# **ORGANOMETALLICS**

#### Article

# Influence of the N→Ru Coordinate Bond Length on the Activity of New Types of Hoveyda–Grubbs Olefin Metathesis Catalysts Containing a Six-Membered Chelate Ring Possessing a Ruthenium–Nitrogen Bond

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**ABSTRACT:** An efficient approach to the synthesis of new types of Hoveyda–Grubbs catalysts containing an N→Ru bond in a sixmembered chelate ring is proposed. The synthesis of the organometallic compounds is based on the interaction of ready accessible 2-vinylbenzylamines and 1,3-bis(2,4,6-trimethylphenyl)-2-trichloromethylimidazolidine ligands with dichloro(3-phenyl-1*H*inden-1-ylidene)bis(tricyclohexylphosphane)ruthenate, and it afforded the target ruthenium complexes in 70–80% yields. Areas of practical utility and potential applications of the obtained chelates were highlighted by tests of the catalysts in different olefin crossmetathesis (CM) and ring-closing-metathesis (RCM) reactions. These experiments revealed a high catalytic performance (up to  $10^{-2}$  mol %) of all the synthesized structures in a broad



temperature range. The structural peculiarities of the resultant ruthenium catalysts were thoroughly investigated by X-ray crystallography, which allowed making a reliable correlation between the structure of the metallo-complexes and their catalytic properties. It was proved that the bond length between ruthenium and nitrogen in the six-membered chelate ring has the greatest effect on the stability and efficiency of the catalyst. As a rule, the shorter and stronger the  $N \rightarrow Ru$  bond, the higher the stability of the complex and the worse its catalytic characteristics. In turn, the coordination  $N \rightarrow Ru$  bond length can be finely tuned and varied over a wide range of values by changing the steric volume of the cyclic substituents at the nitrogen atom, which will make it possible, as appropriate, to obtain in the future metal complexes with predictable stability and the required catalytic activity. Also, it was found that complexes in which the nitrogen atom is included in the morpholine or isoquinoline rings are the most efficient catalysts in this series. An attempt to establish a correlation between the  $N \rightarrow Ru$  bond length and the <sup>1</sup>H and <sup>13</sup>C chemical shifts in the Ru=CH fragment has been made.

# INTRODUCTION

Among the wide variety of ruthenium complexes with N-heterocyclic carbene ligands known to date, the secondgeneration Hoveyda–Grubbs catalysts (Figure 1), in which the coordination bond between ruthenium and oxygen atoms takes place, are the most popular both in synthetic practice and in industry.<sup>1</sup> Stability, tolerance in relation to various functional groups and to reaction conditions, and the high catalytic activity of these metallo-complexes toward alkene metathesis reactions<sup>2</sup> have overshadowed other possible ruthenium derivations comprising  $P \rightarrow Ru$ ,<sup>3</sup>  $S \rightarrow Ru$  (1)<sup>4</sup> and  $N \rightarrow Ru$  (2) coordination bonds which are part of a five-membered chelate ring. Meanwhile, there is only limited information on the synthesis, application, and catalytic activity of ruthenium derivatives (type 2) with an  $N \rightarrow Ru$  coordination bond included in the five-membered ring<sup>5</sup> (many of which have found practical applications),<sup>5g-m</sup> and ruthenium complexes (type 3) where an N $\rightarrow$ Ru intramolecular bond is a part of the six-membered cycle are practically unknown.<sup>6</sup> At the same time, as was shown in our recent publication,<sup>7</sup> metallocomplexes similar to 3 reveal a high catalytic activity toward

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Figure 1. Main types of NHC-ruthenium complexes with known catalytic activity in relation to metathesis reactions.

alkene metathesis reactions, along with ease of preparation and excellent storage stability.

In a previous study<sup>7</sup> we elucidated that among carbene ruthenium complexes of type 3 (R = H, Me, Et), the compound in which the chelating nitrogen atom was included in an additional cycle (3, R + R = heterocycle) possessed the highest catalytic activity toward olefin RCM, ROCM, and CM reactions (the catalyst concentration was less than 2 mol %). This observation was the main prerequisite for the initiation of the present work, in which we tried to synthesize and study in metathesis reactions new Hoveyda-Grubbs catalysts containing the most prevalent azaheterocyclic fragments of pyrrolidine, piperidine, isoindole, tetrahydroquinoline, morpholine, and piperazine. Thus, in the following we have attempted to solve the problem of determination of the dependence of the nature of the N-heterocyclic fragment in the lower hemisphere of a catalyst on the N $\rightarrow$ Ru bond length, which in turn has to define the catalytic potential of ruthenium benzylidene chelates (3).

# RESULTS AND DISCUSSION

**Synthesis of Ruthenium Complexes.** For further investigation, the initial 2-vinylbenzylamines 4 were obtained from tetrahydroisoquinoline according to a preparative method involving two successive one-pot alkylation steps (which give a nearly quantitative yield) and the Hofmann cleavage of the intermediate isoquinolinium salts to form 2-aminomethylstyrenes 4 in overall yields of higher than 60% (Scheme 1 and Table 1).<sup>6a,7,8</sup>

Scheme 1. Synthesis of the Starting N-(2-Ethenylbenzyl)-Substituted Azaheterocycles (4) and the Target Ruthenium Complexes (5)



The subsequent interaction of styrenes 4 with a common precursor for the synthesis of Hoveyda–Grubbs catalysts (Ind II, which was prepared from dichloro(3-phenyl-1*H*-inden-1-ylidene)bis(tricyclohexylphosphane)ruthenate (Ind I) and 2-(trichloromethyl)-1,3-bis(2,4,6-trimethylphenyl)imidazolidine (SIMesH(CCl<sub>3</sub>)))<sup>5i,7,9</sup> led to the formation of ruthenium complexes 5 in rather high yields (Table 1).

The selection of the starting dihalides was dictated by the need for maximum structural diversity of the resulting metallocomplexes. Thus, we obtained derivatives with a donor nitrogen atom included in five- and six-membered rings (5a,b) and in benzo-annellated five- and six-membered rings (5c,d), as well as in heterocycles containing an additional nitrogen or oxygen atom (5e,f). Our attempts to apply the aforementioned alkylation/Hoffmann cleavage procedure to the synthesis of similar styrenes 4 from 1,6-dibromohexane or 1,2-bis(2-bromoethyl)benzene, which should have led to the formation of seven-membered azepine rings, were unsuccessful due to extremely low yields during the alkylation step.

As a result, in the first part of this study, we have proposed and developed a multigram (up to 10 g of 5 in the last stage) convergent two-step method for the preparation of ruthenium complexes 5, based on simple commercially available starting materials: tetrahydroisoquinoline, terminal dihalides, a ruthenium complex (Ind I), and imidazolidine (SIMesH(CCl<sub>3</sub>)). All of the resulting products 5 were green solids of different shades which are stable for at least 3 years in an air atmosphere at r.t.

It should be noted here that in our previous publication,<sup>7</sup> two other *N*,*N*-dialkyl-substituted complexes, **5g**,**h**, were synthesized and characterized by the XRD method (Figure 2).

X-ray Crystallographic Studies of Catalysts 5. In order to establish the spatial structure of catalysts 5a-f, and in particular to measure the more important coordination bond lengths around a ruthenium atom, the Hoveyda-Grubbs-type catalysts synthesized above were crystallized from a CH<sub>2</sub>Cl<sub>2</sub>/ heptane mixture and then explored by X-ray diffraction structural analysis at 100 K (a summary of the crystallographic data is presented in Table S1 in the Supporting Information). According to the X-ray data, molecules 5a-f comprise a heterocyclic system with five-coordinated ruthenium. Compounds 5a,b form isostructural crystals with close unit cell parameters and have one CH<sub>2</sub>Cl<sub>2</sub> solvate molecule per each ruthenium complex molecule. Complexes 5c,f are also isostructural but crystallize without solvent. The asymmetric unit of the morpholine derivative 5e includes three independent molecules, but all three units have almost the same conformation, and bond lengths and angles vary only slightly (see Table 2 and the Tables S15 and S16 in the Supporting Information). All other compounds have one symmetrically independent ruthenium complex molecule. In all crystal structures, two chlorine atoms occupy typical trans positions relative to the central ruthenium atom. The ruthenium-containing six-membered ring has a slightly distorted envelope conformation for  $5a-d_{,f}$  (Table 2). The ruthenium atom and four carbon atoms lie in the same plane (the displacement is 0.01-0.08 Å), but the sixth pyramidal nitrogen atom deviates from it. The dihedral angles between the Ru–C<sub>4</sub> and Ru–N–C planes vary from 52.3 to  $58.2^{\circ}$ . The spatial structure of the catalyst 5e falls out of the range, which is important for further discussion. In the structure of 5e, the ruthenium-containing six-membered ring is more distorted: only four carbon atoms lie in the same plane (the displacement is 0.02 Å), while the Ru and N atoms deviate from it and form another plane with two adjacent carbon atoms (the displacement is 0.08-0.10 Å). The dihedral angle between the C<sub>4</sub> plane and the Ru-N-C plane is 43.8-46.7° (Table 2). This distortion is probably associated with the dipole-dipole interaction of the oxygen atom of the morpholine fragment and the chlorine atoms connected to the ruthenium. At least in

Entry	Initial alkyl halide	Styrene 4	Yield of 4, %	Complex 5	Yield of 5, %
a	Br(CH <sub>2</sub> ) <sub>4</sub> Br		70		79
b	Br(CH2)5Br		76		74
c	Cl		69		78
đ	Br		71	CI-	69
e	(ClCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O		78		75
f	(CICH2CH2)2NMe	Me	62	SIMes CI-,, CI-, N Me	71

#### Table 1. Structures and Yields of N-(2-Vinylbenzyl)heterocycles (4) and the Target Metallo-Complexes (5)



Figure 2. Previously obtained<sup>7</sup> ruthenium complexes.

all three crystallographically independent molecules of **5e**, both the chlorine atoms and the oxygen atom tend to be located as far as possible from each other (the  $N \rightarrow Ru$  bond occupies the axial position in the chair conformation of the morpholine ring).

Each of the ruthenium-containing heterocycles 5a-f has its own additional structural features, some of which will be briefly discussed below. The configuration of the dihydroisoindoline ring in 5c is typical for complexes with other metals;<sup>12</sup> all of the carbon atoms are in the same plane and the nitrogen atom deviates from that plane (the displacement is 0.4887(14) Å). For the tetrahydroisoquinoline conformation in 5d, all atoms except nitrogen and the methylene group closest to the nitrogen atom lie in the same plane. The deviation of the methylene carbon from the  $C_8$  plane is -0.5387(14) Å, and the deviation of the nitrogen atom is 0.2542(13) Å. Such a conformation is typical for tetrahydroisoquinoline (THQ); however, it is worth mentioning that there are a few examples where a nitrogen atom of THQ coordinates to a metal.<sup>13</sup> The morpholine cycle in 5e and the N-methylpiperazine cycle in 5f have the usual chair conformation, which is typical for a

morpholine moiety coordinated to a metal<sup>14</sup> and for piperazine when it coordinates to a metal by one nitrogen atom.<sup>15</sup>

However, the orientations of the heterocyclic fragments in complexes 5c,f and 5d,e toward the ruthenium center are different. The isoquinoline (5d) and morpholine (5e) substituents are skewed toward the chlorine atom, while isoindoline (5c) and methylpiperazine (5f) are twisted in the other direction (Figure 3). The torsion angles between the N $\rightarrow$ Ru bond and the neighboring C–C bonds of the heterocyclic moiety, going in opposite directions through the cycle, are 157.1 and 173.7° for 5c,f, respectively, and 61.6 and  $68.9^{\circ}$  for 5d,e, respectively, going in one direction and -149.6 and  $-167.0^{\circ}$  for 5c,f, respectively, and -79.1 and  $-69.4^{\circ}$ , respectively, for 5d,e in the other direction (for 5e the average value is given for three symmetrically independent molecules).

In all crystal structures 5a-f, the mesityl substituents are twisted to the imidazole plane on angles in the range of 82.7– 102.2°. The weak intramolecular hydrogen bonds C–H···Cl which form in all structures are given in Tables S5, S8, S11, S14, S17, and S20.

The length of the longest  $N(2) \rightarrow Ru(1)$  bond could have the strongest effect with regard to the possible catalytic activity. An analysis of the crystal structure data (Table 2) allows the conclusion that the ruthenium–nitrogen coordination bond elongates with an increase in the steric hindrance of the substituents at the nitrogen atom. Moreover, the volume of the part closest to the N(2) nitrogen atom has a stronger influence than the summary volume of the whole N substituent. Indeed, pyrrolidine-substituted compounds 5a,c have the shortest N $\rightarrow$  Ru bonds in the cyclic series because the nitrogen atom is part

Compd.	Molecular structure <sup>1</sup>	Angle RuC4/RuNC planes, °	N(2)→Ru(1),Å	Ru(1)—C(2),Å	Ru(1)=CH, Å
5a		58.2	2.223	2.043	1.832
5b	Rul Rul Rul	55.5	2.243	2.035	1.826
5c	Rut 2.227	54.7	2.227	2.037	1.829
5d	Ru1 N2 N2	52.3	2.297	2.030	1.832
5e	Ru1 2332340 N2	43.8—46.7 <sup>2</sup>	2.323-2.340	2.015-2.027	1.820—1.831
5f	Ru1 2.251	57.0	2.251	2.027	1.815
5g <sup>3</sup>	2243	56.8	2.243	2.034	1.820
5h <sup>3</sup>		53.3—54.3	2.282—2.297	2.0472.049	1.835—1.838
HG-II	Second-generation Hoveyda-Grubbs catalyst (O-i-Pr) <sup>10</sup>	-	2.2624	1.980	1.824
G-III	Third-generation Grubbs catalyst ( <i>bis</i> -3- bromopyridyl) <sup>11</sup>	-	2.383	2.075	1.848

<sup>1</sup>Thermal ellipsoids are shown at the 50% probability level, and all hydrogen atoms are omitted for clarity. <sup>2</sup>The dihedral angle between the C<sub>4</sub> plane and the = $CH-Ru(1)-N(2)-CH_2$  plane. <sup>3</sup>*N*,*N*-Dialkyl-substituted complexes **5g**,**h** were synthesized previously<sup>7</sup> and added to the table for comparison. <sup>4</sup>Length of the O→Ru bond.



Figure 3. Comparison of orientations of the N-heterocyclic substituent: overlay of complexes  $5c_{,f}$  with the same orientation (a); overlay of  $5c_{,d}$  with different orientations (b). Complexes are shown in red (5c), green (5f), and blue (5d).

of the five-membered rings. In metal complexes 5b,d,f, the nitrogen atom is part of the larger six-membered ring, which makes the  $N \rightarrow Ru$  bond longer. At the same time, a comparison of the ruthenium pyrrolidine derivatives 5a,c shows that the bulky isoindole substituent in 5c makes the bond slightly longer than in the case of 5a with the pyrrolidinium substituent. On comparison of the structures of compounds 5b,f and 5d, comprising six-membered azaheterocycles, a similar trend may be observed. The summary trend, i.e. an increase in the coordination  $N \rightarrow Ru$ bond length along the series 5a (2.223 Å)-5c (2.227 Å)-5b (2.243 Å) - 5f (2.251 Å) - 5d (2.297 Å) - 5e (2.326 Å),suggests that compound 5e, bearing a morpholine ring, is expected to be the most active as a metathesis catalyst. The opposite trend is observed in the variation of the length of the  $C(2) \rightarrow Ru(1)$  bond (see Table 2); this bond has the shortest length in the theoretically most active metal complex 5e (2.015-2.027 Å) and the largest length in compound 5a (2.043 Å).

From the point of view of the further practical application of chelates 5 synthesized in this work, it seems important to compare the  $N \rightarrow Ru$  bond lengths (i.e., theoretical activity) of the "cyclic" complexes 5a-f with the simplest "open" or "linear" N,N-dimethyl (5g) and N,N-diethyl (5h) benzylidene ruthenium analogues<sup>7</sup> as well with the structures of the most common commercially available HG-II<sup>10</sup> and G-III<sup>11</sup> catalysts. X-ray data for compound 5g reveal a distance of 2.24 Å between the key heteroatoms, which is close to similar values in heterocycles 5a-f (2.22–2.25 Å), while a longer N $\rightarrow$ Ru bond (2.28–2.30 Å) is observed in the diethyl analogue 5h, which is almost the same as the length in tetrahydroisoquinoline 5d (2.30 Å). Thus, there is every reason to believe that the catalytic activity of ruthenium derivatives 5a-f will be close to that of dimethyl-substituted 5g, whereas diethyl catalyst 5h will have properties similar to those of the isoquinoline derivative **5d**. The morpholine derivative has the longest rutheniumnitrogen coordination bond comparable with the same fragment of the third-generation Grubbs catalyst,<sup>11</sup> 2.326 Å (for **5e**) versus 2.383 Å (for **G-III**), which in our opinion implies their approximate catalytic activity.

**NMR Studies of Catalysts 5.** The main prerequisite for this part of the work was the idea of establishing of a possible correlation between the  $N \rightarrow Ru$  bond length and the chemical shifts of the nuclei surrounding the ruthenium center. The successful solution of this problem would make it possible to predict the catalytic performance of ruthenium complexes **5** on the basis of only the readily available data of the NMR spectra without resorting to X-ray structural studies, which are not always feasible.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the Ru complexes **5a-h** have signals characteristic of the CH=Ru fragment in strongly downfield spectral regions typical for ruthenium Grubbs catalysts. The scatter of chemical shifts for various substituents in the series of complexes **5a-h** is very narrow for both <sup>1</sup>H and <sup>13</sup>C and is too narrow for the possibility of a reliable prediction and relationship with Ru=C or N→Ru bond lengths. Only the 18.71–18.94 ppm range for <sup>1</sup>H and the 311.2–316.2 ppm diapason for <sup>13</sup>C NMR were detected in CD<sub>2</sub>Cl<sub>2</sub> solutions at r.t. (Figure 4).



Figure 4. Example of the representative downfield regions of  ${}^{1}$ H and  ${}^{13}$ C NMR spectra for ruthenium complex 5d.

Mostly, the chemical shifts of the signals in these regions are randomly distributed in comparison with the Ru=C and N $\rightarrow$ Ru bond lengths (see Tables 2 and 3). Moreover, exact chemical shifts quite strongly depend on concentration and solvation effects for the same samples in ranges to  $\pm 0.1$  ppm for <sup>1</sup>H and  $\pm 2.0$  ppm for <sup>13</sup>C (which is too great in comparison with the difference in chemical shifts for different complexes). Apparently, the <sup>1</sup>H and <sup>13</sup>C chemical shifts of the CH=Ru fragment depend primarily on nonlinear effects associated with the 3D conformation in solution of one of the two mesitylene aromatic rings and the anisotropic effect of its  $\pi$  system (see Xray structures in Table 2 and Figure 5 for a clear representation). It should also be noted that both the <sup>1</sup>H and <sup>13</sup>C signals of the CH=Ru fragment have no  ${}^{1}\text{H}-{}^{99}\text{Ru}/{}^{101}\text{Ru}$  or  ${}^{13}\text{C}-{}^{99}\text{Ru}/{}^{101}\text{Ru}$  coupling constants due to the very high quadrupole moments of the <sup>99</sup>Ru and <sup>101</sup>Ru isotopes. For the same reason, we also failed to obtain any <sup>99</sup>Ru signals even after numerous attempts.

Table 3. N $\rightarrow$ Ru and Ru=CH Bond Lengths in Complexes 5 in Comparison to <sup>1</sup>H and <sup>13</sup>C Chemical Shifts of the Ru=CH Fragment

Compd.	Bond length, Å		<b>δ CH=Ru</b> (in CD <sub>2</sub> Cl <sub>2</sub> ),		
			ppm		
	N→Ru	Ru=C	$\delta(^{1}H)$	δ( <sup>13</sup> C)	
5a	2.223	1.832	18.84	312.6	
5b	2.243	1.826	18.75	313.9	
5c	2.227	1.829	18.77	311.2	
5d	2.297	1.832	18.80	312.3	
5e	2.323-2.340	1.820-1.831	18.94	316.2	
5f	2.251	1.815	18.79	313.8	
5g	2.243	1.820	18.71	311.6	
5h	2.282-2.297	1.835-1.838	18.74	312.6	



**Figure 5.** Schematic representation of the influence of the anisotropic effect of the mesitylene  $\pi$  system on the CH=Ru fragment in **5***f*, as an example.

Moreover, even when the difficult-to-predict through-space effect of the mesityl fragment in solution is taken into account, the chemical shifts of the <sup>1</sup>H and <sup>13</sup>C nuclei (highlighted in dark gray in Table 3) of the Ru=CH moiety in catalyst 5e turn out to be the greatest in value in comparison to all other metal derivatives 5. The greatest difference is observed in the carbon spectra: 316.2 ppm for 5e versus 311.2–313.8 ppm for all other complexes 5, which is in good correlation with the length of the N→Ru coordination bond: ~2.33 Å in 5e vs 2.22–2.30 Å in all other complexes 5.

**Catalytic Activity of Complexes 5 in Metathesis Reactions.** The theoretical predictions of the catalytic performance of complexes 5 made in the precedent part, based on consideration of the length of the coordination  $N \rightarrow$ Ru bond, were practically confirmed using standard metathesis objects.

The simplest olefin metathesis reactions of a self-crossmetathesis of styrene (6) were conducted to investigate the catalytic properties in the series of complexes 5a-f and to evaluate its behavior in these testing transformations (Scheme 2).

The results have shown that almost all of the studied catalysts were inefficient without thermal activation in the self-CM reaction of styrene, with the notable exception of 5e, which provided an 86% yield of stilbene (7) (Table 4). Evaluation of the reaction temperature allowed us to better distinguish the difference in catalytic behavior in the series. To

Scheme 2. Self-CM Reaction of Styrene Used for Characterization of Catalysts 5a-f



Table 4. Reaction Conditions and Conversion in the Reaction of Self-CM of Styrene (6) with a 0.1 mol % Loading of Catalysts under an Ar Atmosphere

Entry	Catalyst	Solvent	Conditions	Ratio of 6/7 <sup>1</sup>
1	5a	CHCl <sub>3</sub>	1 h, r.t.	100/0
2	5b	CHCl <sub>3</sub>	1 h, r.t.	90/10
3	5c	CHCl <sub>3</sub>	1 h, r.t.	94/6
4	5d	CHCl <sub>3</sub>	1 h, r.t.	69/31
5	5e	CHCl <sub>3</sub>	1 h, r.t.	14/86
6	5f	CHCl <sub>3</sub>	1 h, r.t.	83/17
7	5a	$CH_2Cl_2$	1 h, reflux	94/6
8	5b	$CH_2Cl_2$	1 h, reflux	74/26
9	5c	$CH_2Cl_2$	1 h, reflux	81/19
10	5d	$CH_2Cl_2$	1 h, reflux	0/100
11	5e	$CH_2Cl_2$	1 h, reflux	0/100
12	5f	$CH_2Cl_2$	1 h, reflux	39/61

 $^16/7$  ratio was determined by  $^1\mathrm{H}$  NMR analysis of the crude reaction mixtures.

our satisfaction, the experimental data matched with our expectations of the catalytic properties of complexes in this range (Tables 2 and 4). Indeed, the morpholine-containing ruthenium derivative **5e** exhibited the highest efficiency in both dichloromethane and chloroform at r.t. in a 0.1 mol % concentration.

In the medium of boiling absolute chloroform under an argon atmosphere, the complexes 5 all provided 100% conversion of styrene in a 0.1 mol % concentration.

For further determination of the catalytic properties of complexes 5a-f, we investigated their activity toward the standard ring-closing-metathesis (RCM) reaction of diallyl amide 8 (Scheme 3).

Scheme 3. RCM of *N*,*N*-Diallyltosylamide Used for Characterization of Catalysts 5a-f



In contrast, in this type of metathesis reaction, all of the investigated catalysts 5 gave moderate to high yields of pyrrolidine 9 even at r.t. with low catalyst loading (0.05-0.1 mol %) for 1 h (Table 5). Catalysts 5d,e were found to be the most efficient in this case. Using 0.25 mol % of the catalyst and a 1 h reaction time resulted in 100% conversion of the initial diallyltosylamide 8 in all cases. It should be noted that if the reaction time was increased to 2 h or more in the case of the 0.1 mol % catalyst loading, the difference in the catalytic activity of metal complexes 5 became insignificant; all reactions exhibited a conversion of close to 100%.

Another attempt in catalytic trials was to study the selectivity of the obtained catalysts. For this purpose, one of the most used model reactions of cross-metathesis coupling between styrene (6) and (Z)-1,4-diacetoxy-2-butene (10) was chosen (Scheme 4).

In this reaction all of the catalysts showed no activity in both  $CHCl_3$  and 1,2-dichlorethane up to a temperature of about 85 °C with 0.1 mol % loading. An increase in temperature to 120

Table 5. Reaction Conditions<sup>1</sup> and Conversion in the RCM Reaction of *N*,*N*-Diallyltosylamide (8)

	Catalyst	Ratio <sup>2</sup> of 8/9			
Entry		Catalyst loading	Catalyst loading		
		0.1 mol %	0.05 mol %		
1	5a	25/75	85/15		
2	5b	6/94	57/43		
3	5c	10/90	58/42		
4	5d	0/100	29/71		
5	5e	0/100	9/91		
6	5f	5/95	50/50		

<sup>1</sup>All reactions were performed at r.t. for 1 h, and absolute  $CHCl_3$  was used as the solvent. <sup>2</sup>8/9 ratio was determined by <sup>1</sup>H NMR analysis of the crude reaction mixtures.

Scheme 4. CM Reaction of Styrene Used for Characterization of Catalysts 5a-f



°C under microwave irradiation was more efficient. Under these conditions, there was almost no difference in efficiency of the catalysts. All of them provided a mixture of the target molecule **10** and the byproducts: stilbene (7) formed by the self-CM of styrene (6), (E)-1,4-diacetoxy-2-butene (11) due to the isomerization of **10**, and CM products **12** and **13** (Table 6). The yields of targeted products were low and the catalysts

Table 6. Reaction Conditions<sup>1</sup> and Conversion in the CM Reaction of Styrene (6) and (Z)-1,4-Diacetoxy-2-butene (10) with a 0.1 mol % Loading of Catalysts

Enter	Catalyst	Ratio of	Yield of 12 +	12/13	3 04 0.03	
Епігу		$7/10/11/12/13^2$	13 (%)	(E/Z)	%ee-	
1	5a	24/13/33/26/4	17	87/13	74	
2	5b	38/16/3/39/4	24	91/9	82	
3	5c	40/14/4/39/3	24	93/7	86	
4	5d	36/17/7/36/4	23	90/10	80	
5	5e	43/15/2/38/2	22	95/5	90	
6	5f	38/18/4/37/3	23	93/7	86	

<sup>1</sup>All reactions were performed under microwave irradiation (0.25 h, 200 W, 120 °C), and absolute CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent. <sup>2</sup>The ratio was determined by <sup>1</sup>H NMR analysis of the crude reaction mixtures after catalyst separation. <sup>3</sup>ee denotes an excess of the predominant geometric isomer.

exhibited poor selectivity in this type of metathesis reaction, possibly due to the high temperature applied to initiate the reaction.

The difference in catalytic performance among the investigated catalysts has proved our suggestion about the strong influence of the length of the ruthenium-nitrogen coordination bond on the catalytic behavior of these complexes, at least at moderate temperatures. Moreover,

catalytic studies revealed a very high efficiency of catalyst **5e** in these types of reactions, making it a perfect candidate for further catalytic trials toward various challenging metathesis transformations, especially in ROMP reactions, in which its unique properties, such as latency at r.t. and very good performance at elevated temperatures, might become a very useful tool, for example, in the synthesis of highly tactic polymers.

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The present work reports on an efficient method for the synthesis of 2-(N,N-dialkylaminomethyl)styrenes. The resultant vinylbenzenes are excellent precursors for the two-step synthesis of new Hoveyda–Grubbs-type catalysts bearing an  $N \rightarrow Ru$  coordinate bond in a six-membered ring. This process does not require the use of complex equipment or extremely expensive or toxic reagents. The structure of the catalysts was elucidated in detail by 2D NMR and X-ray crystallography. The high catalytic performance of the metallo-complexes was demonstrated by several examples of cross-metathesis (CM) and ring-closing (RCM), and it was proven by these examples that the longer the N $\rightarrow$ Ru bond, the better the catalytic performance of the catalytic performance performance

Furthermore, almost all of the steps of the ligand and catalyst syntheses were accomplished in preparative and multigram scales under conditions close to those used in industrial processes.

#### ASSOCIATED CONTENT

# **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00647.

Details of catalyst syntheses, NMR spectra for all previously unreported compounds, and X-ray crystallog-raphy data (PDF)

### **Accession Codes**

CCDC 1957385–1957390 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

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