Methylation of a nitrosylruthenium complex bearing a hydridotris(pyrazolyl)borate ligand

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Abstract

Reaction of [TpRuCl$_2$(NO)] (**1**) (Tp = HB(pyrazol-1-yl)$_3$) with dimethylzinc, Zn(Me)$_2$, gave rise to a dimethyl complex [TpRu(Me)$_2$(NO)] (**2**) and a monomethyl complex [TpRuCl(Me)(NO)] (**3**) in good yields, while the use of a Grignard reagent, MeMgCl, as the alkylating agents led to isolation of **2** in low yield. Complexes **2** and **3** were confirmed by single-crystal X-ray diffraction analyses. Treatment of **2** with triflic acid, CF$_3$SO$_3$H, afforded a triflato complex [TpRu(Me){OS(O)$_2$CF$_3$}(NO)] (**4**).

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1. Introduction

The chemistry of transition-metal alkyl and aryl complexes with nitrosyl co-ligands has considerable variety, especially of the group 8 elements [1]. Representative are the complexes [Cp*Ru(R)$_2$(NO)], which have been prepared from [Cp*RuCl$_2$(NO)] with some alkylating

reagents, such as Grignard ones RMgX and organo-aluminiums AlR$_3$ [2]. These complexes have been subjected to the mono-protonolyses with HCl [2], HOTf (OTf = OS(O)$_2$CF$_3$) [3], and [H(OEt$_2$)$_2$][BAr'$_4$] (Ar' = 3,5-(CF$_3$)$_2$C$_6$H$_3$) [4] to give Cp*Ru(R)(X)(NO) (X = Cl, OTf, BAr'$_4$) [5], respectively. Interestingly, the latter two complexes with significantly weak or almost non-coordinating X have demonstrated synthetically useful information in carbon-carbon bond formation reactions, exemplified by those of unsaturated hydrocarbons, such as diphenylacetylene [3b] and methyl acrylate [4]. Thermolysis of [Cp*Ru(Ph)$_2$(NO)] also has been conducted in the presence of alkenes or arenes, leading to the release of Ph-Ph and formation of [Cp*Ru(π-alkene)(NO)] [6]. In addition, heating of hetero dihydrocarbyl complex [Cp*Ru(Et)(Ph)(NO)] in the presence of tertiary phosphines (L) has afforded N-coordinated nitrosoalkyl rutheniums [Cp*Ru(Ph){N(=O)CH$_2$CH$_3$}(L)] and N-bound ruthenium oximate [Cp*Ru{N(O)=CHCH$_3$}(L)$_2$] [2a].

On the other hand, for the ruthenium complexes with κ^3-polypyrazolylborato ligands BR(pz)$_3$ (pz = pyrazol-1-yl), to our knowledge, even simple dialkyl (nitrosyl) derivatives have not been reported, while there are several precedent literatures about monoalkyl ruthenium complexes with BR(pz)$_3$, but free of nitrosyl co-ligands [7], being obtainable by use of similar alkylating reagents.

We have been interested in the chemical reactivity of the nitrosyl(polypyrazolylborato)ruthenium [TpRuCl$_2$(NO)] (**1**) (Tp = BH(pz)$_3$) [8], and observed N-C coupling of the ligating NO in the reactions with 2-vinylpyridines [8c] and aliphatic tertiary amines [8a]. Recent reactions of **1** with Super-Hydride solution (LiBHEt$_3$) gave a monoethyl ruthenium [TpRuCl(Et)(NO)], but formation of other species, such as hydrido(nitrosyl) "RuH(NO)", N-bound nitroxyl "Ru{N(=O)H}" [9], and diethyl "Ru(Et)$_2$" species were not found [10]. These findings led us to examine dialkylation of **1** by use of Grignard reagents RMgCl (R = Me, Et, CH$_2$SiMe$_3$) and dimethylzinc ZnMe$_2$, and herein we present the preparations of a dimethyl(nitrosyl)ruthenium complex [TpRu(Me)$_2$(NO)] (**2**) and a monomethyl(nitrosyl)ruthenium [TpRuCl(Me)(NO)] (**3**). Protonolysis of **2** with HOTf is also described.

2. Results and Discussion

To prepare the methyl complexes, reactions with Grignard reagents were initially carried out. Treatment of [TpRuCl$_2$(NO)] (**1**) with MeMgCl (*ca.* 4 eq.) in distilled THF at -78 ºC followed by stirring at room temperature overnight afforded a red-purple solution (Scheme 1). After work-up, from the hexane extract a dimethyl(nitrosyl)ruthenium complex [TpRu(Me)$_2$(NO)] (**2**) was isolated as a pink solid in 11% yield. When the amount of MeMgCl was increased to 6

or 10 eq., a detrimental effect on the yield of **2** was observed (6 eq., 3.9%; 10 eq., 0%). Concerning other Grignard reagents RMgCl (R= Et, CH$_2$SiMe$_3$), the dialkyl analogues [TpRu(R)$_2$(NO)] failed to be obtained.

(Scheme 1 here)

The low yields of **2** motivated us to find more effective alkylating reagents. The transformation of **1** to **2** using alkylzinc reagents was found to proceed cleanly. Complex **1** was mixed with 7 eq. of Zn(Me)$_2$ in distilled THF at -78 °C (Scheme 1), and stirred at room temperature for 91 h with a view of complete reaction proceeding. Reaction mixture was chromatographed on a silica gel column to give **2** in 81% yield. Interestingly, under certain conditions {lesser amount of Zn(Me)$_2$ (5 eq.) and stirring at lower temperature (0 °C) for shorter period (1.5 h)}, a monomethyl(nitrosyl)ruthenium [TpRuCl(Me)(NO)] (**3**) was isolated as a purple solid in 52% yield, concomitant with **2** in 3.6% yield. It is noted that transformation of **3** to **2** was observed in the reaction of **3** with Zn(Me)$_2$ (3 eq.) (53% yield).

Two methyl complexes (**2** and **3**) were characterized by IR, NMR, and EI MS spectroscopic methods. Their IR spectra exhibited intense bands at 1819 and 1803 cm^{-1} for **2** [11] and 1851 cm^{-1} for **3**, indicating the respective retention of terminal linear-type Ru-(NO)$^+$ coordination mode. The ν(NO) value of **2** is larger than that of [Cp*Ru(Me)$_2$(NO)] (1735 cm^{-1}) [2a], demonstrating a smaller degree of π-back donation on the Ru-NO moiety supported with Tp. Similar comparisons of ν(NO) bands [12] have been described in connection with π-electron delocalization systems for a few BR(pz)$_3$ and Cp* ruthenium complexes. The ^{1}H NMR signals of three Tp-pyrazolyl groups in **2** and **3** show two signal sets in the intensity ratio of 1:2 and three distinct signal sets, respectively. Concerning methyl groups of these complexes in C$_6$D$_6$, complex **2** gave signals at δ_H 1.70 and δ_C 5.08 ppm, and complex **3** gave at δ_H 2.05 and δ_C 8.85 ppm, respectively. These chemical shift values of the complexes with Tp ligands were found to be larger than the respective Cp* counterpart complexes, indicating probably lesser electron-density around Ru(Me) moieties [13,14,15]. The EI MS spectra of **2** and **3** exhibit the parent molecular ion signals, respectively, and moreover their structures were confirmed by single-crystal X-ray diffraction analyses. The X-ray crystal structures of **2** and **3** are shown in Fig. 1. Unfortunately, the crystallographic disorder between one methyl group and the NO ligand in **2** and **3** causes the uncertainty of the metric structural parameters, but their skeletal frameworks are established.

(Fig. 1 here)

Chemical reactivity of **2** was preliminary examined. The dimethyl complex **2** is thermally stable toward reductive elimination, since the ^{1}H NMR spectrum of **2** (C$_6$D$_6$) at 70 °C for a week was unchanged. Protonation of **2** with an equimolar triflic acid HOTf was conducted in distilled CH$_2$Cl$_2$ at -78 °C, followed by column chromatographic separation with a silica gel, to

afford a triflato complex [TpRu(Me)(OTf)(NO)] (**4**) as a purple solid in 76% yield (Scheme 2). The IR spectrum of **4** exhibits a ν(NO) band (1863 cm^{-1}) which is higher frequencies than that of **2** and similar to that of **3**. The ^{1}H NMR spectrum of **4** in CDCl$_3$ shows three distinct sets of Tp-pyrazolyl groups in addition to the methyl proton signal at δ_H 1.79 ppm (3H), indicating lowering the symmetry (C_1). In the FAB MS spectra, the parent molecular ion signal [M+1]$^+$ at m/z 510.1 and the fragment signals due to the loss of one Me (m/z 494.0) or one OTf group (m/z 360.1), respectively, are observed. Further reaction of **4** with HOTf failed to obtain a ditriflato complex [TpRu(OTf)$_2$(NO)].

(Scheme 2 here)

3. Conclusion

We have reported the preparations of the mono- and dimethyl(nitrosyl)ruthenium complexes supported by a Tp ligand. The use of dimethylzinc as alkylating reagents led to isolation of these two methyl complexes in good yields. The methyl complexes are characterized by single-crystal X-ray diffraction analyses. In addition, protonation of the dimethyl complex with triflic acid succeeded in isolating the monomethyl triflato complex.

4. Experimental

4.1. General

All reactions were carried out under N$_2$ or Ar unless otherwise noted and subsequent work-up manipulations were performed in air. The starting material [TpRuCl$_2$(NO)] (**1**) [12] was prepared according to the previously reported method. Reaction solvents were distilled from sodium/benzophenone ketyl (THF) or from CaH$_2$ (CH$_2$Cl$_2$). Other organic solvents and all other reagents were commercially available and used without further purification, including 3.0 M MeMgCl solution of THF (Aldrich) and 1.0 M Zn(Me)$_2$ solution of hexane (Kanto Chemical). NMR spectra in C$_6$D$_6$ or CDCl$_3$ were recorded on a Varian Gemini-300 and a JEOL JNM-AL-400 spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ_H and δ_C) are quoted with respect to TMS and the solvent signals, respectively. Infrared spectra in KBr pellets were obtained on JASCO FT-IR-4100 spectrometers. Electron ionization mass spectra (EI MS) and fast atom bombardment mass spectra (FAB MS) were recorded on a JEOL JMS-700N spectrometer. Elemental analyses (C, H, N) were performed on a Perkin Elmer 2400II elemental analyzer.

4.2. Syntheses of [TpRu(Me)$_2$(NO)] (2)

Reaction with MeMgCl: Methylmagnesium chloride solution (0.964 mL, 2.89 mmol) was added dropwise to [TpRuCl$_2$(NO)] (1) (308.4 mg, 0.743 mmol) in distilled THF at -78 ºC. The reaction mixture was warmed gradually to room temperature and stirred overnight. After addition of small amounts of acetone and methanol to quench the remaining MeMgCl, the mixture was evaporated to dryness. The CH$_2$Cl$_2$-soluble product was collected from the dried residue, and its successive extraction with hexane gave complex 2 as a pink solid (31.5 mg, 11%).

Reaction with Zn(Me)$_2$: Dimethylzinc solution (7.0 mL, 7.0 mmol) was added dropwise to [TpRuCl$_2$(NO)] (1) (416.7 mg, 1.00 mmol) in distilled THF (60 mL) at -78 ºC. The reaction mixture was warmed to room temperature and stirred for 91 h with a view of complete reaction proceeding. After addition of methanol (20 mL) to quench any reactive methylzinc species, the mixture was evaporated to dryness. Column chromatographic separation of CH$_2$Cl$_2$ extract from the dried residue was performed on a silica gel with CH$_2$Cl$_2$ elution to give the complex 2 (304.1 mg, 81%).

4.2.1. [TpRu(Me)$_2$(NO)] (2)

IR (KBr): ν(BH) 2478 (m), ν(NO) 1819 (s), 1803 (s) cm^{-1}; (CH$_2$Cl$_2$): ν(BH) 2489 (m), ν(NO) 1810 (s) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ_H 7.45 (d, J = 1.5 Hz, 2H, pz), 7.34 (d, J = 2.4 Hz, 2H, pz), 7.33 (d, J = 2.9 Hz, 1H, pz), 6.99 (d, J = 2.2 Hz, 1H, pz), 5.88 (t, J = 2.0 Hz, 2H, pz), 5.55 (t, J = 2.1 Hz, 1H, pz), 1.70 (s, 6H, Me). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ_C □140.9 (pz), 140.8 (pz), 134.9 (pz), 134.6 (pz), 106.3 (pz), 105.6 (pz), 5.08 (s, Me). Selected ^{1}H NMR (CDCl$_3$): δ_H 1.30 (s, 6H, Me). Selected ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C □4.10(s, Me). EI MS (*m/z*): 375 ([*M*]$^+$), 360 ([*M*-Me]$^+$), 345 ([*M*-Me$_2$]$^+$ or [*M*-(NO)]$^+$), 315 ([TpRu]$^+$). Elemental analysis (%) calcd for C$_{11}$H$_{16}$N$_7$BORu: C 35.31, H 4.31, N 26.20; found: C 35.42, H 4.12, N 26.29.

4.3. Syntheses of [TpRuCl(Me)(NO)] (3)

Dimethylzinc solution (1.25 mL, 1.25 mmol) was added dropwise to [TpRuCl$_2$(NO)] (1) (105.1 mg, 0.253 mmol) in distilled THF (30 mL) at -78 ºC. The reaction mixture was warmed slowly to 0 ºC and stirred at 0 ºC for additional 1.5 h. Then, methanol (4 mL) was added to quench any reactive methylzinc species at this temperature, and the mixture was evaporated to dryness. After extraction of the residue with CH$_2$Cl$_2$ and filtration, the column chromatographic separation with a silica gel by use of a CH$_2$Cl$_2$ eluent afforded complex 3 as a purple solid (51.1 mg, 52%) along with 2 (3.4 mg, 3.6%).

4.3.1. [TpRuCl(Me)(NO)] (3)

IR (KBr): ν(BH) 2496 (m), ν(NO) 1851 (s) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ_H 7.97 (d, J = 1.9 Hz, 1H, pz), 7.85 (d, J = 2.1 Hz, 1H, pz), 7.24 (d, J = 2.2 Hz, 1H, pz), 7.17 (d, J = 2.7 Hz, 1H, pz), 6.91 (d, J = 1.9 Hz, 1H, pz), 6.82 (d, J = 2.1 Hz, 1H, pz), 5.83 (t, J = 2.1 Hz, 1H, pz), 5.69 (t, J = 2.3 Hz, 1H, pz), 5.51 (t, J = 2.3 Hz, 1H, pz), 2.05 (s, 3H, Me). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ_C ☐142.9 (pz), 142.6 (pz), 141.6 (pz), 136.3 (pz), 134.9 (pz), 134.5 (pz), 107.3 (pz), 106.6 (pz), 106.0 (pz), 8.85 (s, Me). Selected ^{1}H NMR (CDCl$_3$): δ_H 1.79 (s, 3H, Me). Selected ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C ☐8.24 (s, Me). EI MS (m/z): 395 ([M]$^+$), 380 ([M-Me]$^+$), 350 ([TpRuCl]$^+$), 315 ([TpRu]$^+$). Elemental analysis (%) calcd for C$_{10}$H$_{13}$N$_7$BClORu: C 30.44, H 3.32, N 24.85; found: C 30.84, H 3.13, N 24.20.

4.4. Protonolysis of 2 with HOTf to give [TpRu(Me)(OTf)(NO)] (4).

To a distilled CH$_2$Cl$_2$ (30 mL) solution of [TpRu(Me)$_2$(NO)] (2) (75.5 mg, 0.202 mmol) at -78 °C was added HOTf (18 µL, 0.203 mmol). The reaction mixture was warmed to room temperature and stirred for 24 h. After evaporation, the residue was separated by column chromatography with a silica gel using a CH$_2$Cl$_2$ eluent to give complex 2 (4.6 mg, 6.1%) and complex 4 as a purple solid (78.1 mg, 76%).

4.4.1. [TpRu(Me)(OTf)(NO)] (4)

IR (KBr): ν(BH) 2521 (w), ν(NO) 1863 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ_H 8.11 (d, J = 1.9 Hz, 1H, pz), 7.84 (d, J = 2.5 Hz, 1H, pz), 7.73 (d, J = 3.2 Hz, 1H, pz), 7.72 (d, J = 2.6 Hz, 1H, pz), 7.64 (d, J = 2.3 Hz, 1H, pz), 7.34 (d, J = 2.1 Hz, 1H, pz), 6.40 (t, J = 2.4 Hz, 1H, pz), 6.35 (t, J = 2.2 Hz, 1H, pz), 6.27 (t, J = 2.3 Hz, 1H, pz), 1.79 (s, 3H, Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ_C ☐142.6 (pz), 142.3 (pz), 141.1 (pz), 137.6 (pz), 135.4 (pz × 2), 118.8 (q, CF$_3$), 107.9 (pz), 106.7 (pz), 106.4 (pz), 9.54 (s, Me). FAB MS (m/z): 510.1 ([M+1]$^+$), 494.0 ([M-Me]$^+$), 360.1 ([M-OTf]$^+$). Elemental analysis (%) calcd for C$_{11}$H$_{13}$N$_7$BF$_3$O$_4$SRu: C 26.00, H 2.58, N 19.29; found: C 26.12, H 1.98, N 19.01.

4.5. X-ray crystal structural analyses of [TpRu(Me)$_2$(NO)] (2) and [TpRuCl(Me)(NO)] (3)

Crystallographic data are summarized in Table 1. X-ray quality single crystals were obtained by sublimation (for 2) and from a solvent mixture CH$_2$Cl$_2$/hexane (for 3), respectively. Diffraction data were collected at -180ºC under a stream of cold N$_2$ gas on a Rigaku RA-Micro7 HFM instrument equipped with a Rigaku Saturn724+ CCD detector by using

graphite-monochromated Mo-Kα radiation. The intensity images were obtained at the exposure of 8.0 s/° (**2**) and 2.0 s/° (**3**). The frame data were integrated using a Rigaku CrystalClear program package, and the data sets were corrected for absorption using a REQAB program.

The calculations were performed with a CrystalStructure software package. The structures were solved by direct methods (for **2**) and Patterson methods (for **3**), and refined on F^2 by the full-matrix least squares methods. For **2**, one of the methyl ligands and the NO ligand were disordered with occupancy factors of 0.5/0.5. For **3**, there was a disorder between the methyl and NO ligands with occupancy factors of 0.5/0.5. Anisotropic refinement was applied to all non-hydrogen atoms except for the disordered atoms (methyl and NO atoms). Hydrogen atoms for all structures were put at calculated positions.

(Table 1 here)

Supplementary material

CCDC 967762 (**2**) and 967763 (**3**) 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. Supplementary data associated with this article can be found, in the online version, at ********.

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[13] NMR data of the methyl signals of the counterpart complexes in C_6D_6: [Cp*Ru(Me)$_2$(NO)] [2a], δ_H 0.87 and δ_C -0.50 ppm; [Cp*RuCl(Me)(NO)] [2b], δ_H 1.64 and δ_C 4.15 ppm.

[14] Based on the electrochemical series study on the $E°\{[Ru(III)]/[Ru(II)]\}$ redox potentials of the complexes [Ru(L^1)(L^2)] (L^1, L^2; polypyrazolylborates and cyclopentadienyls) [15] together with successive modifications, evaluated trend of ligand electron-donating capabilities toward Ru(II) ions would be expressed as the following order; Cp* > BH(pz)$_3$ > B(pz)$_4$ > Cp, with ca. -110 mV of $\Delta E°\{$Cp* vs. BH(pz)$_3$ gap$\}$, ca. -65 mV of $\Delta E°\{$BH(pz)$_3$ vs. B(pz)$_4$ gap$\}$, and ca. -60 mV of $\Delta E°\{$B(pz)$_4$ vs. Cp gap$\}$ in CH_2Cl_2.

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Table 1. Crystallographic data for **2** and **3**

	2	**3**
formula	$C_{11}H_{16}N_7BORu$	$C_{10}H_{13}N_7BClORu$
fw	374.17	394.59
cryst system	tetragonal	monoclinic
space group	$P4_12_12$ (No. 92)	$P2_1/m$ (No. 11)
colour of crystal	pink	purple
crystal size (mm)	0.105 x 0.105 x 0.095	0.30 x 0.18 x 0.10
a (Å)	12.056(2)	8.175(3)
b (Å)	12.056(2)	10.486(4)
c (Å)	20.960(4)	8.627(3)
α (deg)	90	90
β (deg)	90	94.442(4)
γ (deg)	90	90
V (Å^3)	3046.5(8)	737.3(4)
Z	8	2
ρ_{calc} (g cm^{-3})	1.631	1.777
μ (cm^{-1})	10.384	12.527
$2\theta_{max}$ (deg)	54.9	54.9
no. of all reflns collected	25562	5947
no. of unique reflns	3489	1756
R_{int}	0.0744	0.0179
no. of obsd reflns [a]	3171	1700
no. of parameters	190	107
$R1$ [a,b]	0.0466	0.0199
Rw (all data)[c]	0.0973	0.0520
GOF (all data)[d]	1.066	1.063

[a] $I > 2\sigma(I)$. [b] $R1 = \Sigma \,||Fo| - |Fc||/\Sigma \,|Fo|$. [c] $Rw = \{\Sigma w \,(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2\}^{1/2}$.
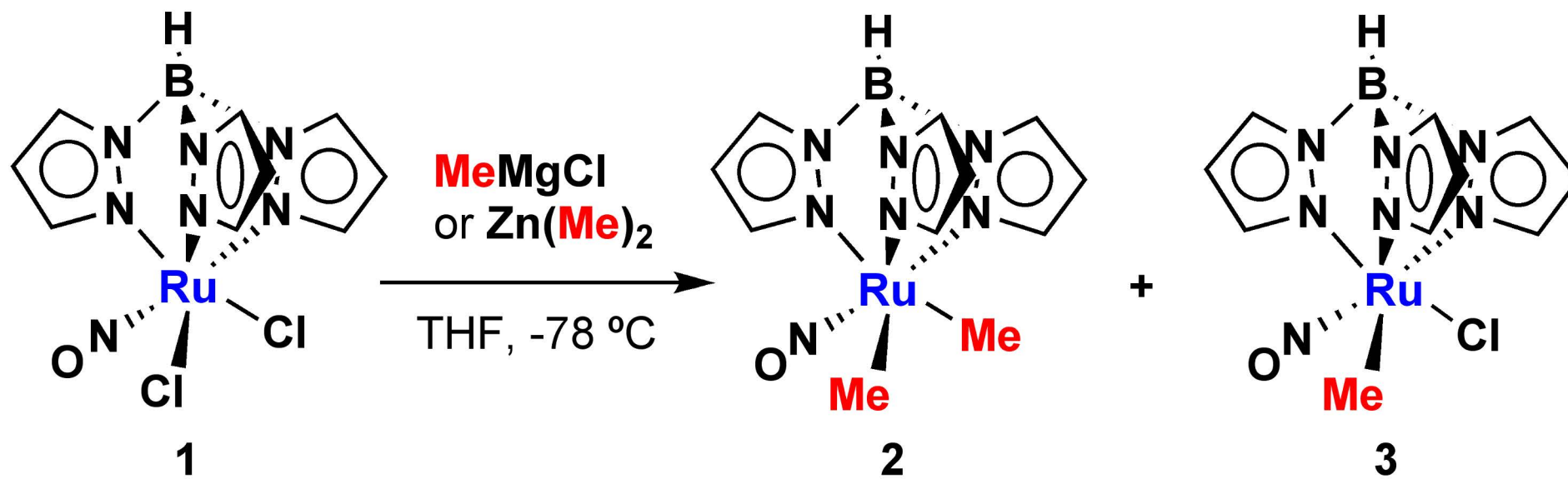
[d] $GOF = [\{\Sigma w(Fo^2 - Fc^2)^2\}/(No - Np)]^{1/2}$, where No and Np denote the number of data and parameters.
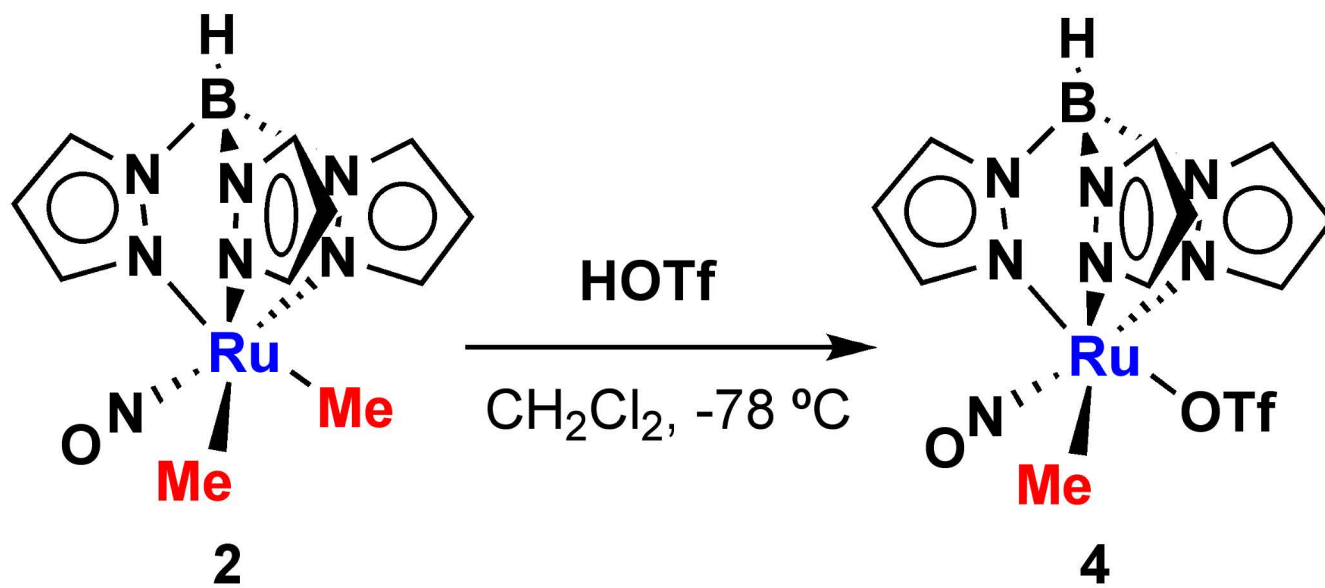
[Captions]

Scheme 1. Methylation of the nitrosylruthenium complex [TpRuCl$_2$(NO)] (**1**).

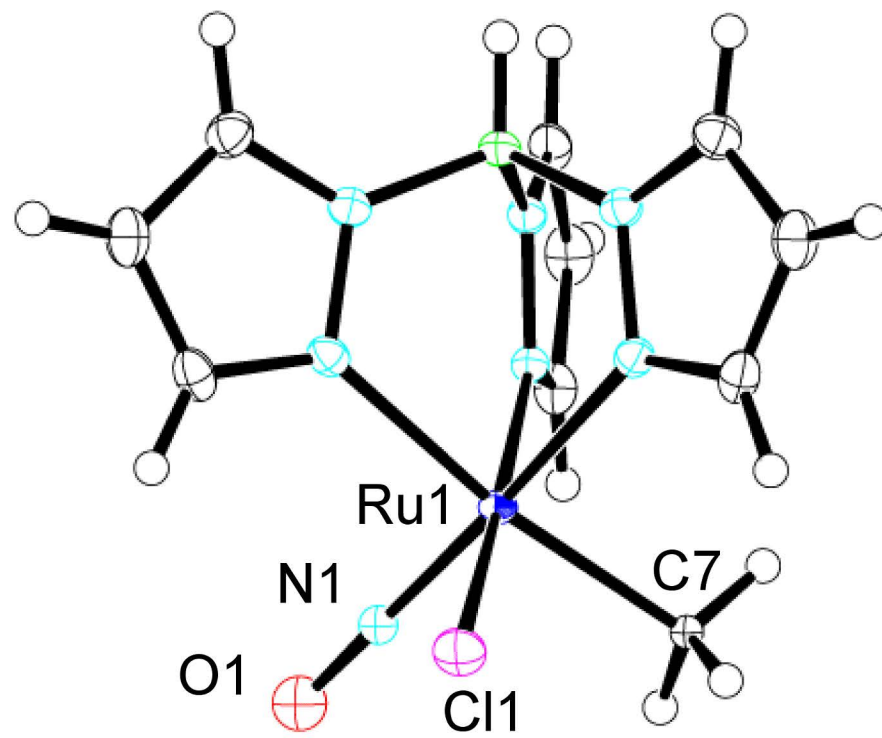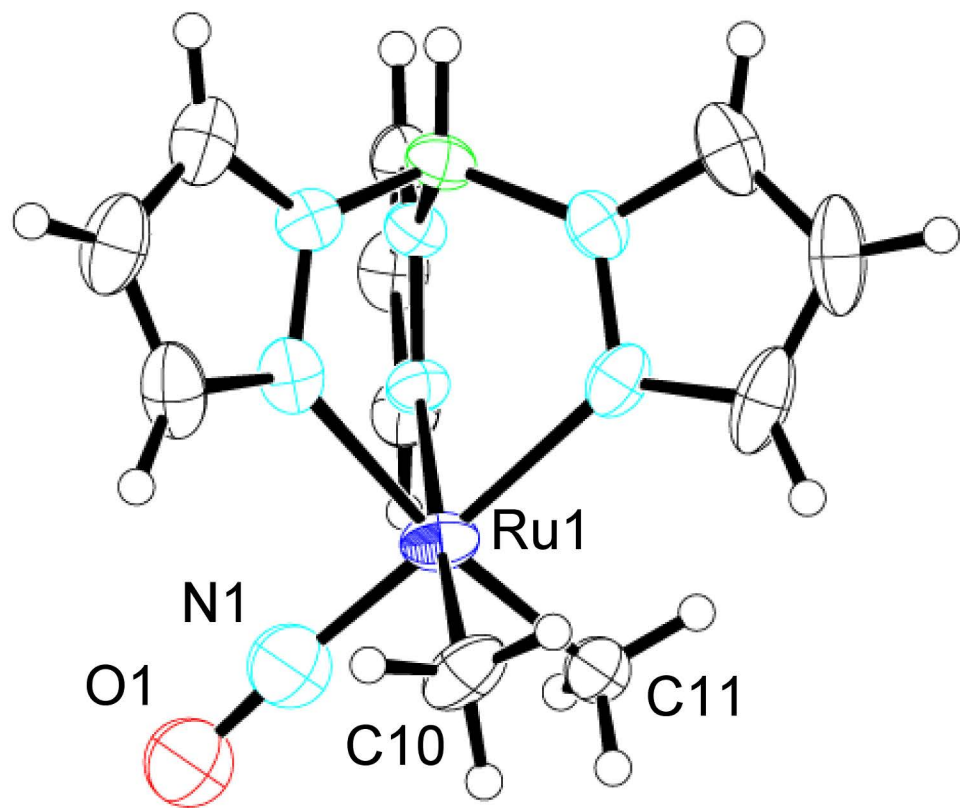**Scheme 2.** Protonation of the dimethylruthenium **2** with HOTf.

Fig. 1. Molecular structures of **2** (left) and **3** (right) with thermal ellipsoids at the 50% probability level. For each structure, one set of the disordered atoms is shown, respectively.

Scheme 1.

HOTf

CH_2Cl_2, -78 ºC

2

4

Scheme 2.

Fig. 1.