Journal of Organometallic Chemistry, 431 (1992) 227–231
Elsevier Sequoia S.A., Lausanne
JOM22591

Methylation of bis(oxazolinyl)pyridinerhodium(III) chlorides with trimethylaluminum

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(Received November 22, 1991)

Abstract

Treatment of bis(oxazolinyl)pyridinerhodium(III) trichloride (**1**) with trimethylaluminum gave the corresponding stable methylrhodium complexes, the mono *axial*-methyl complex (**2**) and the *cis*-dimethyl complex (**3**), stereoselectively. It is also found that the scrambling of the methyl groups at the axial and the equatorial positions, accompanied with the mutual exchange between the methyl group on the rhodium metal and the methyl group on the aluminum atom during the methylation.

Introduction

We have developed 2,6-bis(oxazolinyl)pyridine *pybox*, providing *meridional*-coordination sites for the rest of ligands, as a novel auxiliary for transition metal-catalyzed reactions [1]. We have been interested in organo-transition metal chemistry around the *meridional (trans-cis)* stereochemical environment, especially, with the nitrogen ligand *pybox*. We report here the methylation of pyboxrhodium(III) chlorides giving the methylated complexes and discuss their stereochemistry and reactivities.

Results and discussion

Treatment of bis(4,4-dimethoxyloxazolin-2-yl)pyridinerhodium(III) chloride (**1**) [1,2], (dm-pybox)$RhCl_3$, in dichloromethane at 0°C for 1 h with trimethylaluminum (2.1 *N* in hexane, 1.0 to 5.0 equiv. to **1**) gave the mono *axial*-methylrhodium complex **2** and the *cis*-dimethylrhodium complex **3** (Scheme 1). The stoichiometry and the yields are summarized in Table 1. The stereochemistry of **2** and **3** was readily determined on the basis of unsymmetrical patterns of their ^1H NMR spectra (Fig. 1). Other stereoisomers (**5** and **6**, Scheme 2) for **2** and **3** were not detected.

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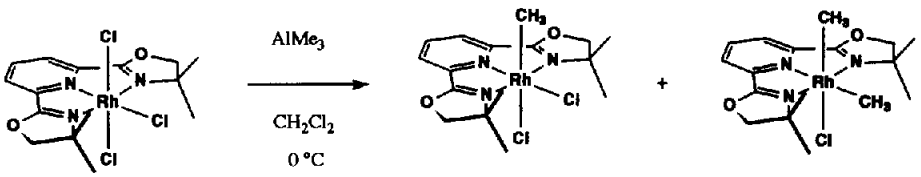


1 2 3

Scheme 1.

Table 1

Methylation of (dm-pybox)$RhCl_3$ (1) with trimethylaluminum [a]

Run	$AlMe_3$ (equiv.)	Isolated yield (%)			
		1	2	3	dm-pybox
1	1.0	20	70	0	0
2	2.0	0	69	11	0
3	3.0	0	55	23	9
4	4.0	0	38	37	6

[a] 1 (100 mg, 0.207 mmol), CH_2Cl_2 (4.0 ml), $AlMe_3$ (1.0–4.0 equiv. to 1, 2.1 *N* in hexane), at 0°C, for 1 h. Work up with water at −30°C.

Large amounts of trimethylaluminum (> *ca.* 4 equiv.) were necessary for the second methylation giving **3** predominantly. However, on starting from the monomethyl complex **2**, the methylation with trimethylaluminum (3.0 equiv.) gave **3** in good yield (72%) and 16% of **2** was recovered. Use of more than 6 equiv. of trimethylaluminum to **1** gave almost metallic rhodium and free pybox in *ca.* 50%

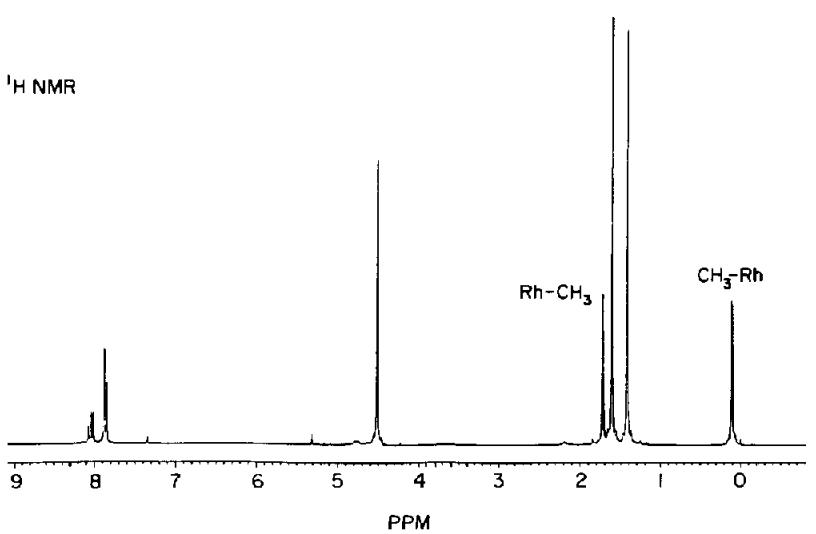
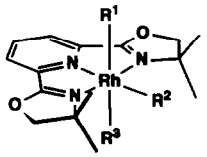


Fig. 1. ^1H NMR spectrum of (dm-pybox)Rh(*cis*-Me_2)Cl (3) (in $CDCl_3$).



	R^1	R^2	R^3
4	Me	Me	Me
5	Cl	Me	Cl
6	Me	Cl	Me
7	CD_3	Cl	Cl
8	$ClCH_2$	Cl	Cl
9	CD_3/CH_3	CD_3/CH_3	Cl
10	-	Cl	-

Scheme 2.

yield. The formation of the trimethylrhodium complex **4** could not be detected even by careful NMR study below 0°C.

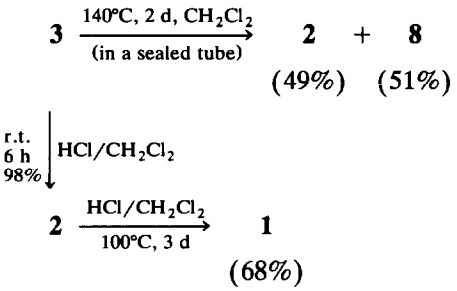
On the basis of the extended Hückel molecular orbital calculation of the *axial* methyl complex **2** and the *equatorial* methyl isomer **5**, the total electron energy of **2** proved to be smaller than that of **5** by 0.244 eV/mol (5.63 kcal/mol) and the overlap population of the Rh–N(pyridine) bond of **2** is also larger than that of the equatorial isomer **5**. Therefore, **2** is thought to be the stable complex rather than **5**. However, we could not find any significant difference of the total electron energy between the *cis*-dimethyl complex **3** and the *trans*-dimethyl complex **6** (< 0.053 eV/mol). Therefore we could not define the critical reason why the *cis*-dimethyl complex **3** forms exclusively rather than **6**.

We examined the stereochemistry of the second methylation by using (dmpybox)Rh(Me-d_3)Cl_2 (**7**), which is readily prepared by the decomposition of the chloromethylrhodium complex **8** in MeOH-d_3 as previously reported [2]. Treatment of **7** with trimethylaluminum (3.0 equiv.) at 0°C for 1 h produced the corresponding *cis*-dimethylrhodium complex **9** (69%) exhibiting the same integral values of the proton signals for the *axial* and the *equatorial* methyl groups (2.3 H and 2.3 H, respectively) (eq. 1). The fact indicates that during the methylation, the facile scrambling of the *axial* methyl group and the *equatorial* one took place. Furthermore the increase in their integrals (theoretically 1.5 H), *i.e.* the loss of the CD_3 group on the rhodium metal, indicates that the methyl migration occurred mutually between the rhodium species and the aluminum species. By the mutual exchange, the increase of the proton integral (2.85 H) of the CH_3–Rh of the recovered methyl complex (**7**) (11% recovered) was also observed (Scheme 3).

We have then examined the reactivity of the methylrhodium complexes. The dimethyl complex **3** readily decomposes in dichloromethane by treatment with hydrochloric acid (5.0 equiv., 0.2 *N*) at room temperature for 6 h to give the monomethyl complex **2** in 98% yield. Although the dimethyl complex **3** is stable in a dichloromethane solution in a sealed tube at 100°C, **3** decomposes at 140°C for 2

$$\mathbf{7} \xrightarrow[-0°C,\ 1\ h,\ CH_2Cl_2]{AlMe_3\ (3.0\ eq)} \mathbf{9}\ (69\%)$$

Scheme 3.



Scheme 4.

d to give the monomethyl complex **2** in 49% and *axial*-$ClCH_2$–Rh complex **8** in 51%, accompanied by the formation of methane and ethane (1/1, > 90%). The activation energy for the decomposition is 33.9 kcal/mol at 140–150°C.

We assume that the decomposition took place via two paths, (i) a homolytic cleavage of the carbon–rhodium bond of **3** giving **2** and methane by the reaction with dichloromethane; (ii) a reductive elimination giving ethane and the monovalent rhodium species **10**, followed by an oxidative addition of dichloromethane to **10** giving **8**. The monomethyl complex **2** proved to be very stable at 100°C in a sealed tube in dichloromethane but decomposed at 100°C for 3 d in hydrochloric acid (20 eq., 1 *N*) to give the trichloride **1** in 68% yield (Scheme 4).

Conclusion

We have synthesized the methylrhodium complexes having the terdentate nitrogen ligand *pybox*. We also found a new type of exchange reaction between the methyl groups on the rhodium atom and the aluminum atom and examined some reactions of the methylrhodium(pybox) species. We think that it is of importance to clarify the basic properties of the alkyl–rhodium bonds. We are currently investigating various reactions of pybox-rhodium-alkyl complexes including catalytic reactions.

Experimental

All reactions were carried out under an atmosphere of nitrogen. Dichloromethane was distilled under nitrogen over $CaCl_2$. ^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded on a JEOL JNM-GX 270 spectrometer using tetramethylsilane as the internal reference. Infrared spectra were recorded on a Jasco A-3 spectrometer. Microanalysis was performed with Yanagimoto CHN corder MT-3. Analytical TLC was performed on Merck (Art 5715) precoated silica gel plates (0.25 mm). Column chromatography was performed with silica gel (Merck, Art 7734). The (dm-pybox)$Rh^{III}Cl_3$ complex **1** was prepared by reaction of dm-pybox and rhodium(III) chloride; see ref. 1. For the preparation of **7** and **8** see ref. 2.

Methylation of mer-trichloro[2,6-bis(4',4'-dimethyloxazolin-2'-yl)pyridine]rhodium-(III) (1) with trimethylaluminum (Table 1, run 3)

To a solution of **1** (100 mg, 0.207 mmol) in dichloromethane (4.0 ml) was added a solution of trimethylaluminum in n-hexane (2.1 *N*, 0.30 ml) at 0°C. After the mixture was stirred for 1 h at 0°C, water (2.0 ml) was added at −30°C. The mixture was extracted with dichloromethane (*ca.* 25 ml) and the extract was dried over anhydrous sodium sulfate. After filtration and concentration, the residue was purified by column chromatography (silica gel, CH_2Cl_2/MeOH = 50/1 ~ 5/1) at 0°C to give **2** (52.4 mg, 0.113 mmol, 55%), **3** (20.6 mg, 0.047 mmol, 23%), and dm-pybox (5.0 mg, 9%); TLC (CH_2Cl_2/MeOH = 5), R_f value: 0.50 for **2** and 0.55 for **3**. For the analytical data of **2**, see ref. 2. For **3**; orange solids, m.p. 225°C (dec); Anal. Found: C, 46.04; H, 5.70; N, 9.54. $C_{17}H_{25}N_3O_2ClRh$ calc.: C, 46.22; H, 5.70; N, 9.51%. ^1H NMR ($CDCl_3$) δ 0.10 (d, J(Rh–H) = 2.5 Hz, 3H), 1.42 (s, 6H), 1.61 (s, 6H), 1.73 (d, J(Rh–H) = 2.5 Hz, 3H), 4.50 (m, 4H, $CH_2O \times 2$), 7.84 (d, J = 8.3 Hz, 2H), 7.98 (t, J = 8.3 and 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$) −5.25 (d, J(Rh–C) = 25.4 Hz), −5.10 (d, J(Rh–C) = 25.4 Hz), 27.26, 27.49, 68.68, 83.29, 124.00, 135.72, 144.50, 163.61. IR (KBr): ν = 1590, 1560, 1410, 1380, 1200, 980, 730 cm^{-1}.

Decomposition of cis-dimethyl(chloro)[2,6-bis(4',4'-dimethyloxazolin-2'-yl)pyridine]-rhodium(III) (3) in dichloromethane in a sealed tube

The dimethylrhodium complex **3** (60 mg, 0.136 mmol) and anhydrous dichloromethane were placed into a glass tube under argon atmosphere. After the glass tube was sealed, the mixture was heated at 140°C for 2 d. After the gas phase was analyzed by GLPC, the residue was analyzed by ^1H NMR to have the monomethyl complex **2** in 49% and the chloromethyl complex **8** in 51%. The decomposition rates: first order for **3**, 2.053×10^{-5} s^{-1} ($t_{1/2}$ = 9.39 h) at 140°C; 2.93×10^{-5} s^{-1} ($t_{1/2}$ = 6.56 h) at 150°C; 33.9 kcal/mol.

The extended Hückel molecular orbital calculation of the pybox-rhodium complexes

The calculation was performed with a NEC PC-9801 RX personal computer and the extended Hückel molecular orbital calculation program (MS-DOS version, 1989), edited by K. Nishimoto and A. Imamura, purchased from Kodansha Scientific, Tokyo. The cartesian coordinate of the pybox-rhodium skeleton is determined on the basis of the X-ray analysis for the related complex [1a].

References

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