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Thermal Switchability of N-Chelating Hoveyda-type Catalyst Containing a Secondary Amine Ligand

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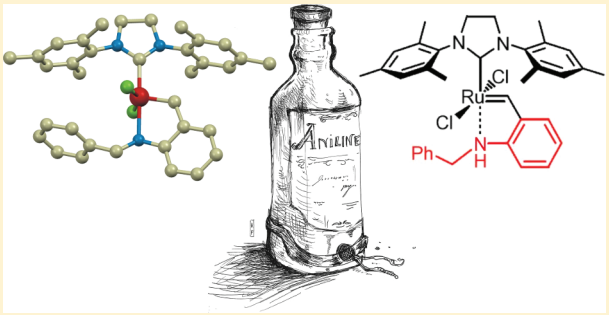
Supporting Information

ABSTRACT: An investigation of aza analogues of the popular Hoveyda−Grubbs catalyst containing a secondary amine ligand is presented, proving the crucial impact of steric as well as electronic factors on the catalyst's stability and performance. The issue of latency in the reactivity profile of studied catalysts is examined, followed by structural and application studies.



1. INTRODUCTION

Olefin metathesis seems to be the most important field of research in organometallic chemistry over the last decades.[1] It allows chemists to form C−C double bonds in complicated natural products and is vital in polymer synthesis. The introduction of well-defined metal-based catalysts resulted in an enormous scientific progress and enabled wide industrial applications. Ruthenium catalysts are especially valued for their air and moisture stability, making them easy to handle. First complexes of this kind were synthesized in the Grubbs group and contained phosphine ligands,[2] which were later partially replaced by N-heterocyclic ligands being stronger σ-donors.[3] Further improvements came from substituting the remaining phosphine ligand by a chelating moiety connected to the benzylidene. Catalysts developed using this idea are presented in Figure 1 with the parent Hoveyda complex marked as **1**.[4] The influence of the heteroatom forming the chelate and its closest substitution was closely examined. Various studies were published on sulfide-,[5] sulfoxide-,[6] or sulfone-chelated[7] ruthenium initiators. Research concerning nitrogen-chelating complexes involves tertiary aliphatic amines (**2**),[8] structures containing nitrogen-containing aromatic heterocycles (**3**−**5**),[9] and those based on Schiff base motifs (**6**−**8**).[10] Although the field seems to be fairly explored, some other N-chelating benzylidenes have not been tested as ligands for ruthenium initiators.

The chelation caused by the presence of nitrogen, oxygen, or sulfur atoms in the structure of ruthenium compounds favors the precatalyst over its metathesis-active form. Such complexes, known as "latent" or "dormant",[11] have a characteristic reduced initiation speed that is found beneficial in some industrial setups involving polymerization or multitransformation sequences. Initiators of this type tend to be thermo- or chemoswitchable: they exhibit a lack of activity in certain conditions, such as ambient temperature or the absence of a chemical agent. Elevating the temperature or introducing a proper agent, usually a Brønsted or Lewis acid, leads to the initiation of the metathesis reaction. Recently, in cooperation with Lemcoff, we comparatively studied a series of O-, S-, and N-chelated ruthenium complexes.[12] The replacement of the oxygen-chelating atom by a sulfur or nitrogen atom resulted in catalysts that were inert at room temperature for typical metathesis reactions and showed catalytic activity only at higher temperatures. Furthermore, nitrogen-chelated catalysts bearing an *N*,*N*-dialkyl aniline motif demonstrated also an interesting thermoswitchable behavior in ring-closing metathesis (RCM). However, the monoalkyl anilines were not tested. Intrigued by this, we decided to study now a set of selected ruthenium chelates containing an *N*-alkyl monosubstituted aniline motif. It shall be noted that amines are known to be problematic substrates for olefin metathesis. Therefore, we expected that these complexes, if formed, shall exhibit in catalysis a rather latent nature. In addition to stability-activity issues relevant to catalysts, we were interested in studying the structural properties of such Ru···NH(R)Ar chelating complexes.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of New Complexes. To study the aforementioned group of ruthenium compounds, we planned a synthesis presented in Scheme 1 leading to ligands **11a**−**11e**. The mentioned ligand precursors

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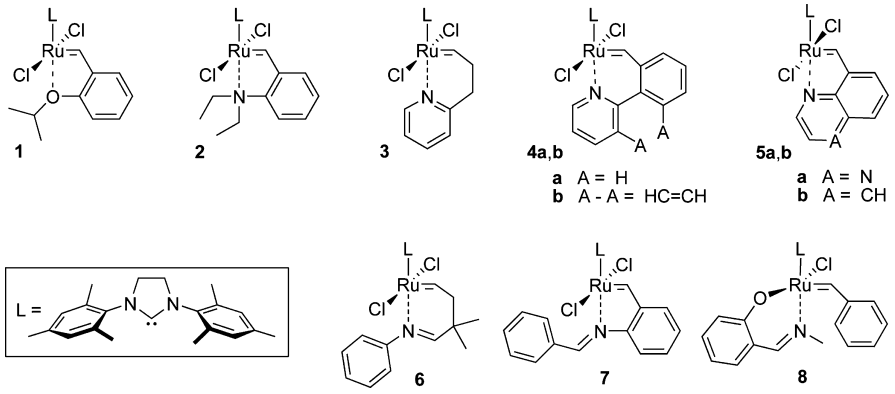
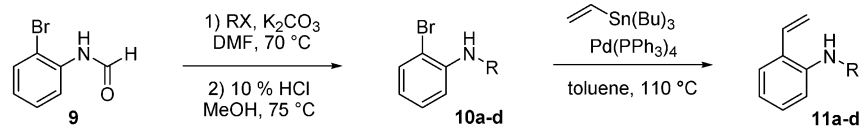
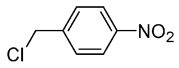
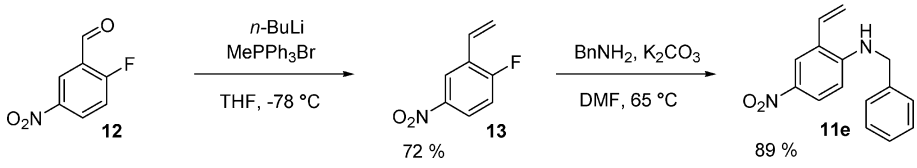


Figure 1. Grubbs–Hoveyda catalyst and selected N-chelating latent catalysts for olefin metathesis.

Scheme 1. Synthetic Pathways of Ligand Precursors 11a–11e



	RX	yield (%) 10	11
a	Me_2SO_4	64	50
b	*i*-PrI	65	62
c	BnCl	83	50
d		77	70

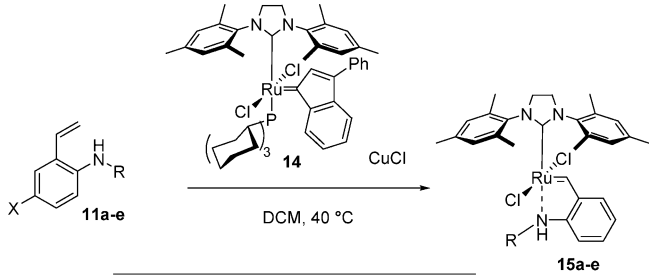


differ in steric hindrance (Me vs *i*-Pr) and electron density (Bn vs *p*-$O_2NC_6H_4CH_2$). These particular structures were chosen in order to explore main factors effecting ruthenium complexes' stability. Starting materials were commercially available compounds **9** and **12** subjected to two-step syntheses. The first stage involved alkylation of (2-bromophenyl)formamide **9**, followed by hydrolysis to yield secondary amines **10a–10d**. The next transformation was Stille coupling leading to compounds **11a–11d**. Ligand precursor **11e** was produced by a Wittig reaction, followed by alkylation.

The final ligand-exchange reaction presented in Scheme 2 was performed in DCM, at 40 °C, in the presence of CuCl with a second-generation indenylidene complex **14** as a ruthenium source. After an hour of heating in such conditions, catalysts **15a**, **15c**, and **15d** were formed and isolated as green crystals.

Interestingly, the reaction with ligand precursor **11b** did not lead to the isolation of a ruthenium compound. Formation of a catalyst containing an isopropyl substituent at the nitrogen atom was visible as a green spot on the TLC plate; however, it was too unstable to allow isolation. This fact leads to a conclusion that catalysts containing a secondary nitrogen atom in their structures are very sensitive for steric hindrance, which seems to be destabilizing them. This phenomenon is peculiar as steric hindrance is known to enhance the stability of some other heteroatom-chelated catalysts **1–4**.[3–6] Performing the ligand-exchange reaction with **11e** led to another failure. Rapid decomposition of complex **14** was observed, suggesting the formation of a new ruthenium complex (presumably the desired compound) and its instant degradation. The electron-withdrawing

Scheme 2. Synthesis of Catalysts 15a–15e



15	R	X	yield (%)
a	Me	H	40
b	*i*Pr	H	-
c	Bn	H	52
d	4-NO_2Bn	H	52
e	Bn	NO_2	-

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effect of the nitro group placed at the para position with respect to the amine group caused the catalyst to be extremely unstable. Similar observations were made when the reaction was performed in different conditions or when different ruthenium sources were used, such as second- and third-generation Grubbs complexes or a Hoveyda–Grubbs catalyst.

The structure of catalyst **15c** (Figure 2) has been determined using single-crystal X-ray diffraction. The compound crystallizes

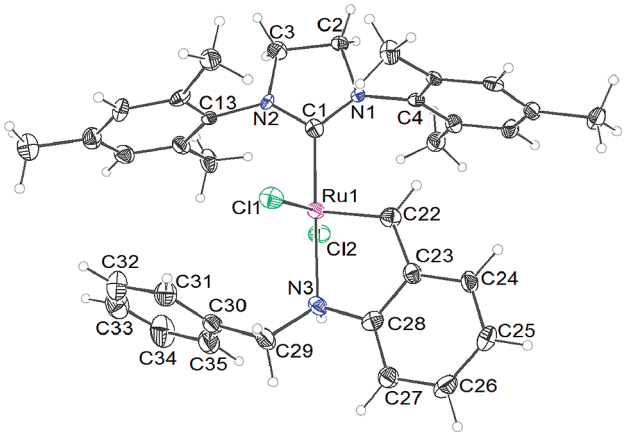


Figure 2. ADPs and the labeling of atoms of **15c**. Thermal ellipsoids at 50% level of probability.

in the monoclinic *P*21/*n* space group with one molecule in the asymmetric part of the unit cell.

The main difference between the Hoveyda parent catalyst and aminoaklylidene derivatives is the E chelating atom determining the position of the R substituent, partially the geometry around the ruthenium center, and the planarity of the benzylidene group. In the Hoveyda catalyst **1**, this is an oxygen atom that keeps the isopropyl group C29 coplanar with the benzylidene group. In consequence, the C23–C28–O1–C29 torsion angle is equal to 169° and C22–Ru1–O1–C28 equals only 7° (see Table 1). The structures of the nitrogen-chelating

Table 1. Comparison of the Most Important Geometrical Parameters of 1 (ABEJUM01[13]), 2, and 15c[a]

		1	2	15c
selected bonds/Å	Ru1–E	2.256	2.336(6)	2.209(4)
	Ru1–Cl1	2.328	2.359(2)	2.331(1)
	Ru1–Cl2	2.338	2.367(2)	2.340(1)
	Ru1–C22	1.829	1.830(8)	1.816(5)
	Ru–C1	1.979	2.010(7)	2.016(5)
	E–C28	1.370	1.451(9)	1.458(6)
	E–C29	1.469	1.515(10)	1.491(6)
			1.503(10)	
selected angles/deg	C28–E–C29	119.93	109.7(6)	113.7(4)
			112.3(7)	
	C28–E–Ru1–C22	7.08	28.61	10.4(3)

[a]The labeling scheme is presented in Figure 1. E stands for O1 in **1** and N3 in **2** and **15c**.

complexes involving secondary and tertiary aliphatic amines, such as **15c** and **2**, have a tetrahedral arrangement around the N3 atom (ex. C28–N3–C29; see Table 1). This has an influence on the geometry of the C23–C28–N3–Ru1 ring and positions of substituents at N3 (ethyl groups in **2** and benzyl group in the **15c**), which begin to depart from planarity (Figure 3).

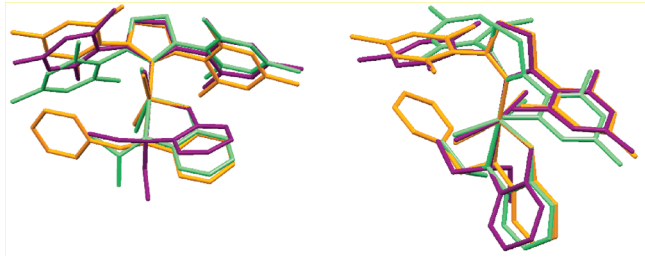
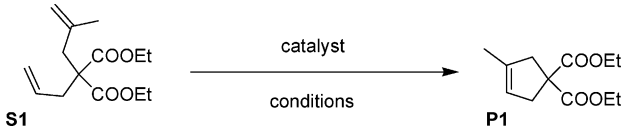


Figure 3. Superposition of **1** (green), **2** (purple), and **15c** (yellow). Hydrogen atoms were omitted for clarity.

Changes of geometry of the molecular fragments containing the E substituents are visible also in the strength of the Ru–E bond, which is surprisingly short in **15c**: decreased by 0.047 Å in comparison to **1** and by 0.127 Å to **2**. Corresponding changes concerns the Ru1–C22 bond, regarded as the catalytic center in this type of compound (this value is also the shortest for **15c**). The other bond lengths around the ruthenium and nitrogen atoms are rather conserved and seem to be independent of the substituent effects.

2.2. Activity Studies and Kinetic Profiles. To study the activity of the synthesized complexes, we selected compound **S1**[14] as a model substrate for the ring-closing metathesis reactions during which a substituted double bond is formed (Scheme 3). All reactions were analyzed by GC using internal

Scheme 3. Model RCM Reaction



standards to ensure that the proper product was obtained. During the metathesis reactions promoted by our new catalysts, the isomerization of **P1** was not observed (according to GC comparison with an authentic sample of **P1**).

Within this reaction catalyzed by 5 mol % **15c**, we examined a number of factors influencing catalyst reactivity, such as temperature, solvent, and additives. Our motivation in utilizing such a relatively high loading was to observe the change in behavior of prepared catalysts under various reaction conditions. For preparative applications of these catalysts, much lower catalyst loadings allow us to obtain desired products in good yields (see Scheme 4). The detailed conditions of conducted RCM of **S1** are listed in Table 2.

Table 2. Detailed Conditions of RCM Reactions

entry	*T* [°C]	solvent	additive	conversion after 8 h [%]	conversion after 24 h [%]
I	80	toluene	none	94	94
II	50	DCE	none	60	67
III	50	toluene	TMSCl	60	72
IV	50	C_6F_6	none	57	70
V	50	toluene	none	45	61
VI	50	toluene	HCl	21	31

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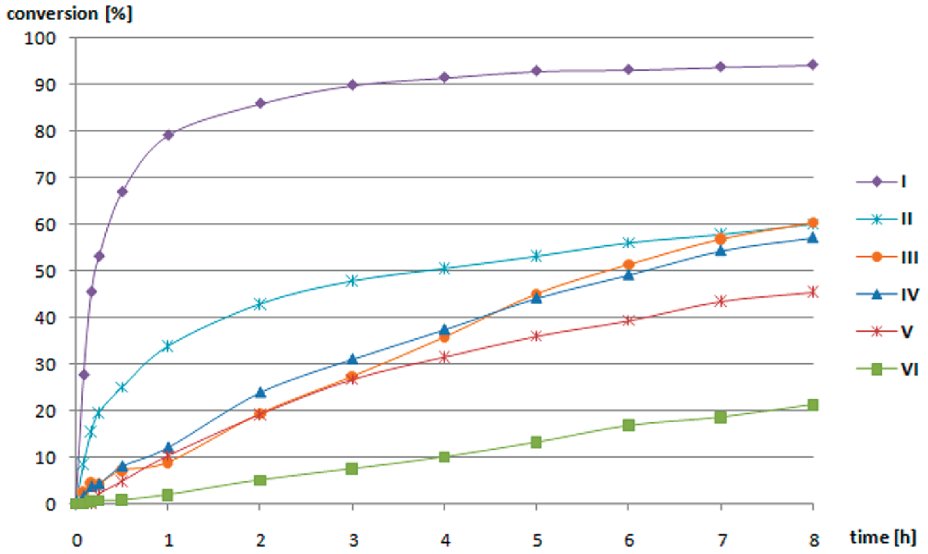

Figure 4. Reaction profile measurements of **S1** (C = 0.1 M) RCM catalyzed by 5 mol % **15c** (for description of labels I–VI, see Table 2).

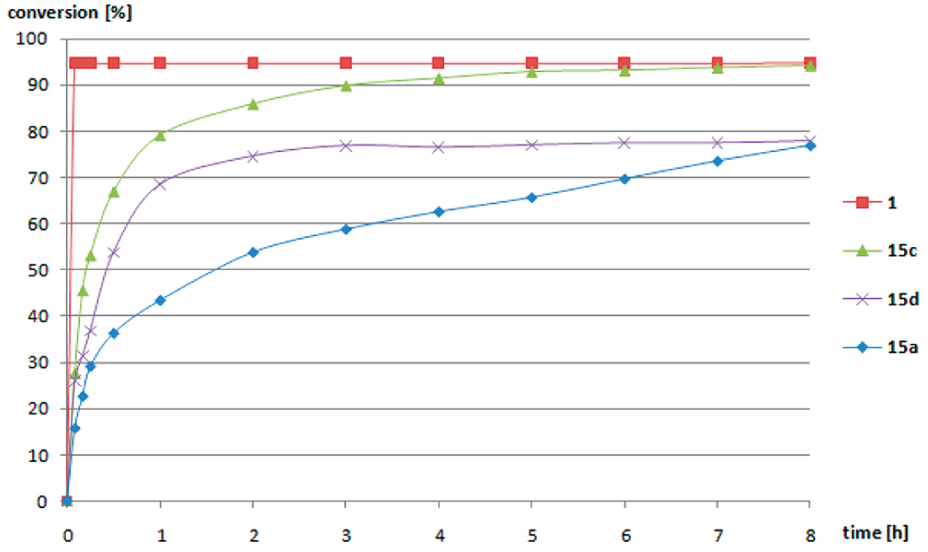

Figure 5. Catalytic activity of Ru initiators in RCM of **S1** (C = 0.1 M). Conditions: 5 mol % catalyst, 80 °C, toluene.

The results of reaction profile measurements are presented in Figure 4.

As a starting point, we performed RCM of **S1** in 50 °C, with toluene (entry V). Obviously, elevating the temperature to 80 °C (entry I) led to a higher conversion of the substrate, simultaneously shortening the lifespan of the **15c**: almost no change in conversion was noticed after 6 h of the reaction, whereas at a lower temperature, the improvement was visible until 24 h. At this point, it is important to underline that the complex **15c** presents no activity at ambient temperature, thus presenting a high degree of thermal switchability. Further experiments involved changing the reaction media. Reports in the literature suggest a possibility of in situ activation of some ruthenium catalysts by applying fluorinated aromatic hydrocarbons (FAH) as solvents.[15] To check this hypothesis, we conducted a comparative experiment utilizing a "classical solvent": dichloroethene (DCE, entry II) and hexafluorobenzene (entry IV). Both solvents gave improved conversions, although FAH allowed us to obtain slightly higher conversions after 48 h. In the case of the N-chelated **15c**, however, the observed activating effect of FAH was not as strong as in the case of fast-initiating phosphine-containing Ru catalysts.[15] The last examined factor was the influence of Lewis and Brønsted acids.[10] For this experiment, we selected TMSCl (entry III) and HCl (entry VI), respectively. The results showed that the Brønsted acid causes instability by protonation of the catalyst and accelerates its decomposition, resulting in a noticeably lower conversion.[16] On the other hand, TMSCl was found to be a milder activating agent that does not affect strongly the catalyst stability, allowing improvement of conversion with respect to the starting conditions (TMSCl is being frequently used as the activator for commercially established Verpoort catalysts, such as Umicore M4x), thus proving a certain degree of chemoswitchability of the system.[11b]

After optimizing the conditions for catalyst **15c**, complexes **15a** and **15b** were tested in the same reaction utilizing the conditions from entry I in Table 2. The results of these measurements are presented in Figure 5.

To allow comparison, the RCM reaction of **S1** catalyzed by the Hoveyda catalyst **1** was performed. Kinetic profiles show clearly that **15c** leads to the same conversion, but with a highly

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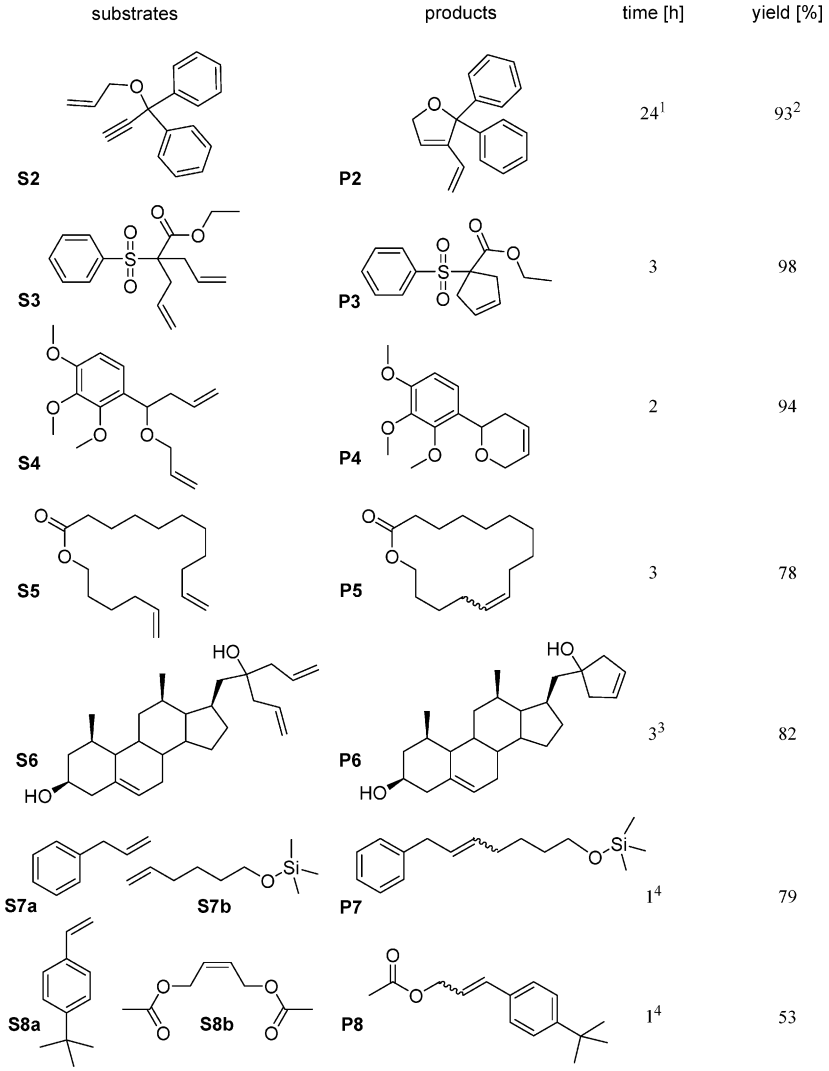
Scheme 4. Metathesis Reaction Catalyzed by 15c[a]



[a]Conditions: C = 0.1 M, 1 mol % **15c**, 80 °C, toluene. Superscript numbers: (1) 40 °C, DCM; (2) GC conversion; (3) 5 mol % **15c**; (4) 2 mol % **15c**.

reduced initiation speed. The time of achieving the same performance is 6 h for **15c** compared with 5 min for **1**, which suggests its great potential for applications requiring latency. Catalysts **15a** and **15d** exhibit a similar catalytic behavior but do not lead to conversions this high. This system show some structural differences. **15a**, bearing a methyl group, lacks proper stabilization of active species by steric hindrance. In complex **15d**, on the other hand we observed a disadvantageous electron-deficient character of the nitro group. Although the conversions in metathesis of **S1** catalyzed by **15a** and **15d** are lower, they are still above the satisfactory level of 75%.

After initial studies involving RCM of **S1**, we have decided to present the preparative applications of **15c**, thus broadening the range of substrates used to explore the catalytic activity of amine catalysts. The results are presented in Scheme 4.

Activity of the complex **15c** was checked in model reactions of ene-yne **P2**[17] and cross metathesis (**P7**, **P8**). Further examples of RCM are presented (**P2**–**P6**),[18] including musk and steroid derivatives synthesis. Yields of the products prove the potential of the ruthenium complexes studied herewith.

3. CONCLUSIONS

A novel class of ruthenium complexes containing an amine chelation is presented with detailed synthesis and X-ray characterization. The investigation of their catalytic activity revealed thermal switchability of the examined complexes with simultaneous high activity toward olefinic substrates. The latent character of synthesized catalysts makes them potentially useful in syntheses requiring an initiation step of reduced ratio. Applications of the newly developed amino catalysts in polymerization reactions will be tested by us in due time, to fully utilize the thermal switchability noted by us in the present study.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Ligands 11a–11e. *4.1.1. Alkylation Reactions.* Commercially available (2-bromophenyl)formamide (2.5 mmol, 500 mg) and potassium carbonate (5 mmol, 691 mg) were put in a flask equipped with a stir bar, dissolved in 10 mL of DMF, and stirred for 10 min at 70 °C. The appropriate halide was added (5 mmol), and the stirring was continued for 16 h. The reaction was then poured onto 10 mL of water and extracted with DCM (2 × 10 mL). Combined organic phases were dried over $MgSO_4$ and evaporated.

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The residue was filtered through a plug of silica gel, evaporated, and redissolved in a 10% solution of hydrochloric acid in methanol. The reaction was then stirred at 75 °C for an hour and cooled to room temperature. Neutralization with a diluted solution of NaOH followed. The mixture was poured onto 10 mL of water and extracted with DCM (2 × 10 mL). Combined organic phases were dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography, providing the corresponding product 64−83%.

10a, (*N*-methyl)-2-bromoaniline. Colorless oil (1.6 mmol, 300 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89 (s, 3H), 4.42 (s, 1H), 6.54−6.66 (m, 2H), 7.17−7.23 (m, 1H), 7.38−7.44 (m, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 30.6, 109.6, 110.6, 117.6, 128.5, 132.2, 145.9 ppm. IR (CH_2Cl_2 film): ν 3426, 2913, 2874, 2821, 2583, 1889, 1761, 1599, 1513, 1461, 1431, 1421, 1320, 1292, 1169, 1155, 1106, 1073, 1019, 926, 893, 836, 662, 541, 434 cm^{-1}, MS (EI; *m*/*z*): 51 (23), 52 (22), 63 (18), 77 (54), 91 (19), 104 (18), 105 (54), 184 (91), 185 (100), 186 (97, $M^{+\bullet}$). Anal. Calcd for C_7H_8BrN (186.05): C, 45.19; H, 4.33; N, 7.53; Br, 42.95. Found: C, 44.97; H, 4.43; N, 7.39; Br, 43.06.

10b, (*N-iso*-propyl)-2-bromoaniline. Colorless oil (1.6 mmol, 345 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (d, *J* = 6.2 Hz, 6H), 3.64−3.71 (m, 1H), 4.16 (s, 1H), 6.52−6.56 (m, 1H), 6.64−6.66 (m, 1H), 7.15−7.19 (m, 1H), 7.41−7.44 (dd, *J* = 7.8, 1.4 Hz, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 22.8, 44.3, 109.8, 111.8, 117.2, 128.4, 132.5, 144.3 ppm. IR (CH_2Cl_2 film): ν 3406, 3070, 3027, 2967, 2927, 2927, 2870, 1920, 1882, 1845, 1755, 1664, 1596, 1511, 1463, 1453, 1426, 1384, 1366, 1319, 1285, 1246, 1176, 1154, 1123, 1112, 1048, 1018, 983, 944, 924, 858, 833, 739, 707, 667, 492, 434 cm^{-1}. MS (EI; *m*/*z*): 92 (12), 118 (35), 119 (40), 171 (9), 198 (100), 199 (11), 200 (93), 201 (9), 213 (31), 215 (29, $M^{+\bullet}$). Anal. Calcd for $C_9H_{12}BrN$ (214.11): C, 50.49; H, 5.65; N, 6.54; Br, 37.32. Found: C, 50.55; H, 5.54; N, 6.48; Br, 37.35.

10c, (*N*-benzyl)-2-bromoaniline. Colorless oil (2.1 mmol, 542 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.39 (s, 2H), 4.75 (s, 1H), 6.54−6.62 (m, 2H), 7.08−715 (m, 1H), 7.22−7.38 (m, 5H), 7.41−7.45 (m, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 48.0, 56.4, 109.7, 111.6, 118.0, 124.5, 124.7, 127.0, 127.2, 127.3, 127.6, 128.2, 128.5, 128.6, 128.7, 132.4, 133.8, 138.0, 138.7, 144.8 ppm. IR (CH_2Cl_2 film): ν 3418, 3084, 3063, 3029, 2925, 2856, 2584, 2525, 1950, 1883, 1807, 1753, 1797, 1510, 1469, 1452, 1427, 1361, 1322, 1295, 1264, 1235, 1194, 1175, 1161, 1129, 1089, 1067, 1045, 1019, 989, 924, 832, 789, 742, 697, 669, 658, 627, 540, 515, 457, 433 cm^{-1}. MS (EI; *m*/*z*): 65 (10), 91 (100), 92 (10), 171 (7), 180 (9), 182 (12), 260 (13), 261 (43), 262 (19) 263 (41, $M^{+\bullet}$). Anal. Calcd for $C_{13}H_{12}BrN$ (262.15): C, 59.56; H, 4.61; N, 5.34; Br, 30.48. Found: C, 59.85; H, 4.73; N, 5.45; Br, 30.20.

10d, (*N*-(*p*-nitrobenzyl))-2-bromoaniline. Bright yellow crystals, mp 98−100 °C (1.9 mmol, 592 mg, 77% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 4.55 (d, *J* = 5.77 Hz, 2H), 4.93 (s, 1H), 6.44 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.61 (td, *J* = 6.4, 1.3 Hz, 1H), 7.09−7.12 (m, 1H), 7.49 (dd, *J* = 7.9, 1.4 Hz, 2H), 8.18−8.22 (m, 2H) ppm, ^{13}C NMR (500 MHz, $CDCl_3$): δ 47.4, 109.9, 111.6, 118.7, 124.0, 127.5, 128.5, 132.6, 144.0, 146.6, 147.3 ppm. IR (CH_2Cl_2 film): ν 3415, 3075, 2852, 2451, 1925, 1726, 1597, 1516, 1457, 1428, 1345, 1319, 1285, 1235, 1162, 1130, 1110, 1083, 1046, 1019, 989, 926, 858, 842, 787, 737, 698, 656, 539, 462, 434 cm^{-1}. MS (EI; *m*/*z*): 77 (21), 78 (30), 89 (48), 90 (39), 91 (25), 106 (16), 136 (23), 184 (36), 186 (28), 306 (100, $M^{+\bullet}$). Anal. Calcd for $C_{13}H_{11}BrN_2O_2$ (307.15): C, 50.84; H, 3.61; Br, 26.01; N, 9.12. Found: C, 50.87; H, 3.65; N, 9.12; Br, 26.11.

4.1.2. Stille Couplings. Appropriate substituted amine (1 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.03 mmol, 35 mg) were put in a Schlenk tube under argon and dissolved in 5 mL of anhydrous toluene. Tributyl(vinyl)tin (1.1 mmol, 0.32 mL) was added, and the reaction was stirred at 120 °C for 3 h. After that, that the mixture was cooled to an ambient temperature and stirred with an aqueous solution of KF for an hour. After that, it was extracted with DCM (2 × 10 mL). Combined organic phases were washed with 10 mL of water, dried over $MgSO_4$, and evaporated. The residue was purified on the chromatography column, resulting in the corresponding styrene (50−70%).

11a, (*N*-methyl)-2-vinylaniline. Light yellow oil (0.5 mmol, 67 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.86 (s, 3H), 3.92 (s, 1H), 5.26−5.32 (m, 1H), 5.56−5.64 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.69−6.79 (m, 2H), 7.16−7.28 (m, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 30.8, 110.1, 116.2, 117.2, 124.2, 127.3, 129.0, 132.9, 146.2 ppm. IR (CH_2Cl_2 film): ν 3430, 3083, 3044, 2985, 2917, 2870, 2815, 2581, 1889, 1704, 1622, 1602, 1577, 1511, 1478, 1461, 1426, 1318, 1307, 1292, 1262, 1186, 1166, 1125, 1106, 1063, 1018, 993, 910, 823, 745, 694, 661, 472, 434 cm^{-1}. MS (EI; *m*/*z*): 51 (7), 65 (7), 77 (11), 91 (28), 117 (30), 118 (100), 119 (7), 130 (10), 132 (10), 133 (50, $M^{+\bullet}$). Anal. Calcd for $C_9H_{11}N$ (133.19): C, 81.16; N, 10.52; H, 8.32. Found: C, 80.95; N, 10.43; H, 8.15.

11b, (*N-iso*-propyl)-2-vinylaniline. Light yellow oil (0.1 mmol, 62 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.4 Hz, 6H), 3.50−3.75 (m, 2H), 5.30 (dd, *J* = 11.2, 2.0 Hz, 1H), 5.59 (dd, *J* = 17.2, 1.6 Hz, 1H), 6.63−6.79 (m, 3H), 7.15−7.20 (m, 1H), 7.24−7.28 (m, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 22.6, 23.1, 43.9, 44.2, 111.3, 116.0, 116.4, 116.8, 119.0, 124.2, 126.5, 127.6, 128.9, 129.0, 129.2, 130.1, 133.1, 144.4 ppm. IR (CH_2Cl_2 film): ν 3418, 3081, 3037, 2966, 2929, 2870, 2623, 1891, 1816, 1623, 1601, 1576, 1506, 1456, 1438, 1383, 1314, 1281, 1256, 1176, 1156, 1123, 1058, 1026, 996, 909, 861, 744, 696, 658, 619, 501 cm^{-1}. MS (EI; *m*/*z*): 77 (13), 91 (14), 117 (15), 118 (100), 119 (11), 130 (21), 131 (29), 144 (11), 146 (77), 161 (38, $M^{+\bullet}$). Anal. Calcd for $C_9H_{12}BrN$ (161.25): C, 81.94; H, 9.38; N, 8.69. Found: C, 81.68; H, 9.24; N, 8.76.

11c, (*N*-benzyl)-2-vinylaniline. Light yellow oil (0.5 mmol, 105 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.21 (s, 1H), 4.35 (s, 2H), 5.30 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.62 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.61−6.66 (d, 1H), 6.70−6.82 (m, 2H), 7.10−7.17 (m, 1H), 7.24−7.30 (m, 2H), 7.31−7.40 (m, 4H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 48.4, 111.0, 116.4, 117.6, 124.3, 127.3, 127.4, 127.5, 128.5, 128.7, 129.0, 133.0, 139.2, 145.0 ppm. IR (CH_2Cl_2 film): ν 3453, 2928, 2854, 1624, 1601, 1577, 1508, 1453, 1416, 1361, 1321, 1298, 1185, 1162, 1121, 1061, 1028, 994, 917, 823, 589, 519, 498, 457 cm^{-1}. MS (EI; *m*/*z*): 65 (7), 91 (38), 117 (9), 118 (100), 119 (6), 130 (5), 132 (7), 194 (7), 208 (4), 209 (27, $M^{+\bullet}$). Anal. Calcd for $C_{15}H_{15}N$ (209.29): C, 86.08; H, 7.22; N, 6.69. Found: C, 85.79; H, 7.22; N, 6.73.

11d, (*N*-(*p*-nitrobenzyl))-2-vinylaniline. Bright yellow crystals, mp 57−59 °C (0.7 mmol, 178 mg, 70% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 4.38 (s, 1H), 4.50 (d, *J* = 3.5 Hz, 2H), 5.37 (dd, *J* = 11.1, 1.6 Hz, 1H), 5.66 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.43−6.47 (m, 1H), 6.74−6.84 (m, 2H), 7.07−7.12 (m, 1H), 7.26 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 8.17−8.21 (m, 2H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 47.6, 111.0, 117.0, 118.2, 123.9, 124.7, 127.7, 128.9, 132.7, 144.2, 147.2 ppm. IR (CH_2Cl_2 film): ν 3415, 3075, 2852, 2451, 1925, 1726, 1597, 1516, 1457, 1428, 1345, 1319, 1285, 1235, 1162, 1130, 1110, 1083, 1046, 1019, 989, 926, 858, 842, 787, 737, 698, 656, 539, 462, 434 cm^{-1}. MS (EI; *m*/*z*): 77 (6), 89 (10), 90 (9), 91 (17), 117 (15), 118 (100), 119 (11), 130 (5), 132 (6), 254 (15, $M^{+\bullet}$). Anal. Calcd for $C_{15}H_{14}N_2O_2$ (254.29): C, 70.85; H, 5.55; N, 11.02. Found: C, 70.64; H, 5.50; N, 11.11.

4.1.3. Synthesis of ***11e****. 4.1.3.1. Wittig Reaction.* Predried methyl(triphenyl)phosphonium bromide (7 mmol, 2.5 g) was placed in a Schlenk flask under argon and dissolved in 5 mL of THF. The solution was cooled to −78 °C, and a 2.5 M butyllithium solution (7 mmol, 3 mL) was added dropwise. The mixture was then warmed to RT and stirred for an hour. Subsequently, the reaction mixture was again cooled to −70 °C and a solution of 2-fluoro-5-nitrobenzaldehyde (5 mmol) in 2 mL of THF was added dropwise. After that, the reaction was warmed to RT and stirred for 4 h. When completion was reached, the mixture was washed with a solution of saturated NH_4Cl and extracted with DCM (2 × 10 mL). Combined organic phases were dried over $MgSO_4$ and evaporated. The residue was purified on the chromatography column, resulting in a colorless oil crystallizing in the fridge (3.3 mmol, 556 mg, 72% yield).

13, 2-fluoro-5-nitrostyrene. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.56 (d, *J* = 11.2 Hz, 1H), 5.98 (d, *J* = 17.7, 1H), 6.58 (dd, *J* = 17.7, 11.2 Hz, 1H), 7.19 (t, *J* = 9.2 Hz, 1H), 8.42 (dd, *J* = 6.4, 2.8 Hz, 1H), 8.38−8.47 (m, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 122.9, 123.0, 124.4, 124.5, 126.6, 126.7, 127.3, 127.4 ppm. IR (CH_2Cl_2 film): ν 3096, 2926,

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2867, 1865, 1634, 1622, 1578, 1529, 1484, 1427, 1348, 1302, 1241, 1204, 1119, 1102, 1081, 990, 919, 907, 833, 813, 770, 740, 698, 636, 534, 493, 430 cm^{-1}. MS (EI; *m*/*z*): 51 (8), 75 (27), 95 (8), 101 (77), 109 (19), 120 (13), 121 (17), 137 (8), 167 (100, $M^{+\bullet}$). Anal. Calcd for $C_8H_6FNO_2$ (167.14): C, 57.49; H, 3.62; N, 8. 38; F, 11.37. Found: C, 53.37; H, 3.71; N, 8.51; F, 11.19.

4.1.3.2. Alkylation Reaction. Benzylamine (2 mmol, 0.2 mL), 2-fluoro-5-nitrostyrene (0.1 mmol, 160 mg), and potassium carbonate (2 mmol, 270 mg) were placed in a Schlenk tube under argon and dissolved in 4 mL of DMF. The reaction was stirred for 12 h in 40 °C. After that, the mixture was poured onto 15 mL of water and extracted with DCM (2 × 10 mL). Combined organic phases were dried over $MgSO_4$ and evaporated. The residue was purified on the chromatography column, resulting in yellow crystals (0.9 mmol, 224 mg, 89% yield). mp 79−81 °C.

11e, (*N*-benzyl)-5-nitro-2-vinylaniline. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.48 (d, *J* = 5.4 Hz, 1H), 4.93 (s, 1H), 5.49 (dd, *J* = 11.0, 1.3 Hz, 1H), 5.75 (dd, *J* = 17.2, 1.1 Hz, 1H), 6.58 (d, *J* = 9.1 Hz, 1H), 6.64−6.71 (m, 1H), 7.23−7.40 (m, 5H), 8.04 (dd, *J* = 9.2, 2.7 Hz, 1H), 8.15 (dd, *J* = 2.7, 0.4 Hz, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): 47.9, 109.3, 119.8, 123.5, 123.8, 125.6, 127.3, 127.9, 129.0, 130.8, 137.3, 138.3, 150.0 ppm. IR (CH_2Cl_2 film): ν 3393, 3180, 3085, 3059, 3025, 2931, 2644, 1959, 1886, 1671, 1623, 1602, 1581, 1528, 1494, 1454, 1431, 1366, 1326, 1287, 1170, 1146, 1095, 1078, 1027, 982, 903, 810, 764, 756, 741, 703, 644, 584, 532, 505, 474 cm^{-1}. MS (EI; *m*/*z*): 65 (16), 89 (7), 90 (5), 91 (100), 92 (8), 117 (53), 118 (5), 146 (5), 163 (49), 254 (19 $M^{+\bullet}$). Anal. Calcd for $C_{15}H_{14}N_2O_2$ (254.29): C, 70.85; H, 5.55; N, 11.02. Found: C, 70.68; H, 5.50; N, 10.84.

4.2. Synthesis of Catalysts 15a, 15c, 15d. Copper(I) chloride (0.35 mmol, 34 mg) and M21 (0.32 mmol, 300 mg) were placed in a Schlenk tube under argon and dissolved in 5 mL of anhydrous DCM. The mixture was heated to 40 °C, and a solution of an appropriate ligand precursor (0.35 mmol) in 1 mL of DCM was added. Heating was continued for an hour. After this time, the solvent was evaporated and the residue was redissolved in ethyl acetate and filtered through a Pasteur pipet containing cotton. The mixture was then purified utilizing column chromatography. The resulting product was concentrated in vacuo and the green solid was dissolved in a minimal amount of DCM and was washed with cold *n*-heptane (5 mL). The percipitate was filtered off, washed with 5 mL of *n*-heptane, and dried to afford green crystals (40−52%).

15a. Green solid (0.13 mmol, 76 mg, 40% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.35−2.65 (m, 21H), 3.42 (d, *J* = 6.0 Hz, 1H), 4.09 (s, 4H), 6.89 (dd, *J* = 6.5, 1.0 Hz, 1H), 7.07 (d, *J* = 11.5 Hz, 4H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.52−7.58 (m, 1H), 16.89 (s, 1H) ppm. ^{13}C NMR (500 MHz, CD_2Cl_2): δ 14.3, 19.3, 19.4, 21.3, 23.0, 29.4, 32.3, 35.0, 52.0, 119.9, 123.2, 128.1, 128.6, 129.6, 129. 7, 136.9, 138.8, 138.9, 138.9, 144.1, 155.7, 213.3, 296.1 ppm. IR (CH_2Cl_2 film): ν 3426, 3198, 3002, 2916, 2854, 2735, 1935, 1732, 1709, 1606, 1481, 1463, 1445, 1416, 1379, 1315, 1306, 1264, 1165, 1153, 1100, 1032, 929, 851, 797, 746, 699, 644, 618, 601, 590, 578, 528, 474, 446, 418 cm^{-1}. MS (FD/FI) (*m*/*z*): [$M^{+\bullet}$] 597.1. Anal. Calcd for $C_{29}H_{35}Cl_2N_3Ru$ (597.59): C, 58.29; H, 5.90; N, 7.03; Cl, 11.87. Found: C, 58.10; H, 5.75; N, 6.91; Cl, 12.16.

15c. Green solid (0.16 mmol, 111 mg, 52% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.40−2.54 (m, 18H), 3.67 (d, *J* = 10.5 Hz, 1H), 4.08 (s, 4H), 4.24 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.40−447 (m, 1H), 6.94 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.09 (s, 4H), 7.17−7.35 (m, 6H), 7.42−7.46 (m, 1H), 7.58−7.63 (m, 1H), 16.99 (s, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 51.8, 52.4, 120.5, 124.8, 127.7, 128.3, 129.1, 129.2, 129.9, 130.1, 137.4, 138.8, 138.9, 143.1, 155.8, 212.6, 297.0 ppm. IR (CH_2Cl_2 film): ν 3160, 3064, 3023, 2916, 2853, 2734, 1943, 1734, 1607, 1586, 1577, 1481, 1448, 1414, 1400, 1378, 1308, 1294, 1265, 1192, 1167, 1151, 1103, 1030, 999, 938, 932, 912, 887, 870, 851, 795, 768, 747, 741, 712, 696, 644, 626, 594, 577, 538, 506, 452, 432, 419 cm^{-1}. MS (FD/FI) (*m*/*z*): [$M^{+\bullet}$] 673.0. Anal. Calcd for $C_{35}H_{39}Cl_2N_3Ru$ (673.69): C, 62.40; H, 5.84; N, 6.24; Cl, 10.52. Found: C, 62.11; H, 5.96; N, 6.12; Cl, 10.76.

15d. Green solid (0.17 mmol, 119 mg, 52% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.32−2.48 (m, 18H), 3.78 (d, *J* = 11.5 Hz, 2H), 4.01 (s, 4H), 4.36−4.42 (m, 1H), 4.46−4.54 (m, 1H), 6.93 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.98−7.06 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.4 (d, *J* = 6.5, 2.0 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.59−7.64 (m, 1H), 8.04 (dd, *J* = 6.5, 2.0 Hz, 2H), 16.94 (s, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 50.5, 52.3, 120.6, 123.9, 124.4, 128.3, 129.4, 129.8, 129.9, 129.9, 138.6, 138.7, 139.0, 141.9, 144.2, 147.3, 155.4, 211.6, 296.5 ppm. IR (CH_2Cl_2 film): ν 3181, 2950, 2917, 2856, 1735, 1606, 1588, 1519, 1480, 1449, 1415, 1380, 1344, 1318, 1264, 1187, 1165, 1155, 1106, 1033, 1015, 991, 920, 853, 826, 796, 743, 737, 697, 644, 597, 579, 542, 443, 420 cm^{-1}. MS (FD/FI) (*m*/*z*): [$M^{+\bullet}$] 718.1. Anal. Calcd for $C_{35}H_{39}Cl_2N_4O_2Ru$ (719.7): C, 58.49; H, 5.33; N, 7.80; Cl, 9.87. Found: C, 58.22; H, 5.38; N, 8.06; Cl, 9.63.

■ ASSOCIATED CONTENT

Supporting Information

Equipment and chemicals used; general procedures of metathesis reactions; RCM time-conversion studies; preparative RCM, CM, and ene-yne reactions; CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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