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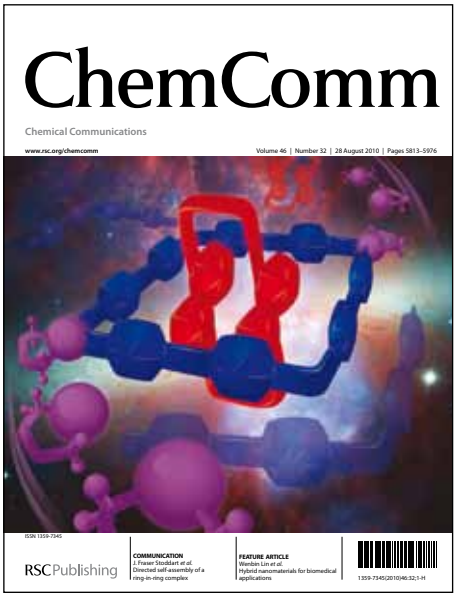

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Ruthenium Nitronate Complexes as Tunable Catalysts for Olefin Metathesis and Other Transformations

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Novel ruthenium(II) complexes were obtained as a result of a stoichiometric reaction of Grubbs' benzylidene second generation catalysts with 3-nitropropene. These stable complexes, formally ruthenaisoxazole *N*-oxide derivatives, display activity in both metathesis and non-metathetic processes such as cycloisomerisation, isomerization and hydrogenation.

Since the discovery of stable molybdenum and ruthenium catalysts, olefin metathesis has became powerful tool in organic synthesis.[1] During the last twenty years the large number of reports concerning new improved catalysts was published, and the scope of the metathesis transformation was greatly extended.[2] Moreover, application of these catalysts in non-metathetic transformations has been also reported.[3] In the ruthenium-branch of metathesis, a great deal of work was invested to fine-tuning the properties of the "parent" ruthenium benzylidene (**1**), indenylidene (**2**) and 2-alkoxy-benzylidene (**3**) complexes (Fig. 1).[4,5]

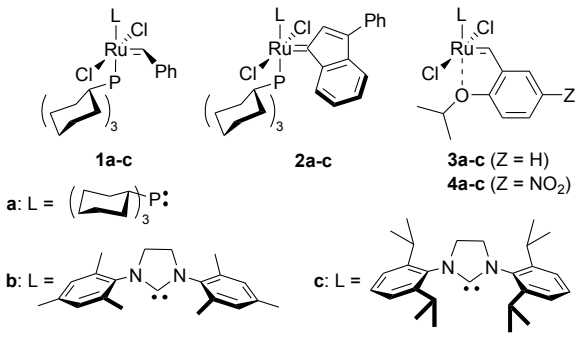
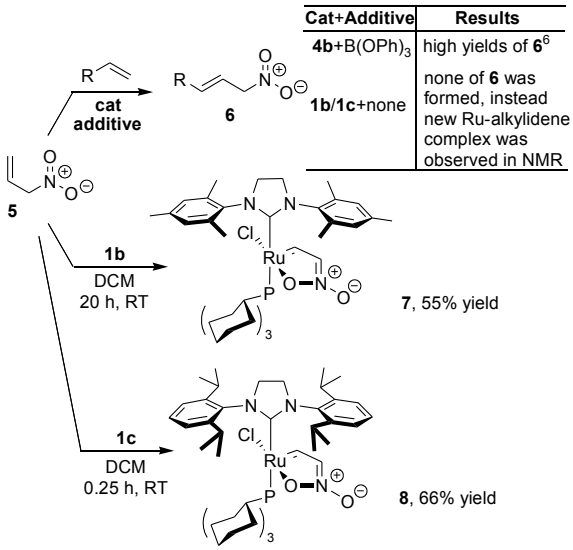


Fig. 1 Selected catalyst for olefin metathesis

Recently we have reported on the application of 3-nitropropene **5** as a partner for cross-metathesis (CM) of terminal olefins.[6] This transformation was possible only when catalyst **4b** was applied in the presence of a Lewis acid, while no CM product was observed when Grubbs' second generation catalysts **1b** was used.[6] Interestingly, NMR inspection of the reaction mixture suggested that the reaction of **1b** with 3-nitropropene probably leads to a new alkylidene complex.

As a result of this serendipitous observation, we describe herewith a study on preparation and chemical properties of new ruthenium alkylidene complexes formed in the reaction between Grubbs' benzylidene complexes **1b**,**c** and 3-nitropropene **5**. Complex **7** was easily obtained in the reaction of **1b** and 3-nitropropene (1.25 equiv.) at room temperature in 55% yield as a green micro-crystalline solid (Scheme 1). Under the same conditions analogue **8** was obtained from complex **1c** in slightly higher yield.



Scheme 1 Preliminary results of CM of 3-nitropropene **5** with complexes **4b** and **1b** and the optimised synthesis of **7** and **8**

These complexes were stable enough for isolation using standard silica gel column chromatography *on air*. Structures of new complexes were determined using NMR spectroscopy and mass spectrometry. Complexes **7** and **8**, bearing a cyclic nitronate (*azinate*) skeleton, can be formally classified as ruthenaisoxazole *N*-oxides.[7] To confirm the connectivity of atoms in the complex **8** (see Fig. 2), the single-crystal X-ray structure analysis has been determined. The collection and refinement parameters for the crystallographic analysis are presented in the Supporting Information. The distance between the ruthenium atom and carbon atom from NHC ligand is equal to 2.07(1) Å (Ru(1)-C(1)) and the bond length between Ru(1)-P(1) is 2.406(3) Å. The five-membered azinate ring is flat with the Ru(1)O(1)N(3)C(30) torsion angle equal to −3(1)º. The formation of the bond between the ruthenium and oxygen atoms (Ru(1)-O(1) = 2.059(8) Å) causes the elongation of the N(3)-O(1) bond (1.33(1) Å comparing to the N(3)-O(2) bond 1.27(1) Å). The bond distance between the metal centre and carbon atom C(31) is equal to 1.88(1) Å. A repulsion between the azinate, mesyl and trialkylo-phosphane groups results in the decrease of the P(1)Ru(1)C(1) angle to 165.0(3)º.

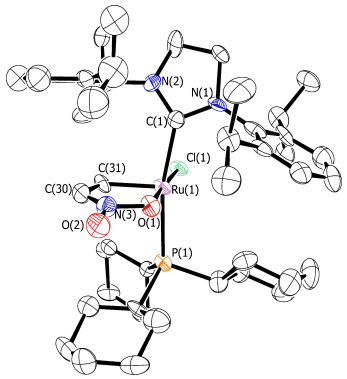


Fig. 2 ORTEP representation of **8** (CCDC 905000; probability ellipsoids at 50% level, hydrogen atoms omitted for clarity)

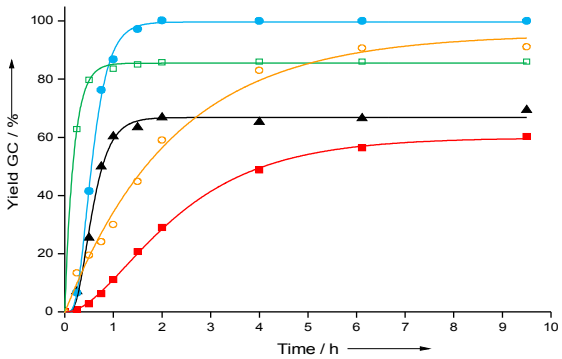
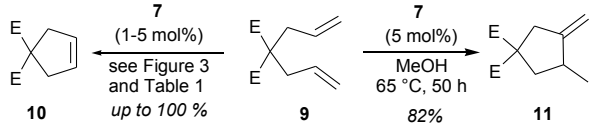


Fig. 3 RCM of **9**: promoted by **7** (1 mol%). GC yield of **10** determined by GC using internal standard. ■ - in toluene (80 °C); ▲ - in CCl_4 (60 °C); □ - in toluene (80 °C) with TMSCl (4 mol%); ○ - in toluene (80 °C) with CSA (4 mol%); ● - in toluene (80 °C) with C_2Cl_6 (4 mol%)

According to Cambridge Structural Database (CSD, version 5.33, November 2012) this is the first example of the ruthenaisoxazole *N*-oxide catalyst structure reported.

The unusual structure of these complexes has raised a question concerning their chemical reactivity, therefore we tested **7** and **8** in the ring closing metathesis (RCM) transformation of a standard model diene – diethyl diallylmalonate **9** (Scheme 2).[8]



Scheme 2 Reactivity profiles of complex **7** with diene **9** (E = CO_2Et)

RCM of diene **9** in the presence of 1 mol% of **7** in DCM at room temperature was not successful. The same reaction conducted at higher temperature in toluene gave RCM product **10** but in rather low yield (Fig. 3, curve ■). Interestingly, after prolonged heating in methanol, a product of cycloizomerization (**11**) was observed instead of the RCM product **10** (Scheme 2).

Therefore, we decided to investigate this reaction in more detail. We found that both activity of **7** and its selectivity towards RCM can be increased by addition of camphorosulfonic acid (CSA) or TMSCl (Fig. 3, curves □ and ○). On the other hand, our unsuccessful trials of application of **7** in Kharasch-type additions[9] made possible to discover that CCl_4, used as a solvent, activates strongly catalysts **7** and **8** towards RCM. For example, reaction of **9** promoted by **8** (5 mol%) in CCl_4 at 60 °C gave product **10** in 97% yield after 2 h (Table 1). Other haloalkanes, such as CBr_4 and C_2Cl_6, used as additives, activate the nitroniate catalyst to a similar extend (Fig. 3 and Table 1).

It may be reasonable to expect that acids (CSA or TMSCl) and chlorinating agents can open the ruthenaisoxazole ring to form catalytically more active species $L_2Cl(X')Ru{=}CHCH{=}N(O)OR$ (R = H or TMS) and $L_2Cl(X')Ru{=}CHCH(X)NO_2$.[10] Unfortunately, we were not able to isolate nor characterise in solution the catalytically active species formed from **7** or **8** upon action of these additives.

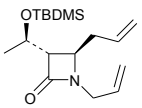
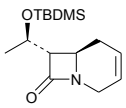
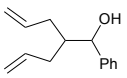
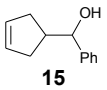
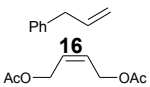
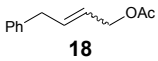
Table 1 Influence of additives on RCM of **9**

Entry	Cat (mol%)	Solvent	Temp [°C]	Additive (mol%)	Yield **10** [%][a]
1	**7** (5)	$CHCl_3$	60	none	45
2	**8** (5)	CCl_4	60	none	97
3	**7** (5)	Toluene	80	CBr_4 (20)	74

[a] Yield of **10** after 2 h determined by GC using internal standard

Using the optimised conditions, i.e. 1 mol% of **7**, 4 mol% of hexachloroethane in toluene at 80 °C leads to formation of **10** in high yield (Figure 3, ●). Application of this system to other dienes and alkenes was also successful (Table 2).[11]

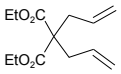
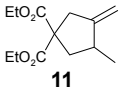
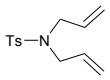
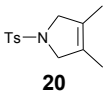
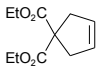
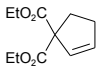
Table 2 Catalytic RCM and CM reactions promoted by **7** and **8**. TBDMS = *tert*-butyldimethylsilyl, Ac = acetyl

Entry	Cat	Substrate	Product	Yield [%][a]
1[b]	**7**	 **12**	 **13**	96
2[b]	**7**	 **14**	 **15**	88
3[c]	**7**	 **16** + **17** (2 equiv.)	 **18**	65 *E*/*Z* = 4:1

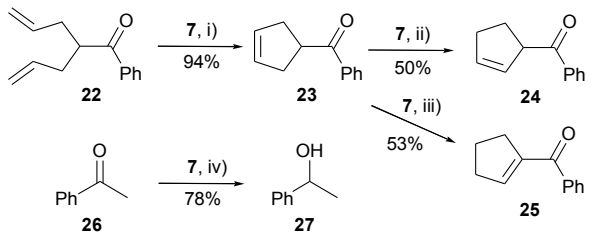
[a] Isolated yield of analytically pure product; [b] **7** (1 mol%) + C_2Cl_6 (4 mol%) in toluene (80 °C), 3 h; [c] **7** (2 mol%) + C_2Cl_6 (8 mol%) in toluene (80°C), 24 h

Formation of cycloisomer **11** as a product of reaction of **9** conducted in a protic solvent (Scheme 2) encouraged us to study a possibility of using the Ru-nitronate complexes in selective isomerisation and cycloisomerisation reactions (Table 3). It should be noted that the sulphonamide derivative **19** (Table 3, entry 2) leads upon action of **7** in methanol to product **20** containing a tetrasubstituted double bond.[12] Finally, the double bond in cyclopentene **10** can be isomerised to yield **21**, by using the nitronate complex in more acidic CF_3CH_2OH (entry 3). Also other conditions can be used to isomerise the C-C double bond in **10**, such as heating in toluene with addition of vinyloxytrimethylsilane and **8**.

Table 3 Reactivity of complexes **7** in isomerisation and cycloisomerisation reactions. Ts = tosyl.

Entry	Substrate	Product	Yield [%] [b]
1[a]	 **9**	 **11**	82
2[a]	 **19**	 **20**	88
3[c]	 **10**	 **21**	75

[a] Conditions: 5 mol% of **7**, methanol, 65 °C; [b] Yield after 50 h determined by GC using internal standard. Products identifed by comparison with independently prepared samples; [c] Conditions: 5 mol % of **8**, trifluoroethanol 70 °C



Scheme 3 Diverse reactivity of **7** in RCM and non-metathetic processes. i) **7** (1 mol%), C_2Cl_6 (4 mol%), toluene, 80 °C, 3 h; ii) **7** (5 mol%), methanol 65 °C, 50 h; iii) **7** (5 mol%), KHMDS (10 mol %), toluene 80 °C, 65 h; iv) **7** (2 mol%), NaH (7 mol%), *i*-PrOH (50 equiv.), THF, 70 °C, 5 h.

Next, we have found that depending on conditions, Ru-nitronate catalyst can induce a C-C double bond shift over one or over two positions in the RCM product **23** (Scheme 3).[3,13] Separate "blind" experiments, conducted under identical conditions but without the metal complex, have shown that these transformations do not undergo in the absence of **7**. We have also checked preliminary that reduction of a carbonyl group is also possible with **7**, however, under different conditions. Using isopropyl alcohol and NaH, we successfully carried out of the reduction of acetophenone **26** (Scheme 3).[14]

In conclusion, our studies shown that the reaction of Grubbs' second generation catalysts with 3-nitropropene leads to new chelating Ru-alkylidene complexes bearing a nitronate ligand. These complexes show catalytic activity both in olefin metathesis and in non-metathetic processes. Applications of these complexes in metathesis requires activation by hexachloroethane or trimethylsilyl chloride. Other processes such as cycloisomerisation, isomerization of a C-C double bond and hydrogenations are possible under precisely selected conditions. While there are known other olefin metathesis catalysts of higher activity, the diverse reactivity exhibited by **7** and **8** makes these complexes of interest in organic synthesis.

Notes and references

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