Ruthenium(II)−MeO−Biphep−Arene Dications: Acetylene Reactions and Unexpected Cyclometalation

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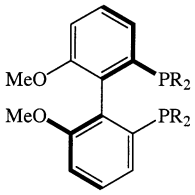
Reactions of [Ru(arene)(MeO−Biphep)]$(SbF_6)_2$ (arene = *p*-cymene, **4**, or benzene, **5**; MeO−Biphep = (6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine)) with several terminal acetylene compounds lead to products derived from cyclometalation of one of the P-phenyl rings, followed by insertion of the acetylene derivative into the new Ru−C bond. The solid-state structure of one of these compounds, an η^6-benzene complex derived from phenylacetylene, has been determined by X-ray diffraction. The dicationic complexes **4** and **5** catalyze the reaction of benzoic acid with 1-pentyne or 1-octyne to form enol-ester organic products. Using octyne-d_1, deuterium-labeling experiments show scrambling of the deuterium atom. A new Ru−carbene complex was prepared and used in the catalytic reaction.

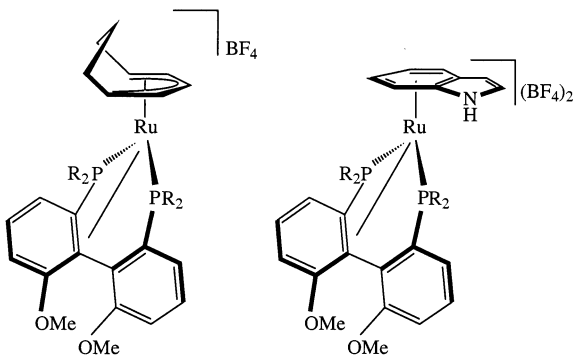
Introduction

Ruthenium phosphine chemistry remains an active area of research.[1−6] Homogeneous hydrogenation, ring-opening and ring-closing metathesis, and C−C bond formation reactions represent a few of the synthetic applications currently under study.[7−11] Frequently, tertiary phosphine ligands are involved as either stabilizing or chiral auxiliaries.



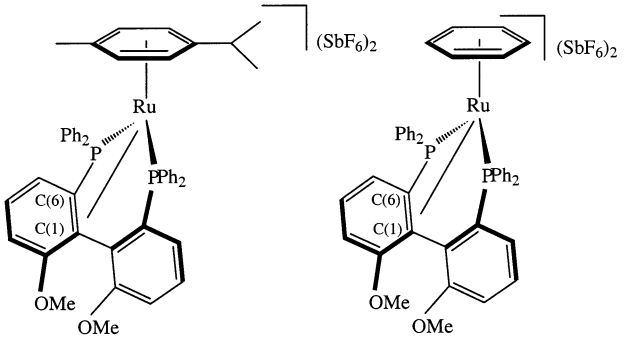
1a, R = Ph, **1b**, R = 3,5-di-t-butylphenyl

We have recently noticed that the chelating ligand MeO−Biphep,[12−17] **1**, can act as a 6e-donor to Ru(II). The third pair of electrons stems from a double bond immediately adjacent to one of the two tertiary phosphine donors. A number of these complexes have now been prepared including **2**−**5**.[18,19]



2 R = 3,5-di-t-butylphenyl **3**

The relatively simple compounds, **4** and **5**, as SbF_6 cationic salts, not only reveal an additional η^2-bonding but have been recently shown to have interesting ^{13}C NMR characteristics; for **4** δ = 93.0 (C1) and δ = 80.1 (C6) and for **5** δ = 90.9 (C1) and δ = 86.0 (C6).[18]



4 **5**

In principle dications **4** and **5** should be catalyst precursors, as the biaryl double bond is not strongly coordinated to Ru(II),[19] thus allowing 16e species to be

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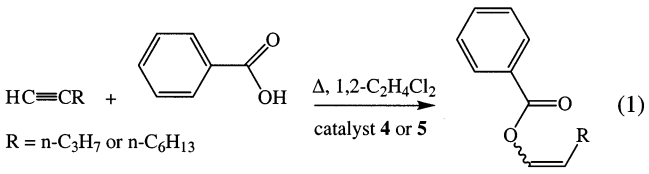
formed. We report here on some alkyne chemistry associated with these two compounds.

Results and Discussion

Catalysis. Bruneau and Dixneuf[20−22] have shown that a variety of enol esters can be prepared by the ruthenium-catalyzed reaction of carboxylic acids with terminal alkynes. We find that the reaction of 1-pentyne (at 35 °C) or 1-octyne (at 60 °C) with benzoic acid, catalyzed by the Ru−arene complexes **4** and **5** (5 mol %), proceeds smoothly, but relatively slowly (96 and 24 h, respectively) as shown in eq 1.

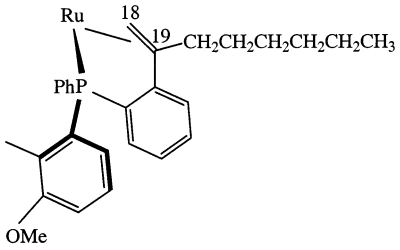


(1)

We find little or no trace of the terminal olefin, so that the reaction is highly regioselective. However, both cis and trans internal olefin products are observed in the ratio 7:3. Phenylacetylene did not afford an enol-ester product, and we will suggest an explanation for this below.

Using **4** as precursor, a catalytic reaction involving 1-octyne and benzoic acid has been monitored using ^{31}P NMR. The signals for complex **4** are present at the beginning of the transformation (although its ^{31}P resonances are broad, suggesting dynamic behavior) along with two additional species. One of these, which we have not yet satisfactorily identified, **6**,[23] slowly disappears to leave a second complex, **7a**, as an isolable material (see Scheme 1). However, if **7a** is allowed to remain in the catalytic solution, it slowly converts completely to an isomer, **7b**, which is also isolable and readily identified. Since the reaction is slow at room temperature, we have isolated both **7a** and **7b** separately.

Structural Studies. Reactions of the *p*-cymene complex **4** and the benzene analogue **5** with only the appropriate terminal alkyne afforded a new series of complexes, as shown in Scheme 1. These are neither carbene nor acetylide complexes, but rather the unexpected cyclometalation/insertion Ru−arene products. The isomers differ in that, in one case, we find a terminal, but in the other an internal olefin. A fragment of product **7a** is shown above.

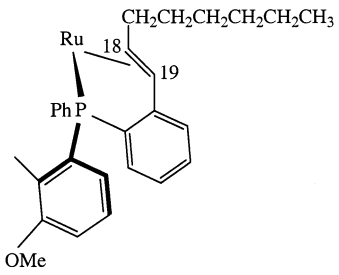


Fragment of 7a

The *p*-cymene complex **7a** could be characterized via multidimensional NMR methods. The routine one-bond and long-range ^{13}C,^{1}H-correlations proved to be the most useful of these NMR methods in that, for **7a**, they reveal the two olefinic carbons at δ = 55.4 (C18) and δ = 133.0[24] (C19) at relatively low frequency. ^{13}C NMR data for the analogous *n*-propyl, **8a**, and phenyl, **9**, complexes are given in Table 1.

Figure 1 reveals a section of the 2D ^{13}C−^{1}H NMR one-bond correlation for the phenyl complex **9** and shows the two terminal olefinic protons (H18a and H18b) on the terminal olefinic carbon (C18). These terminal olefinic protons are somewhat unusual in that (a) they do not show a significant $^{2}J_{H,H}$ value and (b) only one of the two protons (H18b) is coupled to a single ^{31}P spin.

The internal olefin isomeric complexes **7b** and **8b** are also readily recognized via ^{13}C NMR; for example, for **7b** δ = 85.2 (C18) and δ = 89.1 (C19). A fragment of the structure of **7b** is shown below.



Fragment of 7b

The assignment of the trans isomer has been made via the relatively large 12.6 Hz $^{3}J_{H,H}$ coupling constant observed for H19.

The analogous reaction of HC≡CR (R = *n*-hexyl, *n*-propyl, and phenyl) with the benzene complex **5** afforded exclusively the terminal isomer products, **10**−**12**. We believe that **7a**, **8a**, and **9**, as well as **10**−**12**, are the kinetic products. For **12**, a crystal suitable for X-ray diffraction could be obtained.

Solid-State Structure of 12. The solid-state structure of **12** has been determined by X-ray diffraction methods. An ORTEP view of the cation is shown in Figure 2. The immediate coordination sphere around the Ru(II) consists of the two P-donors, the complexed olefin, and the six carbon atoms of the η^6-benzene ligand. The structure shows a distorted piano-stool arrangement

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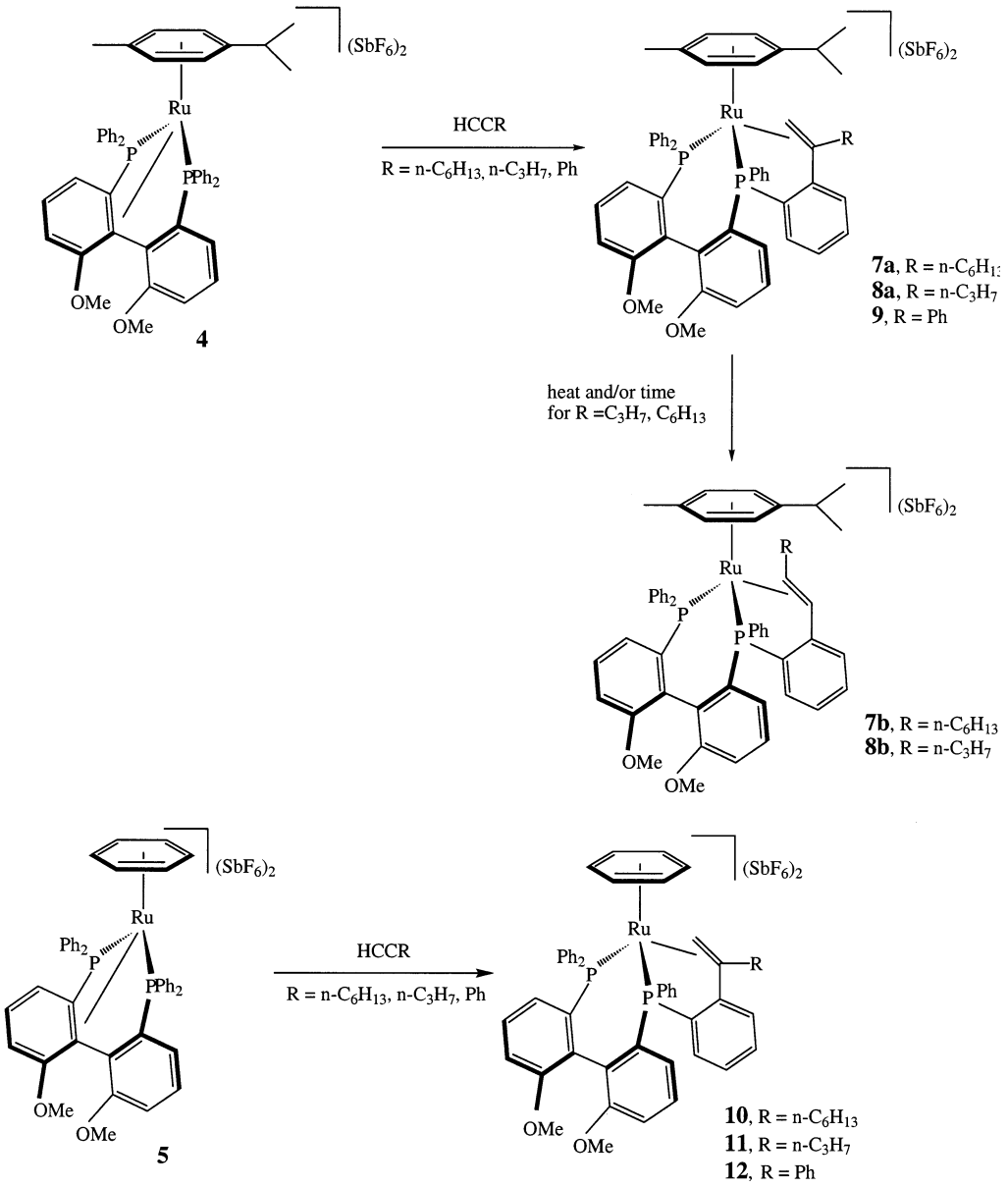
(23) The ^{31}P NMR characteristics for **6** (δ = 22.5 ($J_{P,P}$ = 45 Hz) and δ = 45.0 ($J_{P,P}$ = 45 Hz) are normal, i.e., within the region observed for the complexes **7**−**12**, but not consistent with a cyclometalated four-membered ring (Umeza-Vizzini, K.; Lee, T. R. *Organometallics* **1997**, *16*, 5613−5615). One possibility for **6** is the η^2-acetylene complex.

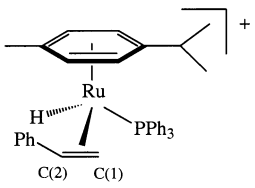
(24) The estimated ^{13}C NMR chemical shifts of the uncomplexed olefin carbons of CH_2=C(Ph)C_6H_{13} are 112.6 and 148.1 ppm for the terminal and internal olefinic carbons, respectively. Consequently, 133.0 ppm represents a coordination chemical shift of ca. 15 ppm for the internal olefin carbon.

Scheme 1



with the olefinic double bond as the third leg. Selected bond lengths and bond angles are listed in Table 2.

The two Ru−C(olefin) separations are markedly different: 2.413(14) Å for Ru(1)−C(18) and 2.246(12) Å for Ru(1)−C(19). This corresponds to a strongly asymmetric arrangement of the double bond with respect to the Ru(II).[25−27]



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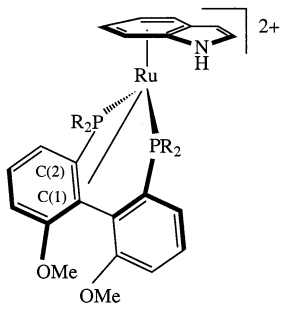
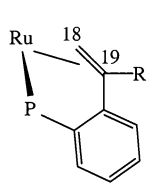
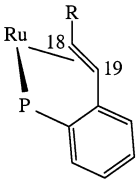


14 (R = 3,5-di-t-butylphenyl)

Table 1. Selected ^{13}C and ^{1}H Data for 7−12



7a, 8a, 9-12



7b,8b

complex	C(18)	C(19)	H(18a/b)	H(19)
p-cymene				
7a, R = *n*-Hex	55.4	133.0	5.00/3.75	
7b, R = *n*-Hex	85.6	89.2	3.11	5.91
8a, R = *n*-Pr	55.1	*a*	5.03/3.73	
8b, R = *n*-Pr	85.2	89.1	3.12	5.92
9, R = Ph	47.0	*a*	5.93/3.42	
benzene				
10, R = *n*-Hex	55.1	137.4	5.38/3.31	
11, R = *n*-Pr	55.4	137.0	5.37/3.30	
12, R = Ph	51.0	*a*	6.18/2.98	

[a] Not assignable due to the lack of long-range correlations.

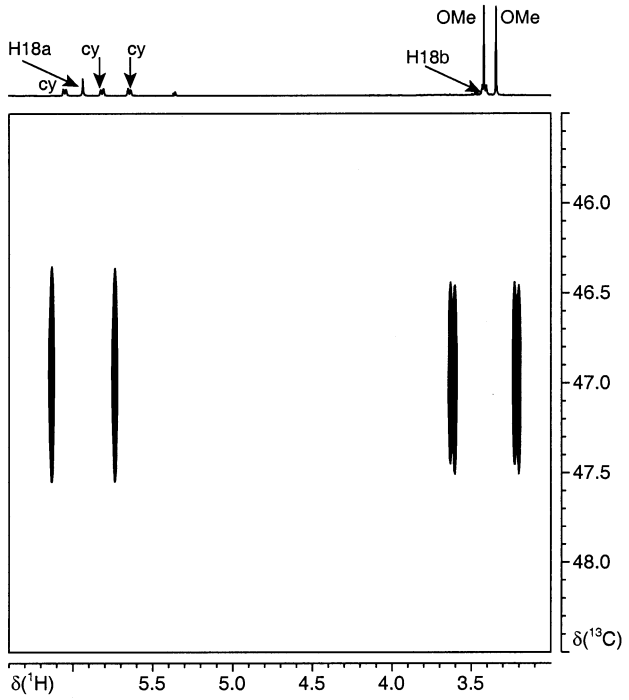


Figure 1. Section of the $^{13}C-^{1}H$ one-bond correlation of **9** showing the two terminal olefinic protons (H18a and H18b) on the terminal olefinic carbon (C18) (400 MHz, CD_2Cl_2, ambient temperature).

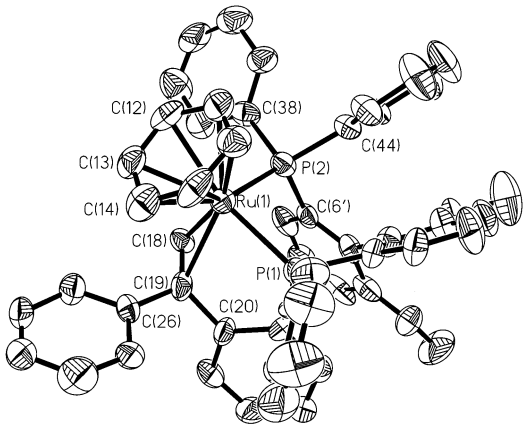


Figure 2. ORTEP view of the cation of **12**, 50% ellipsoids, from one of the two molecules present in the unit cell. Hydrogen atoms are omitted for clarity.

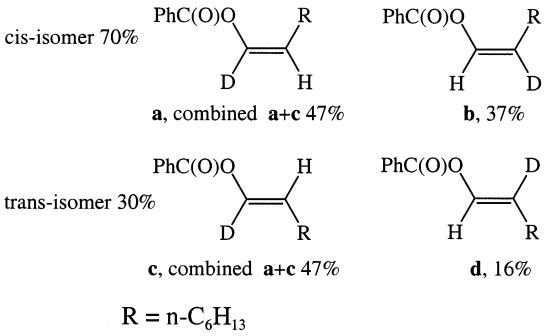
Faller et al.[28] have reported the structure of **13** as having Ru−C(1) and Ru−C(2) bond distances of 2.195(6) and 2.216(6) Å, respectively, i.e., relatively short separations. In the arene olefin Ru(II) complex, **14**, the bond distances between Ru−C(1) and Ru−C(2), 2.34(3) and 2.31(3) Å, respectively, are relatively long.[19] The η^2-bonding distances in [Ru{(η^3-1−3):(η^2-5,6)-C_8H_{18}}(CH_3CN)(Binap)]BF_4 at ca. 2.40 Å are also quite long.[27] Taken together with the observed olefinic C(18)−C(19) distance of 1.362(19) Å (which is only slightly longer than a normal uncomplexed double bond, ca. 1.34 Å), we conclude that the molecular crowding in **12** results in a fairly weak olefin bond.

The six Ru−C(arene) separations fall in the range 2.290(14)−2.331(16) Å, with the average ca. 2.30 Å. Inspection of the X-ray literature[29−32] for η^6-benzene Ru(II) complexes suggests that routine Ru−C separations should be on the order of 2.15−2.24 Å, with the average at ca. 2.20 Å. Consequently, these data also suggest some crowding.

Table 2. Selected Bonds Lengths (Å) and Bond Angles (deg) for the Cation in 12

Ru(1)−C(18)	2.246(12)	C(18)−C(19)	1.362(19)
Ru(1)−C(19)	2.413(14)	C(19)−C(20)	1.510(19)
Ru(1)−P(1)	2.353(4)	C(19)−C(26)	1.499(19)
Ru(1)−P(2)	2.361(4)	P(1)−C(6)	1.844(13)
Ru(1)−C(9)	2.286(14)	P(2)−C(6′)	1.830(14)
Ru(1)−C(10)	2.290(15)	P(2)−C(38)	1.808(15)
Ru(1)−C(11)	2.297(17)	P(2)−C(44)	1.812(14)
Ru(1)−C(12)	2.330(16)		
Ru(1)−C(13)	2.289(15)		
Ru(1)−C(14)	2.305(15)		
P(1)−Ru(1)−P(2)	86.67(13)	C(18)−C(19)−C(20)	117.3(12)
P(1)−Ru(1)−C(18)	98.9(4)	C(18)−C(19)−C(26)	123.7(12)
P(1)−Ru(1)−C(19)	77.4(3)	C(20)−C(19)−C(26)	112.8(13)
P(2)−Ru(1)−C(18)	82.4(3)		
P(2)−Ru(1)−C(19)	106.6(3)		
C(18)−Ru(1)−C(19)	33.7(5)		

Reactions with Octyne-d_1. It was hoped that deuterium labeling might provide mechanistic insight. However, the catalytic reaction of **4** with $C_6H_{13}C{\equiv}CD$ (>95% D) and benzoic acid resulted in almost random deuterium incorporation; that is, we observed the four isomers (**a**−**d**) shown:



The lack of observed selectivity[35] is consistent with H(D) exchange of the complexed alkyne with the acid proton of the benzoic acid. There is no indication of

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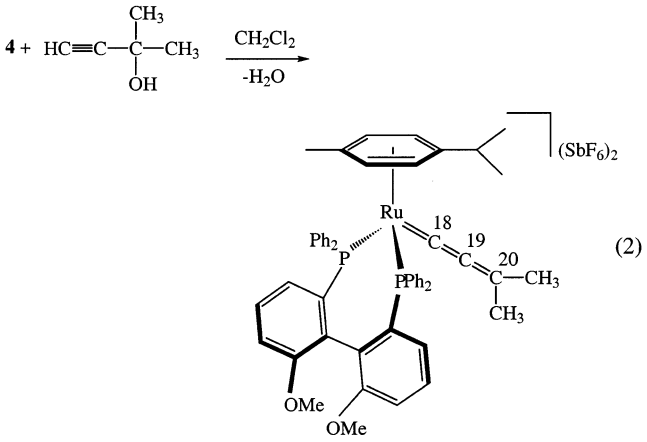
(35) We cannot exclude the presence of doubly deuterated and fully protonated olefinic compounds. Both carbene and acetylene mechanisms could involve exchange of the terminal-D and the benzoic acid-H.

deuterium incorporation into the ortho position of the phenyl groups in **4**.

Allenylidene Complex (15). It was conceivable that a carbene complex might be involved in the catalytic reaction. Consequently, the allenylidene compound **15** was synthesized as shown in eq 2.



(2)

15

The allene carbons of complex **15** were characterized by using $^{13}C-^{1}H$ long-range NMR methods. Carbons C(18), C(19), and C(20) show characteristic ^{13}C NMR chemical shifts, $\delta = 305.1$, $\delta = 204.0$, and $\delta = 178.2$, respectively, in accordance with the ^{13}C NMR literature.[36]

The reaction of 1-octyne and benzoic acid catalyzed by **15** gives the cis and trans internal olefin products of eq 1 in the ratio 7:3 in slightly lower yield (60%). During the catalysis with compound **15** the ^{31}P NMR spectra indicated several complexes as products from the allenylidene complex. Complex **15** disappears and the main component was found to be **7b**. The reaction rate is about the same as for **4**. This suggests that the new carbene itself is not responsible for the catalysis.

Comment. The chemistry of Scheme 1 is readily summarized. There would seem to be a not very stable, as yet not detected, cyclometalated species, which reacts with the three alkynes to give **7**−**12**. There is a kinetic, terminal olefin, insertion product, which can be isolated, and in some cases, a more thermodynamically stable trans olefin insertion product, also isolable. The cyclometalation/phenylacetylene insertion products **9** and **12** are sufficiently stable such that they do not react further to afford organic product. An indication for this is the stability of **12** over weeks in solution during crystal growth.

On the other hand, the 1-pentyne and 1-octyne reaction products are capable of catalyzing the chemistry of eq 1. The mechanism of the reaction remains uncertain.

Experimental Section

X-ray. Air-stable, orange crystals of **12** were obtained by slow diffusion of pentane into a saturated CH_2Cl_2 solution. A prismatic single crystal was mounted on a glass capillary, and a data set covering a hemisphere was collected on a Siemens SMART platform diffractometer equipped with a CCD detector. Data reduction plus corrections for Lorentz polarization and absorption were performed using the programs SAINT[37] and SADABS.[38] The structure was solved by direct methods and refined by full-matrix least-squares (versus F^2) with the SHELXTL program package.[39] The SbF_6 molecules are disordered and were described as a rigid group. Crystal data and structure refinements are summarized in Table 3. Two molecules are present in the unit cell; their bond distances and conformations are not significantly different.

Table 3. Crystal Data and Structure Refinement for 12

formula	$C_{52}H_{44}F_{12}O_2P_2RuSb_2$
fw	1335.38
temperature	293(2) K
wavelength	0.71073 Å
cryst syst, space group	triclinic, *P*1
unit cell dimens	$a = 13.976(2)$ Å, $\alpha = 72.619(3)°$ $b = 14.859(2)$ Å, $\beta = 66.23(3)°$ $c = 15.136(2)$ Å, $\gamma = 78.34°$
volume	2733.2(7) Å^3
Z, calcd density	2, 1.623 Mg/m^3
abs coeff	1.391 mm^{-1}
F(000)	1312
cryst size, mm^3	0.64 × 0.08 × 0.02 mm
θ-range for data collection, deg	1.44−23.27
limiting indices	$-15 \le h \le 15$, $-16 \le k \le 16$, $-11 \le l \le 16$
reflns collected/unique	15541/10624 [*R*(int) = 0.0478]
completeness to θ, deg, %	23.27, 99.7
max. and min. transmn	0.9727 and 0.4697
no. of data/restraints/params	10624/27/1283
GOOF on F^2	1.036
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0477, wR2 = 0.1269
R indices (all data)	R1 = 0.0672, wR2 = 0.1475
largest diff peak and hole, e Å^{-3}	1.346 and −0.614

Synthesis. All manipulations were carried out under argon atmosphere. Methanol was distilled from magnesium. Diethyl ether was distilled from Na−K amalgam. Dichloromethane, dichloromethane-d_2, and pentane were distilled from CaH_2. 1,2-Dichloroethane was distilled from P_2O_{10}. [Ru({S}-MeO−Biphep)(*p*-cymene)]$(SbF_6)_2$ (**4**) and [Ru({S}-MeO−Biphep)(benzene)]$(SbF_6)_2$ (**5**) were prepared according to the literature.[18] (cy = *p*-cymene, backbone = backbone of MeO−Biphep).

Synthesis of 7a. 1-Octyne (8 μL, 0.051 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(*p*-cymene)]$(SbF_6)_2$ (**4**) (66.2 mg, 0.051 mmol) in 2 mL 1,2-$C_2H_4Cl_2$. After 2.5 h at room temperature the ^{31}P NMR spectrum indicated a full conversion to the product. The solvent was evaporated in vacuo, and the resulting powder was washed with 5 × 1 mL of Et_2O. The orange product was dried in vacuo to afford the complex in 93% yield. During the 2D NMR characterization the thermodynamically more stable product **7b** appeared. Color: orange. Yield: 66.4 mg (93%). Anal. Calcd for $C_{56}H_{60}P_2O_2RuSb_2F_{12}\cdot H_2O$ (1399.7): C, 47.45; H, 4.40. Found: C, 47.09; H, 4.40. FAB-MS: calcd M^{2+} 928.2; found M^{2+} − *p*-cymene − C_8H_{15} + $2SbF_6$, 1031.0; M^{2+} − *p*-cymene − C_8H_{15} + SbF_6, 919.0; M^{2+} − *p*-cymene, 792.0; M^{2+} − *p*-cymene − C_8H_{15}, 682.9. $^{31}P\{^1H\}$ NMR (298 K, CD_2Cl_2): 38.7 (d, $^2J_{PP} = 48$), 45.6 (d, $^2J_{PP} = 48$). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2): 14.1 ($-(CH_2)_5CH_3$), 20.0 (cy), 20.5 (cy), 22.8 ($-(CH_2)_4CH_2CH_3$), 22.9 (cy), 25.1 ($-(CH_2)_3CH_2$-CH_2CH_3),31.0(cy),31.8($-(CH_2)_2CH_2(CH_2)_2CH_3$),32.3($-CH_2CH_2(CH_2)_3$-$CH_3$), 46.3 ($-CH_2(CH_2)_4CH_3$), 55.4 ($H_2C{=}CRPh-$), 100.8 (cy), 102.5 (cy), 103.3 (cy), 106.3 (cy), 114.6 (backbone), 114.7

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(backbone), 121.7 (cy), 123.3 (backbone), 124.9 (backbone), 126.7−136.0, 145.4 (H_2C=CR*Ph*−), 158.0 (backbone), 158.3 (backbone). ^{1}H NMR (298 K, CD_2Cl_2): 0.70 (d, 7.0, 3H, cy), 0.89 (t, 7.2, 3H, −$(CH_2)_5CH_3$), 0.96 (d, 7.0, 3H, cy), 1.09−1.68 (m, 10H, −$(CH_2)_5CH_3$), 2.18 (br s, 3H, cy), 2.35 (m, 1H, cy), 3.25 (s, 3H, O*Me*), 3.44 (s, 3H, O*Me*), 3.75 (d, 10.3, 1H, H_2C=CRPh−), 5.00 (s, 1H, H_2C=CRPh−), 5.88 (d, 6.8, 1H, cy), 5.97 (d, 6.8, 1H, cy), 6.18 (d, 6.8, 1H, cy), 6.43 (d, 8.4, 1H, backbone), 6.55 (d, 8.4, 1H, backbone), 6.86 (d, 6.8, 1H, cy), 6.92 (dd, 11.2, 11.6, 1H, H_2C=CR*Ph*−), 7.10−7.94 (m, 22H).

Synthesis of 7b. 1-Octyne (7 μL, 0.047 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(*p*-cymene)]$(SbF_6)_2$ (**4**) (61.0 mg, 0.047 mmol) in 0.5 mL of CD_2Cl_2. The resulting orange solution was heated at 35 °C for 48 h. The solvent was then evaporated in vacuo, and the resulting powder was washed with 5 × 1 mL of Et_2O and 1 × 1 mL of CH_2Cl_2. The orange product was dried in vacuo to afford the product. Color: orange. Yield: 28.3 mg (92%). Anal. Calcd for $C_{56}H_{60}P_2O_2RuSb_2F_{12}\cdot H_2O$ (1399.7): C, 47.45; H, 4.41. Found: C, 47.33; H, 4.46. FAB-MS: calcd M^{2+}, 928.2; found M^{2+} − *p*-cymene− C_8H_{14} + 2SbF_6, 1031.0; M^{2+} − *p*-cymene − C_8H_{14} + SbF_6, 919.0; M^{2+} − *p*-cymene, 792.0; M^{2+} − *p*-cymene − C_8H_{14}, 682,9. ^{31}P-{^{1}H} NMR (298 K, CD_2Cl_2): 39.9 (d, $^2J_{PP}$ = 56), 45.5 (d, $^2J_{PP}$ = 56). ^{13}C{^{1}H} NMR (298K, CD_2Cl_2): 14.2 (−$(CH_2)_5CH_3$), 18.5 (cy), 20.2 (cy), 23.0 (−$(CH_2)_2CH_2CH_3$), 25.1 (cy), 29.5 (−$(CH_2)_3CH_2CH_2CH_3$), 32.2 (cy), 32.3 (−$(CH_2)_2CH_2(CH_2)_2CH_3$), 34.7 (−$CH_2CH_2(CH_2)_3CH_3$), 42.8 (−$CH_2(CH_2)_4CH_3$), 55.4 (O*Me*), 55.6 (O*Me*), 85.6 (RH*C*=CHPh−), 89.2 (RHC=*C*HPh−), 95.4 (cy), 103.0 (cy), 106.3 (cy), 108.6 (cy), 114.5 (backbone), 115.3 (backbone), 123.1 (backbone), 124.9 (backbone), 126.0 (backbone), 126.1 (cy), 126.6 (backbone), 127.6 (backbone), 128.1−130.9, 132.0−135.5, 144.0 (RHC=CH*Ph*−), 158.0 (backbone), 159.4 (backbone). ^{1}H NMR (298 K, CD_2Cl_2): 0.59 (d, 7.0, 3H, cy), 1.12 (d, 7.0, 3H, cy), 2.00 (br s, 3H, cy), 2.65 (m, 1H, cy), 3.11 (d, 12.7, 1H, R*H*C=CHPh−), 3.31 (s, 3H, O*Me*), 3.37 (s, 3H, O*Me*), 5.01 (br s, 1H, cy), 5.10 (d, 6.8, 1H, cy), 5.91 (d, 12.7, 1H, RHC=C*H*Ph−), 6.11 (d, 6.8, 1H, cy), 6.54 (br s, 1H, backbone), 6.62 (d, 8.4, 1H, cy), 6.84 (dd, 7.5, 10.8, 1H, RHC=CH*Ph*−), 7.04−8.08 (m, 25H).

In Situ Preparation and Characterization of 8a. 1-Pentyne (6 μL, 0.061 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(*p*-cymene)]$(SbF_6)_2$ (**4**) (54.2 mg, 0.042 mmol) in 0.5 mL of CD_2Cl_2. After 12 h at room temperature the ^{31}P NMR spectrum indicated a full conversion to one product, which was characterized in situ by 2D NMR methods (only selected NMR data for **8a** are given). The reaction proceeded to the thermodynamically more stable isomer **8b** during these measurements. ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2): 39.0 (d, $^2J_{PP}$ = 49), 45.7 (d, $^2J_{PP}$ = 49). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2): 13.8 (−$CH_2CH_2CH_3$), 19.8 (cy), 20.0 (cy), 23.1 (cy), 25.6 (−$CH_2CH_2CH_3$), 30.9 (cy), 48.0 (−$CH_2CH_2CH_3$), 55.0 (O*Me*), 55.1 (H_2C=CRPh−), 55.4 (O*Me*), 100.1 (cy), 102.3 (cy), 103.5 (cy), 106.7 (cy), 114.5 (backbone), 114.6 (backbone), 122.1 (cy), 123.4 (backbone), 124.9 (backbone), 126.4 (backbone), 126.7 (H_2C=CR*Ph*−), 127.2 (backbone), 128.4 (backbone), 128.4 (backbone), 129.1 (HC_2=CR*Ph*−), 129.6 (backbone), 130.5 (backbone), 134.2 (H_2C=CR*Ph*−), 133.8 (cy), 134.2 (H_2C=CR*Ph*−), 136.3 (H_2C=CR*Ph*−), 145.2 (H_2C=CR*Ph*−),157.9 (backbone), 158.3 (backbone). ^{1}H NMR (298 K, CD_2Cl_2): 0.66 (d, 6.8, 3H, cy), 0.96 (d, 6.8, 3H, cy), 0.96 (t, 7.4, 3H, −$CH_2CH_2CH_3$), 1.32 (m, 1H, −$CH_2CH_2CH_3$), 1.50 (m, 1H, −$CH_2CH_2CH_3$), 2.09 (br s, 3H, cy), 2.20 (m, 1H, −$CH_2CH_2CH_3$), 2.29 (m, 1H, cy), 2.47 (m, 1H, −$CH_2CH_2CH_3$), 3.24 (s, 3H, O*Me*), 3.73 (d, 9.9, 1H, H_2C=CRPh−), 3.40 (s, 3H, O*Me*), 5.03 (s, 1H, H_2C=CRPh−), 5.97 (d, 7.2, 1H, cy), 6.04 (d, 7.2, 1H, cy), 6.14 (d, 7.2, 1H, cy), 6.42 (d, 8.4, 1H, backbone), 6.54 (d, 8.4, 1H, backbone), 6.89 (d, 7.2, 1H, cy), 6.91 (H2C=CR*Ph*−), 7.12 (backbone), 7.16 (H_2C=CR*Ph*−), 7.21 (H_2C=CR*Ph*−), 7.24 (backbone), 7.28 (backbone), 7.40 (H_2C=CR*Ph*−), 7.64 (backbone).

Synthesis of 8b. 1-Pentyne (4 equiv, 10 μL, 0.10 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(*p*-cymene)]$(SbF_6)_2$ (**4**) (31.6 mg, 0.025 mmol) in 0.5 mL of CD_2Cl_2. The remaining orange solution was heated at 35 °C for 48 h. The solvent was evaporated in vacuo, and the resulting powder was washed with 5 × 1 mL of Et_2O. The orange product was dried in vacuo. Color: orange. Yield: 29.5 mg (87%). Anal. Calcd for $C_{53}H_{54}P_2O_2RuSb_2F_{12}\cdot Et_2O$ (1357.6): C, 47.82; H, 4.51. Found: C, 47.45; H, 4.48. FAB-MS: calcd M^{2+} 886.1; found M^{2+}, 887.1; M^{2+} − *p*-cymene, 750.0; M^{2+} − *p*-cymene − C_5H_9, 682.9. ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2): 39.7 (d, $^2J_{PP}$ = 56), 45.4 (d, $^2J_{PP}$ = 56). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2): 14.0 (−$CH_2CH_2CH_3$), 18.3 (cy), 20.1 (cy), 25.1 (cy), 27.7 (−$CH_2CH_2CH_3$), 31.9 (cy), 44.4 (−$CH_2CH_2CH_3$), 55.3 (*Me*O), 55.5 (O*Me*), 85.2 (RH*C*=CHPh−), 89.1 (RHC=*C*HPh−), 95.2 (cy), 102.6 (cy), 106.2 (cy), 108.4 (cy), 114.2 (backbone), 115.0 (backbone), 123.1 (backbone), 124.9 (backbone), 126.1 (cy), 125.3 (backbone), 126.3 (backbone), 127.6 (backbone), 129.5−131.1, 132.4−134.9, 144.8, 157.4 (backbone), 159.1 (backbone). ^{1}H NMR (298 K, CD_2Cl_2): 0.59 (d, 6.9, 3H, cy), 1.29 (t, 7.3, 3H, −$CH_2CH_2CH_3$), 1.10 (d, 6.9, 3H, cy), 1.92 (m, 1H, −$CH_2CH_2CH_3$), 1.92 (m, 1H, −$CH_2CH_2CH_3$), 2.00 (br s, 3H, cy), 2.10 (m, 1H, −$CH_2CH_2CH_3$), 2.65 (m, 1H, cy), 2.79 (m, 1H, −$CH_2CH_2CH_3$), 3.12 (m, 1H, R*H*C=CHPh−), 3.31 (s, 3H, O*Me*), 3.36 (s, 3H, O*Me*), 5.00 (d, 6.4, 1H, cy), 5.07 (d, 7.2, 1H, cy), 5.92 (d, 12.6, 1H, RHC=C*H*Ph−), 6.09 (d, 7.2, 1H, cy), 6.53 (d, 8.3, 1H, backbone), 6.61 (d, 8.1, 1H, backbone), 6.83 (dd, 1H, H_2C=CR*Ph*−), 6.91−8.09 (m, 24H).

Synthesis of 9. Phenylacetylene (5 μL, 0.046 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(*p*-cymene)]-$(SbF_6)_2$ (**4**) (30.0 mg, 0.023 mmol) in 1 mL of 1,2-$C_2H_4Cl_2$. After 2.5 h at room temperature the ^{31}P NMR spectrum showed full conversion to the product. The solvent was evaporated in vacuo, and the resulting powder was washed with 5 × 1 mL of Et_2O. The orange product was dried in vacuo. Color: orange. Yield: 30.7 mg (96%). Anal. Calcd for $C_{56}H_{52}P_2O_2RuSb_2F_{12}$ (1391.5): C, 48.34; H, 3.77. Found: C, 48.29; H, 3.72. FAB-MS: calcd M^{2+}, 920.1; found M^{2+}, 919.1; M^{2+} − *p*-cymene, 785.0; M^{2+} − *p*-cymene − C_8H_7, 683.0. ^{31}P{^{1}H} NMR (298 K, CD_2Cl_2): 41.4 (d, $^2J_{PP}$ = 54), 45.0 (d, $^2J_{PP}$ = 54). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2): 17.6 (cy), 19.4 (cy), 24.5 (cy), 26.4 (cy), 47.0 (H_2C=CPhPh−), 55.3 (O*Me*), 55.4 (O*Me*), 93.1 (cy), 102.5 (cy), 108.8 (cy), 113.9 (backbone), 114.6 (backbone), 120.3, 120.9, 126.0−135.2, 147.9, 157.8 (backbone), 158.8 (backbone). ^{1}H NMR (298 K, CD_2Cl_2): −0.41 (m, 1H, cy), −0.22 (d, 6.6, 1H, cy), 0.53 (d, 7.0, 1H, cy), 1.50 (br s, 1H, cy), 3.34 (s, 3H, O*Me*), 3.42 (s, 3H, O*Me*), 3.42 (d, 1.10, 1H, H_2C=CPhPh−), 5.65 (d, 7.2, 1H, cy), 5.82 (d, 7.2, 1H, cy), 5.93 (s, 1H, H_2C=CPhPh−), 6.05 (d, 6.7, 1H, cy), 6.44 (d, 8.4, 1H, backbone), 6.53 (d, 8.3, 1H, backbone), 6.92−8.12 (m, 29H).

Synthesis of 10. 1-Octyne (7 μL, 0.048 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(benzene)]$(SbF_6)_2$ (**5**) (51.4 mg, 0.042 mmol) in 1 mL of CD_2Cl_2. The remaining orange solution was heated at 35 °C for 48 h. The solvent was evaporated in vacuo, and the resulting powder was washed with 5 × 1 mL of Et_2O. The orange product was dried in vacuo. Color: orange. Yield: 61.3 mg (95%). Anal. Calcd for $C_{52}H_{52}P_2O_2RuSb_2F_{12}$ (1343.5): C, 46.49; H, 3.90. Found: C, 46.83; H, 4.38−26. FAB-MS: calcd. M^{2+} 872.1; found M^{2+} − benzene − C_8H_{15} + 2SbF_6, 1029.1; M^{2+} − benzene − C_8H_{15} + SbF_6, 919.1; M^{2+} − benzene, 793.1; M^{2+} − benzene − C_8H_{15}, 683.0. ^{31}P-{^{1}H} NMR (298 K, CD_2Cl_2): 36.2 (d, $^2J_{PP}$ = 51), 45.8 (d, $^2J_{PP}$ = 51). ^{13}C{^{1}H} NMR (298 K, CD_2Cl_2): 14.0 (−$(CH_2)_5CH_3$), 22.6 (−$(CH_2)_4CH_2CH_3$),29.3(−$(CH_2)_3CH_2CH_2CH_3$),30.6(−$(CH_2)_2CH_2(CH_2)_2CH_3$), 31.7 (−$CH_2CH_2(CH_2)_3CH_3$), 45.5 (−$CH_2(CH_2)_4CH_3$), 55.1 (H_2C=CRPh−), 55.1 (O*Me*), 55.1 (O*Me*), 104,3 (benzene), 114.3 (backbone), 114.7 (backbone), 123.1 (backbone), 125.6 (backbone), 125.9 (backbone), 126.4 (backbone), 126.9 (backbone), 129.4−135.3, 137.4 (H_2C=*C*RPh−), 146.4 (H_2C=CR*Ph*−), 157.8 (backbone), 158.8 (backbone). ^{1}H NMR (298 K, CD_2Cl_2): 2.09 (m, 1H, −$CH_2(CH_2)_4CH_3$), 3.24 (m, 1H, −$CH_2(CH_2)_4CH_3$), 3.24 (s, 3H, O*Me*), 3.31 (d, 10.6, 1H, H_2C=CRPh−), 3.41 (s, 3H, O*Me*), 5.38 (s, 1H, H_2C=CRPh−), 6.14 (s, 6H, benzene), 6.43

(d, 8.4, 1H, backbone), 6.60 (d, 8.6, 1H, backbone), 6.98 (dd, 7.7, 11.5, 1H), 7.15−7.89 (m, 22H).

Synthesis of 11. 1-Pentyne (2.5 equiv, 10 μL, 0.048 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(benzene)]-$(SbF_6)_2$ (**5**) (47.4 mg, 0.038 mmol) in 1 mL of CD_2Cl_2. The remaining orange solution was heated at 35 °C for 48 h. The solvent was evaporated in vacuo, and the resulting powder was washed with 5 × 1 mL of Et_2O. The orange product was dried in vacuo. Color: orange. Yield: 47.5 mg (96%). Anal. Calcd for $C_{49}H_{46}P_2O_2RuSb_2F_{12}\cdot Et_2O$ (1301.5): C, 46.28; H, 4.11. Found: C, 46.28; H, 4.11. FAB-MS: calcd M^{2+} 830.0; found M^{2+} − benzene, 749.0; M^{2+} − benzene $-C_5H_9$, 683.0. $^{31}P\{^1H\}$ NMR (298 K, CD_2Cl_2): 36.2 (d, $^2J_{PP} = 51$), 45.7 (d, $^2J_{PP} = 51$). $^{13}C\{^1H\}$ NMR (298K, CD_2Cl_2): 13.8 ($-CH_2CH_2\mathit{C}H_3$), 23.6 ($-CH_2\mathit{C}H_2CH_3$), 47.4 ($-\mathit{C}H_2CH_2CH_3$), 55.2 (O*Me*), 55.4 (O*Me*), 55.4 ($H_2\mathit{C}$=CRPh−), 104.4 (benzene), 114.5 (backbone), 114.8 (backbone), 132.1 (backbone), 126.6 (backbone), 129.3−131.1, 132.2, 132.8, 133.1−134.0, 137.0 (H_2C=*C*RPh−), 146.2 (backbone), 157.9 (backbone), 158.9 (backbone). ^1H NMR (298 K, CD_2Cl_2): 0.77 (m, 1H, $-CH_2\mathit{C}H_2CH_3$), 0.89 (t, 7.5, 3H, $-CH_2CH_2\mathit{C}H_3$), 1.33 (m, 1H, $-CH_2\mathit{C}H_2CH_3$), 2.12 (m, 1H, $-\mathit{C}H_2CH_2CH_3$), 3.19 (m, 1H, $-\mathit{C}H_2CH_2CH_3$), 3.25 (s, 3H, O*Me*), 3.30 (d, 10.8, 1H, H_2C=CRPh−), 3.41 (s, 3H, O*Me*), 5.37 (s, 1H, H_2C=CRPh−), 6.18 (s, 6H, benzene), 6.43 (d, 8.5, 1H, backbone), 6.60 (d, 8.5, 1H, backbone), 6.97 (dd, 8.1, 11.0, 1H), 7.13−7.93 (m, 22H).

Synthesis of 12. Phenylacetylene (10 μL, 0.091 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(benzene)]$(SbF_6)_2$ (**5**) (39.5 mg, 0.032 mmol) in 0.5 mL of CD_2Cl_2. The remaining orange solution was heated at 35 °C for 3 h. The solvent was evaporated in vacuo, and the resulting powder was washed with 5 × 1 mL of Et_2O. The orange product was dried in vacuo. Color: orange. Yield: 41.5 mg (97%). Anal. Calcd for $C_{52}H_{44}P_2O_2$-$RuSb_2F_{12}$ (1335.4): C, 47.72; H, 3.86. Found: C, 47.38; H, 3.62. FAB-MS: calcd M^{2+}, 884.1; found M^{2+} − benzene + SbF_6, 1021.7; M^{2+} − benzene, 785.9. $^{31}P\{^1H\}$ NMR (298 K, CD_2Cl_2): 36.4 (d, $^2J_{PP} = 53$), 46.0 (d, $^2J_{PP} = 53$). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2): 51.0 ($H_2\mathit{C}$=CPhPh−), 55.4 (O*Me*), 55.6 (O*Me*), 114.5 (backbone), 115.0 (backbone), 123.6 (backbone), 125.8 (backbone), 125.8 (backbone), 126.2 (backbone), 126.7(backbone), 129.9−133.4 (overlapping), 147.1 (H_2C=CPh*Ph*−), 158.0 (backbone),159.2 (backbone). ^1H NMR (298 K, CD_2Cl_2): 2.98 (d, 10.5, 1H, H_2C=CPhPh−), 3.31 (s, 3H, O*Me*), 3.47 (s, 3H, O*Me*), 5.64 (s, 6H, benzene), 6.18 (s, 1H, H_2C=CPhPh−), 6.42−8.59 (m, 30H).

Synthesis of 15. 2-Methyl-3-butyn-2-ol (6 μL, 0.101 mmol) was added to a solution of [Ru({S}-MeO−Biphep)(*p*-cymene)]-$(SbF_6)_2$ (**4**) (61.4 mg, 0.048 mmol) in 1.5 mL of CD_2Cl_2. The remaining solution changed color from red to yellow. ^{31}P NMR indicated after 1.5 h full conversion to the product. The solvent was evaporated in vacuo, and the remaining powder was washed with 3 × 1 mL of Et_2O, upon which the color changed to purple. The purple powder was dried at in vacuo. Color: orange. Yield: 58.6 mg (90%). Anal. Calcd for $C_{53}H_{52}P_2O_2$-$RuSb_2F_{12}$ (1355.49): C, 46.96; H, 3.87. Found: C, 46.80; H, 3.96. FAB-MS: calcd M^{2+}, 884.1; found M^{2+}, 885.2; M^{2+} − *p*-cymene, 749.8; M^{2+} − *p*-cymene − C_5H_6, 683.1. $^{31}P\{^1H\}$ NMR (298 K, CD_2Cl_2): 31.9 (d, $^2J_{PP} = 38$), 47.7 (d, $^2J_{PP} = 38$). ^{13}C-$\{^1H\}$ NMR (298 K, CD_2Cl_2): 21.9 (cy), 20.2 (cy), 23.0 (cy), 32.3 (cy), 38.3 (CCC*Me*$_2$), 55.7 (O*Me*), 56.1 (O*Me*), 105.5 (cy), 107.2 (cy), 108.8 (cy), 114.3 (cy), 114.3 (backbone), 114.4 (backbone), 120.6, 120.1, 123.4, 126.1, 129.5−133.3 (overlapping), 158.3 (backbone), 159.9 (backbone), 178.2 (CC*C*Me$_2$), 204.0 (C*C*C-Me$_2$), 305.1 (*C*CCMe$_2$). ^1H NMR (298 K, CD_2Cl_2): 1.02 (d, 7.0, 3H, cy), 1.49 (d, 7.0, 3H, cy), 1.81 (s, 6H, CCC*Me*$_2$), 2.04 (br s, 3H, cy), 2.90 (m, 1H, cy), 3.44 (s, 3H, *Me*O), 3.61 (s, 3H, O*Me*), 4.72 (d, 7.2, 1H, cy), 4.87 (d, 6.5, 1H, cy), 6.57 (d, 8.6, 1H, backbone), 6.81−7.77 (m, 27H).

Pent-1-enyl Ester (cat 4). Benzoic acid (105.0 mg, 0.86 mmol), 1-pentyne (85 μL, 0.86 mmol), and catalyst **4** (55.7 mg, 0.043 mmol) in 1 mL of 1,2-$C_2H_4Cl_2$ were stirred at 35 °C for 96 h in a closed ampule under inert atmosphere (Ar). The product was purified by preparative TLC (eluent 95% hexane/5% ethyl acetate) to afford 39.3 mg (24%) of the pent-1-enyl ester (cis:trans, 69%:31%).

Pent-1-en-yl Ester (cat 5). Benzoic acid (104.8 mg, 0.86 mmol), 1-pentyne (85 μL, 0.86 mmol), and catalyst **5** (55.3 mg, 0.045 mmol) in 1 mL of 1,2-$C_2H_4Cl_2$ were stirred at 35 °C for 96 h in a closed ampule under inert atmosphere (Ar). The product was purified by preparative TLC (eluent 95% hexane/5% ethyl acetate) to afford 29.4 mg (18%) of the pent-1-enyl ester (cis:trans, 75%:25%).

Characterization of Pent-1-en-yl Ester. $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): (major product, cis-product) 14.1, 22.8, 27.1, 115.1, 128.9, 129.9, 130.3, 133.8, 134.7, 164.0; (minor product, trans product) 14.0, 23.1, 29.8, 115.9, 128.8, 129.7, 130.3, 133.7, 136.1, 164.3. ^1H NMR (298 K, $CDCl_3$): 0.97 (t, 7.4), 0.99 (t, 7.4), 1.41−1.57, 2.08 (m), 2.30 (m), 5.04 (dt, 7.4, 6.4), 5.63 (dt, 12.3, 7.7), 7.30 (m, 6.4), 7.34 (m, 12.3), 7.44−7.54, 7.57−7.66, 8.08−8.16.

Oct-1-enyl Ester (cat 4). Benzoic acid (106.0 mg, 0.87 mmol), 1-octyne (130 μL, 0.88 mmol), and catalyst **4** (54.6 mg, 0.044 mmol) in 1 mL of 1,2-$C_2H_4Cl_2$ were stirred at 60 °C for 24 h in a closed ampule under inert atmosphere (Ar). The reaction mixture was washed with aqueous $NaHCO_3$ solution and dried over $MgSO_4$. The product was purified by silica gel chromatography (eluent 95% hexane/5% ethyl acetate) to afford 135.7 mg (71%) of the oct-1-enyl ester (cis:trans, 73%:27%).

Oct-1-enyl Ester (cat 5). Benzoic acid (105.4 mg, 0.86 mmol), 1-octyne (130 μL, 0.88 mmol), and catalyst **5** (56.0 mg, 0.043 mmol) in 1 mL of 1,2-$C_2H_4Cl_2$ were stirred at 60 °C for 24 h in a closed ampule under inert atmosphere (Ar). The reaction mixture was washed with aqueous $NaHCO_3$ solution and dried over $MgSO_4$. The product was purified by silica gel chromatography (eluent 95% hexane/5% ethyl acetate) to afford 122.4 mg (64%) of the oct-1-enyl ester (cis:trans, 80%:20%).

Oct-1-enyl Ester (cat 15). Benzoic acid (53.9 mg, 0.44 mmol), 1-octyne (65 μL, 0.44 mmol), and catalyst **15** (31.2 mg, 0.023 mmol) in 0.5 mL of 1,2-$C_2H_4Cl_2$ were stirred at 60 °C for 24 h in a closed ampule under inert atmosphere (Ar). The reaction mixture was washed with aqueous $NaHCO_3$ solution and dried over $MgSO_4$. The product was purified by silica gel chromatography (eluent 95% hexane/5% ethyl acetate) to afford 60.6 mg (62%) of the oct-1-enyl ester (cis:trans, 70%:30%).

Characterization Oct-1-enyl Ester. $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): (major product, cis-product) 14.5, 23.0, 25.0, 29.3, 29.6, 32.7, 115.3, 128.9, 129.9, 130.3, 133.8, 134.6, 164.0; (minor isomer, trans-product) 14.5, 23.1, 27.8, 29.2, 30.0, 32.0, 116.1, 128.8, 129.8, 133.7, 136.0, 164.0. ^1H NMR (298 K, $CDCl_3$): 0.81−1.00 (m), 1.20−1.55 (m), 2.10 (minor isomer, m), 2.32 (major isomer, m), 5.03 (major isomer, dt, 7.4, 6.4), 5.63 (minor isomer, dt, 12.5, 7.4), 7.29 (major isomer, dt, 6.4, 1.5), 7.34 (minor isomer, dt, 12.5, 1.5), 7.44−7.54 (m), 7.56−7.66 (m), 8.09−8.17 (m).

Synthesis of Octyne-d_1. To 1-octyne (1 mL, 6.8 mmol) was slowly added MeLi (5 mL, 0.1584 M in Et_2O). After 0.5 h stirring, the reaction mixture was quenched with 5 mL of D_2O. The volume of the reaction mixture was increased by adding 5 mL of dried Et_2O. The two liquid layers were separated, and the Et_2O layer was dried over $MgSO_4$. Evaporation of the Et_2O lead to the colorless product. ^2H NMR (298 K, acetone): 2.23 (br s). ^1H NMR (298 K, acetone-d_6): 0.90 (3H, t, 6.9), 1.22−1.57 (8H, m), 2.16 (2H, t, 6.6).

Catalytic Reaction with Octyne-d_1. Benzoic acid (105.7 mg, 0.87 mmol), octyne-d_1 (130 μL, 0.88 mmol), and catalyst **4** (54.0 mg, 0.043 mmol) in 1 mL of 1,2-$C_2H_4Cl_2$ were stirred at 60 °C for 24 h. The same conditions and workup as for catalysis with 1-octyne were applied. ^2H NMR (298 K, acetone):

5.09 (47%, br s), 5.70 (16%, br s), 7.31 (37%, br s). ^{1}H NMR (298 K, acetone-d_6): 0.80−0.99 (m), 1.21−1.57 (m), 2.10 (minor isomer, m), 2.32 (major isomer, m), 5.08 (major isomer, dt, 7.4, 6.4), 5.58 (minor isomer, dt, 12.5, 7.4), 7.27 (major isomer, dt, 6.4, 1.5), 7.33 (minor isomer, dt, 12.5, 1.5), 7.51−7.60 (m), 7.64−7.73 (m), 8.05−8.15 (m).

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Supporting Information Available: Atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters and calculated hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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