

# Proton-assisted addition reactions on trimethylsilylalkynyl nitrosylrutheniums of hydrotris(pyrazolyl)borate

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## Abstract

Incorporation of H<sub>2</sub>O or HCl on treatment of trimethylsilylalkynyl nitrosylruthenium TpRuCl(C≡CSiMe<sub>3</sub>)(NO) (**1**) (Tp = hydrotris(pyrazolyl)borate) with protic acid, and the dependence of its product formation on the reaction solvents, are reported. Reactions of **1** with HBF<sub>4</sub> or HCl (aq.) in MeOH gave rise to the mixture of the mono(ethynyl) TpRuCl(C≡CH)(NO) (**2**) and the mono(acyl) TpRuCl{C(O)CH<sub>3</sub>}(NO) (**3**). The H<sub>2</sub>O-incorporated **3** was quantitatively obtained from the reactions of **2** with HCl (aq.) in MeOH. On the other hand, reactions of **1** with HCl (aq.) in CH<sub>2</sub>Cl<sub>2</sub> gave the η<sup>1</sup>-α-chlorovinyl TpRuCl{C(Cl)=CH<sub>2</sub>}(NO) (**4**). In the bis(alkynyl) system TpRu(C≡CSiMe<sub>3</sub>)<sub>2</sub>(NO) (**5**), the similar reactivities were observed. Proton-assisted hydration of **5** afforded the bis(acyl) TpRu{C(O)CH<sub>3</sub>}<sub>2</sub>(NO) (**6**), while the HCl-treatment led to the formation of the bis(α-chlorovinyl) TpRu{C(Cl)=CH<sub>2</sub>}<sub>2</sub>(NO) (**7**).  
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**Keywords:** Nitrosyl ruthenium; Addition reaction; Trimethylsilylalkynyl; Hydrotris(pyrazolyl)borate

## 1. Introduction

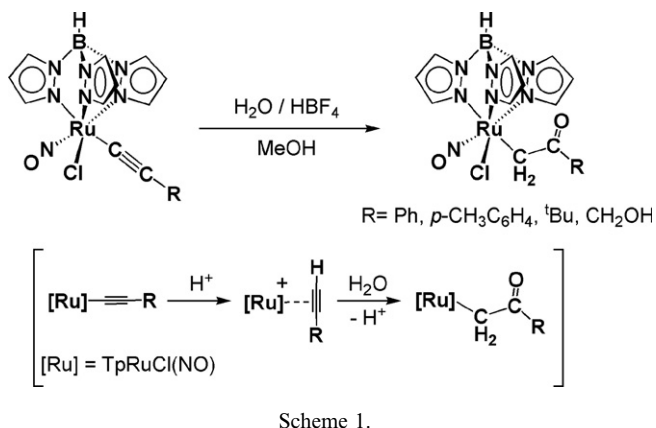
Syntheses and chemical reactivity studies of transition-metal alkynyl complexes have been a subject of considerable interest over two decades, in connection with their simple derivation to well-known vinylidene, allenylidene, and some other cumulenyldene species [1]. Many of them have been proposed as key intermediates in terminal alkyne-utilizing catalytic reactions, such as anti-Markovnikov hydration [2] and propargylic substitution reactions [3]. Furthermore, their linear π-conjugated system with the C≡C bonds has been also attributed to the potentiality developable as functional materials (e.g., optical nonlinearity, luminescence, and liquid crystallinity) [4].

In these laboratories, mono(alkynyl) complexes TpRuCl(C≡CR)(NO), containing a hydrotris(pyrazolyl)borate (Tp) and a characteristic nitrosyl (NO) ligand, have been

prepared and their structural and chemical properties have been investigated in these years. In the course of our protonation studies of the ligating alkynyl groups, we have accidentally disclosed that their H<sub>2</sub>O-addition reactions were induced by HBF<sub>4</sub>, producing the novel ketonyl complexes TpRuCl{CH<sub>2</sub>C(O)R}(NO) (R = Ph, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, <sup>t</sup>Bu, CH<sub>2</sub>OH) (Scheme 1) [5]. The formation of less common ketonyl complexes was generated through π-alkyne intermediates. The appearance of the π-alkyne intermediates has also been established by the proton-assisted phosphine addition reactions in our system [6]. Moreover, application of this hydration chemistry to the bis(alkynyl) complexes TpRu(C≡CPh)<sub>2</sub>(NO) have led to the unprecedented hydrative dimerization to produce the five-membered metallacycle [7]. These results were probably attributed to the presence of the NO ligand. With the intention to make clear the effect of substituent R of the alkynyl ligand, proton-assisted hydration of trimethylsilylalkynyl rutheniums ([Ru]C≡CSiMe<sub>3</sub>) was studied. Interestingly, the use of HCl (aq.) instead of HBF<sub>4</sub> led us to isolate the novel α-chlorovinyl complexes.

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## 2. Results and discussion

### 2.1. Protonation reactions of $TpRuCl(C\equiv CSiMe_3)(NO)$ (1)

Treatment of mono(trimethylsilylalkynyl) complex  $TpRuCl(C\equiv CSiMe_3)(NO)$  (**1**) with an equimolecular amount of  $HBF_4$  in MeOH for 15 min gave two species, mono(ethynyl) complex  $TpRuCl(C\equiv CH)(NO)$  (**2**) and mono(acyl) complex  $TpRuCl\{C(O)CH_3\}(NO)$  (**3**) in a 52:1 ratio (Scheme 2). Similar reaction using  $HCl$  (aq.) in MeOH also afforded the mixture of **2** and **3** (5:1). The column chromatographic separation of the mixture provided **2** in 48% yield, while **3** was not purified owing to unavoidable contamination with a trace amount of **2**. However, separation of **3** was achieved by further protonation of the isolated **2** with 10 equiv of  $HCl$  (aq.) in MeOH.

Complexes **2** and **3** were characterized by IR, NMR, and EI-MS spectroscopic methods together with the elemental analyses. For complex **2**, the  $C\equiv C$  stretching band ( $1999\text{ cm}^{-1}$ ) remains in the IR spectrum. The  $^1H$  NMR spectrum shows a characteristic acetylenic proton at  $\delta$  2.55 at the expense of the trimethylsilyl proton signal at  $\delta$  0.13. In addition, its EI-MS spectrum exhibits the parent molecular ion signal at  $m/z$  405.0 in conformity with its formulation. As for **3**, the presence of the acyl moiety ( $C(O)CH_3$ ) was revealed by the strong IR band of  $\nu_{C=O}$  at  $1685\text{ cm}^{-1}$ , the Me proton resonance at  $\delta$  2.86, and the carbonyl carbon resonance at  $\delta$  235.0. The EI-MS spectrum also shows the parent molecular ion signal ( $m/z$

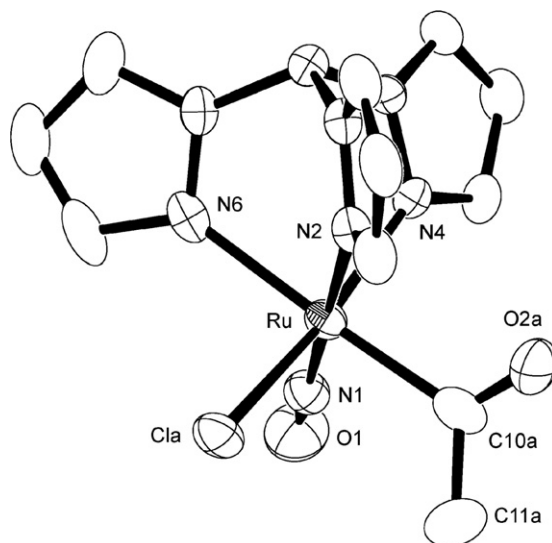
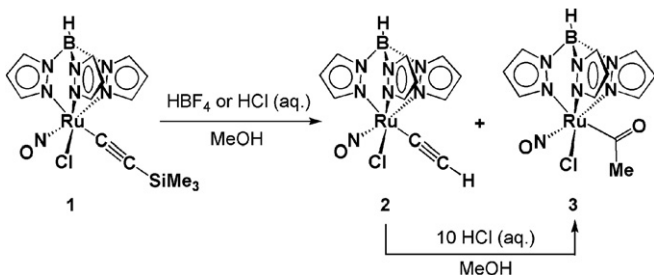


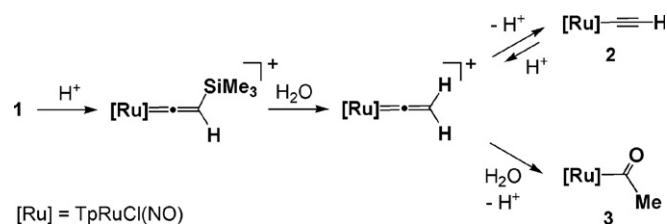
Fig. 1. ORTEP diagram of complex **3** (thermal ellipsoids set at 30% probability). The chloride atom and the acyl moiety are disordered with occupancy factors of 0.7 (a)/0.3 (b). Hydrogen atoms and minor set of the disordered atoms (Clb, C10b, C11b, O2b) have been omitted for clarity.

422.8), indicating one- $H_2O$  mass increment as compared with **2**. Moreover, the structure of **3** was confirmed by an X-ray crystallographic analysis. The ORTEP view is shown in Fig. 1, and selected bond lengths and angles are summarized in Table 1. Unfortunately, the metrical parameters cannot be discussed owing to the crystallographic disorder between the chloride atom and the acyl moiety, but the configuration of **3** was established.

A plausible mechanism is proposed for the formation of **2** and **3** (Scheme 3). Initial protonation of the trimethylsilylalkynyl group would result in the formation of trimethylsilylvinylidene derivative ( $[Ru]=C=CH(SiMe_3)$ ), followed by desilylation to give the primary vinylidene ( $[Ru]=C=CH_2$ ). This facile desilylation is attributed to

Table 1  
Selected bond distances (Å) and angles ( $^\circ$ ) for  $TpRuCl\{C(O)CH_3\}(NO)$  (**3**)

|                                      |          |                                       |          |
|--------------------------------------|----------|---------------------------------------|----------|
| Ru–Cl <sub>a</sub>                   | 2.375(2) | Ru–C10 <sub>a</sub>                   | 2.07(1)  |
| Ru–N1                                | 1.765(3) | O1–N1                                 | 1.099(4) |
| Ru–N2                                | 2.092(3) | O2 <sub>a</sub> –C10 <sub>a</sub>     | 1.17(1)  |
| Ru–N4                                | 2.108(3) | C10 <sub>a</sub> –C11 <sub>a</sub>    | 1.42(1)  |
| Ru–N6                                | 2.161(3) |                                       |          |
| Ru–N1–O1                             | 175.6(3) | Ru–C10 <sub>a</sub> –C11 <sub>a</sub> | 119.0(7) |
| Ru–C10 <sub>a</sub> –O2 <sub>a</sub> | 117.3(8) |                                       |          |



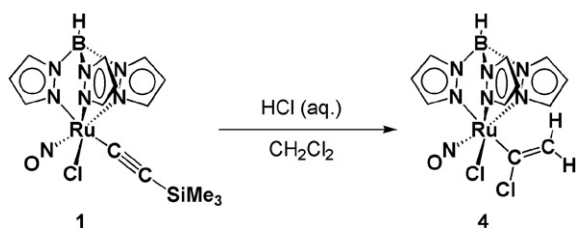
the high susceptibility of the C(sp<sup>2</sup>)-Si bond toward water molecules. The hydrolytic cleavage of the C-Si bonds in ruthenium complexes is well documented in the literatures [8]. Deprotonation of the primary vinylidene would afford **2**, but addition of water molecules on the  $\alpha$  carbon of the vinylidene would yield the acyl complex **3**. The mechanism of this hydration is different from that of our previous alkynyl complexes TpRuCl(C $\equiv$ CR)(NO) (R = Ph, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, <sup>*t*</sup>Bu, CH<sub>2</sub>OH), where hydration proceeded via  $\pi$ -alkyne intermediates (Scheme 1) [5]. Similar formation of the acyl species from ethynyl ruthenium has been described [9].

On the other hand, in CH<sub>2</sub>Cl<sub>2</sub>, the reaction of **1** with HCl (aq.) brought about HCl-incorporation without the hydration processes (Scheme 4). After column chromatographic separation, the  $\alpha$ -chlorovinyl complex TpRuCl{C(Cl)=CH<sub>2</sub>} (NO) (**4**) was isolated as a purple solid (78%). Complex **4** in CH<sub>2</sub>Cl<sub>2</sub> or MeOH solution was slowly subjected to hydrolysis to generate **3**. This formation of **4**, to our knowledge, is the first reported example of HCl-incorporation on alkynylrutheniums [10].

The IR spectrum of **4** shows a  $\nu$ (C=C) stretching band at 1576 cm<sup>-1</sup>. The <sup>1</sup>H NMR signals of the  $\alpha$ -chlorovinyl geminal protons were observed as two doublet resonances coupled with each other (<sup>2</sup>*J* = 1.1 Hz) at  $\delta$  5.97 and 5.02. The EI-MS spectrum indicates the incorporation of HCl into **2**, and the complex **4** was determined to be the  $\alpha$ -chlorovinyl complex by a preliminary X-ray diffraction analysis [11]. The low accuracy of the structural analysis data and the presence of the crystallographic disorder between the  $\alpha$ -chlorovinyl and nitrosyl ligands precluded a precise discussion of the metrical parameters.

In consideration of separation of **4**, the addition of Cl<sup>-</sup> on the  $\alpha$ -carbon reveals the formation of the vinylidene intermediate. Protonation of the Me<sub>3</sub>SiC $\equiv$ C group and desilylation would lead to the primary vinylidene ([Ru]=C=CH<sub>2</sub>), followed by the nucleophilic attack of Cl<sup>-</sup> on the  $\alpha$ -carbon of the resulting vinylidene to afford **4**. When the addition reaction had proceeded through the  $\pi$ -alkyne intermediate, the  $\beta$ -chlorovinyl complex TpRuCl{CH=CH(Cl)}(NO) would have been separated.

The solvent effect in the formation of **3** and **4** was probably attributed to solvation of chloride ion [12]. In MeOH, increased solvation, i.e., weakened nucleophilic character of Cl<sup>-</sup>, would cause the hydration to give **3**, while, in CH<sub>2</sub>Cl<sub>2</sub>, less solvation would lead to **4** via HCl-addition process. Moreover, in the reaction of **1** with HCl (aq.) in



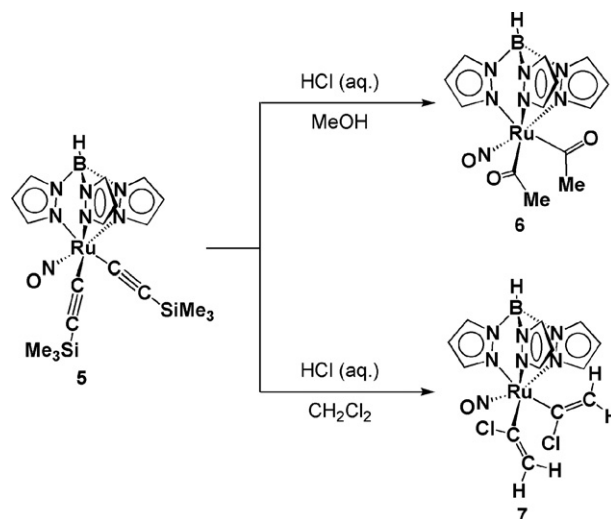
Scheme 4.

CH<sub>2</sub>Cl<sub>2</sub>, the formation of **4**, rather than **3**, may be partially due to the resulting heterogeneous reaction conditions.

## 2.2. Protonation reactions of TpRu(C $\equiv$ CSiMe<sub>3</sub>)<sub>2</sub>(NO) (**5**)

Similar chemical reactivities were shown in the protonations of the bis(trimethylsilylalkynyl) complex TpRu(C $\equiv$ CSiMe<sub>3</sub>)<sub>2</sub>(NO) (**5**). The **5**/HCl (aq.) reaction system in MeOH and CH<sub>2</sub>Cl<sub>2</sub> were carried out to give the bis(acyl) TpRu{C(O)CH<sub>3</sub>}<sub>2</sub>(NO) (**6**) as the H<sub>2</sub>O-incorporated product (39%) and the bis( $\alpha$ -chlorovinyl) TpRu{C(Cl)=CH<sub>2</sub>}<sub>2</sub>(NO) (**7**) as the HCl-addition product (59%), respectively (Scheme 5). In the present system, hydrolysis of the bis(vinyl) **7** in CH<sub>2</sub>Cl<sub>2</sub> or MeOH solution to the bis(acyl) **6** also proceeded slowly as a concomitant side reaction pathway.

Spectroscopic data and elemental analyses of **6** and **7** are consistent with their respective formulation. Both <sup>1</sup>H



Scheme 5.

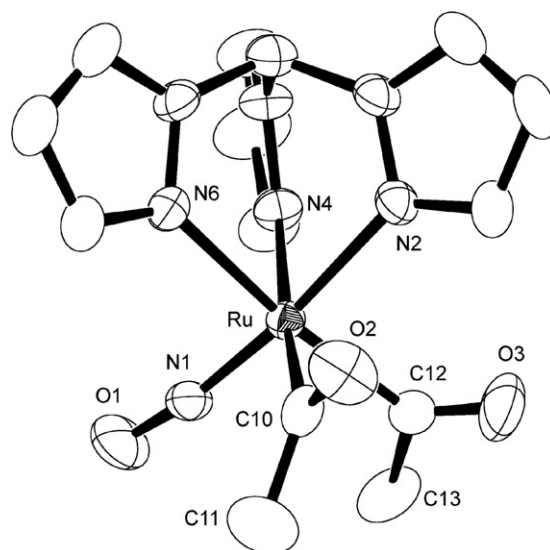
Fig. 2. ORTEP diagram of complex **6** with thermal ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

Table 2  
Selected bond distances (Å) and angles (°) for  $\text{TpRu}\{\text{C}(\text{O})\text{CH}_3\}_2(\text{NO})$  (**6**)

|            |          |            |          |
|------------|----------|------------|----------|
| Ru–N1      | 1.726(2) | O1–N1      | 1.156(3) |
| Ru–N2      | 2.130(2) | O2–C10     | 1.200(4) |
| Ru–N4      | 2.232(2) | O3–C12     | 1.189(4) |
| Ru–N6      | 2.205(2) | C10–C11    | 1.495(4) |
| Ru–C10     | 2.063(3) | C12–C13    | 1.505(4) |
| Ru–C12     | 2.074(3) |            |          |
| Ru–N1–O1   | 170.4(2) | Ru–C12–O3  | 123.7(2) |
| Ru–C10–O2  | 120.2(2) | Ru–C12–C13 | 118.5(2) |
| Ru–C10–C11 | 120.2(2) |            |          |

NMR spectra exhibit two sets of resonances (1:2) for their pyrazolyl groups. Moreover, characteristic methyl signal at  $\delta$  2.58 for **6** and geminal  $\alpha$ -chlorovinyl protons at  $\delta$  5.98 and 5.27 (d,  $^2J = 1.1$  Hz) for **7** are also observed. The EI-MS spectra show signals of their parent ions. In addition, the molecular structure of **6** was X-ray crystallographically confirmed (Fig. 2 and Table 2).

As depicted in Fig. 2, complex **6** adopts a distorted octahedral coordination that is surrounded by Tp, nitrosyl ligands, and two acyl groups. The Ru–C(acyl) bond lengths (2.063(3), 2.074(3) Å) fall within the ranges found previously for the acyl–ruthenium complexes (2.038–2.099 Å) [9,13]. The C(10)–O(2) (1.200 (4) Å) and C(12)–O(3) (1.189(4) Å) are regarded to be a typical C–O double bond. The planes defined by the acyl moiety (O2–C10–C11, O3–C12–C13) are nearly coincident with the respective equatorial coordination plane (N1–Ru–N2–N4, dihedral angle 16.5°; N1–Ru–N2–N6, dihedral angle 18.8°), thus favoring formation of the  $\pi$ -electron delocalization over the Ru–C–O moiety.

### 3. Conclusion

We have observed H<sub>2</sub>O- or HCl-addition reactions of  $\text{TpRuCl}(\text{C}\equiv\text{CSiMe}_3)(\text{NO})$  (**1**). In MeOH, the mono(ethynyl)  $\text{TpRuCl}(\text{C}\equiv\text{CH})(\text{NO})$  (**2**) and the H<sub>2</sub>O-incorporated mono(acyl)  $\text{TpRuCl}\{\text{C}(\text{O})\text{CH}_3\}(\text{NO})$  (**3**) species were isolated, where the latter was also obtained from the further protonation of the former. In CH<sub>2</sub>Cl<sub>2</sub>, using HCl (aq.) as protic acid, the  $\alpha$ -chlorovinyl complex  $\text{TpRuCl}\{\text{C}(\text{Cl})=\text{CH}_2\}(\text{NO})$  (**4**) was isolated as a result of HCl addition. Mechanism for these transformations include the formation of the trimethylsilylvinylidene ( $[\text{Ru}]=\text{C}=\text{CH}(\text{SiMe}_3)$ ), followed by desilylation to afford the primary vinylidene intermediate ( $[\text{Ru}]=\text{C}=\text{CH}_2$ ). Consistent with this mechanism, hydration (in MeOH) and HCl-addition reaction (in CH<sub>2</sub>Cl<sub>2</sub>) of the bis(trimethylsilylalkynyl) complex  $\text{TpRu}(\text{C}\equiv\text{CSiMe}_3)_2(\text{NO})$  (**5**) proceeded to give the bis(acyl)  $\text{TpRu}\{\text{C}(\text{O})\text{CH}_3\}_2(\text{NO})$  (**6**) and the bis( $\alpha$ -chlorovinyl)  $\text{TpRu}\{\text{C}(\text{Cl})=\text{CH}_2\}_2(\text{NO})$  (**7**), respectively.

### 4. Experimental

#### 4.1. General

Reactions were carried out under an atmosphere of dry dinitrogen, whereas subsequent workup was performed in

air. Commercially available reagent grade chemicals were used without any further purification, including 54% HBF<sub>4</sub> solution of diethyl ether (Fluka), 1.0 M HCl solution of diethyl ether (Aldrich), and “dehydrated” MeOH (Wako). The starting material  $\text{TpRuCl}_2(\text{NO})$  was prepared by previously reported methods [14]. <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectra were recorded at ambient temperature in CDCl<sub>3</sub> using a Varian Gemini 300 spectrometer, referenced to the signals of TMS. Infrared spectra (KBr pellets) were run on a JASCO FT/IR-420 spectrometer. Electron ionization mass spectra (EI-MS) were obtained on a JEOL JMS-DX303 spectrometer. Elemental analyses were performed using a PERKIN ELMER 2400II elemental analyzer.

#### 4.2. Preparation of $\text{TpRuCl}(\text{C}\equiv\text{CSiMe}_3)(\text{NO})$ (**1**)

To a solution of  $\text{TpRuCl}_2(\text{NO})$  (300 mg, 0.72 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added HC≡CSiMe<sub>3</sub> (720 mg, 7.33 mmol) and Et<sub>3</sub>N (3.66 g, 36.2 mmol) and then the mixture was heated under reflux for 50 min. After removal of the volatiles, the residue was separated by chromatography on a silica gel using a CH<sub>2</sub>Cl<sub>2</sub> eluent. From the fourth brown band,  $\text{TpRuCl}(\text{C}\equiv\text{CSiMe}_3)(\text{NO})$  (**1**) was isolated as a brown solid (160 mg, 47%). IR (KBr, pellet):  $\nu(\text{BH})$  2514 (w),  $\nu(\text{C}\equiv\text{C})$  2066 (m),  $\nu(\text{N}\equiv\text{O})$  1869 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  8.08 (d,  $J = 1.9$  Hz, 1H, pz), 7.98 (d,  $J = 1.9$  Hz, 1H, pz), 7.82 (d,  $J = 1.9$  Hz, 1H, pz), 7.78 (d,  $J = 2.5$  Hz, 1H, pz), 7.75 (d,  $J = 2.2$  Hz, 1H, pz), 7.53 (d,  $J = 2.5$  Hz, 1H, pz), 6.39 (t,  $J = 2.2$  Hz, 1H, pz), 6.38 (t,  $J = 2.5$  Hz, 1H, pz), 6.20 (t,  $J = 2.4$  Hz, 1H, pz), 0.13 (s, 9H, SiMe<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR:  $\delta$  144.8 (s, pz) 143.5 (s, pz), 142.1 (s, pz), 136.7 (s, pz), 135.7 (s, pz), 134.9 (s, pz), 118.8 (s, Ru–C≡C), 115.1 (s, Ru–C≡C), 107.2 (s, pz), 107.0 (s, pz), 105.9 (s, pz), 1.09 (s, Me). EI-MS ( $m/z$ ): 476.7 (M<sup>+</sup>), 461.7 ([M – Me]<sup>+</sup>), 446.7 ([M – (NO)]<sup>+</sup>), 344.8 ([TpRu(NO)]<sup>+</sup>), 314.8 ([TpRu]<sup>+</sup>). Elemental Anal. (%) Calc. for C<sub>14</sub>H<sub>19</sub>N<sub>7</sub>BClORuSi: C, 35.27; H, 4.02; N, 20.57. Found: C, 35.57; H, 4.03; N, 20.41%.

#### 4.3. Preparation of $\text{TpRu}(\text{C}\equiv\text{CSiMe}_3)_2(\text{NO})$ (**5**)

To a solution of  $\text{TpRuCl}_2(\text{NO})$  (200 mg, 0.48 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) were added HC≡CSiMe<sub>3</sub> (720 mg, 7.33 mmol) and Et<sub>3</sub>N (9.75 g, 96.4 mmol) and then the mixture was refluxed for 12 h. The volatiles were removed and the residue was separated by chromatography on a silica gel. The third brown band was eluted with CH<sub>2</sub>Cl<sub>2</sub> and the solvent were removed under vacuum to give  $\text{TpRu}(\text{C}\equiv\text{CSiMe}_3)_2(\text{NO})$  (**5**) as a brown solid (86 mg, 33%). IR (KBr, pellet):  $\nu(\text{BH})$  2501 (w),  $\nu(\text{C}\equiv\text{C})$  2065 (m), 2056 (m),  $\nu(\text{N}\equiv\text{O})$  1867 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  8.03 (d,  $J = 2.2$  Hz, 1H, pz), 7.90 (d,  $J = 1.9$  Hz, 2H, pz), 7.71 (d,  $J = 1.9$  Hz, 2H, pz), 7.47 (d,  $J = 2.2$  Hz, 1H, pz), 6.33 (t,  $J = 2.2$  Hz, 2H, pz), 6.13 (t,  $J = 2.4$  Hz, 1H, pz), 0.14 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR:  $\delta$  145.4 (s, pz), 142.6 (s, pz) 135.5 (s, pz), 134.6 (s, pz), 122.5 (s, Ru–C≡C), 115.0 (s, Ru–C≡C), 106.4 (s, pz), 105.2 (s, pz), 1.13 (s, SiMe<sub>3</sub>).

EI-MS ( $m/z$ ): 538.7 ( $M^+$ ), 523.7 ( $[M - Me]^+$ ), 508.7 ( $[M - (NO)]^+$ ), 344.8 ( $[TpRu(NO)]^+$ ), 314.8 ( $[TpRu]^+$ ). Elemental Anal. (%) Calc. for  $C_{19}H_{28}N_7BORuSi_2$ : C, 42.38; H, 5.24; N, 18.21. Found: C, 42.66; H, 5.08; N, 18.00%.

#### 4.4. Preparation of $TpRuCl(C\equiv CH)(NO)$ (**2**)

A solution of  $TpRuCl(C\equiv CSiMe_3)(NO)$  (**1**) (51 mg, 0.11 mmol) in MeOH (5 mL) was treated with  $HBF_4 \cdot Et_2O$  (15  $\mu$ L, 0.11 mmol) at room temperature. After stirring for 15 min, the protic acid remained in the solution was quenched by  $NaHCO_3$  powder. The mixture was filtered and the volatiles were evaporated in vacuo. The residue was separated by chromatography (silica gel) using a  $CH_2Cl_2$  eluent to afford the mixture of  $TpRuCl(C\equiv CH)(NO)$  (**2**) and  $TpRuCl\{C(O)CH_3\}(NO)$  (**3**) in a 52:1 ratio. The resulting purple solid was purified by additional chromatographic separation (silica gel) using a ether eluent, followed by  $CH_2Cl_2$  eluent, to give  $TpRuCl(C\equiv CH)(NO)$  (**2**) (21 mg, 48%). Use of conc. HCl (aq.) as protic acid in MeOH also gave rise to the mixture of **2** and **3** (5:1). IR (KBr, pellet):  $\nu(BH)$  2517 (w),  $\nu(C\equiv C)$  1999 (w),  $\nu(N\equiv O)$  1867 (s)  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  8.13 (d,  $J = 2.2$  Hz, 1H, pz), 7.99 (d,  $J = 1.9$  Hz, 1H, pz), 7.86 (d,  $J = 1.9$  Hz, 1H, pz), 7.79 (d,  $J = 2.5$  Hz, 1H, pz), 7.76 (d,  $J = 2.2$  Hz, 1H, pz), 7.54 (d,  $J = 2.2$  Hz, 1H, pz), 6.41 (t,  $J = 2.5$  Hz, 1H, pz), 6.40 (t,  $J = 2.4$  Hz, 1H, pz), 6.22 (d,  $J = 2.4$  Hz, 1H, pz), 2.55 (s, 1H,  $C\equiv C-H$ ).  $^{13}C\{^1H\}$  NMR:  $\delta$  144.8 (s, pz), 143.6 (s, pz), 142.2 (s, pz), 136.7 (s, pz), 135.9 (s, pz), 135.0 (s, pz), 107.5 (s, pz), 107.1 (s, pz), 106.1 (s, pz), 95.4 (s,  $C\equiv C-H$ ), 92.3 (s,  $C\equiv C-H$ ). EI-MS ( $m/z$ ): 405.0 ( $M^+$ ), 375.0 ( $[M - (NO)]^+$ ), 345.0 ( $[TpRu(NO)]^+$ ), 315.0 ( $[TpRu]^+$ ). Elemental Anal. (%) Calc. for  $C_{11}H_{11}N_7BClORu$ : C, 32.66; H, 2.74; N, 24.23. Found: C, 33.07; H, 2.73; N, 23.79%.

#### 4.5. Preparation of $TpRuCl\{C(O)CH_3\}(NO)$ (**3**)

To a MeOH solution (4 mL) of  $TpRuCl(C\equiv CH)(NO)$  (**2**) (21 mg, 0.052 mmol) was added conc. HCl (aq.) (44  $\mu$ L, 0.53 mmol). The solution was stirred at room temperature for 90 min. After the addition of  $NaHCO_3$ , filtration, and evaporation of the filtrate, the residue was chromatographed on a silica gel column using  $CH_2Cl_2$  as an eluent to give  $TpRuCl\{C(O)CH_3\}(NO)$  (**3**) (16 mg, 74%). IR (KBr, pellet):  $\nu(BH)$  2499 (w),  $\nu(N\equiv O)$  1858 (s),  $\nu(C=O)$  1685 (s)  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  7.87 (d,  $J = 1.6$  Hz, 1H, pz), 7.81 (d,  $J = 2.2$  Hz, 1H, pz), 7.79 (d,  $J = 1.9$  Hz, 1H, pz), 7.69 (d,  $J = 2.2$  Hz, 1H, pz), 7.53 (d,  $J = 2.4$  Hz, 1H, pz), 7.52 (d,  $J = 1.9$  Hz, 1H, pz), 6.37 (t,  $J = 2.2$  Hz, 1H, pz), 6.30 (t,  $J = 2.1$  Hz, 1H, pz), 6.18 (t,  $J = 2.4$  Hz, 1H, pz), 2.86 (s, 3 H, Me).  $^{13}C\{^1H\}$  NMR:  $\delta$  235.0 (s,  $C=O$ ), 144.0 (s, pz), 142.7 (s, pz), 141.6 (s, pz), 136.7 (s, pz), 135.3 (s, pz), 134.9 (s, pz), 107.3 (s, pz), 106.4 (s, pz), 105.7 (s, pz), 43.7 (s, Me). EI-MS ( $m/z$ ): 422.8 ( $M^+$ ), 407.8 ( $[M - CH_3]^+$ ), 379.8 ( $[TpRuCl(NO)]^+$ ),

344.9 ( $[TpRu(NO)]^+$ ), 314.9 ( $[TpRu]^+$ ). Elemental Anal. (%) Calc. for  $C_{11}H_{13}N_7BClO_2Ru$ : C, 31.26; H, 3.10; N, 23.20. Found: C, 31.69; H, 3.06; N, 22.64%.

#### 4.6. Preparation of $TpRuCl\{C(Cl)=CH_2\}(NO)$ (**4**)

The complex  $TpRuCl(C\equiv CSiMe_3)(NO)$  (**1**) (30 mg, 0.063 mmol) in  $CH_2Cl_2$  (4 mL) was treated with conc. HCl (aq.) (52  $\mu$ L, 0.63 mmol) at room temperature, and then the mixture was stirred for 30 min. The mixture was quenched by  $NaHCO_3$  powder and filtered, and the volatiles were evaporated to dryness. The residue was extracted with  $CH_2Cl_2$  and loaded onto a silica gel column. The second purple band was eluted with  $CH_2Cl_2$  and collected to yield  $TpRuCl\{C(Cl)=CH_2\}(NO)$  (**4**) as a purple solid (22 mg, 79%). IR (KBr, pellet):  $\nu(BH)$  2514 (w),  $\nu(N\equiv O)$  1868 (s),  $\nu(C=C)$  1576 (m)  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  7.95 (d,  $J = 1.9$  Hz, 2H, pz), 7.81 (d,  $J = 2.5$  Hz, 1H, pz), 7.72 (d,  $J = 1.6$  Hz, 2H, pz), 7.57 (d,  $J = 2.2$  Hz, 1H, pz), 6.41 (t,  $J = 2.4$  Hz, 1H, pz), 6.36 (d,  $J = 2.2$  Hz, 1H, pz), 6.21 (d,  $J = 2.2$  Hz, 1H, pz), 5.97 (d,  $J = 1.1$  Hz, 1H,  $CH_2$ ), 5.02 (d,  $J = 1.1$  Hz, 1H,  $CH_2$ ).  $^{13}C\{^1H\}$  NMR:  $\delta$  155.7 (s,  $Ru-C=C$ ), 144.7 (s, pz), 143.4 (s, pz), 142.3 (s, pz), 136.6 (s, pz), 135.6 (s, pz), 135.0 (s, pz), 124.2 (s,  $=CH_2$ ), 107.3 (s, pz), 106.7 (s, pz), 105.9 (s, pz). EI-MS ( $m/z$ ): 440.9 ( $M^+$ ), 374.9 ( $[M - (NO) - Cl]^+$ ), 345.0 ( $[TpRu(NO)]^+$ ), 315.0 ( $[TpRu]^+$ ). Elemental Anal. (%) Calc. for  $C_{11}H_{12}N_7BCl_2ORu$ : C, 29.96; H, 2.74; N, 22.23. Found: C, 30.28; H, 2.73; N, 22.45%.

#### 4.7. Preparation of $TpRu\{C(O)CH_3\}_2(NO)$ (**6**)

A MeOH solution (4 mL) of  $TpRu(C\equiv CSiMe_3)_2(NO)$  (**5**) (32 mg, 0.059 mmol) and conc. HCl (aq.) (50  $\mu$ L, 0.61 mmol) was stirred at room temperature for 1 h. After addition of  $NaHCO_3$ , filtration, and evaporation, the residue was chromatographed on a silica gel column using a  $CH_2Cl_2$ -acetone (20/1) eluent to give  $TpRu\{C(O)CH_3\}_2(NO)$  (**6**) as an orange solid (10 mg, 39%). IR (KBr, pellet):  $\nu(BH)$  2483 (w),  $\nu(N\equiv O)$  1844 (s),  $\nu(C=O)$  1665 (s), 1630 (s)  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  8.09 (d,  $J = 2.2$  Hz, 1H, pz), 7.72 (d,  $J = 2.5$  Hz, 2H, pz), 7.66 (d,  $J = 1.6$  Hz, 2H, pz), 7.55 (d,  $J = 2.2$  Hz, 1H, pz), 6.30 (d,  $J = 2.1$  Hz, 2H, pz), 6.20 (d,  $J = 2.2$  Hz, 1H, pz), 2.59 (s, 6H, 2Me).  $^{13}C\{^1H\}$ -NMR:  $\delta$  242.5 (s,  $C=O$ ), 144.0 (s, pz), 141.6 (s, pz), 135.5 (s, pz), 135.5 (s, pz), 106.1 (s, pz), 104.9 (s, pz), 44.6 (s,  $CH_3$ ). EI-MS ( $m/z$ ): 431.0 ( $M^+$ ), 416.1 ( $[M - CH_3]^+$ ), 401.1 ( $[M - (NO)]^+$ ), 388.0 ( $[M - \{C(O)CH_3\}]^+$ ), 360.0 ( $[M - (CO) - \{C(O)CH_3\}]^+$ ), 343.0 ( $[M - CH_3 - (NO) - \{C(O)CH_3\}]^+$ ), 315.0 ( $[TpRu]^+$ ). Elemental Anal. (%) Calc. for  $C_{13}H_{16}N_7BO_3Ru$ : C, 36.30; H, 3.75; N, 22.79. Found: C, 36.64; H, 3.73; N, 22.30%.

#### 4.8. Preparation of $TpRu\{C(Cl)=CH_2\}_2(NO)$ (**7**)

A  $CH_2Cl_2$  solution (4 mL) of  $TpRu(C\equiv CSiMe_3)_2(NO)$  (**5**) (94 mg, 0.17 mmol) and conc. HCl (aq.) (0.15 mL,

1.8 mmol) was stirred at room temperature for 1 h. The mixture was quenched by NaHCO<sub>3</sub> powder and filtered, and the volatiles were evaporated to dryness. The residue was extracted with *n*-hexane to afford TpRu{C(Cl)=CH<sub>2</sub>}<sub>2</sub>(NO) (**7**) as a red-purple solid (47 mg, 59%). IR (KBr, pellet):  $\nu(\text{BH})$  2498 (w),  $\nu(\text{N}\equiv\text{O})$  1854 (s),  $\nu(\text{C}=\text{C})$  1568 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.92 (d, *J* = 1.7 Hz, 1H, pz), 7.88 (d, *J* = 1.5 Hz, 2H, pz), 7.72 (d, *J* = 2.2 Hz, 2H, pz), 7.57 (d, *J* = 2.2 Hz, 1H, pz), 6.32 (t, *J* = 2.1 Hz, 2H, pz), 6.18 (t, *J* = 2.4 Hz, 1H, pz), 5.98 (d, *J* = 1.1 Hz, 2H, =CH<sub>2</sub>), 5.27 (d, *J* = 1.1 Hz, 2H, =CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  158.5 (s, Ru–C(Cl)=CH<sub>2</sub>), 144.9 (s, pz), 142.4 (s, pz), 135.3 (s, pz), 128.1 (s, pz), 123.0 (s, Ru–C(Cl)=CH<sub>2</sub>), 106.1 (s, pz), 105.1 (s, pz). EI-MS (*m/z*): 466.8 (M<sup>+</sup>), 436.9 ([M – (NO)]<sup>+</sup>), 344.9 ([TpRu(NO)]<sup>+</sup>), 314.9 ([TpRu]<sup>+</sup>). Elemental Anal. (%) Calc. for C<sub>13</sub>H<sub>14</sub>N<sub>7</sub>BCl<sub>2</sub>ORu: C, 33.43; H, 3.02; N, 20.99. Found: C, 33.93; H, 3.17; N, 20.18%.

#### 4.9. X-ray crystal structural analyses of complexes **3** and **6**

Single crystals suitable for X-ray structural analyses were grown from slow evaporation of CH<sub>2</sub>Cl<sub>2</sub> solution. 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  $\omega$ , in order to assess the crystal quality and preliminary unit cell parameters. The intensity images were obtained with  $\omega$  scans of 0.5° interval per frame for duration of 30 s. The frame data

Table 3  
Crystallographic data for TpRuCl{C(O)CH<sub>3</sub>}<sub>2</sub>(NO) (**3**) and TpRu{C(O)CH<sub>3</sub>}<sub>2</sub>(NO) (**6**)

|                                             | <b>3</b>                                                            | <b>6</b>                                                          |
|---------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------------------|
| Formula                                     | C <sub>11</sub> H <sub>10</sub> N <sub>7</sub> O <sub>2</sub> BClRu | C <sub>13</sub> H <sub>16</sub> N <sub>7</sub> O <sub>3</sub> BRu |
| <i>F</i> <sub>w</sub>                       | 419.58                                                              | 430.19                                                            |
| Crystal system                              | Trigonal                                                            | Orthorhombic                                                      |
| Space group                                 | <i>R</i> -3 (No. 148)                                               | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)    |
| Color of crystal                            | Red                                                                 | Wine red                                                          |
| Crystal size (mm)                           | 0.50 × 0.25 × 0.20                                                  | 0.30 × 0.15 × 0.12                                                |
| <i>a</i> (Å)                                | 30.660(1)                                                           | 7.6811(6)                                                         |
| <i>b</i> (Å)                                |                                                                     | 13.0175(4)                                                        |
| <i>c</i> (Å)                                | 11.4543(2)                                                          | 17.2567(5)                                                        |
| <i>V</i> (Å <sup>3</sup> )                  | 9324.6(4)                                                           | 1725.5(2)                                                         |
| <i>Z</i>                                    | 18                                                                  | 4                                                                 |
| $\rho_{\text{calc}}$ (g cm <sup>-3</sup> )  | 1.345                                                               | 1.656                                                             |
| $\mu$ (cm <sup>-1</sup> )                   | 9.00                                                                | 9.37                                                              |
| 2 $\theta_{\text{max}}$ (°)                 | 55.0                                                                | 55.0                                                              |
| Number of unique reflections                | 4729                                                                | 2184                                                              |
| <i>R</i> <sub>int</sub>                     | 0.026                                                               | 0.022                                                             |
| Number of observed reflections <sup>a</sup> | 4681                                                                | 3800                                                              |
| Number of parameters                        | 224                                                                 | 226                                                               |
| <i>R</i> <sup>b</sup>                       | 0.061                                                               | 0.035                                                             |
| <i>R</i> <sub>w</sub> <sup>c</sup>          | 0.088                                                               | 0.051                                                             |
| Goodness-of-fit <sup>d</sup>                | 1.17                                                                | 1.03                                                              |

<sup>a</sup> All data.

<sup>b</sup>  $R = \sum |F_o^2 - F_c^2| / \sum F_o^2$ .

<sup>c</sup>  $R_w = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$ .

<sup>d</sup> GOF =  $\{ \sum w(|F_o| - |F_c|)^2 / (N_o - N_p) \}^{1/2}$ , where *N*<sub>o</sub> and *N*<sub>p</sub> denote the number of data and parameters.

were integrated using an MSC d\*TREK program package, and the data set were corrected for absorption using a REQAB program.

The calculations were performed with a TEXSAN program package. Crystal structures were solved by direct methods, and refined on *F*<sup>2</sup> by the full-matrix least squares method. In the case of **3**, the acyl fragment and the chloride atom are crystallographically disordered with occupancy factors of 0.7/0.3. Anisotropic refinement was applied to all non-hydrogen atoms with the exception of the minor configuration in disordered **3**. Hydrogen atoms were put at calculated positions with C–H distances of 0.97 Å, except for those of B–H, while three hydrogen atoms of the acyl moiety in **3** were not located. The crystal data and refinement results are summarized in Table 3.

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#### Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 298893 and 298894 for complexes **3** and **6**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.040.

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