Hydration of Nitrosylruthenium Acetylide Complexes Having a Tris(pyrazol-1-yl)borate in the Presence of Protic Acid: Formation of Ketonyl and Acyl Complexes

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*Summary: Treatment of the monoacetylide complexes TpRuCl(C≡CR)(NO) (R = Ph (**1a**), p-$CH_3C_6H_4$ (**1b**), ^{t}Bu (**1c**), CH_2CH_2OH (**1d**), CH_2OH (**1e**), $C(Me)_2OH$ (**1f**), $C(Ph)_2OH$ (**1g**); Tp = BH(pyrazol-1-yl)$_3$) with HBF_4·Et_2O in methanol afforded the ketonyl complexes TpRuCl($CH_2C(O)R$)(NO) (R = Ph (**2a**), p-$CH_3C_6H_4$ (**2b**), ^{t}Bu (**2c**), CH_2CH_2OMe (**2d**), CH_2OH (**2e**)) and the α,β-unsaturated acyl complexes TpRuCl(C(O)CH=CR′$_2$)(NO) (R′ = Me (**3f**), Ph (**3g**)), respectively. While the latter were produced by hydration via allenylidene species, the former were presumably generated from the reaction of η^2-coordinated 1-alkyne species with adventitious water.*

The chemistry of ruthenium vinylidene and allenylidene complexes has attracted increasing attention because of their occurrence as key intermediates in stoichiometric and catalytic transformations of organic molecules.[1] Their complexes supported by cyclopentadienyl or tris(pyrazolyl)borate have been widely studied.[2] Many coligands in TpRu (Tp = BH(pyrazol-1-yl)$_3$) complexes have not been used other than phosphines, amines, and diene. We are interested in the electron-withdrawing coligand NO^+ and have begun to investigate the use of $TpRuCl_2(NO)$[3] as a starting material. We first attempted to prepare the vinylidene and allenylidene species with a TpRuCl(NO) fragment by the reactions with terminal acetylenes and propargyl alcohols in the presence of the appropriate salts such as NH_4PF_6, $AgBF_4$, and $NaBAr^F_4$ (Ar^F = 3,5-C_6H_3-$(CF_3)_2$). These reactions, however, did not take place. Thus another strategy for their syntheses focused on the protonation of σ-acetylide complexes. However, the ketonyl and α,β-unsaturated acyl complexes were generated because of the reactions with adventitious water. The former is the first structurally characterized example of ketonyl ruthenium complexes that are formed through hydration of acetylide complexes.

The σ-acetylide complexes TpRuCl(C≡CR)(NO) (R = Ph (**1a**), *p*-$CH_3C_6H_4$ (**1b**), ^{t}Bu (**1c**), CH_2CH_2OH (**1d**), CH_2OH (**1e**), $C(Me)_2OH$ (**1f**), $C(Ph)_2OH$ (**1g**)) were prepared from $TpRuCl_2(NO)$ and an excess of the corresponding terminal alkynes HC≡CR in the presence of Et_3N, producing poly(acetylene) as byproducts in the cases of **1a** and **1b**. The ^1H NMR spectra of complexes **1a**−**g** exhibit three distinct sets of pyrazol-1-yl resonances in addition to those of acetylide units. In the IR spectra of these complexes, characteristic NO^+ and C≡C stretching bands were observed.

When TpRuCl(C≡CPh)(NO) (**1a**) was reacted with HBF_4·Et_2O in THF (distilled) under reflux for 6 h, the ketonyl complex TpRuCl($CH_2C(O)Ph$)(NO) (**2a**) was obtained in 38% yield. No reaction was found between **1a** and acetic acid in refluxing THF.

The IR spectrum of **2a** shows two characteristic bands at 1855 and 1633 cm^{-1}, which are assigned to NO^+ and CO stretching, respectively. In the ^1H NMR spectrum of **2a**, two doublets at δ 4.82 and 3.45, coupled to each other (J = 6.0 Hz), were attributed to nonequivalent, i.e. diastereotopic, protons in the ruthenium-bonded methylene group. The carbonylic and methylene carbons give rise to $^{13}C\{^1H\}$ NMR signals at δ 204.8 and 31.7, respectively. The former is very close to those for ketonyl complexes described in the literatures.[4] A ^{13}C-DEPT experiment confirms these assignments. Furthermore, released acetophenone was detected by GC analysis when the mixture of complex **2a** and concentrated HCl in benzene was refluxed. Since ^1H NMR shows that **2a** was produced quantitatively before column chromatographic purification, the formation of **2a** would occur by the reaction with traces of water present in the reaction mixture. Addition of H_2O to the mixture increased the yield of **2a** (75%). Analogous high reactivity toward water has been found in protonation reaction of (arene)ruthenium alkynyl complex, where the vinylidene intermediate is proposed, followed by hydration

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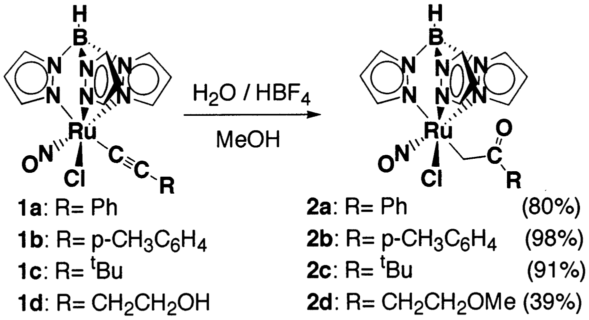
Scheme 1



to produce the acyl complex.[5] When **1a** was treated with $HBF_4\cdot Et_2O$ in methanol instead of THF, the reaction was immediately completed at room temperature and a slight increase of the yield was observed (80%).[6a]

Similarly, other ketonyl complexes TpRuCl(CH_2C-(O)R)(NO) (R = *p*-$CH_3C_6H_4$ (**2b**), ᵗBu (**2c**), CH_2CH_2OMe (**2d**)) also were synthesized by reactions between TpRuCl-(C≡CR)(NO) (R = p-$CH_3C_6H_4$ (**1b**), ᵗBu (**1c**), CH_2CH_2-OH (**1d**)) and $HBF_4\cdot Et_2O$ in methanol (Scheme 1). The terminal hydroxide of **1d** is converted into an OMe group during the formation of **2d**. These complexes were characterized spectroscopically. The presence of NO^+ and CO groups was identified by the IR spectra of **2b**−**d**, and characteristic diastereotopic protons in the ruthenium-bonded methylene groups are also observed in the ^1H NMR spectra. In particular, in the $^1H-^1H$ 2D COSY spectrum of **2d**, the resonances of methylene protons (RuCH_2C(O)R) clearly do not show any cross-peaks except for geminal ones. The chemical shifts in $^{13}C\{^1H\}$ NMR for the carbonylic carbons in **2b**−**d** are similar to that in **2a**. Moreover, the EI mass spectrum of **2c** shows the signal of $[TpRuCl(CH_2C(O))(NO)]^+$ (*m*/*z*: 422) along with the parent ion, which assists its formulation. The ketonyl form was confirmed by X-ray analysis of **2b**.[6b]

Although two molecules are present per one asymmetric unit, both structures are not significantly different. One of the molecular structures is presented in Figure 1. The ruthenium center possesses a distorted octahedral geometry defined by a facial Tp ligand together with ketonyl group, nitrosyl, and chloride ligands. The $CH_2-C(O)$ (1.474(4), 1.479(3) Å) and C=O (1.237(3), 1.227(3) Å) distances in the ketonyl group correspond well to single and double bonds, respectively.

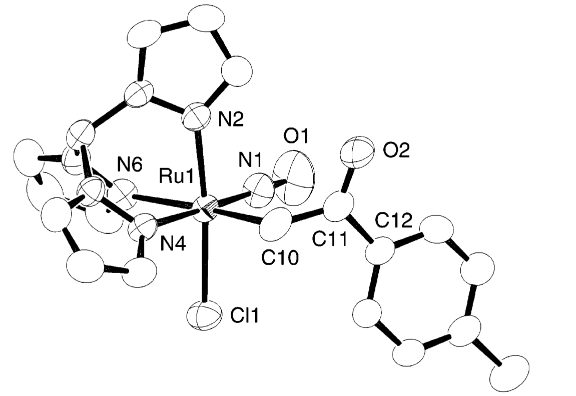
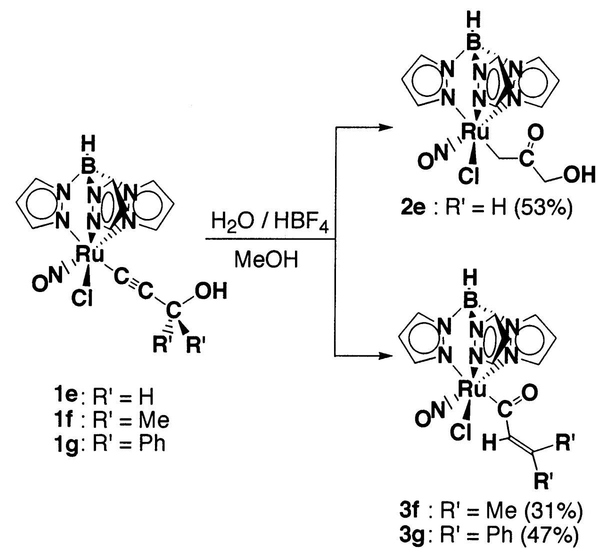


Figure 1. Molecular structure of **2b** (thermal ellipsoids at the 50% level). One of the two crystallographically independent molecules of **2b** is drawn. Crystal solvent and hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Ru(1)−Cl(1), 2.3627(7); Ru(1)−N(1), 1.742(2); Ru(1)−C(10), 2.151(2); O(1)−N(1), 1.128(3); O(2)−C(11), 1.237(3); C(10)−C(11), 1.474(4). Selected bond angles (deg): Ru(1)−N(1)−O(1), 178.9(3); Ru(1)−C(10)−C(11), 113.2(2); O(2)−C(11)−C(10), 120.8(2); O(2)−C(11)−C(12), 118.0(2); C(10)−C(11)−C(12), 121.2(2).

Scheme 2



On the other hand, for the γ-hydroxyacetylide derivatives of **1e**−**g**, TpRuCl(C≡CC(R′)$_2$OH)(NO) with H, Me, and Ph as R′, respectively, similar treatment with $HBF_4\cdot Et_2O$ afforded the ketonyl complex TpRuCl-($CH_2C(O)CH_2OH$)(NO) (**2e**) and the α,β-unsaturated acyl complexes TpRuCl(C(O)CH=CR′$_2$)(NO) (R′ = Me (**3f**), Ph (**3g**)) (Scheme 2).

Spectroscopic data observed for **2e** are sufficient for the assignment to the ketonyl complex, while the presence of α,β-unsaturated acyl groups in **3f** and **3g** is also confirmed. The EI-MS spectra of **3f** and **3g** include the fragment peak corresponding to $[TpRu(CO)]^+$ (*m*/*z*: 343) without the signal at *m*/*z* 422 of $[TpRuCl(CH_2C$-$(O))(NO)]^+$. The most relevant features of the ^1H NMR spectra of **3f** and **3g** are the resonances of the olefinic protons, which are observed as singlets at δ 6.72 (**3f**) and 7.63 (**3g**). An X-ray structural analysis carried out

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(6) (a) Representative procedure: Tetrafluoroboric acid, HBF_4 (14 μL, 0.10 mmol, 54% in diethyl ether), was added to a MeOH solution (10 mL) of TpRuCl(C≡CPh)(NO) (**1a**) (50 mg, 0.10 mmol). The solution was stirred for 1 h at room temperature and was concentrated to dryness. The residue was chromatographed on a silica gel column using CH_2Cl_2 as an eluent to give **2a** as a red solid (40 mg, 80%). IR (KBr, pellet): ν(BH) 2508 (w), ν(N≡O) 1855 (s), ν(C=O) 1633 (s). ^1H NMR-($CDCl_3$): δ 8.35 (d, J = 6.8 Hz, 2H of Ph), 8.25 (d, J = 2.0 Hz, 1H of pz), 7.94 (d, J = 2.2 Hz, 1H of pz), 7.85 (d, J = 1.9 Hz, 1H of pz), 7.80 (d, J = 2.4 Hz, 1H of pz), 7.70 (d, J = 2.2 Hz, 1H of pz), 7.62 (d, J = 2.4 Hz, 1H of pz), 7.6−7.4 (3H of Ph), 6.40 (t, J = 1.8 Hz, 1H of pz), 6.33 (t, J = 2.2 Hz, 1H of pz), 6.29 (t, J = 2.2 Hz, 1H of pz), 4.82 (d, J = 6.0 Hz, 1H of CH_2), 3.45 (d, J = 6.0 Hz, 1H of CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 204.8 (s, *C*O), 143.6 (s, pz), 142.5 (s, pz), 142.2 (s, pz), 137.9 (s, Ph), 137.0 (s, pz), 135.5 (s, pz), 132.5 (s, Ph), 129.0 (s, Ph), 128.3 (s, Ph), 107.3 (s, pz), 106.9 (s, pz), 106.4 (s, pz), 31.7 (s, *C*H_2). EI-MS (*m*/*z*): 481 (M^+), 451 ($[TpRuCl(CH_2C(O)Ph)]^+$), 345 ($[TpRu(NO)]^+$), 315 ($[TpRu]^+$). Anal. Calcd for $C_{17}H_{17}ClBN_7O_2Ru$: C, 40.94; H, 3.44; N, 19.66. Found: C, 40.93; H, 3.57; N, 19.30. (b) Crystal data for **2b**: $C_{18}H_{19}N_7O_2BClRu\cdot 1/2(CH_3OH)$ (M_r = 528.24); triclinic, space group $P\bar{1}$ (No. 2), a = 10.0179(3) Å, b = 12.2652(7) Å, c = 19.6601(8) Å, α = 94.213(2)°, β = 95.7850(9)°, γ = 109.8535(5)°, V = 2245.5(2) Å^3, Z = 4, ρ_{calcd} = 1.562 g cm^{-3}, R (R_w) = 0.043 (0.069) for 559 variables and 9571 unique reflections (all data).

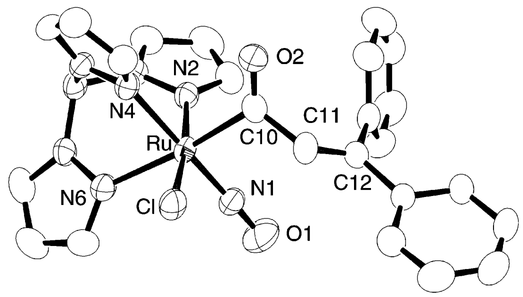

Figure 2. Molecular structure of **3g** (thermal ellipsoids at the 50% level). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Ru–Cl, 2.3654(8); Ru–N(1), 1.737(2); Ru–C(10), 2.064(3); O(1)–N(1), 1.138(3); O(2)–C(10), 1.180(4); C(10)–C(11), 1.517(4); C(11)–C(12), 1.345(4). Selected bond angles (deg): Ru–N(1)–O(1), 177.0(3); Ru–C(10)–C(11), 114.7(2); Ru–C(10)–O(2), 123.8(2); O(2)–C(10)–C(11), 121.0(3); C(10)–C(11)–C(12), 126.5(3). Torsion angle (deg): O(2)–C(10)–C(11)–C(12), −87.5(4).

on a single crystal of **3g**, which was grown from benzene/hexane, confirmed the $TpRuCl(C(O)CH{=}CPh_2)(NO)$ formulation.[7]

The molecular structure of **3g** is depicted in Figure 2. The coordination geometry is approximately octahedral, with the Tp ligand occupying three facial sites. The Ru–C(10) distance of 2.064(3) Å is very close to that of $CpRu(C(O)CH{=}CPh_2)(CO)(P^iPr_3)$ (2.060(2) Å).[8] The C(10)–O(2) and C(11)–C(12) distances are 1.180(4) and 1.345(4) Å, respectively, which are in the region of double-bond distances, indicating no appreciable conjugation over them.

Tautomerism of η^2-coordinated 1-alkyne to the vinylidene form is well-known.[9] Stoichiometric hydration via vinylidene species "M=C=CHR" has been reported in detail by Bianchini et al. to give a Ru(II)–CO complex by C–C triple-bond cleavage reactions, where metal–acyl intermediates "$M{-}C(O)CH_2R$" are involved.[10] A recent mechanistic study of catalytic hydration also proposes the vinylidene intermediate.[11] On the other hand, the 1-alkyne hydration reactions with some metal catalysts such as Hg(II),[12] Pt(II),[13] and Ru(III)[14] give rise to methyl ketones as the Markovnikov products, where formation of ketonyl species has been suggested as an important catalytic process, which involves the nucleophilic attack of H_2O on η^2-coordinated alkynes. Ketonyl platinum(III) dinuclear complexes were reported to be generated by a similar mechanism.[15] Therefore, in the production of **2a–e**, the protonation of the acetylide complexes would afford the vinylidene species, which rapidly isomerize to η^2-alkyne intermediates.[16] Vinylidene species of ruthenium(II) have been regarded to be thermodynamically more stable than tautomeric η^2-alkyne species.[9,11] The back-bonding $d\pi$(metal)–$p\pi$-(vinylidene) interaction would be essential to the stability of the vinylidene species. The presence of the NO^+ ligand, which is a strong π-acceptor group, reduces the interaction to convert vinylidene into η^2-alkyne species. Kirchner et al. have reported a similar view, based on the experimental and theoretical results.[17] To detect the η^2-alkyne intermediate or its tautomers, reaction of **1a** with $HBAr^F{}_4$ ($Ar^F = 3{,}5\text{-}C_6H_3(CF_3)_2$) was monitored by ^1H NMR experiments in dried CD_3OD, on warming from −40 °C to room temperature. Only a mixture of **1a** and **2a** was observed at −20 °C without any intermediates, although no reaction occurred at lower temperatures. Even if the ^1H NMR experiment was carried out using ^tBu analogue **1c**, where the hydration reaction proceeded more slowly than that of **1a**, the η^2-alkyne species were not detected either.

In the case of γ-hydroxyacetylide derivatives except for **1e**, the protonation easily leads to the allenylidene species through the dehydration process at the γ-carbon and then the addition of H_2O at the α-carbon resulted in the α,β-unsaturated acyl complexes. Since the dehydration of the protonated **1e** is likely difficult as expected for a primary alcohol,[18] the reaction does not proceed via the allenylidene form but the η^2-alkyne form.

In conclusion, the protonation of the monoacetylide complexes **1a–g** caused a hydration reaction, producing ketonyl complexes **2a–e** via the η^2-alkyne form and α,β-unsaturated acyl complexes **3f** and **3g** via the allenylidene species. Future work will be focused on the preparation of bis-acetylide complexes with TpRu(NO) fragments and their reactivities.

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Supporting Information Available: Spectroscopic data for the compounds prepared in this study and X-ray crystallographic data for **2b** and **3g**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data for **3g**: $C_{24}H_{21}N_7O_2BClRu$ (M_r = 586.81), triclinic, space group $P\bar{1}$ (No. 2), a = 8.9275(6) Å, b = 10.182(2) Å, c = 14.495(3) Å, α = 98.086(4)°, β = 91.767(2)°, γ = 107.388(1)°, V = 1241.2(4) Å^3, Z = 2, ρ_{calcd} = 1.570 g cm^{-3}, R (R_w) = 0.053 (0.075) for 325 variables and 5386 unique reflections (all data).

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