

Highly stereoselective formation of *cis*-enediones from α -diazo carbonyl compounds catalysed by $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$

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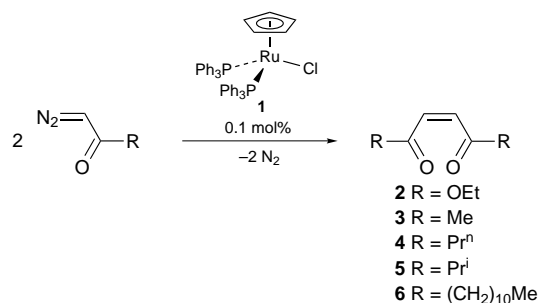
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Stereoselective decomposition of the α -diazo carbonyl compounds N_2CHCOR [$\text{R} = \text{Me}$, Pr^n , Pr^i , $(\text{CH}_2)_{10}\text{CH}_3$] catalysed by $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ (0.1 mol%) in toluene at 65 °C affords quantitatively $\text{RCOCH}=\text{CHCOR}$ carbene dimers, the *cis* isomers being formed in 95–97% yield; under the same experimental conditions N_2CHCOEt gives diethyl maleate in a purity of greater than 99%, the highest value for a stereoselective carbene–carbene dimer formation reported to date.

The metal-catalysed reactions of α -diazo carbonyl compounds have attracted a great deal of attention in recent years and have been used in an increasing number of syntheses, such as alkene cyclopropanation, carbene dimerisation and C–H insertion.¹ It is generally accepted that transition-metal complexes react with diazo compounds to generate transient metal–carbenes, although a few catalytically active species have been isolated.² Tuning of the electronic and steric properties of the catalyst has been proved to strongly affect the product distribution in reactions with diazo compounds, the control of both chemo- and stereo-selectivity still remaining an important goal.³

It has been reported that the metal-catalysed decomposition of diazo compounds occurs with loss of nitrogen to give alkenes, and both yield and *cis*:*trans* ratio vary according to the catalyst employed. We have now found that the readily available ruthenium(II) complex $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ **1** catalyses the highly stereoselective formation of *cis*-enediones⁴ from α -diazo carbonyl compounds. Thus, **1** in toluene at 65 °C converts ethyl diazoacetate (EDA) into diethyl maleate **2** quantitatively and in a purity of greater than 99%, diethyl fumarate being the only byproduct.† A comparison with other group 8 metal complexes shows that the metal–porphyrins $[\text{Ru}(\text{TMP})]^{1c}$ and $[\text{Os}(\text{TTP})]_2^5$ induce formation of diethyl maleate in 94 and 96% purity, respectively, the highest values reported to date. Moreover, other complexes such as $[\text{Rh}_2(\text{OAc})_4]$, $[\text{RuCl}_2(\text{PPh}_3)_3]$ and $[\text{Ru}_2\text{Cl}_4(\text{p-cymene})_2]$ also catalyse the conversion of EDA into alkenes, but with a considerably lower *cis*:*trans* ratio. Complex **1** has been previously used as a catalyst for the coupling of terminal alkynes with allyl alcohols,⁶ but no investigations concerning its catalytic activity towards diazo compounds decomposition have been reported to date.

In order to explore the potential of **1** in the stereocontrolled carbene dimerisation reaction, other substrates have been tested (see Scheme 1). The conversion into alkene is always quantitative and the *cis* isomer is present in the reaction mixture in yields higher than 95%. Thus, when a toluene solution of N_2CHCOR [$\text{R} = \text{Me}$, Pr^n , Pr^i , $(\text{CH}_2)_{10}\text{CH}_3$] is treated with 0.1 mol% of **1** under an inert atmosphere, dinitrogen evolution takes place rapidly (within 10 min) at 65 °C with quantitative formation of the product, as monitored by NMR spectroscopy. After removal of toluene, the *cis*-enediones **3–5** were distilled off *in vacuo* and isolated in 81–87% yield, while **6** was chromatographed on SiO_2 (84% isolated yield).† No cyclopropanation products, or other byproducts except *trans*-enediones were detected in the reaction mixtures by NMR and GC–mass spectrometry.

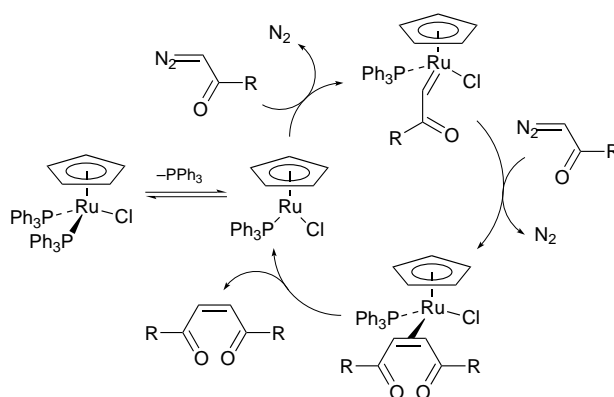


Scheme 1 Reaction conditions: toluene, 65 °C, argon atmosphere

The catalytic carbene dimer formation has been extended to α,ω -bis(diazo carbonyl) compounds. For example, $\text{N}_2\text{CHCO}(\text{CH}_2)_4\text{COCHN}_2$ reacts in THF solution at 60 °C in the presence of **1** to give a mixture of cyclic *cis*-enediones, the *trans*-isomers being formed in less than 5% yield. The mononuclear *cis*-cyclooct-2-ene-1,4-dione⁷ was distilled off from the reaction mixture and isolated in 19% yield. The solid residue, obtained in 60% yield, is a mixture of dicarbene dimer and trimer (in *ca.* 2:3 molar ratio), as inferred by ¹H and ¹³C NMR and mass spectrometry.

Other ruthenium(II) cyclopentadienyl complexes obtained by substitution of one or both PPh₃ of **1**, such as $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)]$, $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)(\text{PPh}_3)]$, $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)\{\text{P}(\text{O}Ph)_3\}_2]$ and $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$, have been shown not to be catalytically active for the decomposition of EDA. In contrast, the indenyl complex $[\text{RuCl}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ **7** decomposes all the N_2CHCOR compounds reported above, at a temperature (45 °C) lower than that necessary with **1**, but with similar high selectivity for the *cis*-enedione.

The decomposition of EDA catalysed by **1** has been examined in some detail and a plausible mechanism for the *cis*-enedione formation is depicted in Scheme 2. Since at room temperature no catalytic activity is shown by **1**, it is likely that the diazo compound decomposition takes place on the 16-electrons species $[\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$, which is formed upon



Scheme 2 Proposed mechanism and catalytic cycle

PPh₃ dissociation induced by high temperature and concomitant reaction of the phosphine with EDA. In fact, it is known that EDA and PPh₃ give in an equilibrium reaction the phosphazine EtOCOCHN₂=PPh₃, and traces of this product were always found in our reaction mixtures. Furthermore, solutions containing equimolar amounts of EDA and PPh₃ and **1** as catalyst do not show dinitrogen evolution at 65 °C. At 90 °C only traces of diethyl maleate (< 1%) are detected after 2 h reaction, the ylide EtOCOCH=PPh₃ being the major product present in solution.

As stated above, the indenyl complex **7** decomposes EDA at a lower temperature (45 °C) than **1** (65 °C), and this result is consistent with the kinetic studies of Gamasa *et al.*,⁸ who found that complex **7** dissociates PPh₃ an order of magnitude faster than **1** to form [RuCl(η⁵-ligand)(PPh₃)].

In the proposed catalytic cycle a neutral Ru^{II} cyclopentadienyl carbene complex is involved, which is similar to [RuCl(η⁵-C₅H₅)(CPh₂)(PPh₃)], recently reported by Braun *et al.*⁹ The high stereoselectivity observed for the nucleophilic attack of the α-diazo carbonyl compound on the coordinated carbene is probably related to the preferred orientation of the carbene moiety caused by the cyclopentadienyl ligand.¹⁰ Furthermore, the steric constraint of the RuCl(η⁵-C₅H₅)(PPh₃) fragment may favour the formation of the less sterically demanding *cis* alkene.¹¹

The extension of this research towards the synthesis of unsymmetrical *cis*-enediones by using two different α-diazo-carbonyl compounds is in progress. In particular, decomposition of a 1 : 1 mixture of EDA and N₂CHCOMe yields **2**, **3** and *cis*-EtOCOCH=CHCOMe in *ca.* 1 : 1 : 3 molar ratio, respectively. The double coupling between carbene units derived from mono- and α,ω-bis-diazo carbonyl compounds is also under investigation and seems to give promising results.

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Footnotes and References

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† The typical procedure adopted for the synthesis of *cis*-enediones **2–6** is described here in detail for **3**. A solution of 1-diazopropan-2-one (700 mg, 8.33 mmol) in 5 ml of toluene was added dropwise to a solution of **1** (6 mg; 8 μmol) in 10 ml of toluene, at 65 °C under Ar atmosphere. The solvent was

evaporated *in vacuo* and **3** was obtained as a pale yellow oily liquid by distillation at 55 °C and 1 mmHg (377 mg, 81%).

Compounds **2–6** gave satisfactory analytical and spectroscopic (¹H and ¹³C NMR and MS) data.

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