Hydration of Nitrosylruthenium Bis(alkynyl) Complexes with Hydrotris(pyrazolyl)borate: Insertion/Hydration and Double Hydration Products

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Lately, the use of organic transformation reactions which have high atom efficiency is attracting great interest in transition-metal-mediated synthetic chemistry,[1] and a typical example is the hydration of unsaturated hydrocarbon compounds, especially alkynes, which are currently under wide and active investigation.[2] While we were examining the protonation of mono(alkynyl) ruthenium complexes having hydrotris(pyrazolyl)borate (Tp) and nitrosyl (NO) ligands, hydration accidentally took place, to yield unusual ketonyl complexes through a π-alkyne intermediate, which was communicated recently.[3a] Extending this chemistry to bis-(alkynyl) complexes gave rise to metallacycle complexes, as well as two double-hydrated regioisomers. The combination of insertion and subsequent hydration processes resulted in the unprecedented formation of the metallacycle complexes.

The bis(alkynyl) ruthenium complex TpRu(C≡CPh)$_2$(NO) (**1**)[3b] was allowed to react with 1 equiv of H$_2$O in the presence of HBF$_4$·Et$_2$O in distilled MeOH to give the metallacycle complex TpRu{CH=C(Ph)C(O)CH(Ph)}(NO) (**2**) (39% yield) and the bis(ketonyl) complex TpRu(CH$_2$C(O)Ph)$_2$(NO) (**3**) (37% yield) after silica gel column separation using a CH$_2$Cl$_2$ eluent (Scheme 1). When the reaction proceeded using 10 equiv of H$_2$O, the yield of **3** was increased (54%) in contrast to that of **2** (7.7%). The C=O stretching bands for **2** and **3** were observed at 1654 and 1632 cm^{-1}, respectively. The EI-MS spectra exhibit parent molecular ion signals at m/z 565 (**2**) and 583 (**3**), showing one- and two-H$_2$O mass increments, respectively, as compared to **1**.

The metallacycle **2** shows two sets of ^{1}H NMR signal patterns; one set has two singlets at δ 9.42 and 5.06, and the second set has singlets at δ 9.81 and 5.08. The ^{13}C {^{1}H} NMR exhibits two carbonyl carbons at δ 208.1 and 207.7, and four olefinic carbons at δ 149.5, 151.3, 167.9, and 171.9. These indicate a mixture of two diastereomers with a varying abundance ratio. The ratio was changed by heating the isolated mixture in MeOH under acidic conditions, but did not change without acids.[4] The p-tolyl derivatives TpRu{CH=C(C$_6$H$_4$Me)C(O)CH(C$_6$H$_4$Me)}(NO) (**2***) were also isolated by similar methods, and in this case both single crystals of the diastereomers were obtained from CH$_2$Cl$_2$/MeOH.

The molecular structure of the major isomer of **2*** is shown in Figure 1.[5] The most remarkable feature is the presence of the metallacyclopentenone with a chiral carbon center, C(10). The steric interaction between pyrazole rings and the tolyl ring at C(10) was assumed to favor this thermodynamically stable isomer via keto−enol tautomerism.[4]

The bis(ketonyl) complex TpRu(CH$_2$C(O)Ph)$_2$(NO) (**3**) has been characterized by spectroscopic and elemental analyses. The ^{1}H NMR spectrum of **3** showed characteristic diastereotopic methylene protons with an integral intensity of 4H. The structure of **3** was confirmed by X-ray crystallographic analysis.
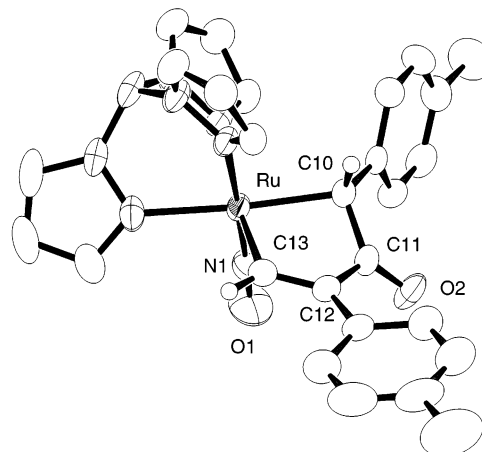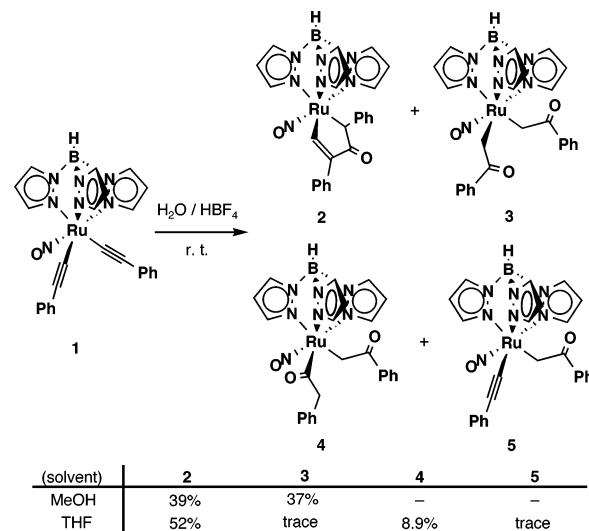

Figure 1. Molecular structure of the major diastereomer of **2***.

Scheme 1

(solvent)	2	3	4	5
MeOH	39%	37%	–	–
THF	52%	trace	8.9%	trace

On the other hand, a similar reaction was performed in THF instead of MeOH, to afford **2** (52%) and trace, but ^{1}H NMR spectroscopically detectable, amounts of **3** and **5** (see below) (Scheme 1). Concomitantly, TpRu(C(O)CH$_2$Ph)(CH$_2$C(O)Ph)−(NO) (**4**) as the regioisomer of **3**, which contains both mono(acyl) and mono(ketonyl) fragments, was obtained in 8.9% yield. Characterization of **4** was performed on the basis of ^{1}H and ^{13}C {^{1}H} NMR, IR, EI-MS, and elemental analysis. Each of the two methylene groups appeared as an AB spin system in the ^{1}H NMR spectrum. In the ^{13}C {^{1}H} NMR spectrum, the presence of an acyl fragment was confirmed by the appearance of a low field signal at δ 243 for the acyl carbonyl carbon along with that at δ 205 for the
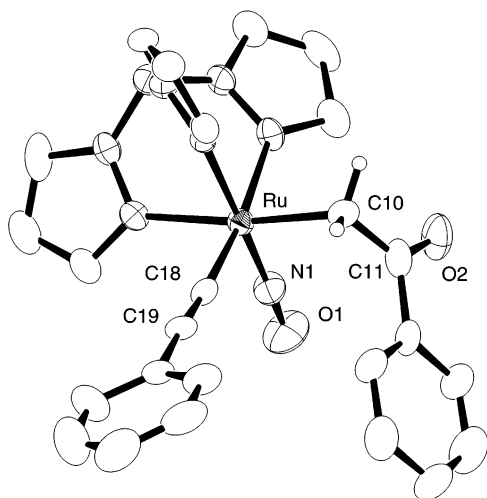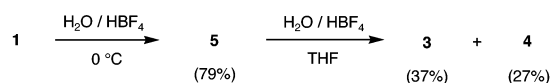
Figure 2. Molecular structure of **5**.

Scheme 2

Scheme 3

ketonyl carbon. Furthermore, the EI-MS spectrum shows a [TpRu-(CO)(CH₂C(O)Ph)(NO)]⁺ fragment due to the loss of a benzyl group, which differs from **3**.

Intriguingly, the **1**/HBF₄·Et₂O/H₂O reaction system in MeOH was carried out at 0 °C to produce the alkynyl-ketonyl complex TpRu(C≡CPh)(CH₂C(O)Ph)(NO) (**5**) exclusively (Scheme 2). Formation of **5** would result from hydration of the η^2-coordinated 1-alkyne intermediate, similarly to that of the mono(alkynyl) nitrosylrutheniums.[3a] The spectroscopic data were sufficient to unequivocally assign the structure of **5**. The methylene group resonates as an AB pattern in the ¹H NMR spectrum, and the IR spectrum shows $\nu_{C≡C}$ (2124 cm⁻¹) and $\nu_{C=O}$ (1627 cm⁻¹). Single crystals were obtained from CH₂Cl₂/MeOH, and the X-ray structural determination is presented in Figure 2.[6] The bond lengths of C(18)−C(19) (1.17(1) Å) and C(11)−O(2) (1.23(1) Å) are typical of triple and double bonds, respectively.

Hydration of isolated **5** under acidic conditions in THF gave rise to **3** and **4**, revealing that **5** is the intermediate in their formation (Scheme 2).[7] While **5** would be further hydrated via the π-alkyne form to give **3**, complex **4** was presumably generated through the ketonyl-vinylidene species, because the acyl fragment is often prepared by hydration of vinylidene complexes (Scheme 3).[2,8] Regrettably, the vinylidene intermediate was not isolated, even using [H(OEt₂)₂][BArᶠ₄] (Arᶠ = 3,5-C₆H₃(CF₃)₂) as a protic acid.

The formation mechanism of **2** would be that protonation of **1** led to insertion of one protonated π-alkyne fragment into the other ruthenium−phenylacetylide bond, followed by nucleophilic attack by H₂O on the γ carbon of the resulting ene-yne intermediate to afford 3-hydroxymetallacyclopentadiene species,[9] which were converted to **2** (Scheme 3).[10] Probable π-interaction between the central metal and the alkynyl part in the intermediate may facilitate the hydration step.[11] These reaction processes are in sharp contrast to the formation of alkenyl ketone complexes from Cp*RhCl₂(PPh₃) by incorporation of two 1-alkyne molecules and one H₂O molecule, through initial hydration of vinylidene species and subsequent insertion of alkyne into the metal−acyl bond.[12]

In conclusion, hydration of the bis(alkynyl) complexes resulted in the formation of **2**−**5**, where the product distribution depended on the reaction conditions (solvent, amount of water, and temperature). The combination of insertion and subsequent hydration
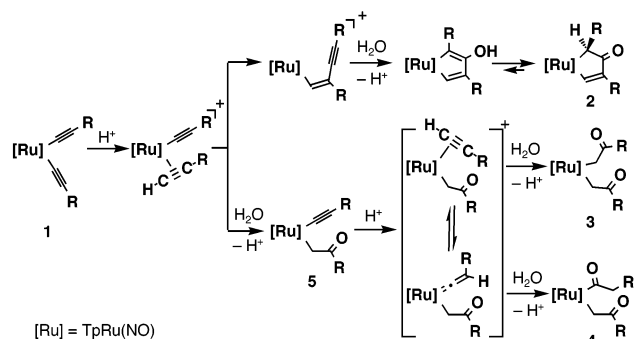
processes afforded the metallacyclopentenone complex **2**. On the other hand, the regioisomers **3** and **4** were produced by double hydration, where the intermediate product, alkynyl-ketonyl complex **5**, was also isolated.

Supporting Information Available: Full experimental and spectroscopic details for all new compounds and X-ray structural data for complexes **2***, **3**, and **5** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) (a) Arikawa, Y.; Nishimura, Y.; Kawano, H.; Onishi, M. *Organometallics* **2003**, *22*, 3354−3356. (b) Complex **1** was prepared from TpRuCl₂(NO) and an excess of PhC≡CH in the presence of Et₃N and catalytic amounts of CuI.

(4) Under MeOH-d₄ at 60 °C for 1 h, while the ratio of diastereoisomers **2** (1:1) was changed to 3.4:1, that of **2*** varied from 1:1 to 2.1:1. The marked difference in steric effect between the two sets of diastereomers (i.e., with and without 4-Me substituent) was not observed.

(5) Crystal data for major isomer of **2***: monoclinic, *P2₁/c* (No. 14), *a* = 10.5206(8) Å, *b* = 19.820(2) Å, *c* = 13.2299(2) Å, *β* = 101.9368(3)°, *V* = 2699.0(3) Å³, *Z* = 4, ρ_{calcd} = 1.458 g cm⁻³, *R* (*R*ₗ) = 0.038 (0.059) for 343 variables and 6060 unique reflections (all data).

(6) Crystal data for **5**: monoclinic, *C2/c* (No. 15), *a* = 23.365(4) Å, *b* = 10.1610(8) Å, *c* = 23.375(1) Å, *β* = 101.440(1)°, *V* = 5439(1) Å³, *Z* = 8, ρ_{calcd} = 1.378 g cm⁻³, *R* (*R*ₗ) = 0.176 (0.206) for 325 variables and 6122 unique reflections (all data).

(7) Another possible isomer, the alkynyl-acyl species TpRu(C≡CPh)(C(O)-CH₂Ph)(NO), was not detected in any reactions.

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(9) If the addition of H₂O to the α carbon proceeded, the organic product, 2,4-diphenyl-3-butynal, could be released.

(10) Formation of a ruthenacyclopentatriene intermediate also cannot be ruled out at the present stage, as another possible route for **2**. See ref 1g.

(11) Treatment of the mono(alkynyl) complex TpRuCl(C≡CPh)(NO) with HC≡CC(O)OMe gave rise to the similar ene-yne complex, TpRuCl[C{C-(O)OMe}=CH(C≡CPh)](NO). This complex, where the alkynyl part has no interaction with the metal center, was not hydrated.

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