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Reactions of ruthenium benzylidenes with H_2O to give benzaldehyde and (aqua)ruthenium complex

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Abstract

The second generation of Grubbs type catalyst, $(PCy_3)(H_2IMes)Cl_2Ru{=}CHPh$ (**1**) undergoes the Cl replacement with CH_3CN to give cationic ruthenium carbene complexes, $[(RCN)_3(H_2IMes)Ru{=}CHPh](OTf)_2$ (**2**, R = CH_3 (**a**), Ph (**b**)) in the presence of AgOTf. The reaction of **2a** with H_2O in the presence of CH_3CN gives (aqua)ruthenium complex, $[Ru(H_2IMes)(NCCH_3)_4(H_2O)](OTf)_2$ (**3**) and benzaldehyde. Benzaldehyde is also observed in the reaction of **1** with H_2O. Plausible reaction pathways are suggested for the degradation of ruthenium benzylidenes to give benzaldehyde on the basis of the isotope labeling experiments.

Keywords: Ruthenium benzylidene; Aquaruthenium complex; Ruthenium; Degradation

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1. Introduction

Transition metal carbene complexes are useful catalysts and important intermediates in organic reactions such as olefin metathesis, cyclopropanation, furan synthesis, and C–C coupling reactions [1]. Especially, ruthenium alkylidenes have been of special interest as olefin metathesis catalyst over the past decade, since they possess significant advantages in terms of stability and ease of storage and handling [1b,2].

In spite of this interest, the studies on the deactivation of ruthenium alkylidenes by water, alcohol, and others have been rarely reported while hydrolysis and nucleophilic substitution are well known in Fischer carbene complexes [3–5]. Furthermore, although the degradations of ruthenium benzylidenes with primary alcohol and water have been recently reported [3a,3b], the mechanism is still not unambiguously elucidated. Particularly, the behavior of the benzylidene moiety in the complex during the reaction is not understood yet.

Herein, we wish to report the degradation of the second generation of Grubbs type ruthenium benzylidene $(PCy_3)(H_2IMes)Cl_2Ru{=}CHPh$ (**1**) [6] and cationic ruthenium benzylidenes $[(RCN)_3(H_2IMes)Ru{=}CHPh](OTf)_2$ (**2**, R = CH_3 (**a**), Ph (**b**)) by reacting with H_2O to give benzaldehyde, and to suggest their deactivation pathways based on isotope labeling experiments.

2. Results and discussion

Since considerable efforts have been recently focused on modification of the ligand environment of the second

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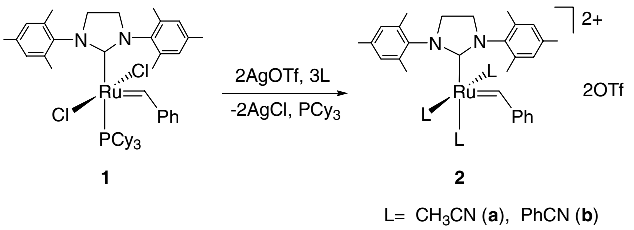
generation of Grubbs type catalyst due to the needs for new catalyst with stability and activity [6,7]. We also have been encouraged to try the replacement of Cl ligand of **1** with neutral ligand by the previous reports on cationic ruthenium catalysts which are highly active in olefin metathesis [8].

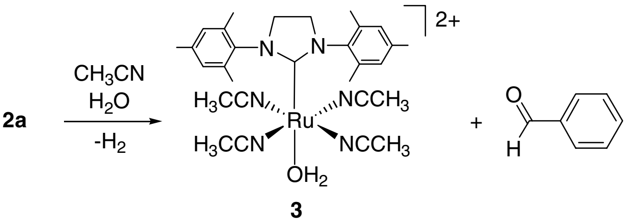
New cationic ruthenium carbenes $[(RCN)_3(H_2IMes)Ru{=}CHPh](OTf)_2$ (**2**, R = CH_3 (**a**), Ph (**b**)) are obtained from reactions of $(PCy_3)(H_2IMes)Cl_2Ru{=}CHPh$ (**1**) with RCN in the presence of AgOTf.



(1)

The most characteristic spectroscopic feature of **2** is the resonance of carbene proton Ru=C*H*Ph in the ^1H NMR spectra at δ 17.34 (for **2a**) and 17.81 (for **2b**), which are considerably shifted to lower field compared with **1**. And the absence of phosphine ligand in **2** is confirmed by no signal in ^{31}P NMR spectra of **2**, and the free phosphine in the reaction solution. This is in agreement with the previous report that phosphine of **1** can be replaced with N-donor ligand [9].

It is observed that ruthenium benzylidenes **1** and **2a** are decomposed to give unknown metal mixtures and the only organic product, benzaldehyde in the presence of H_2O. To obtain well defined decomposition metal product, the reaction of **2a** with H_2O is carried out in the presence of excess CH_3CN, which resulted in the formation of cationic (aqua)ruthenium complex $[Ru(H_2IMes)(NCCH_3)_4(H_2O)](OTf)_2$ (**3**) (75%) and benzaldehyde (93%) in high yields (Eq. (2)). Unlike **2a**, however, well defined decomposition metal product has not been obtained from the reaction of **1** with H_2O even in the presence of excess CH_3CN or PCy_3.



(2)

The molecular structure of **3** is determined by X-ray crystallography which shows the hydrogen bonding interaction between proton of H_2O ligand and oxygen of triflate anion (see Fig. 1 and Supporting Information). From X-ray crystallographic data it was observed that the distance of $O(H_2O){-}H\cdots O(OTf_1)$ is 2.70(1) Å and $O(H_2O){-}H\cdots O(OTf_2)$ is 3.08(1) Å, and bond angle of $O(H_2O){-}H\cdots O(OTf_1)$ is 171(8)° and $O(H_2O){-}H\cdots O(OTf_2)$ is 152(5)°. Two CH_3CN ligands located parallel to the aromatic rings of *N*-heterocyclic carbene of **2a** have bigger angles of C–Ru–N and smaller angles of Ru–N–C than those of the other two CH_3CN ligands of **2a** probably due to steric interactions (Fig. 1).

In order to get some information on the decomposition pathways of ruthenium carbenes **1** and **2** with H_2O, labeling experiments were carried out. In this work, deutrated benzaldehyde ($DCOC_6D_5$) is observed in both reactions of $(PCy_3)(H_2IMes)Cl_2Ru{=}CDC_6D_5$ (**1**-d_6) [3b] and $[(CH_3CN)_3(H_2IMes)Ru{=}CDC_6D_5](OTf)_2$ (**2a**-d_6) with H_2O while both **1** and **2a** react with D_2O to yield undeutrated benzaldehyde (HCOPh). These results strongly suggest that the proton of *H* COPh is oriented from benzylidene proton (Ru=C*H* Ph) of **1** and **2a**. It is also found that the source of the oxygen required for formation of benzaldehyde is H_2O by formation of ^{18}O-labeled benzaldehyde from the reaction of **1** and **2a** with $H_2{}^{18}O$.

These results clearly demonstrate that benzaldehyde is formed from benzylidene group and H_2O. A speculative mechanism is shown in Scheme 1. In the proposed mechanism, first, nucleophilic attack of H_2O on the α-carbon of carbene ligand of **2a** would occur to give intermediate **A**, which would undergo β-hydrogen abstraction to lead to an (aqua)ruthenium complex **3** and benzaldehyde. Nucleophilic attacks on the carbene carbon of methylidene [10a,10b] alkylidene [10a], benzylidene [10c] and dialrylcarbene [10d] have been rarely reported while they are well known for Fisher carbenes [4,11]. The formation of Ru–H bond, though cannot be supported by any direct evidence, can be speculated in a

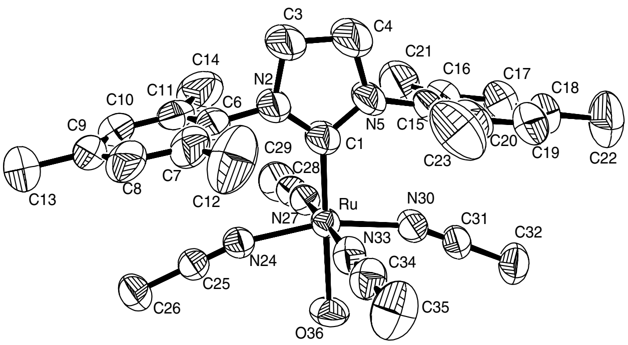
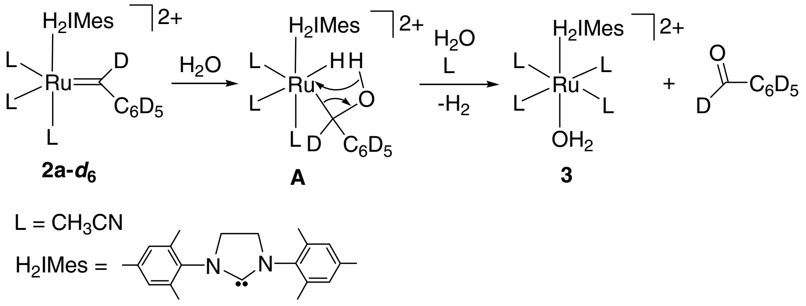


Fig. 1. ORTEP drawing of $[Ru(H_2IMes)(NCCH_3)_4\ (H_2O)](OTf)_2$ (3) with 50% thermal ellipsoids probability. Selected bond distances (Å) and angles (°): $Ru{-}C_1 = 2.015(5)$; $Ru{-}N_{24} = 2.035(4)$; $Ru{-}N_{27} = 2.024(5)$; $Ru{-}N_{30} = 2.041(4)$; $Ru{-}N_{33} = 2.018(5)$; $Ru{-}O_{36} = 2.199(4)$; $C_1{-}Ru{-}O_{36} = 178.79(19)$; $C_1{-}Ru{-}N_{24} = 97.41(19)$; $C_1{-}Ru{-}N_{27} = 92.4(2)$; $C_1{-}Ru{-}N_{30} = 97.82(19)$; $C_1{-}Ru{-}N_{33} = 92.9(2)$; $N_{24}{-}Ru{-}N_{30} = 164.72(18)$; $N_{27}{-}Ru{-}N_{33} = 174.69(18)$; $N_{24}{-}Ru{-}N_{27} = 88.10(17)$; $N_{24}{-}Ru{-}N_{33} = 91.85(17)$; $N_{22}{-}Ru{-}N_{30} = 92.57(17)$; $N_{30}{-}Ru{-}N_{33} = 86.08(17)$; $Ru{-}N_{24}{-}C_{25} = 165.4(4)$; $Ru{-}N_{27}{-}C_{28} = 175.1(4)$; $Ru{-}N_{30}{-}C_{31} = 162.4(4)$; $Ru{-}N_{33}{-}C_{34} = 172.8(5)$.



Scheme 1.

similar way of the formation of metal to H bond suggested in the reaction of Fischer carbene with RSH [5a].

During the investigation on degradations of **1** and **2a** by H_2O, it is found that the cationic ruthenium carbene **2a** is more stable than **1** toward H_2O. The benzylidene signal of **2a** is observed with the significant size even after 2 days while that of **1** disappears within 36 h in the mixed solution of DCE-d_4 (1.5 mL)/H_2O (1.0 mL) in the air at room temperature. Kharasch addition [12] products and ruthenium hydride [3a,3b,12] are not observed during these experiments in $CHCl_3$ and dichloroethane, respectively (Fig. 2).

In the preliminary experiments for the ring opening metathesis polymerization (ROMP) of norbornene, **2a** shows good catalytic activity (60 °C, 10 min, [Monomer]/[catalyst] = 300, yield = 94%) and the resulting polynorbornenes have significantly high *cis* contents of 76% determined by ^1H NMR spectroscopy (Fig. 3) while complex **1** produce polynorbornenes with predominant *trans* contents [6a].

In summary, we demonstrated new cationic ruthenium benzylidenes **2** obtained by Cl abstraction of the second generation Grubbs catalyst **1** and suggested the reaction pathways for the degradation of **1** and **2a** by H_2O to give benzaldehyde by labeling experiments. Further studies to apply **2** to various olefin metathesis reactions and to understand their mechanism are underway in our laboratory.

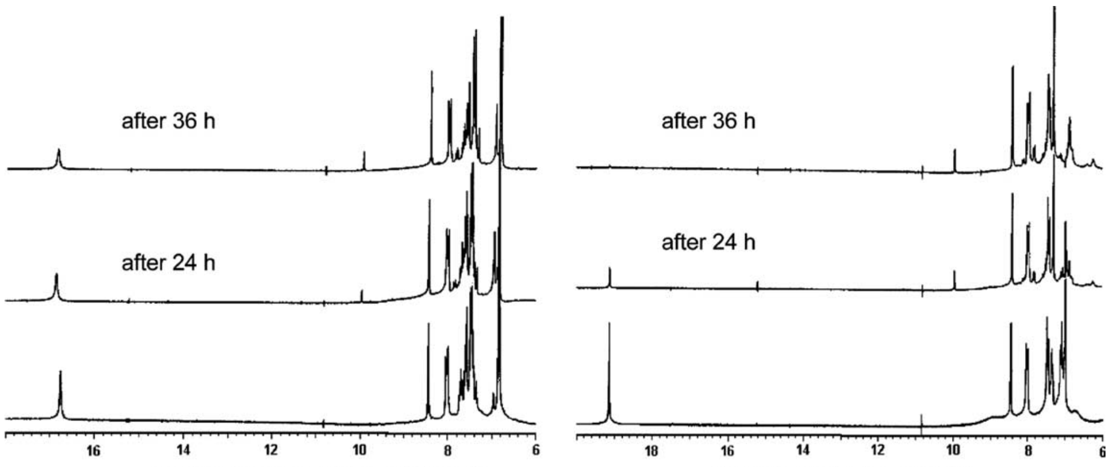
3. Experimental

3.1. General information

A standard vacuum system and Schlenk type glassware were used in most of experimental procedures in handling ruthenium compounds.

$(PCy_3)(H_2IMes)Cl_2Ru{=}CHPh$ (**1**) was purchased from Strem and D_2O, $H_2{}^{18}O$, and styrene-d_8 were purchased from Aldrich. $(PCy_3)(H_2IMes)Cl_2Ru{=}CDC_6D_5$ (**1**-d_6) was prepared from the reaction of **1** and styrene-d_8 by the literature method [3b].

NMR spectra were recorded on either a Varian Gemini 200, 300 or 500 spectrometer (^1H, 300 or 500 MHz; ^{13}C, 126 MHz; ^{31}P, 81.0 MHz). IR spectra were obtained on a Nicolet 205 spectrophotometer. Elemental analyses



$[(CH_3CN)_3(H_2IMes)Ru{=}CDC_6H_5](OTf)_2$(**2a**) $(PCy_3)(H_2IMes)Cl_2Ru{=}CHPh$ (**1**)

Fig. 2. ^1H NMR spectra of compounds of **1** and **2a** in the solution of DCE–d_4 (1.5 mL)/H_2O (1.0 mL) and an internal standard (anthracene) at room temperature in air.

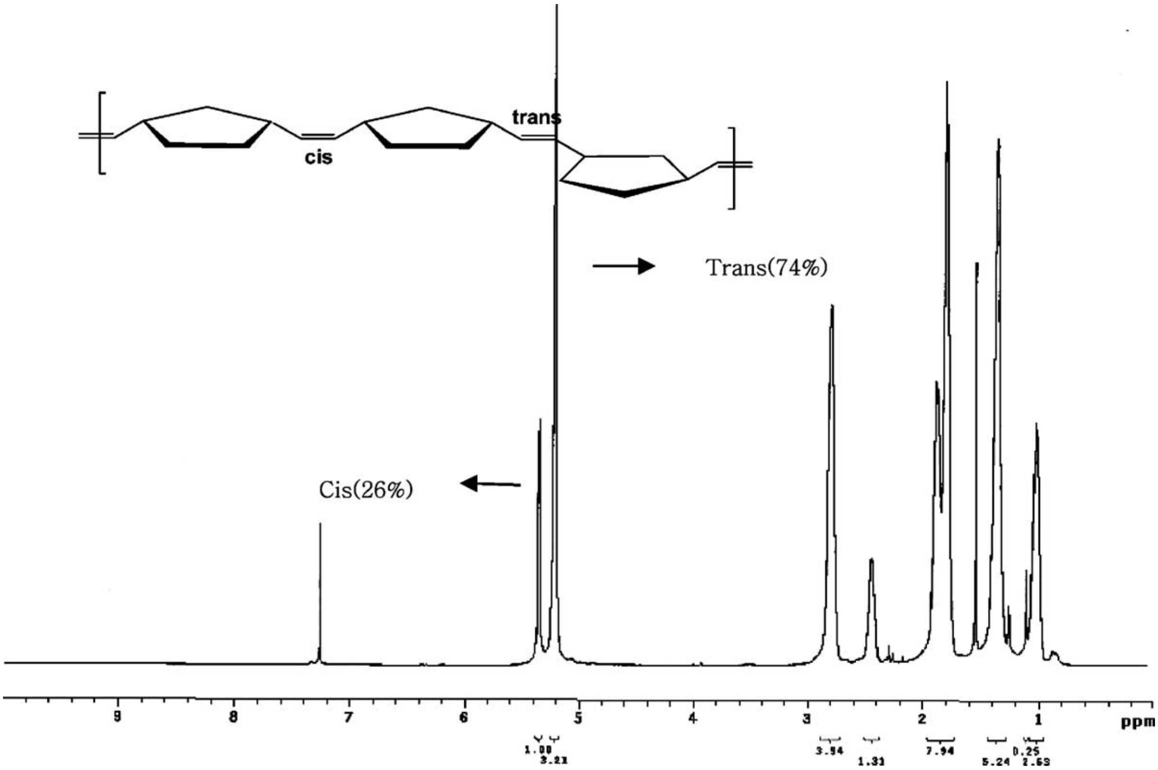


Fig. 3. ^1H NMR spectrum of polynorbornene by **2a** at 500 MHz in $CDCl_3$.

were carried out by a Carlo Erba EA 1108 CHNS-O analyzer. Gas chromatography/mass spectra were measured with Hewlett–Packard HP 5890A VG-trio 2000. FAB-Mass measurements were carried out with JMS-DX303Mass Spectrometer.

3.2. Synthesis

*3.2.1. Synthesis of $[(RCN)_3(H_2IMes)Ru{=}CHPh](OTf)_2$ (**2**, R = CH_3 (**a**), Ph (**b**))*

These compounds were prepared by the same method as described below for **2a**. The reaction mixture of **1** (0.1 g, 0.12 mmol) and AgOTf (0.06 g, 0.24 mmol) in $CHCl_3$ (10 mL) was stirred in the presence of CH_3CN (0.02 mL, 0.36 mmol) at 25 °C for 30 min before the white solid (AgCl) was removed by filtration. Addition of *n*-pentane (20 mL) resulted in precipitation of greenish beige microcrystals that were collected by filtration, washed with *n*-pentane (3 × 10 mL) and dried under vacuum. The yield was 0.1 g or 96% based on $[Ru(=CH-Ph)(IMes)(CH_3CN)_3](OTf)_2$ (**2a**).

*$[Ru(=CHPh)(IMes)(CH_3CN)_3](OTf)_2$ (**2a**).* ^1H NMR (500 MHz, $CDCl_3$): δ 17.34 (s, 1H, Ru=C*H*Ph), 7.61 (t, *J*(H–H) = 7.0 Hz, 1H, *para* C*H* of Ru=CH*Ph*), 7.45 (d, *J*(H–H) = 7.0 Hz, 2H, *ortho* C*H* of Ru=CH*Ph*), 7.35 (t, *J*(H–H) = 7.0 Hz, 2H, *meta* C*H* of Ru=CH*Ph*), 6.87 (s, 4H, C*H* of H_2IMes), 3.98 (s, 4H, CH_2 of H_2IMes), 2.34 (s, 6H, CH_3CN), 2.23 (s, 6H, *para* CH_3 of H_2IMes), 2.19 (s, 12H, *ortho* CH_3 of H_2IMes), 2.11 (s, 3H, CH_3CN). ^{13}C NMR (126 MHz, $CDCl_3$): δ 325.6 (s, Ru=*C*HPh), 202.4 (s, carbene carbon of H_2IMes), 134.1 (*para C* H of Ru=CH*Ph*), 130.2 (*ortho C* H of Ru=CH*Ph*), 129.9 (s, *C*H of H_2IMes), 128.3 (s, *meta C*H of Ru=CH*Ph*), 52.1 (s, CH_2 carbons of H_2IMes), 20.9 (s, *para* CH_3 of H_2IMes), 17.9 (*ortho* CH_3 of H_2IMes), 4.1 ($NCCH_3$), 2.9 ($NCCH_3$), 202.4, 151.2, 140.1, 136.9, 127.4, 121.5, 118.9. HETCOR (^1H (500 MHz) → ^{13}C (126 MHz)): δ 17.34 → 325.6; 7.61 → 134.1; 7.45 → 130.2; 7.35 → 128.3; 6.87 → 129.9; 3.98 → 52.1; 2.34 → 4.1; 2.23 → 20.9; 2.19 → 17.9; 2.11 → 2.9. IR (KBr, cm^{-1}): 2295 (s, $\nu_{C\equiv N}$), 1269, 1160 and 1031 (s, due to uncoordinated OTf^-). Anal. Calc. for $Ru_1S_2F_6O_6N_5C_{36}H_{41}$: C, 47.05; H, 4.50; N, 7.62. Found: C, 47.15; H, 4.55; N, 7.57%. MS (FAB) *m/z* Calc. for $[M^+ - OTf - CH_3CN]$: 729.

*$[Ru(=CHPh)(IMes)(PhCN)_3](OTf)_2$ (**2b**) (89% yield).* ^1H NMR (500 MHz, $CDCl_3$): δ 17.81 (s, 1H, Ru=C*H*Ph), 6.82 (s, 4H, C*H* of H_2IMes), 4.10 (s, 4H, CH_2 of H_2IMes), 2.30 (s, 12H, *ortho* CH_3 of H_2IMes), 2.09 (s, 6H, *para* CH_3 of H_2IMes). ^{13}C NMR (126 MHz, $CDCl_3$): δ 328.4 (s, Ru=*C*HPh), 200.0 (carbene carbon of $H_{2Imes)}$, 134.1, 133.1, 130.2, 129.8, 129.6 (CH carbons), 52.5 (s, CH_2 carbons of IMes), 20.7 (s, *para* CH_3 of IMes), 18.3 (*ortho C* H_3 of IMes), 151.9, 140.5, 137.0, 128.7, 127.6, 125.1, 124.0, 121.4, 118.9, 110.8, 109.8. HETCOR (^1H (500 MHz) → ^{13}C (126 MHz)): δ 17.81 → 328.4; 6.82 → 129.8; 7.45 → 130.2; 7.35 → 128.3; 6.87 → 129.9; 4.10 → 52.5; 2.30 → 20.7;

2.09 → 18.3. IR (KBr, cm^{-1}): 2258 (s, $\nu_{C\equiv N}$), 1269, 1155 and 1030 (s, due to uncoordinated OTf^-). Anal. Calc. for $RuS_2C_{51}H_{47}F_6N_5O_6$:C, 55.43; H, 4.29; N, 6.34. Found: C, 55.82; H, 4.53; N, 6.36%.

3.2.2. Synthesis of $[(CH_3CN)_3(H_2IMes)Ru{=}CDC_6D_5](OTf)_2$ (**2a**-d_6)

This compound was prepared by the same method as described above for **2a** using $(PCy_3)(H_2IMes)Cl_2Ru{=}CDC_6D_5$ (**1**-d_6). The yield was 0.1 g or 95% based on **2a**-d_6. ^1H NMR spectrum of **2a**-d_6 shows all the signals for **2a** except the disappearance of the singlet signal at δ 17.34 due to Ru=C*H*Ph and the signals at δ 7.61, 7.45, and 7.35 due to Ru=CH*Ph*.

3.3. Reactions of **1**, **1**-d_6, **2a** and **2a**-d_6 with H_2O, D_2O, and $H_2{}^{18}O$

These reactions were carried out by the same manner as described below for **2a** and H_2O. A reaction mixture of **2a** (0.10 g, 0.11 mmol) and H_2O (15 mL) in $CHCl_3$ (10 mL) was stirred for 4 days at 25 °C in the presence of CH_3CN (0.006 mL, 0.12 mmol). Addition of *n*-pentane (20 mL) to the $CHCl_3$ solution resulted in precipitation of beige microcrystals that were collected by filtration, washed with *n*-pentane (3 × 10 mL) and dried under vacuum (0.09 g, and 75%). The filtrate was distilled at 25 °C under vacuum to less than 1.0 mL, and the residue was eluted with *n*-pentane on a column packed with silica gel to obtain benzaldehyde (ca. 93% yield), which was detected by ^1H NMR and GC/MS.

*$[Ru(H_2IMes)(NCCH_3)_4(H_2O)](OTf)_2$ (**3**).* ^1H NMR (500 MHz, $CDCl_3$): δ 6.98 (s, 4H, C*H* of H_2IMes), 5.26 (s, 2H, OH_2), 3.91 (s, 4H, CH_2 of H_2IMes), 2.28–2.22 (30H, CH_3 of H_2IMes and NCCH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 206.35 (carbene carbon of H_2IMes), 129.6 (*C*H carbons of H_2IMes), 52.7 (*C*H_2 carbons of H_2IMes), 21.1 and 17.7 (*C*H_3 carbons of H_2IMes), 4.5 (NC*C*H_3), 138.9, 138.1, 124.7. IR (KBr, cm^{-1}): 2296 and 2286 (s, $\nu_{C\equiv N}$), 1266, 1155 and 1031 (s, OTf^-). Anal. Calc. for $RuS_2C_{31}H_{40}F_6N_6O_7$: C, 41.94; H, 4.54; N, 9.47. Found: C, 42.03; H, 4.58; N, 9.34%.

*$[Ru(H_2IMes)(NCCH_3)_4(D_2O)](OTf)_2$ (**3**-d_2).* ^1H NMR spectra of **3**-d_2 show all the signals for **3** except the disappearance of one singlet at 5.26 due to Ru–OH_2.

$DCOC_6D_5$ (benzaldehyde-d_6). MS *m/z* = 112 [M^+].

$HC^{18}OC_6H_5$ (benzaldehyde-^{18}O). MS *m/z* = 108 [M^+].

4. X-ray structure determination

Crystals of **3** were grown by slow evaporation from $CHCl_3$ solution. A pale yellow plate crystal of the title compound was coated with epoxy glue in order to prevent spontaneous liberation of ligands from the specimen under ambient conditions. The epoxy-coated crystal was mounted on an Bruker P4 four-circle X-ray diffractometer and the intensity data were collected in the θ–2θ scan mode using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters and an orientation matrix for the compound were determined from the least-squares fit of 41 accurately centered reflections with θ range of 3.33–12.48°. Three standard reflections were monitored every 97 reflections; no remarkable decays were observed through data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the psi-scans was applied [13a].

All calculations in the structural solution and refinement were performed using the Bruker SHELXTL crystallographic software package [13b]. Space groups were assigned on the basis of the systematic absences and intensity statistics, and were confirmed by successful refinements. The structure was solved by the direct method [13c] and successively refined by the full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms were put into calculated positions with the isotropic thermal parameters. Final difference of electron density maps contained no

Table 1
Details of crystallographic data collection for **3**

Chemical formula	$C_{31}H_{41}F_6N_6O_7RuS_2$
Formula weight	888.89
Temperature (K)	286(2)
Crystal dimension (mm)	0.50 × 0.38 × 0.12
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	14.222(7)
b (Å)	14.995(4)
c (Å)	18.824(3)
α (°)	90
β (°)	90.105(18)
γ (°)	90
V ($Å^3$)	4015(2)
Z	4
$\rho_{(calc)}$ (g cm^{-1})	1.471
μ (mm^{-1})	5.72
F(000)	1820
Radiation	Mo Kα
Wavelength	0.71073
θ Range (°)	1.79 to 26.51
hkl range	$-1 \leqslant h \leqslant 17$ $-1 \leqslant k \leqslant 18$ $-23 \leqslant l \leqslant 23$
No. of reflections	9184
No. of independent reflections	7520
No. of obs. ($\lvert F_o \rvert > 2\sigma F_o$) data	8170
No. of parameters	482
R_1	0.0602
wR_2	0.1624
GOF	1.023

significant features. Further details of the crystallographic and experimental data of **3** are given in Table 1.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.08.017.

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