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Ruthenium aryloxide catalysts: Synthesis and applications in ring-closing metathesis

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Abstract

Advances in design of ruthenium catalysts for olefin metathesis are described, in which problems of catalyst decomposition via formation of chloride-bridged species are addressed by replacing the chloride ligands of the Grubbs-class catalysts with aryloxides as "pseudohalide" ligands. The best of the new catalysts offer activity comparable to or greater than that of the parent chloride systems in ring-closing metathesis, with some intriguing differences in selectivity, particularly in macrocycle formation. Unexpected advantages associated with removal of spent catalyst following reaction are also reviewed.

Keywords: Alkene metathesis; Ruthenium; Deactivation; Aryloxide; Macrocycle

1. Introduction

Metathesis chemistry has emerged as one of the major success stories of homogeneous catalysis, recently highlighted by the announcement of the 2005 Nobel Prize in Chemistry honouring the pioneering accomplishments of Chauvin, Schrock, and Grubbs. Spectacular developments in organic and materials synthesis have emerged from ring-closing metathesis (RCM), cross-metathesis (CM), and ring-opening metathesis polymerization (ROMP), with applications ranging from renewable resources to photonics, tissue engineering, and pharmaceutical synthesis. Overviews of these subjects appear in a recent Handbook, which also presents cogent reviews of the fundamental issue of catalyst design [1]. To date, high selectivity remains the province of the Group 6 catalysts developed by Schrock and Hoveyda, of which chiral Mo systems are of particular interest for their capacity to impart precise control over tacticity in ROMP, as well as high enantioselectivity in asymmetric ring-closing and ring-opening metathesis [2]. The important Mo systems are limited, however, by their high sensitivity to air and water. The tremendous impact of Ru initiators of type **1** and their second-generation derivatives of type **2** is due to their greater robustness, which permits metathesis of a wide range of substrates under less stringent reaction conditions. They are more limited, however, in terms of selectivity, and despite the greater tolerance of the metal, short lifetimes necessitate the use of high catalyst loadings. A major goal is thus the design of long-lived, robust catalysts, which integrate the tolerance of the ruthenium systems with the selectivity of the Group 6 systems. This paper provides an overview of our progress toward these goals.

2. Results and discussion

Efforts in design of ruthenium metathesis catalysts have so far focused chiefly on increasing the activity of the Grubbs catalyst **1**. Following the major breakthrough associated with incorporation of an *N*-heterocyclic carbene (NHC) ligand [3], attention turned to derivatives of **2** containing more labile donor ligands. Examples include triphenylphosphine [3c,4–6] and pyridine [7,8] derivatives (**3** and **4**; Fig. 1), styrene ethers (e.g. **5b** and **5c**) in which the intramolecular donation from the chelated ether group of the Hoveyda catalyst **5a** is destabilized by electronic or steric factors [9,10], and four-coordinate phosphonium alkylidenes **6** [11].

These approaches have led to significant gains in catalyst activity, owing to improvements in the rate and efficiency with which the 14-electron intermediate **7** can be generated. However, a correlation exists between high activity and shorter lifetime in these complexes, which limits catalyst productivity [12]. The high catalyst loadings consequently required are of heightened concern as ruthenium-catalyzed metathesis technologies enter

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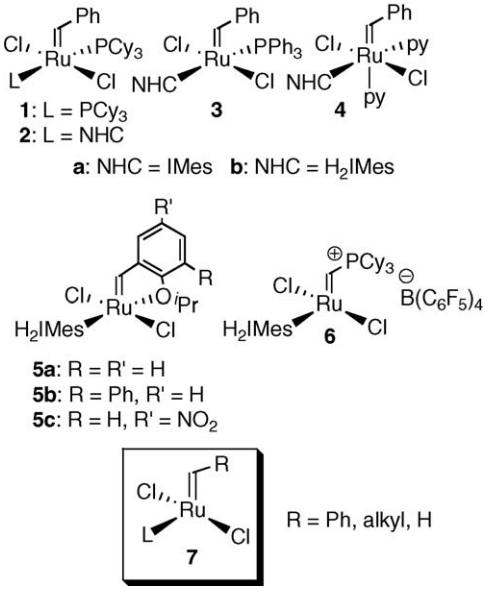


Fig. 1. High-performing Ru metathesis catalysts leading to intermediate **7**.

the industrial arena. Compounding the problem are difficulties in separating the heavy-metal residues from the organic products, especially when the residues are present in high concentrations. We earlier showed that a range of ruthenium alkylidene complexes of the Grubbs type is susceptible to deactivation via formation of chloride-bridged species [13]. While deactivation of the methylidene intermediates in the Grubbs systems apparently proceeds via a poorly understood unimolecular pathway (at least for $RuCl_2(PCy_3)_2(=CH_2)$ [14b]), Grubbs has recently proposed that such species can likewise decompose via chloride-bridged intermediates [15]. We considered that replacement of chloride by aryloxide ligands might improve catalyst lifetimes and total productivity, as well as providing a "handle" for modulation of catalyst properties such as solubility, electrophilicity, etc. In addition, the aryloxide ligand set encodes expanded capabilities for stereoelectronic tuning, as evidenced by the remarkable selectivity of the biphenolate and binaphtholate complexes developed in the Group 6 chemistry [2].

2.1. First-generation pseudohalide derivatives

Earlier work examined of the chloride ligands of the Grubbs catalyst **1** with alkoxide [16], tris(pyrazolyl)borate [17], salicylaldiminato [18,19], iminopyrrolato [20], or carboxylate [21] ligands (Fig. 2). In general, the metathesis activity of the resulting catalysts was moderate to low (though significant advances subsequently emerged with second-generation carboxylate [22] and Schiff base [23] derivatives, in parallel with our own work, while an NHC-binaphtholate derivative [24] is of interest for asymmetric metathesis). Among the original catalyst systems, examination of the ligand sets employed in **8–13** revealed several limiting factors. These limitations arise from: (a) steric congestion, which inhibits substrate binding (see **8**); (b) the low lability of the "placeholder" ligand that must be lost in order to bind olefin (in **9**, **10**, and possibly **11**, this is a PCy_3 ligand, though

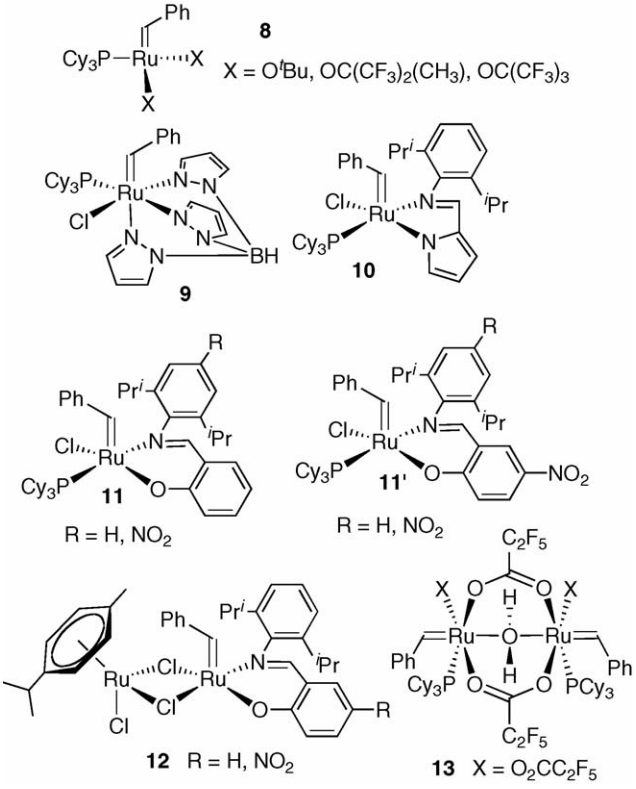
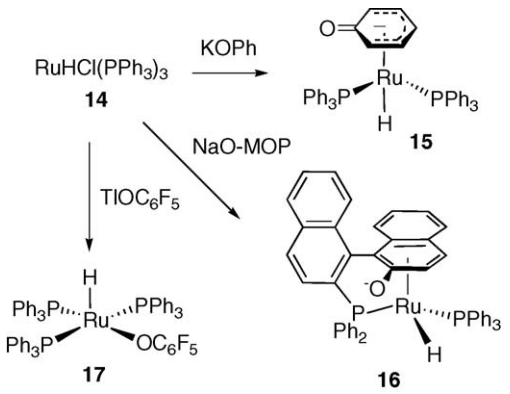


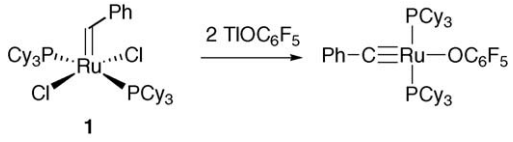
Fig. 2. First-generation Ru-pseudohalide derivatives.

decoordination of the salicylaldiminato nitrogen may provide an alternative initiation pathway in certain cases [25]); and (c) the low donor ability of the neutral donor ligand still present after initiation (**9–12**).

Aryloxide groups offer a number of attractive features as potential pseudohalide ligands. These include the two-dimensional geometry of the ligand, which minimizes steric congestion, and the absence of potentially chelating secondary donor sites, as found in the carboxylates [21]. A further major asset is the ease with which the aryloxide group can be modified to modulate steric, electronic, atropisomeric, and other properties. However, we rapidly became aware that the aryloxide complexes presented some synthetic challenges. Initially disappointing results, in which mixtures of unidentified products were obtained, led us to undertake probe reactions of aryloxide salts with $RuHCl(PPh_3)_3$ **14**. This complex was chosen as a model for the synthetic and catalytic intermediate $RuCl_2(PR_3)_2(CHR)$: the high trans-influence hydride ligand serves as a mimic for alkylidene, while the lability of the triphenylphosphine group provides insight into the likely behaviour of coordinatively unsaturated or labile intermediates that can be expected to participate in catalysis. Reaction of **14** with phenoxide afforded solely piano–stool complex **15**, formed by $\sigma \rightarrow \pi$ isomerization of the aryloxide ligand (Scheme 1) [26]. Subsequent efforts indicated that isomerization could not be suppressed by chelation to form a seven-membered ring (complex **16** instead being obtained) [27], though very recent work in our group indicates that smaller, five- and six-membered chelates are stable [28]. As formation of the piano–stool complexes is clearly a function of the donor ability



Scheme 1. Stabilizing the Ru–O bond against $\sigma \rightarrow \pi$ isomerization.



Scheme 2. Reaction of **1** with perfluorophenoxide.

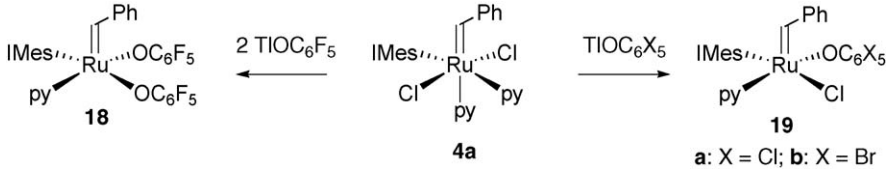
of the aromatic ring, we turned our attention to incorporation of electron-deficient aryloxide ligands. High yields of complex **17** could be obtained on reaction of **14** with the perfluorophenoxide ion, confirming that it was possible to stabilize the Ru(σ-OAr) moiety by depleting the donor ability of the aromatic ring. X-ray crystallographic data provided unequivocal confirmation of the presence of the Ru–O bond, and the complex shows no signs of either isomerization or reductive elimination on standing in solution.

Installation of phenoxide ligands into ruthenium alkylidene complexes presents a further set of challenges. Work by Caulton and co-workers [29] demonstrated that reaction of $RuCl_2(PPr^i_3)_2(CHPh)$ with phenoxide ion effected deprotonation of the benzylidene group, eliminating phenol and forming the four-coordinate carbyne. We were surprised to discover that this reaction path also dominates on treatment of **1** with perfluorophenoxide ion (Scheme 2) [30], in spite of the acidity of the perfluorophenol coproduct. This behaviour is in striking contrast with the corresponding reaction of **1** with potassium *tert*-butoxide, which yields the bis(OBu^t) species **8** in preference to the corresponding carbyne and *tert*-butanol [16,29]. We attributed the difference to the steric pressure exerted by the bulky trialkylphosphine ligands within the five-coordinate intermediate $Ru(OAr)_2(PCy_3)_n(CHPh)$, which forces the phenolic oxygen into proximity of the benzylidene proton: these steric constraints are relieved by elimination of the phenol. Modelling studies suggested that this interaction is inhibited in the *tert*-butoxide system by the combined bulk of the alkoxide and PCy_3 ligands, which inhibits formation of the five-coordinate intermediate, and the greater steric shielding of the alkoxide oxygen.

2.2. Second-generation pseudohalide derivatives

The apparent importance of steric parameters in dictating benzylidene deprotonation led us to explore the reaction of perfluorophenoxide with the second-generation complex **4a**, the steric bulk of which is minimized by the presence of planar NHC and pyridine ligands [30]. Added advantages include the activating effect of the NHC ligand versus PCy_3, and the higher lability of the pyridine "placeholder" ligand. Consistent with the analysis above, the reduced steric pressure in this system enabled synthesis of the desired five-coordinate alkylidene complex **18** in high yield, with no evidence for deprotonation of the benzylidene group. Use of bulkier pentachloro- or pentabromophenoxide gives the monoaryloxide species **19a/b** (Scheme 3) [31]. Derivatives containing the more labile 3-bromopyridine ligand were also prepared from the corresponding $RuCl_2$(IMes)(3-bromopyridine)(CHPh) precursor [8]. In all of these syntheses, the thallium aryloxides are employed, despite well-founded concerns about their toxicity [32], because the electrophilic "pull" by the heavy-metal cation [33] significantly accelerates the rate of halide substitution. Use of alkali metal salts results in much slower reaction, as we earlier commented [27] in context of reaction of alkali aryloxides with $RuHCl(PPh_3)_3$. Slow exchange is particularly problematic in syntheses involving the pyridine precursors, because the heightened lability of these ligands permits decomposition of the Ru-alkylidene precursor over the timescale of ligand substitution. The correlation between lability, catalyst activity, and accelerated decomposition for **4** [34] and related complexes [12] has been discussed elsewhere.

These pseudohalide catalysts exhibit high RCM activity, even at low catalyst loadings (<0.5 mol% Ru), as well as tolerance toward a variety of functional groups, including sulfide (Fig. 3) [30,31]. In all cases, elevated temperatures are required (40–60 °C; chlorocarbon or aromatic solvents), owing to the rather low lability of the pyridine ligand. Catalyst productivity is particularly high for the perfluorophenoxide complex, which achieved up to 40,000 turnovers in RCM of diethyldiallyl malonate. Turnovers in the thousands were achieved for the corresponding chloro- and bromo-phenoxide catalysts. The shorter lifetimes may be associated with the retention of one chloride ligand in these complexes. As a compensating factor, they exhibit higher reactivity than **18**. The performance of **19b**, in particular, is notable: this complex effects ring-closing of a range of substrates with an efficiency superior to that of the important catalyst



Scheme 3. Synthesis of aryloxide derivatives of second-generation Ru metathesis catalysts.

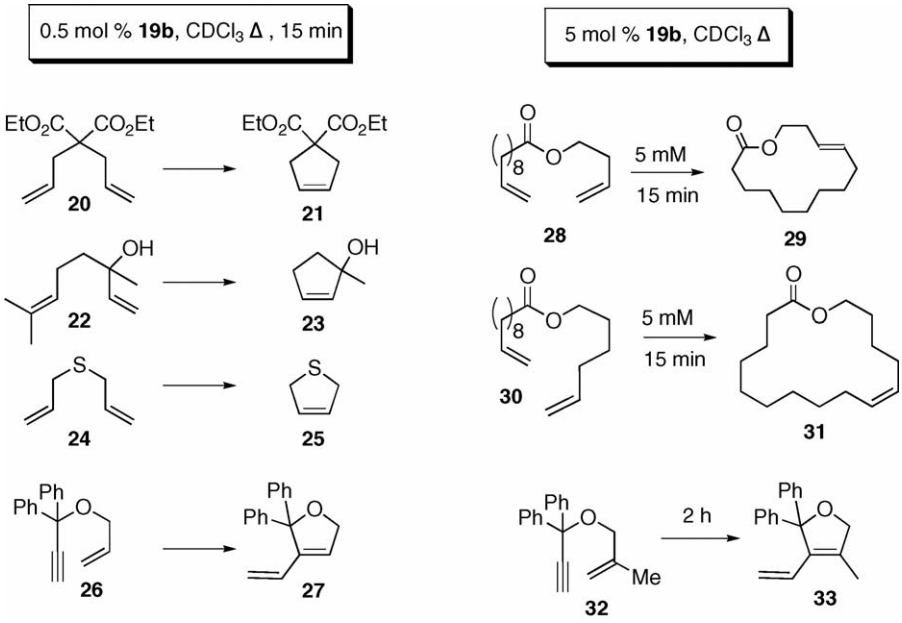


Fig. 3. RCM of representative substrates promoted by aryloxide catalyst **19b**.

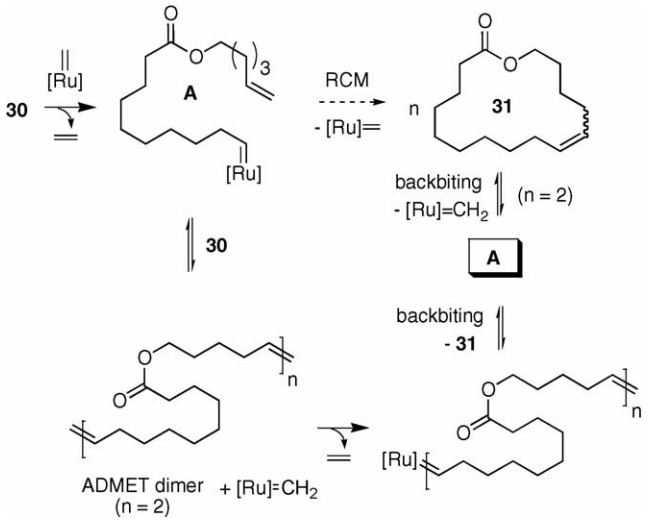
2a. RCM of ene–yne substrates, including sterically encumbered substrate **32**, proceeds at rates considerably higher than those previously attainable. Similarly, quantitative ring-closing to give macrocycles **29** and **31** is effected by catalyst **19b** in 15 minutes, versus a timescale of hours for the chloride catalysts.

2.3. Mechanistic insights into macrocyclizations catalyzed by Ru–NHC complexes

The high efficiency of macrocyclization using **19b** is of particular interest. While RCM methodologies have attained a high profile in macrocycle synthesis, the conditions employed are experimentally inconvenient. Concerns about the competion between intramolecular RCM and intermolecular oligomerization (acyclic diene metathesis, ADMET) processes date back to the first report of macrocycle synthesis by olefin metathesis, in which Villemin noted preferential polymerization at substrate concentrations above 15 mM, but formation of macrocycles at 6 mM [35]. High dilutions, typically achieved by dropwise addition, are thus routinely used to favour RCM, in keeping with long-established protocols for ring-closing of bifunctional molecules. These conditions exacerbate the inherently slower rates of ring-closing for large rings [36], requiring use of elevated temperatures to overcome the unfavourable kinetic effects of dilution and large ring size. Catalyst decomposition under these conditions, however, can limit yields, and addition of catalyst in several batches is thus common.

Given these precedents, we were struck by the high efficiency with which **19b** effects macrocyclization. In examining more closely the relative behaviour of **19b**, **2a**, and **4a** in this reaction, we uncovered an unexpected pathway for the cyclization reaction. While **19b** effects quantitative RCM of diene **30** within 15 min, the majority species produced by **2a** or **4a** at the same stage is the ADMET oligomer, even at dilutions of 5 mM. Importantly, however, macrocyclization is near-quantitative on longer reaction time (9 h for **2a**, 1 h for **4a**) [37]. Formation of ADMET oligomers en route to the macrocyclic products is consistent with the operation of ring-chain equilibria long recognized in ROMP chemistry [38–40] (Scheme 4), but little considered in context of RCM. The key participants in this equilibrium are the macrocyclic rings, and the ruthenium-terminated "ROMP" polymers initially generated by reaction of the ADMET oligomers with the Ru-methylidene species.

In this equilibrium process, formation of progressively smaller cyclic species is favoured with increasing dilution, as expected from Jacobson–Stockmayer theory [41]. We observed oligomers as the dominant species at high concentrations (10 mM in diene), cyclooligomers at 1 mM, and the target macrocycles at high dilution (5 mM). The product distribution can thus be manipulated by altering the concentration, providing



Scheme 4. ADMET-backbiting mechanism for macrocycle formation. Reactions evolving ethylene are shown as irreversible.

that catalyst deactivation has not occurred. The fact that the ADMET oligomers are intermediates in the ring-closing reaction implies that it is unnecessary to minimize the intermolecular reaction by dropwise addition of substrate and catalyst. The experimental protocol is simplified, and reaction times significantly decreased, by rapid mixing of substrate and catalyst. The kinetic bias toward ADMET, even at high dilution, means that the effect of concentration has little impact on the efficiency of the initial oligomerization process, and the reaction can therefore be conveniently set up at the high dilution required to shift the ring-chain equilibrium in favour of the RCM product. Elevated temperatures are essential, possibly reflecting the barrier to reinstallation of the rather unreactive Ru methylidene species as an endgroup on the ADMET oligomer. In comparison to the conventional method, which required 9 h to achieve >95% RCM of **30** using **2a**, simply mixing **30** and **2a** at high dilutions, then heating to reflux, reduces reaction times to 1 h [37]. The reaction rate depends on ring size, as expected [36]: RCM to give the corresponding 16- and 20-membered macrolactones under these conditions requires 3 h or 5 h, respectively, to proceed to >95% completion. We are presently exploring a broader range of ring sizes with differing conformational constraints, in order to establish the generality of this behaviour.

2.4. Removal of ruthenium residues

An unexpected advantage of the aryloxide catalysts is their ease of removal following metathesis. The corresponding chloride catalysts decompose to coloured products that are difficult to remove from the organic products. Purification by chromatography is hampered by "streaking" on the column, while distillation is generally inadvisable, as this can trigger isomerization and other undesirable reactions that can reduce the quality and quantity of organic products. Standard protocols for evaluation of methods for removing Ru residues involve RCM of diethyldiallyl malonate with 5 mol% **2a**, followed by addition of some agent to modify or sequester the metal complex. Chromatography on silica gel in the absence of such an agent is rather ineffective, as noted above: a ruthenium content of thousands of ppm remains after flash chromatography using 5% EtOAc-hexanes [31]. Residues of **2a** can be reduced to 200–1200 ppm by use of additives such as lead tetraacetate [42], DMSO or triphenylphosphine oxide [43], water-soluble phosphines [44], or a polymer-bound diarylphosphine scavenger [45]. Alternatively, incubation with activated charcoal for 12 h, followed by two cycles of chromatography, decreases the Ru content to ca. 60 ppm [46]. In comparison, the high affinity of the Ru–aryloxide complexes for silica gel simplifies their separation from nonpolar organic compounds: a single cycle of flash chromatography afforded products in which the Ru content was below the 100 ppm detection limit of ICP-AES [31].

3. Conclusions

Development of metathesis catalysts that are highly active, long-lived, and selective will enable new advances in challenging metathesis reactions. Ruthenium aryloxide complexes exhibit advantages in terms of catalyst efficiency, product selectivity, and ease of removal from organic products, though the shorter lifetimes of the monoaryloxide derivatives, in which one chloride ligand is retained, relative to the bis(OAr) catalysts, is notable. Parallel work focusing on deconvolution of deactivation pathways in the aryloxide systems, particularly in chlorinated media, will aid in iterative catalyst redesign, as well as identification of optimum or undesirable reaction conditions. Finally, the new systems offer clear potential for modulation of solubility and selectivity, avenues currently under intensive investigation in our group.

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