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Novel Polymetallic Vinylidene- and Allenylideneruthenium(II) Complexes

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Two new triynes, C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)C≡CH]$_3$ (**3**) and C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)-PhC(OH)C≡CH]$_3$ (**5**), have been prepared and used for the facile synthesis of several tris(vinylideneruthenium) and tris(allenylideneruthenium) complexes via metal-mediated activation and tautomerization or isomerization and dehydration of the alkyne moieties, respectively. Complexes C_6Me_3-1,3,5-{[CH_2O(*p*-C_6H_4)CH=C=Ru(dppe)$_2$Cl]BF_4}$_3$ (**6**) and C_6Me_3-1,3,5-{[CH_2O(*p*-C_6H_4)PhC=C=C=Ru(dppe)$_2$Cl]BF_4}$_3$ (**8**) were obtained by activation of **3** and **5** by [RuCl(dppe)$_2$]BF_4. C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)CH=C=Ru(PCy_3)$_2$$Cl_2$]$_3$ (**7**) and C_6Me_3-1,3,5-{[CH_2O(*p*-C_6H_4)PhC=C=C=Ru(PCy_3)(*p*-cymene)Cl]OTf}$_3$ (**9**) resulted from the reaction of **3** with [$RuCl_2$(*p*-cymene)]$_2$/2PCy_3 and of **5** with [RuCl(PCy_3)(*p*-cymene)]OTf.

Introduction

The design of functional star molecules and dendrimers is the focus of a fast evolving field of chemistry.[1,2] This interest arises from their potential to incorporate guest molecules within their cavities and to bind active molecules in their outer sphere.[2] Star molecules constitute key starting components for the synthesis of new multisite catalyst precursors by interaction of the multiple periphery functions, acting as ligands, with suitable metal complexes.[2b,c] Recently, it was shown that conjugated terminal polyalkynes can be activated and easily converted into the isomeric vinylidenes in the coordination sphere of ruthenium complexes to give trimetallic complexes in the form of an organometallic triskelion.[3] These complexes displayed a fully conjugated, rigid organic spine. Such compounds are of interest for applications as electron storage devices[4] or as modified electrodes,[5] and their model ruthenium-carbene moieties may become suitable to open the way to new types of functional star polymers, via ring-opening metathesis polymerization (ROMP).[6,7]Indeed, vinylidene- and allenylideneruthenium(II) complexes are known as efficient catalysts for olefin metathesis and provide the advantage that they can be conveniently prepared from conventional terminal alkynes and alkynols.[8] However, for catalysis purposes coordinatively unsaturated complexes with a nonconjugated backbone are of better value to avoid communication between the metal centers through the core[3] and ensure the possibility of equal reactivity of all identical catalytic moieties within the same molecule. This challenge led us to design new simple organic nonconjugated polyynes as precursors for suitable stable 18-electron vinylideneruthenium(II) and allenylideneruthenium(II) complexes. We report here the controlled activation of star triynes by suitable ruthenium derivatives and the synthesis of novel star trisvinylidene- and trisallenylideneruthenium(II) complexes with identical ruthenium sites.

Results and Discussion

Synthesis of the Tritopic Polyynes. Compound C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)C≡CH]$_3$ (**3**) was synthesized in three reaction steps via the iodo derivative C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)I]$_3$ (**1**) and the protected alkyne C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)C≡CSi(CH_3)$_3$]$_3$ (**2**). Following a procedure described for the synthesis of dendrons carrying alkoxyaryl moieties in their side chains[9] the tris(*p*-iodophenoxy)-terminated compound **1** was obtained from the reaction of 4-iodophenol and tris(bromomethyl)mesitylene in the presence of a base (Scheme 1).

The product is insoluble in almost all common organic solvents but can be recrystallized from a hot solution of DMF by addition of methanol. Compound **1** could be

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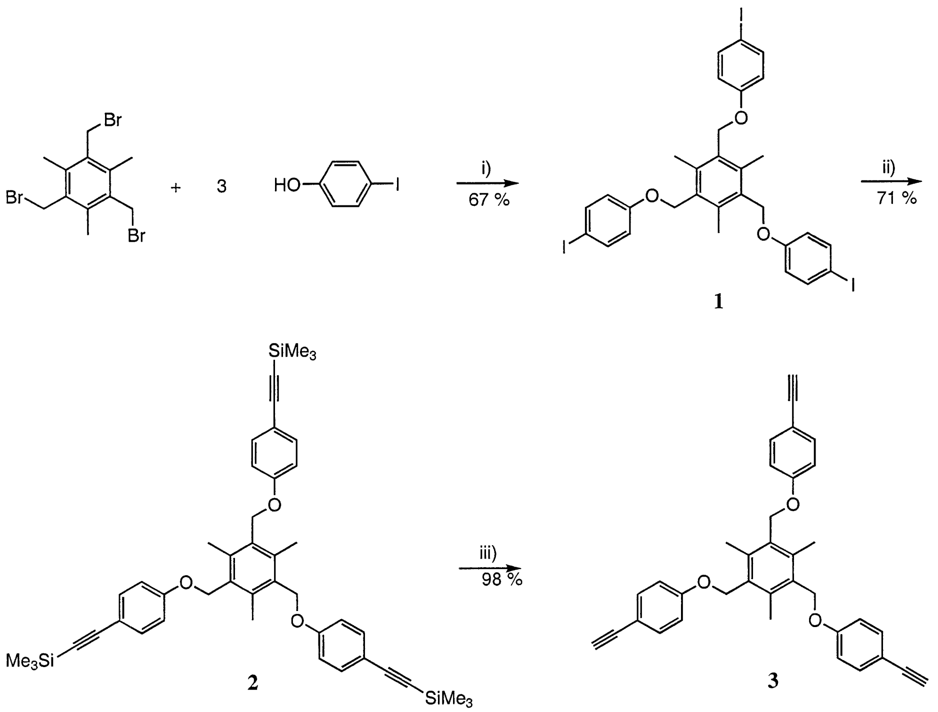
10.1021/om0300326 CCC: $25.00

Scheme 1[a]



[a] (i) K_2CO_3, NaI, DMF, 75 °C, 24 h; (ii) $PdCl_2(PPh_3)_2$, CuI, HN(*i*-Pr)$_2$, $Me_3SiC{\equiv}CH$, THF, rt, 48 h; (iii) K_2CO_3, MeOH/H_2O, 50 °C, 5 h.

readily transformed in high yield into the trimethylsilyl-protected alkyne C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)$C{\equiv}CSi(CH_3)_3$]$_3$ (**2**) by a classical Sonogashira coupling reaction. Quantitative deprotection of the alkyne was achieved using aqueous potassium carbonate.[10]

The ^1H NMR spectrum of the product C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)$C{\equiv}CH$]$_3$ (**3**) showed two doublets, each corresponding to six protons, assignable to the aryl protons of the branches ($\delta = 7.49$ and 6.98, $^3J_{HH} = 8.81$ Hz) along with two singlets in a ratio of 6:9 at δ 5.10 and 2.42, respectively, attributed to the methyleneoxy and methyl groups of the core. Additionally, a resonance corresponding to three protons was observed within the typical range for terminal alkynes (δ 3.01). The characterization by ^{13}C NMR spectroscopy was not possible due to the low solubility of **3**, but a distinct IR absorption band at 2104 cm^{-1}, consistent with the presence of $C{\equiv}C$ bonds, as well as the results of mass spectrometry (*m*/*e* 509: $[M - H]^+$) support the proposed structure.

For the synthesis of the trisalkynol C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)PhC(OH)$C{\equiv}CH$]$_3$ (**5**), in the first step of the sequence depicted in Scheme 2, the benzophenone derivative C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)COPh]$_3$ (**4**) was obtained in a similar manner as compound **1** by a typical Williamson ether synthesis. The addition of **4** to a solution of a large excess of lithium ethynyl generated in situ by reaction of acetylene gas with *n*-butylithium at low temperature, following a procedure described by Midland,[11] resulted in the selective formation of the alkynol C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)PhC(OH)$C{\equiv}CH$]$_3$ (**5**) in 76% isolated yield. No other side product was detected when a 2-fold excess of the alkynylating reagent and a sufficient amount of solvent were used. With an excess of only 10% of lithium ethynyl only the 2-fold alkynylated compound was obtained as a result of the decreasingly solubility of the 1-, 2-, and 3-fold lithium-alcoholate-substituted intermediates formed during the reaction.

The ^1H NMR spectrum of **5** is consistent with the proposed structure depicted in Scheme 2 and shows singlet resonances typical for the CH_2O and CH_3 units at δ 5.14 and 2.49 and for the alcohol and alkyne protons at δ 3.07 and 2.97, respectively, in a ratio of 6:3:3:3. Interesting features of the $^{13}C\{^1H\}$ NMR spectrum are the two signals assignable to the six carbon atoms of the alkyne moieties at δ 87.10 and 75.88, reflecting the high symmetry of the complex. The chemical shifts of the methyleneoxy and the methyl groups at δ 65.43 and 16.38 ppm are similar for all compounds discussed in this publication. Only a weak $\nu(C{\equiv}C)$ absorption band was observed in the IR spectrum at 2113 cm^{-1}. However, fast atom bombardment mass spectrometry revealed a mass peak of *m*/*e* 828 consistent with a $[M - H]^+$ ion. Unfortunately, the crystallization solvent could not be completely removed from the target compound, even after several days under vacuum and mild heating. This problem persisted whether methanol, ethanol, diethyl ether, or tetrahydrofuran was used for the purification and might be a consequence of weak hydrogen bonds between the ether functions and hydroxy groups of both solvent and **5**. The corresponding solvent molecules within the product could be easily replaced by those of another solvent by simple stirring **5** in the new solvent. They could not be replaced by a solvent of lower polarity such as dichloromethane.

Synthesis of the Tris(vinylideneruthenium) and tris(allenylideneruthenium) Model Complexes 6 and 8. The synthetic approach was based on known activation processes of terminal alkynes and propargyl

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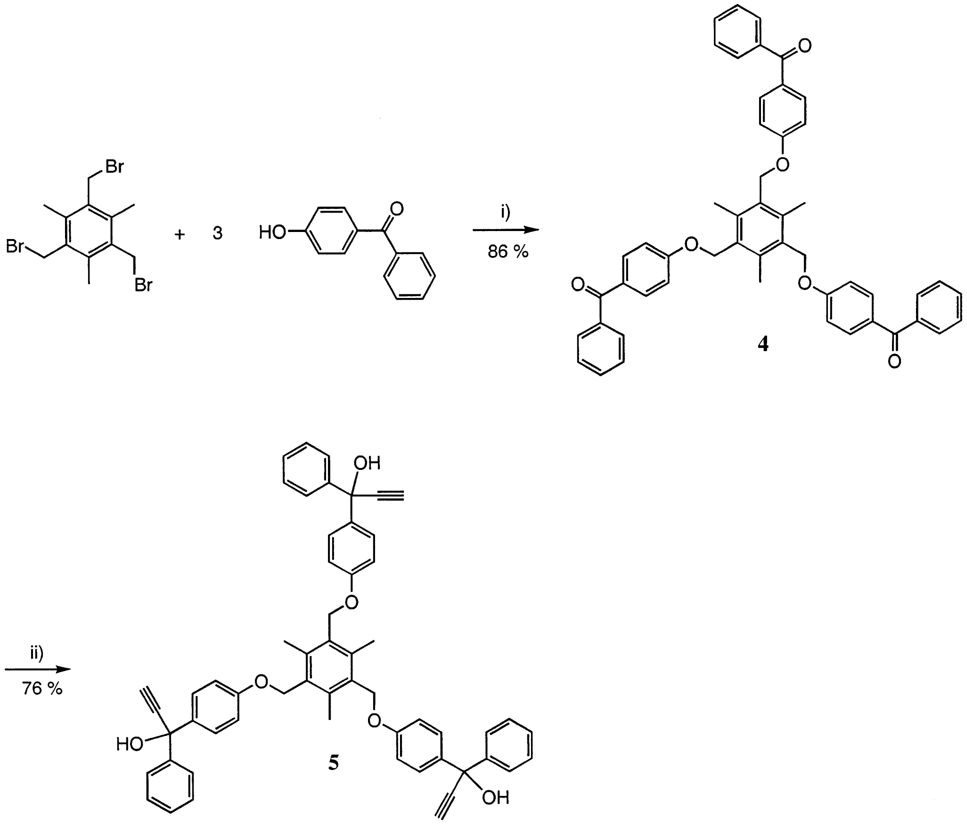
Scheme 2[a]



[a] (i) K_2CO_3, NaI, DMF, 75 °C, 24 h; (ii) a) $LiC{\equiv}CH$ (from *n*-BuLi and $HC{\equiv}CH$ at −100 °C), THF, −100 °C, rt, 48 h; (b) HCl/H_2O.

alcohols[12] with $RuCl_2(dppe)_2$,[13] and then with $RuCl_2(PR_3)(arene)$[14]complexes, the former leading to more stable vinylidene and allenylidene complexes. The stable 18-electron complexes C_6Me_3-1,3,5-$\{[CH_2O(p\text{-}C_6H_4)CH{=}C{=}Ru(dppe)_2Cl]BF_4\}_3$ (**6**) and C_6Me_3-1,3,5-$\{[CH_2O(p\text{-}C_6H_4)PhC{=}C{=}C{=}Ru(dppe)_2Cl]BF_4\}_3$ (**8**), displaying C_3-symmetry triskelion shapes,[15] were prepared similarly and in high yield by reaction of the complex $[(dppe)_2RuCl]BF_4$, in situ generated from $(dppe)_2RuCl_2$ in the presence of $AgBF_4$, with the respective trialkynes **3** and **5** in dichloromethane at ambient temperature (Schemes 3 and 4). Complexes **6** and **8** were isolated as deep brown and purple solids, respectively.

This method was already applied to the synthesis of the fully conjugated bimetallic C_6H_4-1,4-$\{[CH{=}C{=}C{=}Ru(dppe)_2Cl]PF_6\}_2$[16] and trimetallic C_6H_3-1,3,5-$\{[C{\equiv}C(p\text{-}C_6H_4)CH{=}C{=}Ru(dppe)_2Cl]PF_6\}_3$[3] complexes. Whereas in the case of the vinylidene **6** the conversion was complete after 17 h according to ^{31}P NMR spectroscopy, the formation of the allenylidene **8** was only complete after three weeks. This might be due to steric reasons with respect to the crowded environment of both the dppe-substituted ruthenium center and the alkyne moiety of the propargylic alcohol derivative **5**. The trisilylated triyne derivative **2** reacted under similar conditions only to a small extent with $[(dppe)_2RuCl]BF_4$, and the conversion could not be driven to completeness.

The ^1H NMR spectrum of **6** showed the expected characteristics and the high symmetry of the molecule: one singlet for the six protons of the methyleneoxy moiety at δ 4.96 and one singlet for the nine protons of the methyl groups of the core at δ 2.40 are observed. A multiplet at δ 3.49 is assigned to the β-H atom of the ruthenium vinylidene moiety $Ru{=}C{=}CHR$. The corresponding signal of the conjugated complex C_6H_3-1,3,5-$\{[C{\equiv}C(p\text{-}C_6H_4)CH{=}C{=}Ru(dppe)_2Cl]PF_6\}_3$ appears as a broad resonance at δ 3.75. Characteristic features in the $^{13}C\{^1H\}$ NMR spectrum of **6** are the positions of the signals of the α- and β-C atoms of the vinylidene ligand which appear as a quintet ($^2J_{PC} = 13$ Hz) at δ 358.77 and as a multiplet at δ 108.83 (for C_6H_3-1,3,5-$\{[C{\equiv}C(p\text{-}C_6H_4)CH{=}C{=}Ru(dppe)_2Cl]PF_6\}_3$: δ 356.6 and 109.5). During the reaction a $^{31}P\{^1H\}$ singlet increased at δ 39.69, which indicates the formation of a regularly 3-fold ruthenium-substituted complex with 12 equivalent ^{31}P nuclei, with the vinylidene and the chloro ligands in a *trans* arrangement. At the same time in the IR spectrum the vibration band at 2104 cm^{-1}, typical for the presence of alkyne, disappeared, while a new band ascribed to the $\nu(C{=}C)$ stretching frequency of the $Ru{=}C{=}C$ group was observed at 1637 cm^{-1}.

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(15) The triskelion (plural: triskelia) is a sign related to celtic symbolism representing three forces and is constituted of three branches (legs), radiating from a center. A typical example can be found in the arms of Isle of Man. See also: Doyle, M.; Parker, W.; Gum, P. A.; Martin, J.; Macnicol, D. D. *Tetrahedron Lett.* **1970**, *42*, 3619 and ref 3.

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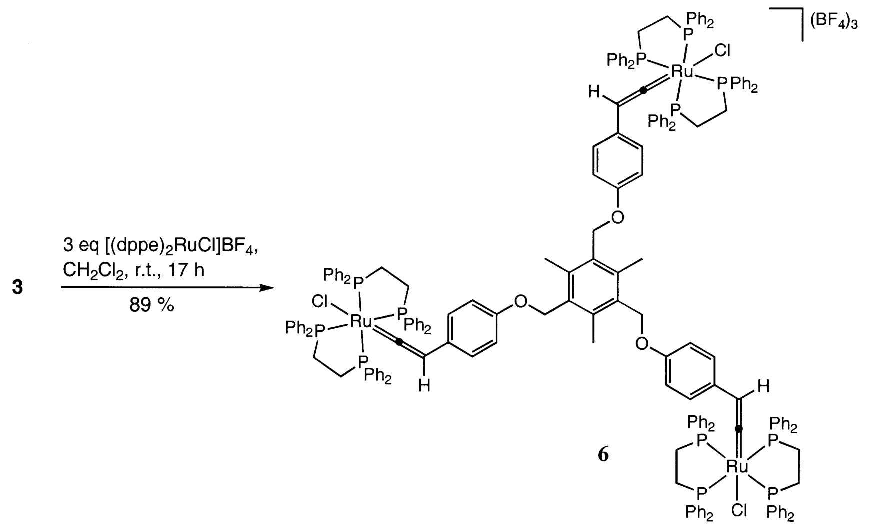
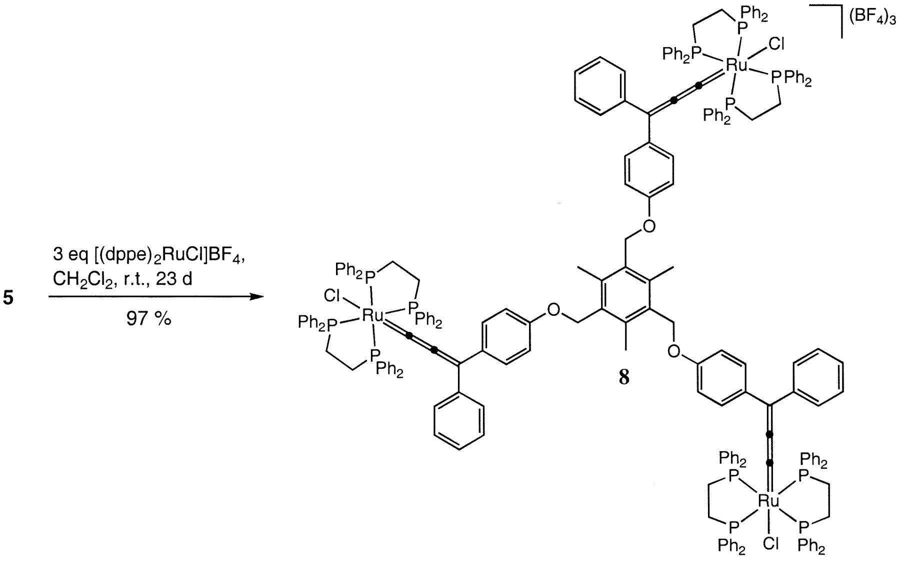
Scheme 3



Scheme 4



The ^{1}H NMR spectrum of complex **8** displays two singlets at δ 5.25 and 2.49 arising from the methyleneoxy and methyl protons of the core. The three allenylidene ligands are equivalent by $^{13}C\{^1H\}$ NMR spectroscopy and give rise to three resonances at δ 298.30, 204.21 (m), and 160.44 corresponding to the α, β, and γ carbons of the allenylidene spine, the former showing coupling to the phosphorus nuclei (quintet, $^2J_{PC} = 14$ Hz). The high symmetry of the complex is also reflected by the presence of a discrete singlet ($\delta = 38.6$) in the $^{31}P\{^1H\}$ NMR spectrum for the 12 Ph_2P groups, only consistent with a *trans* arrangement of the chloro and allenylidene ligands. The IR spectrum of the deep violet solid shows the expected strong absorption peak at 1925 cm^{-1} for the C=C=C stretching frequency of the allenylidene unit. Similar values were reported for the corresponding mononuclear ruthenium complex $[(dppe)_2ClRu{=}C{=}C{=}CPh_2]PF_6$ [17] ($^{13}C\{^1H\}$ NMR δ 308.57 (Ru=C, $^2J_{PC} = 14$ Hz), 215.90 (Ru=C=*C*), 161.47 (Ru=C=C=*C*); ^{31}P NMR δ 37.98; IR 1923 cm^{-1} (s, ν(C=C=C)).

Synthesis of the Trisvinylidene Complex C_6Me_3-1,3,5-$[CH_2O(p\text{-}C_6H_4)CH{=}C{=}Ru(PCy_3)_2Cl_2]_3$ (7). Another method to produce stable vinylideneruthenium complexes from terminal alkyne is based on the concomitant modification of the ruthenium source by addition of stabilizing ligands. Recently, Ozawa et al. described the synthesis of the vinylidene analogue of the Grubbs catalyst, $(PCy_3)_2RuCl_2({=}C{=}CHPh)$.[18] This synthetic method was applied to the triyne **3**. The reaction of **3** with 3 equiv of $[RuCl_2(p\text{-cymene})]_2$ in the presence of 6 equiv of PCy_3 proceeded very cleanly at 80 °C and led to the isolation of the trisvinylidene **7**, as a grayish-brown solid in high purity and essentially quantitative yield (Scheme 5).

The ^{1}H NMR spectrum of complex **7** exhibits a triplet with an integral corresponding to 3 H atoms at low-field resonance typical for the vinylidene β-hydrogen atoms at δ 4.33 ($^4J_{PH} = 3$ Hz). This value compares well to the corresponding β-H shift of the single-site complex $[(PCy_3)_2RuCl_2({=}C{=}CHPh)$: $\delta = 4.70$, $^4J_{PH} = 3.6$ Hz[18]]. The $^{13}C\{^1H\}$ NMR spectrum of **7** shows a characteristic resonance at δ 345.27 (t, $^2J_{PC} = 14$ Hz) and δ 107.95 (t,

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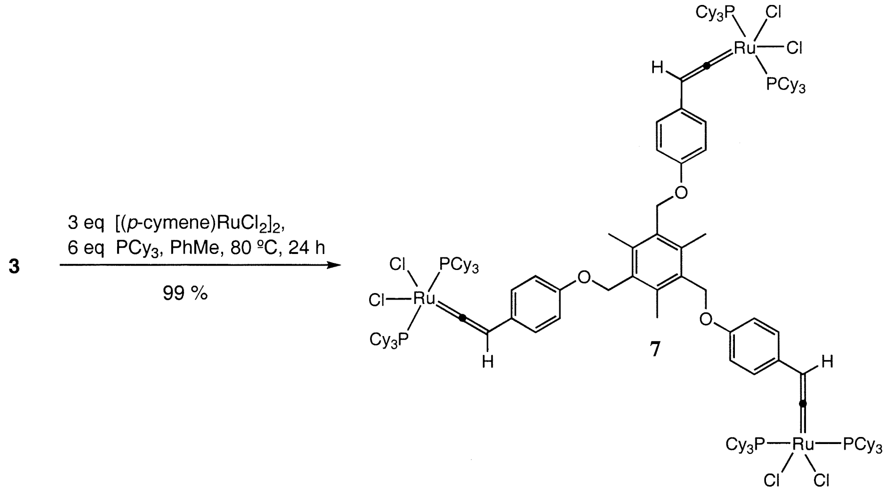
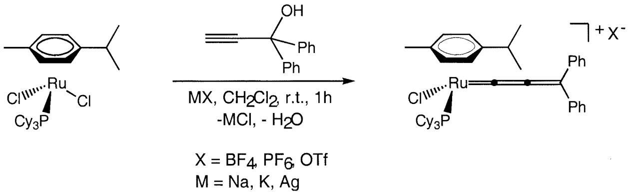
(18) Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190.

Scheme 5



Scheme 6



$^3J_{PC}$ = 4 Hz) comparable to the shifts of the α- and β-vinylidene carbon atoms in $(PCy_3)_2RuCl_2({=}C{=}CHPh)$[18] (δ 342.1 (t, $^2J_{PC}$ = 14 Hz), 109.6 (t, $^3J_{PC}$ = 5 Hz)).

Synthesis and Reactivity of C_6Me_3-1,3,5-$\{[CH_2O(p\text{-}C_6H_4)PhC{=}C{=}C{=}Ru(PCy_3)(p\text{-cymene})Cl]OTf\}_3$ (9). Ruthenium allenylidene complexes were shown recently to be efficient catalysts for alkene metathesis.[8] They were easily obtained by activation and dehydration of propargyl alcohols with (*p*-cymene)-$(PCy_3)RuCl_2$ in the presence of a noncoordinating salt according to Scheme 6.

Molecule **5**, offering three identical propargyl alcohol functions, was thus a good candidate for access to the first tris(allenylidenemetal) complex, a possible multiple "single-site" catalyst with three active moieties. Treatment of alkynol **5** with 3 equiv of [(*p*-cymene)(PCy_3)RuCl]OTf in dichloromethane at ambient temperature resulted in the instantaneous formation of a deep purple solution. The reaction was monitored by in situ ^{31}P NMR spectroscopy and stopped after 55 min, when about 95% conversion of the starting material was obtained. Evaporation of the solvent led to a dark violet, somewhat air-sensitive solid (Scheme 7).

The shift of the $^{31}P\{^1H\}$ NMR signal of the resulting product **9** at δ 56.36 (s) is in good agreement with the chemical shift observed for the mononuclear allenylideneruthenium complex [(*p*-cymene)(PCy_3)RuCl(=C=C=CPh_2]OTf (δ 59.21).[14b] The disappearance of the ^1H NMR signals attributed to the protons of the terminal alkyne moieties and hydroxy functionalities together with the IR spectroscopy data shows clearly that no simple coordination of the alkyne groups by the ruthenium centers took place. Besides, four doublets, each corresponding to 3 H atoms, were found between δ 6.58 and 6.00; this is the typical range for the four different signals of the aromatic protons of the three equivalent *p*-cymene ligands in comparable chiral allenylideneruthenium(II) complexes.[8,14] The appearance of a strong allenylidene absorption in the infrared spectrum of **9** at 1962 cm^{-1} is comparable to the respective value for the Ru=C=C=CPh_2 moiety in [(*p*-cymene)(PCy_3)RuCl-(=C=C=CPh_2]OTf (1963 cm^{-1}).[14b] These data allow us to propose a structure corresponding to a tripodal allenylidene complex of the formula C_6Me_3-1,3,5-$\{[CH_2O(p\text{-}C_6H_4)PhC{=}C{=}C{=}Ru(PCy_3)(p\text{-cymene})Cl]OTf\}_3$ for product **9**.

Conclusion

New nonconjugated triynes have been prepared in order to investigate the first step of possible involvement of polyvinylidene- and polyallenylidene-metal intermediates in the preparation of star polymers by ROMP. These triynes were suitable substrates for the synthesis of model tris(vinylideneruthenium) and tris(allenylideneruthenium) complexes in high yield. Whereas complexes containing the $RuCl(dppe)_2$ moiety are stable, two of the novel trimetallic compounds, $C_6H_3Me_3$-1,3,5-$[CH_2O(p\text{-}C_6H_4)CH{=}C{=}Ru(PCy_3)_2Cl_2]_3$ (**7**) and C_6Me_3-1,3,5-$\{[CH_2O(p\text{-}C_6H_4)PhC{=}C{=}C{=}Ru(PCy_3)(p\text{-cymene})Cl]OTf\}_3$ (**9**), represent interesting arrangements that may become useful as catalyst precursors for olefin metathesis and related reactions.

Experimental Section

General Procedures. All manipulations involving organometallic compounds and ruthenium complexes were performed under an inert atmosphere of argon, using standard Schlenk techniques. Dichloromethane, tetrahydrofuran, and methanol were dried by standard methods and freshly distilled under argon prior to use. $PdCl_2(PPh_3)_2$,[8b] $(dmso)_4RuCl_2$,[19] *cis*-$(dppe)_2RuCl_2$,[20] [(*p*-cymene)$RuCl_2]_2$,[21] (*p*-cymene)$(PCy_3)RuCl_2$,[8b] and [(*p*-cymene)(PCy_3)RuCl]OTf[8b] have been prepared according to literature procedures. $[(dppe)_2RuCl]BF_4$ was synthesized by the reaction of *cis*-$(dppe)_2RuCl_2$ with a stoichiometric amount of $AgBF_4$ in dichloromethane at room temperature for 2 h and after filtration of the resulting solution was used without isolation of the product. *N*,*N*-Di-isopropylamine was

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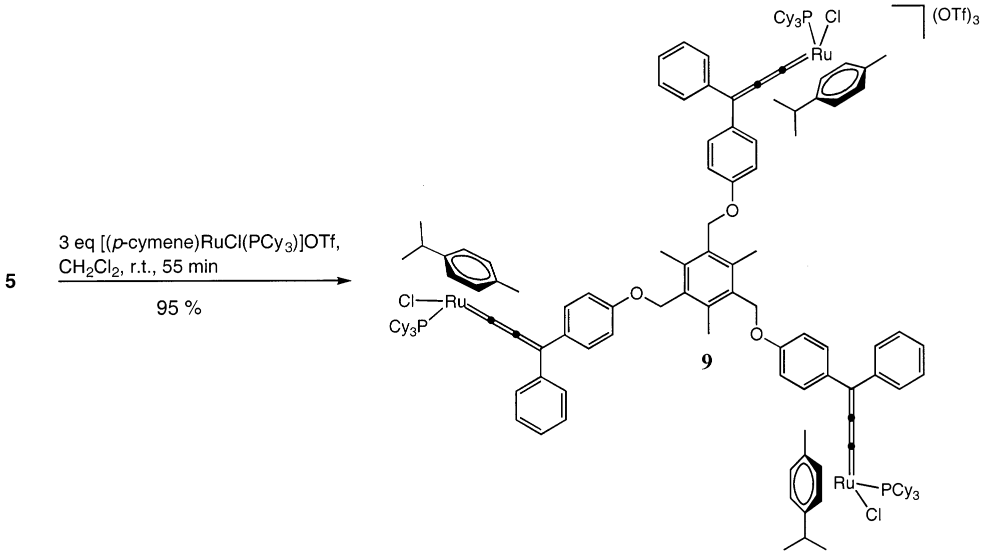
Scheme 7



distilled and stored under argon. All other commercially available chemicals were used without further purification.

Infrared spectra were recorded on a Bruker IFS 28 spectrometer. The C, H, and N analyses and mass spectra were carried out by the Regional Centre of Physical Measurement (CRMPO) at the University of Rennes 1. High-resolution mass spectra were recorded using a ZabSpec TOF Micromass spectrometer (ionization method, LSIMS with Cs^+; matrix, mNBA; acceleration, 8 kV). NMR spectra were recorded on a Bruker Avance DPX 200 instrument at 200.13 MHz (^{1}H), 81.02 MHz (^{31}P), and 50.33 MHz (^{13}C) or on a Bruker AC 300 P instrument at 75.47 MHz (^{13}C). Chemical shifts are reported in ppm and referenced to the residual protons and ^{13}C signals of deuterated solvents or to the ^{31}P signal of external 85% H_3PO_4.

Synthesis of C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)I]$_3$ (1). Tris(bromomethyl)mesitylene (3.00 g, 7.52 mmol), 4-iodophenol (4.96 g, 22.56 mmol), K_2CO_3 (6.24 g, 45.12 mmol), and NaI (845 mg, 5.64 mmol) were suspended in 90 mL of DMF, and the reaction mixture was stirred at 75 °C for 48 h. The hot solution was decanted, and 150 mL of MeOH was added under vigorous stirring. A white crystalline solid of very low solubility in common organic solvents was obtained. It was stirred two times for 30 min in 100 mL of distilled water to remove residual salt impurities. The product was filtered off, dissolved in 100 mL of hot DMF, and precipitated again by addition of 100 mL of MeOH. After filtration the product was washed several times with MeOH and with diethyl ether. Yield: 4.10 g (67%). IR (KBr): ν 2904 (w), 1673 (w), 1582 (m), 1481 (s), 1370 (w), 1280 (m), 1236 (s), 1173 (m), 985 (m), 816 (m), 634 (w), 503 (w) cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 7.61 (d, 6H, $^3J_{HH}$ = 8.90 Hz, CH_{meta}, ArO), 6.81 (d, 6H, $^3J_{HH}$ = 8.90 Hz, CH_{ortho}, ArO), 5.04 (s, 6H, CH_2O), 2.40 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 138.72 (C_{meta}, ArO), 117.43 (C_{ortho}, ArO), 65.70 (CH$_2$O), 16.19 (CH$_3$), quarternary carbon atoms could not be detected because of the low solubility of the product. Anal. Calcd for $C_{30}H_{27}I_3O_3$: C, 44.14; H, 3.33. Found: C, 43.99; H, 3.53. MS(FAB$^+$): *m*/*e* 816 ($M^{+\bullet}$).

Synthesis of C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)C≡CSiMe$_3$]$_3$ (2). 1,3,5-Tris(*p*-iodo-phenoxymethyl)mesitylene (**1**) (3.00 g, 3.68 mmol), $Pd(PPh_3)_2Cl_2$ (77 mg, 0.110 mmol), and CuI (42 mg, 0.220 mmol) were suspended in 50 mL of dry THF under argon atmosphere. Subsequently 70 mL of *N*,*N*-di-isopropylamine and trimethylsilylacetylene (1.88 mL, 1.30 g, 13.23 mmol) were added with a syringe, and the reaction mixture was stirred for 62 h at ambient temperature. After filtration and evaporation of all volatile components the resulting product was redissolved in a small amount of CH_2Cl_2 and precipitated with a 10-fold volume of heptane. After filtration, the white crystalline material was washed with heptane (3 × 30 mL) and pentane (20 mL) and dried in vacuo. Yield: 1.89 g (71%). IR (KBr): 2958 (w), 2156 (m, ν(C=C)), 1604 (m), 1506 (s,), 1237 (vs, ν(C−O), CH_2−O−Ar), 171 (w), 992 (m), 843 (s), 759 (w) cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 7.53 (d, 6H, $^3J_{HH}$ = 8.61 Hz, CH_{meta}, ArO), 7.02 (d, 6H, $^3J_{HH}$ = 8.81 Hz, CH_{ortho}, ArO), 5.15 (s, 6H, CH_2O), 2.48 (s, 9H, CH_3, Mes), 0.32 (s, 27H, Si(CH_3)$_3$). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$): 159.65 (C_{ipso}, ArO), 139.89 (CCH$_2$O, Mes), 133.98 (C_{meta}, ArO), 131.99 (CH$_3$, Mes), 116.11 (C_{para}, ArO), 114.93 (C_{ortho}, ArO), 105.56 (C≡CSiMe$_3$), 93.10 (C≡CSiMe$_3$), 65.43 (CH$_2$O), 16.40 (CH$_3$, Mes), 0.55 (Si(CH$_3$)$_3$). Anal. Calcd for $C_{45}H_{54}O_3Si_3$: C, 74.33; H, 7.49. Found: C, 73.41; H, 7.44. MS(FAB$^+$): *m*/*e* 726 ($M^{+\bullet}$).

Synthesis of C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)C≡CH]$_3$ (3). 1,3,5-Tris[*p*-(trimethylsilylethynyl)phenoxymethyl]mesitylene (**2**) (1 g, 1.38 mmol) was dissolved in 100 mL of MeOH. Following the addition of a solution of K_2CO_3 (855 mg, 6.19 mmol) in ca. 6 mL of distilled water the white suspension was stirred at 50 °C for 5 h. After the evaporation of the solvents the residue was extracted carefully with PhCl (3 × 40 mL, stirred for 30 min each time). After removing the solvent using an additional solvent trap the product was obtained as an electrostatic white powder with very low solubility in all common solvents besides PhCl. Yield: 688 mg (98%). IR (KBr): ν 3283 (s, ν(C−H), C=CH), 2971 (m), 2908 (m), 2104 (m, ν(C=C)), 1604 (s), 1502 (s), 1370 (m), 1285 (s), 1235 (s, br, ν(C−O), CH_2−O−Ar), 1170 (s), 1109 (m) 1025 (m), 988 (s), 851 (m), 830 (s), 743 (m), 686 (m), 666 (m), 605 (m), 536 (s) cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 7.49 (d, 6H, $^3J_{HH}$ = 8.81 Hz, CH_{meta}, ArO), 6.98 (d, 6H, $^3J_{HH}$ = 8.81 Hz, CH_{ortho}, ArO), 5.10 (s, 6H, CH_2O), 3.01 10 (s, 3H, C=CH), 2.42 (s, 9H, CH_3). The characterization by ^{13}C NMR spectroscopy was not possible because of the low solubility of **3**. Anal. Calcd for $C_{36}H_{30}O_3$: C, 84.68; H, 5.92. Found C, 84.18; H, 5.89. MS(FAB$^+$): *m*/*e* 509 [M − H]$^+$.

Synthesis of C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)COPh]$_3$ (4). Tris(bromomethyl)mesitylene (1.50 g, 3.76 mmol), 4-hydroxybenzophenone (2.24 g, 11.28 mmol), K_2CO_3 (3.12 g, 2.56 mmol), and NaI (423 mg g, 2.82 mmol) were suspended in 50 mL of neat DMF, and the reaction mixture was stirred at 75 °C for 24 h. The hot solution was filtered through a glass frit, and 250 mL of MeOH was added under vigorous stirring. After filtration the white solid was washed several times with MeOH and dried in vacuo. Yield: 2.43 g (86%). IR (KBr): 3053−2910 (w), 1652 (s, ν(C=O), Ar(CO)Ar), 1599 (s), 1506 (m), 1445 (m), 1418 (m), 1372 (m), 1317 (s), 1281 (s), 1243 (vs, br, ν(C−O), CH_2−O−Ar), 1173 (s), 1148 (s), 1026 (w), 988 (s), 937 (w), 922 (m), 841 (s), 793 (m), 742 (s), 698 (s), 630 (m) cm^{-1}. ^{1}H NMR

(δ, $CDCl_3$): 7.96 (d, 6H, $^3J_{HH}$ = 8.79 Hz, CH_{meta}, ArO), 7.87 (d, 6H, $^3J_{HH}$ = 8.26 Hz, CH_{ortho}, Ph), 7.58 (m, 9H, CH_{meta}, Ph + CH_{para}, Ph), 7.19 (d, 6H, $^3J_{HH}$ = 8.82 Hz, CH_{ortho}, ArO), 5.28 (s, 6H, CH_2O), 2.56 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 195.96 (*C*=O), 163.07 (C_{ipso}, ArO), 140.14 (C_{ipso}, Ph), 138.65 (CCH_2O, Mes), 133.11 (C_{meta}, ArO), 132.46 (C_{para}, Ph), 131.87 (C_{para}, ArO), 130.98 (CCH_3, Mes), 130.23 (C_{ortho}, Ph), 128.69 (C_{meta}, Ph), 114.60 (C_{ortho}, ArO), 65.63 (CH_2O), 16.50 (CH_3). Anal. Calcd for $C_{51}H_{42}O_6$: C, 81.58; H, 5.64. Found: C, 81.69; H, 5.65. MS(FAB$^+$): *m/e* 751 ([M + H]$^+$).

Synthesis of C_6Me_3-1,3,5-[CH_2O(*p*-C_6H_4)C(Ph)(OH)C≡CH]$_3$ (5). A 160 mL sample of dry THF was cooled to −100 °C (pentane/N_2). The argon was removed in vacuo, and the solution was saturated with acetylene gas (2.0 L, 89 mmol). *n*-BuLi was added at −100 °C via a syringe (10 mL of a 1.6 M solution in hexanes, 15.98 mmol), and the solution was stirred 1 h at this temperature. After the slow addition of a solution of 1,3,5-tris[*p*-(phenylcarbonyl)phenoxymethyl]mesitylene (**4**) (2.00 g, 2.66 mmol) in 60 mL of THF with a syringe the resulting clear solution was kept at −100 °C for another 1 h, then slowly warmed to ambient temperature within the cold bath and stirred at ambient temperature for 48 h. Following hydrolysis of the excess lithium ethynyl with ice and distilled water, the emulsion was neutralized with concentrated HCl and the organic phase was washed with distilled water. The combined aqueous phases were extracted with ether (2 × 100 mL). The combined organic phases were dried with $MgSO_4$ and filtrated, and the solvent was evaporated. The obtained yellowish oily residue was redissolved in a small amount of CH_2Cl_2 and purified by flash chromatography (SiO_2 (2 × 6 cm)/pentane): after extraction of the column with 500 mL of pentane to remove impurities the product was extracted with 300 mL of MeOH. The solvent was removed in vacuo, 20 mL of THF were added, the solution was stirred for 30 min, and the ether was evaporated to remove traces of MeOH (which otherwise cannot be removed even within 16 h in vacuo). The product was obtained in the form of a light yellowish solid. Yield: 1.92 g (76 %). IR (KBr): 3539−3423 (m-s, br) and 3282 (s, ν(O−H)), 3058−2913 (w), 2113 (w, ν(C≡C)), 1607 (m), 1507 (s), 1448 (w), 1370 (w), 1297 (w), 1237 (vs, ν(C−O), CH_2−O−Ar), 1174 (s), 1050 (w), 1029 (w), 986 (s), 896 (w), 829 (m), 761 (w), 699 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.70 (d, 6H, $^3J_{HH}$ = 8.21 Hz, CH_{ortho}, Ph), 7.66 (d, 6H, $^3J_{HH}$ = 8.81 Hz, CH_{meta}, ArO), 7.40 (m, 9H, CH_{meta}, Ph + CH_{para}, Ph), 7.08 (d, 6H, $^3J_{HH}$ = 8.81 Hz, CH_{ortho}, ArO), 5.14 (s, 6H, CH_2O), 3.07 (s, br, 3H, O*H*), 2.97 (s, 3H, C≡C*H*), 2.49 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 159.16 (C_{ipso}, ArO), 145.10 (C_{ipso}, Ph), 139.81 (CCH_2O, Mes), 137.58 (C_{para}, ArO), 132.15 (CCH_3, Mes), 128.79 (C_{meta}, Ph), 128.29 (C_{para}, Ph), 127.93 (C_{meta}, ArO), 126.46 (C_{ortho}, Ph), 114.73 (C_{ortho}, ArO), 87.10 (*C*≡CH), 75.88 (C≡*C*H), 74.44 (*C*-OH), 65.43 (CH_2O), 16.38 (CH_3). Anal. Calcd for $C_{57}H_{48}O_6$·1.5THF: C, 81.27; H, 5.86. Found: C, 80.81; H, 6.04. MS-(FAB$^+$): *m/e* 828 ([M − H]$^+$).

Synthesis of C_6Me_3-1,3,5-{CH_2O(*p*-C_6H_4)CH=C=Ru-(dppe)$_2$Cl]BF_4}$_3$ (6). *cis*-(dppe)$_2RuCl_2$ (1.138 g, 1.175 mmol) and $AgBF_4$ (229 mg, 1.175 mmol) were dissolved in 40 mL of CH_2Cl_2, stirred for 2 h, and filtrated, and the formed AgCl residue was washed with 10 mL of CH_2Cl_2. The deep red filtrate was added to a solution of trisalkyne **3** (200 mg, 0.392 mmol) in 10 mL of CH_2Cl_2, and the reaction mixture was stirred at ambient temperature for 17 h. Within that time the color of the solution changed from deep red to light brown. Complete conversion was confirmed by ^{31}P NMR spectroscopy, and then the solvent was evaporated to give a brown crystalline solid. The product was washed several times with ether and dried under vacuum. Yield: 1.30 g (89%). IR (KBr): ν 3054 (m), 2921 (w), 1637 (s, br, ν(C=C), Ru=*C*=*C*HR), 1680 (m), 1503 (s), 1485 (m), 1434 (s), 1231 (s), 1057 (s, br), 998 (m), 827 (m), 711 (s), 696 (vs), 530 (s), 492 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.48−6.83 (m, 120H, Ph, dppe), 6.43 (d, 6H, $^3J_{HH}$ = 8.7 Hz, CH_{meta}, ArO), 5.70 (d, 6H, $^3J_{HH}$ = 8.5 Hz, CH_{ortho}, ArO), 4.96 (s, 6H, CH_2O), 3.49 (m, 3H, Ru=C=C*H*), 3.00−2.63 (m, b, 24H, CH_2CH_2, dppe), 2.40 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 358.77 (t, $^2J_{PC}$ = 13 Hz, Ru=*C*), 157.51 (C_{ipso}, ArO), 139.10 (CCH_2O, Mes), 134.14 (Ar), 133.45 (Ar), 131.60 (Ar), 131.34 (Ar), 130.75 (Ar), 128.81 (Ar), 128.03 (Ar), 117.59 (C_{para}, ArO), 114.68 (C_{ortho}, ArO), 108.83 (m, Ru=C=*C*), 65.16 (CH_2O), 28.82 (virtual triplet, *J* = 11 Hz, PCH_2CH_2P, dppe), 16.04 (CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 39.69 (s). Anal. Calcd for $C_{192}H_{174}B_3Cl_3F_{12}O_3P_{12}Ru_3$: C, 64.58; H, 4.91. Found: C, 63.66; H, 5.06.

Synthesis of C_6Me_3-1,3,5-{CH_2O(*p*-C_6H_4)CH=C=Ru-(PCy_3)$_2Cl_2$]$_3$ (7). 1,3,5-Tris(*p*-ethynylphenoxymethyl)mesitylene (**3**) (303 mg, 0.594 mmol), [(*p*-cymene)$RuCl_2$]$_2$ (545 mg, 1.78 mmol), and PCy_3 (999 mg, 3.56 mmol) were dissolved in 40 mL of toluene, and the suspension was stirred for 24 h at 80 °C to give a dark brown solution. After complete conversion was confirmed by ^{31}P NMR spectroscopy the solvent was removed in vacuo and the resulting residue was washed with dry MeOH (3 × 10 mL). Yield: 1.593 g (99%). IR (KBr): ν 2926 (s), 2849 (s), 1618 (s, ν(C=C), Ru=*C*=*C*HR), 1504 (s), 1446 (s), 1222 (m, b), 1173 (m), 1003 (m), 848 (m), 829 (w−m), 729 (w), 511 (w-m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 6.85 (s, 12H, Ar), 5.00 (s, 6H, CH_2O), 4.33 (t, $^4J_{PH}$ = 3.33 Hz, 3H, Ru=C=C*H*), 2.38 (s, 9H, CH_3), 2.72−2.47, 2.15−1.92, 2.85−1.43, 1.36−1.01 (each m, 198H, Cy). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 345.27 (t, $^2J_{PC}$ = 14 Hz, Ru=*C*), 156.02 (C_{ipso}, ArO), 138.99 (CCH_2O), 132.04 (C_{para}, ArO), 129.01 (C_{ipso}, CCH_3), 126.31 (C_{meta}, ArO), 114.83 (C_{ortho}, ArO), 107.95 (t, $^3J_{PC}$ = 4 Hz, Ru=C=*C*), 65.48 (CH_2O), 33.15 (virtual triplet, *J* = 9 Hz, C^1 of Cy), 30.13 ($C^{3,5}$ of Cy), 28.01 ($C^{2,6}$ of Cy), 26.95 (C^4 of Cy), 15.97 (CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 22.02 (s). Anal. Calcd for $C_{144}H_{228}Cl_6O_3P_6Ru_3$: C, 63.84; H, 8.48. Found: C, 63.92; H, 8.53.

Synthesis of C_6Me_3-1,3,5-{CH_2O(*p*-C_6H_4)PhC=C=C=Ru(dppe)$_2$Cl]BF_4}$_3$ (8). *cis*-(dppe)$_2RuCl_2$ (88 mg, 0.091 mmol) and $AgBF_4$ (18 mg, 0.091 mmol) were dissolved in 10 mL of CH_2Cl_2, stirred for 2 h, and filtrated, and the resulting AgCl residue was washed with 2 mL of CH_2Cl_2. The deep red filtrate was added to a solution of triyne (**5**) (25 mg, 0.030 mmol) in 10 mL of CH_2Cl_2, and the reaction mixture was stirred at ambient temperature for 23 days. Within that time the color of the solution changed from red to deep violet. After complete conversion was confirmed by ^{31}P NMR spectroscopy, the solution was evaporated to dryness to give a violet crystalline solid. Yield: 113 mg (97%). IR (KBr): ν 3054 (m), 2921 (w), 1925 (vs, b, ν(C=C=C), Ru=*C*=*C*=*C*R_2), 1637 (s, b), 1680 (m), 1503 (s), 1485 (m), 1434 (s), 1231 (s, ν(C−O), CH_2−O−Ar), 1057 (s, b), 998 (m), 827 (m), 711 (s), 696 (s), 530 (s), 492 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 7.32−6.64 (m, 147H, Ar), 4.96 (s, 6H, CH_2O), 3.19−2.68 (m, b, 24H, CH_2CH_2, dppe), 2.49 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 208.30 (t, $^2J_{PC}$ =14 Hz, Ru=*C*), 204.21 (m, Ru=C=*C*), 163.44 (C_{ipso}, ArO), 160.85 (Ru=C=C=*C*), 144.70 (C_{ipso}, Ph, PhC(Ar)=C=C=Ru), 140.26 (C_{para}, ArO), 138.88 (C_{ipso}, CCH_2O), 134.86 (Ar), 134.29 (Ar), 133.85 (Ar), 133.61 (Ar), 133.16 (Ar), 133.01 (Ar), 132.86 (Ar), 132.73 (Ar), 132.10 (Ar), 131.96 (Ar), 131.63 (Ar), 131.45 (Ar), 130.81 (Ar), 129.40 (Ar), 129.29 (Ar), 128.96 (Ar), 128.70 (Ar), 128.60 (Ar), 128.45 (Ar), 127.45 (Ar) 115.4 59 (C_{para}, ArO), 66.14 (CH_2O), 28.0, 16.3. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 38.64 (s). Anal. Calcd for $C_{213}H_{186}B_3Cl_3F_{12}O_3P_{12}Ru_3$: C, 66.70; H, 4.89. Found: C, 65.68; H, 5.19.

Synthesis of C_6Me_3-1,3,5-{CH_2O(*p*-C_6H_4)PhC=C=C=Ru(PCy_3)(*p*-cymene)Cl]OTf}$_3$ (9). Triyne **5**·1.5THF (100 mg, 0.107 mmol) and 3 equiv of [(*p*-cymene)RuCl(PCy_3)]OTf (224 mg, 0.320 mmol) were dissolved in 20 mL of CH_2Cl_2 and stirred at room temperature for 55 min. An immediate color change from red to deep violet was observed. After about 95% conversion was confirmed by ^{31}P NMR spectroscopy the solvent was removed under vacuum. At longer reaction times a degradation of the product **9**, which seems to possess a limited stability in solution, was observed accompanied by a color change to deep red. Even in the solid state and at low temperatures around 0 °C slow but continuous decomposition of compound **9** could be observed. Yield: 298 mg (97%) of about 95% purity. IR (KBr): ν 2930 (m), 2853 (w-m), 1962 (vs, ν(C=C=C), Ru=C=C=CR$_2$), 1586 (m-s), 1506 (w), 1448 (w), 1258 (s, b, ν(C−O), CH$_2$−O−Ar), 1172 (m), 1030 (m), 849 (w), 729 (w), 699 (w), 637 (m), 516 (w) cm^{-1}. ^{1}H NMR (δ, CDCl$_3$): 8.07 (d, 6H, J = 8.3 Hz, CH, Ar), 7.86 (d, 6H, J = 8.4 Hz, CH, Ar), 7.71 (t, 3H, J = 6.8 Hz, CH_{para}, Ph), 7.50 (t, 6H, J = 7.6 Hz, CH$_{meta}$, Ph), 7.22 (d, 6H, J = 8.9 Hz, CH, Ar), 6.58 (d, 3H, J = 6.0 Hz, CH, Ar, *p*-cymene), 6.49 (d, 3H, J = 6.6 Hz, CH, Ar, *p*-cymene), 6.12 (d, 3H, J = 6.6 Hz, CH, Ar, *p*-cymene), 6.00 (d, 3H, J = 5.8 Hz, CH, Ar, *p*-cymene), 5.32 (s, 6H, CH_2O), 2.75 (m, 3H, CH, *i*-Pr of *p*-cymene), 2.53−1.03 (broad superpositions, 135H, PCy$_3$, CH_3 of Mes and *p*-cymene). The characterization by ^{13}C NMR spectroscopy was not possible because of the low long-term stability of **9** in solution. ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 56.36 (s).

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