Communications

The First Highly Active, Halide-Free Ruthenium Catalyst for Olefin Metathesis

Jay C. Conrad, Dino Amoroso,† Pawel Czechura, Glenn P. A. Yap, and Deryn E. Fogg*

Center for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, Canada K1N 6N5

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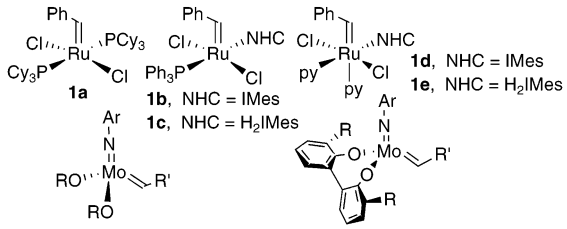
Summary: New ruthenium alkylidyne and alkylidene complexes are prepared, in which aryloxide groups function as pseudohalide ligands. The selectivity for alkylidene or alkylidyne products is controlled by steric matching or mismatching between pseudohalide and ancillary donor ligands. Alkylidene ***5*** *achieves up to 40 000 turnovers in ring-closing metathesis of diethyl diallylmalonate.*

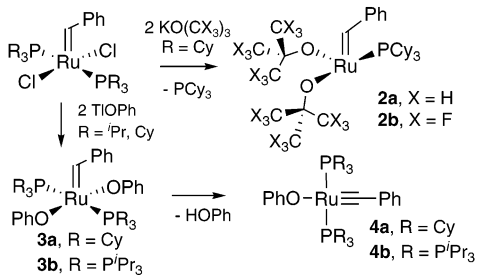
Over the past decade, advances in catalyst design have transformed olefin metathesis into a powerful synthetic tool in organic[1a−c] and materials[1d] chemistry. Two dominant lines of experimental progress have emerged (Chart 1), centered around the Mo and Ru catalysts pioneered by Schrock and Grubbs, respectively. A key feature of the former systems is the presence of aryloxide or alkoxide ligands that enable steric and electronic tuning.[1c] Chiral biphenolate and binaphtholate derivatives, in particular, have led to impressive advances in asymmetric ring-closing metathesis (ARCM).[2] The simple chloride ligands ubiquitous in the Ru chemistry offer no such opportunity, but can enable[3] bimolecular deactivation pathways[4,5] which limit the robustness that constitutes a key advantage of the Ru systems.

While much effort has focused on modification of neutral "L-donor" ligands in the ruthenium systems (an important recent addition being highly reactive N-heterocyclic carbene (NHC) species with labile donors;[6−9] Chart 1, IMes = *N*,*N*′-bis(mesityl)imidazol-2-ylidene[10]), modification of the anionic ligands is much less explored. Metathesis catalysts of low to moderate activity are obtained by replacing chloride with carboxylate,[4,11] or on use of heterobifunctional salicylaldimine[12] or NHC-naphtholate ligands.[13] Installation of alkoxide ligands affords the four-coordinate species **2a**,**b** (Scheme 1)[14,15] which—despite their nominal coordinative unsaturation—exhibit near-zero metathesis activity[14] (Table 1), prob-

Chart 1. Olefin Metathesis Catalysts



Scheme 1. Reactions of Ru Alkylidenes with Phenoxides or Alkoxides



* To whom correspondence should be addressed. E-mail: dfogg@science.uottawa.ca. Fax: (613) 562-5170.
† Present address: Promerus L.L.C., 9921 Brecksville Rd., Brecksville, OH 44141-3829.

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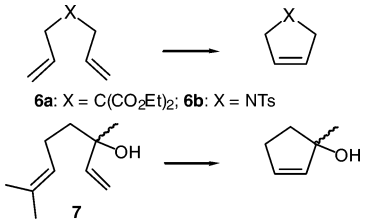
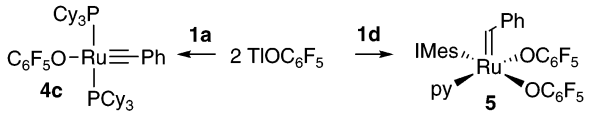
Table 1. Ring-Closing Metathesis via Ru−Alkylidene Catalysts[a]



entry	cat.	S	[S]/[C][b]	solvent	time (min)	conversn (%)	TOF (h^{-1})
1[c]	**2a**	**6a**	5	C_6D_6	5760	<5	≪1
2[c]	**2b**	**6a**	5	C_6D_6	720	40	≪1
3	**5**	**6a**	10	C_6D_6	15	56[d]	22[d]
4	**5**	**6a**	20	C_6F_6	120	>99	10
5	**5**	**6a**	20	$CDCl_3$	20	>99	60
6	**5**	**6b**	20	$CDCl_3$	20	>99	60[e]
7	**5**	**7**	20	$CDCl_3$	90	>99	13
8	**5**	**6a**	2000	$CDCl_3$	180	>99	667
9	**5**	**6a**	200000	$CDCl_3$	1440	20	333

[a] Conditions: [S] = 0.1−0.5 M; [C] = (2.5×10^{-6}) − 0.01 M; reactions under Ar, at 60 °C (C_6D_6) or at reflux; conversions determined by ^{1}H NMR. TOF = turnover frequency. [b] [S]/[C] = substrate-to-catalyst ratio. [c] Reference 14. [d] Catalyst incompletely dissolved. [e] 92% selectivity for the expected 2,5-dihydropyrrole product.[21]

Scheme 2. Sterically Determined Selectivity in Reactions of Ru Alkylidene Precursors with Aryloxide



ably owing to steric crowding, compounded by thermal instability.

While use of planar *aryloxide* ligands, in place of alkoxide, could potentially relieve these steric constraints, reaction of **1a** or $RuCl_2(P^iPr_3)_2(CHPh)$ with phenoxide anion unexpectedly yields alkylidynes **4a**,**b**, via deprotonation of the benzylidene ligand and liberation of phenol.[15] Given the higher basicity of *tert*-butoxide, vs phenoxide,[16] we speculated that the product selectivity in Scheme 1 might be driven by steric interactions between incoming pseudohalide and ancillary donor ligands. We now report that steric matching/mismatching strategies enable selective synthesis of four-coordinate carbyne *or* five-coordinate alkylidene complexes. The latter catalyzes RCM of diethyl diallylmalonate at very low catalyst loadings.

Consistent with our view that the nucleophilicity of the aryloxide is extraneous to alkylidyne formation, we find that treatment of **1a** with $TlOC_6F_5$ effects quantitative conversion to **4c** within 3 h at 22 °C (Scheme 2).[17] The complex is isolated as a green, air-stable, ether-soluble powder; high solubility limits yields to ca. 60%. The approximately square-planar molecular structure (Figure 1; for details see Supporting Information) closely resembles that reported for **4b**.[15] Formation of **4c**,

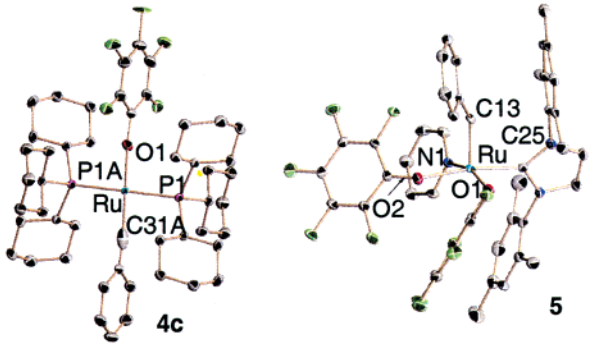


Figure 1. ORTEP representations of **4c** and **5**, with hydrogen atoms and solvates omitted. Thermal ellipsoids are given at 30% probability level. Aryloxide and alkylidyne ligands in **4c** are related by a center of inversion.

despite the acidity of the perfluorophenol coproduct,[16] implies a powerful driving force for reaction. Modeling studies point toward steric crowding within the five-coordinate intermediate (cf. **3**), sufficient to promote interaction between the alkylidene proton and the phenoxide oxygen. This is ultimately relieved by elimination of perfluorophenol. Failure to observe the corresponding reaction for the *tert*-butoxide system,[14,15] despite the thermodynamically more favorable liberation of *tert*-butyl alcohol, is consistent with prohibition of the alkylidene−alkoxide interaction by the bulk of the *tert*-butyl substituent. Relief of steric pressure can then only be accommodated by phosphine loss.

This analysis suggested that alkylidene complexes of simple aryloxide ligands could potentially be accessed by attenuating the bulk of the neutral ligands *as well as* the pseudohalide. We therefore turned our attention to NHC complexes of type **1d**,[9] containing an approximately two-dimensional IMes ligand. Reaction of $TlOC_6F_5$ with **1d** is selective for transmetalation, yielding solely alkylidene **5**. Complex **5** was isolated in 92% yield and characterized by spectroscopic, microanalytical, and crystallographic analysis. Its geometry is square pyramidal, with alkylidene occupying the apical site (Figure 1), consistent with the high trans influence of this ligand.

Retention of the potentially labile pyridine ligand within **5** attests to the absence of steric constraints in this five-coordinate complex. Importantly, it also signifies the presence of an incipient coordination site for incoming substrate in **5**, in contrast with the sterically encumbered alkoxide complexes of type **2**.[14,15] Indeed, **5** exhibits dramatically increased activity for ring-closing metathesis (Table 1). Metathesis activity is retained in fluorocarbon solvents (entry 4) and at exceptionally low catalyst loadings (entries 8 and 9). Up to 40 000 turnovers are observed for RCM of the benchmark substrate diethyl diallylmalonate, using only 5×10^{-4} mol % of **5**. A lower limit of 0.05 mol % has been established for chlororuthenium catalyst **1c** under comparable conditions.[18] Catalyst loadings of 5−20 mol % are typical in Ru-catalyzed RCM, owing to the short lifetimes of the active Ru−methylidene intermediate.[5,19,20] Even at 20 mol %, however, complexes **2a**,**b** achieve turnover numbers of only 0.25 and 2, respectively.[14]

(16) pK_a values: perfluorophenol, 5.52 (Birchall, J. M.; Haszeldine, R. N. *J. Chem. Soc.* **1959**, 3653); phenol, 10; *tert*-butyl alcohol, 18 (Streitwieser, A. J.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; McMillan: New York, 1981).

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In summary, we have established strategies for selective synthesis of alkylidene or alkylidyne derivatives of ruthenium, via steric matching/mismatching between two- or three-dimensional "L-donor" ligands and an incoming pseudohalide. Alkylidene complex **5** exhibits excellent activity for ring-closing metathesis, even at very low catalyst loading. This chemistry affords convenient access to a new, active, and potentially broad class of ruthenium catalysts for olefin metathesis. Investigation of the selectivity and activity conferred by other pseudohalide ligands, as well as immobilization strategies, is in progress.

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Supporting Information Available: Text and tables giving synthetic, spectroscopic, and crystallographic data for **4c** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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