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Chelating η^6-Arene-η^1-carbene Ligands in Ruthenium Complexes

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N-Heterocyclic carbene (NHC) ruthenium complexes containing a chelating NHC-η^6-arene ligand have been prepared and evaluated as precursors for ring opening metathesis polymerization (ROMP). The reaction of $[RuCl_2(p\text{-cymene})]_2$ with electron-rich olefins of the bis(imidazolinylidene) type containing at least one arylmethyl-*N* chain (aryl: 2,4,6-trimethylphenyl, 3,4,5-trimethoxyphenyl) selectively leads, upon heating, to ruthenium(II) complexes **2** containing a chelating bridged carbene η^6-arene ligand. The reaction of complexes containing an additional $ROCH_2CH_2N$ group with AgOTf leads to ionic complexes **5** with a tridentate trifunctional carbene/arene/ether ligand. The X-ray structure of $[RuCl_2\{\eta^1\text{-}CN(CH_2\{\eta^6\text{-}C_6H_2Me_3\text{-}2,4,6\})CH_2CH_2N(CH_2\{C_6H_2(OMe)_3\text{-}3,4,5\})\}]$ (**2c**) and that of the ionic ruthenium complex containing a trifunctional carbene/arene/ether ligand that provides ten electrons, $[RuCl\{\eta^1\text{-}CN(CH_2\{\eta^6\text{-}C_6H_2Me_3\text{-}2,4,6\})CH_2CH_2N(CH_2CH_2OCH_3)\}][CF_3SO_3]$ (**5e**), have been determined. The precursors **2** in the presence of AgOTf and propargyl alcohol, in order to produce an allenylidene initiator, and complexes **5** in the presence of propargyl alcohol lead to ROMP of norbornene. It is shown that initial chloride abstraction is required and that the catalyst activity is increased by using mesityl–ruthenium precursors and coordinated branched ether complexes.

Introduction

Electron-releasing heterocyclic carbenes have been identified in the early days of their coordination chemistry as phosphane ligand equivalents.[1] Recently, sterically hindered N-heterocyclic carbenes (NHCs) of the 1,3-imidazolylidene and 1,3-imidazolinylidene type have been used to stabilize novel organometallic structures[2] and to generate new catalyst precursors especially in the field of C–C bond formation[3–5] and in alkene metathesis.[6] Their success in catalysis is largely due to their ability to increase the electron density at the metal site and to protect coordinatively unsaturated active metal species by their high steric hindering effect.

It is expected that when the NHC orientation is perturbed in space, the catalytic activity of the linked metal site should be largely modified. This influence has lead to the design of new chelating NHCs. Examples of bis(NHC)s,[7] mixed pyridine-carbene[8] and oxazoline-carbene[9] complexes have already been reported. We have recently shown the route to metal complexes containing mixed arene and carbene ligands providing eight electrons to the metal, and have demonstrated that the natural orientation of the carbene in these complexes is significantly modified.[10]

We now present new eight-electron bridged (η^6-arene-η^1-carbene)ruthenium complexes from related electron-rich bis(1,3-imidazolin-2-ylidene) olefins containing at least one arylmethylene group linked to a nitrogen atom. We also show that the resulting (η^6-arene-η^1-carbene)$RuCl_2$ complexes can be used to generate intermediates of the type [(η^6-arene-η^1-carbene)RuCl]OTf and that these are catalyst precursors, associated to propargyl alcohol, for the polymerization of cyclic olefins by the ring opening metathesis polymerization (ROMP) process. The X-ray structure of the neutral complex $[RuCl_2\{\eta^1\text{-}CN(CH_2\{\eta^6\text{-}C_6H_2Me_3\text{-}2,4,6\})CH_2CH_2N(CH_2\{C_6H_2(OMe)_3\text{-}3,4,5\})\}]$ and those of two ionic ruthenium complexes containing di- or tridentate NHC ligands are also reported.

Results and Discussion

The electron-rich olefins that contain one (**1a**–**1b**) or two (**1c**–**1d**) arylmethylene group(s) attached to a nitrogen atom[11] were treated with the ruthenium source $[RuCl_2(p\text{-cymene})]_2$[12] in toluene at 100 °C for 4 h in order to bring about complete conversion of $[RuCl_2(p\text{-cymene})]_2$ and substitution of the *p*-cymene ligand. The ruthenium complexes containing the bridged carbene-arene ligand were isolated as brown solids: **2a** (90%), **2b** (93%), **2c** (89%), **2d** (82%) (Scheme 1).

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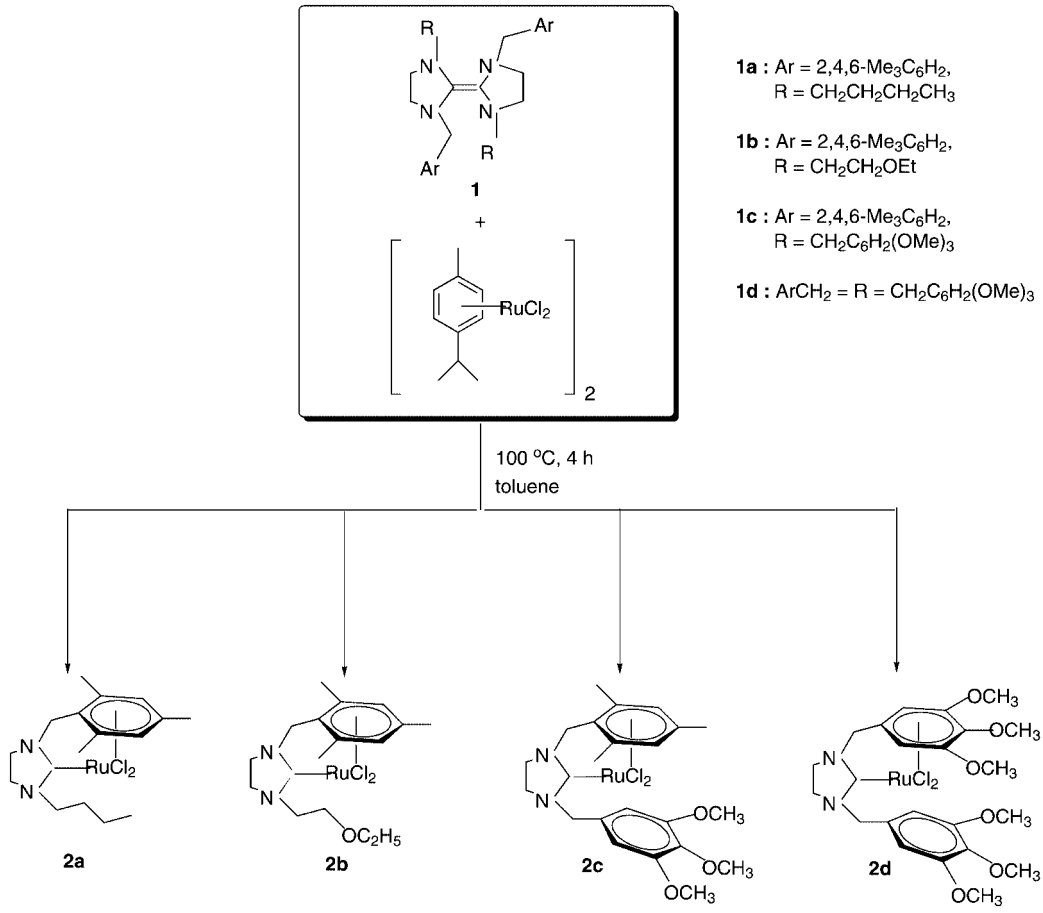


Scheme 1. Preparation of (η⁶-arene-η¹-carbene)$RuCl_2$ complexes.

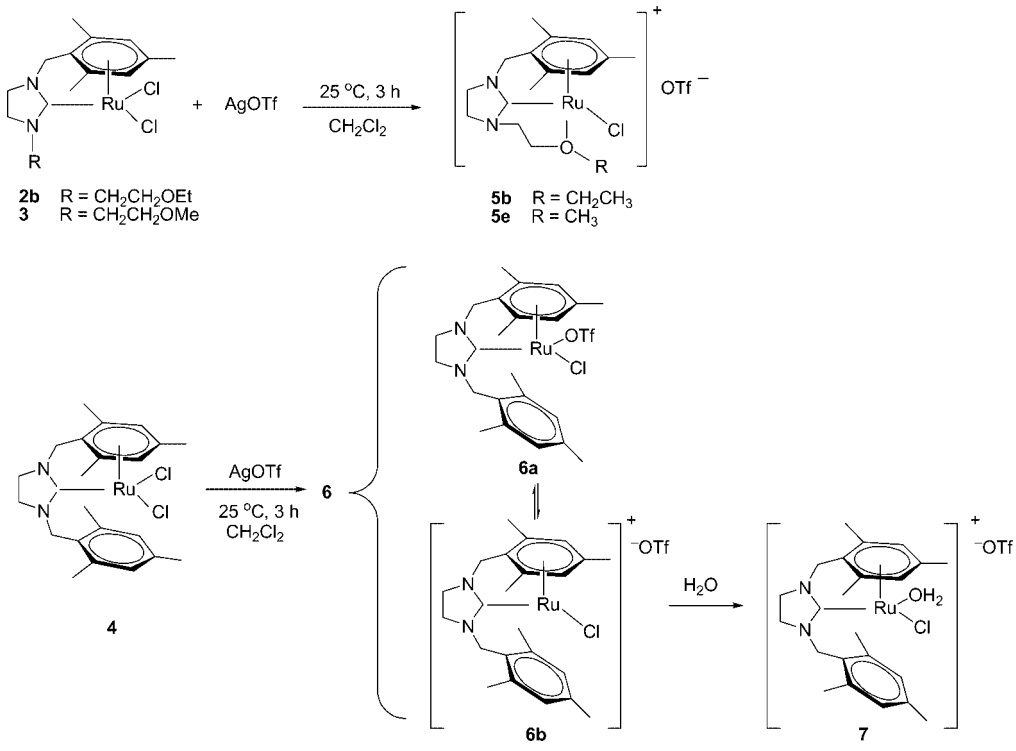
The ^1H NMR spectra show the absence of the *p*-cymene ligand and the presence of a coordinated mesityl group in **2a**–**c** with equivalent ortho methyl groups and equivalent high-field aryl CH proton resonances at δ = 5.36–5.43 ppm (cf. δ = 6.7 ppm for **1a**–**1c**). Complex **2d** shows a coordinated aryl CH proton signal at δ = 4.78 ppm and noncoordinated aryl proton signals at δ = 6.79 ppm, whereas the aryl proton signal appears at δ = 6.90 ppm in the related olefin precursor **1d**. The coordination of the carbene carbon is evidenced by a low-field singlet in the ^{13}C NMR spectrum at δ = 200–201.5 ppm for **2a**–**2d**.

These syntheses show that the intramolecular displacement of the *p*-cymene ligand by the mesityl group is quantitative and rather easy. They also show (**2c**) that the coordination of the mesityl group is favoured over that of the 3,4,5-$(MeO)_3C_6H_2$ group likely because of steric repulsion between the methoxy group and the chloride ligands. The complexes **2** that do not contain an alkene-metathesis-initiating carbene are inert as catalysts for the ROMP of cyclic olefins. In order to change them into active catalysts for alkene metathesis, attempts were made to transform them into related allenylidene–ruthenium complexes according to Equation (1).[12]

$$\mathrm{LnRuCl_2} \xrightarrow[-\mathrm{AgCl}]{\mathrm{Ag^+}} \mathrm{LnRuCl}^+ \xrightarrow{\mathrm{HC{\equiv}CC(OH)Ph_2}} \mathrm{LnRuCl(=C=C=CPh_2)}^+ \quad (1)$$

Indeed, the [Ru=C=C=CPh_2(Cl)(PCy_3)(*p*-cymene)]X[13] complexes were shown to be active precursors for ROMP on either thermal[14] or acid-promoted[15] transformations into indenylidene–ruthenium derivatives. The indenylidene carbene plays the role of alkene metathesis initiator in these catalyst precursors. Attempts to isolate the 16-electron ruthenium intermediates were made by the abstraction of one chloride ion from complexes **2**, before attempting allenylidene–ruthenium complex formation by addition of propargylic alcohol.

Complex **2b** and complexes **3** and **4**, analogous to **2b** and **2d**, were treated with one equivalent of AgOTf in dichloromethane at room temperature for 3 h, and the ionic complexes **5b**, **5e**, **6** were isolated in 78–85% yields (Scheme 2). The ^1H and ^{13}C NMR spectra show that the arene group remains coordinated to the metal, the (Ru=C) carbene carbon (δ = 197 ppm) is only slightly shielded relative to that in complexes **2** (δ = 200 ppm). In their ^1H NMR spectra at



Scheme 2. Preparation of ionic mixed arene carbene ruthenium complexes **5**, **6** and **7**.

room temperature, complexes **5** show nonequivalent coordinated mesityl CH protons, which is consistent with a chiral ruthenium centre. Complex **6** is an orange solid that reacts with wet solvents to give the aquo complex **7** for which an X-ray structure has been determined (Figure 1, Table 1).[16] The nature of **6** can be understood as an 18-electron complex **6a** with a weak Ru–OTf bond in equilibrium with a 16-electron complex **6b**. The latter reacts with water in the same way that the intermediates obtained from the reaction between **2b** or **3** and AgOTf react with the ether branch to give complexes **5b** and **5e**.

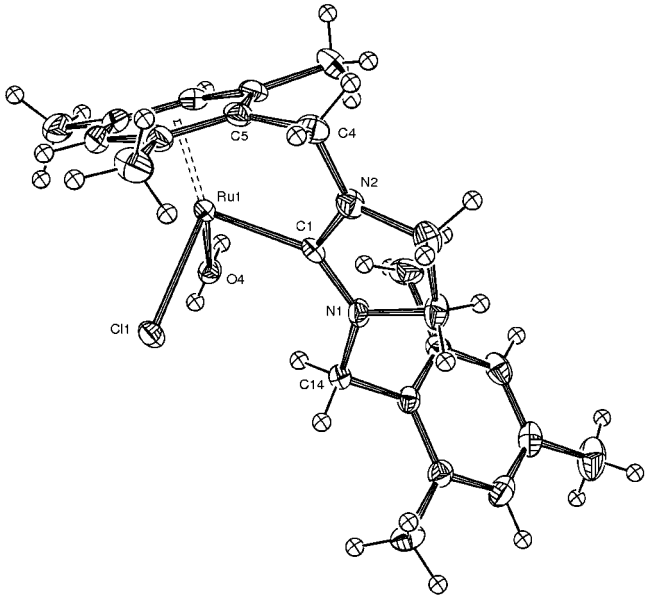


Figure 1. Molecular structure of complex **7** showing 50% ellipsoid probability. A triflate and a chloroform molecule are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for the molecular structure of **7**.

Ru1–C1	2.058(3)	Ru1–O4	2.190(2)
N1–C11	1.357(3)	Ru1–C5	2.107(3)
N2–C4	1.465(4)	N1–C14	1.458(3)
Ru1–Cl1	2.408(7)	Ru1–C6	2.158(3)
Ru1–C7	2.239(3)	Ru1–C8	2.283(3)
Ru1–C9	2.197(3)	Ru1–C10	2.201(3)
C1–Ru1–Cl1	82.62(7)	C1–Ru1–O4	95.95(9)
C1–Ru1–N1	136.23(19)	C1–Ru1–N2	115.1(2)
C1–N2–C4	122.9(2)	N2–C4–C5	106.1(2)
Ru1–C5–C4–N2	14.00		

X-ray Diffraction Study of 2c and 5e

In order to evaluate the ligand modification brought about by the abstraction of one chloride ion from complexes **2**, structural studies were carried out on a neutral complex **2c**[17] and an ionic complex **5e**[18] containing a coordinating chain.

Molecular structures of **2c** and **5e** with selected data are presented in Figure 2 with Table 2, and Figure 3 with Table 3, respectively. The structure of **2c** confirms that one of the mesityl groups is coordinated to the ruthenium atom. The structure of **5e** shows that formally a chlorine atom has been displaced by the methoxy oxygen atom and that the ligand is tricoordinate, donating ten electrons to the ruthenium atom. The mesityl–ruthenium bond length is not sig-

nificantly modified: the Ru–arene distance is 1.690 Å in **2c** and 1.693 Å in **5e**. By contrast, we can observe a slightly shorter carbene C–Ru bond when the NHC is tricoordinate: 1.996(3) Å in **5e** and 2.050(2) Å in **2c**.

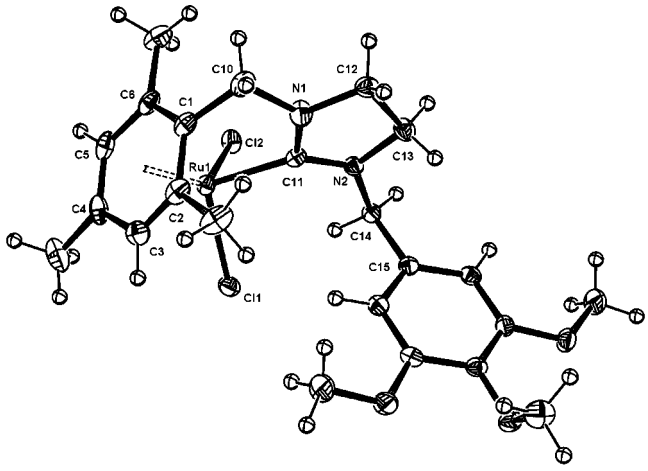


Figure 2. Molecular structure of **2c** showing 50% ellipsoid probability. A dichloromethane molecule is omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for the molecular structure of **2c**.

Ru1–C11	2.050(2)	Ru1–C4	2.182(2)
N1–C11	1.357(3)	Ru1–C5	2.321(2)
N2–C11	1.328(3)	Ru1–C2	2.112(2)
N1–C10	1.452(3)	Ru1–C3	2.194(2)
Ru1–Cl1	2.3936(5)	Ru1–Cl2	2.4416(6)
N2–C13	1.474(3)	N2)–C14	1.458(3)
N1–C12	1.462(3)	Ru1–C6	2.278(2)
Ru1–C1	2.153(2)	N1–C11–N2	107.4(2)
C1–C2–C10	120.6(2)	N1–C10–C1	106.24(18)
N2–C14–C15	110.15(17)	C11–Ru1–Cl1	85.11(6)
C11–Ru1–Cl2	100.14(6)	N1–C11–Ru1	115.74(16)
Ru1–C1–C10–N1	13.99		

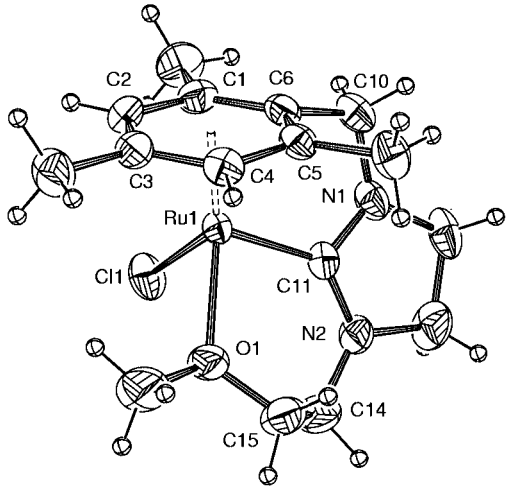


Figure 3. Molecular structure of **5e** showing 50% ellipsoid probability. A triflate molecule is omitted for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for the molecular structure of **5e**.

Ru1–C11	1.996(3)	Ru1–O1	2.175(2)
Ru1–C6	2.101(3)	Ru1–C3	2.330(3)
Ru1–C1	2.154(3)	Ru1–C5	2.197(3)
Ru1–C4	2.200(3)	Ru1–C2	2.274(3)
Ru1–Cl1	2.3885(8)	N1–C11	1.324(4)
N1–C10	1.451(5)	N2–C11	1.325(4)
N2–C14	1.458(5)	C6–C10	1.533(5)
C11–Ru1–O1	86.89(11)	N1–C11–Ru1	118.0(2)
N2–C11–Ru1	131.4(2)	Ru1–C6–C10–N1	15.3

ROMP Promoted by Complexes 2 and 5

ROMP of norbornene was studied under two sets of conditions by taking into account that complexes **2** do not react with norbornene in the absence or presence of propargylic alcohol. Thus, the catalysts were generated directly from the precursors **2** by in situ treatment first with AgOTf in PhCl followed by the addition of propargylic alcohol, without isolation of the intermediate of type **5**. The resulting allenylidene or indenylidene intermediate could not be isolated, consequently the ROMP reaction was performed in situ as soon as the propargylic alcohol was added to complexes **5**, and chlorobenzene was used as solvent (conditions [a], Table 4). An analogously successful approach for the in situ generation of alkene metathesis catalysts was used for the ring closing metathesis (RCM) of dienes.[10] Another polymerization procedure was used by combining the isolated ionic complexes **5** and propargylic alcohol, $HC{\equiv}CCPh_2OH$, in order to generate the allenylidene intermediate and then the indenylidene initiator in situ

Table 4. ROMP of norbornene in PhCl catalyzed by various N-heterocyclic carbene-ruthenium intermediates in situ generated from **2** and **5**.

Catalyst precursor	Conditions	Yield [%]	$10^{-3} \times M_n$[d]	PDI[e]	*cis* [%][f]
2a[a]	15 min 80 °C	84	71	1.8	41
2a[a]	30 min room temp.	82	136	1.8	41
2b[c]	30 min 80 °C	15	162	1.9	–
2c[a]	30 min room temp.	78	68	1.7	38
2c[a]	15 min 80 °C	94	53	2.2	39
2d[a]	20 min 80 °C	74	76	1.7	47
2d[a]	480 min room temp.	19	121	1.8	39
4[b]	420 min 80 °C	60	74	1.8	23
5e[b]	5 min 80 °C	71	60	1.8	34
5e[b]	480 min room temp.	30	132	1.7	31
5b[b]	5 min 80 °C	97	75	1.5	36
5b[b]	40 min room temp.	95	54	1.6	34

[a] Catalyst precursor (1.5×10^{-5} mol), AgOTf (1.5×10^{-5} mol), $HC{\equiv}C{-}CPh_2(OH)$ (1.7×10^{-5} mol), norbornene (4.5×10^{-3} mol), PhCl (5 mL). [b] Catalyst precursor (1.5×10^{-5} mol), $HC{\equiv}C{-}CPh_2(OH)$ (1.7×10^{-5} mol), norbornene (4.5×10^{-3} mol), PhCl (5 mL). [c] Catalyst precursor (1.5×10^{-5} mol), norbornene (4.5×10^{-3} mol), PhCl (5 mL). [d] Determined by GPC in THF vs. polystyrene standards. [e] Polydispersity index M_w/M_n. [f] Determined by ^{1}H NMR spectroscopy.

(conditions [b], Table 4). Precursor **2a**, under conditions [a], led to similar yields at 80 °C and room temperature, but higher molecular mass was obtained at room temperature. This indicates that a lower number of active initiators are produced at room temperature. Precursor **2b**, in the absence of AgOTf and propargylic alcohol, leads to very low activity, thus showing that the initial halide abstraction from complexes **2** is required to trigger efficient polymerization. Precursor **2c** gives a higher yield (94%) after 15 min at 80 °C, but with a broad polydispersity. Complexes **2a** and **2d** afford similar yields and polydispersity at 80 °C. However, at room temperature, precursors **2a** and **2c** with a coordinated mesityl group are much more active than **2d** with the coordinated trimethoxybenzyl group, thus showing the influence of the nature of the coordinated arene.

The ROMP, performed directly with ionic complexes **5b** and **5e**, shows that the most efficient precursor is **5b** both at room temperature and at 80 °C with high yield (>95%) and good polydispersity (PDI = 1.5). The comparison of this result to that obtained from **2b** alone indicates that the preliminary chloride ion abstraction by silver salt treatment is essential to obtain high yield and low polydispersity. The nature of the coordinated OR group, e.g. OEt or OMe, has a strong influence. The precursor **5b** (OEt) exhibits a much higher activity than **5e** (OMe).

Conclusions

The above results show that bis(imidazolinylidene) olefins containing an arylmethyl-*N* group always displace the *p*-cymene to give (η^1-carbene-η^6-arene)$RuCl_2$ complexes upon reaction with $[RuCl_2(p\text{-cymene})]_2$. Upon chloride abstraction, these complexes containing an additional $ROCH_2CH_2$–N group lead to the tridentate carbene/arene/ether ionic complexes **5b** and **5e**. The mixed arene-NHC precursors **2** are ROMP initiators after chloride abstraction and reaction with propargylic alcohol to initially produce allenylidenes. The most active precursors **2a**, **2b** and **5b**, operate at room temperature.

Experimental Section

Syntheses were carried out by using standard Schlenk techniques under an inert argon atmosphere with previously dried solvents. The starting complex $[RuCl_2(p\text{-cymene})]_2$ was prepared by known methods.[12] Electron-rich olefins **1** were prepared according to Lappert's procedure.[11] Infrared spectra were recorded by using KBr pellets in the range 400–4000 cm^{-1} with an ATI UNICAM 2000 spectrometer. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded with a Bruker AM 300 WB FT spectrometer, and the chemical shifts were referenced to $CDCl_3$. Microanalyses were performed by the TÜBITAK analysis centre in Ankara.

A**[$RuCl_2${η^1-CN(CH_2{η^6-$C_6H_2Me_3$-2,4,6})$CH_2CH_2N(CH_2CH_2CH_2CH_3)$}] (2a):** A solution of the electron-rich olefin **1a** (284 mg, 0.55 mmol) and the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.5 mmol) in degassed toluene (15 mL) was heated at 100 °C for 4 h to give **2a** in 90% yield (387 mg), after extraction into and crystallization from dichloromethane/hexane (5:20). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.4 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.21 (hex., J = 7.4 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.42 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.11 (s, 6 H, 2 CH_3 Mes), 2.23 (s, 3 H, CH_3 Mes), 3.53 (t, J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 3.75 (s, 4 H, NCH_2CH_2N), 4.07 (s, 2 H, NCH_2 Mes), 5.38 (s, 2 H, CH Mes) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.5 ($CH_2CH_2CH_2CH_3$), 17.2 (2 CH_3 Mes), 17.7 ($CH_2CH_2CH_2CH_3$), 20.1 (CH_3 Mes), 31.2 ($CH_2CH_2CH_2CH_3$), 47.4 ($CH_2CH_2CH_2CH_3$), 48.3 and 49.5 (NCH_2CH_2N), 50.0 (NCH_2 Mes), 88.8, 94.2, 99.4 and 100.6 ($CH_2C_6H_2Me_3$-2,4,6), 200.1 (Ru=C) ppm. $C_{17}H_{26}Cl_2N_2Ru$ (430.08): calcd. C 47.44, H 6.09, N 6.51; found C 47.47, H 6.02, N 6.39. M.p. 256–257 °C.

[$RuCl_2${η^1-CN(CH_2{η^6-$C_6H_2Me_3$-2,4,6})$CH_2CH_2N(CH_2CH_2OCH_2CH_3)$}] (2b): A solution of the electron-rich olefin **1b** (302 mg, 0.55 mmol) and the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.5 mmol) in degassed toluene (15 mL) was heated at 100 °C for 4 h to give **2b** in 93% yield (415 mg) after extraction into and crystallization from dichloromethane/hexane (5:20). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.07 (t, J = 6.36 Hz, 3 H, $CH_2CH_2OCH_2CH_3$), 2.07 (s, 6 H, 2 CH_3 Mes), 2.21 (s, 3 H, CH_3 Mes), 3.35 (q, J = 6.20 Hz, 2 H, $CH_2CH_2OCH_2CH_3$), 3.49 and 3.73 (s, 4 H, NCH_2CH_2N), 3.76 (m, 2 H, $CH_2CH_2OCH_2CH_3$), 3.94 (t, J = 4.76 Hz, 2 H, $CH_2CH_2OCH_2CH_3$), 4.07 (s, 2 H, NCH_2 Mes), 5.36 (s, 2 H, CH Mes) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 17.1 (2 CH_3 Mes), 15.7 (CH_3 Mes), 17.7 ($CH_2CH_2OCH_2CH_3$), 47.4 and 49.7 (NCH_2CH_2N), 48.6 (NCH_2 Mes), 52.3 ($CH_2CH_2OCH_2CH_3$), 66.4 ($CH_2CH_2OCH_2CH_3$), 72.8 ($CH_2CH_2OCH_2CH_3$), 88.8, 94.2, 99.3 and 100.8 ($CH_2C_6H_2Me_3$-2,4,6), 200.5 (Ru=C) ppm. $C_{17}H_{26}Cl_2N_2ORu$ (446.38): calcd. C 45.74, H 5.87, N 6.27; found C 45.71, H 5.90, N 6.25. M.p. 213–214 °C.

[$RuCl_2${η^1-CN(CH_2{η^6-$C_6H_2Me_3$-2,4,6})$CH_2CH_2N(CH_2{C_6H_2(OMe)_3-3,4,5})$}] (2c): A solution of the electron-rich olefin **1c** (420 mg, 0.55 mmol) and the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.5 mmol) in degassed toluene (15 mL) was heated at 100 °C for 4 h to give **2c** in 89% yield (493 mg) after extraction into and crystallization from dichloromethane/hexane (5:20). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.10 (s, 6 H, 2 CH_3 Mes), 2.26 (s, 3 H, CH_3 Mes), 3.52 (t, J = 10.38 Hz, 2 H, NCH_2CH_2N), 3.67 (t, J = 10.37 Hz, 2 H, NCH_2CH_2N), 3.74 [s, 3 H, $NCH_2C_6H_2(OMe)_3$-3,4,5], 3.76 [s, 6 H, $NCH_2C_6H_2(OMe)_3$-3,4,5], 4.05 (s, 2 H, NCH_2 Mes), 4.66 [s, 2 H, $NCH_2C_6H_2(OMe)_3$-3,4,5], 5.43 (s, 2 H, CH Mes), 6.67 [s, 2 H, $NCH_2C_6H_2(OMe)_3$-3,4,5] ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 17.3 (2 CH_3 Mes), 17.9 (CH_3 Mes), 47.6 and 49.9 (NCH_2CH_2N), 48.5 (NCH_2 Mes), 54.2 [$NCH_2C_6H_2(OMe)_3$-3,4,5], 56.9 [$NCH_2C_6H_2(OMe)_3$-3,4,5], 61.5 [$NCH_2C_6H_2(OMe)_3$-3,4,5], 89.5, 94.8, 99.9 and 101.5 ($CH_2C_6H_2Me_3$-2,4,6), 107.7, 133.3, 138.4 and 154.2 [$NCH_2C_6H_2(OMe)_3$-3,4,5], 200.9 (Ru=C) ppm. $C_{23}H_{30}Cl_2N_2O_3Ru$ (554.47): calcd. C 49.82, H 5.45, N 5.05; found C 49.85, H 5.41, N 5.12. M.p. 254–255 °C.

[$RuCl_2${η^1-CN(CH_2{η^6-$C_6H_2(OMe)_3$-3,4,5})$CH_2CH_2N(CH_2{C_6H_2(OMe)_3-3,4,5})$}] (2d): A solution of the electron-rich olefin **1d** (473 mg, 0.55 mmol) and the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.5 mmol) in degassed toluene (15 mL) was heated at 100 °C for 4 h. After the mixture had been cooled to 25 °C, *n*-hexane (15 mL) was added, and the solution was cooled to –15 °C. The precipitated brown solid was filtered and recrystallized from dichloromethane/hexane (10:30). Compound **2d** was isolated in 82% yield (494 mg). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.46 and 3.58 (t, J = 10.38 Hz, 4 H, NCH_2CH_2N), 3.73 [s, 3 H, coord. $NCH_2C_6H_2(OMe)_3$-3,4,5], 3.76 [s, 6 H, coord. $NCH_2C_6H_2$-

(O*Me*)$_3$-*3*,4,*5*], 3.90 [s, 2 H, coord. NC*H*$_2$C$_6$H$_2$(OMe)$_3$-3,4,5], 3.94 [s, 6 H, free NCH$_2$C$_6$H$_2$(O*Me*)$_3$-*3*,4,*5*], 4.13 [s, 3 H, free NCH$_2$C$_6$H$_2$(O*Me*)$_3$-3,*4*,5], 4.66 [s, 2 H, free NC*H*$_2$C$_6$H$_2$(OMe)$_3$-3,4,5], 4.78 [s, 2 H, coord. NCH$_2$C$_6$*H*$_2$(OMe)$_3$-3,4,5], 6.79 [s, 2 H, free NCH$_2$C$_6$*H*$_2$(OMe)$_3$-3,4,5] ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 48.2 [coord. N*C*H$_2$C$_6$H$_2$(OMe)$_3$-3,4,5], 49.7 [free N*C*H$_2$C$_6$H$_2$(OMe)$_3$-3,4,5], 52.1 and 54.6 (N*C*H$_2$*C*H$_2$N), 54.9 [coord. NCH$_2$C$_6$H$_2$(O*Me*)$_3$-3,4,5], 56.8 and 58.2 [free NCH$_2$C$_6$H$_2$(O*Me*)$_3$-3,4,5], 99.3, 107.7, 107.9 and 110.1 [coord. NCH$_2$*C*$_6$H$_2$(OMe)$_3$-3,4,5], 131.9, 137.7, 138.6 and 153.3 [free NCH$_2$*C*$_6$H$_2$(OMe)$_3$-3,4,5], 201.2 (Ru=C) ppm. $C_{23}H_{30}Cl_2N_2O_6Ru$ (602.47): calcd. C 45.85, H 5.02, N 4.65; found C 45.89, H 5.00, N 4.61. M.p. 214–215 °C.

[RuCl{η^1-CN(CH$_2${η^6-C$_6$H$_2$Me$_3$-2,4,6})CH$_2$CH$_2$N(CH$_2$CH$_2$OCH$_2$CH$_3$)}][CF$_3$SO$_3$] (5b): Complex **2b** (223 mg, 0.5 mmol) and silver triflate (128 mg, 0.5 mmol) in degassed CH_2Cl_2 were stirred for 3 h at room temperature, then filtered and crystallized from CH_2Cl_2/diethylether (10:20). Compound **5b** was isolated in 78% yield (218 mg). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 2.20 (t, *J* = 6.8 Hz, 3 H, CH$_2$CH$_2$OCH$_2$C*H*$_3$), 3.03 (s, 3 H, CH$_3$ Mes), 3.32 and 3.38 (s each, 3 H; 2 CH$_3$ Mes), 4.58 (t, *J* = 3.0 Hz, 2 H, CH$_2$CH$_2$OC*H*$_2$CH$_3$), 4.62 and 4.98 (m, 4 H, NC*H*$_2$C*H*$_2$N), 5.10 (m, 2 H, C*H*$_2$CH$_2$OCH$_2$CH$_3$), 5.37 (q, *J* = 12.8 Hz, 2 H, CH$_2$C*H*$_2$OCH$_2$CH$_3$), 5.84 (s, 2 H, NCH$_2$ Mes), 6.87 and 6.93 (s each, 1 H, CHMes) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 14.3 (CH$_3$ Mes), 15.9 (2 CH$_3$ Mes), 16.9 (CH$_2$CH$_2$OCH$_2$*C*H$_3$), 48.9 and 50.7 (N*C*H$_2$*C*H$_2$N), 66.9 (NCH$_2$ Mes), 68.5 (*C*H$_2$CH$_2$OCH$_2$CH$_3$), 83.2 (CH$_2$CH$_2$O*C*H$_2$CH$_3$), 92.7 (CH$_2$*C*H$_2$OCH$_2$CH$_3$), 93.9, 96.4, 99.9 and 102.3 (CH$_2$*C*$_6$H$_2$Me$_3$-2,4,6), 124.0 (*C*F$_3$SO$_3$), 197.7 (Ru=C) ppm. $C_{18}H_{26}ClF_3N_2O_4RuS$ (559.99): calcd. C 38.61, H 4.68, N 5.00, S 5.73; found C 38.67, H 4.61, N 5.03, S 5.71.

[RuCl{η^1-CN(CH$_2${η^6-C$_6$H$_2$Me$_3$-2,4,6})CH$_2$CH$_2$N(CH$_2$CH$_2$OCH$_3$)}][CF$_3$SO$_3$] (5e): Compound **5e** was prepared in the same way as **5b** and isolated in 81% yield (221 mg). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 2.33 (s, 3 H, CH$_3$ Mes), 2.38 (s, 6 H, 2 CH$_3$ Mes), 2.85 (s, 3 H, CH$_2$CH$_2$OC*H*$_3$), 3.32–4.13 (m, 8 H, NC*H*$_2$C*H*$_2$N and C*H*$_2$C*H*$_2$OCH$_3$), 4.51 (s, 2 H, NCH$_2$ Mes), 5.80 and 5.88 (each: s, 1 H, CHMes) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 15.9 (2 CH$_3$ Mes), 16.9 (CH$_3$ Mes), 49.3 and 58.3 (N*C*H$_2$*C*H$_2$N), 50.9 (NCH$_2$ Mes), 71.1 (*C*H$_2$CH$_2$OCH$_3$), 83.5 (CH$_2$CH$_2$O*C*H$_3$), 92.8 (CH$_2$*C*H$_2$OCH$_3$), 93.8, 96.2, 99.6 and 102.4 (CH$_2$*C*$_6$H$_2$Me$_3$-2,4,6), 124.0 (*C*F$_3$SO$_3$), 197.6 (Ru=C) ppm. $C_{17}H_{24}ClF_3N_2O_4RuS$ (545.97): calcd. C 37.40, H 4.43, N 5.13, S 5.87; found C 37.45, H 4.39, N 5.15, S 5.83. M.p. 227–228 °C.

[RuCl{η^1-CN(CH$_2${η^6-C$_6$H$_2$Me$_3$-2,4,6})CH$_2$CH$_2$N(CH$_2${η^6-C$_6$H$_2$Me$_3$-2,4,6})}][CF$_3$SO$_3$] (6): Compound **6** was prepared in the same way as **5b** and isolated in 85% yield (264 mg). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 2.19 (s, 12 H, coord. and free NCH$_2$C$_6$H$_2$*Me*$_3$-*2*,4,*6*), 2.29 (s, 6 H, coord. and free NCH$_2$C$_6$H$_2$*Me*$_3$-2,*4*,6), 3.77 and 4.27 (dd, *J* = 10.4 and *J* = 9.4 Hz, 4 H, NC*H*$_2$C*H*$_2$N), 4.32 (s, 2 H, coord. NC*H*$_2$C$_6$H$_2$Me$_3$-2,4,6), 4.81 (s, 2 H, free NC*H*$_2$C$_6$H$_2$Me$_3$-2,4,6), 5.71 and 5.91 (each :s, 1 H, coord. NCH$_2$C$_6$*H*$_2$Me$_3$-2,4,6), 6.80 (s, 2 H, free NCH$_2$C$_6$*H*$_2$Me$_3$-2,4,6) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 16.9 (coord. NCH$_2$C$_6$H$_2$*Me*$_3$-*2*,4,*6*), 17.4 (coord. NCH$_2$C$_6$H$_2$*Me*$_3$-2,*4*,6), 19.5 (free NCH$_2$C$_6$H$_2$*Me*$_3$-*2*,4,*6*), 20.0 (free NCH$_2$C$_6$H$_2$*Me*$_3$-2,*4*,6), 47.8 and 49.3 (N*C*H$_2$*C*H$_2$N), 48.0 (coord. NC*H*$_2$C$_6$H$_2$Me$_3$-2,4,6), 48.9 (free N*C*H$_2$C$_6$H$_2$Me$_3$-2,4,6), 93.7, 95.2, 97.8 and 103.4 (coord. NCH$_2$*C*$_6$H$_2$Me$_3$-2,4,6), 124.0 (*C*F$_3$SO$_3$), 128.3, 129.4, 137.9 and 138.2 (free NCH$_2$*C*$_6$H$_2$Me$_3$-2,4,6), 197.6 (Ru=C) ppm. $C_{24}H_{30}ClF_3N_2O_3RuS$ (620.07): calcd. C 46.49, H 4.87, N 4.52, S 5.17; found C 46.54, H 4.79, N 4.58, S 5.20. M.p. 242–243 °C.

Polymerization of Norbornene by [(Arene)(NHC)RuCl$_2$)] 2: Ruthenium complex **2** (1.5×10^{-5} mol), AgOTf (1.5×10^{-5} mol), HC≡C-CPh$_2$(OH) (1.7×10^{-5} mol), and norbornene (4.5×10^{-3} mol) were mixed in dry chlorobenzene (5 mL) under an argon atmosphere. The suspension was stirred at the desired temperature for the required time. After reaction, the resulting viscous mixture was dissolved in $CHCl_3$ (20 mL) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT) (0.1%) as a radical scavenger and ethyl vinyl ether (0.3 mL). The solution was poured into methanol (300 mL) to precipitate the polymer, which was collected by filtration, dried under vacuum, and characterized by ^{1}H and ^{13}C NMR spectroscopy. Average molecular weights were determined by using GPC calibrated with polystyrene standards.

Polymerization of Norbornene by [(Arene)(NHC)RuCl)]OTf 5: Ruthenium complex, **5** (1.5×10^{-5} mol), HC≡C–CPh$_2$(OH) (1.7×10^{-5} mol), and norbornene (4.5×10^{-3} mol) were mixed in dry chlorobenzene (5 mL) under an argon atmosphere. The suspension was stirred at the desired temperature for the required time. After reaction, the resulting viscous mixture was treated as for polymerization with complexes **2**.

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[16] A few crystals suitable for X-ray structure determination were taken out of an NMR solution. Crystal data for compound **7**: $RuClC_{23}H_{32}ON_2$, CF_3SO_3, $CHCl_3$, M_r = 757.46, triclinic, $P\bar{1}$, a = 8.9960(4), b = 12.9478(5), c = 14.1936(6) Å, α = 95.034(3), β = 89.390(3), γ = 111.241(3)°, V = 1534.6(1) Å^3, Z = 2, D_X = 1.639 Mg m^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 9.80 cm^{-1}, F(000) = 768, T = 120(1) K. The sample (0.21 × 0.16 × 0.14 mm) was studied with an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized Mo-K_α radiation. The data collection[19] ($2\theta_{max}$ = 54°, omega scan frames via 0.75° omega rotation and 20 s per frame, index ranges: $0 \le h \le 11$, $-16 \le k \le 16$, $-18 \le l \le 18$) gives 11443 reflections. The data leads to 6541 independent reflections, 5524 of which with $I > 2.0\sigma(I)$. The structure was solved with SIR-97,[20] which reveals the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97[21] by the full-matrix least-squares techniques (use of F square magnitude; x, y, z, β_{ij} for Ru, Cl, C, O, S, F and N atoms, x, y, z in riding mode for H atoms; 361 variables and 5524 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.032, R_w = 0.098 and S_w = 1.137, $\Delta\rho < 0.8$ e. Å^{-3}. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[22] CCDC-290024 contains the supplementary crystallographic data of compound **7** 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.

[17] Crystal data for compound **2c**, CCDC : $C_{23}H_{30}N_2O_3Cl_2Ru$, CH_2Cl_2, M_r = 639.39, orthorhombic, *Pbca*, a = 15.1773(1), b = 14.9059(1), c = 23.7686(3) Å, V = 5377.2(1) Å^3, Z = 8, D_X = 1.580 Mg m^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 10.09 cm^{-1}, F(000) = 2608, T = 110 K. The crystal (0.32 × 0.22 × 0.20 mm) was studied with a NONIUS Kappa CCD with graphite monochromatized Mo-K_α radiation. The cell parameters are obtained with Denzo and Scalepack[23] with 10 frames (psi rotation: 1° per frame). The data collection[24] ($2\theta_{max}$ = 54°, 297 frames via 1.5° omega rotation and 22 s per frame, index ranges: $0 \le h \le 19$, $0 \le k \le 19$, $0 \le l \le 30$) gave 52555 reflections. The data reduction with Denzo and Scalepack[23] led to 6170 independent reflections [5345 with $I > 2.0\sigma(I)$]. The structure was solved with SIR-97,[20] which revealed the non-hydrogen atoms of the structure. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97[21] by the full-matrix least-squares techniques (use of F square magnitude; x, y, z, β_{ij} for Ru, Cl, O, N and C atoms, x, y, z in riding mode for H atoms; 307 variables and 5345 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 7.15P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting R = 0.032, R_w = 0.082 and S_w = 1.053, $\Delta\rho < 0.70$ e Å^{-3}. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[22] CCDC-249335 contains the supplementary crystallographic data of compound **2c** 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.

[18] Crystal data for complex **5e**: $C_{16}H_{24}N_2ORuClRu,CF_3SO_3$, M_r = 545.96 monoclinic, *P*21/*c*, a = 7.8439(1), b = 15.6482(2), c = 17.3026(2) Å, β = 95.648(1)°, V = 2113.46(5) Å^3, Z = 4, D_X = 1.716 Mg m^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 10.19 cm^{-1}, F(000)= 1104, T = 293 K. The crystal (0.35 × 0.33 × 0.25 mm) was studied with a NONIUS Kappa CCD with graphite monochromatized Mo-K_α radiation. The cell parameters are obtained with Denzo and Scalepack[23] with 10 frames (psi rotation: 1° per frame). The data collection[24] ($2\theta_{max}$ = 54°, 216 frames via

2.0° omega rotation and 20 s per frame, index ranges: $0 \le h \le 10$, $0 \le k \le 20$, $-22 \le l \le 22$) gives 34723 reflections. The data reduction with Denzo and Scalepack[23] led to 4849 independent reflections, 4324 of which with $I > 2.0\sigma(I)$. The structure was solved with SIR-97,[20] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97[21] by the full-matrix least-squares techniques (use of F square magnitude; x, y, z, β_{ij} for Ru, S, F, N C and O atoms, x, y, z in riding mode for H atoms; 263 variables and 4324 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 2.4P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.045$, $R_w = 0.116$ and $S_w = 1.041$, $\Delta\rho < 0.96$ e Å^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[22] CCDC-249534 contains the supplementary crystallographic data of complex **5e** 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.

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