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Synthesis and properties of alkylruthenium complexes bearing primary and secondary amine ligands

Takashi Koike, Takao Ikariya *

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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Abstract

A series of 18-electron alkylruthenium complexes, RuR[κ^2(*N*,*N*′)-(*S*,*S*)-R′SO_2NCHPhCHPhNH$_2$](η^6-arene) (Ph = C_6H_5, R′ = *p*-$CH_3C_6H_4$ and CH_3), bearing a N-sulfonylated diamine ligand was synthesized from the reaction of RuCl[κ^2(*N*, *N*′)-(*S*,*S*)-R′SO_2NCHPhCHPhNH$_2$](η^6-arene) with alkylzinc reagents, in which transmetalation proceeded smoothly to give the desired alkyl complexes in good yield and selectivity. Although the isolable amine Ru complexes bearing functionalized alkyl ligands were thermally stable, the simple methyl and ethyl Ru complexes underwent intramolecular deprotonation from NH protons to give the amido Ru complexes with release of the alkanes. The reactivity of the alkyl Ru complexes is highly affected by the structures of the arene ligands.

Keywords: Alkylruthenium; Primary amine ligands; Amido ruthenium complex; Alkylzinc reagents; Transmetalation

1. Introduction

We have recently developed chiral amido Ru complexes, Ru[κ^2(*N*,*N*′)-(*S*,*S*)-R′SO_2NCHPhCHPhNH](η^6-arene) (Ph = C_6H_5, R′ = *p*-$CH_3C_6H_4$ and CH_3) (**1**) [1], bearing a M/NH bifunctional unit as highly efficient chiral catalysts for enantioselective C–C bond formation. For example, chiral amido Ru complexes effect the asymmetric Michael addition of 1,3-dicarbonyl compounds to cyclic enones and nitroalkenes in a 1:1 molar ratio to give the corresponding Michael adducts in almost quantitative yields and with excellent ee's [2]. Because the chiral amido Ru complexes have suitable Brønsted basicity as a result of the nature of their Ru–N bond [3], they could effectively deprotonate acidic organic compounds such as 1,3-dicarbonyl compounds to give the alkyl Ru complexes in a highly diastereoselective manner [3c]. In fact, we have found that the amido Ru complex, Ru[κ^2(*N*,*N*′)-(*R*,*R*)-TsNCHPhCHPhNH$_2$](mesitylene) (Ts = *p*-toluenesulfonyl), readily reacted with dimethyl malonate to give the isolable C-bound malonato complex, Ru[$CH(COOCH_3)_2$][κ^2(*N*,*N*′)-(*R*,*R*)-TsNCHPhCHPhNH$_2$](mesitylene). ^{1}H VTNMR experiments in CD_2Cl_2 revealed that the malonato Ru complex existed in a temperature-dependent equilibrium with the amido complex and free dimethyl malonate (Scheme 1) [2a], suggesting that the Ru–C moiety has sufficient basicity to intramolecularly deprotonate the acidic NH proton. On the basis of NMR spectroscopy and X-ray structural analysis of the malonato complex, we propose the possibility that the C-bound malonato complex is a catalytic intermediate for the Michael addition of malonates to cyclic enones. However, another possible reaction pathway through an O-bound enolato intermediate cannot be ruled out because the O-bound enolato complex can be isolated from the reaction of the amido Ru complex with β-keto esters acting as a Michael donor [2d]. These results prompted us to investigate the properties of alkyl Ru complexes bearing primary amine ligands to gain further insight into the mechanism of the enantioselective C–C bond formation with the chiral Ru catalysts **1**. However, detailed properties of the C-bound alkyl Ru complexes

* Corresponding author. Tel.: +81 3 5734 2636; fax: +81 3 5734 2637.
E-mail address: tikariya@apc.titech.ac.jp (T. Ikariya).

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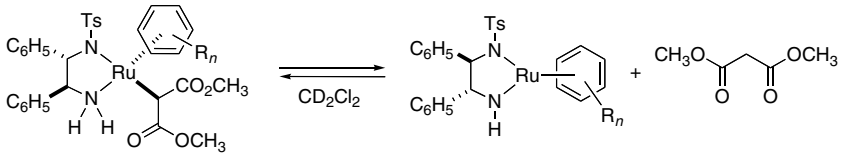


Scheme 1.

have not been clarified yet, mainly due to the difficulty in isolating stable alkyl Ru complexes bearing primary amine ligands [3c]. We now report the synthesis, structure, and properties of alkyl Ru complexes bearing primary amine ligands.

2. Results and discussion

2.1. Synthesis and structure of methyl Ru complexes

The reaction of 18-electron chloro Ru complex, RuCl-[κ^2(*N*,*N*′)-(*S*,*S*)-TsNCHPhCHPhNH$_2$](*p*-cymene) (**2a**), with $Zn(CH_3)_2$ as an alkylating agent in THF at 0 °C gave the corresponding methylruthenium complex, Ru(CH_3)[κ^2(*N*,*N*′)-(*S*,*S*)-TsNCHPhCHPhNH$_2$](*p*-cymene) (**3a**), as the sole product in reasonably high yield (Scheme 2). The choice of the alkylating agent is crucial in obtaining the alkyl Ru complex. When $LiCH_3$ was used in THF at −78 °C, facile elimination of HCl proceeds possibly by a D_{cb} mechanism [4] (deprotonation of the NH group followed by dechlorination) to give the amido Ru complex; the Li reagent serves as a strong base [1]. The less basic $Sn(CH_3)_4$ did not react with the chloro Ru complex in CH_2Cl_2 at room temperature. The transmetalation with the zinc reagent proceeded smoothly without damage of the NH protons to give the desired alkyl Ru complex. Similarly, analogous methyl Ru complexes (**3b**–**e**) and the methyl complex having a secondary amine ligand, Ru(CH_3)[κ^2(*N*,*N*′)-(*S*,*S*)-TsNCHPhCHPhNH(CH_3)](*p*-cymene) (**3f**), were obtainable from the reaction of the 18-electron chloro Ru complex (**2b**–**e**) with $Zn(CH_3)_2$ (Scheme 2).

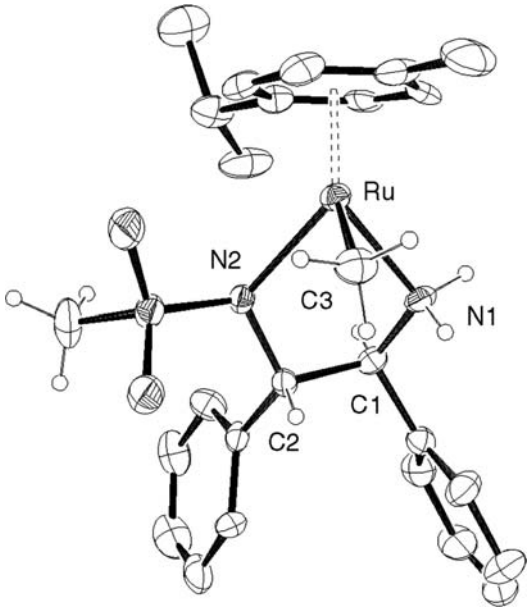
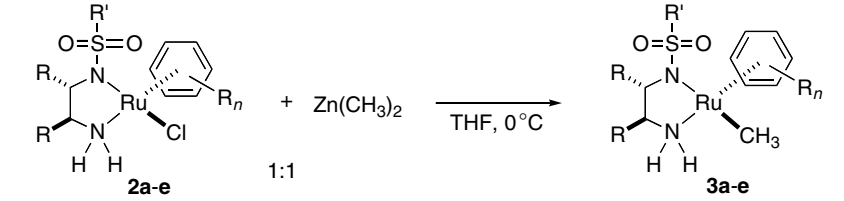


Fig. 1. Structural view of Ru(CH_3)[κ^2(*N*,*N*′)-(*S*,*S*)-MsNCHPh–CHPh-NH$_2$](*p*-cymene) (**3b**).

The ^{1}H NMR spectra of **3a** and **3b** in CD_2Cl_2 each display a singlet due to the methyl protons at 0.88 and 0.84 ppm and a set of two non-equivalent NH protons observed at 2.25 and 4.28, and 2.20 and 4.40 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectra, the peak of the methyl carbon attached to the metal center in complex **3a** and **3b** was observed at 2.84 and 1.91 ppm, respectively. An X-ray crystallographic analysis of the methyl complex,



18e chloro(amine) complex

18e methyl(amine) complex

η^6-arene = *p*-cymene
R = C_6H_5, R' = *p*-$CH_3C_6H_4$: **2a**
R = C_6H_5, R' = CH_3: **2b**
R = -$(CH_2)_2$-, R' = *p*-$CH_3C_6H_4$: **2c**

η^6-arene = 1,2,3,4,5,6-hexamethylbenzene (HMB)
R = C_6H_5, R' = *p*-$CH_3C_6H_4$: **2d**
R = C_6H_5, R' = CH_3: **2e**

Scheme 2.

$Ru(CH_3)[\kappa^2(N,N')$-(S,S)-$MsNCHPhCHPhNH_2](p$-cymene) (Ms = methanesulfonyl) (**3b**), as illustrated in Fig. 1, confirmed that it has a three-legged piano stool coordination environment with *p*-cymene, sulfonamido, amine, and methyl ligands [5]. The chirality of the (*S*,*S*)-diamine ligand determines the *R* configuration around the central metal, indicating that the transmetalation of the chloro Ru complex with the alkylzinc reagent proceeded with complete retention of the stereochemistry around the Ru metal center [6]. The retention of configuration around the Ru atom in the alkylation of a chloro Ru complex, CpRuCl(diphosphine), has been reported [7]; that reaction may have proceeded through bridged intermediates. Another isolable methyl complex, $Ru(CH_3)[\kappa^2(N,N')$-(S,S)-$TsN(C_6H_{10})$-$NH_2](p$-cymene) (**3c**), also has a structure similar to that of complex **3b**. Crystallographic data and selected bond distances and angles of isolable methyl Ru complexes **3b** and **3c** are given in Tables 1 and 2.

In a similar manner, the use of the ethylzinc reagent, $Zn(CH_3CH_2)_2$, gave the corresponding ethyl Ru complexes (**4a**,**b**,**e**), which have a structure similar to those of methyl complexes both in the solid state and in solution (Scheme 3). The ethyl Ru complex, $Ru(CH_2CH_3)[\kappa^2(N,N')$-$(S,S)$-$MsNCHPhCHPhNH_2](p$-cymene) (**4b**), has a three-legged piano stool coordination environment with the *R* configuration around the Ru center as shown in Fig. 2 [8]. The ^1H NMR spectrum of **4b** in CD_2Cl_2 shows the two independent CH_2 protons of the ethyl ligand at 1.07 and 2.41 ppm and the two non-equivalent NH protons at 2.2 and 4.2 ppm. The structure of the analogous ethyl Ru complex **4e** was determined by NMR spectroscopy and X-ray crystallography. Crystallographic data and selected bond

Table 1
Crystallographic data for complexes **3b**, **3c**, **4b**, **4e**, and **5d**

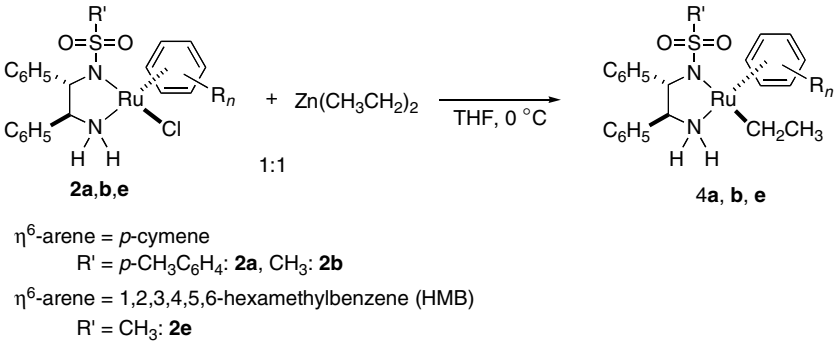
	3b	**3c** · CH_2Cl_2	**4b**	**4e** · CH_2Cl_2	**5d**
(A) Crystal data					
Experimental formula	$C_{26}H_{34}N_2O_2RuS$	$C_{25}H_{38}N_2O_2Cl_2RuS$	$C_{27}H_{36}N_2O_2RuS$	$C_{30}H_{42}N_2O_2Cl_2RuS$	$C_{36}H_{44}N_2O_4RuS$
Formula weight	539.70	602.62	553.72	666.71	701.88
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (#19)	$P2_1$ (#4)	$P2_12_12_1$ (#19)	$P2_1$ (#4)	$P2_1$ (#4)
Lattice parameter					
a (Å)	9.419(2)	14.389(4)	15.575(5)	13.756(5)	10.538(5)
b (Å)	12.402(2)	11.534(3)	17.804(5)	22.113(7)	12.872(6)
c (Å)	21.378(4)	16.830(4)	18.512(5)	15.515(5)	12.846(6)
α (°)					
β (°)		99.175(4)		93.997(5)	104.396(6)
γ (°)					
V (Å)^3	2497.2(8)	2757.4(12)	5133.2(26)	4707.9(27)	1687.8(14)
Z value	4	4	8	6	2
D_{Calc} (g cm^{-3})	1.435	1.452	1.433	1.411	1.381
μ (cm^{-1}) (Mo Kα)	7.36	8.62	7.18	7.65	5.67
(B) Data collections					
Diffractometer	Rigaku Saturn RigakuAFC10	Rigaku Saturn Rigaku AFC10	Rigaku Saturn Rigaku AFC10	Rigaku Saturn Rigaku AFC10	Rigaku Saturn Rigaku AFC10
Radiation	Mo Kα (λ = 0.71070 Å) Graphite monochromated	Mo Kα (λ = 0.71070 Å) Graphite monochromated	Mo Kα (λ = 0.71070 Å) Graphite monochromated	Mo Kα (λ = 0.71070 Å) Graphite monochromated	Mo Kα (λ = 0.71070 Å) Graphite monochromated
T (K)	193	123	193	193	193
Absorption corrections	Empirical	Empirical	Empirical	Empirical	Empirical
$2\theta_{max}$ (°)	55.1	55.0	55.0	55.2	55.0
No. of reflections measured	27,383	27,525	40,091	38,826	13,655
No. of unique reflections	27,315 (R_{int} = 0.127)	23,216 (R_{int} = 0.058)	40,032 (R_{int} = 0.182)	37,637 (R_{int} = 0.114)	3954 (R_{int} = 0.039)
(C) Refinement					
No. of observations ($I > 3.00\ \sigma(I)$)	14,303	11,052	11,349	13,588	2843
No. of variables	323	653	667	1106	411
Goodness-of-fit indicator	1.004	1.031	1.071	1.168	1.198
R_1 ($I > 3.00\ \sigma(I)$)[a]	0.065	0.061	0.069	0.068	0.051
wR_2 ($I > 3.00\ \sigma(I)$)[a]	0.176	0.140	0.129	0.158	0.120

[a] $R_1 = \sum \|F_o| - F_c\| / \sum |F_o|$, $wR_2 = \left[\sum(\omega(F_o^2 - F_c^2)^2) \Big/ \sum(\omega(F_o^2)^2)\right]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for complexes **3b**, **3c**, **4b**, **4e**, and **5d**

	3b	**3c**[a]	**4b**[a]	**4e**[a]	**5d**
$Ru–N_{amine}$	2.136(4)	2.132	2.107	2.132	2.134(8)
$Ru–N_{amido}$	2.164(4)	2.178	2.168	2.192	2.183(6)
Ru–C3	2.127(6)	2.12	2.13	2.12	2.188(9)
$N_{amine}–Ru–N_{amido}$	78.9(2)	78.6	78.6	76.1	77.0(3)
$N_{amine}–Ru–C3$	81.3(2)	82.9	83.9	82.8	84.4(3)
$N_{amido}–Ru–C3$	87.2(2)	86.5	85.0	88.0	87.9(3)
$Ru–N_{amine}–C1$	111.3(3)	110.7	108.0	107.9	112.3(5)
$Ru–N_{amido}–C2$	112.9(3)	111.6	113.0	114.3	113.8(5)
$Ru–N_{amido}–S$	119.2(2)	119.8	121.9	121.6	118.1(4)
$S–N_{amido}–C2$	113.8(3)	115.9	117.3	113.7	113.6(6)

[a] Mean value.



Scheme 3.

distances and angles of isolable ethyl Ru complexes **4b** and **4e** are given in Tables 1 and 2.

2.2. Synthesis and structures of functionalized alkyl Ru complexes

The use of two other functionalized alkylzinc reagents, $ZnBr(CH_2OCOCH_3)$ and $ZnBr(CH_2CN)$, gave the corresponding alkyl Ru complexes, the methoxycarbonylmethyl Ru complex (**5a**,**b**,**d**,**e**) and the cyanomethyl Ru complex (**6a**,**b**,**d**,**e**), respectively. NMR spectroscopic data as well as X-ray crystallographic data confirmed that these complexes have the C-bound structure in both the solid and the solution state as shown in Scheme 4.

An X-ray single-crystal structural analysis of the 18-electron methoxycarbonyl-methyl complex, $Ru(CH_2COOCH_3)[\kappa^2(N,N')$-$(S,S)$-$TsNCHPhCHPhNH_2](hmb)$ (HMB = hexamethylbenzene) (**5d**), shown in Fig. 3 [9], revealed that the (S,S)-diamine ligand establishes an R configuration around the central metal as observed in the methyl and ethyl Ru complexes. This transmetalation also retains the stereochemistry of the metal center. Crystallographic data and selected bond distances and angles are given in Tables 1 and 2. Notably, there is a short $H_2N\cdots O{=}C$ distance of 2.856(8) Å, which is ascribed to an intramolecular hydrogen bond [10], as observed in the C-bound malonato complex, $Ru[CH(COOCH_3)_2]$-$[\kappa^2(N,N')$-(R,R)-$TsNCHPhCHPhNH_2](mesitylene)$ [2a],

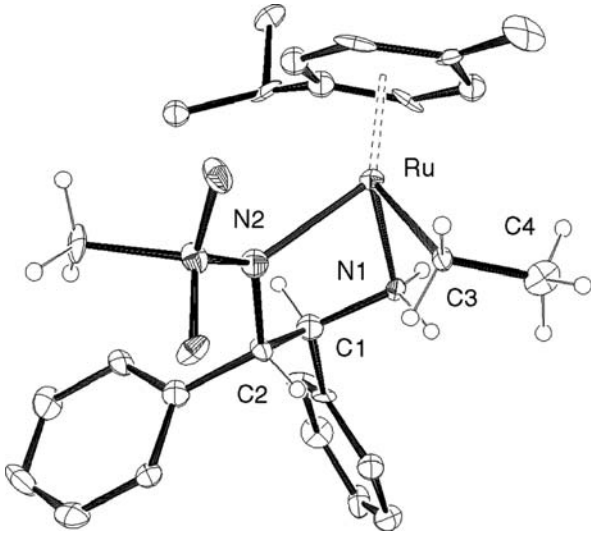
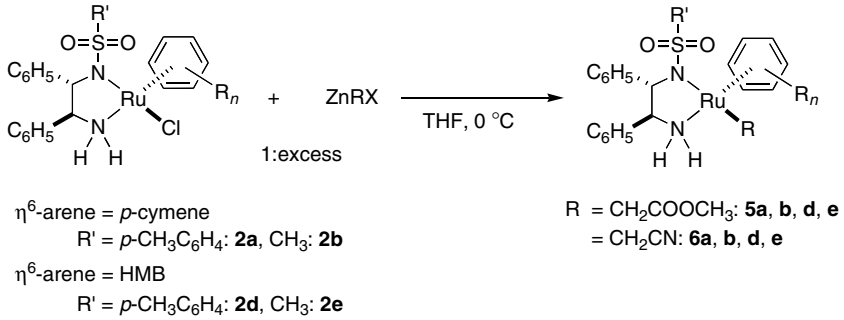


Fig. 2. Structural view of $Ru(CH_2CH_3)[\kappa^2(N,N')$-$(S,S)$-$MsNCHPh–CHPhNH_2](p$-cymene) (**4b**).

and the acetato Ru complex, $Ru(OCOCH_3)[\kappa^2(N,N')$-$(R,R)$-$TsNCHPhCHPhNH_2](p$-cymene) [10b]. The IR spectrum of complex **5d** showed a C=O stretching frequency at 1645 cm^{-1}, indicating that complex **5d** has a methoxycarbonylmethyl ligand with a carbonyl group hydrogen-bonded to the NH group in the diamine ligand.



Scheme 4.

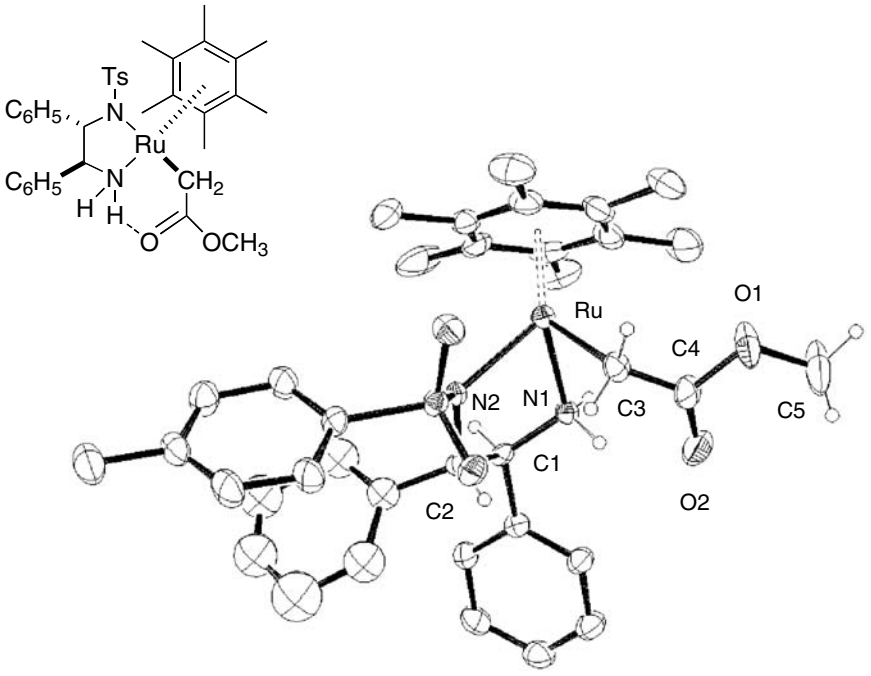


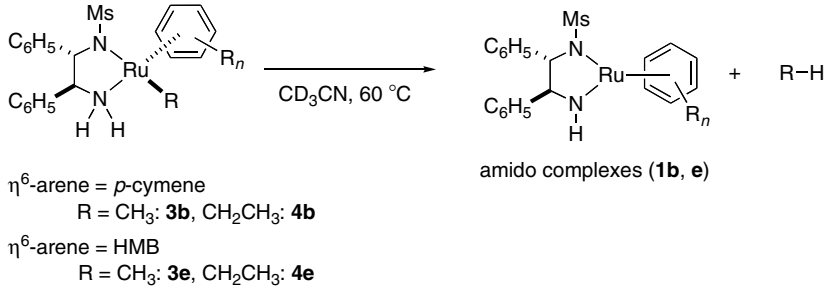
Fig. 3. Structural view of $Ru(CH_2COOCH_3)[\kappa^2(N,N')$-TsNCHPhCHPhNH$_2$](hmb) (**5d**).

In the ^{1}H NMR spectrum of complex **5d** in CD_2Cl_2, two doublet signals due to the diastereotopic methylene protons of the CH_2COOCH$_3$ group were observed at 2.46 and 2.93 ppm ($^2J_{HH} = 7$ Hz) and two signals due to the NH protons at 3.07 and 5.08 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the characteristic C=O carbon signal was observed at 184.3 ppm. These spectroscopic data for **5d** in solution are consistent with its solid structure.

The structure of the 18-electron cyanomethyl Ru complex, $Ru(CH_2CN)[\kappa^2(N,N')$-$(S,S)$-TsNCHPhCHPhNH$_2$]-(hmb) (**6d**), in the solid state was determined to be the C-bound Ru complex by preliminary single-crystal X-ray analysis [11]. In the IR spectrum of complex **6d**, the characteristic C≡N bond stretching frequency at 2175 cm^{-1} also supported the structure of the cyanomethyl Ru complex. The ^{1}H NMR spectrum of **6d** in CD_2Cl_2 displays two doublet signals due to the diastereotopic methylene protons of the CH_2CN group at 2.2 and 2.3 ppm and two signals due to the NH protons at 2.93 and 3.62 ppm. These NMR spectroscopic data for **6d** in solution are consistent with the solid state structure of the C-bound Ru complexes.

2.3. Reactivities of isolable alkyl Ru complexes

As shown in Scheme 1, the malonato Ru complex bearing a C-bound malonato ligand could have sufficient basicity to deprotonate the NH protons in the ligand to give the amido Ru complex with the formation of dimethyl malonate [2a]. The reaction proceeded even at low temperature (−30 °C). In contrast to the malonato complex, the methoxycarbonylmethyl complex **5d** was thermally stable at 60 °C. During the thermal treatment, neither deprotonation leading to the amido Ru complex nor isomerization



Scheme 5.

between the C-bound and O-bound Ru complex took place as observed in the related complexes [12] by NMR spectroscopy.

In a sharp contrast to the functionalized alkyl Ru complexes, when the simple alkyl complexes were thermally treated in solution, these complexes emitted alkanes to give the corresponding amido complexes as shown in Scheme 5 [13]. For example, the methyl Ru complex **3b**, at 60 °C in CD_3CN gradually converted to the amido complex, Ru[κ²(*N*,*N*′)-(*S*,*S*)-MsNCHPhCHPhNH](*p*-cymene) (**1b**), by releasing methane, indicating that the Ru–CH_3 moiety can deprotonate the acidic NH protons in the diamine ligand. Similarly, the alkyl complexes (**3e**,**4b**,**4e**) decomposed through deprotonation to give the amido complexes (**1b**,**e**) as shown in Fig. 4. The deprotonation was monitored by ^{1}H NMR spectroscopy at 60 °C in CD_3CN. First-order kinetics for the disappearance of the signals due to the alkyl complex were obtained at up to 50% conversion of the thermal decomposition of the methyl complex **3b** as shown in Fig. 5. The decomposition rate of the alkyl complexes increases in the order *p*-cymene < HMB as the arene ligand, and $CH_3 < C_2H_5$, as the alkyl group [14,15]. The methyl complex bearing a secondary amine ligand (**3f**) decomposed faster than complex **3a** [16]. The trend of the thermal stability of the alkyl Ru complexes indicates that the electronic and steric factors of the arene and alkyl ligands delicately affect the reactivity of the alkyl complexes as observed in reported transition metal alkyl complexes [14,15]. Noticeably, the thermal reaction of the ethyl Ru complexes (**4b**,**e**) in CD_3CN at 60 °C also proceeded smoothly to give the amido Ru complexes (**1b**,**e**) and ethane through intramolecular deprotonation. No formation of hydrido Ru complexes, RuH[κ²(*N*,*N*′)-(*S*,*S*)-MsNCHPhCHPhNH$_2$](η⁶-arene), and ethylene via β-hydride elimination of the ethyl complexes was observed because the complexes were coordinatively saturated as shown in Scheme 6. Activation parameters for the thermal decomposition of complex **4e**, determined from an Eyring plot of data measured between 45 and 70 °C, were $\Delta H^{\ddagger} = 93.9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -37.2$ J mol^{-1} K^{-1}.

Unfortunately, the isolable alkyl complexes **4e** and **5d** did not react with 2-cyclohexen-1-one in CD_3CN at 50 °C to give any C–C bond formation products, indicating that these alkyl complexes do not posses sufficient nucleophilicity.

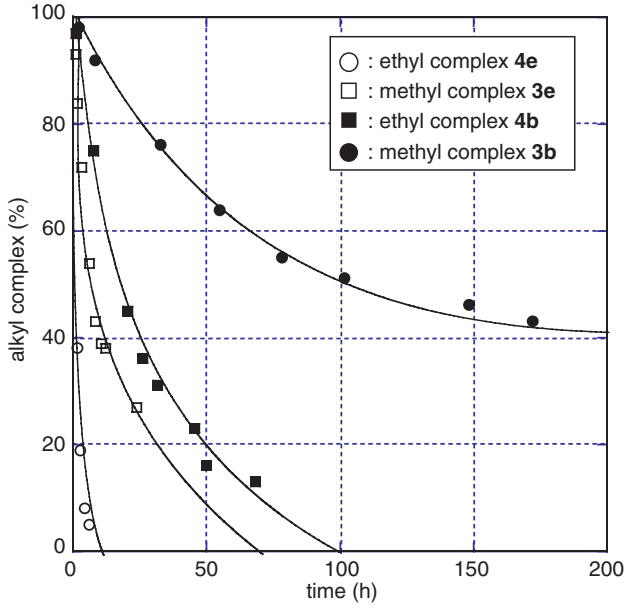


Fig. 4. Time course for the thermolysis of the alkyl complexes.

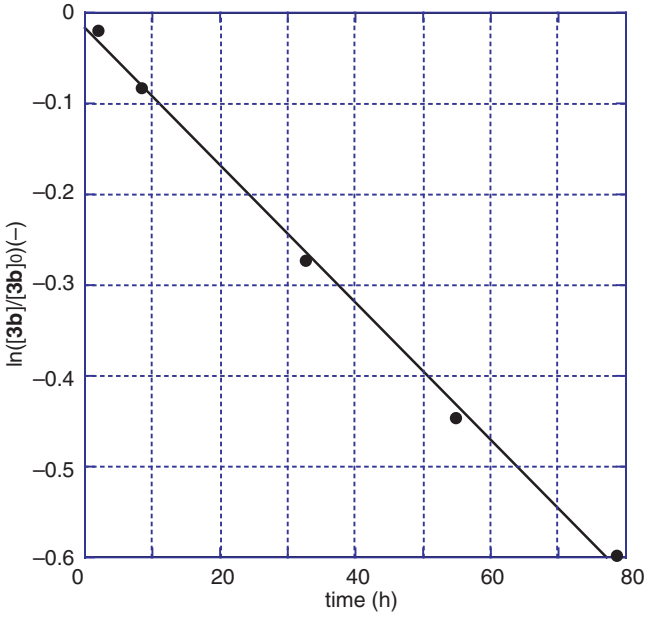
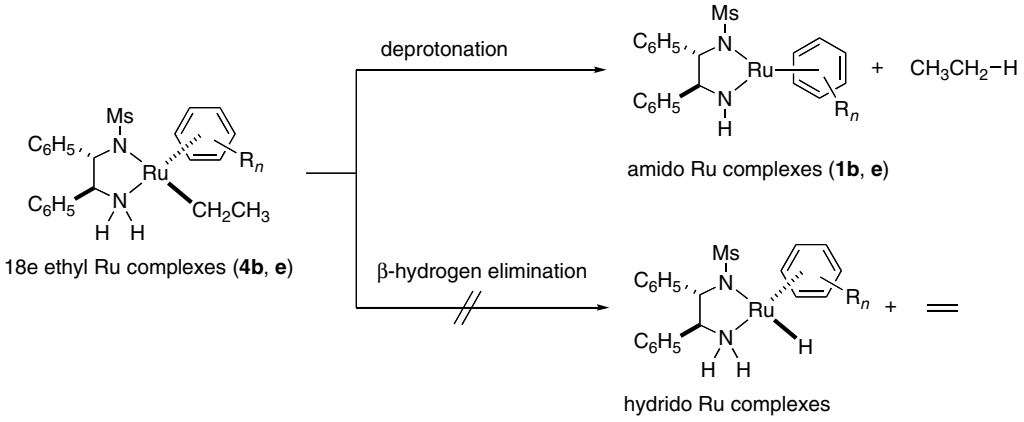


Fig. 5. Linear plot of the thermolysis of **3b**.



Scheme 6.

3. Conclusions

We have developed a general synthetic method for 18-electron alkyl(amine) Ru complexes from the 18-electron chloro(amine) Ru complexes with alkylzinc reagents. Although the functionalized alkyl complexes were thermally stable in solution, the isolable simple alkyl(amine) Ru complexes underwent intramolecular deprotonation of an NH proton in the diamine ligand by the M–C moiety to give the corresponding amido complexes and alkanes. Alkyl Ru complexes bearing a peralkylated arene ligand or an electron-donating alkyl ligand might have more basic metal bound alkyl groups; however, their nucleophilicity could not be sufficiently enhanced to attack the electrophiles. The present work indicates that the intramolecular acid/base interaction between the Ru–C moiety and NH protons, as well as the balance between the basicity and nucleophilicity of the metal bound alkyl groups, are crucially important factors in determining reactivity of the metal bound nucleophiles. Further investigation on the intermediary complexes related to catalytic C–C bond formation is in progress.

4. Experimental

All experiments were conducted under an argon atmosphere using Schlenk techniques. All deuterated NMR solvents were dehydrated and degassed. Amido Ru complexes (**1b**,**e**) and chloro Ru complexes (**2a**–**e**) were prepared according to reported procedures [1]. Alkylzinc reagents were prepared as described in the literature [17]. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300 Fourier transform spectrometer. X-ray single-crystal structural analysis studies were made on a Rigaku Saturn using graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). IR spectra were obtained on JASCO FT/IR-610. Elemental analysis was performed on a Perkin Elmer 2400II CHNS/O or LECO CHNS-932.

4.1. General procedure for synthesis of alkyl Ru complexes

To a THF solution (7 mL) of RuCl[κ^2(*N*,*N*′)-(*S*,*S*)-R′SO_2NCHPhCHPhNH_2](η^6-arene) (**2**) (1.00×10^{-1} g), the alkylzinc reagent, ZnR_2 (R = CH_3, C_2H_5), ZnBr(CH_2OCOCH_3), and ZnBr(CH_2CN) (1.1 equivalents-excess) was slowly added at 0 °C. The reaction solution was stirred at 0 °C for 5 h. Then the reaction mixture was filtered through an alumina column (including 7.0 wt% water). The solvent was removed under reduced pressure, leading to the corresponding alkyl(amine) complexes.

4.2. Ru(*CH*$_3$)[κ^2(*N*,*N*′)-(*S*,*S*)-*TsNCHPhCHPhNH*$_2$](*p*-cymene) (*3a*)

Recrystallization from CH_2Cl_2 and diethyl ether afforded the pale yellow crystals. Isolated yield, 72%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 0.88 (s, 3H; RuC*H*$_3$), 1.28 (d, $^{3}J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 1.36 (d, $^{3}J_{HH} = 7.1$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 2.21, 2.31 (each s, 3H; $CH_3C_6H_4CH(CH_3)_2$ or *p*-$CH_3C_6H_4SO_2N$), 2.25 (br., 1H; N*H*H), 3.00 (m, 1H; $CH_3C_6H_4CH(CH_3)_2$), 4.09, 4.10 (br. m, 2H; TsNC*H*PhC*H*PhNH_2), 4.28 (br., 1H; NH*H*), 4.73, 5.00, 5.11, 5.18 (each d, 1H; $CH_3C_6H_4CH(CH_3)_2$), 6.67–7.14 (14H; *p*-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). $^{13}C\{^{1}H\}$ NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 2.84 (Ru*C*H$_3$), 18.5, 21.1, 22.4, 23.6, 30.7 (*C*H$_3$-$C_6H_4CH(CH_3)_2$, *p*-$CH_3C_6H_4SO_2N$), 68.4, 74.2 (TsN*C*HPh*C*HPhNH_2), 78.9, 80.0, 81.3, 83.5, 98.9, 106.3 ($CH_3C_6H_4CH(CH_3)_2$), 126.3–144.5 (*p*-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). IR (KBr): *ν* ($cm^{-1}$): 3302, 3232, 3150 (H–N), 3060, 3029 (H–C_{arom}), 2959, 2923, 2867 (H–C_{aliph}). Anal. Calc. for $C_{32}H_{38}N_2O_2Ru_1S_1(CH_2Cl_2)_{0.5}$: C 59.30, H 5.97, N 4.26, S 4.87. Found: C 59.60, H 6.22, N 4.27, S 4.87%.

4.3. $Ru(CH_3)[\kappa^2(N,N')$-(S,S)-MsNCHPhCHPhNH$_2$](p-cymene) (**3b**)

Recrystallization from CH_2Cl_2 and hexane afforded the yellow crystals suitable for a single-crystal X-ray analysis. Isolated yield, 64%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 0.84 (s, 3H; RuCH_3), 1.18 (d, $^3J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 1.33 (d, $^3J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 1.89, 2.20 (each s, 3H; $CH_3C_6H_4CH(CH_3)_2$ or CH_3SO_2N), 2.2 (br., 1H; NHH), 2.85 (m, 1H; $CH_3C_6H_4CH(CH_3)_2$), 4.06 (d, $^3J_{HH} =$ 11.0 Hz, 1H; MsNCHPhCHPhNH$_2$), 4.32 (m, 1H; MsNCHPhCHPhNH$_2$), 4.4 (br., 1H; NHH), 4.62, 4.84, 5.29 (4H; $CH_3C_6H_4CH(CH_3)_2$), 6.97–7.18 (10H; MsNCH(C_6H_5)CH(C_6H_5)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 1.91 (RuCH_3), 18.7, 22.2, 23.9, 30.7, 44.1 ($CH_3C_6H_4CH(CH_3)_2$, CH_3SO_2N), 68.2, 74.1 (MsNCHPhCHPhNH$_2$), 77.8, 78.2, 84.7, 85.2, 99.8, 102.3 ($CH_3C_6H_4CH(CH_3)_2$), 127.4–142.0 (MsNCH(C_6H_5)CH(C_6H_5)NH$_2$). IR (KBr): ν (cm^{-1}): 3314, 3237, 3151 (H–N), 3063, 3027 (H–C$_{arom}$), 2961, 2934, 2859 (H–C$_{aliph}$). Anal. Calc. for $C_{26}H_{34}N_2O_2Ru_1S_1$: C 57.86, H 6.35, N 5.19, S 5.94. Found: C 57.63, H 6.35, N 5.13, S 6.04%.

4.4. $Ru(CH_3)[\kappa^2(N,N')$-(S,S)-TsN(C_6H_{10})NH$_2$]-(p-cymene) (**3c**)

Recrystallization from CH_2Cl_2 and diethyl ether afforded the brown crystals suitable for X-ray single-crystal structural analysis. Isolated yield, 31%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 0.58 (s, 3H; RuCH_3), 0.64–2.72 (11H; Ts(C_6H_{10})NHH), 1.23 (d, $^3J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 1.28 (d, $^3J_{HH} = 7.1$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 2.16, 2.36 (each s, 3H; $CH_3C_6H_4CH(CH_3)_2$ or p-$CH_3C_6H_4SO_2N$), 2.86 (m, 1H; $CH_3C_6H_4CH(CH_3)_2$), 4.05 (br., 1H; NHH), 4.55–4.96 (4H; $CH_3C_6H_4CH(CH_3)_2$), 7.17, 7.67 (each d, 2H; p-$CH_3C_6H_4SO_2N$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 2.84 (RuCH_3), 18.2, 21.3, 22.6, 23.7, 25.097, 25.142, 30.9, 33.9, 36.7, 62.4, 66.7 ($CH_3C_6H_4CH(CH_3)_2$, p-$CH_3C_6H_4SO_2N$(C_6H_{10})NH$_2$), 77.9, 80.8, 80.9, 82.5, 97.5, 107.3 ($CH_3C_6H_4CH(CH_3)_2$), 126.7, 128.8, 139.8, 147.0 (p-$CH_3C_6H_4SO_2N$). IR (KBr): ν (cm^{-1}): 3290, 3237, 3156 (H–N), 3060, 3023 (H–C$_{arom}$), 2955, 2925, 2858 (H–C$_{aliph}$). Anal. Calc. for $C_{24}H_{36}N_2O_2Ru_1S_1(CH_2Cl_2)_{0.5}$: C 52.53, H 6.66, N 5.00, S 5.73. Found: C 52.27, H 7.09, N 4.77, S 5.37%.

4.5. $Ru(CH_3)[\kappa^2(N,N')$-(S,S)-TsNCHPhCHPhNH$_2$](hmb) (**3d**)

Recrystallization from CH_2Cl_2 and diethyl ether afforded the yellow crystals. Isolated yield, 46%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 0.73 (s, 3H; RuCH_3), 1.28 (s, 18H; $C_6(CH_3)_6$), 2.09 (s, 3H; p-$CH_3C_6H_4SO_2N$), 2.36 (br. dd, 1H; NHH), 3.01 (br. d, $^3J_{HH} = 10.2$ Hz, 1H; NHH), 4.05 (m, 1H; TsNCHPhCHPhNH$_2$), 4.20 (d, $^3J_{HH} = 11.0$ Hz, 1H; TsNCHPhCHPhNH$_2$), 6.66–7.18 (14H; p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 7.00 (RuCH_3), 15.6, 21.1 ($C_6(CH_3)_6$, p-$CH_3C_6H_4SO_2N$), 68.9, 73.2 (TsNCHPhCHPhNH$_2$), 90.7 ($C_6(CH_3)_6$), 126.0–140.8 (p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). IR (KBr): ν (cm^{-1}): 3322, 3270, 3161 (H–N), 3085, 3062, 3030 (H–C$_{arom}$), 2920, 2868 (H–C$_{aliph}$). Anal. Calc. for $C_{34}H_{42}N_2O_2Ru_1S_1(H_2O)$: C 61.70, H 6.70, N 4.23, S 4.84. Found: C 62.01, H 6.36, N 4.24, S 4.84%.

4.6. $Ru(CH_3)[\kappa^2(N,N')$-(S,S)-MsNCHPhCHPhNH$_2$](hmb) (**3e**)

Recrystallization from toluene afforded the yellow crystals. Isolated yield, 66%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 0.57 (s, 3H; RuCH_3), 1.84 (s, 3H; CH_3SO_2N), 2.04 (s, 3H; $C_6(CH_3)_6$), 2.3 (br. dd, 1H; NHH), 3.06 (br. d, $^3J_{HH} = 9.5$ Hz, 1H; NHH), 4.2 (m, 2H; MsNCHPhCHPhNH$_2$), 7.02–7.21 (10H; MsNCH(C_6H_5)CH(C_6H_5)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 6.72 (RuCH_3), 15.5, 44.6 ($C_6(CH_3)_6$, CH_3SO_2N), 68.6, 72.3 (MsNCHPhCHPhNH$_2$), 90.6 ($C_6(CH_3)_6$), 127.3–142.3 (MsNCH(C_6H_5)CH(C_6H_5)NH$_2$). IR (KBr): ν (cm^{-1}): 3328, 3273, 3160 (H–N), 3061, 3027 (H–C$_{arom}$), 3000, 2925, 2861 (H–C$_{aliph}$). Anal. Calc. for $C_{28}H_{38}N_2O_2Ru_1S_1$: C 59.23, H 6.75, N 4.93, S 5.65. Found: C 58.83, H 6.65, N 4.63, S 5.46%.

4.7. $Ru(CH_3)[\kappa^2(N,N')$-(S,S)-TsNCHPhCHPhNH(CH_3)](p-cymene) (**3f**)

Recrystallization from diethyl ether and hexane afforded the brown crystals. Isolated yield, 20%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 0.98 (s, 3H; RuCH_3), 1.31 (d, $^3J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 1.42 (d, $^3J_{HH} = 7.1$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 2.20, 2.35 (each s, 3H; $CH_3C_6H_4CH(CH_3)_2$ or p-$CH_3C_6H_4SO_2N$), 2.35 (br. m, 1H; NH(CH_3)), 2.49 (d, $^3J_{HH} = 6.1$ Hz, 3H; NH(CH_3)), 3.14 (m, 1H; $CH_3C_6H_4CH(CH_3)_2$), 3.97 (dd, 1H; TsNCHPhCHPhNH(CH_3)), 4.20 (d, $^3J_{HH} = 11.0$ Hz, 1H; TsNCHPhCHPhNH(CH_3)), 4.62, 4.77, 5.23 (4H; $CH_3C_6H_4CH(CH_3)_2$), 6.63–7.14 (14H; p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH(CH_3)$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 2.81 (RuCH_3), 18.7, 21.1, 22.3, 23.4, 30.5 ($CH_3C_6H_4CH(CH_3)_2$, p-$CH_3C_6H_4SO_2N$), 43.7 (NH(CH_3)), 70.3, 79.1 (TsNCHPhCHPhNH(CH_3)), 79.5, 81.9, 82.1, 83.5, 99.3, 107.3 ($CH_3C_6H_4CH(CH_3)_2$), 126.2–144.5 (p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH(CH_3)$). IR (KBr): ν (cm^{-1}): 3266 (H–N), 3083, 3064, 3027, 3002 (H–C$_{arom}$), 2947, 2924, 2869 (H–C$_{aliph}$). Anal. Calc. for $C_{33}H_{40}N_2O_2Ru_1S_1$: C 62.93, H 6.40, N 4.45, S 5.09. Found: C 62.54, H 6.42, N 4.36, S 5.02%.

4.8. Ru(CH$_2$CH$_3$)[κ^2(N,N′)-(S,S)-TsNCHPhCHPhNH$_2$](p-cymene) (**4a**)

Recrystallization from THF and hexane afforded the pale yellow crystals. Isolated yield, 76%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.13 (m, 1H; RuC*H*HCH$_3$), 1.32 (d, $^3J_{HH} = 6.8$ Hz, 3H; CH$_3$C$_6$H$_4$CH(C*H*$_3$)(CH$_3$)), 1.39 (d, $^3J_{HH} = 7.1$ Hz, 3H; CH$_3$C$_6$H$_4$CH(CH$_3$)(C*H*$_3$)), 1.44 (dd, 3H; RuCH$_2$C*H*$_3$), 2.20, 2.35 (each s, 3H; C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$ or *p*-C*H*$_3$C$_6$H$_4$SO$_2$N), 2.28 (br., 1H; N*H*H), 2.66 (m, 1H; RuCH*H*CH$_3$), 2.95 (m, 1H; CH$_3$C$_6$H$_4$C*H*(CH$_3$)$_2$), 4.2 (br. m, 3H; TsNC*H*PhC*H*-PhNH*H*), 4.73, 4.83, 4.95, 5.30 (each d, 1H; CH$_3$C$_6$*H*$_4$CH(CH$_3$)$_2$), 6.65–7.17 (14H; *p*-CH$_3$C$_6$*H*$_4$SO$_2$-NCH(C$_6$*H*$_5$)CH(C$_6$*H*$_5$)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 17.9 18.0, 21.1, 22.7, 23.8, 31.0 (Ru*C*H$_2$*C*H$_3$, *C*H$_3$C$_6$H$_4$*C*H(*C*H$_3$)$_2$, *p*-*C*H$_3$C$_6$H$_4$SO$_2$N), 67.9, 74.4 (TsN*C*HPh*C*HPhNH$_2$), 76.6, 81.0, 81.5, 85.6, 96.2, 107.8 (CH$_3$*C*$_6$H$_4$CH(CH$_3$)$_2$), 126.3–144.7 (*p*-CH$_3$*C*$_6$H$_4$SO$_2$NCH(*C*$_6$H$_5$)CH(*C*$_6$H$_5$)NH$_2$). IR (KBr): ν (cm^{-1}): 3302, 3231, 3150 (H–N), 3061, 3029 (H–C$_{arom}$), 2959, 2920, 2868b (H–C$_{aliph}$). Anal. Calc. for $C_{33}H_{40}N_2O_2Ru_1S_1$: C 62.93, H 6.40, N 4.45, S 5.09. Found: C 62.65, H 6.51, N 4.41, S 5.00%.

4.9. Ru(CH$_2$CH$_3$)[κ^2(N,N′)-(S,S)-MsNCHPhCHPhNH$_2$](p-cymene) (**4b**)

Recrystallization from THF and hexane afforded the yellow crystals suitable for a single-crystal X-ray analysis. Isolated yield, 72%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.07 (m, 1H; RuC*H*HCH$_3$), 1.25 (d, $^3J_{HH} = 6.8$ Hz, 3H; CH$_3$C$_6$H$_4$CH(C*H*$_3$)(CH$_3$)), 1.30 (d, $^3J_{HH} = 7.1$ Hz, 3H; CH$_3$C$_6$H$_4$CH(CH$_3$)(C*H*$_3$)), 1.52 (dd, 3H; RuCH$_2$C*H*$_3$), 1.89, 2.20 (each s, 3H; C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$ or C*H*$_3$SO$_2$N), 2.2 (br., 1H; N*H*H), 2.41 (m, 1H; RuCH*H*CH$_3$), 2.80 (m, 1H; CH$_3$C$_6$H$_4$C*H*(CH$_3$)$_2$), 4.2 (br., 2H; MsNC*H*PhCH-PhNH*H*), 4.46 (m, 1H; MsNCHPhC*H*PhNH$_2$), 4.72, 5.1 (4H; CH$_3$C$_6$*H*$_4$CH(CH$_3$)$_2$), 7.00–7.21 (10H; MsNCH-(C$_6$*H*$_5$)CH(C$_6$*H*$_5$)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 17.1, 18.5, 20.9, 22.6, 24.0, 31.0, 44.0 (Ru*C*H$_2$*C*H$_3$, *C*H$_3$C$_6$H$_4$*C*H(*C*H$_3$)$_2$, *C*H$_3$SO$_2$N), 67.8, 74.6 (MsN*C*HPh*C*HPhNH$_2$), 79.4, 82.0, 82.1, 83.4, 98.0, 102.5 (CH$_3$*C*$_6$H$_4$CH(CH$_3$)$_2$), 127.3–142.2 (MsNCH(*C*$_6$H$_5$)-CH(*C*$_6$H$_5$)NH$_2$). IR (KBr): ν (cm^{-1}): 3296, 3221, 3145 (H–N), 3060, 3029 (H–C$_{arom}$), 2993, 2959, 2922, 2836 (H–C$_{aliph}$). Anal. Calc. for $C_{27}H_{36}N_2O_2Ru_1S_1$: C 58.57, H 6.55, N 5.06, S 5.79. Found: C 58.27, H 6.56, N 5.00, S 5.92%.

4.10. Ru(CH$_2$CH$_3$)[κ^2(N,N′)-(S,S)-MsNCHPhCHPhNH$_2$](hmb) (**4e**)

Recrystallization from toluene and hexane afforded the yellow crystals suitable for a single-crystal X-ray analysis. Isolated yield, 64%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.08 (dd, 3H; RuCH$_2$C*H*$_3$), 1.39 (m, 1H; RuC*H*HCH$_3$), 1.81 (s, 3H; C*H*$_3$SO$_2$N), 2.05 (s, 18H; C$_6$(C*H*$_3$)$_6$), 2.38 (m, 1H; RuCH*H*CH$_3$), 2.48 (br. dd, 1H; N*H*H), 3.22 (br. d, $^3J_{HH} = 10.0$ Hz, 1H; NH*H*), 4.24 (br. m, 2H; MsNC*H*PhC*H*PhNH$_2$), 7.06–7.22 (10H; MsNCH-(C$_6$*H*$_5$)CH(C$_6$*H*$_5$)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 15.5, 15.6, 16.9, 44.7 (Ru*C*H$_2$*C*H$_3$, C$_6$(*C*H$_3$)$_6$, *C*H$_3$SO$_2$N), 68.5, 72.6 (MsN*C*HPh*C*HPhNH$_2$), 90.8 (*C*$_6$(CH$_3$)$_6$), 127.3–142.1 (MsNCH(*C*$_6$H$_5$)CH(*C*$_6$H$_5$)-NH$_2$). IR (KBr): ν (cm^{-1}): 3304, 3239, 3157 (H–N), 3085, 3060, 3028, 3006 (H–C$_{arom}$), 2950, 2910, 2871, 2842 (H–C$_{aliph}$). Anal. Calc. for $C_{29}H_{40}N_2O_2Ru_1S_1$: C 59.87, H 6.93, N 4.82, S 5.51. Found: C 59.55, H 7.01, N 4.65, S 5.32%.

4.11. Ru(CH$_2$COOCH$_3$)[κ^2(N,N′)-(S,S)-TsNCHPhCHPhNH$_2$](p-cymene) (**5a**)

Recrystallization from THF and hexane afforded the yellow crystals. Isolated yield, 58%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.33 (d, $^3J_{HH} = 6.8$ Hz, 3H; CH$_3$-C$_6$H$_4$CH(C*H*$_3$)(CH$_3$)), 1.46 (d, $^3J_{HH} = 6.8$ Hz, 3H; CH$_3$-C$_6$H$_4$CH(CH$_3$)(C*H*$_3$)), 1.80 (d, $^2J_{HH} = 7.3$ Hz, 1H; RuC*H*-HCOOCH$_3$), 2.23, 2.40 (each s, 3H; C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$ or *p*-C*H*$_3$C$_6$H$_4$SO$_2$N), 2.92 (m, 1H; CH$_3$C$_6$H$_4$C*H*(CH$_3$)$_2$), 3.17 (d, $^2J_{HH} = 7.3$ Hz, 1H; RuCH*H*COOCH$_3$), 3.56 (s, 3H; CH$_2$COOC*H*$_3$), 4.01 (br. m, 3H; TsNC*H*PhC*H*PhN*H*H), 4.93 (br. dd, 1H; NH*H*), 4.77, 5.01, 5.24, 5.50 (each d, 1H; CH$_3$C$_6$*H*$_4$CH(CH$_3$)$_2$), 6.65–7.15 (14H; *p*-CH$_3$C$_6$*H*$_4$SO$_2$-NCH(C$_6$*H*$_5$)CH(C$_6$*H*$_5$)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 14.8 (Ru*C*H$_2$COOCH$_3$), 18.2, 21.2, 22.4, 24.0, 30.8 (*C*H$_3$C$_6$H$_4$*C*H(*C*H$_3$)$_2$, *p*-*C*H$_3$C$_6$H$_4$SO$_2$N), 50.6 (CH$_2$COO*C*H$_3$), 68.7, 73.7 (TsN*C*HPh*C*HPhNH$_2$), 77.4, 82.8, 83.3, 85.8, 97.7, 107.1 (CH$_3$*C*$_6$H$_4$CH(CH$_3$)$_2$), 126.4–144.3 (*p*-CH$_3$*C*$_6$H$_4$SO$_2$NCH(*C*$_6$H$_5$)CH(*C*$_6$H$_5$)NH$_2$), 184.5 (CH$_2$*C*OOCH$_3$). IR (KBr): ν (cm^{-1}): 3249, 3150 (H–N), 3085, 3061, 3029 (H–C$_{arom}$), 2958, 2925, 2870 (H–C$_{aliph}$), 1649 (C=O). Anal. Calc. for $C_{34}H_{40}N_2O_4Ru_1S_1$(THF): C 61.19, H 6.49, N 3.76, S 4.30. Found: C 61.22, H 6.86, N 4.00, S 4.34%.

4.12. Ru(CH$_2$COOCH$_3$)[κ^2(N,N′)-(S,S)-MsNCHPhCHPhNH$_2$](p-cymene) (**5b**)

Recrystallization from CH_2Cl_2 and hexane afforded the yellow crystals. Isolated yield, 52%. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.279 (d, $^3J_{HH} = 6.8$ Hz, 3H; CH$_3$C$_6$H$_4$CH(C*H*$_3$)(CH$_3$)), 1.283 (d, $^3J_{HH} = 6.8$ Hz, 3H; CH$_3$C$_6$H$_4$CH(CH$_3$)(C*H*$_3$)), 1.76 (d, $^2J_{HH} = 7.3$ Hz, 1H; RuC*H*HCOOCH$_3$), 1.92, 2.25 (each s, 3H; C*H*$_3$C$_6$H$_4$CH-(CH$_3$)$_2$ or C*H*$_3$SO$_2$N), 2.85 (m, 1H; CH$_3$C$_6$H$_4$C*H*(CH$_3$)$_2$), 3.27 (d, $^2J_{HH} = 7.6$ Hz, 1H; RuCH*H*COOCH$_3$), 3.53 (s, 3H; CH$_2$COOC*H*$_3$), 4.1 (br. m, 3H; MsNC*H*Ph-C*H*PhN*H*H), 4.87 (br. dd, 1H; NH*H*), 4.95, 5.14, 5.26 (4H; CH$_3$C$_6$*H*$_4$CH(CH$_3$)$_2$), 7.02–7.19 (10H; MsNCH-(C$_6$*H*$_5$)CH(C$_6$*H*$_5$)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 13.1 (Ru*C*H$_2$COOCH$_3$), 18.6, 22.3, 24.4, 30.6, 44.3 (*C*H$_3$C$_6$H$_4$*C*H(*C*H$_3$)$_2$, *C*H$_3$SO$_2$N), 50.6 (CH$_2$COO-*C*H$_3$), 68.6, 74.0 (MsN*C*HPh*C*HPhNH$_2$), 81.4, 81.7, 83.36,

83.41, 99.3, 103.6 ($CH_3C_6H_4CH(CH_3)_2$), 127.4–141.6 ($MsNCH(C_6H_5)CH(C_6H_5)NH_2$), 184.3 ($CH_2COOCH_3$). IR (KBr): ν (cm^{-1}): 3293, 3225, 3142 (H–N), 3086, 3063, 3030 (H–C_{arom}), 2960, 2872 (H–C_{aliph}), 1650 (C=O). Anal. Calc. for $C_{28}H_{36}N_2O_4Ru_1S_1$: C 56.26, H 6.07, N 4.69, S 5.36. Found: C 56.49, H 6.01, N 4.64, S 5.44%.

4.13. $Ru(CH_2COOCH_3)[\kappa^2(N,N')$-(S,S)-$TsNCHPhCHPhNH_2](hmb)$ (**5d**)

Recrystallization from THF and hexane afforded the yellow crystals suitable for X-ray single-crystal structural analysis. Isolated yield, 36%. ^1H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 2.14 (s, 21H; $C_6(CH_3)_6$, p-$CH_3C_6H_4SO_2N$), 2.46, 2.93 (each d, $^2J_{HH} = 7.6$ Hz, $^2J_{HH} = 7.3$ Hz, 1H; RuC*HH*COOCH$_3$), 3.07 (br. d, 1H; N*H*H), 3.52 (s, 3H; RuCH$_2$COOC*H*$_3$), 3.79 (m, 1H; TsNCHPhC*H*PhNH$_2$), 4.05 (d, $^3J_{HH} = 11.2$ Hz, 1H; TsNC*H*PhCHPhNH$_2$), 5.08 (br., 1H; NH*H*), 6.63–7.17 (14H; p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 13.0 (Ru*C*H$_2$COOCH$_3$), 15.8 ($C_6(CH_3)_6$), 21.1 (p-$CH_3C_6H_4SO_2N$), 50.3 (CH_2COOCH_3), 69.3, 73.0 (TsN*C*HPh*C*HPhNH$_2$), 91.9 ($C_6(CH_3)_6$), 126.2–143.7 (p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$), 184.3 ($CH_2COOCH_3$). IR (KBr): ν (cm^{-1}): 3259, 3203, 3150 (H–N), 3062, 3027 (H–C_{arom}), 2970, 2937, 2921, 2828 (H–C_{aliph}), 1645 (C=O). Anal. Calc. for $C_{36}H_{44}N_2O_4Ru_1S_1(H_2O)_2$: C 59.32, H 6.50, N 3.84. Found: C 59.16, H 6.36, N 3.81%.

4.14. $Ru(CH_2COOCH_3)[\kappa^2(N,N')$-(S,S)-$MsNCHPhCHPhNH_2](hmb)$ (**5e**)

Recrystallization from CH_2Cl_2, toluene, and hexane afforded the yellow crystals. Isolated yield, 81%. ^1H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.57 (s, 3H; C*H*$_3$SO$_2$N), 2.02 (d, $^2J_{HH} = 7.6$ Hz, 1H; RuC*H*HCOOCH$_3$), 2.08 (s, 18H; $C_6(CH_3)_6$), 2.84 (d, $^2J_{HH} = 7.3$ Hz, 1H; RuCH*H*COOCH$_3$), 3.10 (br. d, 1H; N*H*H), 3.50 (s, 3H; RuCH$_2$COOC*H*$_3$), 3.89 (m, 1H; MsNCHPhC*H*PhNH$_2$), 4.05 (d, $^3J_{HH} = 11.5$ Hz, 1H; MsNC*H*PhCHPhNH$_2$), 5.18 (br. dd, 1H; NH*H*), 7.07–7.22 (10H; $MsNCH(C_6H_5)CH(C_6H_5)NH_2$). $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): 13.6 (Ru*C*H$_2$COOCH$_3$), 15.7 ($C_6(CH_3)_6$), 45.0 (*C*H$_3$SO$_2$N), 50.3 (CH_2COOCH_3), 69.0, 72.1 (MsN*C*HPh*C*HPhNH$_2$), 91.8 ($C_6(CH_3)_6$), 125.6–141.6 ($MsNCH(C_6H_5)CH(C_6H_5)NH_2$), 184.2 ($CH_2COOCH_3$). IR (KBr): ν (cm^{-1}): 3262 (H–N), 3060, 3029 (H–C_{arom}), 2928 (H–C_{aliph}), 1638 (C=O). Anal. Calc. for $C_{30}H_{40}N_2O_4Ru_1S_1(CH_2Cl_2)_{0.25}$: C 56.15, H 6.31, N 4.33, S 4.96. Found: C 56.45, H 6.71, N 4.15, S 4.70%.

4.15. $Ru(CH_2CN)[\kappa^2(N,N')$-(S,S)-$TsNCHPhCHPhNH_2](p\text{-}cymene)$ (**6a**)

Recrystallization from CH_2Cl_2 and hexane afforded the orange crystals. Isolated yield, 38%. ^1H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.33 (d, $^3J_{HH} = 7.1$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 1.34 (d, $^3J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 2.02 (d, $^2J_{HH} = 14.7$ Hz, 1H; RuC*H*HCN), 2.19, 2.35 (each s, 3H; $CH_3C_6H_4CH(CH_3)_2$ or p-$CH_3C_6H_4SO_2N$), 2.78 (d, $^2J_{HH} = 14.9$ Hz, 1H; RuCH*H*CN), 2.97 (m, 1H; $CH_3C_6H_4CH(CH_3)_2$), 3.07 (br. m, 1H; N*H*H), 4.02 (br. m, 2H; TsNC*H*PhC*H*PhNH$_2$), 4.95 (br. d, 1H; NH*H*), 5.07–5.31 (4H; $CH_3C_6H_4CH(CH_3)_2$), 6.56–7.13 (14H; p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): −11.8 (Ru*C*H$_2$CN), 18.5, 21.1, 22.4, 23.5, 30.7 ($CH_3C_6H_4CH(CH_3)_2$, p-$CH_3C_6H_4SO_2N$), 68.7, 74.7 (TsN*C*HPh*C*HPhNH$_2$), 81.7, 81.9, 83.0, 83.9, 99.4, 106.6 ($CH_3C_6H_4CH(CH_3)_2$), 126.5–143.5 (p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$, CH_2CN). IR (KBr): ν (cm^{-1}): 3269, 3229, 3144 (H–N), 3085, 3061, 3030 (H–C_{arom}), 2963, 2922, 2870 (H–C_{aliph}), 2171 (C≡N). Anal. Calc. for $C_{33}H_{37}N_3O_2Ru_1S_1(CH_2Cl_2)$: C 56.27, H 5.42, N 5.79. Found: C 56.12, H 5.60, N 5.83%.

4.16. $Ru(CH_2CN)[\kappa^2(N,N')$-(S,S)-$MsNCHPhCHPhNH_2](p\text{-}cymene)$ (**6b**)

Recrystallization from THF and hexane afforded the pale yellow crystals. Isolated yield, 44%. They do not confirm elemental analysis because of their hygroscopicity. ^1H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.25 (d, $^3J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 1.33 (d, $^3J_{HH} = 6.8$ Hz, 3H; $CH_3C_6H_4CH(CH_3)(CH_3)$), 2.05 (d, $^2J_{HH} = 14.9$ Hz, 1H; RuC*H*HCN), 1.94, 2.28 (each s, 3H; $CH_3C_6H_4CH(CH_3)_2$ or CH_3SO_2N), 2.81 (d, $^2J_{HH} = 14.9$ Hz, 1H; RuCH*H*CN), 2.87 (m, 1H; $CH_3C_6H_4CH(CH_3)_2$), 3.15 (br. dd, 1H; N*H*H), 4.06 (d, $^3J_{HH} = 11.2$ Hz, 1H; MsNC*H*PhCHPhNH$_2$), 4.27 (m, 1H; MsNCHPhC*H*PhNH$_2$), 4.92 (br. d, $^2J_{HH} = 9.3$ Hz, 1H; NH*H*), 5.01, 5.14, 5.34 (4H; $CH_3C_6H_4CH(CH_3)_2$), 7.10–7.19 (10H; $MsNCH(C_6H_5)CH(C_6H_5)NH_2$). $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): −12.8 (Ru*C*H$_2$CN), 18.8, 22.2, 24.0, 30.8, 44.3 ($CH_3C_6H_4CH(CH_3)_2$, CH_3SO_2N), 68.3, 74.8 (MsN*C*HPh*C*HPhNH$_2$), 80.7, 81.6, 84.3, 85.0, 101.3, 103.1 ($CH_3C_6H_4CH(CH_3)_2$), 127.7–141.1 ($MsNCH(C_6H_5)CH(C_6H_5)NH_2$, CH_2CN). IR (KBr): ν (cm^{-1}): 3278, 3222, 3143 (H–N), 3068, 3030 (H–C_{arom}), 2962, 2930, 2868 (H–C_{aliph}), 2178 (C≡N).

4.17. $Ru(CH_2CN)[\kappa^2(N,N')$-(S,S)-$TsNCHPhCHPhNH_2](hmb)$ (**6d**)

Recrystallization from THF and hexane afforded the yellow crystals suitable for X-ray single-crystal structural analysis. Isolated yield, 43%. ^1H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 2.15 (s, 3H; p-C*H*$_3$C$_6$H$_4$SO$_2$N), 2.17 (s, 18H; $C_6(CH_3)_6$), 2.2, 2.3 (each d, 1H; RuC*HH*CN), 2.93 (br. dd, 1H; N*H*H), 3.62 (br. d, 1H; NH*H*), 3.92 (m, 1H; TsNCHPhC*H*PhNH$_2$), 4.16 (d, $^3J_{HH} = 11.0$ Hz, 1H; TsNC*H*PhCHPhNH$_2$), 6.64–7.19 (14H; p-$CH_3C_6H_4SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). $^{13}C\{^1H\}$ NMR (75.6 MHz,

CD_2Cl_2, rt, δ/ppm): −9.68 (Ru*C*H_2CN), 15.6 ($C_6(CH_3)_6$), 21.1 (*p*-$CH_3C_6H_4SO_2N$), 69.0, 73.5 (TsN*C*HPh*C*HPh-NH_2), 92.3 ($C_6(CH_3)_6$), 126.3–143.0 (*p*-$CH_3C_6H_4SO_2N$-$CH(C_6H_5)CH(C_6H_5)NH_2$, CH_2CN). IR (KBr): ν (cm^{-1}): 3276, 3231, 3141 (H–N), 3061, 3029 (H–C_{arom}), 3005, 2973, 2924, 2871 (H–C_{aliph}), 2175 (C≡N). Anal. Calc. for $C_{35}H_{41}N_3O_2Ru_1S_1(H_2O)$: C 61.20, H 6.31, N 6.12. Found: C 61.48, H 6.53, N 5.79%.

4.18. Ru(CH$_2$CN)[κ^2(N,N′)-(S,S)-MsNCHPhCHPhNH$_2$](hmb) (6e)

Recrystallization from toluene and hexane afforded the yellow crystals. Isolated yield, 45%. They do not confirm elemental analysis because of their hygroscopicity. ^{1}H NMR (300.4 MHz, CD_2Cl_2, rt, δ/ppm): 1.76 (d, $^2J_{HH} = 14.9$ Hz, 1H; RuC*H*HCN), 1.89 (s, 3H; CH_3SO$_2$N), 2.11 (s, 18H; $C_6(CH_3)_6$), 2.19 (d, $^2J_{HH} = 14.9$ Hz, 1H; RuCH*H*CN), 2.81 (br. dd, 1H; N*H*H), 3.65 (br. d, 1H; NH*H*), 4.05 (m, 1H; MsNCHPhC*H*PhNH$_2$), 4.19 (d, $^3J_{HH} = 11.5$ Hz, 1H; MsNC*H*PhCHPhNH$_2$), 7.09–7.22 (10H; MsNCH(C_6H_5)CH(C_6H_5)NH$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2, rt, δ/ppm): −9.48 (Ru*C*H$_2$CN), 15.5 ($C_6(CH_3)_6$), 44.8 (CH_3SO_2N), 69.7, 72.6 (MsN*C*HPh*C*H-PhNH$_2$), 92.1 ($C_6(CH_3)_6$), 127.4–141.2 (MsNCH(C_6H_5)-CH(C_6H_5)NH$_2$, CH_2CN). IR (KBr): ν (cm^{-1}): 3239, 3158 (H–N), 3060, 3028 (H–C_{arom}), 2962, 2927 (H–C_{aliph}), 2182 (C≡N).

4.19. Experimental procedure for thermolysis of alkyl(amine) complexes

To an CD_3CN solution of the alkyl(amine) complex (2.6×10^{-2} M), dihexylether as internal standard was added to the NMR tube. The tube was sealed and the signals of the disappearing alkyl complex were traced by ^{1}H NMR spectroscopy. The resulting reaction profile is shown in Fig. 4.

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Appendix A. Supplementary data

Spectral data of amido Ru complexes **1b** and **1e**, X-ray crystallographic data of **3b**, **3c**, **4b**, **4e**, **5d**, and **6d**, the ^{1}H NMR spectra of thermolysis, and kinetic data of **4e**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.047.

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[6] X-ray crystallographic analysis of the chloro(amine) Ru complexes (**2a**–**e**) confirmed that they have a three-legged piano stool coordination environment with arene, chloro, sulfonamido, and amine ligands. The chirality of the (*S*,*S*)-diamine ligands determines the *R* configuration around the central metal [1].
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[8] An X-ray crystallographic analysis of **4b** was performed. In Fig. 2, there are omissions of the other molecule of the same structure. Crystallographic data and structure refinement parameters of complex **4b** is shown in Table 1. All hydrogen atoms were calculated from ideal geometries. See Supporting information.
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