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LETTERS

A series of ruthenium(II) ester-carbene complexes as olefin metathesis initiators: metathesis of acrylates[†]

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Abstract

A series of ester-carbene complexes was synthesized. These complexes were found to be highly active for the metathesis of olefinic substrates, including acrylates and trisubstituted olefins. In addition, the ester-carbene moiety is thermodynamically high in energy. As a result, these complexes react to ring-open cyclohexene by metathesis to alleviate the thermodynamic strain of the ester-carbene ligand. © 2000 Published by Elsevier Science Ltd.

Keywords: olefin metathesis; catalyst; ruthenium; carbene; acrylate; ring-opening.

Over the past several years the use of ruthenium-based olefin metathesis catalysts, of the general formula $L_2X_2Ru{=}CHR$, has become common in organic synthesis.[1] Previous work has examined the effects of the ligand sphere on catalyst activity, including the effect of L-type ligands,[2] X-type ligands,[2a] chelating ligands,[3] and the effect of carbene derivatives on catalyst initiation.[4] With the development of a novel way to make ruthenium carbenes through a double oxidative addition of an α,α-dichloroalkane to a ruthenium(0) precursor,[5] a new method became available for the straightforward synthesis of a variety of new carbene complexes for further studies of catalyst initiation. This letter describes the synthesis and activity of ester-carbenes of the general formula: $Cl_2(PCy_3)_2Ru{=}CHCO_2R$.

The first ruthenium-based metathesis-active ester-carbene, $Cl_2(PPh_3)_2Ru{=}CHCO_2Et$ (**1**), was synthesized by the addition of ethyl diazoacetate to $RuCl_2(PPh_3)_3$.[6,7] However, this complex (**1**) was found to be very unstable in solution, even at low temperature, making isolation of the pure product difficult. Subsequent work allowed the isolation of the methyl ester-carbene complex (**2a**) by the addition of methyl dichloroacetate to ruthenium bis(hydrido) (cyclohexene) bis(tricyclohexyl phosphine) in pentane such that the resulting carbene complex precipitated and decomposition was avoided.[5a]

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[†] Dedicated to Professor Mitsuru Kubota on the occasion of his retirement.

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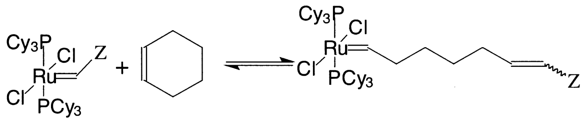
The methyl ester-carbene (**2a**) was found to be thermally unstable at room temperature in solution, decomposing over several hours, but proved to be very active for the initiation of metathesis. A remarkable property of this initiator was that it reacted completely with excess cyclohexene to form the ring-opened metathesis product (Scheme 1). This was unexpected because metathesis reactions are thermodynamically driven and stable six-membered rings are not typically opened in simple metathesis reactions such that the equilibrium of (**3**) reacting with cyclohexene to form (**6**) lies exclusively on the reactant side. The fact that the ester-carbene reacts with cyclohexene suggests that there is enough stabilization achieved by converting the less stable ester-carbene into an alkyl-carbene to drive the equilibrium towards the ring-opened product. In an effort to study the activity and stability of the ester-carbene complexes, a series was prepared with different ester groups (**2**). These complexes vary in stability but all exhibit very high rates of initiation for olefin metathesis and all are capable of the ring-opening of cyclohexene.



2a Z = CO_2-methyl
2b Z = CO_2-*p*-tolyl
2c Z = CO_2-*t*-butyl
2d Z = CO_2-*i*-propyl
2e Z = CO_2-cyclohexyl
2f Z = CO_2-1-adamantyl
3 Z = phenyl

5a Z = CO_2-methyl
5b Z = CO_2-*p*-tolyl
5c Z = CO_2-*t*-butyl
5d Z = CO_2-*i*-propyl
5e Z = CO_2-cyclohexyl
5f Z = CO_2-1-adamantyl
6 Z = phenyl

Scheme 1. Ring opening of cyclohexene by metathesis with ruthenium carbene complexes

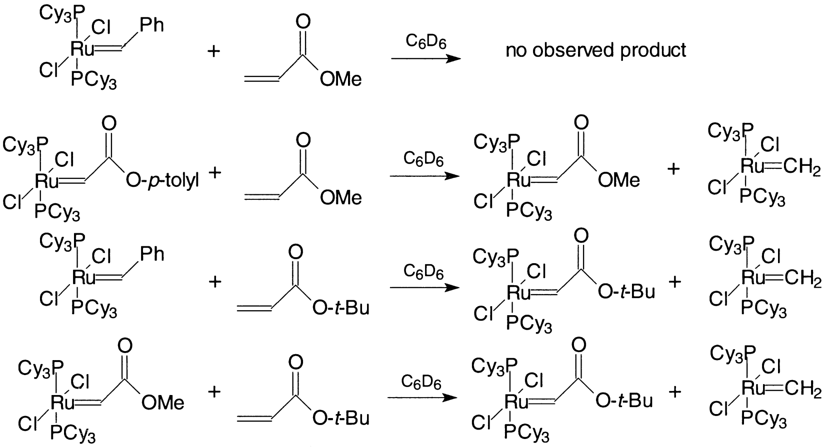
All of the ester-carbenes (Table 1) were synthesized by the addition of $Cl_2CHC(O)$–OR to a benzene suspension of the ruthenium bis(hydrido) (cyclohexene) bis(tricyclohexyl phosphine) complex reported earlier.[5a] The dihalo esters were synthesized in good yield by the addition of the corresponding alcohol to a solution of dichloroacetic anhydride and pyridine in methylene chloride at 0°C.

Table 1
Spectral analysis of ruthenium ester/amide-carbene complexes, $Cl_2(PCy_3)_2Ru{=}CHC(O)$–Y–R

	-Y-R	^1H (C_6D_6)	^{31}P (C_6D_6)	^{13}C (CD_2Cl_2)	k_{dec} (L/molar·min)
2a	-O-Me	20.15 s	38.66 s	276.37 t	0.6
2b	-O-p-tolyl	20.33 s	38.43 s	273.68 t	0.5
2c	-O-t-Bu	20.13 s	37.05 s	281.67 t	0.4
2d	-O-i-Pr	20.18 s	37.75 s	278.90 t	0.3
2e	-O-cyclohexyl	20.21 s	37.70 s	279.38 t	0.2
2f	-O-(1-adamantyl)	20.19 s	37.33 s	282.47 t	0.2
				(C_6D_6)	
4	-NH_2	20.35 s	40.29 s	291.87 t	0

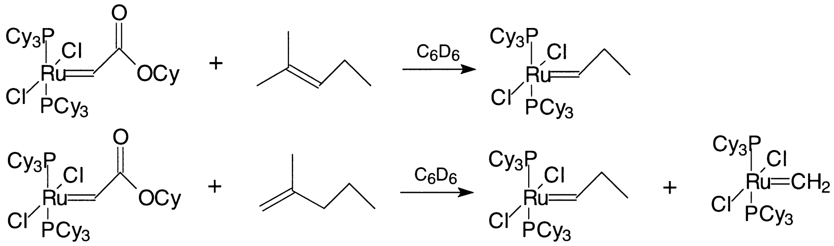
The order of decreasing decomposition rate at room temperature (proceeding through the same bimolecular mechanism observed for the alkyl-carbenes)[8] for the series of ester-carbenes is methyl > *p*-tolyl > *t*-butyl > isopropyl > cyclohexyl≅1-adamantyl. The observed second order rate constants for the decomposition are shown in Table 1. Decomposition data collection was started 20 min after dissolving the samples in benzene (0.016 M) at room temperature and data collection was ceased at 400 min after dissolution.[9] It is interesting to note that the amide carbene (**4**) is stable indefinitely. It is also notable that the *t*-butyl ester-carbene is significantly less stable than expected based on its bulk. In the other cases, the stability was increased by increasing the ester group size to inhibit bimolecular decomposition. An attempt was made to examine the electronic effects of the ester by making the tri-, hexa- and nonofluorinated *t*-butyl esters. However, all attempts at isolating these carbene products failed as the rates of decomposition rival the rate of formation. Similarly, *p*-nitrophenyl dichloroacetate reacted with the cyclohexene ruthenium precursor with no observed ester-carbene formation, suggesting that electron-poor esters are particularly unstable. All the isolated ester-carbene complexes were found to be active for metathesis and readily ring-opened cyclohexene, while the amide-carbene (**4**) was active for acyclic metathesis but did not ring-open cyclohexene.

To further examine the relative thermodynamic stability of ester-carbenes (**2**) and the benzylidene (**3**), the ruthenium benzylidene was reacted with excess methyl acrylate (Scheme 2) in C_6D_6 but no new product was observed, though the benzylidene (**3**) was consumed over the course of 12 hours. Presumably, this is because the rate of product decomposition rivals the slow rate of product formation. Meanwhile, the reaction of the *p*-tolyl ester-carbene (**2b**) with excess methyl acrylate rapidly produced the methyl ester-carbene (**2a**) and a minute amount of methylidene,[4] along with significant decomposition. However, both the benzylidene (**3**) and the methyl ester-carbene (**2a**) react with excess *t*-butyl acrylate to form a mixture of the *t*-butyl ester-carbene (**2c**) and the methylidene, though the benzylidene reacted far slower and to a smaller extent. These observations demonstrate that both the benzylidene and the ester-carbenes react with excess acrylates but the ester-carbenes undergo reaction more readily.



Scheme 2. Metathesis of acrylates

Having established that the ester-carbenes are more active towards olefin metathesis than any ruthenium bis-L-type ligand carbene isolated to date,[10] an attempt was made to take advantage of this high activity and test its limits by reacting the carbenes with olefins which are ordinarily resistant towards ruthenium-catalyzed metathesis (Scheme 3). We first attempted to react dicyclohexyl maleate with the *t*-butyl ester-carbene, hoping that the two of the more stable ester-carbenes would yield the highest chance of observing the product. However, no reaction was observed. The experiment was repeated with the methyl ester-carbene to try to minimize the steric interaction of the carbene and substrate but again no reaction was observed. An attempt was then made to react the ester-carbenes with 2-methyl-2-pentene and 2-methyl-1-pentene, both of which do not react with the ruthenium benzylidene. Reaction of the cyclohexyl ester-carbene with the former olefin produced the propylidene. The latter olefin produced both the propylidene and the methylidene. The propylidene must have been formed from the metathesis of the internal olefin produced from the isomerization of the terminal olefin by ruthenium decomposition products.[8]



Scheme 3. Ester-carbene metathesis of challenging substrates

In conclusion, a new series of ruthenium(II) carbenes have been synthesized which exhibit remarkable olefin metathesis activity but suffer from relatively low solution stability. If used for ring-opening metathesis polymerization (ROMP), these complexes hold promise for the synthesis of telechelic ester-terminated polymers. These complexes should also be useful in other systems where rapid initiation is required. Once initiated, the reaction is identical to that of the well-studied ruthenium benzylidene initiator.

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9. The decomposition data obtained for the first 20 min of decomposition did not fit second order kinetics. For a more detailed discussion of the decomposition pathways for the ruthenium catalysts, see Ref. 8.
10. The catalysts based on *N*-heterocyclic carbene ligands reported in Ref. 2b–e are very active for propagating olefin metathesis but the rates of catalyst initiation are rather slow and significantly lower than for the ester-carbenes. In metathesis initiated by the ester-carbenes, the ester-carbene functionality is lost in the first catalyst turnover so the rates of propagation are equivalent to those achieved with the other bis-phosphine initiators. In claiming that the ester-carbenes are the most active catalysts, the implication is only for the first turnover after which the ester functionality is lost.