Butenynyl and Vinylidene Complexes of Ruthenium

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Reaction of ruthenium bis-acetylide complexes with 2,6-lutidinium tetrafluoroborate gave butenynyl complexes *cis*-[Ru(η^3-RC≡CC═C(H)R)(PMe$_3$)$_4$]BF$_4$ in moderate to good yields. The structure of *cis*-[Ru(η^3-*t*BuC≡CC═C(H)*t*Bu)(PMe$_3$)$_4$]BF$_4$ was determined crystallographically. Attempts to prepare *cis*-[Ru(η^3-MeC≡CC═C(H)Me)(PMe$_3$)$_4$]BF$_4$ resulted in the formation of two isomers, which differ in the stereochemistry about the double bond. The reaction of two bis-acetylide complexes with methyl triflate afforded butenynyl-type complexes *cis*-[Ru(η^3-RC≡CC═C(Me)R)(PMe$_3$)$_4$]$^+$ (R = Me, Ph). The mixed acetylide−vinylidene complex *trans*-[Ru(C≡CSiMe$_3$)(C═CH$_2$)(PMe$_3$)$_4$]PF$_6$ was prepared by the reaction of *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ with ammonium hexafluorophosphate. In addition, the crystal structure of *trans*-[Ru(C≡CH)(C═CH$_2$)(PMe$_3$)$_4$]BF$_4$ is reported.

Introduction

Transition-metal butenynyl complexes have been identified as key intermediates in the metal-catalyzed head-to-head couplings of alkynes leading to *E*/*Z*-1,4-disubstituted-1-buten-3-ynes[1−3] and *E*/*Z*-1,4-disubstituted butatrienes.[4] This dimerization reaction is an attractive, atom-efficient route for the formation of the enyne substructure that plays an important role in a number of medicinal compounds and natural products.[5] We, and others, have been studying the formation of transition-metal butenynyl complexes with a view to better understand the structure and chemistry of these species.[1,6−10]

Butenynyl complexes have been prepared by reaction of transition-metal complexes with terminal alkynes,[9−14] coupling of acetylide units in preformed metal acetylide complexes,[15,16] insertion of 1,4-disubstituted buta-1,3-diynes into a transition-metal hydride bond,[17,18] and protonation of low-valent complexes bearing η^2-coordinated butadiynyl ligands.[7,18] The butenynyl ligand may exhibit either η^1-coordination[4,12,19] or η^3-coordination,[9,13,15,18,20] depending on the requirements of the metal center, and it has been suggested that a change in coordination mode from η^3 to η^1 may be involved in the catalytic formation of C4 units from terminal acetylenes.[21]

Our previous studies on iron butenynes have focused on metal complexes with bidentate[6] or tetradentate phosphine ligands.[14] We report here the synthesis of a range of bis-acetylido and butenynyl complexes of ruthenium(II) bearing the simpler monodentate trimethylphosphine as the ancillary ligand.

Results and Discussion

Formation of Ruthenium Butenynes. Ruthenium bis-acetylides Ru(C≡CR)$_2$(PMe$_3$)$_4$ were prepared by reaction of terminal acetylenes RC≡CH with *cis*-RuMe$_2$(PMe$_3$)$_4$ (Scheme 1), as has been reported previously.[22] The bis-acetylides are obtained as a mixture of *cis*- and *trans*-stereoisomers, with the *cis*-isomer dominating for complexes **1**−**4** and complex **6**, whereas complex **5** is obtained predominately as the *trans*-isomer.

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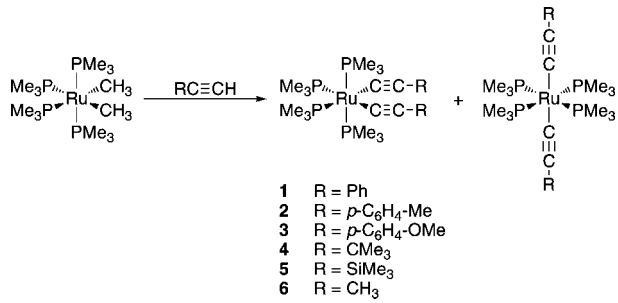
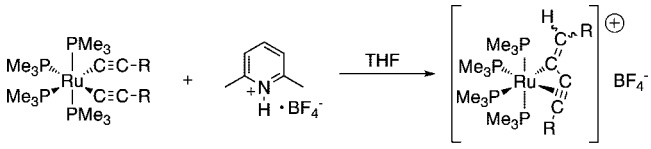
Scheme 1



Scheme 2



Attempts to prepare butenynylruthenium complexes from the metal bis-acetylides by the addition of trifluoroacetic acid, in a manner analogous to that reported for bis-acetylidoiron(II) complexes,[6] did not result in the formation of any desired product butenynyl product. The use of $HBF_4 \cdot Et_2O$ in place of TFA afforded butenynyl products in variable yields, together with other products. Performing the reaction at −78 °C did not result in any noticeable improvement in product yield or purity.

The addition of THF solutions of the bis-acetylidoruthenium complexes **1**−**5** to the mild acid 2,6-lutidinium tetrafluoroborate[23] gave the butenynylruthenium(II) complexes **7**−**11** in good yields (Scheme 2). The reaction is accompanied by a color change from colorless or pale yellow to bright yellow. In many cases, the products precipitated directly from the reaction mixture as yellow solids.

Complexes **7**−**9** all exhibit a clear AM_2X pattern in the $^{31}P\{^1H\}$ NMR spectrum, with two six-line multiplets corresponding to each of two equatorial phosphines and an apparent triplet or doublet of doublets corresponding to the two axial phosphines. An identical AM_2X splitting pattern has been reported for related ruthenium complexes.[9,24] The equatorial phosphorus *trans* to the coordinated vinyl ligand shows coupling to the vinyl proton ($^4J_{PH} \approx 4$ Hz) and, in contrast to that previously reported for butenynyl iron complexes,[6] resonates at higher field than the other phosphorus atoms in the complex. In the cases of complexes **10** and **11**, the ^{31}P chemical shifts are not well dispersed and the $^{31}P\{^1H\}$ NMR spectra are more complex.

The vinyl protons of **7**−**11** all exhibit a strong NOE with the protons of an equatorial phosphine, suggesting an *E*-stereochemistry at the double bond, in which the vinyl proton is directed toward the coordinated phosphines, while the aryl or alkyl substituent on the vinyl group is directed away from the metal−ligand coordination sphere.

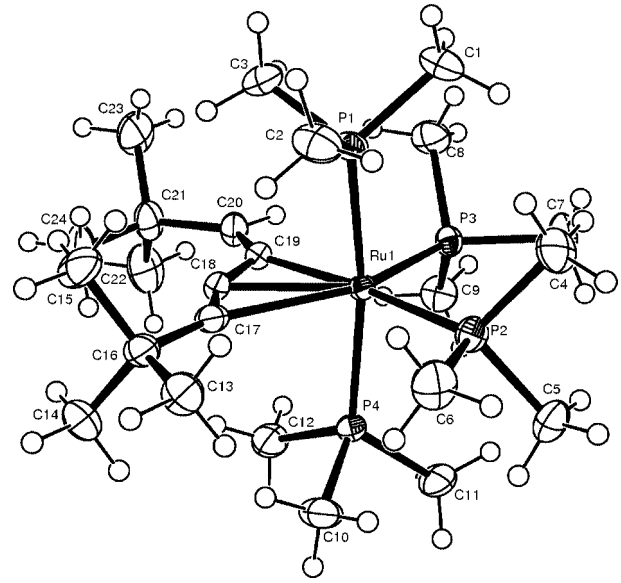


Figure 1. Molecular projection of the complex cation of *trans*-$[Ru(C(\equiv CtBu)=CHtBu)(PMe_3)_4]BF_4 \cdot$acetone (**10**). Thermal ellipsoids are shown at the 50% probability level, while hydrogen atoms have an arbitrary radius of 0.1 Å. The BF_4^- counterion and solvating acetone have been omitted for clarity.

Table 1. Selected Bond Lengths and Angles for $[Ru(C(\equiv CtBu)=CHtBu)(PMe_3)_4]BF_4$ (7)

bond	length (Å)	bond	angle (deg)
C(17)−C(18)	1.249(2)	C(17)−C(18)−C(19)	155.3(2)
C(18)−C(19)	1.389(2)	C(18)−C(19)−C(20)	135.0(1)
C(19)−C(20)	1.332(2)	C(17)−Ru−C(19)	66.30(5)
Ru−C(17)	2.535(2)	P(1)−Ru−P(4)	170.22(1)
Ru−C(18)	2.249(1)	P(2)−Ru−P(3)	99.14(2)
Ru−C(19)	2.139(2)		

Crystals of **10** suitable for X-ray analysis were grown from an acetone solution layered with heptane. The complex crystallizes as an acetone solvate (Figure 1, Table 1). The ruthenium center exhibits a distorted octahedral coordination mode, with the phosphorus atoms of the PMe_3 ligands occupying four sites. The remaining two sites are occupied by the butenynyl fragment, which coordinates in an η^3-fashion.

The Ru−C(17), Ru−C(18), and Ru−C(19) bond distances of 2.535(2), 2.249(1), and 2.139(2) Å, respectively, are comparable with those previously reported for the related complexes $[Ru(\eta^3\text{-}Me_3SiC{\equiv}CC{=}C(H)SiMe_3)(PP_3)]BPh_4$ [$PP_3 = P(CH_2CH_2PPh_2)_3$] (2.485(3), 2.234(3), and 2.144(3) Å),[2] $[Ru(\eta^3\text{-}PhC{\equiv}CC{=}C(H)Ph)(PPhMe_2)_4]PF_6$ (2.510(4), 2.226(4), and 2.119(4) Å),[9] and $[Ru(\eta^3\text{-}\{p\text{-tolyl}\}C{\equiv}CC{=}C(H)\{p\text{-tolyl}\})(PPh\{OEt\}_2)_4]BPh_4$ (2.43(1), 2.24(1), and 2.15(1) Å).[24] The metal−butenyne bond lengths in these tetraphosphine complexes are considerably longer than in butenynyl complexes bearing less sterically demanding ancillary ligands, e.g., $[Ru(\eta^3\text{-}PhC{\equiv}CC{=}C(H)Ph)(CO)_2(PPh_3)_2]PF_6$ (2.32(1), 2.23(1), and 2.170(9) Å)[18] and *anti,mer*-[Ru(C≡CPh)(η^3-PhC≡CC=C(H)-Ph)(PNP)] (PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$) (2.39(1), 2.19(1), and 2.06(1) Å).[25]

The C−C bond lengths (1.249(2), 1.389(2), and 1.332(2) Å) and angles (155.3(2)° and 135.0(1)°) within the butenynyl ligand are virtually indistinguishable from those reported for $[Ru(\eta^3\text{-}\{p\text{-tolyl}\}C{\equiv}CC{=}C(H)\{p\text{-tolyl}\})(PPh\{OEt\}_2)_4]BPh_4$ (1.23(1), 1.39(2), and 1.33(2) Å; 150.9(13)° and 136.0(13)°).[24]

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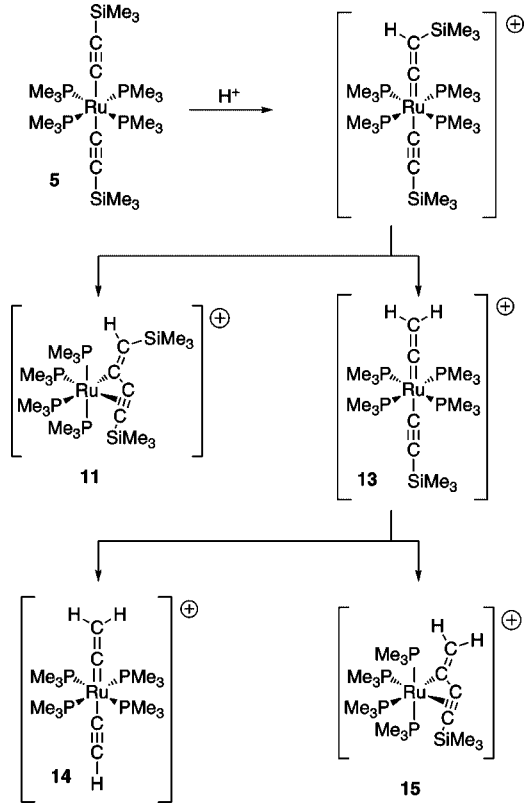
Scheme 3



Comparison of the bond angles P(1)−Ru(1)−P(4) and P(2)−Ru(1)−P(3) (170.22(1)° and 99.14(2)°, respectively) with those of the related bis-acetylide complex *cis*-Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (**6**) (162.71(2)° and 97.77(2)°)[22] suggests that coupling of the acetylide units to form the C4 moiety allows the phosphine ligands to move further apart, relieving some steric strain within the molecule.

Protonation of *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ (5). The initial reaction of the ruthenium bis-acetylides with acid is generally accepted to be protonation at one of the β-carbon atoms to give a cationic vinylidene species, which rapidly rearranges with carbon−carbon bond formation to the observed butenyne products.[13,20,24−26] In the case of bisacetylides **1**−**4**, only the butenyne products are obtained. However, a number of different products were obtained from the reaction of *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ (**5**) with 2,6-lutidinium tetrafluoroborate and other weak acids (Scheme 3) depending on the reaction conditions. The products observed included the expected butenyne (**11**) as well as desilylated products *trans*-[Ru(C≡CSiMe$_3$)(C═CH$_2$)(PMe$_3$)$_4$]BF$_4$ (**13**), *trans*-[Ru(C≡CH)(C═CH$_2$)(PMe$_3$)$_4$]BF$_4$ (**14**), and [Ru(η^3-Me$_3$SiC≡CC═CH$_2$)(PMe$_3$)$_4$]-BF$_4$ (**15**).

The formation of these products can be rationalized by the competition between desilylation and carbon−carbon coupling under the reaction conditions. In the initial part of the reaction, a species with a broad singlet resonance in the ^{31}P{^{1}H} NMR spectrum (at δ −9.52 ppm) and three distinct signals in the ^{1}H NMR spectrum (a two-proton phosphorus-coupled multiplet at δ 3.85 ppm, a broad 36-proton resonance at δ 1.74, and a nine-proton singlet δ 0.08 ppm) is ascribed to complex **13**.

X-ray quality crystals of **14** were grown by diffusion of hexane into an acetone solution of a crude mixture of reaction products containing **11** and **13** (Figure 2, Table 2). The C−Si bond is known to be remarkably inert to cleavage in many organometallic complexes,[22] and the formation of *trans*-[Ru(C≡CH)(C═CH$_2$)(PMe$_3$)$_4$]BF$_4$ (**14**) is somewhat surprising, although HBF$_4$ has been previously shown to cleave trimethylsilyl groups when used as the protonating acid in vinylidene synthesis.[27]

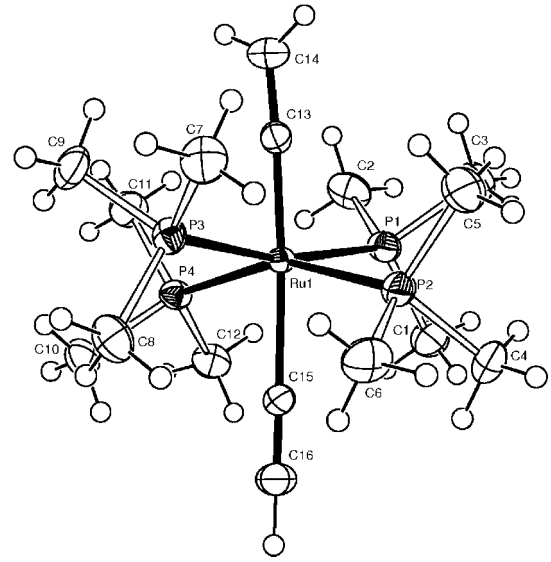


Figure 2. Molecular projection of the complex cation of *trans*-[Ru(C═CH$_2$)(C≡CH)(PMe$_3$)$_4$]BF$_4$ (**14**). Thermal ellipsoids are shown at the 50% probability level, while hydrogen atoms have an arbitrary radius of 0.1 Å. The BF$_4^-$ counterion has been omitted for clarity.

Table 2. Selected Bond Lengths and Angles for *trans*-[Ru(C═CH$_2$)(C≡CH)(PMe$_3$)$_4$]BF$_4$ (14)

bond	length (Å)	bond	angle (deg)
Ru(1)−C(13)	1.871(2)	C(13)−Ru(1)−C(15)	176.63(9)
Ru(1)−C(15)	2.114(2)	P(2)−Ru(1)−P(4)	156.49(2)
Ru(1)−P(1)	2.3733(6)	P(1)−Ru(1)−P(3)	166.394(19)
Ru(1)−P(2)	2.3933(6)	C(14)−C(13)−Ru(1)	177.2(2)
Ru(1)−P(3)	2.3637(5)	C(16)−C(15)−Ru(1)	177.2(2)
Ru(1)−P(4)	2.3672(6)	C(13)−Ru(1)−P(1)	83.55(6)
C(13)−C(14)	1.298(3)	C(15)−Ru(1)−P(1)	98.26(6)
C(15)−C(16)	1.194(3)	C(13)−Ru(1)−P(2)	104.72(7)

While several mixed acetylide−vinylidene complexes have been reported in the past, e.g., *trans*-[Rh(C≡CH)(C═CH$_2$)(P*i*Pr$_3$)$_2$],[28] complex **14** represents the first structurally authenticated complex bearing both the parent unsubstituted acetylide and vinylidene groups.

The ruthenium atom displays a distorted octahedral geometry, with the acetylide and vinylidene ligands occupying mutually *trans* positions. These ligands coordinate in an essentially linear fashion, with the largest deviation from linearity in the C(14)−C(13)−Ru(1)−C(15)−C(16) chain being observed at the ruthenium atom, where a bond angle of 176.63(9)° is observed.

The coordination plane formed by the four phosphorus atoms shows a considerable tetrahedral deformation (e.g., P(2)−Ru−P(4) 156.49(2)°), which is a result of the steric requirements of trimethylphosphine. This out-of-plane staggering of tertiary phosphine ligands has been observed in other *trans*-substituted

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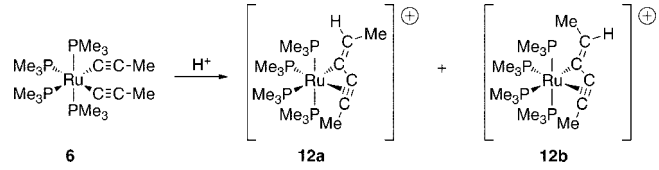
trimethylphosphine complexes, e.g., *trans*-Ru(C≡CPh)$_2$(PMe$_3$)$_4$ (161.12(3)°)[22] and *trans*-Ru(N$_3$)$_2$(PMe$_3$)$_4$ (163.10(2)°).[29]

The ruthenium−vinylidene bond length of 1.871(2) Å is consistent with that observed in related complexes and is indicative of a significant degree of multiple-bond character for the Ru−C bond.[30] The C═C bond length (1.298(3) Å) is unremarkable. The ruthenium−acetylide bond distance (2.114(2) Å) is longer than that observed in other mononuclear ruthenium(II) complexes bearing the parent acetylide ligand.[31] This lengthening may result from a strong *trans* influence exerted by the vinylidene ligand. By contrast, the C≡C bond length (1.194(3) Å) is typical of the bond lengths found in related metal acetylide complexes.

Ammonium hexafluorophosphate has been reported as a reagent that will cleave silyl groups when used for vinylidene synthesis.[32] A sample of the partially desilylated complex **13** was made independently by treatment of *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ (**5**) with NH$_4$PF$_6$ in diethyl ether. The reaction afforded an off-white precipitate that exhibited the same ^{31}P{^{1}H} and ^{1}H NMR spectra as complex *trans*-[Ru(C═CH$_2$)(C≡CSiMe$_3$)(PMe$_3$)$_4$]BF$_4$ (**13**·BF$_4$) and exhibited a resonance consistent with a vinylidene α-carbon at 351.4 ppm in the ^{13}C{^{1}H} NMR spectrum. The product obtained in this fashion was always contaminated with the butenyne **11** (up to about 10%). Complex **15**, which has been observed only during the preparation of **13**, exhibits the expected AM$_2$X pattern in the ^{31}P{^{1}H} NMR spectrum. In the ^{1}H NMR spectrum, the geminal vinyl protons appear as two phosphorus-coupled multiplets at δ 6.51 and 5.81 ppm ($^4J_{PH}$ = 9.9 and 5.7 Hz, respectively). While Scheme 3 rationalizes the products observed in the reaction of **5** with acid, the possibility that [Ru(η^3-Me$_3$SiC≡CC═CH$_2$)(PMe$_3$)$_4$]BF$_4$ (**15**) could also be formed directly by desilylation of **11** cannot be ruled out.

Acetylide−vinylidene complexes are well established in the literature for iron(II)[10,33] and ruthenium(II),[34] while osmium(II) and rhodium(I) examples have also been reported.[35] The factors influencing the stability of acetylide−vinylidene complexes are subtle, with the complex *trans*-[Fe(C≡CMe)(C═C(H)Me)(dmpe)$_2$]BPh$_4$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) being readily isolated from the reaction of *cis*-[Fe(H$_2$)H(dmpe)$_2$]BPh$_4$ with propyne, while *cis*-[Fe(η^3-MeC≡CC═C(H)Me)(depe)$_2$]BPh$_4$ (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$) is the only product from the analogous reaction employing *cis*-[Fe(H$_2$)H(depe)$_2$]BPh$_4$ as starting material.[10] Similarly, protonation of *trans*-[Ru(C≡CPh)$_2$(P{OEt}$_3$)$_4$] at room temperature yields an isolable, albeit unstable, acetylide−vinylidene species, while the related complex with PPh(OEt)$_2$ as the coordinating phosphines gives only the butenynyl complex.[33,34]

Scheme 4



Clearly, in the reaction of of *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ (**5**) with a weak acid, if the compound desilylates before carbon−carbon coupling occurs, the acetylide−vinylidene species *trans*-[Ru(C═CH$_2$)(C≡CSiMe$_3$)(PMe$_3$)$_4$]$^+$ (**13**) is sufficiently stable to permit its isolation and characterization.

Protonation of *cis*-Ru(C≡CCH$_3$)$_2$(PMe$_3$)$_4$ (6). The protonation of *cis*-Ru(CCMe)$_2$(PMe$_3$)$_4$ (**6**) with lutidinium tetrafluoroborate resulted in the formation of two isomeric products, **12a** and **12b**, approximately in the ratio of 2:1, respectively (Scheme 4). The complexes correspond to the isomers with the coordinated butenyne adopting the *E*-stereochemistry (**12a**) or the *Z*-stereochemistry (**12b**). The ^{31}P{^{1}H} and ^{1}H NMR spectra for these two products are remarkably similar, with the only significant difference being in the shift of the vinylic protons in the ^{1}H NMR spectrum: the vinylic protons appear at phosphorus-coupled multiplets at δ 5.63 ppm (**12a**) and 6.80 ppm (**12b**). The stereochemistry of **12a** and **12b** was established by ^{1}H NOESY: in **12a**, the vinylic proton shows a strong correlation to one of the equatorial PMe$_3$ ligands, and in **12b** there is a strong correlation between the vinylic methyl group and one of the equatorial PMe$_3$ groups.

Compared to the other ruthenium acetylides studied in this work, only **6** appears to have a substituent that is sufficiently small to orient either toward the metal or away from it. In all of the other acetylides studied, the butenyne adopts the *E*-stereochemistry where the vinylic proton is oriented toward the metal and the larger substituent away from the metal.

The butenyne unit of the related complex [Fe(η^3-MeC≡CC═C(H)Me)(dmpe)$_2$]BPh$_4$ adopts exclusively the *E*-stereochemistry at the double bond,[10] and the methyl group of the substituted butenyne fragment in [Os(η^3-PhC≡CC═C(Me)Ph)(PP$_3$)]BPh$_4$ (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$) is directed toward the metal with the larger phenyl substituent directed away from the metal.[20]

While both **12a** and **12b** are very stable at low temperature, at temperatures above 30 °C, **12b** gradually rearranges to give **12a**. Kinetic analysis of the thermal *Z* to *E* isomerization gives a $\Delta G^{\ddagger}$ of approximately 98.0 kJ mol^{-1} at 30 °C. There are few examples in the literature of the *Z* → *E* geometric rearrangement of butenynyl complexes; however the photochemical and thermal rearrangement of *trans*-[Rh(η^1-(*Z*)-C(═C(H)^{t}Bu)C≡C^{t}Bu)(CO)(P^{i}Pr$_3$)$_2$] to give the corresponding *E* isomer has been reported.[35b]

While we have no evidence to confirm a mechanism for the isomerization **12b** → **12a**, the isomerization could occur by reversion to the vinylidene acetylide or alternatively by reversible hydride elimination to form an intermediate containing a coordinated butadiyne (Scheme 5). The reaction of butadiynes with metal hydride complexes has been shown to yield butenynyl complexes.[4,6,12,17,21]

Reaction of Ruthenium Bisacetylides with Other Electrophiles. Transition-metal acetylide complexes are known to react with electrophiles other than H$^+$ to generate vinylidene complexes. For example, the reaction of trimethyloxonium salts with RuCp(C≡CPh)(PPh$_3$)$_2$ yields [RuCp(C═CMePh)(PPh$_3$)$_2$]$^+$,[36] where the methylating reagent attacks at the β-carbon.

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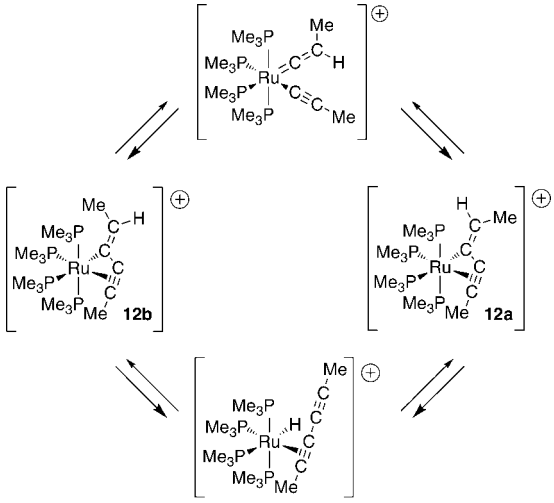
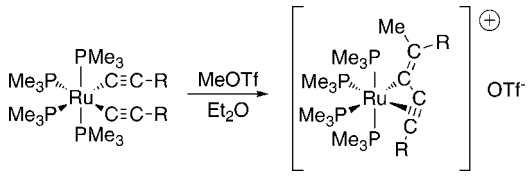
Scheme 5



Scheme 6



16 R = Me
17 R = Ph

Having established above that the presence of a methyl substituent can be accommodated close to the metal center in the product ruthenium butenyne complexes, we examined the possibility that the formation of a butenyne complex could be induced by methylation of a ruthenium bis-acetylide in an analogous fashion to the reaction induced by protonation.

The addition of methyl triflate to *cis*-Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (**6**) in diethyl ether resulted in the rapid precipitation of a white solid from solution in moderate yield (Scheme 6). This complex was identified as *cis*-[Ru(η^3-MeC≡CC═CMe$_2$)(PMe$_3$)$_4$]OTf (**16**) and exhibits the characteristic AM$_2$X pattern in the ^{31}P{^{1}H} NMR spectrum, indicative of the butenynes synthesized in this work. The ^{1}H NMR spectrum shows three distinct resonances corresponding to methyl groups (at 2.52, 2.26, and 2.08 ppm), while the ^{13}C{^{1}H} NMR spectrum displays resonances at 142.9, 133.7, 97.7, and 47.9 ppm, which can be assigned to the carbon backbone of a coordinated butenyne, in addition to signals attributable to the methyl substituents and phosphine ligands.

A similar reaction was undertaken starting with *cis*-Ru(C≡CPh)$_2$(PMe$_3$)$_4$ (**1**) to yield *cis*-[Ru(η^3-PhC≡CC═C(Me)Ph)(PMe$_3$)$_4$]OTf (**17**). The methyl substituent at the double bond exhibits a strong NOE with the protons of an equatorial phosphine ligand, confirming the *E*-stereochemistry at the double bond.

From these experiments it is clear that there is sufficient space around the ruthenium metal center to permit the formation of a butenyne complex with a methyl substituent directed into the pocket close to the metal, and this provides a viable route to methyl-substituted butenynes.

Conclusions

A series of ruthenium complexes bearing substituted, η^3-bound butenynyl ligands were prepared by protonation and rearrangement of ruthenium bis-acetylides with a weak acid (2,6-lutidinium tetrafluoroborate). Under these reaction conditions, the reaction proceeds in good yield and presumably results from initial protonation of the ruthenium bis-acetylide at the nucleophilic β-carbon to give a mixed acetylide vinylidene complex, which then rearranges with carbon−carbon bond formation to give the butenynyl products.

When *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ was the starting material, there was competition between desilylation and ligand coupling under the reaction conditions, and metal complexes containing desilylated and partially desilylated ligands were isolated and characterized from this reaction. The mixed acetylide vinylidene complex *trans*-[Ru(C≡CH)(C═CH$_2$)(PMe$_3$)$_4$]BF$_4$ (**14**) was isolated and characterized crystallographically. This is the first mixed acetylide vinylidene complex to be structurally characterized where the acetylide and vinylidene units are unsubstituted.

In almost all of the coupling reactions, the butenyne product had the *E*-stereochemistry, i.e., with the bulkier substituent on the vinyl group *trans* to the metal center. Only in the case where the substituent was a methyl group was a mixture of *E*- and *Z*-isomers obtained, and this indicates that the vinyl group of the substituted butenynyl ligand can accommodate substituents as large as a methyl group *cis* to the ruthenium center.

The acetylide coupling to form coordinated butenynes was also induced using methyl triflate as the initiating electrophile to form methyl-substituted butenyne complexes.

Experimental Section

All syntheses and manipulations involving air-sensitive compounds were carried out using standard vacuum line and Schlenk techniques under an atmosphere of dry nitrogen or argon. Diethyl ether, tetrahydrofuran, petroleum ether, toluene, and benzene were dried and degassed by refluxing over standard drying agents[37] under an atmosphere of dry nitrogen and were freshly distilled prior to use. All other solvents were dried according to standard methods. THF-d_8 and benzene-d_6 were dried over sodium benzophenone ketyl and vacuum transferred into ampules prior to use. All other NMR solvents were stored over 4 Å molecular sieves.

Nuclear magnetic resonance spectra were recorded on a Bruker DMX600 (operating at 600.13, 150.92, and 242.95 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), Bruker AVANCE DRX400 (operating at 400.13, 100.62, and 161.98 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively), Bruker DPX300 (operating at 300.13 and 121.49 MHz for ^{1}H and ^{31}P, respectively), or a Bruker DPX200 (operating at 200.13 MHz for ^{1}H) at 300 K unless otherwise stated. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances, while ^{31}P NMR spectra were referenced to external H_3PO_4. Infrared spectra were recorded on a Shimadzu 8400 series FTIR. UV irradiation of metal complexes was performed using an Oriel 300-W high-pressure mercury vapor lamp with the incident beam directed through a water-filled jacket to filter infrared radiation.

Terminal acetylenes were purchased from Aldrich and used as received. 2,6-Lutidinium tetrafluoroborate[38] and *cis*-RuMe$_2$(dmpe)$_2$[39] were prepared according to the literature procedures. The complexes Ru(C≡CR)$_2$(PMe$_3$)$_4$ were prepared as previously reported.[22]

cis-[Ru(η^3-PhC≡CC═C(H)Ph)(PMe$_3$)$_4$]BF$_4$ (7). A solution of Ru(C≡CPh)$_2$(PMe$_3$)$_4$ (**1**) (0.136 g, 0.223 mmol) in THF (7 mL) was added to a suspension of 2,6-lutidinium tetrafluoroborate (0.0444 g, 0.228 mmol) in THF (13 mL). A yellow suspension formed quickly, and the mixture was stirred overnight at room temperature. The mixture was concentrated under reduced pressure to 3 mL, the mother liquor was decanted, and the bright yellow

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solid was dried *in vacuo*. The product was recrystallized from acetone/pentane to give *cis*-[Ru(η^3-PhC≡CC═C(H)Ph)(PMe_3)$_4$]BF_4 (**6**) as a yellow solid. Yield: 0.094 g (0.134 mmol, 60%). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.77 (m, 4H, Ar*H*), 7.58−7.37 (m, 5H, Ar*H*), 7.27 (m, 1H, Ar*H*), 7.17 (d, $^4J_{PH}$ = 4.6 Hz, 1H, C═C(Ph)*H*), 1.86 (d, $^2J_{PH}$ = 8.6 Hz, 9H, $P_{eq}(CH_3)_3$), 1.81 (d, $^2J_{PH}$ = 7.9 Hz, 9H, $P_{eq}(CH_3)_3$), 1.20 (apparent t, splitting = 3.5 Hz, 18H, $P_{ax}(CH_3)_3$) ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6): δ −2.72 (dt, $^2J_{PP}$ = 20.7 Hz, $^2J_{PP}$ = 34.6 Hz, 1P, P_{eq}), −12.43 (dd, $^2J_{PP}$ = 30.6 Hz, $^2J_{PP}$ = 34.6 Hz, 2P, 2 × P_{ax}), −19.87 (dt, $^2J_{PP}$ = 20.7 Hz, $^2J_{PP}$ = 30.6 Hz, 1P, P_{eq}) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 148.4 (d, $^2J_{PC}$ = 42.9 Hz, Ru-*C*═C), 138.9 (ArC_{ipso}), 132.6 (ArC_{para}), 130.7 (C═*C*(H)Ph), 130.1, 129.8, 129.43, 129.39 (ArC_{ipso}), 127.7, 126.9 (ArC_{para}), 115.4 (d, $^2J_{PC}$ = 28.3 Hz, PhC≡*C*), 59.7 (Ph*C*≡C), 24.9 (d, $^1J_{PC}$ = 26.5 Hz, $P_{eq}(CH_3)_3$), 23.8 (d, $^1J_{CP}$ = 30.3 Hz, $P_{eq}(CH_3)_3$), 18.3 (apparent t, splitting = 13.3 Hz, $P_{ax}(CH_3)_3$) ppm. MS(ESI) *m*/*z*: 533 (25%) [M − $P(CH_3)_3$]$^+$, 457 (100) [M − $2P(CH_3)_3$]$^+$, 381 (27) [M − $3P(CH_3)_3$]$^+$. ν_{max} (KBr disk): 2975, 2912, 2051, 1591, 1482, 1423, 1307, 1285, 1084, 1055, 1037, 945, 860, 763, 720, 697, 669 cm^{-1}. Anal. Calcd for $C_{28}H_{47}BF_4P_4Ru$: C, 48.36; H, 6.81. Found: C, 48.62; H, 6.93.

***cis*-[Ru(η^3-(*p*-C_6H_4-Me)C≡CC═C(H)(*p*-C_6H_4-Me))(PMe_3)$_4$]BF_4 (8).** Prepared as described for **7** from Ru(C≡C(*p*-C_6H_4-Me))$_2$(PMe_3)$_4$ (**2**) (0.171 g, 0.393 mmol). Yield: 0.134 g (0.188 mmol, 48%). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.70 (m, 4H, Ar*H*), 7.35 (m, AA′ of AA′XX′, 2H, Ar*H*), 7.25 (m, XX′ of AA′XX′, 2H, Ar*H*), 7.09 (d, $^4J_{PH}$ = 4.3 Hz, 1H, C═C(*H*)Ar), 2.40 (s, 3H, Ar-CH_3), 2.33 (s, 3H, Ar-CH_3), 1.84 (m, 18H, $P_{eq}(CH_3)_3$), 1.21 (m, 18H, $P_{ax}(CH_3)_3$) ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6): δ 1.25 (dt, $^2J_{PP}$ = 20 Hz, $^2J_{PP}$ = 34 Hz, 1P, P_{eq}), −8.40 (dd, $^2J_{PP}$ = 29 Hz, $^2J_{PP}$ = 34 Hz, 2P, 2 × P_{ax}), −15.9 (dt, $^2J_{PP}$ = 20 Hz, $^2J_{PP}$ = 29 Hz, 1P, P_{eq}) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 147.0 (Ru-*C*), 139.6 (Ar*C*-CH_3), 137.5 (Ar*C*-CH_3), 136.6 (Ar-C_{ipso}), 132.7 (ArC_{ortho}), 130.9 (ArC_{meta}), 130.5 (ArC_{meta}), 130.4 (C═*C*(H)Ar), 126.9 (ArC_{ortho}), 126.3 (ArC_{ipso}), 114.6 (*C*≡CAr), 58.9 (C≡*C*Ar), 25.1 (d, $^1J_{PC}$ = 25.7 Hz, $P_{eq}(CH_3)_3$), 24.0 (d, $^1J_{PC}$ = 30.0 Hz, $P_{eq}(CH_3)_3$), 21.4 (C-*C*H_3), 21.2 (C-*C*H_3), 18.4 (apparent t, splitting = 13.8 Hz, $P_{ax}(CH_3)_3$) ppm. MS(ESI) *m*/*z* (abundance): 561 (100) [M − PMe_3]$^+$. ν_{max} (KBr disk): 2976, 2913, 1506, 1423, 1308, 1287, 1083, 1051, 1037, 944, 860, 815, 718, 669, 522 cm^{-1}. Anal. Calc for $C_{30}H_{51}BF_4P_4Ru$: C, 49.80; H, 7.11. Found: C, 49.98; H, 7.03.

***cis*-[Ru(η^3-(*p*-C_6H_4-OMe)C≡CC═C(H)(*p*-C_6H_4OMe)(PMe_3)$_4$]BF_4 (9).** Prepared as described for **7**, from Ru(C≡C(*p*-C_6H_4-OMe))$_2$(PMe_3)$_4$ (**3**) (0.226 g, 0.338 mmol) and 2,6-lutidinium tetrafluoroborate (0.066 g, 0.336 mmol). Concentration of the THF solution under reduced pressure and cooling to −20 °C gave a bright yellow microcrystalline solid. Yield: 0.189 g (0.251 mmol, 74%). ^{1}H NMR (600 MHz, acetone-d_6): δ 7.77 (m, AA′ of AA′XX′, 2H, ArH_{ortho}), 7.72 (m, AA′ of AA′XX′, 2H, ArH_{ortho}), 7.10 (m, XX′ of AA′XX′, 2H, ArH_{meta}), 7.03 (d, $^4J_{PH}$ = 4.6 Hz, 1H, C═C(*H*)Ar), 7.01 (m, XX′ of AA′XX′, 2H, ArH_{meta}), 3.88 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 1.85 (d, $^2J_{PH}$ = 8.5 Hz, 9H, $P_{eq}(CH_3)_3$), 1.81 (d, $^2J_{PH}$ = 7.2 Hz, 9H, $P_{eq}(CH_3)_3$), 1.19 (apparent t, splitting = 3.0 Hz, 18H, $P_{eq}(CH_3)_3$) ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6): δ 1.75 (dt, $^2J_{PP}$ = 19.3 Hz, $^2J_{PP}$ = 33.7 Hz, 1P, P_{eq}), −7.79 (dd, $^2J_{PP}$ = 30.2 Hz, $^2J_{PP}$ = 33.7 Hz, 2P, 2 × P_{ax}), −15.1 (dt, $^2J_{PP}$ = 19.3 Hz, $^2J_{PP}$ = 30.2 Hz, 1P, P_{eq}) ppm. ^{13}C{^{1}H} NMR (151 MHz, acetone-d_6): δ 160.9 (*C*-OCH_3), 159.9 (*C*-OCH_3), 144.9 (dq, $^2J_{PC}$ = 42.6, $^2J_{PC}$ = 7.8 Hz, Ru-*C* = C), 134.3 (ArC_{ortho}), 132.4 (d, $^3J_{PC}$ = 4.8 Hz, C═*C*(H)Ar, 129.5 (ArC_{ipso}), 128.1 (ArC_{ortho}), 121.0 (ArC_{ipso}), 115.7 (ArC_{meta}), 115.3 (ArC_{meta}), 113.8 (d, $^2J_{PC}$ = 24.8 Hz, *C*≡CAr), 57.5 (C≡*C*Ar), 55.9 (O-*C*H_3), 55.7 (O-*C*H_3), 25.1 (d, $^1J_{PC}$ = 25.1 Hz, $P_{eq}(CH_3)_3$), 24.0 (dd, $^1J_{PC}$ = 29.5 Hz, $^3J_{PC}$ = 1.7 Hz, $P_{eq}(CH_3)_3$), 18.4 (apparent t, splitting = 14.0 Hz, $P_{ax}(CH_3)_3$) ppm. MS(ESI) *m*/*z* (abundance): 593.15 (100) [M −$P(CH_3)_3$]$^+$. ν_{max} (KBr disk): 2974, 2912, 2837, 1598, 1506, 1438, 1306, 1284, 1248, 1171, 1055, 1033, 971, 944, 860 cm^{-1}. The product was recrystallized from acetone/pentane to yield crystals suitable for microanalysis. Anal. Calcd for $C_{30}H_{51}BF_4O_2P_4Ru \cdot (CH_3)_2CO$: C, 48.72; H, 7.06. Found: C, 48.85; H, 7.02.

***cis*-[Ru(η^3-^{t}BuC≡CC═C(H)^{t}Bu)(PMe_3)$_4$]BF_4 (10).** Prepared as described for **7**, from Ru(C≡C^{t}Bu)$_2$(PMe_3)$_4$ (**4**) (0.239 g, 0.549 mmol) and 2,6-lutidinium tetrafluoroborate (0.1058 g, 0.543 mmol). Yield: 0.286 g (0.430 mmol, 79%). ^{1}H NMR (300 MHz, acetone-d_6): δ 5.87 (m, 1H, ═C(*H*)^{t}Bu), 1.82 (d, $^2J_{PH}$ = 8.7 Hz, 9H, $P(CH_3)_3$), 1.72 (d, $^2J_{PH}$ = 8.7 Hz, 9H, $P(CH_3)_3$), 1.50 (s, 9H, $C(CH_3)_3$), 1.26 (m, 27H, $P(CH_3)_3$ and $C(CH_3)_3$) ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6): δ 5.52 (dt, $^2J_{PP}$ = 15.7 Hz, $^2J_{PP}$ = 36.8 Hz, 1P, P_{eq}), −14.26 (dd, $^2J_{PP}$ = 30.3 Hz, $^2J_{PP}$ = 36.8 Hz, 2P, 2 × P_{ax}), −18.01 (dt, $^2J_{PP}$ = 15.7 Hz, $^2J_{PP}$ = 30.3 Hz, 1P, P_{eq}) ppm. ^{13}C{^{1}H} NMR (151 MHz, acetone-d_6): δ 141.5 (C═*C*(H)^{t}Bu), 139.5 (d, $^2J_{PC}$ = 51.4 Hz, Ru-*C*═C), 118.7 (d, $^2J_{PC}$ = 23.7 Hz, (*C*≡C^{t}Bu), 55.3 (C≡*C*^{t}Bu), 33.6 ($C(CH_3)_3$), 33.3 ($C(CH_3)_3$), 30.7 ($C(CH_3)_3$), 30.4 ($C(CH_3)_3$), 26.8 (d, $^1J_{PC}$ = 24.0 Hz, $P_{eq}(CH_3)_3$), 23.7 (d, $^1J_{PC}$ = 30.7 Hz, $P_{eq}(CH_3)_3$), 18.9 (apparent t, splitting = 13.7 Hz, $P_{ax}(CH_3)_3$) ppm. MS(ESI) *m*/*z* (abundance): 493 (100) [M − PMe_3]$^+$. ν_{max} (KBr disk): 2963, 2909, 1427, 1305, 1286, 1232, 1084, 1055, 1036, 953, 864, 716, 667 cm^{-1}. Anal. Calcd for $C_{24}H_{55}BF_4P_4Ru$: C, 43.98; H, 8.46. Found: C, 43.91; H, 8.71. Crystals suitable for X-ray diffraction were grown by layering an acetone solution of the complex with heptane.

***cis*-[Ru(η^3-Me_3SiC≡CC═C(H)$SiMe_3$)(PMe_3)$_4$]BF_4 (11).** Trimethylsilylacetylene (0.54 mL, 3.82 mmol) was added to a solution of $RuMe_2(PMe_3)_4$ (0.1645 g, 0.377 mmol) in THF (10 mL). The mixture was stirred at 50 °C for 2 h, after which time the volatiles were removed under reduced pressure. The pale brown residue was dissolved in THF (10 mL), and 2,6-lutidinium tetrafluoroborate (0.0716 g, 0.361 mmol) was added as a single solid portion. A suspension was quickly formed. The mixture was stirred overnight at room temperature before the dark green mother liquor was decanted from the precipitate. The residue was dried *in vacuo* to yield *cis*-[Ru(η^3-Me_3SiC≡CC═C(H)$SiMe_3$)(PMe_3)$_4$]BF_4 (**11**) as a pale yellow solid. Yield: 0.165 g (0.259 mmol, 69%). ^{1}H NMR (300 MHz, acetone-d_6): δ 6.82 (m, 1H, C═C(*H*)$SiMe_3$), 1.82 (d, $^2J_{PH}$ = 6.9 Hz, 9H, $P_{eq}(CH_3)_3$), 1.74 (d, $^2J_{PH}$ = 8.7 Hz, 9H, $P_{eq}(CH_3)_3$), 1.21 (apparent t, splitting = 3.06 Hz, 18H, $P_{ax}(CH_3)_3$), 0.43 (s, 9H, $Si(CH_3)_3$), 0.23 (s, 9H, $Si(CH_3)_3$) ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6): δ 8.29 (dt, $^2J_{PP}$ = 15.6 Hz, $^2J_{PP}$ = 35.2 Hz, 1P, P_{eq}), −10.35 (m, 2P, 2 × P_{ax}), −13.26 (m, 2P, P_{eq}) ppm. ^{13}C{^{1}H,^{31}P} NMR (75 MHz, acetone-d_6): δ 170.7 (Ru-*C*═C), 137.2 (C═*C*(H)$SiMe_3$), 110.9 (*C*≡C$SiMe_3$), 81.5 (C≡*C*$SiMe_3$), 26.7 ($P_{eq}(CH_3)_3$), 23.5 ($P_{eq}(CH_3)_3$), 18.5 ($P_{ax}(CH_3)_3$), 2.2 ($Si(CH_3)_3$), −0.6 ($Si(CH_3)_3$) ppm. MS(ESI) *m*/*z* (abundance): 525.1 (100) [M − $P(CH_3)_3$]$^+$. HRMS (LSIMS): 598.18351. Required for $C_{22}H_{55}P_4Si_2{}^{99}Ru$: 598.19351. ν_{max} (KBr disk): 3642, 2953, 2910, 1636, 1588, 1428, 1307, 1289, 1242, 1063, 949, 836, 717, 668 cm^{-1}.

***cis*-[Ru(η^3-MeC≡CC═C(H)Me)(PMe_3)$_4$]BF_4 (12a and 12b).** A mixture of Ru(C≡CMe)$_2$(PMe_3)$_4$ (**6**) (0.0252 g, 0.0521 mmol) and 2,6-lutidinium tetrafluoroborate (0.0070 g, 0.0506 mmol) was dissolved in CD_2Cl_2. The color of the solution immediately turned yellow. **12a** (*E*-stereochemistry): Selected ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.63 (apparent br pentet, splitting = 4.9 Hz, 1H, ═C(*H*)CH_3), 2.39 (s, 3H, ≡CCH_3), 2.05 (d, $^3J_{HH}$ = 6.4 Hz, 3H, ═C(H)CH_3), 1.62 (d, $^2J_{PH}$ = 5.7 Hz, 9H, $P_{eq}(CH_3)_3$), 1.55 (d, $^2J_{PH}$ = 7.7 Hz, 9H, $P_{eq}(CH_3)_3$), 1.06 (apparent t, splitting = 3.0 Hz, 18H, 2 × $P_{ax}(CH_3)_3$) ppm, phosphine proton resonances coincident with **12b**. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 5.03 (dt, $^2J_{PP}$ = 15.5 Hz, $^2J_{PP}$ = 33.1 Hz, 1P, P_{eq}), −5.91 (apparent t, 2P, 2 × P_{ax}), −14.66 (dt, $^2J_{PP}$ = 15.5 Hz, $^2J_{PP}$ = 31.8 Hz, 1P, P_{eq}) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 149.6 (Ru-*C*═C), 124.9 (Ru-C═*C*), 102.1 (*C*≡CCH$_3$), 44.8 (C≡*C*CH$_3$), 25.7 (C═C(H)*C*H$_3$), 24.6 ($P_{eq}(CH_3)_3$), 24.3 ($P_{eq}(CH_3)_3$), 18.1 ($P_{ax}(CH_3)_3$), 11.5 (C≡*C*CH$_3$) ppm. **12b** (*Z*-stereochemistry): Selected ^{1}H NMR (300 MHz,

CD_2Cl_2): δ 6.80 (apparent br pentet, splitting = 8.0 Hz, 1H, =C(*H*)CH_3), 2.38 (s, 3H, ≡CC*H*$_3$), 1.95 (d, $^3J_{HH}$ = 7.1 Hz, 3H, =C(H)C*H*$_3$) ppm, phosphine proton resonances coincident with **12a** (*E*-stereochemistry): $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 3.94 (dt, $^2J_{PP}$ = 18.3 Hz, $^2J_{PP}$ = 33.6 Hz, 1P, P_{eq}), −5.36 (apparent t, 2P, 2 × P_{ax}), −15.03 (dt, $^2J_{PP}$ = 18.3 Hz, $^2J_{PP}$ = 30.6 Hz, 1P, P_{eq}) ppm.

***trans*-[Ru(C≡CSiMe$_3$)(C=CH$_2$)(PMe$_3$)$_4$]PF$_6$ (13·PF$_6$).** NH_4PF_6 (0.0594 g, 0.364 mmol) was added in a single solid portion to an ether solution of *trans*-Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ (**5**) (0.2239 g, 0.372 mmol) at 0 °C. The mixture was stirred at 0 °C for 45 min, then allowed to warm to room temperature and stirred overnight. The mother liquor was decanted and the residue dried *in vacuo* to yield *trans*-[Ru(C≡CSiMe$_3$)(C=CH$_2$)(PMe$_3$)$_4$]PF$_6$ (**13**·PF$_6$) as an off-white solid. Yield: 0.1165 g (0.171 mmol, 46%). ^1H NMR (300 MHz, acetone-d_6): δ 3.85 (m, 2H, C=C*H*$_2$), 1.74 (br s, 36H, P(C*H*$_3$)$_3$), 0.08 (s, 9H, Si(C*H*$_3$)$_3$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, acetone-d_6): δ −9.51 (br s) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (125 MHz, acetone-d_6): δ 351.4 (*C*=CH$_2$), 141.1 (C≡*C*SiMe$_3$), 124.9 (*C*≡CSiMe$_3$), 91.4 (C=*C*H$_2$), 19.4 (br, P(*C*H$_3$)$_3$), 1.28 (Si(*C*H$_3$)$_3$) ppm. MS(ESI) *m*/*z*: 529.0 (100%) [M$^+$], 453.0 (95) [M − PMe$_3$]$^+$. HRMS(LSIMS): 531.14317. Required for $C_{19}H_{47}P_4{}^{104}RuSi$: 531.14518.

***trans*-[Ru(C=CH$_2$)(C≡CH)(PMe$_3$)$_4$]BF$_4$ (14).** A solution of Ru(C≡CSiMe$_3$)$_2$(PMe$_3$)$_4$ (**11**) (0.098 g, 0.163 mmol) in THF (5 mL) was added to 2,6-lutidinium tetrafluoroborate (0.0347 g, 0.177 mmol). The pale yellow solution was stirred at room temperature for 2 h and then concentrated to dryness *in vacuo*. The pale yellow-brown residue was washed with pentane (8 mL) and dried *in vacuo* to yield **13** as a pale brown solid. Complex **13** was taken up in acetone and layered with hexane. X-ray quality crystals of **14** were deposited as long, thin needles.

***cis*-[Ru(η^3-Me$_3$SiC≡CC=CH$_2$)(PMe$_3$)$_4$]BF$_4$ (15).** Trimethylsilylacetylene (0.3 mL, 2.1 mmol) was added to a solution of *cis*-$RuMe_2(PMe_3)_4$ (0.2248 g, 0.516 mmol) in THF (15 mL). The mixture was stirred at 40 °C for 2.5 h before the volatiles were removed under reduced pressure. The residue was redissolved in THF (15 mL) and irradiated (300 W Hg-vapor lamp) for 1 h. Solid NH_4PF_6 (0.0837 g, 0.513 mmol) was added, and the mixture stirred at room temperature for 2 h. The golden-colored solution was filtered, and the volatiles were removed under reduced pressure to yield a pale yellow solid containing approximately 72% **11** and 28% **15**. Yield: 0.223 g. ^1H NMR (600 MHz, acetone-d_6): δ 6.52 (d, $^4J_{PH}$ = 10.2 Hz, 1H, =C*H*H), 5.82 (d, J_{PH} = 4.8 Hz, 1H, =CH*H*), 1.25 (apparent t, splitting = 3.2 Hz, 18H, $P_{ax}(CH_3)_3$), 0.39 (s, 9H, Si(C*H*$_3$)$_3$) ppm. Resonances due to $P_{eq}(CH_3)_3$ were coincident with **11**. $^{31}P\{^1H\}$ NMR (242.9 MHz, acetone-d_6): δ 9.85 (dt, $^2J_{PP}$ = 16.9, 35.5 Hz, 1P, P_{eq}), −11.30 (apparent t, splitting = 35.0 Hz, 2P, P_{ax}), −13.76 (dt, $^2J_{PP}$ = 16.9 Hz, 30.4 Hz, 1P, P_{eq}) ppm.

***cis*-[Ru(η^3-MeC≡CC=CMe$_2$)(PMe$_3$)$_4$]OTf (16).** A solution of Ru(C≡CMe)$_2$(PMe$_3$)$_4$ (**6**) (0.1058 g, 0.219 mmol) in diethyl ether (5 mL) was cooled to 0 °C, and methyl triflate (28 μL, 0.25 mmol) was added. Immediately a white solid formed, and the mixture was stirred for an additional 20 min. The solid was isolated by filtration, washed with ether, and dried *in vacuo*. Yield: 0.0762 g (0.118 mmol, 54%). ^1H NMR (300 MHz, acetone-d_6): δ 2.52 (d, $^4J_{PH}$ = 2.0 Hz, 3H, C≡CC*H*$_3$), 2.26 (s, 3H, C=C(C*H*$_3$)$_2$), 2.08 (s, 3H, C=C(C*H*$_3$)$_2$), 1.78 (d, $^2J_{PH}$ = 1.8 Hz, 9H, $P_{eq}(CH_3)_3$), 1.75 (d, $^2J_{PH}$ = 3.2 Hz, 9H, $P_{eq}(CH_3)_3$), 1.17 (apparent t, splitting = 3.2 Hz, 18H, 2 × $P_{ax}(CH_3)_3$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, acetone-d_6): δ 3.04 (dt, $^2J_{PP}$ = 33.8 Hz, $^2J_{PP}$ = 18.5 Hz, 1P, P_{eq}), −6.06 (dd, $^2J_{PP}$ = 33.8, $^2J_{PP}$ = 29.3 Hz, 2P, 2 × P_{ax}), −16.43 (dt, $^2J_{PP}$ = 29.3 Hz, $^2J_{PP}$ = 18.5 Hz, 1P, P_{eq}) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 142.7 (Ru-*C*=C), 133.8 (Ru-C=*C*), 97.7 (d, $^2J_{PC}$ = 25.9 Hz, *C*≡CCH$_3$), 47.9 (C≡*C*CH$_3$), 33.6 (C=C(*C*H$_3$)$_2$), 26.8 (d, $^1J_{PC}$ = 27.0 Hz, $P_{eq}(CH_3)_3$), 24.6 (m, $P_{eq}(CH_3)_3$ + C=C(*C*H$_3$)$_2$), 18.4 (apparent t, splitting = 14.2 Hz, 2 × $P_{ax}(CH_3)_3$), 11.2 (C≡C*C*H$_3$) ppm. Recrystallization as the BPh_4 salt gave material suitable for MS and microanalysis. MS(ESI) *m*/*z*: 424.7 (10%) [M − PMe$_3$]$^+$, 348.4 (90) [M − 2PMe$_3$]$^+$. Anal. Calcd for $C_{43}H_{65}BP_4Ru$: C, 63.16; H, 8.01. Found: C, 63.33; H, 8.06.

***cis*-[Ru(η^3-PhC≡CC=C(Me)Ph)(PMe$_3$)$_4$]OTf (17).** To a cold (0 °C) suspension of Ru(C≡CPh)$_2$(PMe$_3$)$_4$ (0.0999 g, 0.155 mmol) in diethyl ether (10 mL) was added methyl triflate (20 μL, 0.177 mmol). The mixture was stirred overnight before the resultant precipitate was isolated by filtration, washed with ether, and dried *in vacuo*. The product was recrystallized from a mixture of acetone and pentane. Yield: 0.0834 g (0.104 mmol, 67%). ^1H NMR (300 MHz, acetone-d_6): δ 7.87 (d, J = 8.1 Hz, 2H, Ar*H*), 7.68 (d, J = 8.1 Hz, 2H, Ar*H*), 7.54−7.38 (m, 5H, Ar*H*), 7.28 (t, J = 8.1 Hz, 1H, Ar*H*), 2.67 (s, 3H, *C*=CC*H*$_3$), 1.92 (d, $^2J_{PH}$ = 8.6 Hz, 9H, $P_{eq}(CH_3)_3$), 1.80 (d, $^2J_{PH}$ = 7.0 Hz, 9H, $P_{eq}(CH_3)_3$), 1.24 (apparent t, splitting = 3.0 Hz, 18H, 2 × $P_{ax}(CH_3)_3$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, acetone-d_6): δ 3.06 (dt, $^2J_{PP}$ = 34.5 Hz, $^2J_{PP}$ = 23.9 Hz, 1P, P_{eq}), −4.19 (dd, $^2J_{PP}$ = 34.5 Hz, $^2J_{PP}$ = 28.7 Hz, 2P, 2 × P_{ax}), −13.27 (dt, $^2J_{PP}$ = 28.7 Hz, $^2J_{PP}$ = 23.9 Hz, 1P, P_{eq}) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ 145.3 (d, $^2J_{PC}$ = 5.3 Hz, Ru-*C*=C), 138.2 (Ru-C=*C*), 132.7 (Ar*C*), 130.2 (Ar*C*), 129.4 (Ar*C*), 129.2 (Ar*C*), 127.7 (Ar*C*), 126.2 (Ar*C*), 105.4 (*C*≡CPh), 62.1 (C≡*C*Ph), 26.7 (d, $^1J_{PC}$ = 31.3 Hz, $P_{eq}(CH_3)_3$), 25.3 (d, $^1J_{PC}$ = 25.6 Hz, $P_{eq}(CH_3)_3$), 24.04 (C=C(*C*H$_3$)Ph), 19.1 (apparent t, splitting = 14.1 Hz, 2 × $P_{ax}(CH_3)_3$) ppm. *Ipso* carbons not identified. MS (ESI) *m*/*z*: 546.99 (95%) [M − PMe$_3$]$^+$, 473.0 (100) [M − 2PMe$_3$]$^+$. Anal. Calcd for $C_{30}H_{49}F_3O_3P_4RuS$: C, 46.69; H, 6.40. Found: C, 46.65; H, 6.30.

X-ray Crystallography of 10. A yellow block-like crystal was attached with Exxon Paratone N to a short length of fiber supported on a thin piece of copper wire inserted in a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. A Bruker CCD-1000 area detector diffractometer employing graphite-monochromated Mo Kα radiation generated from a fine-focus sealed tube was used for the data collection. Cell constants were obtained from a least-squares refinement against 8112 reflections located between 4.52° and 56.52° 2θ. Data were collected at 150(2) K with ω scans to 56.60° 2θ. The data integration and reduction were undertaken with SAINT and XPREP,[40] and subsequent computations were carried out with the X-Seed[41] graphical user interface. The intensities of 507 standard reflections re-collected at the end of the experiment did not change significantly during the data collection. An empirical absorption correction determined with SADABS[42] was applied to the data.

The structure was solved in the space group $P2_1/n$ (#14) by direct methods with SHELXS-97[43] and extended and refined with SHELXL-97.[43] Of the 47 non-hydrogen atom sites in the asymmetric unit, 42 were modeled with anisotropic displacement parameters, and the rest were modeled with isotropic displacement parameters. A riding atom model with group displacement parameters was used for the hydrogen atoms. The tetrafluoroborate anion was modeled over two positions (85:15). The atoms in the minor (0.15) occupied position were refined with isotropic displacement parameters. The acetone solvent molecule was modeled over two disordered positions with a 60:40 split in site occupancies.

X-ray Crystallography of 14. A yellow prism-like crystal was attached with Exxon Paratone N to a short length of fiber supported on a thin piece of copper wire inserted in a copper mounting pin. The crystal was quenched in a cold nitrogen gas stream from an

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Oxford Cryosystems Cryostream. A Bruker CCD-1000 area detector diffractometer employing graphite-monochromated Mo Kα radiation generated from a fine-focus sealed tube was used for the data collection. Cell constants were obtained from a least-squares refinement against 14 880 reflections located between 4.82° and 55.88° 2θ. Data were collected at 150(2) K with ω scans to 56.62° 2θ. The data integration and reduction were undertaken with SAINT and XPREP,[40] and subsequent computations were carried out with the XP SHELXTL-Plus[44] graphical user interface. The intensities of 343 standard reflections re-collected at the end of the experiment did not change significantly during the data collection. An empirical absorption correction determined with SADABS[42] was applied to the data.

The structure was solved in the chiral space group $P2_12_12_1$ (#19) by direct methods with SHELXS-97[43] and extended and refined with SHELXL-97.[43] The chirality is in the overall structure rather than in the molecules themselves. The sample was a racemic mixture of chiral single crystals; the crystal was chirally pure, and the absolute structure was established with the Flack parameter[45] refining to −0.031(18). The non-hydrogen atoms in the asymmetric unit were modeled with anisotropic displacement parameters. Of the 39 hydrogen atoms included in the model, three were located and modeled with isotropic displacement parameters, and a riding atom model was used for the remainder.

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Supporting Information Available: A CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800861G

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