Ruthenium Tris(pyrazolyl)borate Complexes. 14.[1] Synthesis and Characterization of (Allyloxy)carbene Complexes

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Summary: *Treatment of RuTp(dmso)$_2$Cl with an excess of HC≡CR (R = Ph, C$_6$H$_9$, COOMe, n-Hex) and allyl alcohol in toluene at reflux affords the (allyloxy)carbene complexes RuTp(=C(CH$_2$R)OCH$_2$CH=CH$_2$)Cl in good yields. With R = C$_7$H$_{15}$, in addition to the carbene complex, also RuTp(η^3(O,C,C)-H$_2$C=CHCH$_2$COC$_7$H$_{15}$)-Cl and the free ketone 4-dodec-1-enone could be isolated. In the case of R = SiMe$_3$, RuTp(COD)Cl instead of RuTp(dmso)$_2$Cl had to be used as the starting material so as to obtain the corresponding (allyloxy)carbene. Representative X-ray structures are reported.*

Introduction

Transition-metal vinylidene complexes have been the subject of recent investigations. Interest in these compounds stems from their potential as reactive intermediates in organic and organometallic synthesis as well as in catalytic processes.[2] A key characteristic of vinylidene complexes is the electrophilicity of the α-carbon, which adds, often easily, amines,[2d,3] alcohols,[2c,3,4] phosphines,[5] and even fluoride.[2c] A noteworthy reaction in this regard is the RuCp(PPh$_3$)$_2$Cl-catalyzed coupling of allylic alcohols and terminal alkynes to yield β,γ-unsaturated ketones.[2k] According to Trost et al., this process might involve addition of allylic alcohol to a vinylidene complex to give (allyloxy)carbene intermediates. None of these species, however, could be isolated or spectroscopically detected in this particular case, but a related ruthenium (allyloxy)carbene complex has been reported recently.[6] Worthy of note is the fact that tungsten (allyloxy)carbene complexes have been reported which, on thermolysis, give β,γ-unsaturated ketones.[7]

Herein we report the addition of allyl alcohol to terminal alkynes mediated by RuTp(dmso)$_2$Cl (dmso = dimethyl sulfoxide) to give stable (allyloxy)carbene complexes. The latter are possible intermediates on the pathway to β,γ-unsaturated ketones. X-ray structures of representative compounds are given.

Results and Discussion

The reaction of RuTp(COD)Cl with 2 equiv of dmso in boiling dmf (dmf = dimethylformamide) for 2 h affords RuTp(dmso)$_2$Cl (**1**) in 81% isolated yield as a thermally robust air-stable yellow solid. Characterization was by a combination of elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In addition, the solid-state structure was determined by single-crystal X-ray diffraction. An ORTEP diagram is depicted in Figure 1 with important bond distances reported in the caption. The coordination geometry of **1** is approximately octahedral with both dmso ligands S-bonded. The Ru−S(1) and Ru−S(2) bond distances are 2.250(1) and 2.288(1) Å, respectively. The two Ru−N(Tp) bond lengths trans to the dmso ligands are longer (Ru−N(2) = 2.135(2) Å, Ru−N(4) = 2.102(2) Å) than that trans to the chloride ligand (Ru−N(6) = 2.076(2) Å). The Ru−Cl bond of 2.414(1) Å is comparable to that found in other Ru(II) Tp complexes, e.g., 2.409(3) Å in [RuTp(PPh$_3$)$_2$(Cl)],[8] 2.401(1) Å in [RuTp(PPh$_3$)(Cl)(=C=CHPh)],[9] and 2.418-(2) Å in [RuTp(PPh$_3$)(Cl)(CO)].[10]

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(1) Part 13: Slugovc, C.; Gemel, C.; Shen, J.-Y.; Doberer, D.; Schmid, R.; Kirchner, K.; Mereiter, K. *Monatsh. Chem.* **1999**, *130*, 363.

(2) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Trost, B. M. *Angew. Chem.* **1995**, *107*, 285. (c) Ting, P. C.; Lin, Y. C.; Lee, G. H.; Cheng, M. C.; Wang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6433. (d) Bianchini, C.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1995**, *14*, 3152. (e) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272. (f) Werner, H.; Wiedmann, R.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1997**, *3*, 127. (g) Duran, R. P.; Amorebieta, V. T.; Colussi, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3154. (h) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (i) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604. (j) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476. (k) Trost, B. M.; Kulawiec, R. *J. Am. Chem. Soc.* **1992**, *114*, 5579. (l) Wang, Y.; Finn, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 8045. (m) Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1997**, 507.

(3) (a) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585. (b) Barrett, G. M.; Carpenter, N. E. *Organometallics* **1987**, *6*, 2249. (c) Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1986**, *317*, C25. (d) Gamasa, M. P.; Gimeno, J.; Gonzalez-Cueva, M.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1996**, 2547. (e) Nombel, P.; Lugan, N.; Mathieu, R. *J. Organomet. Chem.* **1995**, *503*, C22. (f) Bruce, M. I.; Swincer, A. G.; Wallis, R. C. *J. Organomet. Chem.* **1979**, *171*, C5.

(4) (a) Barrett, A. G. M.; Carpenter, N. E. *Organometallics* **1987**, *6*, 2249. (b) Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1986**, *317*, C25. (c) Nombel, P.; Lugan, N.; Mathieu, R. *J. Organomet. Chem.* **1995**, *503*, C22.

(5) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096.

(6) Esteruelas, M. A.; Gómez, A. V.; López, A. V.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 2297.

(7) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736.

(8) Burns, I. D.; Hill, A. F.; Williams, D. J. *Inorg. Chem.* **1996**, *35*, 2865.

(9) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.

(10) Slugovc, C.; Sapunov, V. N.; Wiede, P.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4209.

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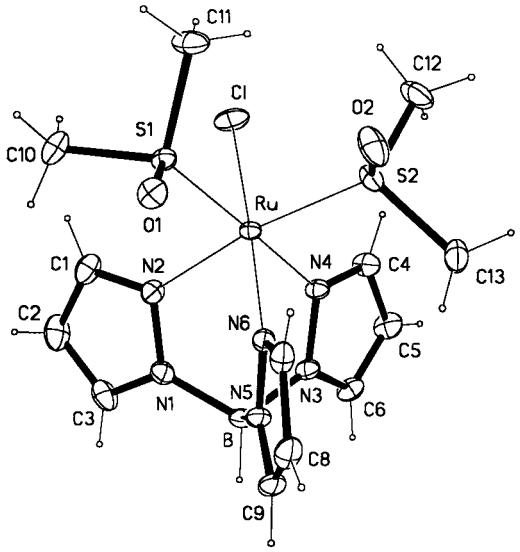
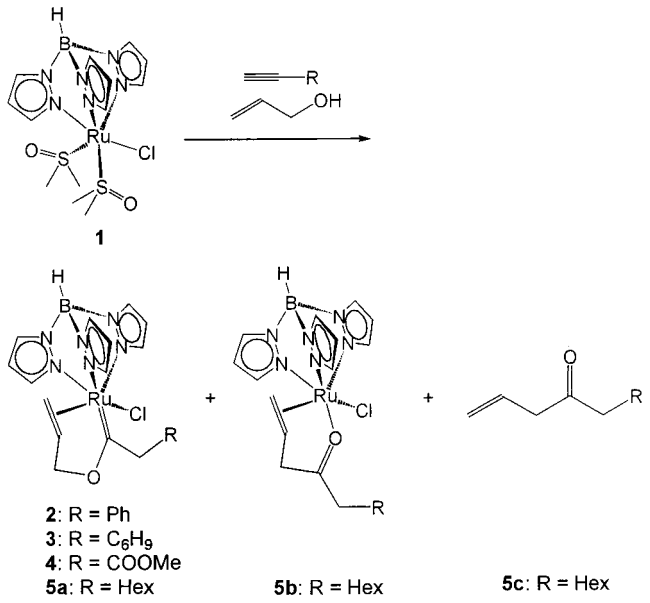


Figure 1. Structural view of $RuTp(dmso)_2Cl\cdot$(solvent) (**1**·(solvent)). Selected bond lengths (Å) and angles (deg): Ru−N(2) = 2.135(2), Ru−N(4) = 2.102(2), Ru−N(6) = 2.076(2), Ru−S(1) = 2.288(1), Ru−S(2) = 2.250(1), Ru−Cl = 2.414(1); N(6)−Ru−N(4) = 88.6(1), N(6)−Ru−N(2) = 87.3(1), N(4)−Ru−N(2) = 82.1(1).

Scheme 1



Treatment of **1** with an excess of HC≡CR (R = Ph, C_6H_9, COOMe, *n*-Hex) and allyl alcohol in toluene at reflux affords, on workup, the (allyloxy)carbene complexes $RuTp(=C(CH_2R)OCH_2CH=CH_2)Cl$ (**2**−**4** and **5a**) in good yields (Scheme 1). With $HC\equiv CSiMe_3$, the reaction was not clean, with just intractable materials obtained. When RuTp(COD)Cl (COD = 1,5-cyclooctadiene) was used as the starting material instead of **1**, despite the fact that COD is more inert than dmso, also $HC\equiv CSiMe_3$ was converted into the expected (allyloxy)carbene complex $RuTp(=C(CH_2SiMe_3)OCH_2CH=CH_2)Cl$ (**6a**). However, this product was not pure but contained about 10% of the hydrolyzed complex $RuTp(=C(CH_3)OCH_2CH=CH_2)Cl$ (**6b**) (Scheme 2). This latter complex was obtained quantitatively in a solution of **6a** in neat MeOH, on standing overnight at room temperature.

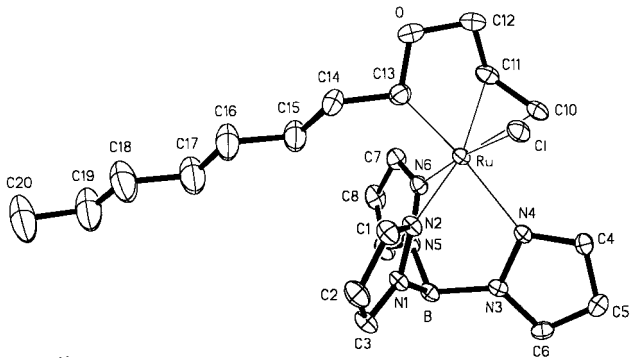
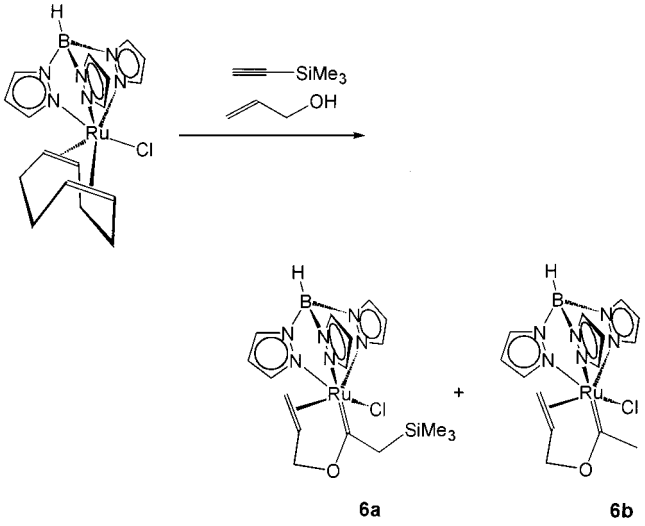


Figure 2. Structural view of $RuTp(=C(CH_2Hex^n)OCH_2CH=CH_2)Cl$ (**5a**). Selected bond lengths (Å) and angles (deg): Ru−N(2) = 2.107(2), Ru−N(4) = 2.204(2), Ru−N(6) = 2.104(1), Ru−C(10) = 2.214(2), Ru−C(11) = 2.199(2), Ru−C(13) = 1.928(2), Ru−Cl = 2.423(1), C(10)−C(11) = 1.377(3); N(6)−Ru−N(4) = 85.1(1), N(6)−Ru−N(2) = 88.8(1), N(4)−Ru−N(2) = 80.7(1).

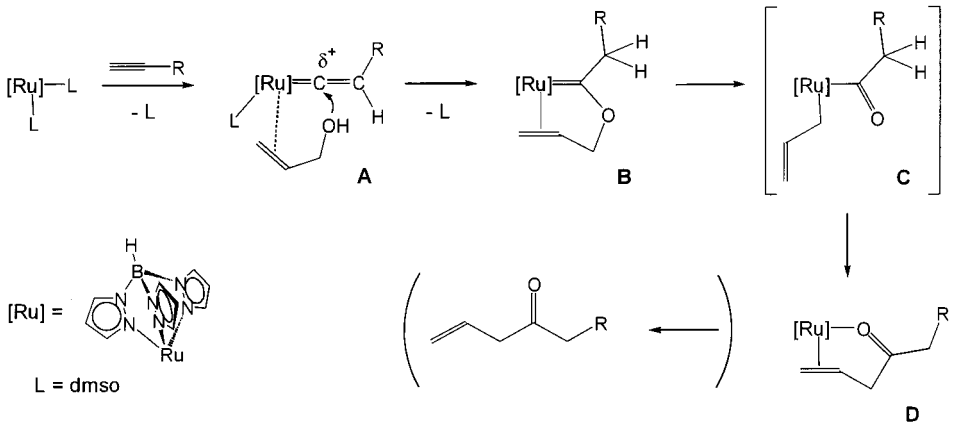
Scheme 2



All these complexes were again characterized by a combination of elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H NMR spectra of **2**−**4**, **5a**, and **6** display the characteristic resonances of coordinated olefin. Thus, for **2**, the terminal protons give rise to two doublets centered at 5.27 (1H, $^3J_{HH,trans}$ = 12.1 Hz) and 3.86 ppm (1H, $^3J_{HH,cis}$ = 8.7 Hz) and a multiplet centered at 4.92 (1H). The CH_2 moiety adjacent to the phenyl substituent exhibits two doublets centered at 4.61 (1H, ^2J = 14.7 Hz) and 4.23 ppm (1H, ^2J = 14.1 Hz). The ^1H NMR spectra of the other complexes are similar. For the $^{13}C\{^1H\}$ NMR spectra of **2**−**6**, it is sufficient to point out that the resonances due to the carbene carbon are characteristically downfield-shifted in the range of 319−332 ppm.

The molecular structures of complexes **5a** and **6a**·$^1/_2C_6H_5CH_3$ have been determined by X-ray crystallography (Figures 2 and 3). Important bond distances and angles are reported in the figure captions. The overall octahedral structure of both complexes is very similar to that of **1**. The two Ru−N(Tp) bond lengths cis to the carbene moiety are shorter (**5a**, Ru−N(2) = 2.107(2) Å, Ru−N(6) = 2.104(2) Å; **6a**·$^1/_2C_6H_5CH_3$, Ru−N(2) = 2.105(5) Å, Ru−N(6) = 2.195(5) Å) than that trans to the carbene moiety (**5a**, Ru−N(4) = 2.204(2)

Scheme 3



Å, **6a**·$^1/_2C_6H_5CH_3$, Ru−N(4) = 2.195(5) Å) due to the strong trans influence of the strong π-accepting carbene. The olefin moiety of the (allyloxy)carbene ligand in both complexes is bonded unsymmetrically to the metal center, with the Ru−C bonds to the internal and terminal carbon atoms C(11) and C(10) being, in the case of **5a**, 2.199(2) and 2.214(2) Å and, in the case of **6a**·$^1/_2C_6H_5CH_3$, 2.188(7) and 2.203(6) Å, respectively. The C=C bond is almost orthogonal to the Ru−Cl bond. The Ru−C(13) distances for **5a** and **6a**·$^1/_2C_6H_5CH_3$ are 1.928(2) and 1.918(7) Å, respectively. For comparison, the Ru=C bond distances in the RuTp carbene complexes RuTp(=CCH_2Ph-aapy)Cl·O$(C_2H_5)_2$ (aapy = 2-acetamidopyridine),[11] RuTp$(PCy_3)_2(Cl)_2$(=CHPh),[12] and RuTp(dippe) (=C(OMe)CH_2COOMe)]BPh_4 (dippe = 1,2-bis(diisopropylphosphine)ethane)[13] are significantly shorter, being 1.897(2), 1.878, and 1.86(2) Å, respectively.

From the reaction of **1** with HC≡CC_6H_{13}, in addition to **5a**, also RuTp(η^3(*O,C,C*)-H_2C=$CHCH_2COC_7H_{15}$)Cl (**5b**) and free 4-dodec-1-enone (**5c**) could be isolated in 7 and 25% yields, respectively (Scheme 1). The ^{1}H NMR spectrum of **5b** reveals two doublets of doublets for the terminal vinyl protons centered at 5.59 ($^3J_{HH,trans}$ = 12.1 Hz, $^2J_{HH}$ = 1.8 Hz) and 4.15 ppm ($^3J_{HH,cis}$ = 7.9 Hz, $^2J_{HH}$ = 1.8 Hz). In the ^{13}C{^{1}H} NMR spectrum the characteristic resonance of the ketonic carbonyl carbon atom is observed at 234.3 ppm, compared with 209.9 ppm in free 4-dodec-1-enone.

A mechanism accounting for the formation of (allyloxy)carbene complexes and β,γ-unsaturated ketones is suggested in Scheme 3. After dissociation of one dmso ligand, the vinylidene intermediate **A** is formed. It is worth noting that in complexes of the type RuTp$(L)_2$Cl (L = PPh_3, pyridine, dmso), in contrast to the isoelectronic complex RuCp$(PPh_3)_2$Cl, L is substitutionally more labile than Cl. In fact, the neutral vinylidene complexes RuTp(PPh_3)(Cl)(=C=CHR) (R = Ph, *n*-Bu, *t*-Bu, $SiMe_3$, C_6H_9, COOEt), but no RuCp(PPh_3)(Cl)-(=C=CHR), have been reported,[9,10] The next step of the reaction is nucleophilic attack of the allyl alcohol at the electrophlic α-carbon atom of the vinylidene moiety and

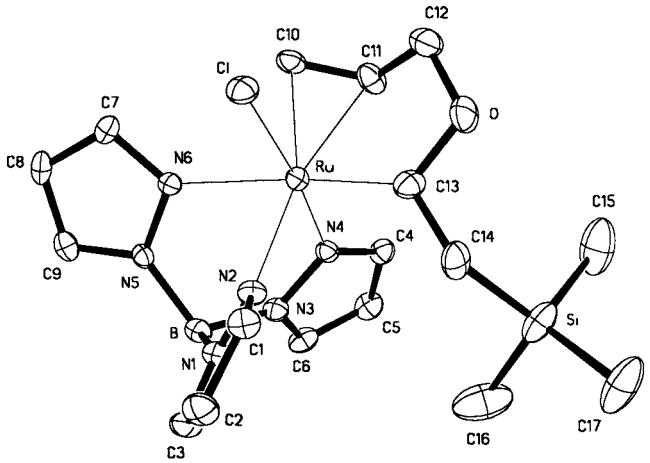


Figure 3. Structural view of RuTp(=$C(CH_2SiMe_3)CH_2$-$CH=CH_2$)Cl·$^1/_2C_6H_5CH_3$ (**6a**·$^1/_2C_6H_5CH_3$). Selected bond lengths (Å) and angles (deg): Ru−N(2) = 2.105(5), Ru−N(4) = 2.095(5), Ru−N(6) = 2.195(5), Ru−C(10) = 2.203-(6), Ru−C(11) = 2.188(7), Ru−C(13) = 1.918(7), Ru−Cl = 2.414(1), C(10)−C(11) = 1.360(10); N(6)−Ru−N(4) = 85.8-(2), N(6)−Ru−N(2) = 80.3(2), N(4)−Ru−N(2) = 88.5(2).

loss of dmso to give the (allyloxy)carbene complexes **B**. It is unclear whether precoordination of the allyl alcohol is necessary for the addition step to occur in these systems. In the case of RuCp such a precoordination step has been proposed,[2j,k] while for a related allenylidene complex a precoordination step was not required.[6]

For **B** two major decomposition pathways have been observed. In the case of L = dmso, exclusively oxidative addition is observed with rupture of the C−O bond to give the allyl acyl species **C**. For steric reasons (seven-coordinate species are not known in RuTp chemistry), we assume that the allyl moiety is bound in an η^1 fashion, although an η^3 bonding mode cannot be conclusively ruled out. Reductive elimination then leads to complex **D**, featuring an η^3(O,C,C)-bound β,γ-unsaturated ketone ligand which may be eventually liberated at elevated temperatures. A 1,2-hydrogen shift has been recently observed for L = pyridine and HC≡CPh as the alkyne, leading to an allyl vinyl ether.[14]

In summary, we have shown that RuTp$(dmso)_2$Cl reacts with allyl alcohol and terminal alkynes to give

(11) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1998**, *17*, 827.
(12) Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, 17, 5384.
(13) Tenorio, M. A. J.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1997**, *16*, 5528.
(14) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998.

stable (allyloxy)carbene complexes. These species are key intermediates on the pathway to β,γ-unsaturated ketones. In fact a complex containing a β,γ-unsaturated ketone ligand could be isolated, as well as free ketone.

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[15] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. For column chromatography silica gel (grade 60, 70−230 mesh, 60 Å) purchased from Merck was used. RuTp(COD)Cl was prepared according to the literature.[16] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalyses were done by the Microanalytical Laboratories, University of Vienna.

Synthesis. RuTp(dmso)$_2$Cl (1). To a suspension of RuTp(COD)Cl (300 mg, 0.664 mmol) in dmf (3 mL) was added dmso (100 μL, 1.328 mmol), and the reaction mixture was kept at 170 °C for 2 h. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (1 mL). Addition of *n*-hexane afforded a bright yellow precipitate, which was collected on a glass frit, washed with *n*-hexane (2 × 2 mL), and dried under vacuum. Yield: 271 mg (81%). Anal. Calcd for $C_{13}H_{22}BClN_6O_2RuS_2$: C, 30.87; H, 4.38; N, 16.61. Found: C, 30.99; H, 4.52; N, 16.48. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.12 (d, 1H, $^3J_{HH}$ = 2.3 Hz, Tp), 7.93 (d, 2H, $^3J_{HH}$ = 2.3 Hz, Tp), 7.85 (d, 1H, $^3J_{HH}$ = 2.5 Hz, Tp), 7.71 (d, 2H, $^3J_{HH}$ = 2.5 Hz, Tp), 6.33 (pt, 1H, $^3J_{HH}$ = 2.3 Hz, Hz, Tp), 6.25 (pt, 2H, $^3J_{HH}$ = 2.3 Hz, Tp), 3.47 (s, 6H, dmso), 2.95 (s, 6H, dmso). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 147.3 (1C, Tp), 144.8 (2C, Tp), 137.8 (1C, Tp), 136.8 (2C, Tp), 107.1 (1C, Tp), 106.8 (2C, Tp), 45.8 (2C, dmso), 45.7 (2C, dmso).

RuTp(=C(CH$_2$Ph)OCH$_2$CH=CH$_2$)Cl (2). To a solution of **1** (100 mg, 0,198 mmol) in toluene (4 mL) were added HC≡CPh (228 μL, 1.977 mmol) and allyl alcohol (403.4 μL, 5.9 mmol), and the reaction mixture was refluxed for 20 h. The solvent was then removed under vacuum and the residue dried under vacuum. The crude product was purified via column chromatography (silica gel). The first yellow band was eluted with CH_2Cl_2 (75 mg, containing intractable materials and some polyphenylacetylene) and was discarded. The second deep yellow band, eluted with acetone, was collected. Evaporation of the solvent, extraction of the residue with *n*-hexane, and evaporation of the *n*-hexane gave analytically pure **2**. Yield: 85 mg (84%). Anal. Calcd for $C_{20}H_{22}BClN_6ORu$: C, 47.12; H, 4.35; N, 16.49. Found: C, 47.19; H, 4.53; N, 16.66. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.28 (d, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 8.03 (d, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 7.80 (d, $^3J_{HH}$ = 2.6 Hz, 1H, Tp), 7.71 (d, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 7.64 (d, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 7.15 (m, 3H, Ph^{2,6}, Tp), 6.81−6.77 (m, 3H, Ph^{3,4,5}), 6.33 (m, 2H, Tp), 5.95 (dd, $^3J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 5.45 (dd, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 4.3 Hz, 1H, CH$_2$=CHCH_2O), 5.27 (d, $^3J_{HH,trans}$ = 12.1 Hz, 1H, CH_2=CHCH$_2$O), 4.99−4.85 (m, 1H, CH$_2$=CHCH$_2$O), 4.73 (m, 1H, CH$_2$=CHCH_2O), 4.61 (d, $^2J_{HH}$ = 14.7 Hz, 1H, CH_2Ph), 4.24 (d, $^2J_{HH}$ = 14.7 Hz, 1H, CH_2Ph), 3.86 (d, $^3J_{HH,cis}$ = 8.7 Hz, 1H, CH_2=CHCH$_2$O). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 325.7 (1C, Ru=*C*), 144.9 (1C, Tp), 143.6 (1C, Tp), 142.5 (1C, Tp), 136.9 (1C, Tp), 135.7 (1C, Tp), 135.0 (1C, Tp), 134.4 (1C, Ph^1), 130.0 (2C, Ph^{2,6}), 128.9 (2C, Ph^{3,5}), 126.9 (1C, Ph^4), 106.7 (1C, Tp), 106.6 (1C, Tp), 106.5 (1C, Tp), 91.8 (1C, CH$_2$=*C*HCH$_2$O), 79.8 (1C, *C*H$_2$=CHCH$_2$O), 78.9 (1C, CH$_2$=CHCH$_2$O), 57.7 (1C, *C*H$_2$Ph).

RuTp(=C(CH$_2$(1-cyclohexenyl)OCH$_2$CH=CH$_2$)Cl (3). This complex was prepared in a fashion similar to that for **2**, with **1** (100 mg, 0.198 mmol), 1-ethynylcyclohexene (70 μL, 0.593 mmol), and allyl alcohol (135 μL, 1.977 mmol) as the starting materials. The crude product was purified via column chromatography (silica gel) with CH_2Cl_2 as the eluant. The second yellow band was collected. Evaporation of the solvent, extraction of the residue with *n*-hexane, and evaporation of the *n*-hexane gave analytically pure **3**. Yield: 45 mg (44%). Anal. Calcd for $C_{20}H_{26}BClN_6ORu$: C, 46.75; H, 5.10; N, 16.36. Found: C, 46.73; H, 5.33; N, 16.24. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.26 (d, $^3J_{HH}$ = 1.8 Hz, 1H, Tp), 7.93 (d, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 7.72 (d, $^3J_{HH}$ = 2.6 Hz, 1H, Tp), 7.68 (d, $^3J_{HH}$ = 2.6 Hz, 2H, Tp), 7.21 (d, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 6.32 (vt, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 6.28 (vt, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 6.15 (vt, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 5.51 (dd, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 4.4 Hz, 1H, CH$_2$=CHCH_2O), 5.25 (d, $^3J_{HH,trans}$ = 12.2 Hz, 1H, CH_2=CHCH$_2$O), 5.09−4.90 (m, 2H, cHex^2, CH$_2$=CHCH$_2$O), 4.70 (dd, $^3J_{HH}$ = 10.8 Hz, $^2J_{HH}$ = 9.7 Hz, 1H, CH$_2$=CHCH_2O), 3.87 (d, $^3J_{HH,cis}$ = 8.5 Hz, 1H, CH_2=CHCH$_2$O), 3.77 (d, $^2J_{HH}$ = 15.5, 1H, CH_2cHex), 3.60 (d, $^2J_{HH}$ = 15.5, 1H, CH_2cHex), 2.02−1.73 (m, 4H, cHex), 1.69−1.41 (m, 4H, cHex). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 328.9 (1C, Ru=*C*), 145.1 (1C, Tp), 143.8 (1C, Tp), 142.8 (1C, Tp), 137.3 (1C, Tp), 135.7 (1C, Tp), 135.1 (1C, Tp), 131.9 (1C, cHex^1), 126.5 (1C, cHex^2), 106.7 (1C, Tp), 106.6 (1C, Tp), 106.4 (1C, Tp), 91.5 (1C, CH$_2$=*C*HCH$_2$O), 79.0 (1C, *C*H$_2$=CHCH$_2$O), 78.6 (1C, CH$_2$=CH*C*H$_2$O), 60.6 (1C, *C*H$_2$-cHex), 30.2 (1C, cHex^3), 26.1 (1C, cHex^5), 23.5 (1C, cHex^4), 22.6 (1C, cHex^6).

RuTp(=C(CH$_2$COOMe)OCH$_2$CH=CH$_2$)Cl (4). This complex was prepared analogously to **2**, with **1** (100 mg, 0.198 mmol), propiolic acid methyl ester (53 μL, 0.593 mmol), and allyl alcohol (135 μL, 1.977 mmol) as the starting materials. Yield: 60 mg (62%). Anal. Calcd for $C_{16}H_{20}BClN_6O_3RuS$: C, 39.08; H, 4.10; N, 17.09. Found: C, 39.34; H, 4.28; N, 16.95. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.28 (d, $^3J_{HH}$ = 1.8 Hz, 1H, Tp), 7.84 (d, $^3J_{HH}$ = 2.1 Hz, 1H, Tp), 7.72 (d, $^3J_{HH}$ = 2.1 Hz, 1H, Tp), 7.69 (vt, $^3J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 2.5 Hz, 2H, Tp), 7.34 (d, $^3J_{HH}$ = 2.5 Hz, 1H, Tp), 6.34 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, Tp), 6.29 (vt, $^3J_{HH}$ = 2.1 Hz, 1H, Tp), 6.17 (vt, $^3J_{HH}$ = 2.5 Hz, 1H, Tp), 5.55 (dd, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, CH$_2$=CHCH_2O), 5.34 (d, $^3J_{HH,trans}$ = 12.5 Hz, 1H, CH_2=CHCH$_2$O), 5.24−5.06 (m, 1H, CH$_2$=CHCH$_2$O), 4.77 (dd, $^3J_{HH}$ = 10.5 Hz, $^2J_{HH}$ = 9.7 Hz, 1H, CH$_2$=CHCH_2O), 4.11 (d, $^2J_{HH}$ = 16.2, 1H, CH_2-COOMe), 3.93 (d, $^3J_{HH,cis}$ = 8.9 Hz, 1H, CH_2=CHCH$_2$O), 3.91 (d, $^2J_{HH}$ = 16.2, 1H, CH_2COOMe), 3.60 (s, 3H, COO*Me*). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 319.1 (1C, Ru=*C*), 167.6 (1C, *C*OOMe), 144.9 (1C, Tp), 143.9 (1C, Tp), 143.3 (1C, Tp), 137.5 (1C, Tp), 135.9 (1C, Tp), 135.3 (1C, Tp), 106.9 (1C, Tp), 106.8 (1C, Tp), 106.7 (1C, Tp), 93.2 (1C, CH$_2$=*C*HCH$_2$O), 81.3 (1C, *C*H$_2$=CHCH$_2$O), 79.5 (1C, CH$_2$=CH*C*H$_2$O), 56.7 (1C, *C*H$_2$-COOMe), 52.8 (1C, COO*Me*).

RuTp(=C(CH$_2$C$_6$H$_{13}$)OCH$_2$CH=CH$_2$)Cl (5a). This complex was prepared analogously to **2**, with **1** (300 mg, 0.593 mmol), 1-octyne (263 μL, 1.779 mmol), and allyl alcohol (202 μL, 2.966 mmol) as the starting materials. The yield of the crude product was 562 mg. The crude product was purified via column chromatography (silica gel) with CH_2Cl_2 as the eluant. The second yellow band was collected. Evaporation of the solvent, extraction of the residue with *n*-hexane, and evaporation of the *n*-hexane gave analytically pure **3**. Yield: 140 mg (46%). The *n*-hexane fraction was used for the isolation of 4-dodec-1-enone (**5c**) (see below). Anal. Calcd for $C_{20}H_{30}BClN_6ORu$: C, 46.39; H, 4.84; N, 16.23. Found: C, 46.57; H, 4.98; N, 16.12. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.27 (d, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 7.89 (d, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 7.72 (d, $^3J_{HH}$ = 2.5 Hz, 1H, Tp), 7.69 (m, 2H, Tp), 7.25 (d, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 6.33 (pt, $^3J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 6.28 (pt, $^3J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, Tp), 6.15 (pt, $^3J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, Tp), 5.50 (dd, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, H$_2$C=CHCH_2O), 5.25 (d, $^3J_{HH,trans}$ = 12.0 Hz, 1H, H_2C=

(15) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

(16) Ashworth, T. V.; Singleton. E.; Hough, J. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1809.

Table 1. Crystallographic Data for 1·(solvent), 5a, and 6a·$^1/_2C_6H_5CH_3$

	1·(solvent)	5a	6a·$^1/_2C_6H_5CH_3$
formula	$C_{13}H_{22}BClN_6O_2RuS_2$[a]	$C_{20}H_{30}BClN_6ORu$	$C_{20.5}H_{30}BClN_6ORuSi$
fw	505.82[a]	517.83	551.92
cryst size, mm	0.44 × 0.30 × 0.16	0.64 × 0.24 × 0.06	0.40 × 0.14 × 0.02
space group	$P2_1/c$ (No. 5)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	7.859(3)	8.272(3)	8.358(3)
b, Å	16.872(6)	8.836(3)	8.725(3)
c, Å	16.566(5)	17.443(6)	18.208(6)
α, deg		103.55(2)	95.19(2)
β, deg	102.30(2)	96.95(2)	95.94(2)
γ, deg		103.51(2)	103.79(2)
V, Å^3	2146(1)	1184.1(7)	1273.5(8)
F(000)	1024[a]	532	566
Z	4	2	2
ρ_{calcd}, g cm^{-3}	1.565[a]	1.452	1.439
T, K	299(2)	297(2)	298(2)
μ, mm^{-1} (Mo Kα)	1.069[a]	0.798	0.791
abs cor	multiscan	multiscan	multiscan
θ_{max}, deg	30	30	25
index ranges	$-11 \le h \le 10$	$-11 \le h \le 11$	$-9 \le h \le 9$
	$-23 \le k \le 23$	$-12 \le k \le 12$	$-10 \le k \le 10$
	$-22 \le l \le 23$	$-24 \le l \le 24$	$0 \le l \le 21$
no. of rflns measd	25 245	17 027	7423
no. of unique rflns	6221	6718	4475
no. of rflns $I > 2\sigma(I)$	5231	5712	3223
no. of params	275	279	280
R1(F) ($I > 2\sigma(I)$)[b]	0.023	0.028	0.059
R1(F) (all data)[b]	0.033	0.037	0.093
wR2(F^2) (all data)[b]	0.055	0.073	0.141
min/max diff Fourier peaks, e Å^{-3}	−0.44/0.40	−0.43/0.42	−0.74/1.24

[a] Without solvent (MeOH/dmso/dmf). [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

$CHCH_2O$), 5.06−4.91 (m, 1H, $H_2C{=}CHCH_2O$), 4.68 (vt, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, $H_2C{=}CHCH_2O$), 3.87 (d, $^3J_{HH,cis}$ = 8.6 Hz, 1H, $H_2C{=}CHCH_2O$), 3.16−2.84 (m, 2H, CH_2Hex^n), 1.79−1.14 (m, 10H), 0.87 (t, 3H). $^{13}C\{^1H\}$ (δ, $CDCl_3$, 20 °C): 332.5 (Ru=*C*), 144.8 (1C, Tp), 143.8 (1C, Tp), 142.7 (1C, Tp), 137.4 (1C, Tp), 135.6 (1C, Tp), 135.1 (1C, Tp), 106.7 (1C, Tp), 106.6 (1C, Tp), 106.5 (1C, Tp), 91.3 (1C, $H_2C{=}CHCH_2O$), 79.3 (1C, $H_2C{=}CHCH_2O$), 78.9 (1C, $H_2C{=}CHCH_2O$), 52.7 (1C, CH_2-Hex), 32.1 (1C, Hep[5]), 30.0 (1C, Hep[4]), 29.4 (1C, Hep[3]), 25.5 (1C, Hep[2]), 23.2 (1C, Hep[6]), 14.7 (1C, Hep[7]).

RuTp(η^3(*O,C,C*)-$H_2C{=}CHCH_2COC_7H_{15}$)Cl (5b). From the reacation above, the fourth yellow band (a third yellow band contained <5 mg of intractable materials) was collected. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (1 mL) and addition of *n*-hexane (5 mL) afforded a pale yellow precipitate which was collected on a glass frit and dried under vacuum. Yield: 23 mg (7%). Anal. Calcd for $C_{20}H_{30}BClN_6ORu$: C, 46.39; H, 4.84; N, 16.23. Found: C, 46.62; H, 4.88; N, 16.20. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.01 (d, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 7.91 (d, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 7.79 (d, $^3J_{HH}$ = 2.6 Hz, 1H, Tp), 7.72 (d, $^3J_{HH}$ = 2.6 Hz, 2H, Tp), 7.68 (d, $^3J_{HH}$ = 2.6 Hz, 1H, Tp), 7.55 (d, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 6.38 (vt, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 6.23 (vt, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 6.20 (vt, $^3J_{HH}$ = 2.2 Hz, 1H, Tp), 5.59 (dd, $^3J_{HH,trans}$ = 12.1 Hz, $^2J_{HH}$ = 1.8 Hz, 1H, $CH_2{=}CHCH_2O$), 5.55−5.41 (m, 1H, $CH_2{=}CHCH_2O$), 4.23 (dd, $^2J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 3.9, 1H, $CH_2{=}CHCH_2O$), 4.15 (dd, $^3J_{HH,cis}$ = 7.9 Hz, $^2J_{HH}$ = 1.8 Hz, 1H, $CH_2{=}CHCH_2O$), 3.56 (dd, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, $CH_2{=}CHCH_2O$), 2.71 (m, 2H, $COCH_2$), 1.79−1.29 (m, 10H, aliphatic protons), 0.89 (t, 3H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 234.3 (1C, *C*=O), 146.7 (1C, Tp), 143.2 (1C, Tp), 142.6 (1C, Tp), 137.4 (1C, Tp), 136.5 (1C, Tp), 134.9 (1C, Tp), 107.1 (1C, Tp), 106.5 (2C, Tp), 92.1 (1C, $CH_2{=}CHCH_2C{=}O$), 83.2 (1C, $CH_2{=}CHCH_2C{=}O$), 51.8 (1C, $CH_2{=}CHCH_2C{=}O$), 42.9 (1C, Hep[1]), 32.2 (1C, Hep[5]), 29.6 (1C, Hep[4]), 29.5 (1C, Hep[3]), 24.9 (1C, Hep[2]), 23.2 (1C, Hep[6]), 14.7 (1C, Hep[7]).

4-Dodec-1-enone (5c). The *n*-hexane fraction obtained during the preparation of **5a** was evaporated to dryness and dried under vacuum. Yield: 75 mg (25% with respect to 1-octyne). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.62; H 11.76. ^1H NMR (δ, $CDCl_3$, 20 °C): 6.03−5.86 (m, 1H, $CH_2{=}CHCH_2COHep^n$), 5.23−5.11 (m, 2H, $CH_2{=}CHCH_2COHep^n$), 3.19 (m, 2H, $CH_2{=}CHCH_2COHep^n$), 2.49−2.42 (m, 2H, $COCH_2Hex^n$), 1.32−1.27 (m, 10H, Hep^n), 0.89 (t, 3H, CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 209.7 ($CH_2{=}CHCH_2COHep^n$), 143.2 ($CH_2{=}CH{-}CH_2COHep^n$), 119.3 ($CH_2{=}CHCH_2COHep^n$), 48.4 ($CH_2{=}CHCH_2COHep^n$), 43.0 ($-COCH_2$-Hex^n), 32.3 (1C, Hep[5]), 29.8 (1C, Hep[4]), 29.7 (1C, Hep[3]), 24.7 (1C, Hep[2]), 23.3 (1C, Hep[6]), 14.7 (1C, Hep[7]).

RuTp(=C(CH_2SiMe_3)$CH_2CH{=}CH_2$)Cl (6a). A solution of RuTp(COD)Cl (200 mg, 0.437 mmol), (trimethylsilyl)acetylene (93 μL, 1.311 mmol), and allyl alcohol (149 μL, 2.185 mmol) in toluene (3 mL) was was heated at reflux for 20 h. After removal of the solvent under reduced pressure, the residue was dissolved in acetone (2 mL). Addition of *n*-hexane afforded a yellow precipitate, which was collected on a glass frit, washed with *n*-hexane (2 × 2 mL), and dried under vacuum. **6a** could not be isolated in pure form containing about 10% of the hydrolyzed complex **6b** (see below). ^1H NMR (δ, acetone-d_6, 20 °C): 8.17 (d, $^3J_{HH}$ = 2.4 Hz, 1H, Tp), 7.89 (d, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 7.87 (d, $^3J_{HH}$ = 2.4 Hz, 1H, Tp), 7.81 (d, $^3J_{HH}$ = 2.4 Hz, 1H, Tp), 7.77 (d, $^3J_{HH}$ = 2.4 Hz, 1H, Tp), 7.58 (d, $^3J_{HH}$ = 2.4 Hz, 1H, Tp), 6.33 (vt, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 6.29 (dd, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 6.19 (dd, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 5.43 (dd, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, $CH_2{=}CHCH_2O$), 5.29−5.14 (m, 1H, $CH_2{=}CHCH_2O$), 5.08 (dd, $^3J_{HH,trans}$ = 12.4 Hz, $^2J_{HH}$ = 1.5 Hz, 1H, $CH_2{=}CHCH_2O$), 4.47 (vt, $^3J_{HH}$ = 9.8 Hz, $^2J_{HH}$ = 9.4 Hz, 1H, $CH_2{=}CHCH_2O$), 3.67 (dd, $^3J_{HH,cis}$ = 8.1 Hz, $^2J_{HH}$ = 1.5 Hz, 1H, $CH_2{=}CHCH_2O$), 2.99 (s, 1H CH_2SiMe_3), 2.98 (s, 1H, CH_2SiMe_3), −0.03 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 330.1 (1C, Ru=*C*), 146.1 (1C, Tp), 144.5 (1C, Tp), 144.2 (1C, Tp), 138.5 (1C, Tp), 136.6 (1C, Tp), 135.9 (1C, Tp), 107.6 (1C, Tp), 107.1 (1C, Tp), 106.9 (1C, Tp), 91.9 (1C, $CH_2{=}CHCH_2O$), 78.7 (1C, $CH_2{=}CHCH_2O$), 78.6 ($CH_2{=}CHCH_2O$), 48.6 (1C, CH_2-$SiMe_3$), 0.9 (3C, $SiMe_3$).

RuTp(=C(CH_3)$CH_2CH{=}CH_2$)Cl (6b). A solution of **6a** (already containing some **6b**) in MeOH was stirred at room temperature for 20 h. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (1 mL).

Addition of *n*-hexane afforded a yellow precipitate, which was collected on a glass frit, washed with *n*-hexane, and dried under vacuum. Anal. Calcd for $C_{14}H_{18}BClN_6ORu$: C, 38.77; H, 4.18; N, 19.38. Found: C, 39.02; H, 4.32; N, 19.24. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.28 (d, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 7.87 (d, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 7.87 (d, $^3J_{HH}$ = 2.4 Hz, 1H, Tp), 7.71 (d, $^3J_{HH}$ = 2.6 Hz, 1H, Tp), 7.69 (d, $^3J_{HH}$ = 2.7 Hz, 1H, Tp), 7.25 (d, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 6.34 (dd, $^3J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 6.23 (dd, $^3J_{HH}$ = 2.3 Hz, $^3J_{HH}$ = 2.0 Hz, 1H, Tp), 6.16 (dd, $^3J_{HH}$ = 2.3 Hz, 1H, Tp), 5.49 (dd, $^2J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, CH_2=CHCH_2O), 5.26 (d, $^3J_{HH,trans}$ = 12.3 Hz, 1H, CH_2=CHCH_2O), 5.09−4.91 (m, 1H, CH_2=CHCH_2O), 4.68 (dd, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 9.8 Hz, 1H, CH_2=CHCH_2O), 3.89 (d, $^3J_{HH,cis}$ = 8.3 Hz, 1H, CH_2=CHCH_2O), 2.58 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 330.2 (1C, Ru=*C*), 145.0 (1C, Tp), 143.9 (1C, Tp), 142.5 (1C, Tp), 137.5 (1C, Tp), 135.5 (1C, Tp), 135.2 (1C, Tp), 106.8 (2C, Tp), 106.5 (1C, Tp), 92.1 (1C, CH_2=*C*HCH_2O), 79.8 (1C, *C*H_2=CHCH_2O), 78.9 (1C, CH_2=CH*C*H_2O), 39.6 (1C, *C*H_3).

X-ray Structure Determination for 1·(solvent), 5a, and 6a·$^1/_2$C$_6$H$_5$CH$_3$. Crystals of **1**·solvent and **5a** were obtained by slow evaporation of the solvent, viz. MeOH and EtOH/CH_2Cl_2, respectively. In the case of **1** not only MeOH but also some dmso and/or dmf—both from the preparation—entered the crystals. Crystals of **6a**·$^1/_2C_6H_5CH_3$ were grown by slow cooling of a hot saturated toluene solution. Only an extremely thin-bladed crystal was available for this compound. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, nominal crystal-to-detector distance of 44.5 mm, 0.3° ω-scan frames). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied (program SADABS[17]). All structures were solved by direct or Patterson methods using the program SHELXS97.[18] Structure refinement on F^2 was carried out with the program SHELXL97.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

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Supporting Information Available: A figure giving a packing diagram of **5a** and listings of atomic coordinates, anisotropic temperature factors, all bond lengths and angles, and least-squares planes for **1**·(solvent), **5a**, and **6a**·$^1/_2C_6H_5CH_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Sheldrick, G. M. SADABS: Program for Absorption Correction; University of Göttingen, Göttingen, Germany, 1996.

(18) Sheldrick, G. M. SHELXS97: Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

(19) Sheldrick, G. M. SHELXL97: Program for Crystal Structure Refinement; University of Göttingen, Germany, 1997.