Six-Coordinate Alkynyldiphenylphosphine Ruthenium(II) Complexes: Synthesis, Structure, and Catalytic Activity as ROMP Initiators

María Bernechea,[†,‡] Noël Lugan,*[,‡] Belén Gil,[†] Elena Lalinde,*[,†] and Guy Lavigne*[,‡]

Departamento de Química-Grupo de Síntesis Química de La Rioja, UA-CSIC, Universidad de La Rioja, 26006, Logroño, Spain, and Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France

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Six-coordinate [*trans*-$RuCl_2(PPh_2C{\equiv}CR)_4$] (R = Ph (**1**), $(4\text{-}CH_3)C_6H_4$ (**2**), $(4\text{-}OCH_3)C_6H_4$, (**3**), $(4\text{-}CF_3)C_6H_4$ (**4**)) were obtained from the reaction of $RuCl_3{\cdot}xH_2O$ with the appropriate alkynylphosphine ($PPh_2C{\equiv}CR$) in ethanol. An X-ray crystal structure analysis of **1**·$4H_2O$ reveals that the complex is obtained as the *trans* isomer, with the halides occupying apical positions and the phosphorus atoms lying in the equatorial plane. The alkynyl substituents of adjacent P ligands are alternatively pointing up and down and are maintained within the vertical plane by a set of weak hydrogen interactions [*intra* C−H···Cl and C−H···π(C≡CPh)] connecting the *ortho*-H of the phenyl rings with the chloride and acetylenic moieties, respectively. Complexes **1** and **2** react cleanly with phenylacetylene via dissociative loss of one alkynyphosphine ligand to yield saturated 18 e^- Ru(II) vinylidene complexes [*mer*,*cis*-$RuCl_2(C{=}CHPh)(PPh_2C{\equiv}CR)_3$] (R = Ph (**12**), Tol (**13**)). The catalytic activity of **1**−**4** in ROMP reactions of norbornene and several functionalized norbornenes in the presence of trimethylsilyldiazomethane (TMSD) as the carbene source is also described.

Introduction

Our current interest in alkynylphosphines[1−10] stems from their now well-established ability to coordinate via the phosphorus atom and/or the C≡C moiety, thus favoring the formation of a rich variety of homo- or hetero-polynuclear species.[1−15] Among other versatile properties of these ligands are (i) their aptitude to act as sources of phosphido and alkynyl fragments via metal-mediated P−C bond cleavage[16] and (ii) their possible engagement in characteristic reactions of the triple bond, namely, intermolecular coupling of the alkynyl moieties leading to association of two coordinated alkynylphosphines,[3,5,8,17] insertion of the triple bond into reactive M−H or M−C bonds,[3,5,8,18−20] or even its activation toward reaction with electrophilic or nucleophilic substrates.[19,21,22]

The chemistry of saturated (18 e^-) and specially unsaturated (16 e^-) halide/cyclopentadienyl and/or arene-phosphine and/or diphosphine ruthenium(II) complexes has gained significance in recent years owing to the current implication of these species as reactive intermediates in organic and organometallic synthesis as well as in homogeneous catalysis.[23−39] Among various

* Corresponding authors. E-mail: elena.lalinde@dq.unirioja.es; lavigne@lcc-toulouse.fr; lugan@lcc-toulouse.fr.
† Universidad de La Rioja, UA-CSIC.
‡ Laboratoire de Chimie de Coordination du CNRS.

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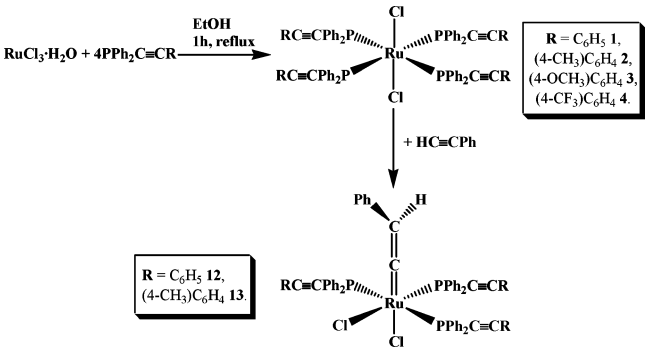
phosphorus-based ligands that may be used to tune the reactivity of the above complexes, heterobifunctional P−N and P−O ligands have received particular attention due to their valuable hemilabile properties.[40−48] By contrast, little is known about the outcome of a heterobifunctional association combining a phosphorus donor atom with vinyl, allyl, or alkynyl groups.[4,7,49−55]

As part of our continuing interest in the chemistry of alkynylphosphines,[1−10] we now report the preparation of the first 18 e$^-$ neutral complexes [*trans*-$RuCl_2(PPh_2C{\equiv}CR)_4$] and their full characterization, including the X-ray crystal structure analysis of [*trans*-$RuCl_2(PPh_2C{\equiv}CPh)_4]{\cdot}4H_2O$. As shown below, preliminary studies of the reactivity of this species toward terminal alkynes led us to observe the clean formation of vinylidene complexes, which were also fully characterized. In addition, considering that vinylidenes are carbenoids, we were logically prompted to examine possibilities to use our alkynylphosphine Ru(II) complexes as precatalysts in the ROMP of norbornene, taken as a test metathesis reaction. To our surprise, preliminary catalytic runs included here revealed an unexpected high efficiency of the above complexes for this reaction.

Results and Discussion

I. Synthesis and Characterization of [*trans*-$RuCl_2(PPh_2C{\equiv}CR)_4$]. Reaction of $RuCl_3{\cdot}xH_2O$ with stoichiometric amounts (1:4 molar ratio) of the appropriate alkynylphosphine, $PPh_2C{\equiv}CR$, in degassed, refluxing EtOH, under N_2, for ca. 1 h yielded the corresponding tetrakis(phosphine) complexes [*trans*-$RuCl_2(PPh_2C{\equiv}CR)_4$] (R = Ph (**1**), $(4\text{-}CH_3)C_6H_4$ (**2**), $(4\text{-}OCH_3)C_6H_4$, (**3**), $(4\text{-}CF_3)C_6H_4$ (**4**)) in high (**1**, **2**, **4**) or low (**3**) yield, which were characterized by the usual analytical and spectroscopic techniques (Scheme 1). These complexes are air stable in the solid state. In solution, they evolve slowly, and after 24 h in $CDCl_3$, $PPh_2C{\equiv}CR$, $O{=}PPh_2C{\equiv}CR$, and an unidentified derivative (similar for all the complexes, $^{31}P\{^1H\}$ NMR: $\delta \sim 37$, broad and ∼30, triplet) together with the corresponding complex (**1**−**4**) were observed. The FAB mass spectra do not show the corresponding molecular peak but exhibit a similar fragmentation pattern with peaks due to $[M - PPh_2C{\equiv}CR]^+$ and $[M - Cl - PPh_2C{\equiv}CR]^+$ as the most abundant species. Their IR spectra show a strong band in the 2173−2184 cm^{-1} range for the $\nu(C{\equiv}C)$ stretching frequency, typical of P-coordinated alkynylphosphines. The small increase in the $\nu(C{\equiv}C)$ relative to free ligands upon coordination ($\Delta\nu(C{\equiv}C)$: 24 (**1**); 27 (**2**); 19 (**3**); 5 (**4**) cm^{-1}) is consistent with the lesser delocalization of the phosphorus lone pair on the π^* C≡C orbitals.[2,4,6−8,56] NMR characterization was carried out at low temperature. The existence of this species in the form of the *trans* isomer can be inferred from $^{31}P\{^1H\}$ NMR spectra showing a singlet signal [δ −4.19 to −5.08 ppm], which is, as expected, clearly downfield with respect to the corresponding free ligand ($PPh_2C{\equiv}CR/\delta$: Ph/−33.5; $(4\text{-}CH_3)C_6H_4$/−33.4; $(4\text{-}OCH_3)C_6H_4$/−32.8; $(4\text{-}CF_3)C_6H_4$/−33.4). In all cases a very small signal due to the free phosphine is also observed, possibly consistent with the occurrence of a dissociative equilibrium. Proton and $^{13}C\{^1H\}$ NMR data indicate that the molecules are relatively rigid on the NMR time scale; indeed, the low-temperature proton spectra (see Figure S1 for complex **1**) exhibit two different sets of *ortho* (δ 9.24−9.14; 6.77−6.83 ppm) and also *meta* resonances clearly indicating hindered rotation around the P−C(Ph) bonds. On the basis of NOESY, COSY, HMQC, $H-^{13}C\{^{31}P\}$, and HMBC experiments carried out on the complex [*trans*-$RuCl_2(PPh_2C{\equiv}C(4\text{-}CH_3)C_6H_4)_4$], **2**, the most deshielded signals (9.24−9.14 ppm) are tentatively attributed to the eight *ortho* protons interacting with the two chlorine axial atoms and therefore the high-field resonances (6.77−6.83 ppm) to the eight *ortho*-protons which are seen in the solid state to be directed toward the alkynyl fragment (vide infra). For complexes **1** and **2**, variable-temperature proton ^1H NMR spectra were recorded. As observed for complex **1** (Figure S1), in the 223−323 K range, signals due to the *ortho*-H rapidly collapse while signals for *meta*-H signals broaden and finally coalesce at ca. 258 K. The analysis of the coalescence behavior of the latter signals led to an activation energy barrier of ca. 12 kcal mol^{-1} for the rotation of the phenyl rings around the P−C bonds.[57] The estimated rotation barrier is considerably higher

Scheme 1



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(57) The activation energy barrier was estimated using the approximation of the Eyring equation: $\Delta G^{\ddagger} = RT_c(22.96 + \ln T_c/\delta\nu)$, where T_c (K) is the coalescence temperature of two signals separated by $\delta\nu$ (Hz).

than in typical phenylphosphine ligands (1−2 kcal mol^{-1} in free triphenylphosphine), and the *ortho*-H···Cl interactions evidenced in the solid state (vide infra) certainly account for such a high value. Upon coordination of the alkynylphosphines, the C_α resonances move upfield (δ 81.3 (**1**); 80.6 (**2**); 79.9 (**3**) ppm), while the C_β shift downfield (δ 112.3 (**1**); 112.6 (**2**); 112.7 (**3**) ppm) with respect to the free ligands (R/δ C_α/δ C_β: Ph/86.5/109; (4-CH_3)C_6H_4/84.6/107.9; (4-OCH_3)C_6H_4/84.1/108.1). In these complexes, the magnitude of the chemical shift difference ($\Delta\delta = \delta C_\beta - \delta C_\alpha$), which is related to the triple-bond polarization ($\Delta\delta$ 31 (**1**); 32 (**2**); 33 (**3**) ppm), is notably higher than those previously observed for the neutral complexes [RuCp*Cl($PPh_2C{\equiv}CPh)_2$] ($\Delta\delta$ 21.1 ppm)[4] and [Ru(η^6-*p*-cymene)Cl_2($PPh_2C{\equiv}CR$)] ($\Delta\delta$ 18.3−26.5 ppm)[7] and comparable to those seen in the cationic derivatives [Ru(η^6-*p*-cymene)Cl($PPh_2C{\equiv}CR)_2$]$^+$ ($\Delta\delta$ 32.2−35.5 ppm).[7]

A search in the Crystallographic Cambridge Data Base[58] revealed that only a small number of dichloride ruthenium(II) complexes incorporating four phosphine ligands have been crystallographically reported.[59−63] These include the *trans* derivatives [*trans*-$RuCl_2(P(OEt)_3)_4$],[59] [*trans*-$RuCl_2${$P(CH_2OH)_3$}$_2${$P(CH_2OH)_2H$}$_2$],[60] and [*trans*-$RuCl_2(PPhH_2)_4$][61,64] stabilized by phosphites and/or secondary and primary phosphine ligands and the water-soluble phosphine complex [*cis*-$RuCl_2(PTA)_4$] (PTA = 1,3,5-triazaphosphaadamantane),[62] which possesses a geometry with *cis* chloride ligands.

Suitable crystals for an X-ray diffraction study were obtained from slow diffusion of *n*-hexane into a saturated solution of complex **1** in CH_2Cl_2. The structure of [$RuCl_2(PPh_2C{\equiv}CPh)_4$]·$4H_2O$ (Figure 1a, Table 1) shows that the molecule has D_{2d} symmetry with the Ru(II) center lying on the S_4 axis. The complex displays an octahedral coordination around the Ru atom with the apical positions occupied by the chloride ligands and the equatorial ones, by the four phenylethynylphosphine ligands. The interatomic Ru−Cl bonding distance (2.4332(10) Å), comparable to those observed in related complexes [*trans*-$RuCl_2L_4$] (L = $PPhH_2$, 2.422(3) Å;[61] L = $POEt_3$, 2.420(2) Å[59]), lies in the expected range. However, the Ru−P bond length (2.4077(8) Å) is significantly longer than those found in *trans*-$RuCl_2L_4$ (L = $PPhH_2$, 2.318(3), 2.319(3) Å; L = $POEt_3$, average of 2.330(5) Å)[59,61] and in other ruthenium complexes containing alkynylphosphine ligands such as [Ru(η^6-*p*-cymene)Cl_2($PPh_2C{\equiv}C$(4-CH_3)C_6H_4)] (2.3289(6) Å)[7] and [Ru(η^6-*p*-cymene)Cl($PPh_2C{\equiv}C^tBu)_2$]$^+$ (2.3278(12) Å),[7] thereby suggesting weaker phosphorus−metal dative bonds probably due to steric crowding. Owing to the crystallographic D_{2h} symmetry, the four phosphorus atoms lie in an exactly planar arrangement around the Ru(II) with no distortion of the Cl−Ru−P or P−Ru−P angles from 90°. It has been previously noted that the introduction of an alkyne spacer between the phosphorus atom and the aryl substituent does not alter the cone angle of the phosphine ligand.[50] In fact, PPh_3 and $PPh_2C{\equiv}CPh$ display identical steric demand (θ = 145°) in porphyrin−Ru(II) complexes [(phosphine)Ru(II)(DPP)] (DPP = 5,15-bis(3′,5′-di-*tert*-butyl)phenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin).[50] However, the analogous reaction of $RuCl_3$·$3H_2O$ with PPh_3 generates the known dichlorotris(triphenylphosphine)ruthenium(II)[65] com-

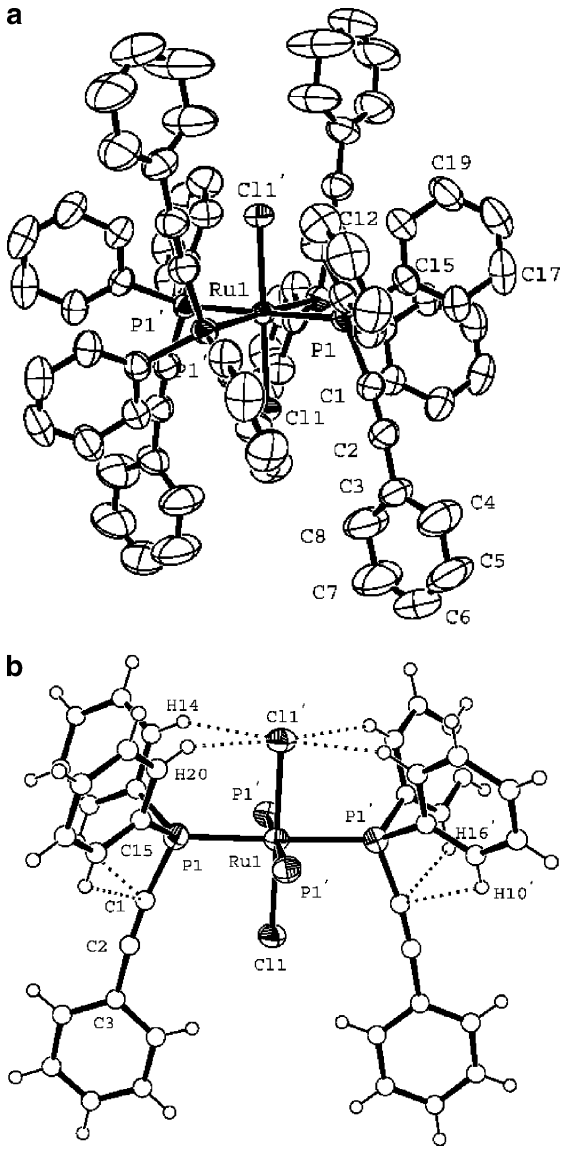

Figure 1. (a) Molecular structure of [*trans*-$RuCl_2(PPh_2C{\equiv}CPh)_4$] (**1**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. (b) View of the H···Cl and H···C interactions in [*cis*-$RuCl_2(PPh_2C{\equiv}CPh)_4$] (**1**). Ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [*trans*-$RuCl_2(PPh_2C{\equiv}CPh)_4$]·$4H_2O$ (1·$4H_2O$)[a]

Ru(1)−P(1)	2.4077(8)	Ru(1)−Cl(1)	2.4332(10)	P(1)−C(9)	1.838(3)
P(1)−C(15)	1.842(3)	P(1)−C(1)	1.757(3)	C(1)−C(2)	1.194(5)
H(14)−Cl(1)	2.629	H(20)−Cl(1)	2.653	H(16)−C(1)	2.495
H(10)−C(1)	2.521				

P(1)−Ru(1)−P(1)′	90.009(1)	P(1)−Ru(1)−P(1)′	178.62(4)
P(1)−Ru(1)−Cl(1)	90.695(18)	P(1)−Ru(1)−Cl(1)′	89.305(18)
C(2)−C(1)−P(1)	173.1(3)	C(1)−C(2)−C(3)	175.7(4)

[a] (′) Symmetry transformations used to generate equivalent atoms are #1 $-x, -y+1/2, z$; #2 $-y+1/4, x+1/4, -z+5/4$; #3 $y-1/4, -x+1/4, -z+5/4$.

(58) A search performed in the Cambridge Structural Data Base updated in February 2005.

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plex, which displays a distorted square-pyramidal coordination with an apical P atom.[66,67] In this complex, the remaining free octahedral site is effectively blocked by a phenyl ring, which establishes an agostic interaction with the ruthenium center (Ru···H = 2.59 Å).[66,67] By contrast, in the present complex (Figure 1b), the four phenyl rings of two $PPh_2C{\equiv}CPh$ ligands and the ethynyl fragments of the two other alkynylphosphine ligands build a cavity that effectively shields the chlorine atom. There is a close spatial contact between the chlorine atom and the four *ortho* protons of the phenyl rings, which results in short intramolecular Ru−Cl···H−C separations of 2.629 (Cl1−H14) and 2.653 Å (Cl1−H20), respectively. These values are shorter than the sum of van der Waals radii of chlorine and hydrogen atoms (2.95 Å) and suggest the presence of weak hydrogen-bonding interactions, which, as commented above, may account for the hindered rotation of the phenyl rings evidenced in solution by NMR. Another interesting structural feature is the existence of close hydrogen-bonding interactions between both *ortho* phenyl protons (PPh_2) and the acceptor C≡C moiety, with H16···C1 and H10···C1 distances of 2.495 and 2.521 Å, respectively. These distances are within the range of those observed in several chloroform solvates of alkynyl complexes[68−71] such as [LAuC≡CAuL$(CHCl_3)_2$] (L = PPh_2naphyl),[68] [LAuC≡CAuL$(CHCl_3)_6$],[69] and [Pt{C≡C(4-CF_3)C_6H_4}$_4$]$^{2-}$ (range 2.446−2.587 Å)[70] and are slightly shorter than those typically found in cyclopentadienyl alkynyl complexes (C(Cp)−H···C≡C 2.6−2.9 Å).[72]

II. Reactivity of [*trans*-$RuCl_2(PPh_2C{\equiv}CR)_4$] Complexes toward Terminal Alkynes. A valuable aspect of the reactivity of chlorophosphine ruthenium(II) complexes is their ability to react with terminal alkynes to give an elusive adduct from which 1-alkyne to vinylidene tautomerization generally takes place,[28−35,73−75] as originally observed by Wakatsuki in the specific case of $RuCl_2(PPh_3)_3$.[75] Considering the obvious steric crowding that could be inferred from the structure analysis of our complex [*trans*-$RuCl_2(PPh_2C{\equiv}CR)_4$] (**1**) in the solid state, a facile dissociative loss of at least one of the alkynylphosphine ligands in solution might be anticipated. Thus, we became interested in determining whether such a property could be exploited in terms of reactivity. Treatment of complexes **1** (R = Ph) and **2** (R = (4-CH_3)C_6H_4) in CH_2Cl_2 with an excess of phenylacetylene at room temperature for 15 h results in the displacement of one of the $PPh_2C{\equiv}CR$ ligands and formation of the vinylidene complexes [*mer*,*cis*-$RuCl_2$(C═CHPh)(PPh_2-C≡CR)$_3$] (R = Ph (**12**), (4-CH_3)C_6H_4 (**13**)) (Scheme 1). It is noteworthy that the reaction, effectively producing a vinylidene species, is accompanied by isomerization of the initial *trans*-(chlorine) derivative to the *cis*-(chlorine), the latter geometry notably avoiding the unfavorable disposition where a strong π-acceptor vinylidene group (:C═CHPh) would be *trans* to a phosphine ligand. The novel vinylidene complexes **12** and **13** have been characterized by various spectroscopic techniques. Characteristic features of the IR spectra are the ν(C≡C) band of the terminal alkynylphosphine ligands (ν(C≡C) 2180 (**12**); 2179 (**13**) cm^{-1}) and those due to ν(C═C) of the vinylidene ligand at 1624 cm^{-1} in **12** and 1627 cm^{-1} in **13**. Further, the $^{13}C\{^1H\}$ NMR spectra display a characteristic low-field resonance at δ 358 ppm (quartet $J_{C-P} \approx 13.7$ Hz (**12**); s br (**13**)) assignable to the α-carbon of the vinylidene moiety, and in the proton spectra the ═CHPh resonance is observed at high field as a triplet of doublets at 5.33 ppm ($J_{H-P} \approx 3.7$ Hz, **12** and **13**), in line with the proposed structure and with those reported for other Ru(II) vinylidenes. The $^{31}P\{^1H\}$ NMR spectra show a triplet (δ 1.58 (**12**); 1.26 (**13**) ppm) and a doublet (δ −0.41 ppm (A_2X spin system) (**12** and **13**) with a $^2J_{P-P} \approx 26.5$ Hz), confirming the *mer* disposition of the alkynylphosphine ligands. The structure of the complex [*mer*,*cis*-$RuCl_2$(C═CHPh)(PPh_2-C≡C(4-CH_3)C_6H_4)$_3$] (**13**) was investigated by X-ray diffraction. An ORTEP drawing of the complex is presented in Figure 2, while selected bond lengths and angles are gathered in Table 2. In agreement with spectroscopic data for **12** and **13** in solution, the ruthenium vinylidene complex **13** exhibits a distorted octahedral geometry around the ruthenium atom, with a *mer* disposition of the alkynylphosphine ligands and a mutually *cis* configuration of both chlorine atoms. Angles around Ru lie between 83.64(9)° (C(1)−Ru(1)−P(1)) and 99.66(9)° (C(1)−Ru(1)−Cl(1)) for the mutually *cis* ligands and between

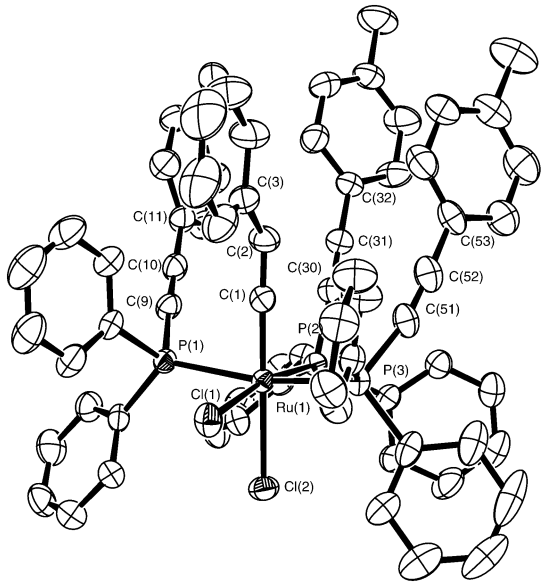

Figure 2. Molecular structure of [*mer*,*cis*-$RuCl_2$(═C═CPh)-($PPh_2C{\equiv}CTol)_3$]·Et_2O (**13**·Et_2O). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [*mer*,*cis*-$RuCl_2$(═C═CPh)($PPh_2C{\equiv}CTol)_3$]·Et_2O (13**·Et_2O)**

Ru(1)−Cl(1)	2.4201(8)	Ru(1)−Cl(2)	2.4862(8)	Ru(1)−C(1)	1.8180(3)
Ru(1)−P(1)	2.3915(7)	Ru(1)−P(2)	2.3642(8)	Ru(1)−P(3)	2.3872(8)
C(9)−C(10)	1.192(4)	C(30)−C(31)	1.1901(4)	C(51)−C(52)	1.190(4)
C(1)−C(2)	1.308(4)	C(2)−C(3)	1.456(5)		

Ru(1)−C(1)−C(2)	175.0(3)	C(1)−Ru(1)−P(1)	83.64(9)
C(1)−C(2)−C(3)	128.2(3)	C(1)−Ru(1)−P(2)	90.84(9)
P(3)−Ru(1)−P(1)	165.53(3)	C(1)−Ru(1)−P(3)	84.04(9)
Cl(2)−Ru(1)−P(1)	94.39(3)	C(1)−Ru(1)−Cl(1)	99.66(9)
Cl(2)−Ru(1)−P(2)	98.53(3)	C(1)−Ru(1)−Cl(2)	174.64(9)
Cl(2)−Ru(1)−P(3)	98.53(3)	Cl(1)−Ru(1)−Cl(2)	85.15(3)
		Cl(1)−Ru(1)−P(2)	169.38(3)
C(10)−C(9)−P(1)	171.2(3)	C(9)−C(10)−C(11)	177.2(4)
C(31)−C(30)−P(2)	174.8(3)	C(30)−C(31)−C(32)	178.4(3)
C(52)−C(51)−P(3)	167.9(3)	C(51)−C(52)−C(53)	177.0(4)

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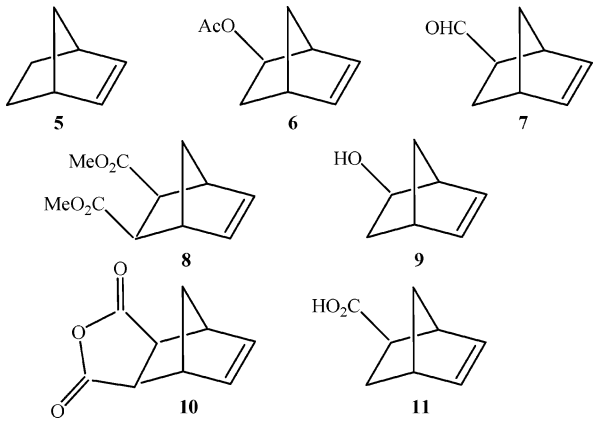
165.53(3)° (P(3)−Ru(1)−P(1)) and 174.64(9)° (C(1)−Ru(1)−Cl(2)) for the mutually *trans* ligands. The three alkynyl fragments of the phosphine ligands are roughly aligned with the vinylidene group, probably for steric reasons. The P−C_α≡C_β−($C_6H_4CH_3$) linkages are almost linear at C_β (177.0(4)−178.4(3)°) but slightly bent at C_α (167.9(3)−174.8(3)°). The Ru(1)−P(2) length *trans* to the chlorine ligand (2.3642(8) Å) is somewhat shorter than the remaining Ru−P distances (Ru(1)−P(1) = 2.3915(7) Å; Ru(1)−P(3) = 2.3872(8) Å) and that found in **1** (Ru(1)−P(1) = 2.4077(8) Å), in agreement with the lesser *trans* influence of the chlorine atom relative to the phosphine ligands. The Ru−Cl bond distance *trans* to the vinylidene (Ru(1)−Cl(2) = 2.4862(8) Å) is significantly longer than the Ru−Cl bond *trans* to P(2) (Ru(1)−Cl(1) = 2.4201(8) Å), thus suggesting a remarkable *trans* influence of the vinylidene ligand, as expected, considering its strong π-acceptor nature. The Ru(1)−C(1)−C(2) unit is almost linear (175.0(3)°), with the C(3)−C(8) phenyl ring being essentially coplanar with the {C(2)−C(1)−Ru(1)−Cl(1)−Cl(2)} mean plane (dihedral angle of 5.3°). The Ru(1)−C(1) and C(1)−C(2) distances of 1.8180(3) and 1.308(4) Å, respectively, compare well with the corresponding distances found in other L_nRu=C=C(H)Ph complexes.[31,63,73,75−77]

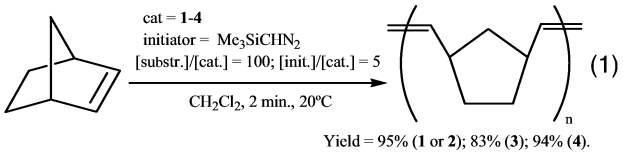
III. Studies of the Use of 1−4, 12, and 13 as ROMP Initiators. In view of the tremendous success of new generations of sophisticated "superfast" olefin metathesis catalysts derived from Hoveyda/Grubbs prototypes,[33,78−80] there is also a practical interest in simpler systems where the catalyst can be generated in situ and at low cost from simple ingredients. In this context, we note that in most commercial processes relevant to metathesis, poorly defined "archaic" catalysts generated in situ from precursors as simple as $RuCl_3$ have been applied.[81]

Keeping in mind that vinylidenes are carbenoids, with interesting applications in catalysis,[28,33−37,82−91] we considered it of interest to test the catalytic activity of the vinylidene complexes **12** and **13** in the ring-opening metathesis polymerization of norbornene (**5**). Unfortunately, they were not active either in CH_2Cl_2 (10 mL, 100 equiv of **5**/1 equiv of **12** or **13**) at room (15 h) or reflux temperature (2.5 h) or in solvent-free norbornene (100 equiv/1 equiv **12** or **13**, 80 °C, 1 h). In view of the fact that these latter complexes (**12**, **13**) are easily generated from the precursors **1** and **2** via phosphine displacement, our focus turned to carrying out some simple tests aimed at determining whether the complexes **1**−**4** could be used as precatalysts for the ROMP of norbornene regarded as a test reaction. We thus decided to adopt the strategy previously used by Noels and co-workers,[92] where an active species is generated in situ upon treatment of a dichlorophosphine ruthenium(II) complex with a diazoalkane as the carbene source.

Chart 1



As shown below, under the standard conditions defined in eq 1, the first tests appeared quite spectacular, the polymerization appearing to be complete in less than 2 min. This result



Yield = 95% (**1** or **2**); 83% (**3**); 94% (**4**).

prompted us to extend our study to other functionalized norbornenes **6**−**11** (Chart 1). All complexes **1**−**4** were active as ROMP precatalysts for monomers **6**−**8**. However, no reaction was found at room temperature or at higher temperatures with monomers **9**−**11**. In the case of monomers **6**−**8** elevated temperatures were necessary to reach the yields obtained with norbornene. The full results of these experiments are displayed in Table 3. Even though the system appears to be of lower efficiency for substituted norbornenes **6**−**8** than for norbornene **5**, the yields obtained after 1 h indicate that these complexes are quite effective precatalysts and present a notable functional-group tolerance. We note that Schrock-type [Mo(=CHR)(N−AR)(O-^{t}Bu)$_2$] (R = ^{t}Bu, CMe_2Ph) and Grubbs-type [$RuCl_2$-(PCy_3)L(=CHPh)] (L = PCy_3, $IMesH_2$) catalysts have shown excellent results in the ROMP reactions with substituted monomers.[93−95] The influence of the nature of the alkynylphosphine on the activity of the ruthenium precursor complex is not remarkable for monomers **5** and **8**. However, a low activity was observed for the precatalyst complex **4**, having the trifluoromethyl group for monomers **6** and **7** (entries 11 and 16). It should be noted that when the precursor **1** is mixed with the diazo compound and the monomer **5** is added 30 min later, the yield of the reaction after 1 h decreases to 50%, thus suggesting that the active species is not stable in solution.

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Table 3. ROMP of 5−8 Initiated by 1−4[a]

entry	precatalyst/monomer	solvent	*T* (K)	yield (%)	TOF[b] (h^{-1})	M_n($\times 10^3$)[c]	PDI (M_w/M_n)[c]	*cis*/*trans*[d]
1[e]	**1/5**	CH_2Cl_2	298	95	2850	188	3.2 (2.1%)	0.56
2[e]	**2/5**	CH_2Cl_2	298	95	2850	115	4.5 (3.2%)	0.54
3[e]	**3/5**	CH_2Cl_2	298	82	2460	44	3.5 (2.6%)	0.55
4[e]	**4/5**	CH_2Cl_2	298	94	2820	498	1.2 (1.2%)	0.56
5	**1/6**	CH_2Cl_2	298	12	12	127	1.5 (1.3%)	
6	**2/6**	CH_2Cl_2	298	9	9	99	1.2 (1.6%)	
7	**3/6**	CH_2Cl_2	298	1	1	146	1.3 (2.5%)	
8	**1/6**	toluene	333	78	78	75	1.5 (1%)	
9	**2/6**	toluene	333	74	74	69	1.4 (0.9%)	
10	**3/6**	toluene	333	76	76	108	1.3 (0.9%)	
11	**4/6**	toluene	333	35	35	127	1.3 (1%)	
12	**1/7**	CH_2Cl_2	298	3	3	11	3.1 (11%)	
13	**1/7**	toluene	333	57	57	126	1.7 (22%)	
14	**2/7**	toluene	333	56	56	420	1.3 (55%)	
15	**3/7**	toluene	333	80	80	239	1.1 (24%)	
16	**4/7**	toluene	333	27	27	11	1.8 (37%)	
17	**1/8**	CH_2Cl_2	298	11	11	53	1.8 (7%)	
18	**2/8**	CH_2Cl_2	298	4	4	300	1.1 (3.4%)	
19	**3/8**	CH_2Cl_2	298	8	8	109	1.4 (2.5%)	
20	**1/8**	toluene	333	73	73	19	1.4 (9%)	
21	**2/8**	toluene	333	92	92	44	2.2 (6%)	
22	**3/8**	toluene	333	89	89	16	1.6 (24%)	
23	**4/8**	toluene	333	78	78	2	1.3 (54%)	

[a] General conditions: precatalyst:initiator:monomer = 1:5:100; reaction time 1 h. Yields are given for isolated polymers. [b] TOF (turnover frequency) = mol monomer converted × mol catalyst^{-1} × hour^{-1}. [c] M_n and PDI calculated by size exclusion chromatography in microfiltrated THF solutions against polystyrene standards. Experimental error in parentheses. [d] Calculated by ^{1}H NMR spectroscopy. [e] In these cases the reaction is stopped after 2 min due to complete gelation of the mixture of reaction.

The characteristics of the polymers have also been examined. The molecular weights were calculated by size exclusion chromatography, and the relative proportion of *cis* and *trans* double bonds was determined by ^{1}H NMR spectroscopy.[96] We would like to note that except for the reactions carried out in toluene (60 °C) with monomer **8**, the initiation efficiency (calculated as $f = M_{n,theor}/M_{n,exp}$) in the reactions is relatively low, as might be expected for a coordinatively saturated precursor on which an alkylidene is installed in situ. The good initiation efficiencies observed for monomer **8** could be tentatively attributed to a possible stabilization of the propagating species owing to the presence of oxygen atoms.[97] In the case of norbornene (entries 1−4) the polymer obtained with the precatalyst **4** having the trifluoromethylalkynyl group presents the highest molecular weight and the lowest polydispersity (entry 4). For the remaining complexes **1**−**3**, the observed polydispersities are quite broad. This fact, together with the high values of the molecular weights, may be indicative that the rate of propagation is faster than the rate of initiation and, probably, that the percentage for generating the catalytically active species is low.[96,98] Although, a broad polydispersity could also indicate that the polymerization is subjected to backbiting and transfer reactions,[99] presumably, the reason for broad molecular weight distribution is due to the slowness of the initiation compared to propagation. The *cis*/*trans* double-bond ratio observed is essentially nondependent on the nature of the precatalyst employed (entries 1−4). In all cases this ratio is near 1:1, contrasting with the *trans* geometry usually observed for other ruthenium catalysts[78,92,100] and indicating a lack of stereoselectivity in the reaction. It has been previously noted that the polymer microstructures are quite sensitive to a wide number of factors: the catalytic system employed, the solvent polarity, the reaction temperature, the dilution, and possibly also the relative amount of byproducts formed in side reactions.[92] Starting from the 2-acetyl-5-norbornene monomer (**6**) the differences in molecular weight and polydispersity of **poly6** are less remarkable than for **poly5**, and curiously, the molecular weights decrease at high temperature. The polydispersities are lower than for **poly5**, pointing to a better control of the reaction or a better efficiency in the initiation. Unfortunately the *cis*/*trans* ratio of **poly6** was not accessible due to extensive overlap of the signals in the proton spectra.

The final polymers obtained using 5-norbornene-2-carboxyaldehyde (**poly7**) and dimethyl-5-norbornene-2,3-dicarboxylate (**poly8**) are not very soluble in THF, and therefore the values of the molecular weights and polydispersities obtained were not very accurate and present an important experimental error. For **poly7** access to the corresponding *cis*/*trans* ratio by solution NMR spectroscopy was not possible due to its lack of solubility and the solid ^{13}C NMR spectra were not informative because only a broad signal in the olefinic region (274.2 ppm at $V_r = 7$ kHz and 234.2 ppm at $V_r = 10$ kHz) was observed. The ^{1}H NMR spectra of **poly8** exhibit only one signal in the olefinic region (5.5 ppm), suggesting that only one type of double bond, probably *trans*, is present. In agreement with this suggestion, this resonance is similar to the one given for the polymer obtained using [Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$] as catalyst (δ 5.45).[93]

By using an approach similar to that of Noels et al.[92] we conducted NMR experiments aimed at getting some insight into the nature of the active species. When 2 equiv of TMSD was added at room temperature to a solution of complex **2** ($CDCl_3$), two weak signals at 19.1 and 18.7 ppm were immediately detected in the ^{1}H NMR spectrum, thus suggesting the formation of small amounts of alkylidene-type [Ru]=CHSiMe$_3$ complexes.[82−84] The corresponding ^{31}P{^{1}H} NMR spectrum showed a main signal due to complex **2** and two additional weak signals, the first one at −32.9 ppm attributable to free phosphine and the second one at 10.4 ppm. When an additional 3 equiv of

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TMSD was added, thus reproducing the conditions of the polymerization reactions, two additional signals at 30.8 and 30.1 ppm were detected in the $^{31}P\{^1H\}$ NMR spectrum. In the ^1H NMR spectrum the two signals at δ 19.1 and 18.7 ppm increased in intensity and two new signals at 19.9 and 17.1 ppm appeared. After 30 min, the $^{31}P\{^1H\}$ NMR spectrum showed the total disappearance of the precursor complex **2**, while the signals at 30.8, 30.1, and 10.4 ppm remained as the most intense ones (small signals probably due to decomposition were also observed). In the proton spectrum only the signal at 17.1 ppm remains. Taken altogether, these observations suggest that the activation of the precatalyst occurs by dissociation of one phosphine (or more) and formation of one (or more) alkylidene-type complexes existing under several isomeric forms. Although we are presently unable to ascertain the nature of the actual active species, the resonances appearing at 19.1 or 18.7 ppm can be reasonably assigned to the H of the active alkylidene species. Besides, the possibility that the diazo compound attacks a coordinated alkynylphosphine cannot be excluded. It has been demonstrated that coordination of alkynylphosphines produces a polarization of the electron density of the triple bond, activating it toward nucleophilic and electrophilic attacks,[19,21,22] and some of the signals observed in the ^{31}P NMR spectra could be generated by this type of reactivity.

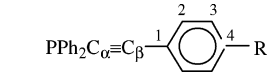
Conclusion

In summary, we have shown that the reaction of alkynylphosphines with a simple and readily available Ru compound like $RuCl_3 \cdot xH_2O$ gives new tetrakis(alkynylphosphine) dichlororuthenium(II) complexes existing in only one [*trans*-$RuCl_2(PPh_2C{\equiv}CR)_4$] isomeric form. An important characteristic of these complexes is their ability to undergo facile dissociative loss of one of the ligands. This can be substantiated in terms of reactivity, as revealed by their clean straightforward reaction with terminal alkynes leading to vinylidene complexes [*mer*,*cis*-$RuCl_2(C{=}CHPh)(PPh_2C{\equiv}CR)_3$] with concomitant reorganization of the geometry. The observed high substitutional lability, possibly involving more than one alkynylphosphine ligand and hence generating a 14 e^- species, certainly also provides a clue to the intriguingly high activity observed when these complexes are used as precatalysts for the ROMP of norbornene upon simple in situ activation by TMSD as carbene source.

Experimental Section

General Procedures. The syntheses were performed using usual vacuum line and Schlenk techniques. All reagents were commercial grade chemicals and were used without further purification. Trimethylsilyldiazomethane (TMSD) came as a solution in hexanes (2 M) and was used without further dilution. Diethyl ether, toluene, and dichloromethane solvent used for the syntheses were dried and distilled by standard methods and stored under nitrogen. The novel alkynylphosphines $PPh_2\{C{\equiv}C(4\text{-}OCH_3)C_6H_4\}$ and $PPh_2\{C{\equiv}C(4\text{-}CF_3)C_6H_4\}$ used in this work have been prepared following the general procedure described by Carty et al.,[101] and their analytical and spectroscopic data are included in this work.

Elemental analyses (C, H) were performed on Carlo Erba CHNS EA-1108 or Perkin-Elmer 2400 CHNS/O instruments. Infrared spectra were recorded on Perkin-Elmer 2000 FT or Perkin-Elmer FT-IR Spectrum 1000 spectrometers using Nujol mulls between polyethylene sheets. The NMR spectra were obtained on Bruker AMX400, DRX500, ARX-300, or AV400 instruments, and NMR spectra in the solid state on Bruker UXNMR. Chemical shifts (δ) are reported in parts per million relative to external standards ($SiMe_4$, $CFCl_3$, and 85% H_3PO_4), and all coupling constants are given in hertz. Mass spectra were obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics or an HP-5989B mass spectrometer. SEC (size exclusion chromatography) analytical data were obtained at 298 K using a SFD RI 2000 differential refractometer, a multiangle laser light scattering detector (Wyatt Technology, miniDAWN), a PLgel 5 μm MIXED-D column (300 $\times$ 7.5 mm), and microfiltrated THF as eluant with a nominal flow of 0.85 mL/min; results are reported relative to poly(styrene) standards.



Data for $PPh_2\{C{\equiv}C(4\text{-}OCH_3)C_6H_4\}$. Yield: 82% (oil). Anal. Calcd for $C_{21}H_{17}OP$: C, 79.73; H, 5.42. The best analyses obtained were: C, 77.23; H, 5.09. These values are lower than expected, probably due to partial oxidation of the phosphine. MS-EI: *m*/*z* 316 $[M]^+$ 22%; 230 $[OPPh_2Me_2]^+$ 67%; 201 $[OPPh_2]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2157 (s). ^1H NMR (δ, 298 K, 300.13 MHz, $CDCl_3$): 7.71 (st), 7.53 (d), 7.40 (m) (12H, Ph and C_6H_4), 6.89 (d, 2H, C_6H_4); 3.82 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (δ, 298 K, 75.48 MHz, $CDCl_3$): 160.2 (C^4, $C_6H_4OCH_3$); 136.7 (d, $^1J_{C-P} = 6.3$, *i*-C, Ph); 133.6 (d, $^4J_{C-P} = 1.2$, C^2, $C_6H_4OCH_3$); 132.6 (d, $^2J_{C-P} = 20.7$, *o*-C, Ph); 129.0 (*p*-C, Ph); 128.7 (d, $^3J_{C-P} = 7.5$, *m*-C, Ph); 114.1 (C^3, $C_6H_4OCH_3$); 108.1 (d, $^2J_{C-P} = 4.6$, C_β); 84.1 (d, $^1J_{C-P} = 4.1$, C_α); 55.4 (OCH_3) (the signal due to C^1 could not be unambiguously assigned). $^{31}P\{^1H\}$ NMR (δ, 298 K, 121.5 MHz, $CDCl_3$): −32.8 (s).

Data for $PPh_2\{C{\equiv}C(4\text{-}CF_3)C_6H_4\}$. Yield: 69%. Anal. Calcd for $C_{21}F_3H_{14}P$: C, 71.19; H, 3.98. Found: C, 70.96; H, 3.49. MS ACPI(+): *m*/*z* 355 $[M + H]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2179 (m), 2164 (m). ^1H NMR (δ, 295 K, 400.14 MHz, $CDCl_3$): 7.69−7.63 (8H); 7.40 (s br, 6H) (Ph, C_6H_4). $^{13}C\{^1H\}$ NMR (δ, 295 K, 100.62 MHz, $CDCl_3$): 135.7 (d, $^1J_{C-P} = 6.0$, *i*-C, Ph); 132.8 (d, $^2J_{C-P} = 21.0$, *o*-C, Ph); 132.13 (d, $^4J_{C-P} = 1.1$, *p*-C, Ph); 130.6 (d, $^1J_{C-P} = 32.6$, *i*-C, Ph); 129.4 (C^2, $C_6H_4CF_3$); 128.9 (d, $^3J_{C-P} = 7.6$, *m*-C, Ph); 126.6 (m, C^4, $C_6H_4CF_3$); 125.4 (q, $^3J_{C-F} = 3.9$, C^3, $C_6H_4CF_3$); 106.1 (d, $^2J_{C-P} = 3.9$, C_β); 89.3 (d, $^1J_{C-P} = 10.6$, C_α) (the signal due to CF_3 could not be unambiguously assigned). $^{31}P\{^1H\}$ NMR (δ, 295 K, 161.98 MHz, $CDCl_3$): −33.4 (s). ^{19}F (δ, 298 K, 282.41 MHz, $CDCl_3$): −63.08 (s, CF_3).

Synthesis of $[RuCl_2(PPh_2C{\equiv}CR)_4]$ (R = C_6H_5 1, (4-CH_3)-C_6H_4 2, (4-OCH_3)-C_6H_4 3, (4-CF_3)-C_6H_4 4). General Procedure. A mixture of $RuCl_3 \cdot xH_2O$ with the appropriate $PPh_2C{\equiv}CR$ (1:4 molar ratio) in degassed commercial ethanol was refluxed for ca. 1 h under nitrogen atmosphere. Upon cooling, the resulting gray (**1** and **2**) or brown (**3** and **4**) solid was filtered off and washed with ethanol, water, and finally diethyl ether, and dried under vacuum.

Data for 1. Yield: 87%. Anal. Calcd for $C_{80}Cl_2H_{60}P_4Ru$: C, 72.95; H, 4.59. Found: C, 72.55; H, 4.14. MS FAB(+): molecular peak (1317.2) not observed; *m*/*z* 1031 $[M - PPh_2C{\equiv}CPh]^+$ 59%; 996 $[M - Cl - PPh_2C{\equiv}CPh]^+$ 70%. IR (cm^{-1}): ν(C≡C) 2177 (vs); ν(Ru−Cl) 296 (w). ^1H NMR (δ, 223 K, 400.14 MHz, $CDCl_3$): 9.24 (s br, 8H, *o*-H, Ph); 8.04 (d, $J_{H-H} = 6.2$, 8H, *o*-H, C≡CPh); 7.61 (m, 12H, C≡CPh); 6.91 (16H, *m*-H, *p*-H, Ph); 6.81 (s br, 8H, *o*-H, Ph); 6.53 (s br, 8H, *m*-H, Ph). Upon heating, the signals due to the *ortho*-H of the PPh_2 groups rapidly collapse (ca. 238 K), while the signals for *meta*-H broaden and finally coalesce at ca. 258 K. Data at 293 K: 8.04 (overlap of a broad resonance due to 16 *o*-H of PPh_2 and a doublet, 8H, *o*-H of C≡CPh); 7.58 (m, 12H, C≡CPh); 6.9 (8H, *p*-H, Ph); 6.71 (s br, 16H, *m*-H, Ph). $^{13}C\{^1H\}$ NMR (δ, 223 K, 125.82 MHz, $CDCl_3$): 138.34 (m, *i*-C, PPh_2), 133.39 (*o*-C, PPh_2), 133.06 (*o*-C, C≡CPh), 129.6 (*p*-C, C≡CPh), 128.92 (*m*-C, C≡CPh), 128.7 (*o*-C, PPh_2), 127.7 (*p*-C, PPh_2), 127.5 (*m*-C, PPh_2), 122.93 (*i*-C, C≡CPh), 112.37 (C_β), 81.30 (m, C_α). $^{31}P\{^1H\}$ NMR (δ, 295 K, 121.5 MHz, $CDCl_3$): −4.85 (s).

(101) Carty, A. J.; Hota, N. K.; Ng, T. W.; Patel, H. A.; O'Connor, T. *J. Can. J. Chem.* **1971**, *49*, 2706.

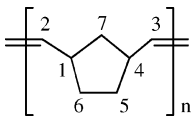
Data for 2. Yield: 93%. Anal. Calcd for $C_{84}Cl_2H_{68}P_4Ru$: C, 73.47; H, 4.99. Found: C, 73.18; H, 4.63. MS FAB(+): molecular peak (1373.3) not observed; *m/z* 1073 [M − $PPh_2C{\equiv}CTol]^+$ 18%; 1038 [M − Cl − $PPh_2C{\equiv}CTol]^+$ 70%. IR (cm^{-1}): ν(C≡C) 2182 (vs); ν(Ru−Cl) 302 (w). ^1H NMR (δ, 223 K, 500.33 MHz, $CDCl_3$): 9.23 (s br, 8H, *o*-H, Ph), 7.93 (d, J_{H-H} = 7.4, 8H, H^2, $C_6H_4{-}CH_3$), 7.41 (d, J_{H-H} = 7.4, 8H, H^3, $C_6H_4{-}CH_3$), 6.89 (s br, 16H, *m*-H and *p*-H, Ph), 6.79 (s br, 8H, *o*-H, Ph), 6.51 (s br, 8H, *m*-H, Ph), 2.53 (12H, $C_6H_4{-}CH_3$). $^{13}C\{^1H\}$ NMR (δ, 223 K, 125.82 MHz, $CDCl_3$): 139.8 (C^4, $C_6H_4{-}CH_3$), 138.5 (m, *i*-C, Ph), 133.5 (*o*-C, Ph), 133.0 (C^2, $C_6H_4{-}CH_3$), 129.6 (C^3, $C_6H_4{-}CH_3$), 128.7 (*o*-C, Ph), 127.6 (*p*-C, Ph), 127.44 (*m*-C, Ph), 127.39 (*m*-C, Ph), 119.96 (C^1, $C_6H_4{-}CH_3$), 112.6 (C_β), 80.60 (m, C_α), 22.29 ($C_6H_4{-}CH_3$) (the assignments of the ^1H and ^{13}C NMR signals have been confirmed by NOESY, COSY, HMQC, H−$^{13}C\{^{31}P\}$, and HMBC experiments). $^{31}P\{^1H\}$ NMR (δ, 223 K, 161.98 MHz, $CDCl_3$): −5.04 (s).

Data for 3. Yield: 24%. Anal. Calcd for $C_{84}Cl_2H_{68}O_4P_4Ru$: C, 70.19; H, 4.77. The best analyses obtained were: C, 67.52; H, 4.55. They fit well for $C_{84}Cl_2H_{68}O_4P_4Ru{\cdot}3H_2O$: C, 67.64; H, 5.00. Evidence of water is an IR band at 3606 cm^{-1}. MS FAB(+): molecular peak (1437.3) not observed; *m/z* 1121 [M − $PPh_2C{\equiv}C(4\text{-}OMe)C_6H_4]^+$ 16%; 1086 [M − Cl − $PPh_2C{\equiv}C(4\text{-}OMe)C_6H_4]^+$ 100%; 1050 [M − 2Cl − $PPh_2C{\equiv}C(4\text{-}OMe)C_6H_4]^+$ 6%. IR (cm^{-1}): ν(C≡C) 2176 (vs); ν(Ru−Cl) 310 (w). ^1H NMR (δ, 223 K, 500.33 MHz, $CDCl_3$): 9.20 (8H, *o*-H, Ph), 8.00 (d, J_{H-H} = 8.5, 8H, H^2, $C_6H_4{-}OCH_3$), 7.12 (d, J_{H-H} = 8.5, 8H, H^3, $C_6H_4{-}OCH_3$), 6.86 (m, 16H, *m*-H and *p*-H, Ph), 6.77 (s br, 8H, *o*-H, Ph), 6.50 (s br, 8H, *m*-H, Ph), 3.98 (12H, $C_6H_4{-}OCH_3$). $^{13}C\{^1H\}$ NMR (δ, 223 K, 125.82 MHz, $CDCl_3$): 160.04 (C^4, $C_6H_4{-}OCH_3$), 138.53 (m, *i*-C, Ph), 134.84 ($C^{2,3}$, $C_6H_4{-}OCH_3$), 133.55 (*o*-C, Ph), 128.80 (*o*-C, Ph), 127.50 (*p*-C, Ph), 127.33 (*m*-C, Ph), 115.29 (C^1, $C_6H_4{-}OCH_3$), 114.19 ($C^{2,3}$, $C_6H_4{-}OCH_3$), 112.65 (tentatively assigned to C_β), 79.87 (m, C_α), 55.81 ($C_6H_4{-}OCH_3$). $^{31}P\{^1H\}$ NMR (δ, 295 K, 161.98 MHz, $CDCl_3$): −5.08 (s).

Data for 4. Yield: 73%. Anal. Calcd for $C_{84}Cl_2F_{12}H_{56}P_4Ru$: C, 63.48; H, 3.55. Found: C, 63.78; H, 3.51. MS FAB(+): molecular peak (1589.2) not observed; *m/z* 1235 [M − $PPh_2C{\equiv}C(4\text{-}CF_3)C_6H_4]^+$ 31%; 1200 [M − Cl − $PPh_2C{\equiv}C(4\text{-}CF_3)C_6H_4]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2184 (vs); ν(Ru−Cl) 304 (w). ^1H NMR (δ, 223 K, 400.14 MHz, $CDCl_3$): 9.14 (8H, *o*-H, Ph), 8.17 (d, J_{H-H} = 7.7, 8H, $C_6H_4{-}CF_3$), 7.88 (d, J_{H-H} = 7.7, 8H, $C_6H_4{-}CF_3$), 6.93 (8H), 6.83 (8H), 6.72 (8H), 6.54 (8H) (Ph). $^{31}P\{^1H\}$ NMR (δ, 295 K, 161.98 MHz, $CDCl_3$): −4.19 (s). ^{19}F (δ, 295 K, 282.41 MHz, $CDCl_3$): −62.99 (s, CF_3). The $^{13}C\{^1H\}$ NMR spectrum could not be obtained because the complex decomposes in solution, even at low temperature.

Polymerization Procedure. The reactions were carried out under inert atmosphere. To the monomer solution (∼2.5 mmol) in 10 mL of CH_2Cl_2 (reaction at room temperature) or toluene (reaction at 60 °C) was added the precatalyst (0.01 equiv) and the initiator Me_3SiCHN_2 (0.05 equiv). The reaction time was 1 h in every case except for norbornene, for which the formation of a gel was complete after 2 min of stirring. The polymerization was quenched and the polymer precipitated by adding ∼40 mL of a solution of 2,6-di(*tert*-butyl)-4-methylphenol in methanol. The resulting polymer was dried under vacuum.

NMR spectra of the polymers produced by the different precatalysts and conditions are similar; therefore only one set of data for each polymer is given.



Poly5: ^1H NMR (δ, 298 K, $CDCl_3$, 300.13 MHz): 5.37−5.36 (s br, 1H, $H^{2,3}$ *trans*), 5.23 (d, 1H, $H^{2,3}$ *cis*); 2.81 (s br, 1H, $H^{1,4}$ *cis*), 2.45 (s br, 1H, $H^{1,4}$ *trans*); 1.86−1.84 (m, 3H, $H^{5,6,7}$); 1.37 (s br, 2H, $H^{5,6}$); 1.08 (m, 1H, H^7).

Poly6: ^1H NMR (δ, 298 K, $CDCl_3$, 300.13 MHz), extensive overlap of the signals is observed: 5.32−5.23 (group of three broad signals of relative intensity 3:1:3H); ∼3.2 (sh), ∼3.11 (d) (relative intensity (1:3H); 2.9 (s br, 4H); 2.4 (s br, 3H); 2.1 (s), 2.05 (s) (relative intensity 3:8H, OCH_3); 1.9 (s br), 1.79 (d) (relative intensity 4:6H); 1.3 (m, 4H). It is not possible to calculate the relative proportion of *cis* and *trans*.

Poly7: ^{13}C NMR (δ, 100.492 MHz): V_r = 7 kHz: 274.191; 203.803; 132.556; 100.375; 55.006; 42.352; 33.637. V_r = 10 kHz: 234.248; 203.966; 133.128; 100.370; 54.714; 42.276; 34.060. It is not possible to find differences between *cis* and *trans* geometries.

Poly8: ^1H NMR (δ, 298 K, $CDCl_3$, 300.13 MHz): 5.5 (s br, 2H, $H^{2,3}$); 3.65 (s, 6H, CO_2CH_3); 3.1 (d, 2H); 2.9 (s br, 2H); 1.95 (s br, 2H).

NMR Probes. To a solution of $[RuCl_2(PPh_2C{\equiv}C(4\text{-}CH_3)C_6H_4)_4]$ (**2**) (0.05 g, 0.037 mmol) in $CDCl_3$ (0.05 mL) was added 0.036 mL (0.073 mmol) of TMSD through a rubber septum. After the recording of the ^1H and $^{31}P\{^1H\}$ NMR spectra, 0.055 mL more of TMSD (0.109 mmol) was added to reproduce the polymerization conditions. The evolution of the solution was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see text).

Synthesis of [*mer*,*cis*-$RuCl_2$(=C=CHPh)($PPh_2C{\equiv}CPh)_3$] (12). A solution of [*trans*-$RuCl_2(PPh_2C{\equiv}CPh)_4$] (**1**) (0.15 g, 0.114 mmol) in CH_2Cl_2 was treated with 15 equiv (0.19 mL) of phenylacetylene. After 15 h of reaction the solution was evaporated to dryness and treated with diethyl ether, giving **12** as a beige solid. Yield: 0.08 g (62%). The best analyses found (C, 71.29; H, 4.67) fit well for $C_{68}Cl_2H_{51}P_3Ru{\cdot}Et_2O$: C, 71.63; H, 5.09. Found: MS ES(+): molecular peak (1133.1) not observed; *m/z* 1062 [M − 2Cl]$^+$ 1%; 1019 [M − (C≡CPh) − Cl + Na]$^+$ 1%; 938 [M − 2(C≡CPh)]$^+$ 2%; 836 [M − Cl − ($PPh_2C{\equiv}CPh$) + Na]$^+$ 7%; 746 [$RuCl_2$-($PPh_2C{\equiv}CPh)_2$ + H]$^+$ 35% (ionized with Na^+). IR (cm^{-1}): ν(C≡C) 2180 (s); ν(=C=C) 1624 (m); ν(Ru−Cl) 312 (w), 294 (w). ^1H NMR (δ, 295 K, 300 MHz, $CDCl_3$): 8.11 (s br), 7.93 (t), 7.69 (s br), 7.24 (m), 7.01 (m), 6.94 (m), 6.75 (s br), 6.31 (s br) (50H, aromatics); 5.33 (td, $^4J_{H-P}$ = 3.7 and 3.8, 1H, =C*H*Ph. ^{13}C NMR (δ, 295 K, 100.64 MHz): 358 (q, $^2J_{C-P} \approx 13.7$, C_α, C_α = CHPh); 134.41 ("t", $^{2+4}J_{C-P}$ = 11.3, *o*-C, PPh_2, *trans*); 133.77 (d, $^2J_{C-P}$ = 10.4, *o*-C, PPh_2, *trans* to Cl); 133.65 (dt, $^1J_{C-P}$ = 55.5, *i*-C, PPh_2, *trans* to Cl); 133.08 ("t", $^{2+4}J_{C-P}$ = 10.1, *o*-C, PPh_2, *trans*); 132.53 (AXX′, $^{1+3}J_{C-P}$ = 85, *i*-C, PPh_2, *trans*); 132.2 (s); 132.14 (s); 129.98 (s br); 129.79 (d, $^4J_{C-P}$ = 1.8, *p*-C, PPh_2); 129.56 (s); 128.85 (s); 128.60 (s); 128.33 (s); 127.93 (s); 127.63 (t, $^{3+5}J_{C-P}$ = 10.7, *m*-C, PPh_2, *trans*); 127.44 (d, $^3J_{C-P}$ = 11.7, *m*-C, PPh_2, *trans* to Cl); 127.10 (t, $^{3+5}J_{C-P}$ = 9.8, *m*-C, PPh_2, *trans*); 126.57 (s); 124.91 (s); 121.91 (s); 120.95 (d, J_{C-P} = 2.11) (aromatics); 110.63 (t, $^3J_{C-P}$ = 8.7, C_β, C=C_βHPh); 110.08 ("t", $^{2+4}J_{C-P}$ = 11.5, C_β, $PPh_2C_\alpha{\equiv}C_\beta$-Ph, *trans*); 107.57 (d, $^2J_{C-P}$ = 12.6, C_β, $PPh_2C_\alpha{\equiv}C_\beta$Ph, *trans* to Cl); 83.64 (d, $^1J_{C-P}$ = 94.93, C_α, $PPh_2C_\alpha{\equiv}C_\beta$Ph, *trans* to Cl); 83.08 (AXX′Y, $^{1+3}J_{C-P} \approx 87.7$, C_α, $PPh_2C_\alpha{\equiv}C_\beta$Ph, *trans*). $^{31}P\{^1H\}$ NMR (δ, 295 K, 121.5 MHz, $CDCl_3$): 1.58 (t), −0.41 (d) ($^2J_{P-P}$ = 26.6).

Synthesis of [*mer*,*cis*-$RuCl_2$(=C=CHPh)($PPh_2C{\equiv}CTol)_3$] (13). This complex was obtained as a beige solid, following the same procedure as for **12**, but starting from 0.15 g (0.109 mmol) of [*trans*-$RuCl_2(PPh_2C{\equiv}CTol)_4$] and 0.184 mL (1.6 mmol) of phenylacetylene. Yield: 0.05 g. (39%). Anal. Calcd for $C_{71}Cl_2H_{57}P_3Ru$: C, 72.57; H, 4.89. Found: C, 72.41; H, 4.92. MS ES(+): molecular peak (1175.1) not observed; *m/z* 1164 [M − Cl + Na + H]$^+$ 24%; 1062 [$RuCl(PPh_2C{\equiv}CTol)_3$ + Na]$^+$ 8%; 863 [M − Cl − (PPh_2-C≡CTol) + Na]$^+$ 100%; 797 [$RuCl_2(PPh_2C{\equiv}CTol)_2$ + Na + H]$^+$ 40%; 760 [$RuCl(PPh_2C{\equiv}CTol)_2$ + Na]$^+$ 14% (ionized with Na^+). IR (cm^{-1}): ν(C≡C) 2179 (vs); ν(=C=C) 1627 (vs); ν(Ru−Cl) 302 (m). ^1H NMR (δ, 295 K, 300 MHz, $CDCl_3$): 8.19 (m, 4H), 8.02 (m, 4H), 7.77 (m, 4H), 7.30 (m, 10H), 7.09 (m, 4H), 7.01 (m, 8H), 6.85 (m, 11H), 6.41 (m, 2H) (aromatics); 5.33 (td, $^4J_{H-P}$ =

Table 4. Crystallographic Data for 1·4H_2O and 13·Et_2O

	1·4H_2O	**13**·Et_2O
empirical formula	$C_{80}H_{60}Cl_2O_4P_4Ru$	$C_{75}H_{67}Cl_2OP_3Ru$
fw	1381.13	1249.17
temperature (K)	293(2)	173(1)
cryst syst	tetragonal	monoclinic
space group	$I4_1/a$	$P2_1/n$
a (Å)	25.4930(8)	11.7880(1)
b (Å)	25.4930(8)	23.1970(3)
c (Å)	12.0850(3)	23.2680(3)
α (deg)	90	90
β (deg)	90	91.751(1)
γ (deg)	90	90
volume (Å^3)	7854.0(4)	6359.58(13)
Z	4	4
D_{calcd} (Mg/m^3)	1.168	1.305
abs coeff (mm^{-1})	0.393	0.451
F(000)	2840	2592
cryst size (mm)	0.15 × 0.15 × 0.12	0.30 × 0.20 × 0.10
θ range for data collection (deg)	1.86 to 27.88	3.10 to 27.89°
no. of data/restraints/params	4666/0/206	15 128/0/744
goodness-of-fit on F^2	1.044	0.986
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0514$, $wR_2 = 0.1240$	$R_1 = 0.0522$, $wR_2 = 0.1034$
R indices (all data)	$R_1 = 0.0932$, $wR_2 = 0.1441$	$R_1 = 0.0956$, $wR_2 = 0.1188$
largest diff peak and hole (e A^{-3})	0.536 and −0.539	0.426 and −0.477

3.6 and 3.8, 1H, =C*H*Ph); 2.48 (s, 3H, C_6H_4−CH_3), 2.36 (s, 6H, C_6H_4−CH_3). ^{13}C NMR (δ, 295 K, 100.64 MHz): 358 (s br, C_α, C_α=CHPh); 140.64 (C^4, C_6H_4−CH_3, *trans* to Cl); 140.23 (C^4, C_6H_4−CH_3, *trans*); 134.78 ("t", $^{2+4}J_{C-P}$ = 11.3, *o*-C, PPh_2, *trans*); 134.2 (d, $^1J_{C-P}$ = 55.1, *i*-C, PPh_2, *trans* to Cl); 133.46 ("t", $^{2+4}J_{C-P}$ = 10, *o*-C, PPh_2, *trans*); 133.12 (*i*-C, PPh_2, *trans*); 132.51 (s br); 133.24 (s); 130.06 (d, $^4J_{C-P}$ = 1.7, *p*-C, PPh_2); 129.5 (s); 129.4 (s); 129.14 (s); 128.29 (s); 127.94 ("t", $^{3+5}J_{C-P}$ = 10.4, *m*-C, PPh_2, *trans*); 127.76 (d, $^3J_{C-P}$ = 11.1, *m*-C, PPh_2, *trans* to Cl); 127.42 ("t", $^{3+5}J_{C-P}$ = 9.8, *m*-C, PPh_2, *trans*); 126.96 (s); 125.20 (s); 119.32 (s); 118.4 (d, $^3J_{C-P}$ = 2.3, tentatively attributed to C_β, C=C_βHPh); 110.95 ("t", $^{2+4}J_{C-P}$ = 11.7, C_β, PPh_2C_α≡C_βTol, *trans*); 108.43 (d, $^2J_{C-P} \approx$ 12.7, C_β, PPh_2C_α≡C_βTol, *trans* to Cl); 83.2 (d, $^1J_{C-P}$ = 96.6, C_α, PPh_2C_α≡C_βTol, *trans* to Cl); 82.6 (AXX′Y, $^{1+3}J_{C-P} \approx$ 88.5, C_α, PPh_2C_α≡C_βPh, *trans*); 22.27 (C_6H_4−CH_3, PPh_2-C≡CTol, *trans* to Cl); 22.14 (C_6H_4−CH_3, PPh_2C≡CTol). ^{31}P{^{1}H} NMR (δ, 295 K, 121.5 MHz, $CDCl_3$): 1.26 (t), −0.41 (d) ($^2J_{P-P}$ = 26.7).

X-ray Crystallography. Table 4 reports details of the structural analyses for the complexes **1**·4H_2O and **13**·Et_2O. Orange-yellow (**1**) or orange (**13**) crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane solution (**1**) or diethyl ether into a chloroform solution (**13**) of each compound at room temperature. For complex **1** only the fragment [RuCl(PPh_2C≡CPh)·H_2O] was in the asymmetric unit, and the absolute structure was obtained using the corresponding symmetry transformations. Complex **13** crystallizes with one diethyl ether molecule. X-ray intensity data were collected with a NONIUS κCCD area-detector diffractometer, using graphite-monochromated Mo Kα radiation (λ(Mo Kα) 0.71071 Å). Images were processed using the DENZO and SCALEPACK suite of programs,[102] and the absorption correction was performed using SORTAV.[103] The structures were solved by direct methods using the SHELXL-97 program[104] for **1** or DIRDIF92[105] for **13** and refined by full-matrix least squares on F^2 with SHELXL-97. All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters of 1.2 times the U_{iso} value of their attached carbons for phenyl and methylene hydrogens and 1.5 for the methyl groups.

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Supporting Information Available: Further details of the structure determinations of **1**·4H_2O and **13**·Et_2O, including atomic coordinates, bond distances and angles, and thermal parameters. Crystallographic data in CIF format. ^{1}H NMR thermal study of compound [$RuCl_2(PPh_2C{\equiv}CPh)_4$] (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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