Coordinatively unsaturated ruthenium allenylidene complexes: highly effective, well defined catalysts for the ring-closure metathesis of α,ω-dienes and dienynes

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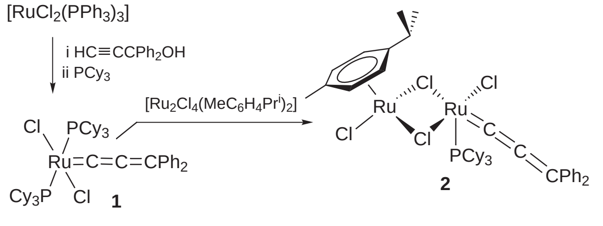
The well defined, conveniently accessible and coordinatively unsaturated allenylidene complexes [$RuCl_2(=C=C=CPh_2)(PCy_3)_2$] and [$Ru_2Cl_4(=C=C=CPh_2)(PCy_3)(\eta\text{-}MeC_6H_4Pr^i\text{-}4)$] are highly effective catalysts for the ambient temperature ring-closure metathesis of *α,ω*-dienes and dienynes, illustrated by the facile and high yielding formation of variously functionalised 5, 6, 7, 8, 15, 16 and 18 membered mono- and bi-cyclic ring systems.

The advent of Grubbs' catalysts [$RuCl_2(=CHR)(PR'_3)_2$] (R = Ph, CH=CPh_2; R′ = Ph, Cy)[1] has revolutionised alkene metathesis technology by offering a combination of functional group tolerance, high activity and catalyst durability. The rapid embrace of these catalysts as tools for organic fine chemicals synthesis has been truly remarkable.[2] The possibility that complexes of unsaturated 'C_1' ligands other than alkylidenes might also serve as pre-catalysts has however received considerably less attention. Recent key observations which however presage a significant role for such ligands include (i) the demonstration that vinylidene complexes may catalyse the ring-opening metathesis polymerisation (ROMP) of strained cyclic olefins,[3] and (ii) the report by one of us of a coordinatively saturated allenylidene complex [$RuCl(=C=C=CPh_2)(PCy_3)(\eta\text{-}MeC_6H_4Pr^i)$]$^+$ serving as a pre-catalyst for the ring-closure of α,ω dienes.[4] The actual nature of the true catalyst(s) in this latter system is open to conjecture, given that the catalysis only proceeds at elevated temperatures. It has been shown that the pre-catalyst may be activated by prior photolysis, possibly inducing arene dissociation, although subsequent heating is still required.[5] Some insight into the possible identity of the active species has been provided by our recent demonstration that the product mixture obtained from the reaction of [$Ru_2Cl_4(\eta\text{-}MeC_6H_4Pr^i)_2$] with HC≡$CCPh_2OH$ and PCy_3 under the conditions of catalysis (toluene, 80 °C) includes the coordinatively unsaturated allenylidene complexes [$RuCl_2(=C=C=CPh_2)(PCy_3)_2$] **1** and [$Ru_2Cl_4(=C=C=CPh_2)(PCy_3)(\eta\text{-}MeC_6H_4Pr^i\text{-}4)$] **2**.[6] Although prior to our report there were no known examples of coordinatively unsaturated allenylidene complexes of group 8 metals,[7] complex **2** is related to the binuclear benzylidene complex [$Ru_2Cl_4(=CHPh)(PCy_3)(\eta\text{-}MeC_6H_4Pr^i\text{-}4)$] reported by Grubbs,[8] whilst complex **1** represents the allenylidene analogue of Grubbs' mononuclear catalyst. Complexes **1** and **2** are conveniently prepared in high yield *via* the synthetic sequence illustrated in Scheme 1.[6] With these complexes readily in hand, we wish to report herein, results of our ongoing study of their catalytic efficacy for alkene metathesis processes.

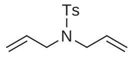
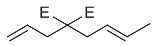
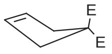
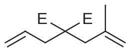
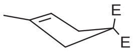
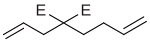
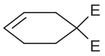
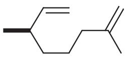
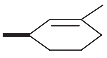
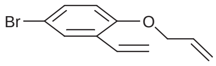
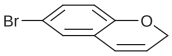
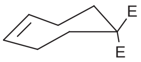
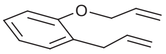
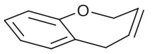
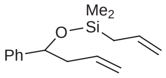
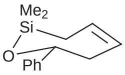
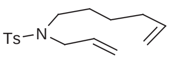
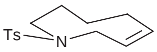
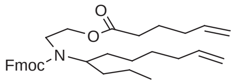
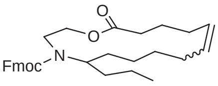
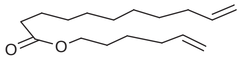
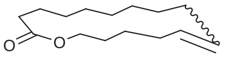
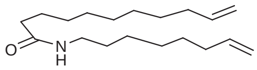
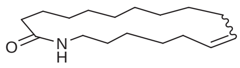
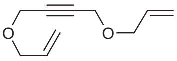
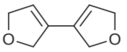
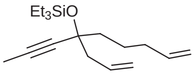
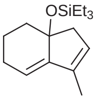
Table 1 summarises representative ring-closure processes mediated effectively by both the mononuclear complex **1** and the binuclear derivative **2**, according to a general procedure outlined below.† To summarise the salient features which emerge: (i) In contrast to previous results with the salt [$RuCl(=C=C=CPh_2)(PCy_3)(\eta\text{-}MeC_6H_4Pr^i\text{-}4)$]$PF_6$,[4] all cyclisations proceed at room temperature and in high to excellent yield, with no need for photolytic pre-activation. (ii) Both catalysts are highly tolerant of functional groups including sulfonamide, ester, bromide, ether, siloxane, amide and fluorenylmethoxycarbonyl substituents. (iii) Both catalysts are suitable for the preparation of buta-1,3-dienes *via* the ring-closure of dienynes. (iv) Five, six, seven, eight, fifteen, sixteen and eighteen membered mono and bicyclic ring systems have been successfully prepared. These include the precursors to Exaltolid®, a musk odored perfume ingredient[9] and epilachnene, an insect repellant alkaloid isolated from the pupae of a Mexican beetle.[10] (v) In general the binuclear catalyst **2**, whilst effective, is slightly less active than the mononuclear complex **1**, requiring somewhat longer reaction times (Table 2) and providing comparable or marginally lower yields. This observation is noteworthy for two reasons: Firstly, by far the most expensive step in the preparative sequence (Scheme 1) involves the synthesis of **2** from **1**. Secondly, Grubbs has shown that for the ROMP of cycloocta-1,5-diene, the binuclear complex [$Ru_2Cl_4(=CHPh)(PCy_3)(\eta\text{-}MeC_6H_4Pr^i\text{-}4)$] shows a substantially greater activity (by a factor of *ca.* 20) than the mononuclear complex [$RuCl_2(=CHPh)(PCy_3)_2$];[8] (vi) The activities and yields observed for complex **1** suggest that it is equipotent to Grubbs' mononuclear benzylidene complex. This is mechanistically reassuring, in that following the initial cycle of catalysis, the propagating species would be expected to be identical for the two catalysts, *viz* the methylene complex [$RuCl_2(=CH_2)(PCy_3)_n$] (n = 1 or 2).

These results taken together illustrate that well defined coordinatively unsaturated allenylidene complexes provide an alternative route into the catalytic cycles which operate from the less conveniently accessible benzylidene complex [$RuCl_2(=CHPh)(PCy_3)_2$]. The study of synthetic approaches to allenylidene complexes, in particular those of ruthenium,[7] has matured considerably in recent times. Although **1** and **2** are, to



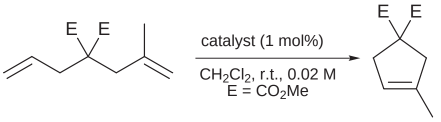
Scheme 1

Table 1. Ring-closure metathesis of α,ω-dienes and dienynes using catalysts **1** and **2**[a]

Cat.	Substrate	Product	Yield(t/h)
1 **2**			98(2) 88(17)
1 **2**			92(20) 89(24)
1 **2**			83(4.5) 75(22)
1 **2**			92(4) 94(4)
1			77(18)
1 **2**			94(3)^b 60(21)^b
1 **2**			94(7) 94(7)
1 **2**			86(18) 77(18)
1 **2**			97(5)^b 86(8)^b
1			70(6)
1 **2**			82(67)^c 81(42)^c
1 **2**			75(19) 69(17)
1			60(72)
1 **2**			84(4)^b 85(3)^b
1 **2**			79(18) 81(5)^b

[a] All reactions were carried out in CH_2Cl_2 at room temperature under Ar. E = CO_2Me, Fmoc = 9-fluorenylmethoxycarbonyl, Ts = toluenesulfonyl. [b] GC-yield. [c] Using 5 mol% of the catalyst.

Table 2



	Conversion (%, GC-yield)	
t/min	Catalyst **1**	Catalyst **2**
20	83	2.5
40	93	5
80	98	11
500	99	33

date, the only coordinatively unsaturated examples, the plethora of recently discovered ruthenium allenylidene complexes provide much scope for the further development and refinement of allenylidene-derived alkene metathesis catalysts, presaged by the high efficacy of catalysts **1** and **2**.

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Notes and references

† *N*,*N*-Bis(allyl)toluene-*p*-sulfonamide (846 mg, 3.37 mmol) and **1** (31.7 mg, 1 mol%) in CH_2Cl_2 (160 cm^3) were stirred for 2 h. The mixture was filtered through silica, freed of volatiles and the residue chromatographed (silica gel, hexane–ethyl ethanoate 4:1 eluent) to provide colorless crystals (742 mg, 98%). Mp = 123 - 124 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, 2 H, J = 8), 7.29 (d, 2 H, J = 8), 5.63 (s, 2 H), 4.10 (s, 4 H), 2.41 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.8, 134.7, 130.1, 127.8, 125.8, 55.2, 21.9. MS: m/z (rel. intensity): 223 (35, $[M]^+$), 155 (32), 91 (77), 68 (100), 41 (24).

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