for $RuC_{42}H_{39}P_3F_6O$: C, 58.13; H, 4.53. Found: C, 58.61; H, 4.45.

(b) $[Ru\{=C=C(NH_2)Me\}(\eta^5\text{-}C_9H_7)(dppm)][PF_6]$ (16c). A mixture of $[RuCl(\eta^5\text{-}C_9H_7)(dppm)]$ (1 mmol), $HC{\equiv}CSiMe_3$ (0.7 mL, 5 mmol), and NH_4PF_6 (0.326 g, 2 mmol) in dichloromethane (*ca.* 40 mL) was heated at 90 °C in a sealed tube over 15 h. The resulting suspension was then concentrated and filtered into an excess of stirred diethyl ether, giving a light yellow precipitate. The solution was decanted and the resulting solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield (%), IR (KBr, $\nu(PF_6^-)$, cm^{-1}) and analytical data are as follows: 65; 840. Anal. Calcd for $RuC_{36}H_{35}P_3F_6N$: C, 54.75; H, 4.43; N, 1.70. Found: C, 55.80; H, 4.35; N, 1.35.

X-ray Diffraction Study. Data collection, crystal, and refinement parameters are collected in Table 4. Diffraction measurements were made on a Enraf-Nonius CAD4 diffractometer. The unit cell parameters were obtained from a least-squares fit of 25 reflections (with θ between 15 and 20°). Data were collected with the $\omega-2\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. On all reflections, profile analysis[37,38] was performed. The final drift correction factors were between 0.99 and 1.04. Some double-measured reflections were averaged (the agreement between equivalent reflections was $R_{\text{int}} = \Sigma(I - \langle I\rangle)/\Sigma I = 0.038$). Lorentz and polarization corrections were applied, and the data were reduced to $|F_o|$ values.

The structure was solved by Patterson methods using the program SHELX86[39] and expanded by DIRDIF.[40] Isotropic least-squares refinement using SHELX76[41,42] converged to $R = 0.108$. At this stage an empirical absorption correction was applied using DIFABS.[43]

Hydrogen atoms were geometrically placed. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. The hydrogen atoms were isotropically refined with a common thermal parameter, riding on their parent atoms.

Finally, a full-matrix least-squares refinement on F^2 was made using SHELXL93.[44] The function minimized was $w = 1/[\sigma^2(F_o^2) + (0.1257P)^2 + 0.0P]$, where $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$, with $\sigma^2(F_o^2)$ from counting statistics (final R factors: $R(I > 2\sigma(I))$ $R1 = 0.066$, w$R2 = 0.173$; R(all data) $R1 = 0.148$, w$R2 = 0.221$). The maximum shift to esd ratio in the last full-matrix least-squares cycle was -0.002. The $CF_3SO_3^-$ anion was affected by strong structural disorder and refined with some fixed positional parameters. The CH_2C_2 solvent molecule was also found to be disordered, and its hydrogens were omitted in the refinement. The methyl group C(4) was found also with two disordered positions with a contribution of C(4) and C(4′) of 42% and 58%, respectively. The final difference Fourier map showed no peaks higher than 1.23 e Å^{-3} near the disordered $CF_3SO_3^-$, nor any deeper than -0.88 e Å^{-3}. Atomic scattering factors were taken from ref 45. Geometrical calculations were made with PARST.[46] The crystallographic plots were made with EUCLID.[47] All calculations were performed on a MicroVAX 3400 at the Scientific Computer Center of the University of Oviedo.

Molecular Orbital Calculations. Calculations were carried out at the extended Hückel level,[48] on the compound **12a** using $[Ru(=C=CMe_2)(\eta^5\text{-}C_9H_7)(PH_3)_2]^+$ as a model, by the weighted H_{ij} formula.[49] Standard atomic parameters were taken for H, C, N, O, and P. The exponents (ζ) an the valence shell ionization potentials (H_{ii}, in eV) for Ru were respectively 2.078 and -8.60 for 5s, 2.043 and -5.10 for 5 p. A linear combination of two Slater-type orbitals ($\zeta_1 = 5.378$, $c_1 = 0.5340$; $\zeta_2 = 2.303$, $c_2 = 0.6365$) was used to represent the atomic d orbitals. The H_{ii} value for 4d was set equal to -12.20 eV.

In our structural model the hydrogen atoms replace the phenyl groups in the phosphine ligands. We optimized the PH_3, CH_3, and indenyl groups with bond distances C—H = 1.080 Å, P—H = 1.437 Å, C—C = 1.421 Å in the five-membered ring and C—C = 1.405 Å in the six-membered ring, keeping the idealized angles.

The calculations were carried out on a MicroVAX 3400 computer at the Scientific Computer Center of the University of Oviedo, with a locally modified version of the program ICON.

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Supplementary Material Available: Crystal structure data for **12a**, including tables of atomic parameters, anisotropic thermal parameters, bond distances, and bond angles and a plot showing all carbon atoms of the PPh_3 ligands, and ^1H NMR spectra for the complexes **4b**, **5b**, and **10b** (26 pages). Ordering information is given on any current masthead page.

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