Ruthenium(II) π-Alkyne and Vinylidene Complexes Derived from Glycoynitols: New Precursors for Water-Soluble Unsaturated Carbenes[⊥]

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Received November 14, 2003

A new class of precursors for water-soluble unsaturated carbenes was synthesized by reaction of $[Cp^*RuCl(PMe_3)_2]$ with a terminal alkyne and a propargyl alcohol, each bearing a polyhydroxylated lateral chain derived from D-xylose. In the reaction with the terminal glycoynitol, the presence of a pair of noninterconverting π-alkyne intermediates of $[Cp^*Ru(PMe_3)_2]^+$ species was observed for the first time and the kinetics of isomerization to the same vinylidene species measured by NMR experiments.

Introduction

Transition metal unsaturated carbenes have become an active and important area of research in organometallic chemistry during the last two decades.[1] In particular, vinylidenes[1,2] and allenylidenes,[1,3] which are the simplest members of this class of compounds, are among the most useful and versatile reagents for organic synthesis and homogeneous catalysis.[4] Although a great number of transition metal unsaturated carbenes have been synthesized, examples of water-soluble vinylidenes and allenylidenes are, to the best of our knowledge, limited to the two ruthenium(II) derivatives, $[RuCl_2\{C{=}C(H)Ph\}(TPPMS)_2]Na_2$ and $[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(TPPMS)_2\}_2]Na_4$, where TPPMS is the sulfonated phosphine $Ph_2P\{2\text{-}OS(O)_2C_6H_4\}^-\}$.[5] Hydrosoluble vinylidenes may find application as water-soluble catalysts, hence allowing the extension of the existing

[⊥] Dedicated to Prof. José Vicente on the occasion of his 60th birthday.

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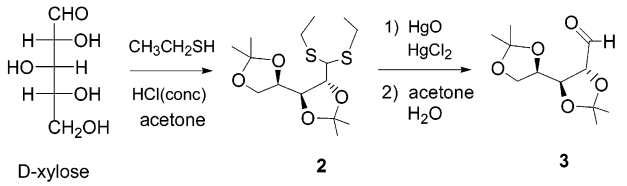
10.1021/om034299g CCC: $27.50
Publication on Web 03/23/2004

Scheme 1



metathesis protocols to the water phase, for the synthesis of drugs and other bioactive compounds related to natural products.[6]

Hereby we report the synthesis of terminal alkynes and propargylic alcohols bearing a polyhydroxylated lateral chain which can be easily derived from simple carbohydrates. The reactions of these glycoynitols with [Cp*RuCl(PMe_3)$_2$] (**1**) to give the corresponding complexes incorporating π-alkyne and vinylidenes bearing the polar lateral chain are also described, together with the first tests on the reactivity of these carbenes toward nucleophiles.

Results and Discussion

Synthesis of Glycoynitol Ligands. The synthetic potential of metal carbenes has been widely investigated by Dötz et al., to develop nonconventional routes to C-glycosides and oligosaccharides.[7] Although some ruthenium vinylidenes and allenylidenes derived from polyhydroxyalkynes have been described and applied to the total synthesis of natural compounds,[8] these species have not been as yet investigated in depth. In our study, naturally occurring D-xylose was chosen as starting material to obtain the corresponding terminal alkyne and propargylic alcohol through standard transformations. The starting material was initially protected on the aldehyde group as dithioacetal[9] and then transformed into the diacetonide (**2**) before being deprotected to afford, with high yield, pure (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)carbaldehyde (**3**) (Scheme 1).

Compound **3** could be used without further purification as suitable starting material to obtain both inytoles (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)ethyne (**4**) and (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi-[[1,3]dioxolanyl]-5(*R*)-yl)propynol (**5**) with one- and two-carbon chain elongation, respectively (Scheme 2) as diasteromerically pure compounds.

The single-carbon homologation required the use of dimethyl-1-diazo-2-oxopropylphosphonate,[10] affording very efficiently the target molecule in high yield and purity via a one-pot reaction, as recently described for differently protected sugars.[11] The two-carbon chain elongation was obtained by reaction of **3** with ethynylmagnesium chloride creating a new asymmetric center, thus affording compound **5** as a mixture of diastereoisomers in a ratio $S/R \cong 1.27$ (**5a**,**b**), which was not resolved at this stage of the work.[12]

Synthesis and Characterization of Ru(II) Carbene Complexes of Glycoynitols. The organometallic chemistry of the polyhydroxyalkynes synthesized as above was explored using the known ruthenium(II) complex **1**, which conjugates high-stability and well-documented reactivity in both stoichiometric[13a] and catalytic processes.[13b] Puerta and co-workers[13] as well as other authors[14] have demonstrated that the reactivity of these complexes with terminal alkynes involves the π-bonding coordination of the alkyne to the metal center followed by tautomerization into the vinylidene derivative. The latter process may follow two different pathways, namely, (a) the alkyne may oxidatively add to give a Ru(IV) hydride-akynyl complex from which the vinylidene forms by a concerted 1,3[H] shift from the metal center to the β-carbon of the alkynyl ligand, or (b) via a concerted 1,2[H] shift from the α-carbon to the β-carbon atom without the intermediacy of the oxidative addition step.[13c,14] The former mechanism has been observed for Rh and Ir,[15] Co,[16] and Ru.[13] In a recent study addressing the reactivity of [Cp*RuCl(PEt_3)$_2$] with acetylene in methanol, the three isomeric species π-alkyne, hydride(alkynyl), and vinylidene have been isolated and characterized by X-ray analysis.[17] In the case of **1**, the presence of the sterically less demanding trimethylphosphine, with basicity comparable to PEt_3, makes the metal center similarly suited to stabilize organometallic alkyne derivatives. In fact, according to our expectations, **1** reacts with **4** in methanol in the presence of $NaBPh_4$ to afford the π-alkyne complex [Cp*Ru(PMe_3)$_2$(η^2-HC≡CR)]BPh_4 [R = (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] (**6**) as a microcrystalline pale yellow solid. Complex **6** is moderately air stable as a solid, but slowly decomposes in chloroform solution unless an inert atmosphere is provided. It has been characterized by elemental analysis and IR and multinuclear NMR spectroscopy. The IR spectrum displays one medium-intensity absorption band at 1828 cm^{-1} due to ν(C≡C) stretching of a dihapto-coordinated π-alkyne ligand. The NMR spectra

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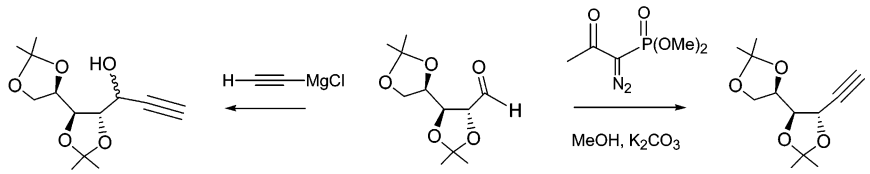
Scheme 2



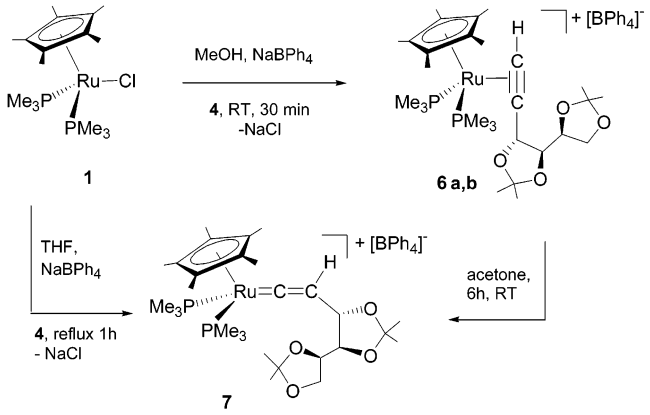
5 3 4

show that **6** exists in acetone-d_6 solution as a 69:31 mixture of two isomers. The $^{31}P\{^1H\}$ NMR spectrum indicates that both isomers exhibit an AB spin system, suggesting the nonequivalence of the two PMe_3 ligands. The major isomer **6a** displays two doublets at 4.16 and 7.56 ppm, while the other isomer **6b** shows two doublets centered at 6.62 and 5.35 ppm, respectively. In the ^1H NMR spectrum, the signals corresponding to the skeleton of the sugar moiety are doubled, in agreement with the existence of a pair of isomers. In particular two doublets of doublets at 5.34 and 5.23 ppm corresponding to **6a** and **6b**, respectively, are assigned to the terminal alkyne proton resonance, *H*C≡CR. $^1H\{^{31}P\}$ NMR experiments indicate that only one of the PMe_3 phosphorus atoms is coupled with this proton, as the other smaller coupling is due to coupling with the nearest proton of the sugar moiety. A reliable ^{13}C NMR analysis could not be run because of the rapid tautomerization of both π-alkyne rotamers into the unique vinylidene complex $[Cp^*Ru(PMe_3)_2\{=C=C(H)R\}]BPh_4$ [R = 2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] (**7**) in acetone and DMSO (see below).

Isomers **6a** and **6b** do not interconvert into each other, as their ratio does not change with the temperature in a series of $^{31}P\{^1H\}$ NMR spectra run at variable temperatures between −60 and 20 °C. Also, no exchange peaks due to the phosphorus atoms of the two AB systems were detected by a 2D $^{31}P\{^1H\}$ exchange spectroscopy experiment.[14,18]

The existence of a pair of *noninterconverting* isomers for the π-alkyne derivative **6** can be attributed to the presence of a pair of rotationally distinct isomers. The two π-alkyne rotamers, which to the best of our knowledge have no precedent in the rich organoalkyne chemistry of $[Cp^*Ru(PR_3)_2]^+$ complexes, are likely to be separated by a significant rotational barrier, which is not crossed at room temperature. The bulkiness of the alkyne sugar substituent is probably responsible for hampering the rotation about the ruthenium−π-alkyne bond. From a theoretical analysis on the model compound $[CpMn(CO)_2(\pi\text{-HC}\equiv\text{CH})]$, Hoffmann and Silvestre suggested that the favored orientation of the C≡C triple bond is almost parallel to the symmetry plane of the $CpMn(CO)_2$ moiety.[19] In contrast, X-ray analysis on the real compounds $[Cp^*Ru(PR_3)_2(\eta^2\text{-HC}\equiv\text{CH})]BPh_4$ (R = Me,[14a] Et[17]) confirmed a rotational orientation, although largely distorted, closer to an orthogonal disposition. Whatever the real orientation in the pair of rotamers of **6** may be, the steric hindrance between the bulky alkyne substituent and the methyl groups on the cyclopentadienyl ring in **6** may well account for a high rotational barrier, which does not allow the two rotamers to equilibrate up to 20 °C.[20]

Scheme 3



Mechanistic Studies and Kinetics. To evaluate the rotational barrier separating the two rotamers in **6**, we ran a series of $^{31}P\{^1H\}$ NMR spectra in DMSO increasing the temperature above 80 °C. Under these conditions, the two AB spin systems experienced a modest drift of their chemical shifts, approaching each other without merging in a unique signal, in line with the behavior shown by π-alkyne CpRu complexes featuring terminal alkynes.[21] At high temperature, the two compounds tautomerize into the vinylidene complex $[Cp^*Ru(PMe_3)_2\{=C=C(H)R\}]BPh_4$ (**7**). The presence of a unique vinylidene derivative for **6** indirectly supports our hypothesis concerning the existence of a pair of noninterconverting rotamers separated by a large rotational barrier. One-pot reaction of **1** with **4** in refluxing tetrahydrofuran directly gives the vinylidene **7** after 1 h heating. The reaction is complete at room temperature in 6 h to yield a yellowish-orange solution from which yellowish-orange microcrystals of **7** are obtained after workup, as shown in Scheme 3.

The kinetics of the isomerization of the π-alkyne complexes **6** into the vinylidene **7** was studied by $^{31}P\{^1H\}$ NMR, monitoring the reaction progress at different temperatures with data collected over 3 half-lives or more. The data were acquired following the rate of decrease of the two AB systems of the π-alkyne complexes and were consistent with a first-order process for both rotamers. The rate constants were comparable (T = 298 K, $k_1 = 5.0 \times 10^{-5}$ M^{-1} s^{-1} for the major isomer, 5.3×10^{-5} M^{-1} s^{-1} for the minor isomer), although the superimposition of the NMR signals increases the error of the measurements. The activation

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(20) A mixture of noninterconverting *exo* and *endo* isomers was found for the η^2-alkyne niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)(\eta^2\text{-HC}\equiv\text{CR})(CO)]$. A computational study indicated a high rotational barrier of 20.9 kcal mol^{-1}. García-Yebra, C.; López-Mardomingo, C.; Fajardo, M.; Antiñolo, A.; Otero, A.; Rodriguez, A.; Vallat, A.; Lucas, D.; Mygnier, Y.; Carbó, J. J.; Lledos, A.; Bo, C. *Organometallics* **2000**, *19*, 1749.

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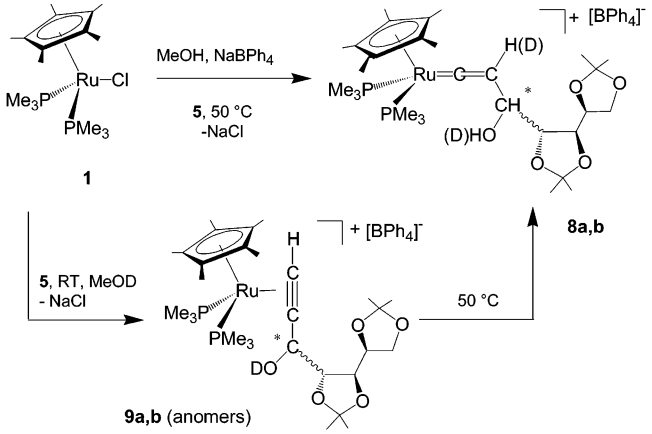
Table 1. Rate Constants for Isomerization Reaction of 6a,b to 7

T/K	$10^5\ k_{iso-a}/s^{-1}$	$\ln(k_{iso-a}/T)$	$10^5\ k_{iso-b}/s^{-1}$	$\ln(k_{iso-b}/T)$
293	3.0	−16.09	3.0	−16.09
299	5.0	−15.60	5.3	−15.55
311	20.0	−14.25	16.0	−14.48
317	22.0	−14.18	20.0	−14.28
323	40.0	−13.60	40.0	−13.60

Scheme 4



enthalpy of the process was calculated as approximately 15.8 kcal mol^{-1} for the major of the two isomers and 15.2 kcal mol^{-1} for the minor one. The closeness of the values, also in accordance with data reported in the literature for analogous processes,[13b,22] agrees with the existence in solution of two rotational π-alkyne isomers which transform, with the same mechanism and same rate law, into a unique vinylidene species. Kinetic data are summarized in Table 1 below.

Encouraged by the outcome of the reaction of **1** with **4**, which resulted in the synthesis of the first unsaturated polyhydroxyvinylidene Ru(II) complex, we decided to study the reaction of **1** with alkynol **5** to verify whether a related allenylidene might be accessible via the well-known Selegue's protocol.[23] The mechanism involves the initial π-coordination of the alkyne, followed by metal-assisted tautomerization to a hydroxyvinylidene species, which, in most cases, gives spontaneous intramolecular dehydration to afford the corresponding allenylidene complex.[23]

In the case of the reaction of **1** with **5** in MeOH, no allenylidene complex was observed,[24] instead stopping at the corresponding hydroxyvinylidene complex [Cp*Ru(PMe$_3$)$_2${=C=C(H)CH(OH)R}]BPh$_4$ (**8**), present as a mixture of diastereoisomers (**8a**,**b** in 3:2 ratio) deriving from the diastereoisomeric excess generated for **5** through the synthetic pathway described above. The pair of anomers in **8** is stable to spontaneous dehydration, as observed by heating the solution close to the boiling point of methanol (Scheme 4). The final product **8** can be recognized by ^{13}C NMR, where a pair of triplets near 344 ppm is observed (Figure 1). These triplets are attributable to the α-carbon atoms of the hydroxyvinylidene ligands in the diastereomeric mixture of **8**, with

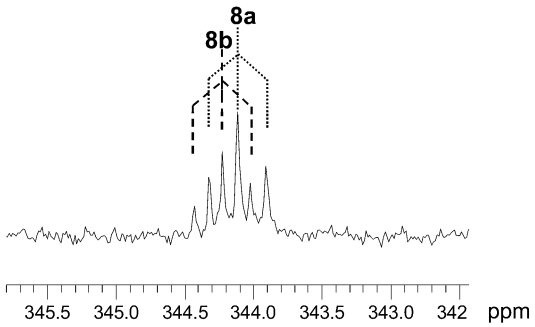


Figure 1. ^{13}C{^{1}H} NMR resonance of the C$_\alpha$ carbon of the vinylidene **8** showing the existence of two diastereomers (3:2 ratio).

the observed multiplicity due to coupling with the two PMe$_3$ ligands.

The reaction was also monitored by ^{31}P{^{1}H} and ^{1}H NMR in a separate experiment using MeOH-d_4 as solvent. Quantitative deuteration of the vinylidene at C$_\beta$ was observed as a consequence of the acidic nature of the M=C=C(H) proton[25] and results in the appearance of a non-binomial triplet (1:1:1 intensity pattern) at δ 106.3 in the ^{13}C{^{1}H} NMR spectrum due to coupling with the deuterium label. Remarkably, a single π-alkyne intermediate existing as a couple of anomers (**9a**,**b** in 3:2 ratio) is formed, in contrast with what is observed for the reaction of **1** with **4**, in which two separate rotamers were identified. The free rotation about the metal−alkyne bond responsible for this behavior may arise from the presence of the propargylic carbon in **5**, allowing for a decrease of the steric hindrance with respect to **4**.

Reactivity of Ru(II)-Glycovinylidenes with Nucleophiles. The reactivity of the vinylidene complex **7** was preliminary evaluated by filling some NMR tube tests with selected nucleophilic reagents such as water and ammonia in order to verify whether the presence of a bulky substituent on the C$_\beta$ carbon has an influence on the known reactivity of these unsaturated carbenes toward nucleophiles and electrophiles.[1b,26] Reaction with ammonia is straightforward and results in the formation of the sugar-functionalized aminocarbene [Cp*Ru(PMe$_3$)$_2${=C(NH$_2$)CH$_2$R}]BPh$_4$ (**10**) as expected.[27] The reaction with water takes place only upon heating a solution of **7** in DMSO-d_6 containing D$_2$O at 80 °C for 12 h (Scheme 5), yielding the known [Cp*Ru(PMe$_3$)$_2$(CO)]BPh$_4$ carbonyl derivative (**11**),[28] together with 1 equiv of the methylated sugar, deriving from the regioselective addition of H$_2$O across the C$_\alpha$=C$_\beta$ vinylidene bond.[25] Although the addition of ammonia and water to ruthenium vinylidenes is a well-understood reaction, they can be used for synthetic purposes to functionalize a protected sugar as described.

Conclusions. In this study, a new class of precursors for water-soluble unsaturated carbenes was synthesized by reaction of [Cp*RuCl(PMe$_3$)$_2$] with a terminal alkyne and propargylic alcohol bearing a fully protected poly-

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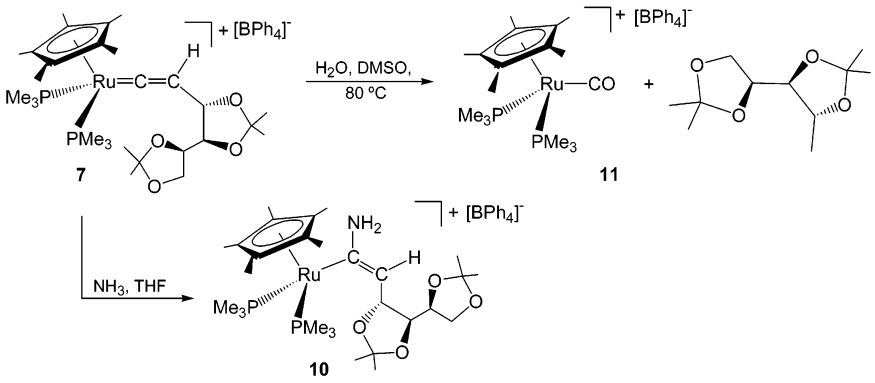
Scheme 5



hydroxylated lateral chain derived from the synthetic elaboration of D-xylose. The reaction proceeds via formation of a pair of noninterconverting π-alkyne intermediates, which were observed for the first time with $[Cp^*Ru(PR_3)_2]^+$ species. Work is in progress to obtain selective deprotection of the diacetonide groups, yielding the water-soluble carbene derivatives in the free form, and to better investigate the scope of the metal-mediated sugar functionalizations.

Experimental Section

Materials and Instruments. All reactions and manipulations involving organometallic syntheses were routinely performed under a dry nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) was freshly distilled over $LiAlH_4$ and purged with nitrogen prior to use. Methanol was purified by distillation over CaH_2 before use. The complex $[Cp^*RuCl(PMe_3)_2]$ (**1**) was prepared according to the procedure reported in the literature.[28] Diazophosphonate was prepared as reported.[10a] All other reagents and chemicals were commercial grade products from Fluka and Aldrich and used as received without further purification except where noted. Solid complexes were collected on sintered glass-frits and washed with light petroleum ether (bp 40−60 °C) before being dried via a stream of nitrogen. Reactions were monitored by TLC plates using Merck Kieselgel silica gel 60 F 254 plates (0.25 nm). Flash chromatography was performed using 400−300 mesh, ICN silica 32-63, ICN Biomedicals, 60 Å. Deuterated chloroform, acetone, and benzene for NMR measurements (Aldrich) were dried over molecular sieves (4 Å). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC200, Varian VXR300, or Bruker AVANCE DRX 500 spectrometers operating at 200.13, 299.94, or 500.13 MHz (^1H), 50.32, 75.42, or 125.80 MHz (^{13}C), and 81.01, 121.42, or 202.45 MHz (^{31}P), respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). ^{31}P NMR chemical shifts were measured relative to external 85% H_3PO_4, with downfield values taken as positive. ^{13}C-DEPT-135 experiments were run on a Bruker AC200 spectrometer. Infrared spectra were recorded as Nujol mulls in a Perkin-Elmer 1600 series FT-IR spectrometer between NaCl plates. Elemental analyses (C, H, N) were performed using a Carlo Erba model 1106 elemental analyzer. Mass spectra were recorded using a Hewlett-Packard 5790 carrying a capillar column OV 101, 30 m, or QMD 1000 Carlo Erba connected to a Mega 5160 gas chromatograph equipped with an SE 54 column, 30 m. In both cases the ionization potential was 70 eV.

(a) Synthesis of 5(*R*)-Bis(ethylsulfanylmethyl)-2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl] (2). d-Xylose (2.0 g, 13.3 mmol) was reacted at room temperature with CH_3CH_2SH (2.9 mL, 40.0 mmol) and concentrated HCl (37%, 0.8 mL). After 15 min, acetone (40 mL) was added, and the final solution was stirred at room temperature overnight. The resulting solution was neutralized with NH_4OH (28% solution), concentrated to a small volume, and then dissolved in H_2O (10 mL) and ethyl acetate (5 mL). The aqueous layer was washed three times with ethyl acetate (5 mL each), and the combined organic phases were dried over dry Na_2SO_4. The solvent was then removed in vacuo, and the crude was purified by flash chromatography using a 1:2 ethyl acetate/light petroleum mixture as eluent. Yield: 3.3 g, 73%. Spectroscopic data were in agreement with those previously reported.[9b] ^1H NMR, δ ($CDCl_3$, 200 MHz): 4.37−4.28 (2H, m, SCH, CH_2CH), 4.16−3.88 (4H, m, CH_2, CH_2CHCH, $CH_2CHCHCH$), 2.83−2.55 (4H, m, 2 × SCH_2), 1.46 (3H, s, CH_3), 1.42 (6H, bs, 2 × CH_3), 1.36 (3H, s, CH_3), 1.26 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3), 1.23 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$, 50.4 MHz): 109.8 (OCO), 109.3 (OCO), 80.0 (CH), 78.5 (CH), 75.1 (CH), 65.7 (CH_2), 52.8 (CHS), 27.2, 27.0, 26.0, 25.4, 25.1, 24.7 (4 CH_3 + 2 CH_2), 14.2, 14.1 (2 × CH_2CH_3). MS, *m*/*z* (%): 217 (6, M^+ − H − 2 SCH═CH_2); 143 (73, M^+ − 2 SCH═CH_2 − CH − 4 CH_3); 135 (100, M^+ − $CH_2CHOCO(CH_3)_2$ − $CHCHOCO(CH_3)_2$), 101 (50, 143 − $CHCHOCO(CH_3)$), 59 (135 − SCH═CH_2−CH).

(b) Synthesis of (2,2,2′,2′-Tetramethyl-[4(*S*),4′(*S*)]bi-[[1,3]dioxolanyl]-5(*R*)-yl)carbaldehyde (3). Compound **2** (1.5 g, 4.6 mmol) was dissolved in acetone (16 mL) and H_2O (1.5 mL) and reacted with HgO (2.3 g, 10.5 mmol) and $HgCl_2$ (2.3 g, 8.3 mmol). The mixture was heated to 55 °C and stirred at this temperature for 3.5 h. After cooling to room temperature the slurry was filtered through a Celite pad and the filtrate concentrated to dryness. The crude was taken with dichloromethane (3 × 10 mL) and filtered again through Celite. The organic layers were washed with a 1 M solution of KI and then dried on dry Na_2SO_4. Removal of the solvent under vacuum gave 0.87 g of aldehyde **3** as an almost pure solid (yield 77%), which was used for the following step without further purification. ^1H NMR, δ ($CDCl_3$, 200 MHz): 9.75 (1H, d, ^3J = 1.6 Hz, CHO), 4.25−4.18 (2H, m, CH_2), 4.13−4.00 (2H, m, CHCHO + CH_2CH), 3.84 (1H, dd, ^3J = 8.4 Hz, ^3J = 6.6 Hz, CH_2CHCH), 1.46 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.35 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$, 50.4 MHz): 201.0 (CHO), 111.8 ($C(CH_3)_2$), 110.0 ($C(CH_3)_2$), 81.3 (CH), 77.1 (CH), 75.5 (CH), 65.3 (CH_2), 26.6 (CH_3), 26.2 (CH_3), 26.0 (CH_3), 25.2 (CH_3). MS, *m*/*z* (%): 215 (16, M^+ − CH_3), 201 (3, M^+ − CHO), 172 (1, 201 − CH_2), 157 (3, 172 − CH_3), 143 (50, 157 − CH_2), 101 (78, 201 − $CHCHOCO(CH_3)$).

(c) Synthesis of (2,2,2′,2′-Tetramethyl-[4(*S*),4′(*S*)]bi-[[1,3]dioxolanyl]-5(*R*)-yl)ethyne (4). Compound **3** (0.75 g, 3.2 mmol) was dissolved in dry methanol (25 mL) under nitrogen and reacted with dimethyl(2-oxo-propyl)diazophosphonate (0.63 g, 3.2 mmol) and K_2CO_3 (0.90 g, 6.5 mmol) at 0 °C for 6 h, then for an additional 4 h at room temperature. The solvent was then removed under reduced pressure, avoiding heating to afford a crude solid, which was dissolved

in a 1:1 mixture of water and ethyl acetate (20 mL). The organic layer was separated, washed with brine, and then dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded 0.61 g of pure **3** as a solid. Yield: 83%; $[\alpha]^{26}_D$ −15.95 [*c* 0.1, $CHCl_3$]. ^1H NMR, δ ($CDCl_3$, 200 MHz): 4.48 (1H, dd, ^3J = 7.6 Hz, ^4J = 2.2 Hz, CHC≡CH), 4.22 (1H, td, ^3J = 7.6 Hz, ^3J = 5.2 Hz, $CHCH_2$), 4.11 (1H, dd, ^3J = 7.6 Hz, ^3J = 5.2 Hz, CHCHC≡CH), 4.07 (1H, dd, ^3J = 8.4 Hz, ^2J = 6.6 Hz, CH_2), 3.93 (1H, dd, ^3J = 8.4 Hz, ^2J = 6.6 Hz, CH_2), 2.56 (1H, d, ^4J = 2.2 Hz, C≡CH), 1.50 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.39 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR, δ ($CDCl_3$, 50.4 MHz): 111.8 ($C(CH_3)_2$), 110.7 ($C(CH_3)_2$), 81.0 (C≡CH), 82.6, 75.7, 67.4 (CH_2CH + CH_2CHCH + CC≡CH + ≡CH), 66.0 (CH_2), 27.3 (CH_3), 26.9 (CH_3), 26.7 (CH_3), 26.0 (CH_3). MS, *m*/*z* (%): 211 (100, M − CH_3), 101 (75, M^+ − CHCHOCO$(CH_3)_2$C≡CH). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 64.20; H, 8.22.

(d) Synthesis of (2,2,2′,2′-Tetramethyl-[4(*S*),4′(*S*)]bi-[[1,3]dioxolanyl]-5(*R*)-yl)propynol (5). To a solution of **3** (1.0 g, 4.34 mmol) in ca. 22 mL of THF was added dropwise 17 mL of a 0.5 M THF solution of CH≡CMgCl through a dropping funnel. The mixture was stirred at room temperature for 4 h before being diluted with diethyl ether (10 mL), water (10 mL), and ammonium buffer (10 mL). The aqueous layers were separated and extracted with ether, and the combined organic phases washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude compound purified by flash chromatography (eluent dichloromethane/diethyl ether, 1:1) to a mixture of diastomers in the ratio *S*/*R* ≅ 1.27 (**5a**,**b**). Yield: 43%. ^1H NMR, δ (C_6D_6, 500 MHz): **5a**, 4.44 (1H, m, CHOH), 4.42 (1H, dd, ^3J = 2.2 Hz, ^3J = 4.9 Hz, CHCHOH), 4.26 (1H, ddd, ^3J = 2.4 Hz, ^3J = 6.8 Hz, ^3J = 7.7 Hz, CH_2CH), 4.15 (1H, dd, ^3J = 2.4 Hz, ^3J = 7.6 Hz, CH_2CHCH), 4.06 (1H, t, *J* = 7.9 Hz, CH_2), 3.86 (1H, dd, ^3J = 6.8 Hz, ^2J = 8.1 Hz, CH_2), 2.09 (1H, s, OH), 2.08 (1H, d, C≡CH), 1.54 (3H, s, CH_3), 1.51 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.45 (3H, s, CH_3); **5b**, 4.43 (1H, m, CHOH), 4.39 (1H, t, ^3J = 3.7 Hz, CHCHOH), 4.13 (1H, dd, ^3J = 2.4 Hz, ^3J = 8.2 Hz, CH_2CHCH), 4.12 (1H, ddd, ^3J = 2.8 Hz, ^3J = 6.7 Hz, ^3J = 8.2 Hz, CH_2CH), 4.02 (1H, t, *J* = 7.0 Hz, CH_2), 3.83 (1H, dd, ^3J = 6.7 Hz, ^2J = 8.1 Hz, CH_2), 2.32 (1H, d, OH), 2.10 (1H, d, C≡CH), 1.52 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.40 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR, δ (C_6D_6 125.75 MHz): **5a**, 81.61 (C≡CH), 79.22 ($CH_2CHCHCH$), 77.22, 76.91 (2 × $C(CH_3)_2$), 76.67 (CH_2CHCH), 75.24 (CH_2CH), 74.55 (C≡CH), 65.86 (CH_2), 62.72 (CC≡CH), 27.13 (CH_3), 27.03 (CH_3), 26.09 (CH_3), 25.72 (CH_3); **5b**, 82.21 (C≡CH), 79.46 ($CH_2CHCHCH$), 77.55, 76.70 (2 × $C(CH_3)_2$), 76.44 (CH_2CHCH), 74.57 (CH_2CH), 74.07 (C≡CH), 65.72 (CH_2), 62.36 (CC≡CH), 27.17 (CH_3), 27.04 (CH_3), 25.99 (CH_3), 25.52 (CH_3). MS, *m*/*z* (%): 241 (4, M^+ − CH − H − H), 201 (2, M^+ − CHOHC≡CH), 101 (31, 201 − CHCHOCO$(CH_3)_2$. Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 61.07; H, 8.01.

(e) Synthesis of [Cp*Ru(PMe$_3$)$_2$(η^2-HC≡CR)]BPh$_4$ [R = (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] (6). To a suspension of **1** (0.19 g, 0.40 mmol) and $NaBPh_4$ (0.34 mg, 1.00 mmol) in 20 mL of methanol were added 1 mL of $CHCl_3$ and 0.1 g of **4** (0.44 mmol) under stirring. The mixture was stirred at room temperature for 1 h to give a yellow solution. Addition of light petroleum ether (30 mL) and ethanol (10 mL) yielded [Cp*Ru(PMe_3)$_2$(π-HC≡CR)]BPh_4 (**6**) as a pale yellow precipitate. Yield: 0.18 g (49%). IR (Nujol, cm^{-1}): 1828 ν(C≡C), 610 ν(B−C) cm^{-1}. $^{31}P\{^1H\}$ NMR, δ (acetone-d_6, 121.42 MHz): **6a** (69%), 7.56, 4.16 (AB system, $^2J_{AB}$ = 46.6 Hz, PMe_3); **6b** (31%), 6.62, 5.35 (AB system, $^2J_{AB}$ = 46.6 Hz, PMe_3). ^1H NMR, δ (acetone-d_6, 300 MHz): **6a** 5.34 (1H, dd, $^3J_{HP}$ = 18.3, ^4J = 1.8 Hz, C≡CH), 4.90 (1H, dbs, ^3J = 9.0 Hz HC≡CCH), 1.76 (15H, t, *J* = 1.2 Hz, ^4J = 1.8 Hz, ($C_5(CH_3)_5$), 1.69 (9H, d, $^2J_{HP}$ = 9.6 Hz, $P(CH_3)_3$); **6b** 5.23 (1H, dd, $^3J_{HP}$ = 19.8 Hz, ^4J = 1.8 Hz, C≡CH), 5.03 (1H, dbs, ^3J = 9.3 Hz, HC≡CCH), 1.75 (15H, t, *J* = 1.2 Hz, ^4J = 1.8 Hz, ($C_5(CH_3)_5$), 1.58 (9H, d, $^2J_{HP}$ = 9.2 Hz, $P(CH_3)_3$). Anal. Calcd for $C_{52}H_{71}BO_4P_2Ru$: C, 66.87; H, 7.66. Found: C, 67.20; H, 7.57.

(f) Synthesis of [Cp*Ru(PMe$_3$)$_2$\{=C=C(H)R\}]BPh$_4$ [R = (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] (7). Method A. Compound **6** (0.4 g, 0.41 mmol; mixture of isomers) was dissolved in 20 mL of acetone and stirred at room temperature for 12 h. After this time a 3:1 mixture of ethanol and light petroleum ether was added to precipitate the vinylidene complex **7**. The yellowish-orange solid was filtered and dried under nitrogen. Yield: 55%.

Method B. A solution of **4** (0.10 g 0.44 mmol) in 1.0 mL of $CHCl_3$ was added to a THF solution of **1** (0.19 g, 0.4 mmol) containing $NaBPh_4$ (0.34 mg, 1.00 mmol). The resulting yellow-orange solution was brought to reflux and stirred for 1 h. After this time, the yellow solution was concentrated almost to dryness. Addition of a 2:1 light petroleum ether/ethanol mixture (13 mL) gave [Cp*Ru(PMe_3)$_2$\{=C=C(H)R\}]BPh_4 (**7**) as a yellow microcrystalline solid. Yield: 0.20 mg (50%). IR (Nujol, cm^{-1}): 1642 ν(C=C), 610 ν(B−C) cm^{-1}. $^{31}P\{^1H\}$ NMR, δ (acetone-d_6, 202.46 MHz): 4.51, 3.66 (AB system, $^2J_{AB}$ = 38.9 Hz, PMe_3). ^1H NMR, δ (acetone-d_6, 500 MHz): 4.80 (1H, dd, ^3J = 9.2 Hz, ^3J = 8.4 Hz, C=CHCH), 4.45 (1H, dt, ^3J = 9.2 Hz, $^4J_{HP}$ = 2.1 Hz, C=CH), 4.25 (1H, ddd, ^3J = 2.4 Hz, ^3J = 6.8 Hz, ^3J = 7.7 Hz, CH_2CH), 4.11 (1H, dd, ^2J = 8.0 Hz, ^3J = 6.8 Hz, CHH), 3.93 (1H, t, ^2J = ^3J = 7.9 Hz, CHH), 3.56 (1H, dd, ^3J = 2.3 Hz, ^3J = 8.4 Hz, CH_2CHCH), 1.97 (15H, t, $^4J_{HP}$ = 1.3 Hz, $C_5(CH_3)_5$), 1.67 (9H, d, $^2J_{HP}$ = 9.8 Hz, $P(CH_3)_3$), 1.66 (9H, d, $^2J_{HP}$ = 9.8 Hz, $P(CH_3)_3$), 1.38 (6H, s, $OC(CH_3)_2$), 1.36 (6H, s, $OC(CH_3)_2$). $^{13}C\{^1H\}$ NMR, δ (acetone-d_6, 125.80 MHz): 344.05 (t, $^2J_{CP}$ = 15.5 Hz, Ru=C), 109.48 (s, $C(CH_3)_2$), 108.58 (s, $C(CH_3)_2$), 105.33 (s, C=CH), 103.57 (s, $C_5(CH_3)_5$), 81.82 (s, CH_2CHCH), 73.62 (s, CH_2CHCH), 70.22 (s, C=CHCH), 66.07 (s, CH_2), 27.16, 26.46, 25.91 (s, $C(CH_3)_2$ + $C(CH_3)(CH_3)$), 25.86 (s, $C(CH_3)(CH_3)$), 20.30 (d, $^1J_{CP}$ = 33.6 Hz, $P(CH_3)_3$), 20.25 (d $^1J_{CP}$ = 33.5 Hz, $P(CH_3)_3$). Anal. Calcd for $C_{52}H_{71}BO_4P_2Ru$: C, 66.87; H, 7.66. Found: C, 66.76; H, 7.59.

(g) Synthesis of [Cp*Ru(PMe$_3$)$_2$\{=C=C(H)CH(OH)R\}]BPh$_4$ [R = (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] (8). To a solution of **1** (0.20 g, 0.47 mmol) in 15 mL of MeOH were added 120 mg of **5** (ca. 0.47 mmol) and 160 mg of $NaBPh_4$ (0.47 mmol). The solution was stirred at room temperature for 3 h, then the slurry was filtered trough Celite and the solution concentrated to dryness. The crude was extracted with ethanol (ca. 5 mL). Addition of light petroleum ether (15 mL) gave **8** as a brownish-orange solid. Yield: 250 mg (65%). Compound **8** is obtained as a 3:2 diastereoisomeric mixture (**8a**,**b**). IR (Nujol, cm^{-1}): 3564 ν(O−H), 1651 ν(C=C), 615 ν(B−C) cm^{-1}. $^{31}P\{^1H\}$ NMR, δ (acetone-d_6, 202.45 MHz): **8a** (60%), 5.87, 2.58 (AB system, $^2J_{AB}$ = 39.0 Hz, PMe_3); **8b** (40%), 6.45, 2.11 (AB system, $^2J_{AB}$ = 39.0 Hz, PMe_3). ^1H NMR, δ (acetone-d_6, 400 MHz): **8a** 4.77 (1H, m, Ru=C=CH−C*H*(OH)R), 4.52 (1H, dt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HP}$ = 6 Hz, Ru=C=C*H*), 3.8−4.1 (5H, m, CH_2CHCH + C=C(H)C*H*), 1.88 (15H, t, $^4J_{HP}$ = 1.2 Hz, ($C_5(CH_3)_5$), 1.52 (9H, d, $^2J_{HP}$ = 9.6 Hz, $P(CH_3)_3$), 1.52 (9H, d, $^2J_{HP}$ = 9.6 Hz, $P(CH_3)_3$), 1.42−1.45 (12H, s, 4 × $OC(CH_3)_2$); **8b** 4.75 (1H, m, Ru=C=CH−C*H*(OH)R), 4.52 (1H, dt, $^3J_{HH}$ = 8.6 Hz, $^4J_{HP}$ = 6.1 Hz, Ru=C=C*H*), 3.8−4.1 (5H, m, CH_2CHCH + C=C(H)C*H*), 1.87 (15H, t, J_{HP} = 1.2 Hz, ($C_5(CH_3)_5$), 1.51 (9H, d, $^2J_{HP}$ = 9.6 Hz, $P(CH_3)_3$), 1.49 (9H, d, $^2J_{HP}$ = 9.6 Hz, $P(CH_3)_3$), 1.42−1.45 (12H, m, 4 × $OC(CH_3)_2$). $^{13}C\{^1H\}$ NMR, δ (acetone-d_6, 125.80 MHz): **8a** 343.95 (t, $^2J_{CP}$ =15.5 Hz, Ru=*C*), 109.60 (s, *C*$(CH_3)_2$), 109.45 (t, $^3J_{CP}$ = 1.5 Hz, C=*C*H), 109.39 (s, *C*$(CH_3)_2$), 104.48 (t, $^3J_{CP}$ = 1.5 Hz, *C*$_5(CH_3)_5$), 81.82 (s, CH_2CHCH), 73.62 (s, *C*H_2CHCH), 70.22 (s, C=CH*C*H), 66.07 (s, CH_2), 27.45, 27.04, 26.19, 25.78 (s, C(*C*H_3)$_2$), 20.52 (dd, $^1J_{CP}$ = 31.2 Hz, $^3J_{CP}$ = 4.1 Hz $P(CH_3)_3$), 20.40 (dd, $^1J_{CP}$ = 31.4 Hz, $^3J_{CP}$ = 4.0 Hz $P(CH_3)_3$), 10.67 (s, $C_5(CH_3)_5$); **8b** $^{13}C\{^1H\}$ NMR, δ (acetone-d_6, 125.80 MHz): 344.05 (t, $^2J_{CP}$ =15.5 Hz, Ru=*C*), 109.27 (s, *C*$(CH_3)_2$), 109.17 (s, *C*$(CH_3)_2$), 108.58 (t, $^3J_{CP}$ = 1.5 Hz, C=*C*H), 104.32 (t, $^3J_{CP}$ = 1.5 Hz, *C*$_5(CH_3)_5$), 81.82 (s, CH_2CHCH), 73.62 (s, *C*H_2CHCH),

70.22 (s, C═CH*C*H), 65.68 (s, CH_2), 27.32, 27.16, 26.24, 25.70 (s, C(CH_3)$_2$), 20.53 (dd, $^1J_{CP}$ = 31.4 Hz, $^3J_{CP}$ = 4.3 Hz, P(CH_3)$_3$), 20.40 (dd, $^1J_{CP}$ = 31.1 Hz, $^3J_{CP}$ = 4.3 Hz, P(CH_3)$_3$), 10.69 (s, C_5(CH_3)$_5$). Anal. Calcd for $C_{53}H_{73}BO_5P_2Ru$: C, 66.04; H, 7.63. Found: C, 66.19; H, 7.85.

(h) Reaction of [Cp*RuCl(PMe$_3$)$_2$] (1) with 2,2,2′,2′-Tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)propynol (5). NMR Tube Test. A solution of **1** (18.5 mg, 0.04 mmol) in MeOH-d_4 (0.8 mL) was added to a 5 mm screw-cap NMR tube containing 13.3 mg (0.05 mmol) of the glycoynitol **5** (1.3 equiv). After inserting the tube in the NMR spectrometer kept at room temperature, a $^{31}P\{^1H\}$ NMR spectrum immediately acquired showed the formation of both the π-alkyne intermediate (two diasteroisomers, **9a** and **9b** in ca. 3:2 ratio) and the hydroxyvinylidene [Cp*Ru(PMe$_3$)$_2${═C═C(H)CH-(OH)R}]Cl (two diasteroisomers, **8a** and **8b** in ca. 3:2 ratio). On standing at room temperature, the complete transformation of **9** into **8** took place in about 20 min. $^{31}P\{^1H\}$ NMR, δ (MeOH-d_4, 81.01 MHz): **9a**, 6.45, 6.70 (AB system, $^2J_{AB}$ = 328.6 Hz); **9b**, 3.60, 2.86 (AB system, $^2J_{AB}$ = 76.0 Hz); **8a**, 5.63, 4.39 (AB system, $^2J_{AB}$ = 46.5 Hz, PMe_3); **8b**, 4.19, 3.04 (AB system, $^2J_{AB}$ = 38.7 Hz, PMe_3).

(i) Reaction of [Cp*Ru(PMe$_3$)$_2${═C═C(H)R}]BPh$_4$ [R = (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] with NH$_3$. NMR Tube Test. Gaseous NH_3 was bubbled throughout an acetone-d_6 (0.8 mL) solution of **7** (35 mg, 0.04 mmol) prepared in a screw-cap 5 mm NMR tube. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of [Cp*Ru(PMe$_3$)$_2${═C(NH_2)CH_2R}]BPh_4 [R = 2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] (**10**) as the only detectable species. $^{31}P\{^1H\}$ NMR, δ (acetone-d_6, 81.01 MHz): 1.05, 0.18 (AB system, $^2J_{AB}$ = 37.2 Hz, PMe_3). ^1H NMR, δ (acetone-d_6, 200.13 MHz): 9.15 (2H, bs, NH_2), 1.76 (15H, t, C_5(CH_3)$_5$), 1.51 (6H, d, P(CH_3)$_2$), 1.48 (6H, d, P(CH_3)$_2$).

(j) Reaction of [Cp*Ru(PMe$_3$)$_2${═C═C(H)R}]BPh$_4$ [R = (2,2,2′,2′-tetramethyl-[4(*S*),4′(*S*)]bi[[1,3]dioxolanyl]-5(*R*)-yl)] with H$_2$O. NMR Tube Test. D_2O (0.1 mL) was syringed into 1.0 mL of a DMSO-d_6 solution of **7** (35 mg, 0.04 mmol) prepared in a NMR tube. The tube was vigorously shaken and then inserted into the NMR spectrometer to be monitored by $^{31}P\{^1H\}$ NMR spectroscopy. No reaction was observed within 12 h. After this time the sample was heated to 80 °C in a thermostated oil bath for 12 h and a new $^{31}P\{^1H\}$ NMR spectrum acquired. A singlet at −0.10 ppm indicated the presence of the carbonyl complex [Cp*Ru(PMe$_3$)$_2$(CO)]BPh_4 (**11**). The solid collected from the NMR tube showed in the IR spectrum a ν(CO) stretching at 1952 cm^{-1}.

Acknowledgment. This work was supported by INTAS (00-00179) and NATO (PST.CLG.978521). Thanks are also due to EC through COST D17 and D29 Chemistry Actions (WGD17/0003/00 and WGD29/0009-003) and RTN no. MRTN-CT-2003-503864 (AQUACHEM) for promoting this scientific activity. I.d.l.R. thanks the MCYT of Spain for a Ramon y Cajal Contract.

OM034299G