

Monothiolate ruthenium alkylidene complexes with tricyclic fluorinated N-heterocyclic carbene ligands

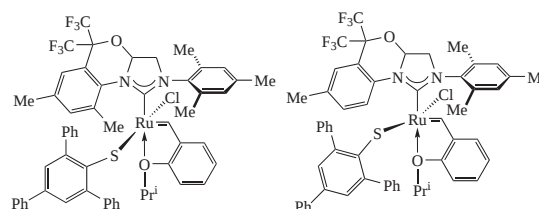
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New monothiolate ruthenium alkylidene complexes bearing bulky tricyclic N-heterocyclic carbene ligands decorated with two geminal trifluoromethyl groups were synthesized. Their catalytic activity in representative olefin metathesis reactions, such as ring closing metathesis of diallyltosylamine and self-metathesis of allylbenzene, has been evaluated.



Over the past decade, olefin metathesis along with the advent of efficient ruthenium alkylidene complexes have experienced a dramatic development becoming the highly versatile method for the catalytic construction of carbon–carbon bonds.¹ Ruthenium metathesis catalysts bearing N-heterocyclic carbene (NHC) ligands, commonly used for various synthetic purposes in academia, have nowadays begun finding industrial applications.²

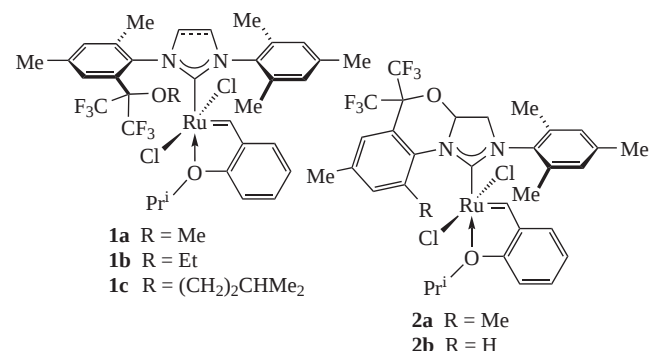
Despite substantial progress in the area highlighting the great potential of these ligands, the particular attention is focused on complexes with unsymmetrical NHCs possessing the unique capability of rapid fine-tuning of their catalytic properties by modifying the NHC stereoelectronics.³ The most attractive recent examples include the application of chelating unsymmetrical NHC ligands in the Ru-catalyzed Z-selective cross-metathesis (CM).⁴ The further development of new catalytic systems bearing unsymmetrical NHC ligands is therefore of current interest.

We have recently developed an efficient procedure for the preparation of novel olefin metathesis catalysts of Hoveyda–Grubbs type based on the sterically demanding unsymmetrical NHC ligands bearing two geminal trifluoromethyl groups.⁵

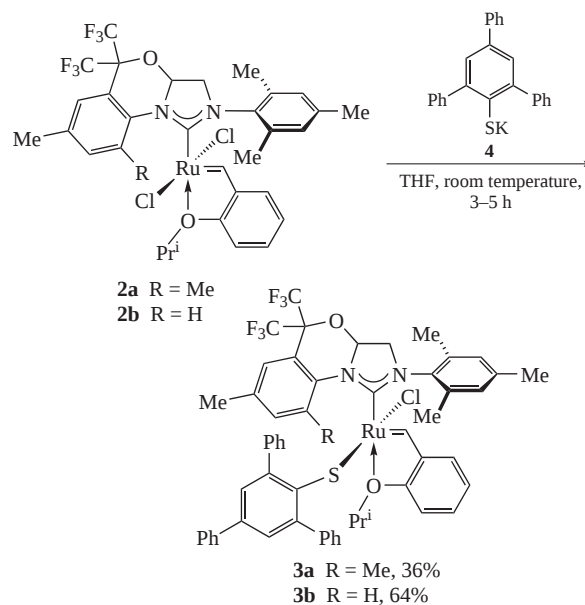
The both types of complexes **1a–c** and **2a,b** have exhibited a good catalytic activity in the ring closing metathesis (RCM) of diallyl and allylmethyl malonates as well as in CM of allylbenzene. Noteworthy, the catalysts **2a,b** comprising sterically rigid

NHC demonstrated promising results in self-metathesis of allylbenzene, outperforming commercially available Hoveyda–Grubbs catalyst HG-II (e.g., remarkably low content of isomerization products along with almost quantitative yields of metathesis product were observed).^{5(d)}

At the same time, Jensen *et al.* have recently reported a series of highly Z-selective olefin metathesis catalysts derived from G-II and HG-II catalysts *via* a simple substitution of one chlorine atom by the bulky 2,4,6-triphenylbenzenethiolate group.⁶ Meanwhile, significant amounts of isomerization products has been observed in the reaction mixtures.^{6(a)} Thus, inspired by Jensen's work and by own findings,^{5(d)} we decided to install into complexes **2a,b**, which are able to hamper the isomerization pathways, the sterically bulky thiolate group and to check the performance and selectivity of resulting complexes **3a** and **3b** (Scheme 1).



Active in RCM and preventing isomerization in CM



Scheme 1

For this purpose, starting complexes **2a,b** were treated with 1.2 equivalent of potassium thiolate **4** prepared from 2,4,6-triphenyl-benzenethiol and potassium hydride.^{6(a)} The reactions proceed at room temperature in anhydrous THF under argon atmosphere for 3 h to afford desired complexes **3a,b** as air stable light green solids in 36 and 64% yields, respectively (see Scheme 1).

The obtained compounds were fully characterized by ¹H, ¹⁹F and ¹³C NMR spectroscopy and elemental analysis. In ¹H NMR spectra of **3a,b** measured at room temperature, the signals of intrinsic benzyldiene protons were observed around 14.96 and 13.65 ppm, respectively, as singlets in each case. Their ¹³C NMR spectra of NHCs contained the corresponding resonances at 215.8 (**3a**) and 215.1 ppm (**3b**) attributed to the carbene center, which are in the expected range for aryl-substituted imidazolylidenes (see Online Supplementary Materials for the complete NMR data). In addition, single crystals of good quality for X-ray analysis were isolated for ruthenium complex **3b** by slow diffusion of hexane into its concentrated solution in a mixture of benzene and CH₂Cl₂ (Figure 1).[†]

The single crystal X-ray analysis of **3b** revealed the presence of two independent molecules (A and B) in the crystal cell, wherein chloride anion of A is hydrogen bonded with solvate molecule of CH₂Cl₂ (distance C...Cl 3.584 Å) leading to some discrepancies in the values of bond length and valence angles. The analogous hydrogen bond with CH₂Cl₂ has been previously reported for a similar monothiolate IMes-complex.^{6(a)}

To ensure that the obtained complexes are metathesis active, their performance was checked on the model RCM reaction of diallyltosylamine **5** (Scheme 2) under the standard conditions

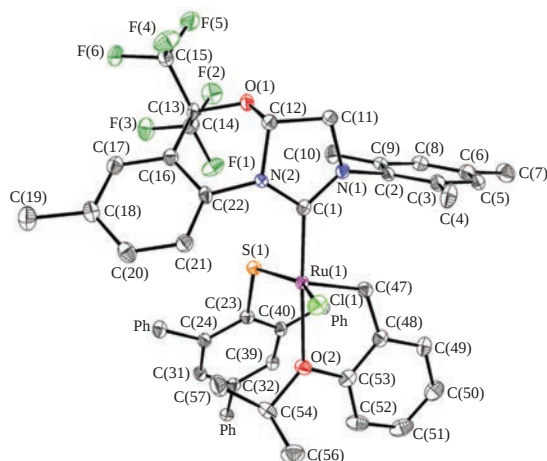


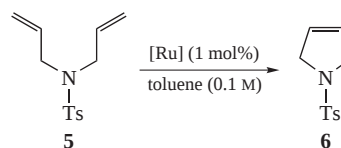
Figure 1 Molecular structure of complex **3b** (two independent molecules, molecule A) showing thermal ellipsoids at the 50% probability level. Only the support carbons of Ph-substituents of arylthiolate ligand are shown. Hydrogen atoms are omitted for clarity. For bond lengths and angles, see Online Supplementary Materials.

[†] Crystal data for **3b**: C₅₆H₄₉ClF₆N₂O₂RuS, *M* = 1107.01, triclinic, space group *P*1̄ (no. 2), at 120 K: *a* = 11.6280(13), *b* = 21.281(2) and *c* = 22.280(3) Å, α = 113.133(2)°, β = 92.415(3)°, γ = 102.219(3)°, *V* = 4906.7(10) Å³, *Z* = 4, *d*_{calc} = 1.499 g cm⁻³. X-ray analysis was performed on a Bruker AXS SMART 1000 instrument equipped with graphite monochromator and CCD-detector operating at λ(MoKα) = 0.71073 Å, ω-scanning, 2θ_{max} = 60°, 28598 measured reflections, 19669 independent reflections with *F*² > 2σ(*I*), μ = 0.540 mm⁻¹, *R*₁ = 0.0506, *wR*₂ = 0.0806. Corrections for absorption were made using SADABS software.⁷ The structure was solved by direct method and refined by full-matrix least squares method for *F*² with anisotropic parameters for all non-hydrogen atoms. All calculations were performed in the SAINT⁸ and SHELXTL-97⁹ software packages.

CCDC 1866377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

Table 1 Activity of catalysts **3a,b** in RCM of diallyltosylamine **5** as compared to that of HG-II and **2a,b**.

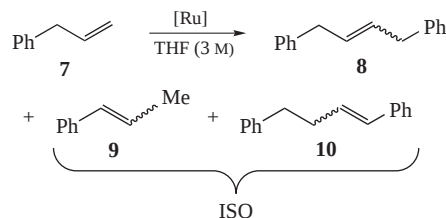
Entry	[Ru]	<i>T</i> /°C	<i>t</i> /h	Yield of 6 (%)
1	HG-II	30	1	100
2	2a	30	1	100
3	2b	30	1	57
			4	82
			24	100
4	3a	30	1	40
			4	62
			24	86
			48	100
5	3b	30	24	0
			48	5
6	3b	100	1	61
			4	81
			24	95
			48	100



Scheme 2

for evaluation of olefin metathesis catalysts.¹⁰ Commercially available complex RuCl₂(H₂IMes)[=CH(2-PrⁱOC₆H₄)] HG-II [H₂IMes = bis(mesityl)imidazolynilidene] was used as reference catalyst.¹¹ As a result, new catalysts **3a** and **3b** were proved to be less active as compared with their dichloride precursors **2a** and **2b** as well as with reference catalyst HG-II (Table 1). Nevertheless, the full conversion can be slowly achieved in 24 h for **3a** (see Table 1, entry 4) and 48 h for **3b** at 100 °C (see Table 1, entry 6), which reflects the high stability of catalysts in solution.

Next, an efficiency of new complexes in the self-metathesis of allylbenzene **7** (Scheme 3) was estimated. Complexes **3a,b** demonstrated a lower catalytic activity and selectivity in this reaction in comparison with their dichloride precursors **2a,b** (Table 2). The best yield of metathesis product (37%) has been achieved for catalyst **3a** at 35 °C in THF in 2 h (see Table 2, entry 4). The enhanced catalyst loading (1 mol%) led to the better yield of **8** (77%, see Table 2, entry 6), but the content of isomerization products (ISO, primarily styrenes **9** and **10**, see Scheme 3) increased several times. Nevertheless, the ISO content in most trails of new catalysts was noticeably lower as compared to HG-II (see Table 2, entry 1). At the same time, catalysts **3a** and **3b** did not induce *Z*-selectivity comparable to their nearest analogue containing IMes ligand^{6(a)} in this reaction. In all cases, the *E/Z* ratios have not exceeded 4 : 1.



Scheme 3

In conclusion, the synthesis of new monothiolate ruthenium alkylidene complexes bearing bulky tricyclic NHC ligands decorated with the two geminal trifluoromethyl groups has been developed. The complexes synthesized have exhibited a moderate catalytic activity in RCM of diallyltosylamine reaching

Table 2 Activity of catalysts **3a,b** in self-metathesis of allylbenzene **7** as compared to that of HG-II and **2a,b**.^a

Entry	[Ru] cat.	Cat. loading (mol%)	t/h	Yield of 8^b (%)	Yield of ISO (%)
1	HG-II	0.1	1	74	14
			2	75	15
2	2a	0.1	1	76	<1
			2	78	<1
3	2b	0.1	1	75	<1
			2	77	<1
4	3a	0.1	1	23	<1
			2	37	<1
5	3b	0.1	1	8	<1
			2	12	<1
6	3a	1.0	1	75	2
			2	77	2
7	3b^c	1.0	1	31	2
			4	46	6

^a Allylbenzene (3 mol dm⁻³), 35 °C. Conversions and yields were determined by ¹H NMR spectroscopy. ^b E/Z ratios in all cases were in a range of 4:1 to 5:1, respectively. ^c Reaction temperature was 60 °C.

the full conversion under heating in THF for two days. In the case of self-metathesis of allyl benzene, these new catalysts were less active than their dichloride precursors demonstrating from moderate to good yields along with an acceptable content of isomerization products under increased catalyst loading. The revealed data can be useful in the design and synthesis of novel more selective olefin metathesis catalysts.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.011.

References

- (a) *Handbook of Metathesis*, 2nd edn., eds. R. H. Grubbs, A. G. Wenzel, D. J. O'Leary and E. Khosravi, Wiley-VCH, Weinheim, 2015; (b) *Olefin Metathesis: Theory and Practice*, 1st edn., ed. K. Grela, John Wiley and Sons, Hoboken, 2014.
- (a) M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953; (b) S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168; (c) L. Jafarpour, H. J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5416.

- (a) J. Tornatzky, A. Kannenberg and S. Blechert, *Dalton Trans.*, 2012, **41**, 8215; (b) F. Hamad, T. Sun, S. Xiao and F. Verpoort, *Coord. Chem. Rev.*, 2013, **257**, 2274; (c) T. P. Montgomery, A. M. Johns and R. H. Grubbs, *Catalysts*, 2017, **7**, 87; (d) V. Paradiso, V. Bertolasi, C. Costabile, T. Caruso, M. Dąbrowski, K. Grela and F. Grisi, *Organometallics*, 2017, **36**, 3692; (e) P. Małecki, K. Gajda, O. Abliatimov, M. Malińska, R. Gajda, K. Woźniak, A. Kajetanowicz and K. Grela, *Organometallics*, 2017, **36**, 2153.
- (a) K. Endo and R. H. Grubbs, *J. Am. Chem. Soc.*, 2011, **133**, 8525; (b) B. K. Keitz, K. Endo, P. R. Patel, M. B. Herbert and R. H. Grubbs, *J. Am. Chem. Soc.*, 2012, **134**, 693; (c) M. B. Herbert, B. A. Suslick, P. Liu, L. Zou, P. K. Dornan, K. N. Houk and R. H. Grubbs, *Organometallics*, 2015, **34**, 2858; (d) A. Dumas, R. Tarrieu, T. Vives, T. Roisnel, V. Dorcet, O. Baslé and M. Mauduit, *ACS Catal.*, 2018, **8**, 3257.
- (a) S. M. Masoud, A. K. Mailyan, V. Dorcet, T. Roisnel, P. H. Dixneuf, C. Bruneau and S. N. Osipov, *Organometallics*, 2015, **34**, 2305; (b) S. M. Masoud, M. A. Topchiy, A. S. Peregodov, T. Roisnel, P. H. Dixneuf, C. Bruneau and S. N. Osipov, *J. Fluorine Chem.*, 2017, **200**, 66; (c) S. M. Masoud, A. K. Mailyan, A. S. Peregodov, C. Bruneau and S. N. Osipov, *Mendelev Commun.*, 2016, **26**, 474; (d) S. M. Masoud, T. R. Akmalov, K. A. Palagin, F. M. Dolgushin, S. E. Nefedov and S. N. Osipov, *Eur. J. Org. Chem.*, 2018, 5988; (e) T. R. Akmalov, S. M. Masoud, D. A. Petropavlovskikh, M. A. Zotova, S. E. Nefedov and S. N. Osipov, *Mendelev Commun.*, 2018, **28**, 609.
- (a) G. Occhipinti, F. R. Hansen, K. W. Törnroos and V. R. Jensen, *J. Am. Chem. Soc.*, 2013, **135**, 3331; (b) G. Occhipinti, V. Koudriavtsev, K. W. Törnroos and V. R. Jensen, *Dalton Trans.*, 2014, **43**, 11106; (c) W. Smit, V. Koudriavtsev, G. Occhipinti, K. W. Törnroos and V. R. Jensen, *Organometallics*, 2016, **35**, 1825; (d) G. Occhipinti, K. W. Törnroos and V. R. Jensen, *Organometallics*, 2017, **36**, 3284.
- G. M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison, WI, 1997.
- SMART*, v. 5.051 and *SAINT*, v. 5.00, Area Detector Control and Integration Software, Bruker AXS Inc., Madison, WI, 1998.
- G. M. Sheldrick, *SHELXTL*, v. 5.10, Bruker AXS Inc., Madison, WI, 1997.
- (a) M. Bieniek, R. Bujok, M. Cabaj, N. Lugan, G. Lavigne, D. Arlt and K. Grela, *J. Am. Chem. Soc.*, 2006, **128**, 13652; (b) Ł. Gułajski, A. Michrowska, R. Bujok and K. Grela, *J. Mol. Catal. A: Chem.*, 2006, **254**, 118; (c) A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos and K. Grela, *J. Am. Chem. Soc.*, 2004, **126**, 9318.
- J. S. Kingsbury, J. P. A. Harrity, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 791.

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