



Note

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

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ABSTRACT

Reaction of [TpRuCl₂(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, CF₃SO₃H, afforded a triflate complex [TpRu(Me){OS(O)₂CF₃}(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*RuCl₂(NO)] with some alkylating reagents, such as Grignard ones RMgX and organo-aluminiums AlR₃ [2]. These complexes have been subjected to the mono-protonolyses with HCl [2], HOTf (OTf = OS(O)₂CF₃) [3], and [H(OEt)₂][BAR'₄] (Ar' = 3,5-(CF₃)₂C₆H₃) [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)CH₂CH₃}(L)] and N-bound ruthenium oximate [Cp*Ru{N(O) = CHCH₃}(L)₂] [2a].

On the other hand, for the ruthenium complexes with κ³-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 literature 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 [TpRuCl₂(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 (LiBHET₃) 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, CH₂SiMe₃) and dimethylzinc ZnMe₂, 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.

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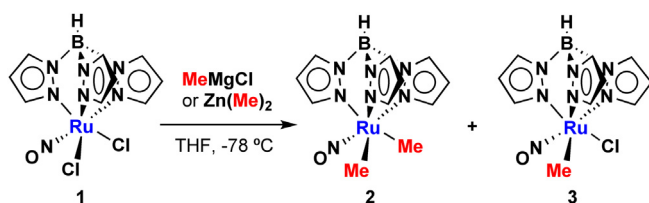
2. Results and discussion

To prepare the methyl complexes, reactions with Grignard reagents were initially carried out. Treatment of $[\text{TpRuCl}_2(\text{NO})]$ (**1**) with MeMgCl (ca. 4 eq.) in distilled THF at -78°C 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 $[\text{TpRu}(\text{Me})_2(\text{NO})]$ (**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 ($\text{R} = \text{Et}, \text{CH}_2\text{SiMe}_3$), the dialkyl analogues $[\text{TpRu}(\text{R})_2(\text{NO})]$ failed to be obtained.

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 $\text{Zn}(\text{Me})_2$ 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 $\text{Zn}(\text{Me})_2$ (5 eq.) and stirring at lower temperature (0°C) for shorter period (1.5 h)}, a monomethyl(nitrosyl)ruthenium $[\text{TpRuCl}(\text{Me})(\text{NO})]$ (**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 $\text{Zn}(\text{Me})_2$ (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 $\text{Ru}(\text{NO})^+$ coordination mode. The $\nu(\text{NO})$ value of **2** is larger than that of $[\text{Cp}^*\text{Ru}(\text{Me})_2(\text{NO})]$ (1735 cm^{-1}) [2a], demonstrating a smaller degree of π -back donation on the $\text{Ru}-\text{NO}$ moiety supported with Tp. Similar comparisons of $\nu(\text{NO})$ bands [12] have been described in connection with π -electron delocalization systems for a few $\text{BR}(\text{pz})_3$ and Cp^* ruthenium complexes. The ^1H 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_6D_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 $\text{Ru}(\text{Me})$ moieties [13–15]. 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.

Chemical reactivity of **2** was preliminary examined. The dimethyl complex **2** is thermally stable toward reductive elimination, since the ^1H NMR spectrum of **2** (C_6D_6) at 70°C for a week was unchanged. Protonation of **2** with an equimolar triflic acid HOTf



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

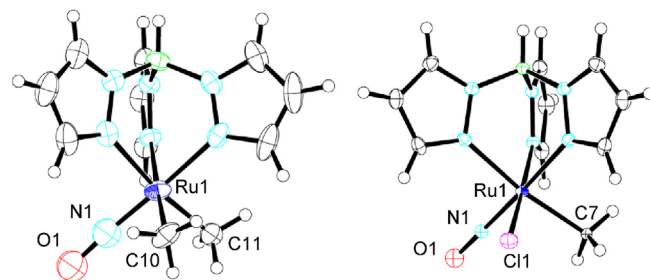


Fig. 1. Molecular structures of **2** (left) and **3** (right) with thermal ellipsoids at the 50% probability level. For each structure, one set of the disordered atoms is shown, respectively.

was conducted in distilled CH_2Cl_2 at -78°C , followed by column chromatographic separation with a silica gel, to afford a triflate complex $[\text{TpRu}(\text{Me})(\text{OTf})(\text{NO})]$ (**4**) as a purple solid in 76% yield (Scheme 2). The IR spectrum of **4** exhibits a $\nu(\text{NO})$ band (1863 cm^{-1}) which is higher frequencies than that of **2** and similar to that of **3**. The ^1H 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 $[\text{M} + 1]^+$ 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 ditriflate complex $[\text{TpRu}(\text{OTf})_2(\text{NO})]$.

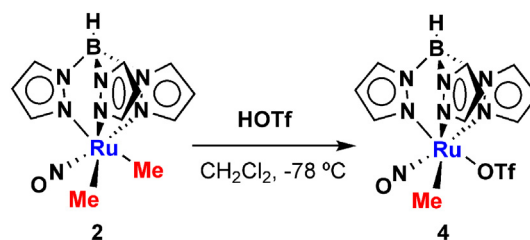
3. Conclusion

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 triflate 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 $[\text{TpRuCl}_2(\text{NO})]$ (**1**) [12] was prepared according to the previously reported method. Reaction solvents were distilled from sodium/benzophenone ketyl (THF) or from CaH_2 (CH_2Cl_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 $\text{Zn}(\text{Me})_2$ solution of hexane (Kanto Chemical). NMR spectra in C_6D_6 or CDCl_3 were recorded on a Varian Gemini-300 and a JEOL JNM-



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

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