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Syntheses of Four-Membered Metallacyclic Complexes with Nitrosylruthenium and Their Ring-Opening upon HCl Addition

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Abstract: Symmetrically disubstituted bis(3-hydroxyalkynyl) complex [TpRu{C≡CCPh$_2$(OH)}$_2$(NO)] (**1**) (Tp = BH(pyrazol-1-yl)$_3$) and unsymmetrically mixed (arylalkynyl)(3-hydroxyalkynyl) congener [TpRu(C≡CC$_6$H$_4$Me){C≡CCPh$_2$(OH)}(NO)] (**2**) were newly prepared. Treatment of **1** or **2** with *p*-toluenesulfonic acid monohydrate was carried out to give unusual four-membered metallacyclic complexes [TpRu{C(=C=CPh$_2$)C(O)C(=CPh$_2$)}(NO)] (**3**) and [TpRu{C(=C=CPh$_2$)C(O)CH(C$_6$H$_4$Me)}(NO)] (**5**), respectively, as major products. Formation mechanism of **3** and **5** would involve insertion of the generated allenylidene group (Ru=C=C=CPh$_2$) into the other Ru–C(alkynyl) bond, followed by hydration of the resulting α-alkynyl–allenyl fragment. With regards to the chemical reactivity of their four-membered metallacycles, treatment with aq. HCl in MeOH afforded the ring-opened one-HCl adducts, [TpRuCl{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(NO)] (**7**) and [TpRuCl{C(=C=CPh$_2$)C(O)CH$_2$(C$_6$H$_4$Me)}(NO)] (**8**). On the other hand, the use of CH$_2$Cl$_2$ and THF as the reaction solvent gave another type of one-HCl adducts [TpRu{CH(C(Cl)=CPh$_2$)C(O)C(=CPh$_2$)}(NO)] (**9a**/**9b**) and [TpRu{CH(C(Cl)=CPh$_2$)C(O)CH(C$_6$H$_4$Me)}(NO)] (**11a**/**11b**) as diastereomeric pairs, still retaining the four-membered ring structure. Moreover, their kinetically controlled products **9b** and **11b** were treated with aq. HCl to afford the ring-opened two-HCl adducts [TpRuCl{C(C(Cl)=CPh$_2$)(H)C(O)CH=CPh$_2$}(NO)] (**10**) and [TpRuCl{CH(C$_6$H$_4$Me)C(O)CH$_2$(C(Cl)=CPh$_2$)}(NO)] (**12**), respectively. In **10** and **12**, each one Ru–C bond is cleaved at mutually different positions in the ring. Protonation on the carbonyl group would trigger the formation of **7**–**12**.

Keywords: alkyne ligands · metallacycles · nitrosyl · ring-opening · ruthenium

Introduction

Addition reactions (such as hydration,[1,2] hydrosilylation,[3] hydroamination[4]) to alkynes hold promise for forming highly valuable organic molecules via atom-economical transformations with no by-products and no troublesome separation processes. Among them, catalytic hydration as one utilization of environmental benign water, has been extensively studied, where Markovnikov's[5] and/or anti-Markovnikov's rule[5f,6] regulate the key reaction processes. Although the former has been examined well through the years, the latter has been developed remarkably in this decade since the first reports by Tokunaga using (phosphine)ruthenium complexes, who disclosed Ru^{IV}–vinylidene species as the key intermediates.[6a] On the other hand, in our continuing research with the [TpRu(NO)] (Tp = BH(pyrazol-1-yl)$_3$) system,[7] proton-assisted hydration of mono(arylalkynyl) complex [TpRuCl(C≡CPh)(NO)] readily proceeded to yield a ketonyl species [TpRuCl{CH$_2$C(O)Ph}(NO)] through a π-alkyne rather than the vinylidene intermediate.[7a] Our ruthenium system has different preference in the hydration from that of usual (phosphine)ruthenium complexes.[2a–d] The presence of the NO$^+$ ligand, being a strong π-acceptor group, would increase a stability of the π-alkyne form with d^6 Ru^{II}, which is generally assumed to be thermodynamically less stable than the isomeric vinylidene form.[8] Interestingly, we have disclosed hydration of a bis(arylalkynyl) TpRu(C≡CPh)$_2$(NO) compound to give an unusual metallacyclopentenone complex [TpRu{CH=C(Ph)C(O)CH(Ph)}(NO)] along with double hydrated products [Eq. (1)].[7b] The five-membered metalla-

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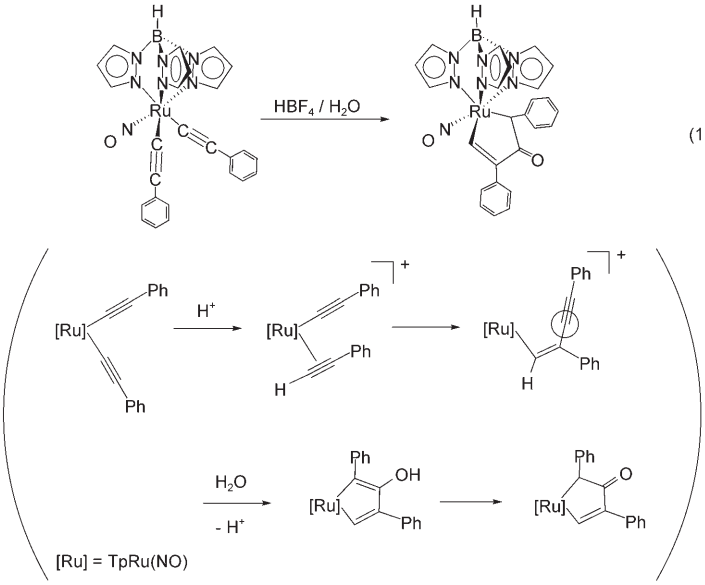


cyclopentenone was formed from two alkyne and one H_2O molecules and its formation mechanism involves the combination of C–C coupling and hydration processes through the π-alkyne intermediate. In spite of abundant ruthenium-catalyzed alkyne oligomerizations, there are only a few examples where an additional hydration process has been incorporated into the reaction sequence.[9]

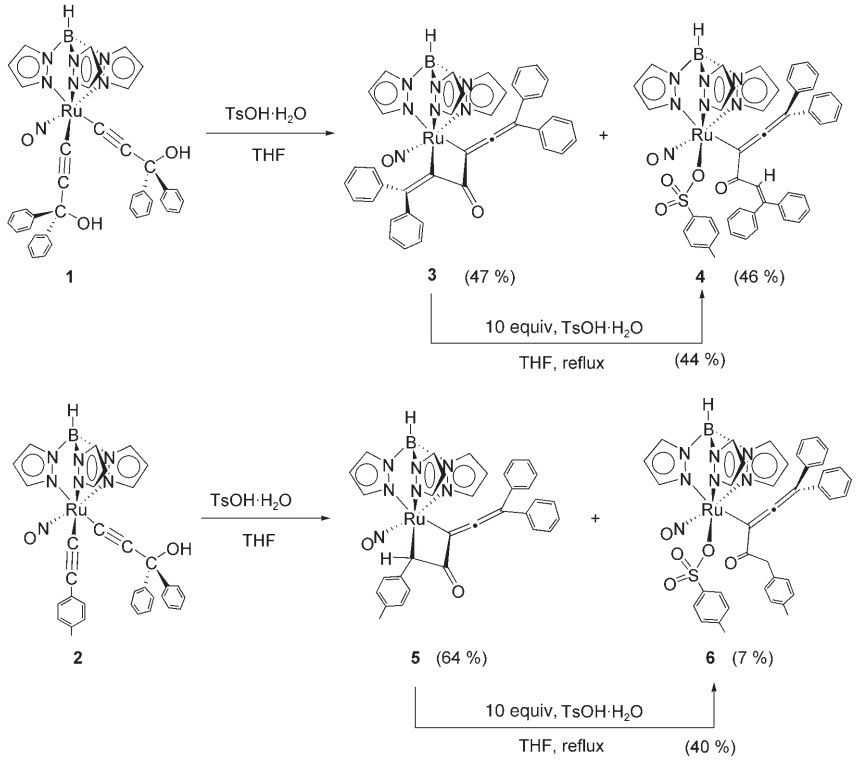
Developing this research, symmetrical and unsymmetrical bis(alkynyl) complexes containing 3-hydroxyalkynyl groups, that is, [TpRu{C≡CCPh$_2$(OH)}$_2$(NO)] (**1**) and [TpRu(C≡CC$_6$H$_4$Me){C≡CCPh$_2$(OH)}(NO)] (**2**) were prepared. Mono(3-hydroxyalkynyl) complexes [TpRuCl{C≡CC(R)$_2$OH}(NO)] (R = Ph, Me) have been hydrated to give acyl species [TpRuCl{C(O)CH=C(R)$_2$}(NO)] through allenylidene intermediates, differently from the mono(arylalkynyl) TpRuCl(C≡CPh)(NO) chemistry.[7a] This finding affected hydration of **1** and **2** to give rare ethenylidene–metallacyclobutan-3-one complexes, and their unprecedented four-membered metallacycles showed also interesting HCl-incorporation reactivities, depending on the reaction solvents used. This is in contrast to the five-membered metallacyclopentenone complex described above,[7b] which is unreactive to further treatment with aqueous HCl.

Results and Discussion

Syntheses of symmetrical and unsymmetrical bis(alkynyl) complexes containing 3-hydroxyalkynyl groups: Reaction of [TpRuCl$_2$(NO)][10] with an excess of HC≡CCPh$_2$(OH) in the presence of Et$_3$N and catalytic amounts of CuI gave the bis(3-hydroxyalkynyl) [TpRu{C≡CCPh$_2$(OH)}$_2$(NO)] (**1**) in 17% yield. Using the mono(3-hydroxyalkynyl) [TpRuCl{C≡CCPh$_2$(OH)}(NO)] as a starting material afforded **1** in 64% yield. On the other hand, treatment of [TpRuCl(C≡CC$_6$H$_4$Me)(NO)] with HC≡CCPh$_2$(OH) in the same conditions afforded the unsymmetrically disubstituted complex [TpRu(C≡CC$_6$H$_4$Me){C≡CCPh$_2$(OH)}(NO)] (**2**) in 50% yield along with the by-products of the mono(3-hydroxyalkynyl) and two possible symmetrically disubstituted bis(alkynyl) complexes. Alternative reaction of the mono(3-hydroxyalkynyl) complex with HC≡CC$_6$H$_4$Me did not proceed. Complexes **1** and **2** were characterized by NMR, IR, FAB-MS spectra, and elemental analyses (see Experimental Section).

Proton-assisted hydration of 1 and 2: Reaction of **1** with *p*-toluenesulfonic acid monohydrate (TsOH·H_2O) in THF at room temperature yielded the ethenylidene–metallacyclobutan-3-one complex [TpRu{C(=C=CPh$_2$)C(O)C(=CPh$_2$)}(NO)] (**3**) and the *p*-toluenesulfonato complex [TpRu{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(OSO$_2$C$_6$H$_4$Me)(NO)] (**4**) in 47 and 46% yield, respectively (Scheme 1). Also, similar treatment of **2** with TsOH·H_2O produced [TpRu{C(=C=CPh$_2$)C(O)CH(C$_6$H$_4$Me)}(NO)] (**5**) (64%) and [TpRu{C(=C=CPh$_2$)C(O)CH$_2$C$_6$H$_4$Me}(OSO$_2$C$_6$H$_4$Me)(NO)] (**6**) (7%). Replacement of the TsOH/THF with HBF$_4$/MeOH in both hydrations provided uncharacterizable products. The four-membered metallacyclic complexes **3** and **5** show characteristic bands $\nu_{C=O}$ (**3**: 1642 cm^{-1}, **5**: 1635 cm^{-1}) and $\nu_{C=C=C}$ (**3**: 1899 cm^{-1}, **5**: 1929 cm^{-1}) together with $\nu_{N\equiv O}$ (**3**: 1826 cm^{-1}, **5**: 1806 cm^{-1}) in the IR spectra. Their ^{1}H NMR spectra exhibit three distinct sets of pyrazolyl protons besides aryl protons. Moreover, for **5**, additional two singlets at $\delta = 4.89$ (methine) and 2.34 ppm (methyl) were observed. Both ^{13}C{^{1}H} NMR spectra exhibit two lower field signals, which were assigned to the carbonyl carbon and the C$_\alpha$ of the ethenylidene groups (=C$_\alpha$=C$_\beta$Ph$_2$).[11] Clearly, in the EI-MS spectra, the parent molecular ion signal of **5** (*m*/*z* 667.1) indicates the mass number remains unaltered during its formation, although, for **3**, a one-H_2O mass decrease compared with **1** is observed (*m*/*z* 741). These complexes were also confirmed by X-ray analyses.

The solid-state structure of **3** reveals two crystallographically unique but chemically identical complexes per one asymmetric unit. One of the molecular structures of **3** and that of **5** are shown in Figure 1. Selected bond lengths and angles are summarized in Table 1. The ethenylidene–metallacyclobutan-3-one frameworks in **3** and **5** are structurally characterized. The C–C$_\alpha$ (**3**: 1.291(3), 1.294(3) Å; **5**: 1.288(4) Å) and C$_\alpha$–C$_\beta$ (**3**: 1.327(3), 1.315(3) Å; **5**: 1.324(4) Å) bond lengths, as well as C-C$_\alpha$-C$_\beta$ angles (**3**: 178.1(2), 177.3(2)°; **5**: 175.2(3)°) of the diphenylethenylidene part, which are in agreement with those of similar literature-described ruthenium complexes,[11c,d] strongly support these allenyl formulation. Comparison between the structures of **3** and **5** reveals that the presence of the diphenylmethylidene (=CPh$_2$) part of the former gives rise to the planarity of its ethenylidene–metallacyclobutan-3-one framework.[12] In spite of conceivable diastereomeric configurations due to the chiral carbon center of C12 in **5**, formation of only one diastereomer was observed in this reaction condition, on the basis of NMR spectra and an X-ray structure analysis.



Scheme 1. Treatment of **1** and **2** with $TsOH{\cdot}H_2O$.

The *p*-toluenesulfonato complexes **4** and **6** exhibit the characteristic olefinic proton for **4** ($\delta = 6.98$ ppm) and diastereotopic methylene protons for **6** ($\delta = 4.37$, 4.07 ppm, $J = 16$ Hz) in the ^1H NMR spectra. The FAB-MS spectra of **4** and **6** show 172 mass increments compared with **3** and **5**, respectively, indicating incorporation of one TsOH into **3** and **5**.

The crystals obtained from a CH_2Cl_2/MeOH solution of **4** were subjected to an X-ray structural analysis, and its molecular structure is shown in Figure 2. Selected bond lengths and angles are summarized in Table 2. The Tp and NO ligands are bound to the Ru atom, and the slightly distorted octahedral geometry is completed by the metallacycle-opened allenyl and the *p*-toluenesulfonato ligands.

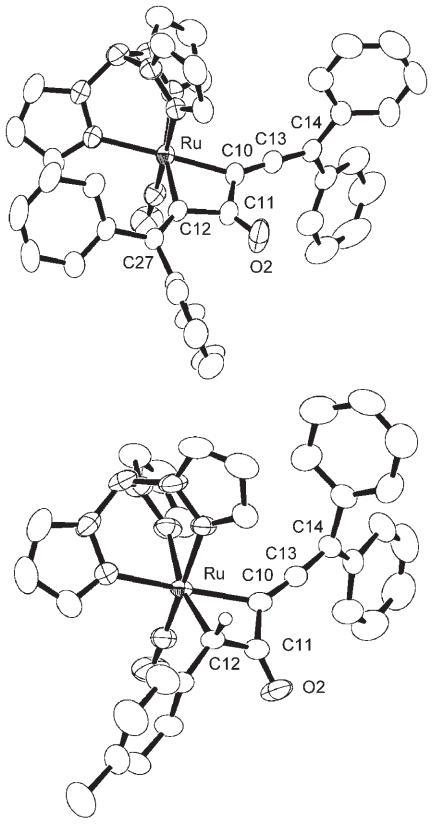


Figure 1. One of the molecular structures of [TpRu{C(=C=CPh$_2$)C(O)C(=CPh$_2$)}(NO)] (**3**) (top) and that of [TpRu{C(=C=CPh$_2$)C(O)CH(C$_6$H$_4$Me)}(NO)] (**5**) (bottom).

Table 1. Selected bond lengths (Å) and angles [°] for [TpRu{C(=C=CPh$_2$)C(O)C(=CPh$_2$)}(NO)] (**3**) and [TpRu{C(=C=CPh$_2$)C(O)CH(C$_6$H$_4$Me)}(NO)] (**5**).

	3	**5**
Ru–C10	2.075(2), 2.075(2)	2.080(3)
Ru–C12	2.106(2), 2.105(2)	2.165(3)
C10–C11	1.501(3), 1.495(3)	1.486(4)
C11–C12	1.493(3), 1.494(3)	1.489(4)
C10–C13	1.291(3), 1.294(3)	1.288(4)
C13–C14	1.327(3), 1.315(3)	1.324(4)
C12–C27	1.351(3), 1.353(3)	1.480(4)
C11–O2	1.203(3), 1.202(3)	1.222(4)
C10-C11-C12	101.4(2), 101.4(2)	104.8(2)
C10-C13-C14	178.1(2), 177.3(2)	175.2(3)

In the α-vinylacyl–allenyl fragment, the dihedral angle between the two planes [Ru-C10-C11-C12-C25] and [C25-C26-C27] is 30.714°, and the O2 atom is situated above the latter plane (0.5383 Å). The bond lengths and angle of C_α-C_β-C_γ in the allenyl part (C_α–C_β 1.300(3) Å, C_β–C_γ 1.328(3) Å, C_α-C_β-C_γ 174.9(2)°) are comparable to those of the diphenylethenylidene part (**3** and **5**). The bond lengths of O2–C25 (1.218(2) Å) and C26–C27 (1.345(3) Å) are typical of double bonds.

Formation mechanism of 3–6: The formation of **3** and **5** would be rationalized according to Scheme 2. Initial protonation of one 3-hydroxyalkynyl group would result in dehydration to give the allenylidene intermediates. This facile dehydration process has been demonstrated in mono(3-hy-

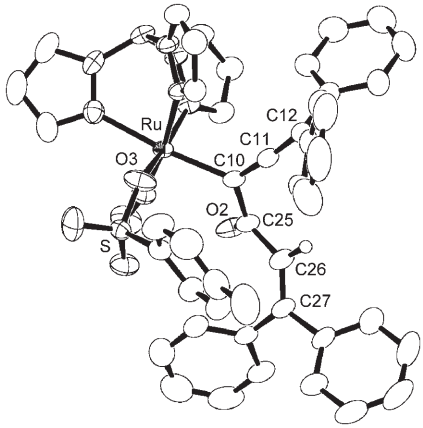


Figure 2. ORTEP drawing of [TpRu{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(OSO$_2$C$_6$H$_4$Me)(NO)] (**4**).

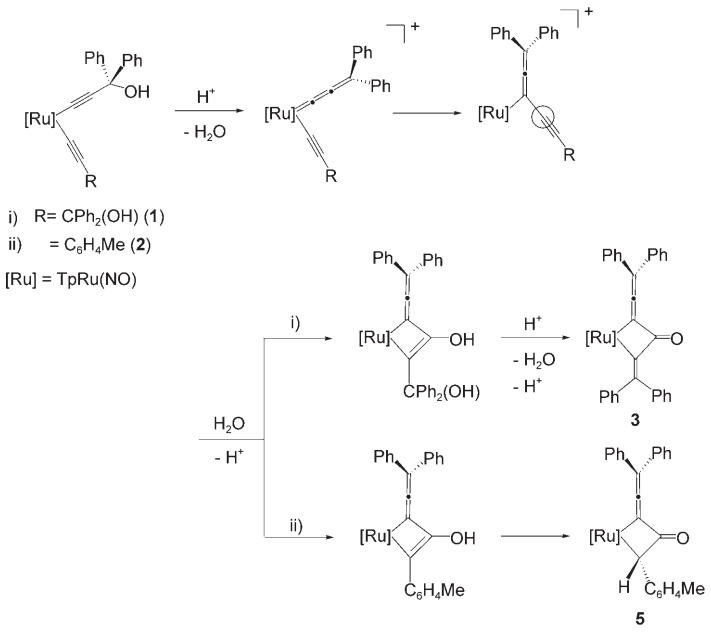
Table 2. Selected bond lengths [Å] and angles [°] for [TpRu{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(OSO$_2$C$_6$H$_4$Me)(NO)] (**4**).

Ru–C10	2.102(2)	C26–C27	1.345(3)
Ru–O3	2.073(1)	C25–O2	1.218(2)
C10–C11	1.300(3)		
C11–C12	1.328(3)	C10-C11-C12	174.9(2)
C10–C25	1.506(2)	C10-C25-C26	117.0(2)
C25–C26	1.477(3)	C25-C26-C27	126.6(2)

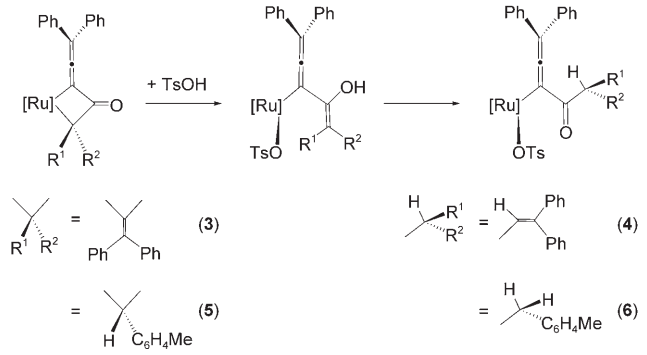
droxyalkynyl) nitrosylruthenium.[7a,c] The other ligating 3-hydroxyalkynyl (**1**) or arylalkynyl (**2**) group would migrate to the α-position of the allenylidene group, followed by nucleophilic addition by H_2O on the β carbon of the resulting α-alkynyl–allenyl intermediates to produce 3-hydroxymetallacyclobutene species. Keto–enol tautomerization would lead to **5**, but in the formation of **3**, after tautomerization further dehydration process would proceed owing to reasonable high reactivity of the generated β-hydroxyketone form.

On the other hand, during the reaction runs to give the four-membered metallacycles **3** and **5**, their additional protonation would lead to the formation of *p*-toluenesulfonato complexes (**4** and **6**) as by-products. Actually, heating the isolated **3** and **5** with TsOH in THF afforded **4** (44%) and **6** (40%), respectively (Scheme 1). The formation mechanism of **4** and **6** would be that protonation of the carbonyl group in **3** and **5** brought about the enol form, accompanying concurrent addition of a TsO^- anion to the metal center, followed by conversion to keto form (**4** and **6**) (Scheme 3).

Reactions of the four-membered metallacycles (3 and 5) with aqueous HCl in MeOH: Isolation of the ring-opened *p*-toluenesulfonato products **4** and **6** has led us to investigate chemical reactivities of the four-membered metallacycles **3** and **5** towards HCl as another protic acid. Treatment of **3** and **5** with aqueous HCl in MeOH was found to give allenyl complexes [TpRuCl{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(NO)] (**7**) (29%) and [TpRuCl{C(=C=CPh$_2$)C(O)CH$_2$(C$_6$H$_4$Me)}(NO)] (**8**) (84%), respectively (Scheme 4). These isolated complexes are ring-opened products, which are similar to **4** and

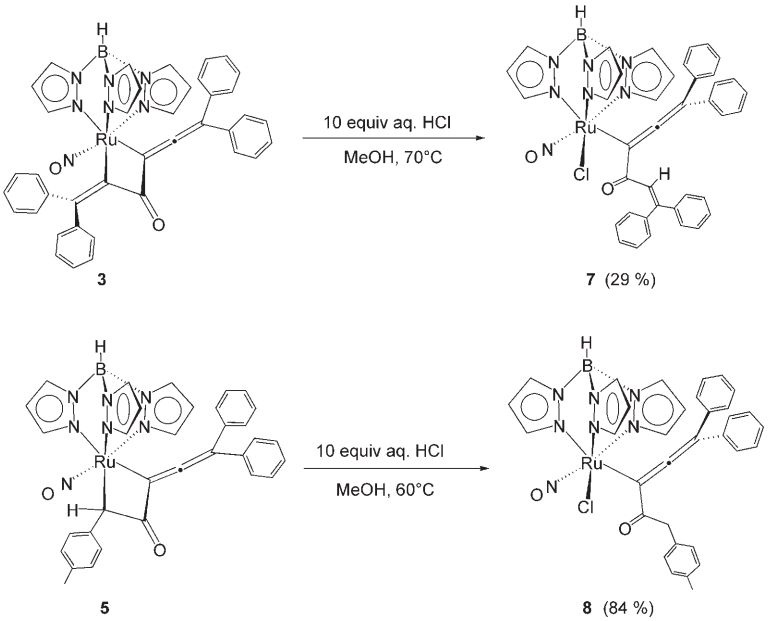


Scheme 2. Formation mechanism of **3** and **5**.



Scheme 3. Formation mechanism of **4** and **6**.

6, but one-HCl adducts. In the ^{1}H NMR spectrum of **8**, the most notable feature is the presence of diastereotopic methylene protons at $\delta = 4.42$ and 4.18 ppm. The NMR signal of the characteristic olefinic proton for **7** was not definitely assigned because of its overlapping with the aromatic Ph signals. Both FAB-MS spectra of **7** and **8** show a [TpRuCl(C=C=CPh$_2$)(NO)]$^+$ fragment signal due to the loss of C(O)CH=CPh$_2$ and C(O)CH$_2$(C$_6$H$_4$Me) groups, respectively, besides their parent molecular ions. In the same manner as **4** and **6** (Scheme 3), the formation of **7** and **8** was triggered by protonation of the carbonyl group in **3** and **5**, followed by coordination of the Cl^- anion to the metal center. Furthermore, the structures of **7** and **8** were confirmed by X-ray crystallographic analyses (Figure 3, Table 3). In the course of their ring-opening, retention of the allenyl part is indicated by C10–C11 (**7**: 1.303(4) Å, **8**: 1.300(3) Å) and C11–C12 (**7**: 1.318(4) Å, **8**: 1.324(3) Å) bond lengths and C10-C11-C12 (**7**: 179.0(3)°, **8**: 177.7(2)°) angles. The C25–O2 (**7**: 1.214(3) Å, **8**: 1.207(3) Å) distances correspond well to



Scheme 4. Treatment of **3** and **5** with aq. HCl in MeOH.

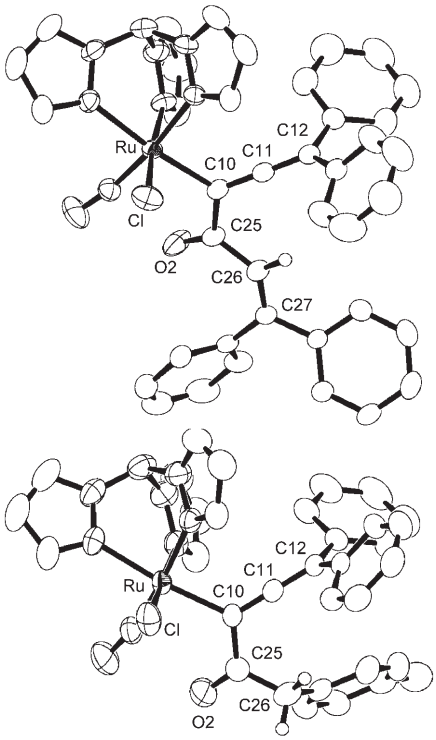


Figure 3. Molecular structures of [TpRuCl{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(NO)] (**7**) (top) and [TpRuCl{C(=C=CPh$_2$)C(O)CH$_2$-(C$_6$H$_4$Me)}(NO)] (**8**) (bottom).

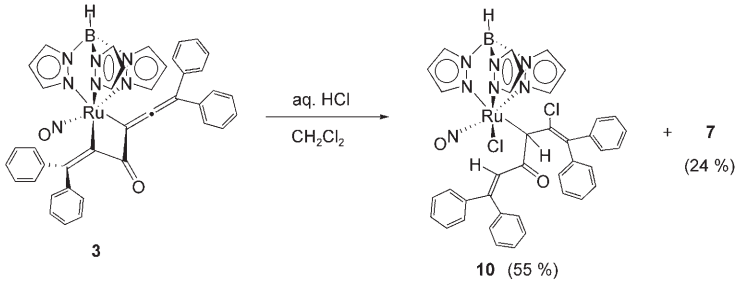
double bonds. Also, the double bond character is seen in C26−C27 of **7** (1.350(3) Å). Complex **8** was not further reacted with aq. HCl even in refluxing CH_2Cl_2, while, from **7** in place of **8**, conversion to **10** was detected in ^{1}H NMR experiments (see below).

Reactivities of the four-membered metallacycles 3 and 5 toward aqueous HCl in CH_2Cl_2 or THF

I) Complex 3: Interestingly, in CH_2Cl_2 instead of MeOH, a similar treatment of the metallacycle **3** with aqueous HCl was run to give other ring-opened complex [TpRuCl{C(C(Cl)=CPh$_2$)(H)C(O)CH=CPh$_2$}(NO)] (**10**) (55 %) along with the complex **7** (24 %) (Scheme 5). In the ^{1}H NMR spectrum of **10**, the most noticeable resonances are two singlets at $\delta = 5.02$ and 5.42 ppm, corresponding to the olefinic and methine protons, respectively. The FAB-MS spectrum exhibits the parent molecular ion signal at *m*/*z* 813.2,

Table 3. Selected bond lengths [Å] and angles [°] for [TpRuCl{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(NO)] (**7**) and [TpRuCl{C(=C=CPh$_2$)C(O)CH$_2$-(C$_6$H$_4$Me)}(NO)] (**8**).

	7	**8**
Ru−C10	2.092(2)	2.094(2)
C10−C11	1.303(4)	1.300(3)
C11−C12	1.318(4)	1.324(3)
C10−C25	1.517(4)	1.499(3)
C25−C26	1.476(4)	1.516(3)
C26−C27	1.350(3)	1.508(3)
C25−O2	1.214(3)	1.207(3)
C10-C11-C12	179.0(3)	177.7(2)
C10-C25-C26	114.4(2)	118.8(2)



Scheme 5. Treatment of **3** with aq. HCl in CH_2Cl_2.

showing two-HCl mass increment as compared with **3**. Elemental analysis and the X-ray diffraction study (Figure 4, Table 4) also support the formulation. The crystal structure of **10** reveals that a Ru−C bond cleavage occurs at the same position as **7**, but that further HCl addition to the diphenylethenylidene part (C=C=CPh$_2$) also takes place. Although C13−C14 (1.37(1) Å) and C12−C27 (1.34(2) Å) bond lengths

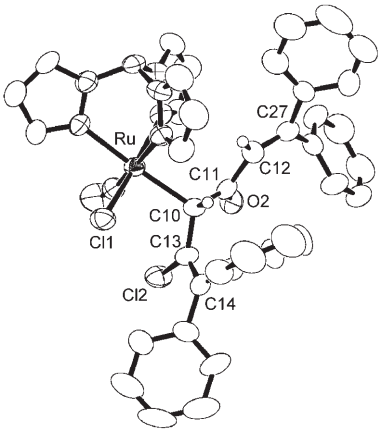


Figure 4. ORTEP drawing of [TpRuCl{C(C(Cl)=CPh$_2$)(H)C(O)CH=CPh$_2$}(NO)] (**10**).

Table 4. Selected bond lengths [Å] and angles [°] for [TpRuCl{CH(C(Cl)=CPh$_2$)C(O)CH=CPh$_2$}(NO)] (**10**).

Ru–C10	2.18(1)	C13–Cl2	1.74(1)
C10–C11	1.47(2)	C11–O2	1.23(1)
C11–C12	1.49(2)		
C12–C27	1.34(2)	C10-C11-C12	112.7(10)
C10–C13	1.48(1)	C11-C12-C27	129(1)
C13–C14	1.37(1)	C10-C13-C14	123(1)

retain double-bond character, elongation of C10–C13 (1.48(1) Å) is observed.

Switching to alternative reaction conditions, that is, in THF at room temperature for 30 min, converted **3** to [TpRu{C(C(Cl)=CPh$_2$)(H)C(O)C(=CPh$_2$)}(NO)] (**9b**) (84%), diastereoselectively (Scheme 6). The ^{1}H NMR of **9b** indicates the presence of methine proton (singlet, δ = 5.03 ppm) and the FAB-MS spectrum shows one-HCl addition to **3**. An X-ray analysis establishes that **9b** retains the four-membered ring, but undergoing HCl addition to the C=C$_\alpha$ bond of the diphenylethenylidene part (C=C$_\alpha$=C$_\beta$Ph$_2$) (Figure 5, Table 5). The bond lengths (C13–C14 1.346(4) Å,

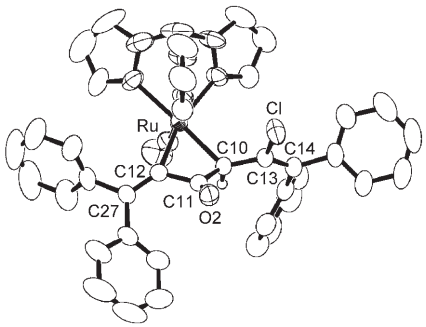


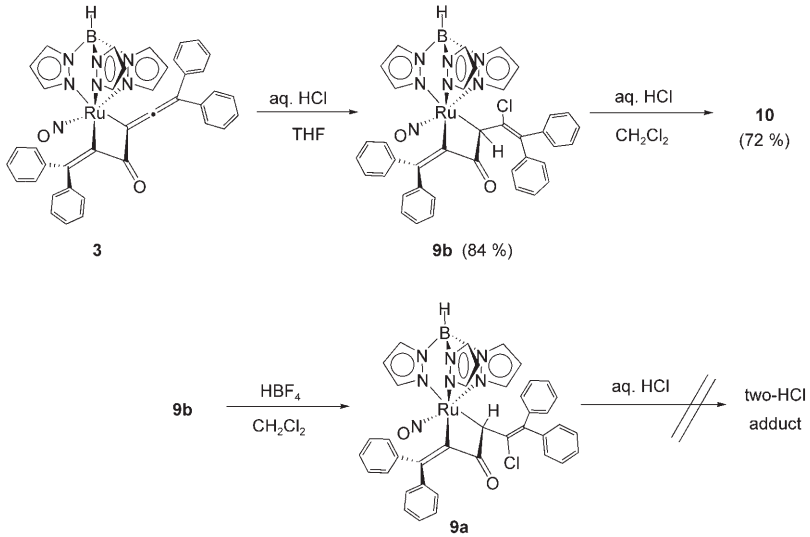
Figure 5. ORTEP drawing of [TpRu{C(C(Cl)=CPh$_2$)(H)C(O)C(=CPh$_2$)}(NO)] (**9b**).

Table 5. Selected bond lengths [Å] and angles [°] for [TpRu{CH(C(Cl)=CPh$_2$)C(O)C(=CPh$_2$)}(NO)] (**9a**) and [TpRu{C(C(Cl)=CPh$_2$)(H)C(O)C(=CPh$_2$)}(NO)] (**9b**).

	9a	**9b**
Ru–C10	2.147(2)	2.180(3)
Ru–C12	2.112(2)	2.101(3)
C10–C11	1.490(2)	1.482(4)
C11–C12	1.498(2)	1.485(4)
C12–C27	1.343(2)	1.334(4)
C10–C13	1.474(2)	1.467(4)
C13–C14	1.330(3)	1.346(4)
C13–Cl	1.756(2)	1.747(3)
C11–O2	1.217(2)	1.227(4)
C10-C11-C12	104.6(1)	103.6(2)
C10-C13-C14	127.1(2)	125.7(3)

C12–C27 1.334(4) Å, C10–C13 1.467(4) Å) of **9b** are similar to those found in **10**. Since the complex **10** is the two-HCl adduct, one can expect that **7** and/or **9b** would be the intermediate in the formation of **10** from **3**. In fact, treatment of **9b** with aq. HCl clearly produced **10** in 72% yield (Scheme 6), while fairly slow conversion of **7** to **10** was observed in ^{1}H NMR spectrum. The intermediate **9b** is also supported by the fact that ruthenium-bonded methine carbons in the crystal structures of **9b** and **10** are in the same diastereomeric configuration.

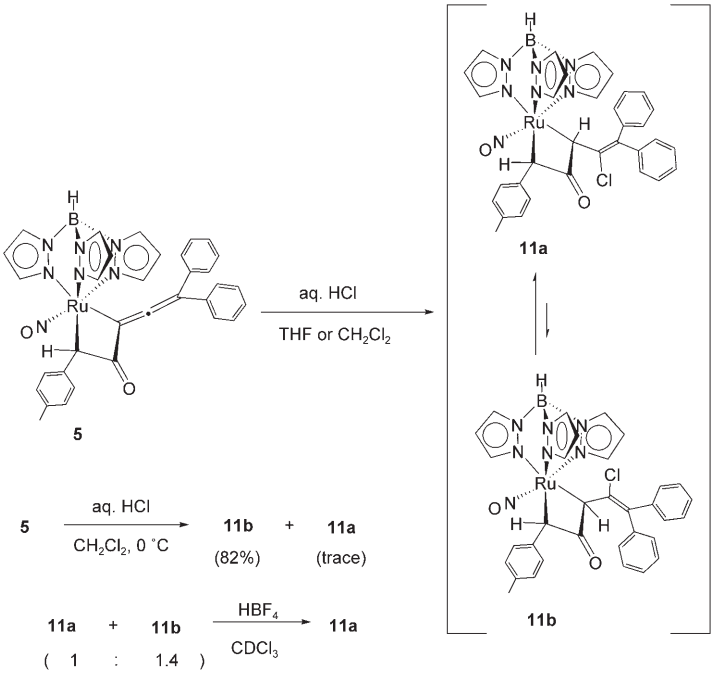
On the other hand, proton-assisted isomerization of **9b** led to the other diastereomer **9a** via keto–enol tautomerization. Complex **9a** has been unambiguously identified by spectral



Scheme 6. Formation of **9a** and **9b**.

data (NMR, IR, and FAB-MS), elemental analysis, and X-ray diffraction (see Supporting Information for Ortep graphic of **9a**). In the comparison of the crystal structures of two diastereoisomers **9a** and **9b**, the configuration at C10 would allow isomer **9a** to be thermodynamically stable, because the chlorovinyl part ($C(Cl)=CPh_2$) at C10 directs away from pyrazolyl rings of the Tp ligand. This character is confirmed by the Ru–C10 bond lengths (**9a**: 2.147(2) Å, **9b**: 2.180(3) Å). Although other significant differences in crystallographic structural data between these two diastereomers are not observed, interestingly, treatment of **9a** with aqueous HCl did not give the corresponding two-HCl adduct like **10**.

II) Complex 5: Reaction of the other four-membered metallacyclic complex **5** with aq. HCl also depends on the reaction solvents. In THF or CH_2Cl_2, treatment of **5** with aq. HCl at room temperature was carried out to give a mixture of two diastereomers [TpRu{CH(C(Cl)=CPh$_2$)C(O)CH-(C$_6$H$_4$Me)}(NO)] (**11a** and **11b**) (Scheme 7; see Supporting Information for Ortep graphic of **11b**). The ^{1}H NMR spectrum of the mixture shows two mutually similar signal patterns assignable to the two diastereomers with a varying abundance ratio. Column chromatographic separation of the mixture was unsuccessful, but each species, **11a** and **11b**, was separately recrystallized. Their structures were revealed by X-ray crystallographic analyses and the molecular structure of **11a** is shown in Figure 6. Selected bond lengths and angles are summarized in Table 6. These species still retain the four-membered metallacycle, containing the chlorovinyl substituent ($C(Cl)=CPh_2$) at α-carbon, indicative of the one-



Scheme 7. Treatment of **5** with aq. HCl in THF or CH_2Cl_2.

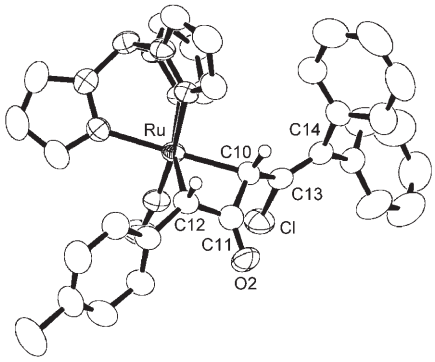


Figure 6. ORTEP drawing of [TpRu{CH(C(Cl)=CPh$_2$)C(O)CH-(C$_6$H$_4$Me)}(NO)] (**11a**).

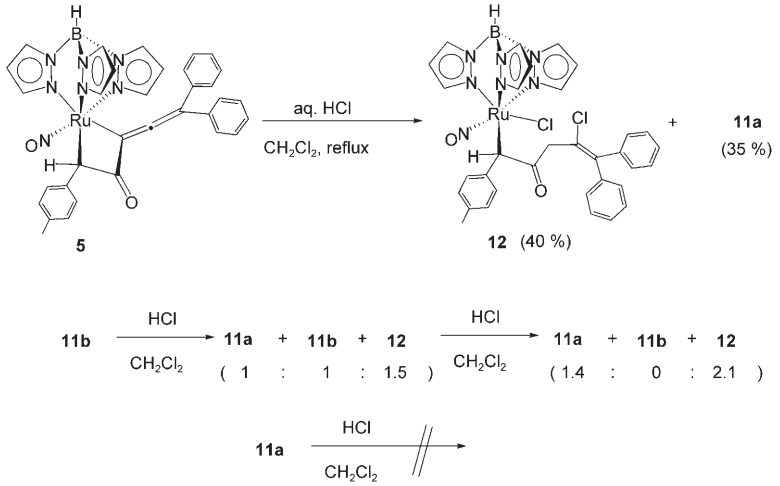
Table 6. Selected bond lengths [Å] and angles [°] for [TpRu{CH(C(Cl)=CPh$_2$)C(O)CH(C$_6$H$_4$Me)}(NO)] (**11a**) and [TpRu{C(C(Cl)=CPh$_2$)(H)C(O)CH(C$_6$H$_4$Me)}(NO)] (**11b**).

	11a	**11b**
Ru–C10	2.140(3)	2.193(4)
Ru–C12	2.156(2)	2.158(4)
C10–C11	1.498(4)	1.475(5)
C11–C12	1.480(4)	1.498(6)
C10–C13	1.478(3)	1.473(5)
C13–C14	1.335(4)	1.348(5)
C13–Cl	1.757(3)	1.747(4)
C11–O2	1.224(3)	1.231(5)
C10-C11-C12	106.3(2)	108.1(3)
C10-C13-C14	127.0(2)	124.7(4)

HCl adduct. The EI-MS spectra also support the formulation. The C10–C13 bond lengths of **11a** (1.478(3) Å) and **11b** (1.473(5) Å) are clearly elongated relative to that of **5**, and the C10-C13-C14 angles are 127.0(2)° (**11a**) and 124.7(4)° (**11b**). The distinguishable difference of the Ru–C10 bond lengths (**11a**: 2.140(3) Å, **11b**: 2.193(4) Å) would reflect the respective steric interaction between pyrazolyl rings and the chlorovinyl substituent.

Taking account of these steric interactions, complex **11b** was presumed to be the kinetically controlled product. In fact, the reaction system of **5**/aq. HCl in CH_2Cl_2 at 0 °C proceeded to give **11b** with trace amounts of **11a**. In the presence of HBF_4, a mixture of two diastereoisomers (**11a**/**11b** 1:1.4) in $CDCl_3$ at room temperature was changed for 48 h to **11a** exclusively.

On the other hand, a similar treatment of **5** with aq. HCl in refluxing CH_2Cl_2 gave rise to **11a** (35%) and newly [TpRuCl{CH(C$_6$H$_4$Me)C(O)CH$_2$(C(Cl)=CPh$_2$)}(NO)] (**12**) (40%) without **11b** (Scheme 8). The most significant features of the ^{1}H NMR spectrum of **12** are a singlet at $\delta =$ 5.12 ppm and an AB pattern at $\delta = 4.36$ and 3.96 ppm ($J =$ 15 Hz). The EI-MS spectrum indicates two-HCl addition to the complex **5**. The complex **12** is crystallographically determined to be a ring-opened species, which is similar to **8**, but where Ru–C bond cleavage occurs at the other Ru-linking side of the metallacycle (Figure 7, Table 7). In the crystal structure of **12**, the bond lengths of O2–C11 (1.209(3) Å)



Scheme 8. Treatment of **5** with aq. HCl in refluxing CH_2Cl_2.

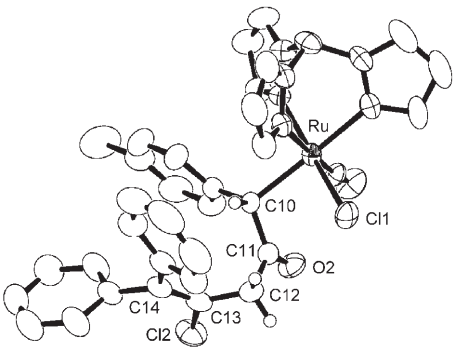


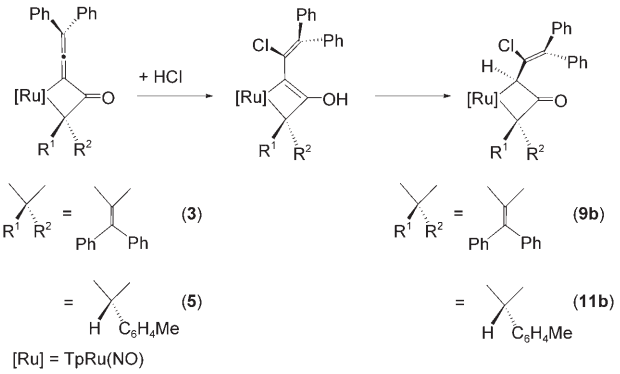
Figure 7. ORTEP drawing of [TpRuCl{CH(C_6H_4Me)C(O)CH_2(C(Cl)=CPh_2)}(NO)] (**12**).

Table 7. Selected bond lengths [Å] and angles [°] for [TpRuCl{CH(C_6H_4Me)C(O)CH_2(C(Cl)=CPh_2)}(NO)] (**12**).

Ru–C10	2.155(2)	C13–Cl2	1.753(2)
C10–C11	1.511(3)	C11–O2	1.209(3)
C11–C12	1.528(3)		
C12–C13	1.499(4)	C10-C11-C12	115.5(2)
C13–C14	1.343(3)	C12-C13-C14	129.6(2)

and C13–C14 (1.343(3) Å) are typical of double bonds. It is noteworthy that complex **12** was formed only from **11b**. The kinetic product **11b** was heated with aq. HCl in CH_2Cl_2 for 24 h to give a mixture of **11a**, **11b**, and **12** (1:1:1.5), and successive heating for another 24 h afforded a mixture of **11a** and **12** (1.4:2.1). Complex **11b** was converted to **11a** and **12**. Under the same reaction conditions, complex **11a** did not react further with aq. HCl.

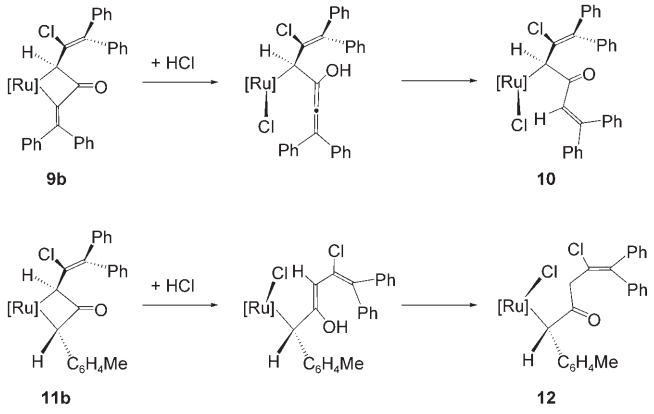
III) Mechanistic aspects in the formation of 9–12: For the formation of **9** and **11**, which are composed of two diastereoisomers, respectively, protonation of the carbonyl group of **3** and **5** would facilitate Cl^- nucleophilic attack on the C_α of the ethenylidene group (=C_α=$C_\beta Ph_2$) (Scheme 9). This Cl^- addition position would be reasonable on the basis of the relatively low-field signal of C_α in their $^{13}C\{^1H\}$ NMR spectra. Following keto–enol tautomerization would complete their formation, retaining the four-membered ring. The reason why **9b** and **11b** are kinetically favored is unclear, but it is presumed that the nitrogen of the NO ligand may assist C_α protonation of the enol form in the transition state during the conversion to the keto form. The steric requirement between pyrazolyl rings of the Tp ligand and the chlorovinyl group would thermodynamically de-



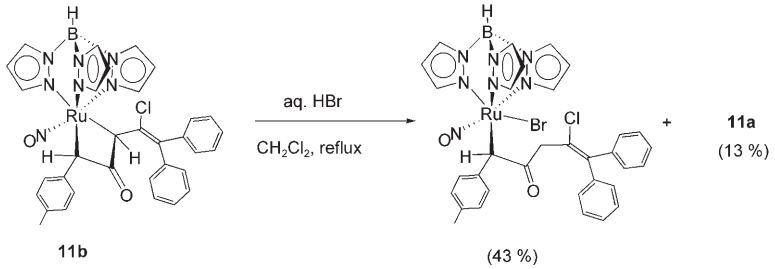
Scheme 9. Formation mechanism of **9b** and **11b**.

termine the relative stability of the diastereoisomers in **9** and **11**. Intriguingly, although additional HCl treatment of **9a** and **11a** did not induce any addition processes under these conditions, both of the thermodynamically less stable isomers (**9b** and **11b**) reacted further with aq. HCl to afford **10** and **12**, respectively. These are ring-opened two-HCl adducts, where each one Ru–C bond is severed at mutually different positions (**10**, Ru–alkenyl bond; **12**, Ru–σ-allyl bond). In either case, protonation on the carbonyl group would also initiate the addition reaction (Scheme 10). Coordination of chloride anion to the ruthenium center, followed by keto–enol tautomerization, would afford **10** and **12**. In the formation of **12**, other mechanism, initial β-chloride elimination of **11b**, followed by 1,4-HCl addition to the resulting α-allenyl–carbonyl form, can be assumed. However, this mechanism was ruled out, because of the results from the treatment of **11b** with aq. HBr, which gave a bromoruthenium [TpRuBr{CH(C_6H_4Me)C(O)CH_2(C(Cl)=CPh_2)}(NO)] without a chlororuthenium complex (Scheme 11).[13]

On the whole, complexes **9** and **11** contain three types of Ru–C bonds (**9**: Ru–alkenyl and Ru–σ-allyl bonds, **11**: Ru–alkyl and Ru–σ-allyl bonds). These HCl addition reactions



Scheme 10. Formation mechanism of **10** and **12**.



Scheme 11. Treatment of **11b** with aq. HBr in refluxing CH_2Cl_2.

indicate the order of the facile bond cleavage (Ru–alkenyl > Ru–σ-allyl > Ru–alkyl bonds).

Conclusion

In this article, we reveal the preparations of the unusual four-membered metallacyclic complexes, [TpRu{C(=C=CPh_2)C(O)C(=CPh_2)}(NO)] (**3**) and [TpRu{C(=C=CPh_2)C(O)CH(C_6H_4Me)}(NO)] (**5**), and their stepwise HCl addition reactions depending on the reaction solvents.

Introduction of the 3-hydroxyalkynyl group to the bis(alkynyl) complexes and their treatment with protic acids allowed us to isolate the four-membered metallacycles **3** and **5**, in contrast to the bis(arylalkynyl) case which afforded the five-membered metallacycles.[7b] Facile generation of allenylidene intermediates through dehydration of the 3-hydroxyalkynyl group affected diverse new attractive reactivities, in combination with ruthenium-mediated C–C coupling processes.

Addition of HCl to the four-membered metallacycles **3** and **5** depended on the reaction solvents. In MeOH (protic solvent), the ring-opened one-HCl adducts **7** and **8** were isolated, while, in CH_2Cl_2 or THF (aprotic solvent), the ring-retained one-HCl adducts **9** and **11** as the respective diastereomers were formed. Although the strict reason for these differences cannot be presently defined, this can be attributed to the solvation of the nucleophile (Cl^-). Since higher nucleophilicities of the chloride anion is produced in non-hydrogen bonding solvents,[14] the aprotic reaction condition would be favored for the formation of the ring-retained products **9** and **11**.

Moreover, each kinetically controlled products **9b** and **11b** rather than **9a** and **11a** was treated with aq. HCl to give the ring-opened two-HCl adducts **10** and **12**, where each one Ru–C bond is cleaved at mutually different positions. Isolation of **10** and **12** through **9b** and **11b** indicates their stepwise HCl addition.

Experimental Section

Reactions were carried out under atmosphere of dry N_2, whereas subsequent workup was performed in air. Solvents were distilled from sodium/benzophenone (THF) or from CaH_2 (CH_2Cl_2). All other organic solvents and reagents were commercially available and used without further purification.

NMR spectra in $CDCl_3$ were acquired on a JEOL JNM-AL-400 and a Varian Gemini-300 spectrometers for ^1H and $^{13}C\{^1H\}$, and their chemical shifts are quoted with respect to TMS and the solvent signals, respectively. IR spectra in KBr pellets were obtained on a JASCO FT-IR-420 spectrometer. Electron ionization mass spectra (EI-MS) and fast atom bombardment mass spectra (FAB-MS) were recorded on a JEOL JMS-DX-303 and a JEOL JMS-700N spectrometers. Elemental analyses (C, H, N) were performed on a Perkin Elmer 2400II elemental analyzer.

[TpRu{C≡CC(Ph)$_2$OH}$_2$(NO)] (1): HC≡CC(Ph)$_2$OH (500 mg, 2.4 mmol), CuI (4.6 mg, 0.024 mmol), and Et_3N (730 mg, 7.2 mmol) were added to a solution of [$TpRuCl_2$(NO)][10] (100 mg, 0.24 mmol) dissolved in CH_2Cl_2 (8 mL), and the reaction mixture was heated under reflux for 1 d. After removal of the volatiles, the residue was separated on column chromatography of a silica gel by use of CH_2Cl_2 and CH_2Cl_2/acetone 40:1, and [TpRu{C≡CC(Ph)$_2$OH}$_2$(NO)] (**1**) was isolated as a brown solid (30 mg, 17%) besides [TpRuCl{C≡CCPh$_2$(OH)}(NO)] (50 mg, 35%). Complex **1** was also prepared (64%) similarly from [TpRuCl{C≡CCPh$_2$(OH)}(NO)].[7a] ^1H NMR ($CDCl_3$): δ = 7.86 (d, J = 1.9 Hz, 2H of pz), 7.83 (d, J = 2.2 Hz, 1H of pz), 7.76–7.71 (m, 10H of pz and Ph), 7.45 (d, J = 2.2 Hz, 1H of pz), 7.25–7.13 (m, 12H of Ph), 6.31 (t, J = 2.4 Hz, 2H of pz), 5.97 (t, J = 2.4 Hz, 1H of pz), 2.91 ppm (s, 2H of O*H*); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 147.1 (s, Ph), 147.0 (s, Ph), 145.4 (s, pz), 142.8 (s, pz), 135.6 (s, pz), 134.6 (s, pz), 127.7 (s, Ph), 127.7 (s, Ph), 126.7 (s, Ph), 126.6 (s, Ph), 126.1 (s, Ph), 126.1 (s, Ph), 112.5 (s, C≡C), 106.6 (s, pz), 105.3 (s, pz), 97.3 (s, C≡C), 75.2 ppm (s, *C*(Ph)$_2$OH); IR (KBr, pellet): $\tilde{\nu}$ = 3416 (w, OH), 2494 (w, BH), 2134 (w, C≡C), 1872 cm^{-1} (s, N≡O); FAB-MS: *m*/*z*: 760 $[M+1]^+$, 742 $[M-OH]^+$; elemental analysis calcd (%) for $C_{39}H_{32}BN_7O_3Ru$: C 61.75, H 4.25, N 12.92; found: C 61.25, H 4.31, N 12.34.

[TpRu(C≡CC_6H_4Me){C≡CC(Ph)$_2$OH}(NO)] (2): Propargylic alcohol HC≡CC(Ph)$_2$OH (420 mg, 2.0 mmol), CuI (8.0 mg, 0.040 mmol), and Et_3N (810 mg, 8.0 mmol) were added to a solution of [TpRuCl(C≡CC_6H_4Me)(NO)][7a] (200 mg, 0.40 mmol) in CH_2Cl_2 (8 mL). The solution was heated under reflux overnight and was concentrated to dryness. The residue was purified by chromatography on a silica gel column using CH_2Cl_2 to give **2** as a red solid (135 mg, 50%). ^1H NMR ($CDCl_3$): δ = 8.01 (d, J = 1.9 Hz, 1H of pz), 8.00 (d, J = 1.9 Hz, 1H of pz), 7.85 (d, J = 1.7 Hz, 1H of pz), 7.81–7.76 (m, 4H of aryl), 7.73 (d, J = 2.2 Hz, 2H of

pz), 7.47 (d, $J=2.2$ Hz, 1H of pz), 7.32 (d, $J=8.0$ Hz, 2H of aryl), 7.26–7.15 (m, 6H of aryl), 7.05 (d, $J=8.0$ Hz, 2H of aryl), 6.36 (t, $J=2.2$ Hz, 1H of pz), 6.32 (t, $J=2.2$ Hz, 1H of pz), 6.05 (t, $J=2.2$ Hz, 1H of pz), 2.94 (br s, 1H of O*H*), 2.32 ppm (s, 3H of C_6H_4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 147.3 (s, aryl), 147.2 (s, aryl), 145.4 (s, pz), 142.7 (s, pz), 142.7 (s, pz), 135.6 (s, aryl), 135.5 (s, pz), 135.5 (s, pz), 134.5 (s, pz), 131.4 (s, aryl), 128.4 (s, aryl), 127.6 (s, aryl), 127.6 (s, aryl), 126.6 (s, aryl), 126.5 (s, aryl), 126.2 (s, aryl), 126.1 (s, aryl), 123.7 (s, aryl), 112.3 (s, C≡C), 110.4 (s, C≡C), 106.7 (s, pz), 106.5 (s, pz), 105.4 (s, pz), 99.9 (s, C≡C), 97.7 (s, C≡C), 75.1 (s, $C(Ph)_2OH$), 21.4 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 3442 (w, OH), 2498 (w, BH), 2127 (w, C≡C), 1868 cm^{-1} (s, N≡O); FAB-MS: *m/z*: 667.1 $[M]^+$, 650.1 $[M-OH]^+$, 637.1 $[M-NO]^+$; elemental analysis calcd (%) for $C_{33}H_{28}BN_7O_2Ru$: C 59.47, H 4.23, N 14.71; found: C 59.99, H 4.30, N 14.07.

Formation of 3 and 4 from treatment of 1 with *p*-toluenesulfonic acid: *p*-Toluenesulfonic acid monohydrate ($TsOH\cdot H_2O$) (15 mg, 0.079 mmol) was added at room temperature to a THF (5 mL) solution of [TpRu{C≡CC(Ph)$_2$OH}$_2$(NO)] (**1**) (60 mg, 0.079 mmol), and the reaction mixture was stirred for 1 h. After the protic acid remained in the solution was quenched by solid powder $NaHCO_3$, the mixture was filtered and the filtrate was evaporated to dryness. The residue was separated on column chromatography (silica gel) to give [TpRu{C(=C=CPh$_2$)C(O)C(=CPh$_2$)}(NO)] (**3**) as an orange solid (27 mg, 47%) and [TpRu{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(OSO$_2$C$_6$H$_4$Me)(NO)] (**4**) as a brown-orange solid (33 mg, 46%) by elution with CH_2Cl_2/acetone 50:1 and 30:1, respectively. Complex **4** was also prepared (44%) in refluxing THF for 4 h from **3** (29 mg, 0.039 mmol) and $TsOH\cdot H_2O$ (76 mg, 0.39 mmol).

Complex 3: ^1H NMR ($CDCl_3$): δ = 7.77 (d, $J=1.9$ Hz, 1H of pz), 7.72 (d, $J=1.9$ Hz, 1H of pz), 7.66 (d, $J=1.9$ Hz, 1H of pz), 7.60 (d, $J=1.9$ Hz, 1H of pz), 7.48 (d, $J=7.1$ Hz, 2H of Ph), 7.42 (d, $J=1.7$ Hz, 1H of pz), 7.36 (t, $J=7.3$ Hz, 2H of Ph), 7.32–7.28 (m, 5H of Ph), 7.05–6.98 (m, 3H of Ph), 6.90 (t, $J=7.7$ Hz, 2H of Ph), 6.87 (t, $J=7.4$ Hz, 2H of Ph), 6.61 (d, $J=6.9$ Hz, 2H of Ph), 6.49 (d, $J=6.9$ Hz, 2H of Ph), 6.21 (t, $J=2.3$ Hz, 1H of pz), 6.19 (d, $J=1.9$ Hz, 1H of pz), 6.08 (t, $J=2.2$ Hz, 1H of pz), 5.86 ppm (t, $J=2.2$ Hz, 1H of pz); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 197.9 (s, *C*O), 195.5 (s, allenyl), 155.3 (s, vinyl), 150.1 (s, vinyl), 144.2 (s, Ph), 142.8 (s, pz), 142.5 (s, Ph), 142.2 (s, pz), 141.9 (s, pz), 137.5 (s, Ph), 136.6 (s, Ph), 135.4 (s, pz), 134.8 (s, pz), 134.5 (s, pz), 129.4 (s, Ph), 129.0 (s, Ph), 128.4 (s, Ph), 128.4 (s, Ph), 128.2 (s, Ph), 127.8 (s, Ph), 127.7 (s, Ph), 127.4 (br s, Ph, overlapping), 127.0 (s, Ph), 126.9 (s, Ph), 126.3 (s, Ph), 110.2 (s, allenyl), 106.2 (s, allenyl), 106.1 (br s, pz, overlapping), 105.9 ppm (s, pz); IR (KBr, pellet): $\tilde{\nu}$ = 2492 (w, BH), 1899 (m, C=C=C), 1826 (s, N≡O), 1642 cm^{-1} (m, C=O); EI-MS: *m/z*: 741 $[M]^+$, 711 $[M-NO]^+$, 683 $[M-NO-CO]^+$, 615 $[M-NO-CO-pz-1]^+$, 535 [TpRu(C=C=CPh$_2$)(NO)]$^+$), 505 [TpRu(C=C=CPh$_2$)]$^+$, 315 $[TpRu]^+$; elemental analysis calcd (%) for $C_{39}H_{30}BN_7O_2Ru$: C 63.25, H 4.08, N 13.24; found: C 62.96, H 3.99, N 13.24.

Complex 4: ^1H NMR ($CDCl_3$): δ = 8.26 (d, $J=2.2$ Hz, 1H of pz), 7.85 (d, $J=2.5$ Hz, 1H of pz), 7.80 (d, $J=8.2$ Hz, 2H of aryl), 7.69 (d, $J=2.5$ Hz, 1H of pz), 7.52 (d, $J=2.2$ Hz, 1H of pz), 7.32–7.17 (m, 12H of aryl and 2H of pz), 7.12–7.03 (m, 4H of aryl), 6.98 (s, 1H of -C*H*=CPh$_2$), 6.92–6.86 (m, 4H of aryl), 6.32 (t, $J=2.1$ Hz, 1H of pz), 6.19 (t, $J=2.3$ Hz, 1H of pz), 6.08 (d, $J=7.4$ Hz, 2H of aryl), 5.80 (t, $J=2.3$ Hz, 1H of pz), 2.39 ppm (s, 3H of C_6H_4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 210.3 (s, *C*O), 194.6 (s, allenyl), 149.5 (s, vinyl), 145.4 (s, pz), 143.9 (s, pz), 142.7 (s, pz), 141.2 (s, aryl), 140.8 (s, aryl), 139.7 (s, aryl), 139.0 (s, aryl), 136.8 (s, aryl), 136.5 (s, pz), 136.3(s, aryl), 135.6 (s, pz), 135.2 (s, pz), 129.6 (s, aryl), 128.8 (s, aryl), 128.6 (s, aryl), 128.3 (s, aryl), 128.0 (s, aryl), 128.0 (br s, aryl, overlapping), 127.8 (s, aryl), 127.7 (s, aryl), 127.5 (s, aryl), 127.3 (s, aryl), 127.3 (s, aryl), 127.1 (s, aryl), 126.5 (s, aryl), 126.4 (s, vinyl), 120.0 (allenyl), 108.9 (s, allenyl), 107.6 (s, pz), 106.8 (s, pz), 105.6 (s, pz), 21.5 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 2497 (w, BH), 1882 (s, N≡O), 1640 cm^{-1} (m, C=O); FAB-MS: *m/z*: 913.2 $[M]^+$, 742.2 $[M-OTs]^+$, 535.1 [TpRu(C=C=CPh$_2$)(NO)]$^+$; elemental analysis calcd (%) for $C_{46}H_{38}BN_7O_5RuS$: C 60.53, H 4.20, N 10.74; found: C 60.15, H 4.21, N 10.69.

Formation of 5 and 6 from treatment of 2 with *p*-toluenesulfonic acid: A mixture of **2** (60 mg, 0.090 mmol) and $TsOH\cdot H_2O$ (17 mg, 0.090 mmol) was stirred in THF (4 mL) at room temperature for 1 h. After addition of $NaHCO_3$ powder, filtration, and evaporation of the filtrate, the residue was purified by chromatography on silica gel with CH_2Cl_2 and CH_2Cl_2/acetone 20:1 to yield [TpRu{C(=C=CPh$_2$)C(O)CH(C$_6$H$_4$Me)}(NO)] (**5**) as an orange solid (39 mg, 64%) and [TpRu{C(=C=CPh$_2$)C(O)CH$_2$C$_6$H$_4$Me}(OTs)(NO)] (**6**) as a brown solid (5.0 mg, 7.0%), respectively. Complex **6** was also prepared (40%) in refluxing THF for 3 h from **5** (20 mg, 0.030 mmol) and $TsOH\cdot H_2O$ (57 mg, 0.30 mmol).

Complex 5: ^1H NMR ($CDCl_3$): δ = 7.77 (d, $J=2.5$ Hz, 1H of pz), 7.73 (d, $J=2.2$ Hz, 1H of pz), 7.62 (d, $J=2.2$ Hz, 1H of pz), 7.59 (d, $J=1.9$ Hz, 1H of pz), 7.52 (d, $J=7.1$ Hz, 2H of aryl), 7.41 (d, $J=1.9$ Hz, 1H of pz), 7.37 (t, $J=7.7$ Hz, 2H of aryl), 7.27 (t, $J=7.1$ Hz, 1H of aryl), 7.16 (d, $J=8.2$ Hz, 2H of aryl), 7.10–7.08 (m, 3H of aryl), 7.00 (t, $J=7.6$ Hz, 2H of aryl), 6.60 (d, $J=7.7$ Hz, 2H of aryl), 6.54 (d, $J=1.9$ Hz, 1H of pz), 6.19 (t, $J=2.1$ Hz, 1H of pz), 6.15 (t, $J=2.1$ Hz, 1H of pz), 6.08 (t, $J=2.3$ Hz, 1H of pz), 4.89 (s, 1H of RuC*H*), 2.34 ppm (s, 3H of C_6H_4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 193.4 (s, *C*O), 192.3 (s, allenyl), 143.1 (s, pz), 142.1 (s, pz), 141.1 (s, pz), 139.8 (s, aryl), 138.0 (s, aryl), 136.5 (s, aryl), 135.7 (s, pz), 135.6 (s, pz), 135.4 (s, aryl), 135.1 (s, pz), 128.9 (s, aryl), 128.8 (s, aryl), 128.4 (s, aryl), 128.0 (s, aryl), 127.9 (s, aryl), 127.7 (s, aryl), 126.8 (s, aryl), 126.5 (s, aryl), 109.3 (s, allenyl), 107.9 (s, allenyl), 106.5 (s, pz), 106.2 (s, pz), 105.7 (s, pz), 58.7 (s, Ru*C*H), 21.3 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 2493 (m, BH), 1929 (m, C=C=C), 1806 (s, N≡O), 1635 cm^{-1} (s, C=O); EI-MS: *m/z*: 667.1 $[M]^+$, 637.1 $[M-NO]^+$, 608.9 $[M-NO-CO]^+$), 535.0 [TpRu(C=C=CPh$_2$)(NO)]$^+$, 505.0 [TpRu-(C=C=CPh$_2$)]$^+$; elemental analysis calcd (%) for $C_{33}H_{28}BN_7O_2Ru$: C 59.47, H 4.23, N 14.71; found: C 59.01, H 4.18, N 14.77.

Complex 6: ^1H NMR ($CDCl_3$): δ = 8.19 (d, $J=1.7$ Hz, 1H of pz), 7.86 (d, $J=1.9$ Hz, 1H of pz), 7.79 (d, $J=8.2$ Hz, 2H of aryl), 7.69 (d, $J=1.6$ Hz, 1H of pz), 7.53 (d, $J=1.7$ Hz, 1H of pz), 7.39–6.87 (m, 14H of aryl), 7.37 (d, $J=1.4$ Hz, 2H of pz), 6.31 (t, $J=2.2$ Hz, 1H of pz), 6.23 (t, $J=2.5$ Hz, 1H of pz), 6.15 (d, $J=8.2$ Hz, 2H of aryl), 5.79 (t, $J=2.3$ Hz, 1H of pz), 4.37 (d, $J=16$ Hz, 1H of CH_2), 4.07 (d, $J=16$ Hz, 1H of CH_2), 2.42 (s, 3H of C_6H_4Me), 2.27 ppm (s, 3H of C_6H_4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 208.0 (s, *C*O), 201.5 (s, allenyl), 145.2 (s, pz), 144.0 (s, pz), 142.8 (s, pz), 141.0 (s, aryl), 139.5 (s, aryl), 136.9 (s, aryl), 136.6 (s, pz), 136.5 (s, aryl), 135.7 (s, aryl), 135.6 (s, pz), 135.2 (s, pz), 132.4 (s, aryl), 129.5 (s, aryl), 128.9 (s, aryl), 128.8 (s, aryl), 128.6 (s, aryl), 128.0 (s, aryl), 127.8 (s, aryl), 127.8 (s, aryl), 127.2 (s, aryl), 126.5 (s, aryl), 117.6 (s, allenyl), 108.8 (s, allenyl), 107.8 (s, pz), 106.9 (s, pz), 105.7 (s, pz), 48.3 (s, CH_2), 21.6 (s, Me), 21.2 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 2511 (w, BH), 1884 (s, N≡O), 1658 cm^{-1} (m, C=O); FAB-MS: *m/z*: 839 $[M]^+$, 668 $[M-OTs]^+$, 535 [TpRu(C=C=CPh$_2$)(NO)]$^+$, 516 [TpRu(OTs)(NO)]$^+$, 486 [TpRu(OTs)]$^+$, 315 $[TpRu]^+$; elemental analysis calcd (%) for $C_{40}H_{36}BN_7O_5RuS$: C 57.28, H 4.33, N 11.69; found: C 56.92, H 4.27, N 11.67.

Formation of 7 from reaction of 3 with aq. HCl in MeOH: 10 equiv of conc. HCl (37 wt%, 12 mol L^{-1}) was added to a solution of **3** (20 mg, 0.027 mmol) in MeOH (4.0 mL) with a small amount of anhydrous powder $MgSO_4$. After the mixture was stirred at 70 °C for 2 h, the solvent was removed in vacuo. The residue was separated on column chromatography of a silica gel with CH_2Cl_2 to afford [TpRuCl{C(=C=CPh$_2$)C(O)CH=CPh$_2$}(NO)] (**7**) contaminated by a small amount of $[TpRuCl_2(NO)]$. Recrystallization from CH_2Cl_2 and MeOH gave a pure sample of **7** (6.0 mg, 29%).

Complex 7: ^1H NMR ($CDCl_3$): δ = 7.91 (d, $J=1.7$ Hz, 1H of pz), 7.83 (d, $J=2.5$ Hz, 1H of pz), 7.70 (d, $J=1.9$ Hz, 1H of pz), 7.46 (d, $J=2.5$ Hz, 1H of pz), 7.45 (d, $J=3.3$ Hz, 1H of pz), 7.39–7.19 (m, 1H of pz, 10H of Ph, and 1H of C*H*=CPh$_2$), 7.12–7.06 (m, 6H of Ph), 6.94 (t, $J=7.6$ Hz, 2H of Ph), 6.33 (t, $J=2.2$ Hz, 1H of pz), 6.22–6.20 (m, 1H of pz and 2H of Ph), 5.71 ppm (t, $J=2.3$ Hz, 1H of pz); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 210.2 (s, *C*O), 195.0 (s, allenyl), 149.6 (s, vinyl), 145.2 (s, pz), 144.6 (s, pz), 141.5 (s, pz), 141.5 (s, Ph), 139.2 (s, Ph), 137.1 (s, Ph), 136.7 (s, Ph), 135.9 (s, pz), 135.5 (s, pz), 134.9 (s, pz), 129.9 (s, vinyl or Ph), 128.6 (s, vinyl or Ph), 128.4 (s, vinyl or Ph), 128.2 (s, vinyl or Ph), 128.1 (br s, vinyl and/or Ph, overlapping), 128.0 (s, vinyl or Ph), 127.9 (s, vinyl or Ph), 127.8 (s, vinyl or Ph), 127.7 (s, vinyl or Ph), 127.5 (s, vinyl or Ph), 127.0 (s, vinyl or Ph), 126.4 (s, vinyl or Ph), 119.6 (s, allenyl), 108.6

(s, allenyl), 107.4 (s, pz), 106.8 (s, pz), 105.4 ppm (s, pz); IR (KBr, pellet): $\tilde{\nu}$ = 2496 (w, BH), 1869 (s, N≡O), 1638 cm^{-1} (m, C=O); FAB-MS: *m/z*: 778.2 $[M+1]^+$, 742.2 $[M-Cl]^+$, 711.2 $[M-Cl-NO-1]^+$, 570.1 $[TpRuCl(C=C=CPh_2)(NO)]^+$, 535.2 $[TpRu(C=C=CPh_2)(NO)]^+$, 380.0 $[TpRuCl(NO)]^+$; elemental analysis calcd (%) for $C_{39}H_{31}BClN_7O_2Ru$: C 60.28, H 4.02, N 12.62; found: C 60.46, H 3.91, N 12.75.

Formation of 8 from reaction of 5 with aq. HCl in MeOH: Conc. HCl (40 μL, 0.48 mmol) was added to a solution of **5** (30 mg, 0.045 mmol) in MeOH (4 mL). The solution was stirred at 60 °C for 1 d. After addition of $NaHCO_3$ powder, filtration, and evaporation of the filtrate, the residue was purified by chromatography on a silica gel column using CH_2Cl_2 to give $[TpRuCl\{C(=C=CPh_2)C(O)CH_2C_6H_4Me\}(NO)]$ (**8**) as a brown-orange solid (27 mg, 84%).

Complex 8: ^1H NMR ($CDCl_3$): δ = 7.90 (d, J = 1.9 Hz, 1H of pz), 7.80 (d, J = 2.2 Hz, 1H of pz), 7.69 (d, J = 2.2 Hz, 1H of pz), 7.47 (d, J = 1.9 Hz, 1H of pz), 7.44 (d, J = 2.2 Hz, 1H of pz), 7.33–7.25 (m, 5H of aryl), 7.12–6.98 (m, 1H of pz and 7H of aryl), 6.32–6.30 (m, 1H of pz and 2H of aryl), 6.16 (t, J = 2.3 Hz, 1H of pz), 5.71 (t, J = 2.3 Hz, 1H of pz), 4.42 (d, J = 15 Hz, 1H of C(O)CH_2), 4.18 (d, J = 15 Hz, 1H of C(O)CH_2), 2.29 ppm (s, 3H of C_6H_4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 208.3 (s, *C*O), 201.0 (s, allenyl), 144.9 (s, pz), 143.9 (s, pz), 141.3 (s, pz), 136.7 (s, aryl), 136.6 (s, aryl), 135.7 (s, pz), 135.6 (s, aryl), 135.3 (s, pz), 134.7 (s, pz), 132.2 (s, aryl), 129.3 (s, aryl), 128.7 (s, aryl), 128.3 (s, aryl), 127.9 (s, aryl), 127.8 (s, aryl), 127.7 (s, aryl), 126.8 (s, aryl), 126.4 (s, aryl), 116.8 (s, allenyl), 108.4 (s, allenyl), 107.1 (s, pz), 106.6 (s, pz), 105.2 (s, pz), 48.5 (s, *C*H_2), 21.0 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 2495 (w, BH), 1869 (s, N≡O), 1652 cm^{-1} (m, C=O); FAB-MS: *m/z*: 703 $[M]^+$, 668 $[M-Cl]^+$, 570 $[TpRuCl(C=C=CPh_2)(NO)]^+$, 535 $[TpRu(C=C=CPh_2)(NO)]^+$, 505 $[TpRu(C=C=CPh_2)]^+$, 380 $[TpRuCl(NO)]^+$, 315 $[TpRu]^+$; elemental analysis calcd (%) for $C_{33}H_{29}BClN_7O_2Ru$: C 56.38, H 4.16, N 13.95; found: C 56.20, H 4.14, N 13.90.

Reactions of 3 with aq. HCl in other solvents

In CH_2Cl_2 (formation of 7 and 10): Addition of conc. HCl (30 μL, 0.36 mmol) to a solution of **3** (28 mg, 0.038 mmol) in CH_2Cl_2 (4 mL) gave a brown-orange solution. The mixture was stirred at room temperature for 1 h, followed by addition of $NaHCO_3$ powder. After filtration and removal of the solvent under vacuum, the residue was separated on column chromatography (silica gel) to give $[TpRuCl\{CH(C(Cl)=CPh_2)C(O)CH=CPh_2\}(NO)]$ (**10**) as a yellow-orange solid (17 mg, 55%) and **7** (6.6 mg, 24%) from a CH_2Cl_2 eluent.

In THF (formation of 9b): The synthetic procedure is analogous to that of the above reaction in CH_2Cl_2. Treatment of **3** (28 mg, 0.038 mmol) with conc. HCl (35 μL, 0.42 mmol) in THF (4 mL) for 30 min afforded $[TpRu\{C(C(Cl)=CPh_2)(H)C(O)C(=CPh_2)\}(NO)]$ (**9b**) as a red-orange solid (25 mg, 84%).

Ring cleavage of the metallacycle 9b with aq. HCl to give 10: By analogy with the above reaction of **3** with aq. HCl, complex **9b** (25 mg, 0.032 mmol) was mixed with conc. HCl (30 μL, 0.36 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred for 24 h to give **10** (19 mg, 72%).

Proton-assisted isomerization of the metallacycle 9b to 9a: Complex **9b** (25 mg, 0.032 mmol) in CH_2Cl_2 (5 mL) was treated with HBF_4 (22 μL, 0.12 mmol, 54% in diethyl ether) and stirred for 19 h to give $[TpRu\{CH(C(Cl)=CPh_2)C(O)C(=CPh_2)\}(NO)]$ (**9a**) (15 mg, 60%).

Complex 9a: ^1H NMR ($CDCl_3$): δ = 7.90 (d, J = 1.9 Hz, 1H of pz), 7.85 (d, J = 2.2 Hz, 1H of pz), 7.73 (d, J = 2.2 Hz, 1H of pz), 7.56 (d, J = 2.2 Hz, 1H of pz), 7.51–7.49 (m, 2H of Ph), 7.32–7.21 (m, 1H of pz and 8H of Ph), 6.91–6.85 (m, 2H of Ph), 6.78–6.74 (m, 1H of pz and 2H of Ph), 6.66 (t, J = 7.7 Hz, 2H of Ph), 6.47 (d, J = 7.1 Hz, 2H of Ph), 6.40 (t, J = 2.1 Hz, 1H of pz), 6.24 (d, J = 7.1 Hz, 2H of Ph), 6.11 (t, J = 2.3 Hz, 1H of pz), 5.90 (t, J = 2.1 Hz, 1H of pz), 4.96 ppm (s, 1H of RuCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 185.2 (s, *C*O), 157.9 (s, vinyl), 146.5 (s, vinyl), 143.2 (s, vinyl or Ph), 142.7 (s, pz), 142.5 (s, pz), 141.4 (s, vinyl or Ph), 141.2 (s, pz), 141.0 (s, vinyl or Ph), 140.5 (s, vinyl or Ph), 139.3 (s, vinyl or Ph), 135.7 (s, vinyl or Ph), 135.6 (s, pz), 135.4 (s, pz), 134.3 (s, pz), 129.6 (s, Ph), 129.0 (s, Ph), 128.4 (s, Ph), 128.2 (s, Ph), 127.6 (s, Ph), 127.6 (s, Ph), 127.5 (s, Ph), 127.2 (s, Ph), 127.1 (s, Ph), 126.8 (s, Ph), 126.2 (s, Ph), 126.1 (s, Ph), 106.7 (s, pz), 106.2 (s, pz), 106.1 (s, pz), 64.3 ppm (s, Ru*C*HC(Cl)=); IR (KBr, pellet): $\tilde{\nu}$ = 2483 (w, BH), 1832 (s, N≡O), 1627 cm^{-1} (m, C=O); FAB-MS: *m/z*: 778.2 $[M+1]^+$, 380.0 $[TpRuCl(NO)]^+$; elemental analysis calcd (%) for $C_{39}H_{31}BClN_7O_2Ru$: C 60.28, H 4.02, N 12.62; found: C 60.39, H 3.95, N 12.74.

Complex 9b: ^1H NMR ($CDCl_3$): δ = 8.23 (d, J = 2.1 Hz, 1H of pz), 7.81 (d, J = 2.4 Hz, 1H of pz), 7.79 (d, J = 1.7 Hz, 1H of pz), 7.58 (d, J = 2.9 Hz, 1H of pz), 7.57 (d, J = 3.0 Hz, 1H of pz), 7.54–7.52 (m, 2H of Ph), 7.45 (t, J = 7.6 Hz, 2H of Ph), 7.37–7.10 (m, 12H of Ph), 7.02 (t, J = 7.7 Hz, 2H of Ph), 6.88–6.86 (m, 2H of Ph), 6.44 (t, J = 2.2 Hz, 1H of pz), 6.09 (t, J = 2.3 Hz, 1H of pz), 5.86 (t, J = 2.2 Hz, 1H of pz), 5.67 (d, J = 1.8 Hz, 1H of pz), 5.03 ppm (s, 1H of RuCH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 189.8 (s, *C*O), 156.6 (s, vinyl), 149.2 (s, vinyl), 143.6 (s, vinyl or Ph), 142.7 (s, pz), 142.6 (s, pz), 142.1 (s, pz), 142.0 (s, vinyl or Ph), 141.5 (s, vinyl or Ph), 140.6 (s, vinyl or Ph), 140.0 (s, vinyl or Ph), 136.2 (s, pz), 135.1 (s, pz), 134.7 (s, pz), 133.7 (s, vinyl or Ph), 130.0 (s, Ph), 130.0 (s, Ph), 129.7 (s, Ph), 129.5 (s, Ph), 128.4 (s, Ph), 128.0 (s, Ph), 127.8 (s, Ph), 127.7 (s, Ph), 127.5 (s, Ph), 127.4 (s, Ph), 126.8 (s, Ph), 126.7 (s, Ph), 106.2 (s, pz), 105.4 (s, pz), 105.0 (s, pz), 51.5 ppm (s, Ru*C*HC(Cl)=); IR (KBr, pellet): $\tilde{\nu}$ = 2484 (w, BH), 1824 (s, N≡O), 1634 cm^{-1} (m, C=O); FAB-MS: *m/z*: 778 $[M+1]^+$, 380 $[TpRuCl(NO)]^+$, 315 $[TpRu]^+$; elemental analysis calcd (%) for $C_{39}H_{31}BClN_7O_2Ru$: C 60.28, H 4.02, N 12.62; found: C 59.78, H 4.16, N 12.45.

Complex 10: ^1H NMR ($CDCl_3$): δ = 7.90 (d, J = 1.6 Hz, 1H of pz), 7.73 (d, J = 1.9 Hz, 1H of pz), 7.65 (d, J = 2.5 Hz, 1H of pz), 7.63 (d, J = 2.5 Hz, 1H of pz), 7.57–7.55 (m, 2H of Ph), 7.56 (d, J = 2.5 Hz, 1H of pz), 7.40–7.18 (m, 12H of Ph), 7.10–7.05 (m, 4H of Ph), 6.74 (d, J = 2.2 Hz, 1H of pz), 6.41 (d, J = 7.4 Hz, 2H of Ph), 6.30 (t, J = 2.4 Hz, 1H of pz), 6.30 (t, J = 2.2 Hz, 1H of pz), 6.02 (t, J = 2.3 Hz, 1H of pz), 5.42 (s, 1H of RuCH), 5.02 ppm (s, 1H of CH=CPh$_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 200.7 (s, *C*O), 152.3 (s, vinyl), 143.6 (s, pz), 143.5 (s, pz), 142.9 (s, vinyl or Ph), 142.2 (s, vinyl or Ph), 142.1 (s, pz), 141.8 (s, vinyl or Ph), 139.4 (s, vinyl or Ph), 138.6 (s, vinyl or Ph), 138.0 (s, vinyl or Ph), 137.2 (s, pz), 135.5 (s, pz), 135.3 (s, pz), 130.7 (s, Ph), 130.0 (s, Ph), 129.5 (s, Ph), 128.5 (s, Ph), 128.0 (s, Ph), 127.8 (s, Ph), 127.7 (s, Ph), 127.6 (s, Ph), 127.4 (s, Ph), 126.6 (s, Ph), 124.8 (s, *C*H=CPh$_2$), 107.9 (s, pz), 106.8 (s, pz), 106.8 (s, pz), 60.2 ppm (s, Ru*C*HC(Cl)=); IR (KBr, pellet): $\tilde{\nu}$ = 2494 (w, BH), 1852 (s, N≡O), 1662 cm^{-1} (m, C=O); FAB-MS: *m/z*: 813.2 $[M]^+$; elemental analysis calcd (%) for $C_{39}H_{32}BCl_2N_7O_2Ru$: C 57.58, H 3.96, N 12.05; found: C 57.11, H 3.97, N 12.04.

Reactions of 5 with aq. HCl in other solvents

In THF or CH_2Cl_2 (formation of 11a and 11b): A mixture of **5** (30 mg, 0.045 mmol) and conc. HCl (40 μL, 0.48 mmol) was stirred in THF (4 mL) at room temperature for 3 h. After addition of $NaHCO_3$ powder, the resulting mixture was filtered and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel with CH_2Cl_2. A mixture of **11a** and **11b** was obtained (24 mg, 78%). The ratio of **11a**/**11b** was 1:1.4 based on the ^1H NMR spectrum. The use of CH_2Cl_2 as the reaction solvent gave a similar mixture. However, the **5**/aq. HCl reaction system in CH_2Cl_2 carried out at 0 °C produced **11b** with a trace amount of **11a**.

In refluxing CH_2Cl_2 (formation of 11a and 12): In analogous procedures to the above reactions in THF or CH_2Cl_2, treatment of **5** (30 mg, 0.045 mmol) with aq. HCl (40 μL, 0.48 mmol) in CH_2Cl_2 under reflux for 24 h gave rise to **11a** (11 mg, 35%) and $[TpRuCl\{CH(C_6H_4Me)C(O)CH_2C(Cl)=CPh_2\}(NO)]$ (**12**) (13.3 mg, 40%).

$[TpRu\{CH(C(Cl)=CPh_2)C(O)CH(C_6H_4Me)\}(NO)]$ (11a): ^1H NMR ($CDCl_3$): δ = 7.97 (d, J = 1.9 Hz, 1H of pz), 7.87 (d, J = 2.2 Hz, 1H of pz), 7.70 (d, J = 2.5 Hz, 1H of pz), 7.63 (d, J = 2.5 Hz, 1H of pz), 7.37–7.21 (m, 7H of aryl), 7.09 (d, J = 2.2 Hz, 1H of pz), 7.05 (d, J = 8.0 Hz, 2H of aryl), 6.99 (t, J = 7.4 Hz, 1H of aryl), 6.81 (t, J = 7.6 Hz, 2H of aryl), 6.54 (d, J = 7.2 Hz, 2H of aryl), 6.44 (t, J = 2.2 Hz, 1H of pz), 6.17 (d, J = 1.7 Hz, 1H of pz), 6.09 (t, J = 2.2 Hz, 1H of pz), 6.07 (t, J = 2.2 Hz, 1H of pz), 4.58 (d, J = 1.4 Hz, 1H of RuCHC$_6$H$_4$Me), 4.31 (br s, 1H of RuCHC(Cl)=), 2.32 ppm (s, 3H of C_6H_4Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 184.5 (s, *C*O), 142.9 (s, pz), 141.5 (s, pz), 141.4 (s, vinyl or aryl), 141.3 (s, vinyl or aryl), 139.2 (s, vinyl or aryl), 139.0 (s, pz), 138.8 (s, vinyl or aryl), 135.9 (s, pz), 135.8 (s, vinyl or aryl), 135.7 (s, pz), 135.5 (s, pz), 135.0 (s, vinyl or aryl), 129.5 (s, aryl), 128.7 (s, aryl), 128.5 (s, aryl), 128.0 (s, aryl),

127.7 (brs, aryl, overlapping), 126.8 (s, aryl), 126.3 (s, aryl), 106.7 (s, pz), 106.2 (s, pz), 105.9 (s, pz), 62.3 (s, Ru*C*HC$_6$H$_4$Me), 60.9 (s, Ru*C*HC(Cl)=), 21.4 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 2494 (w, BH), 1819 (s, N≡O), 1656 (m, C=C), 1628 cm^{-1} (m, C=O); EI-MS: *m*/*z*: 703 [*M*]$^+$, 673 [*M*−NO]$^+$, 637 [*M*−NO−Cl−1]$^+$, 571 [*M*−{C(O)CH(C$_6$H$_4$Me)}]$^+$, 535 [*M*−{C(O)CH(C$_6$H$_4$Me)}−Cl−1]$^+$, 505 [*M*−{C(O)CH-(C$_6$H$_4$Me)}−Cl−NO−1]$^+$, 380 [*M*−{CH(C(Cl)=CPh$_2$)}−NO−(pz)]$^+$; elemental analysis calcd (%) for C$_{33}$H$_{29}$BClN$_7$O$_2$Ru·CH$_3$OH: C 55.56, H 4.53, N 13.34; found: C 55.01, H 4.24, N 13.21.

[TpRu{C(C(Cl)=CPh$_2$)(H)C(O)CH(C$_6$H$_4$Me)}(NO)] (11b): ^{1}H NMR (CDCl$_3$): δ = 8.35 (d, *J*=2.2 Hz, 1H of pz), 7.81 (d, *J*=2.2 Hz, 1H of pz), 7.73 (d, *J*=2.2 Hz, 1H of pz), 7.69 (brs, 1H of pz), 7.61 (d, *J*=2.2 Hz, 1H of pz), 7.48 (d, *J*=7.1 Hz, 2H of aryl), 7.40 (t, *J*=7.3 Hz, 2H of aryl), 7.33–7.16 (m, 6H of aryl and 1H of pz), 6.98–6.91 (m, 4H of aryl), 6.40 (t, *J*=2.1 Hz, 1H of pz), 6.23 (brs, 1H of pz), 6.16 (brs, 1H of pz), 5.17 (s, 1H of Ru*CH*C$_6$H$_4$Me), 4.82 (brs, 1H of Ru*CH*C(Cl)=), 2.26 ppm (s, 3H of C$_6$H$_4$*Me*); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 184.5 (s, *C*O), 142.7 (s, pz), 141.8 (s, vinyl or aryl), 141.2 (s, pz), 141.2 (brs, vinyl and/or aryl, overlapping), 140.3 (s, pz), 136.5 (s, pz), 135.4 (brs, pz, overlapping), 134.1 (s, vinyl or aryl), 133.3 (s, vinyl or aryl), 130.0 (s, aryl), 129.6 (s, aryl), 128.9 (s, aryl), 128.4 (s, aryl), 127.6 (s, aryl), 127.5 (s, aryl), 126.7 (s, aryl), 124.8(s, aryl), 106.4 (s, pz), 106.2 (s, pz), 104.9 (s, pz), 59.0 (s, Ru*C*HC(Cl)=), 51.5 (s, Ru*C*HC$_6$H$_4$Me), 21.1 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 2489 (w, BH), 1831 (s, N≡O), 1644 (m, C=C), 1616 cm^{-1} (w, C=O); EI-MS: *m*/*z*: 703 [*M*]$^+$, 673 [*M*−NO]$^+$, 637 [*M*−NO−Cl−1]$^+$, 535 [*M*−{C(O)CH(C$_6$H$_4$Me)}−Cl−1]$^+$, 505 [*M*−{C(O)CH-(C$_6$H$_4$Me)}−Cl−NO−1]$^+$, 380 [*M*−{CH(C(Cl)=CPh$_2$)}−(NO)−(pz)]$^+$; elemental analysis calcd (%) for C$_{33}$H$_{29}$BClN$_7$O$_2$Ru·CH$_3$CH$_2$OH: C 56.12, H 4.71, N 13.09; found: C 55.55, H 4.70, N 12.96.

Complex 12: ^{1}H NMR (CDCl$_3$): δ = 7.77 (d, *J*=1.9 Hz, 1H of pz), 7.64 (d, *J*=2.2 Hz, 1H of pz), 7.62 (d, *J*=2.5 Hz, 1H of pz), 7.57 (d, *J*=3.0 Hz, 1H of pz), 7.56 (d, *J*=1.8 Hz, 1H of pz), 7.26–7.19 (m, 8H of aryl), 7.01–6.98 (m, 2H of aryl), 6.81–6.75 (m, 4H of aryl), 6.41 (d, *J*=2.2 Hz, 1H of pz), 6.23 (t, *J*=2.2 Hz, 2H of pz), 5.91 (t, *J*=2.3 Hz, 1H of pz), 5.12 (s, 1H of Ru*CH*), 4.36 (d, *J*=15 Hz, 1H of C*H*$_2$), 3.96 (d, *J*=15 Hz, 1H of C*H*$_2$), 2.20 ppm (s, 3H of *Me*); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 209.2 (s, *C*O), 142.8 (s, pz), 142.0 (s, pz), 141.8 (s, pz), 141.4 (s, vinyl or aryl), 141.1 (s, vinyl or aryl), 140.3 (s, vinyl or aryl), 139.8 (s, vinyl or aryl), 135.8 (s, pz), 135.5 (s, pz), 134.9 (s, pz), 134.6 (s, vinyl or aryl), 129.5 (s, aryl), 129.4 (s, aryl), 128.7 (s, aryl), 128.3 (s, aryl), 127.6 (s, aryl), 127.3 (s, aryl), 127.3 (s, aryl), 126.9 (s, aryl), 126.6 (s, vinyl or aryl), 106.5 (s, pz), 106.4 (s, pz), 106.2 (s, pz), 58.1 (s, Ru*C*), 55.2 (s, *C*H$_2$), 21.0 ppm (s, Me); IR (KBr, pellet): $\tilde{\nu}$ = 2496 (w, BH), 1858 (s, N≡O), 1692 cm^{-1} (m, C=O); EI-MS: *m*/*z*: 739 [*M*]$^+$, 512 [TpRuCl{CH(C$_6$H$_4$Me)C(O)}(NO)]$^+$; elemental analysis calcd (%) for C$_{33}$H$_{30}$BCl$_2$N$_7$O$_2$Ru: C 53.60, H 4.09, N 13.26; found: C 53.29, H 4.07, N 13.19.

X-ray crystal structure determinations: Crystal data and refinement parameters for the structurally characterized complexes are summarized in Table 8. X-ray quality single crystals were obtained from slow evaporation of CH$_2$Cl$_2$/MeOH or EtOH. Diffraction data were collected at room temperature on a Rigaku AFC7 diffractometer equipped with a MSC/ADSC Quantum CCD area detector by using graphite-monochromated Mo$_{K\alpha}$ radiation. Seven preliminary data frames were measured at 0.5° increments of ω, in order to assess the crystal quality and preliminary unit cell parameters. The intensity images were obtained with ω scans of 0.5°

Table 8. Crystal data for **3**, **4**, **5**, **7**, **8**, **9a**, **9b**·MeOH, **10**, **11a**·MeOH, **11b**·EtOH, and **12**.

	3	**4**	**5**	**7**	**8**	**9a**
formula	$C_{39}H_{30}N_7O_2BRu$	$C_{46}H_{38}N_7O_5BRuS$	$C_{33}H_{28}N_7O_2BRu$	$C_{39}H_{31}N_7O_2BClRu$	$C_{33}H_{29}N_7O_2BClRu$	$C_{39}H_{31}N_7O_2BClRu$
molecular wt	740.59	912.79	666.51	777.05	702.97	777.05
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (no.2)	$C2/c$ (no.15)	Cc (no.9)	$P2_1/n$ (no.14)	$P2_1/a$ (no.14)	$P\bar{1}$ (no.2)
color	red	red	red	orange	red	red
a [Å]	14.6570(4)	38.857(1)	15.805(1)	9.772(1)	17.527(1)	10.1577(4)
b [Å]	16.1833(9)	11.3244(5)	13.8455(8)	17.254(2)	9.2613(3)	10.5063(7)
c [Å]	17.1016(7)	20.3138(2)	15.3318(2)	21.3846(2)	20.5539(3)	18.977(2)
α [°]	91.048(2)					98.493(3)
β [°]	111.5577(8)	106.1137(2)	111.1040(3)	91.6023(3)	105.7026(3)	97.243(2)
γ [°]	110.2894(7)					118.294(2)
V [Å^3]	3488.9(3)	8587.5(5)	3130.1(3)	3604.3(6)	3211.8(2)	1718.4(2)
Z	4	8	4	4	4	2
R[a]	0.048	0.043	0.041	0.057	0.044	0.036
Rw[b]	0.071	0.069	0.059	0.084	0.071	0.063
GOF[c]	1.31	1.56	1.04	0.94	1.43	1.66

	9b·MeOH	**10**	**11a**·MeOH	**11b**·EtOH	**12**
formula	$C_{39}H_{31}N_7O_2BClRu·MeOH$	$C_{39}H_{32}N_7O_2BCl_2Ru$	$C_{33}H_{29}N_7O_2BClRu·MeOH$	$C_{33}H_{29}N_7O_2BClRu·EtOH$	$C_{33}H_{30}N_7O_2BCl_2Ru$
molecular wt	808.09	813.51	735.01	749.04	739.43
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (no.2)	$P2_12_12_1$ (no.19)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P\bar{1}$ (no.2)
color	red	orange	red	pale yellow	orange
a [Å]	11.5417(7)	9.813(2)	15.9320(8)	12.157(1)	10.7407(6)
b [Å]	12.834(2)	18.2705(7)	13.0876(9)	21.522(4)	11.9940(6)
c [Å]	14.366(1)	20.9554(4)	16.4424(2)	13.5394(3)	14.586(1)
α [°]	100.802(3)				72.928(2)
β [°]	101.6607(7)		98.3945(3)	93.3908(6)	83.123(1)
γ [°]	91.809(1)				69.5119(8)
V [Å^3]	2041.8(3)	3757.2(7)	3391.7(3)	3536.2(7)	1682.4(2)
Z	2	4	4	4	2
R[a]	0.073	0.137	0.054	0.085	0.048
Rw[b]	0.101	0.238	0.081	0.122	0.071
GOF[c]	1.61	0.93	1.32	0.92	1.17

[a] $R=\Sigma|F_o^2-F_c^2|/\Sigma F_o^2$. [b] $Rw=\{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] GOF$=[\{\Sigma w(|F_o|-|F_c|)^2\}/(N_o-N_p)]^{1/2}$, where N_o and N_p denote the number of observations and parameters.

interval per frame for duration of 35 s, except for **5** (30 s). The frame data were integrated using an MSC d*TREK program package, and the data sets were corrected for absorption using a REQAB program.

All calculations were performed with a TEXSAN program package. Crystal structures were solved by direct methods, except for **3** and **10** by Patterson methods, and refined on F^2 by full-matrix least squares. In complex **3**, the asymmetric unit contains two crystallographically independent molecules of **3**. Anisotropic refinement was applied to all non-hydrogen atoms, and hydrogen atoms were put at calculated positions with C-H distances of 0.97 Å, except for those of all B-H and O-H (**11a**·MeOH and **11b**·EtOH), while the O-H hydrogen atom in **9b**·MeOH was not included in the calculations. For **11a**·MeOH and **11b**·EtOH, the positions of the O-H hydrogen atoms were located from the Fourier map, but not refined.

CCDC-617502–617512 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) J. March, *Advanced Organic Chemistry*, Wiley, New York, **1992**, p. 762; b) M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem.* **2004**, *116*, 3448–3479; *Angew. Chem. Int. Ed.* **2004**, *43*, 3368–3398.

[2] For some hydration with Ru complexes, see: a) C. Bianchini, J. A. Casares, M. Peruzzini, A. Romerosa, F. Zanobini, *J. Am. Chem. Soc.* **1996**, *118*, 4585–4595; b) C.-W. Chang, P.-C. Ting, Y.-C. Lin, G.-H. Lee, Y. Wang, *J. Organomet. Chem.* **1998**, *553*, 417–425; c) C. Bianchini, M. Peruzzini, F. Zanobini, C. Lopez, I. de los Rios, A. Romerosa, *Chem. Commun.* **1999**, 443–444; d) C. Bianchini, I. de los Rios, C. Lopez, M. Peruzzini, A. Romerosa, *J. Organomet. Chem.* **2000**, *593–594*, 485–488; e) L. Bonomo, C. Stern, E. Solari, R. Scopelliti, C. Floriani, *Angew. Chem.* **2001**, *113*, 1497–1500; *Angew. Chem. Int. Ed.* **2001**, *40*, 1449–1452; f) C. Menéndez, D. Morales, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2001**, *20*, 2775–2781.

[3] a) I. Ojima, in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, p. 1479; b) T. D. Tilley, in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, p. 1415; c) T. Hiyama, T. Kusumoto, in *Comprehensive Organic Synthesis, Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, p. 763; d) B. Marciniec, *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, **1992**; e) B. M. Trost, Z. T. Ball, *Synthesis* **2005**, 853–887.

[4] a) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–704; b) J. J. Brunet, D. Neibecker in *Catalytic Heterofunctionalization* (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, **2001**, p. 91; c) M. Nobis, B. Driessen-Hölscher, *Angew. Chem.* **2001**, *113*, 4105–4108; *Angew. Chem. Int. Ed.* **2001**, *40*, 3983–3985; d) R. Taube in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2002**, p. 513; e) F. Pohlki, S. Doye, *Chem. Soc. Rev.* **2003**, *32*, 104–114; f) J. F. Hartwig, *Pure Appl. Chem.* **2004**, *76*, 507–516; g) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673–686.

[5] For recent reactions, see: a) T. Tsuchimoto, T. Joya, E. Shirakawa, Y. Kawakami, *Synlett* **2000**, 1777–1778; b) L. W. Francisco, D. A. Moreno, J. D. Atwood, *Organometallics* **2001**, *20*, 4237–4245; c) E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, *Angew. Chem.* **2002**, *114*, 4745–4747; *Angew. Chem. Int. Ed.* **2002**, *41*, 4563–4565; d) R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, *J. Am. Chem. Soc.* **2003**, *125*, 11925–11935; e) A. Vasudevan, M. K. Verzal, *Synlett* **2004**, 631–634; f) S. Ogo, K. Uehara, T. Abura, Y. Watanabe, S. Fukuzumi, *J. Am. Chem. Soc.* **2004**, *126*, 16520–16527.

[6] a) M. Tokunaga, Y. Wakatsuki, *Angew. Chem.* **1998**, *110*, 3024–3027; *Angew. Chem. Int. Ed.* **1998**, *37*, 2867–2869; b) T. Suzuki, M. Tokunaga, Y. Wakatsuki, *Org. Lett.* **2001**, *3*, 735–737; c) D. B. Grotjahn, C. D. Incarvito, A. L. Rheingold, *Angew. Chem.* **2001**, *113*, 4002–4005; *Angew. Chem. Int. Ed.* **2001**, *40*, 3884–3887; d) P. Alvarez, M. Bassetti, J. Gimeno, G. Mancini, *Tetrahedron Lett.* **2001**, *42*, 8467–8470; e) M. Tokunaga, T. Suzuki, N. Koga, T. Fukushima, A. Horiuchi, Y. Wakatsuki, *J. Am. Chem. Soc.* **2001**, *123*, 11917–11924; f) D. B. Grotjahn, D. A. Lev, *J. Am. Chem. Soc.* **2004**, *126*, 12232–12233; g) F. Chevallier, B. Breit, *Angew. Chem.* **2006**, *118*, 1629–1632; *Angew. Chem. Int. Ed.* **2006**, *45*, 1599–1602; h) C. Bruneau, P. H. Dixneuf, *Angew. Chem.* **2006**, *118*, 2232–2260; *Angew. Chem. Int. Ed.* **2006**, *45*, 2176–2203.

[7] a) Y. Arikawa, Y. Nishimura, H. Kawano, M. Onishi, *Organometallics* **2003**, *22*, 3354–3356; b) Y. Arikawa, Y. Nishimura, K. Ikeda, M. Onishi, *J. Am. Chem. Soc.* **2004**, *126*, 3706–3707; c) Y. Nishimura, Y. Arikawa, T. Inoue, M. Onishi, *Dalton Trans.* **2005**, 930–937.

[8] a) C. Slugovc, V. N. Sapunov, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, *J. Chem. Soc. Dalton Trans.* **1997**, 4209–4216; b) E. Bustelo, J. J. Carbó, A. Lledós, K. Mereiter, M. C. Puerta, P. Valerga, *J. Am. Chem. Soc.* **2003**, *125*, 3311–3321; c) F. De Angelis, A. Sgamellotti, N. Re, *Dalton Trans.* **2004**, 3225–3230; d) Y. Wakatsuki, *J. Organomet. Chem.* **2004**, *689*, 4092–4109.

[9] a) B. M. Trost, M. T. Rudd, *J. Am. Chem. Soc.* **2001**, *123*, 8862–8863; b) B. M. Trost, M. T. Rudd, *J. Am. Chem. Soc.* **2002**, *124*, 4178–4179; c) B. M. Trost, M. T. Rudd, *J. Am. Chem. Soc.* **2003**, *125*, 11516–11517; d) Y. Chen, D. M. Ho, C. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 12184–12185; for a Rh-mediated reaction, see: Y. J. Park, B.-I. Kwon, J.-A. Ahn, H. Lee, C.-H. Jun, *J. Am. Chem. Soc.* **2004**, *126*, 13892–13893.

[10] M. Onishi, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3039–3045.

[11] a) C. E. Shuchart, R. R. Willis, A. Wojcicki, *J. Organomet. Chem.* **1992**, *424*, 185–198; b) M. A. Esteruelas, A. V. Gómez, F. J. Lahoz, A. M. López, E. Oñate, L. A. Oro, *Organometallics* **1996**, *15*, 3423–3435; c) V. Cadierno, M. P. Gamasa, J. Gimeno, M. C. López-González, J. Borge, S. García-Granda, *Organometallics* **1997**, *16*, 4453–4463; d) P. Crochet, B. Demerseman, M. I. Vallejo, M. P. Gamasa, J. Gimeno, J. Borge, S. García-Granda, *Organometallics* **1997**, *16*, 5406–5415; e) M. A. Esteruelas, A. V. Gómez, A. M. López, J. Modrego, E. Oñate, *Organometallics* **1997**, *16*, 5826–5835; f) M. A. Esteruelas, A. V. Gómez, A. M. López, J. Modrego, E. Oñate, *Organometallics* **1998**, *17*, 5434–5436; g) B. Buriez, D. J. Cook, K. J. Harlow, A. F. Hill, T. Welton, A. J. P. White, D. J. Williams, J. D. E. T. Wilton-Ely, *J. Organomet. Chem.* **1999**, *578*, 264–267; h) H. D. Hansen, J. H. Nelson, *Organometallics* **2000**, *19*, 4740–4755; i) M. Jiménez-Tenorio, M. D. Palacios, M. C. Puerta, P. Valerga, *J. Organomet. Chem.* **2004**, *689*, 2776–2785.

[12] In the crystal structure of **3**, the mean deviation from the least-squares plane (C14, C13, C10, C11, O2, Ru1, C12, and C27) is 0.0288 Å. The other crystallographically independent molecule in the same asymmetric unit shows the deviation of 0.0327 Å.

[13] Treatment of **11b** with aq. HBr gave rise to the bromoruthenium complex [TpRuBr{CH(C_6H_4Me)C(O)CH_2(C(Cl)=CPh_2)}(NO)] (43%) without a chlororuthenium [TpRuCl{CH(C_6H_4Me)C(O)CH_2(C(Br)=CPh_2)}(NO)], along with the other diastereoisomer **11a** (13%). The bromoruthenium complex was fully characterized by NMR, IR, and MS spectra and X-ray structural analysis.

[14] J. March, *Advanced Organic Chemistry*, Wiley, New York, **1992**, p. 348.

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