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Reactions of Diazo Compounds with Alkenes Catalysed by [RuCl(cod)(Cp)]: Effect of the Substituents in the Formation of Cyclopropanation or Metathesis Products**

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Abstract: The reaction of diazo compounds with alkenes catalysed by complex [RuCl(cod)(Cp)] (cod = 1,5-cyclooctadiene, Cp = cyclopentadienyl) has been studied. The catalytic cycle involves in the first step the decomposition of the diazo derivative to afford the reactive [RuCl(Cp){=C(R^1)R^2}] intermediate and a mechanism is proposed for this step based on a kinetic study of the simple coupling reaction of ethyl diazoacetate. The evolution of the Ru–carbene intermediate in the presence of alkenes depends on the nature of the substituents at both the diazo N_2=C(R^1)R^2 (R^1, R^2 = Ph, H; Ph, CO_2Me; Ph, Ph; C(R^1)R^2 = fluorene) and the olefin substrates R^3(H)C=C(H)R^4 (R^3, R^4 = CO_2Et, CO_2Et; Ph, Ph; Ph, Me; Ph, H; Me, Br; Me, CN; Ph, CN; H, CN; CN, CN). A remarkable reactivity of the complex was recorded, especially towards unstable aryldiazo compounds and electron-poor olefins. The results obtained indicate that either cyclopropanation or metathesis products can be formed: the first products are favoured by the presence of a cyano substituent at the double bond and the second ones by a phenyl.

Keywords: coupling · cyclopropanation · diazo compounds · metathesis · ruthenium

Introduction

Ruthenium cyclopentadienyl complexes are widely used catalysts in a series of C–C bond-forming reactions.[1] In most cases the prototype complex is [RuCl(Cp)(PPh_3)$_2$], not only because of its thermal stability and easy preparation, but also because of its interesting inherent reactivity. In fact, in apolar solvents it dissociates one phosphine at moderate temperatures to give a coordinatively unsaturated reactive intermediate, which is capable of activating the decomposition of diazo derivatives to give selective *cis* coupling of the carbene fragment,[2] cyclopropanation[3] or insertion into X–H (X = S, N) bonds.[4] Reactions involving diazo derivatives (mostly N_2CHSiMe_3 or N_2CHCO_2Et) as carbene sources are reportedly catalysed also by Ru complexes based on the Cp* ligand or its derivatives.[5–7] In particular, many extensive reports deal with the use of [RuCl(cod)(Cp*)] as the catalyst for addition reactions to alkynes in the synthesis of conjugated dienes[6] or to enynes to give alkenylbicyclo-[3.1.0]hexane derivatives.[7]

No reports are present in the literature dealing with the catalytic efficiency of the related cyclopentadienyl complex [RuCl(cod)(Cp)] in this kind of reaction; this complex in principle should exhibit a rather characteristic reactivity pattern, as a consequence of the formation of the highly unsaturated intermediate [RuCl(Cp)] resulting from the facile dissociation of the chelated COD ligand. The ability of COD to be readily displaced has been exploited to easily

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[**] cod = 1,5-cyclooctadiene, Cp = cyclopentadienyl.

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synthesise a large number of $[RuCl(Cp)(L)_2]$ complexes (L = phosphines, amines, dienes, isocyanides); the thermodynamics of these substitution reactions have been accurately determined.[8] Despite its utility as a synthetic intermediate, the catalytic efficiency of [RuCl(cod)(Cp)] has at present been evaluated only in the coupling of alkynes with alkenes or allylic alcohols to produce 1,4-dienes or γ,δ-unsaturated ketones, respectively.[9,10] Remarkably, the absence of methyl substituents on the cyclopentadienyl ring leads to the prediction of a different electronic and steric environment for the metal centre and consequently a different reactivity compared to [RuCl(cod)(Cp*)].[11] This is confirmed for example in the coupling of an alkyne with an allylic alcohol: the activity of both complexes is comparable, but the selectivity toward the linear or branched γ,δ-unsaturated ketones is opposite.[11]

The lack of studies on the use of [RuCl(cod)(Cp)] as the catalyst in carbene-transfer reactions utilizing diazo derivates prompted us to start a systematic study on the simplest C–C bond-forming reactions involving carbene fragments (coupling, cyclopropanation and metathesis). We report here the results of an extensive synthetic and mechanistic study on the reaction of a series of diazo derivatives with alkenes catalysed by [RuCl(Cp)(cod)]. The main goals of this study were to gain information on the mechanism of catalysis and to define how the nature of the substituents at the diazo and at the alkene reagents directs the reaction towards metathesis or cyclopropanation products. Our aim is to establish the potential of this complex as a catalyst for cyclopropanations. Indeed, in recent years an increasing number of Ru-based catalysts, besides those listed above, have been proposed for this reaction.[12,13] Remarkably, although these catalysts are usually less active than the more popular Rh- and Cu-based catalytic systems,[14] they often display unusual selectivities, which complement those obtained with Rh or Cu complexes.

Results and Discussion

In the first part of this study the decomposition of ethyl diazo acetate (EDA) catalysed by [RuCl(cod)(Cp)] has been investigated in detail.

Mechanism of the decomposition of EDA catalysed by [RuCl(cod)(Cp)] in $CHCl_3$ or $CDCl_3$: This ruthenium complex is a very active catalyst at room temperature. To gain information on the mechanism of catalysis we have studied the rate of consumption of EDA as a function of the concentration of the catalyst and of EDA itself (Table 1 and Figure 1).

In most cases the EDA concentration decreases linearly with time. This indicates that, for [EDA]/[Ru] molar ratios between approximately 10 and 25, the rate of consumption of ethyl diazoacetate $\Delta[EDA]/\Delta t$ does not depend on its concentration. Furthermore, as shown in Figure 1, under these experimental conditions the rate depends linearly on the concentration of the ruthenium catalyst, with a constant TOF of $2.7\times10^{-3}\,s^{-1}$.

Table 1. Kinetic data on the decomposition rate of EDA catalysed by [RuCl(cod)(Cp)] at 20 °C in $CHCl_3$.[a]

Run	[Ru] [M]	[EDA] [M]	rate [$M\,s^{-1}$][a]	[EDA]/[Ru]
1	2.2×10^{-3}	2.0×10^{-1}	2.7×10^{-5}[b]	100
2	2.2×10^{-3}	1.0×10^{-2}	6.6×10^{-6}[b]	50
3	1.1×10^{-3}	1.0×10^{-2}	3.2×10^{-6}	10
4	1.1×10^{-3}	1.0×10^{-2}	2.9×10^{-6}	10
5	1.1×10^{-3}	1.0×10^{-2}[c]	1.1×10^{-6}	10
6	1.1×10^{-3}	1.0×10^{-2}[d]	8.0×10^{-6}	10
7	1.1×10^{-3}	1.0×10^{-2}[e]	1.2×10^{-7}	10
8	4.4×10^{-4}	1.0×10^{-2}	1.1×10^{-6}	25

[a] The rates are determined from the ratio $\Delta[EDA]/\Delta t$, which is generally constant with time. [b] Initial rate. [c] In the presence of diethyl maleate and diethyl fumarate, 1.0×10^{-1} M. [d] In the presence of $(Et_4N)Cl$, 1.0×10^{-1} M. [e] In the presence of COD, 1.0×10^{-1} M.

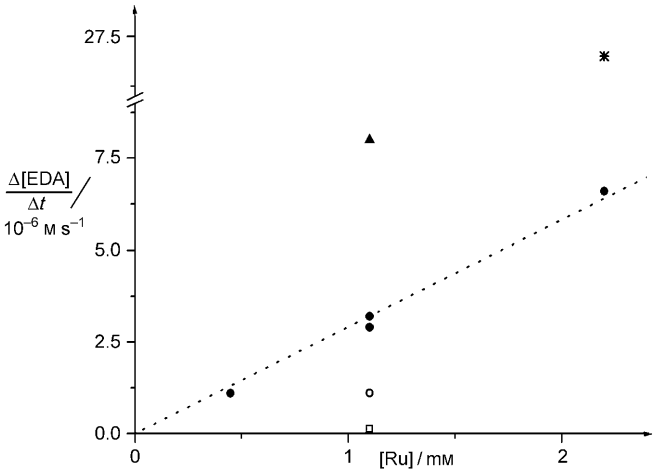
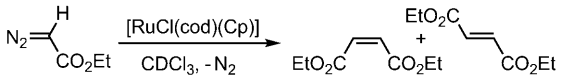


Figure 1. Dependence of the decomposition rate of EDA on the concentration of [RuCl(cod)(Cp)], $CHCl_3$, 20 °C. (●): $[EDA]_0=10^{-2}$ M; (○): $[EDA]_0=10^{-2}$, $[DEM]_0=[DEF]_0=10^{-1}$ M; (□): $[EDA]_0=10^{-2}$, $[COD]=10^{-1}$ M; (▲): $[EDA]_0=10^{-2}$, $[(Et_4N)Cl]=10^{-1}$ M; (*): $[EDA]_0=2\times10^{-1}$ M.

Addition of diethyl maleate and diethyl fumarate, which are the coupling products of this catalysis, decreases the rate of EDA consumption, so that, for example, with $[Ru]_0=1.1\times10^{-3}$, $[EDA]_0=10^{-2}$ and $[DEM]_0=[DEF]_0=10^{-1}$ M (DEM = diethyl maleate, DEF = diethyl fumarate) the rate remains zero order in EDA concentration, but its value lowers from 3.2×10^{-6} to $1.1\times10^{-6}\,M\,s^{-1}$, $TOF=1.0\times10^{-3}\,s^{-1}$. Added COD exhibits a more marked effect and with $[COD]=10^{-1}$ M the rate reduces to approximately $1.2\times10^{-7}\,M\,s^{-1}$, $TOF=1.1\times10^{-4}\,s^{-1}$. The effect of adding $[Et_4N]Cl=10^{-1}$ M is somewhat surprising because the rate increases by more than 160%. This effect fairly contrasts with that observed by using $[RuCl(Cp)(PPh_3)_2]$ complex as the catalyst: in fact, Del Zotto suggested in the N-methylation of amines the simultaneous dissociation of both phosphine and chloride in methanol and this was inferred from the slowing down effect of added chloride on the reaction rate.[15] The opposite effect observed in our case may be attributed to the higher polarity of the reaction medium in the

presence of the ammonium salt. As a further comment on the mechanism, the effect of increasing the initial EDA concentration on its rate of disappearance is rather complex, so that, for example, maintaining constant $[Ru]=2.2\times10^{-3}$ M, $\Delta[EDA]/\Delta t$ for $[EDA]_0=2\times10^{-1}$ M is no longer constant with time (run 1) and the initial rate is about four times higher (TOF_{iniz} = ca. 1.2×10^{-2} s^{-1}) than with $[EDA]_0=10^{-2}$ M (run 2).

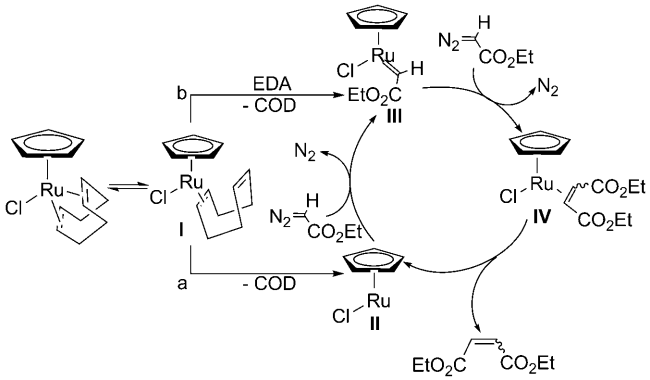
Parallel studies on $CDCl_3$ solutions, in which the evolution of EDA in the presence of [RuCl(cod)(Cp)] was monitored by ^{1}H NMR spectroscopy, have shown that in the range of ruthenium concentrations studied by IR spectroscopy (4.4×10^{-4}–2.2×10^{-3} M) and for low [EDA]/[Ru] ratios (<50), the unique reaction products are diethyl maleate and diethyl fumarate.



To check the effect of catalyst and EDA concentrations on the isomer distribution we have run a series of experiments with $[Ru]=2.5\times10^{-3}$–5.0×10^{-2} M and $[EDA]=2.5\times10^{-3}$–5.5 M. The results are as follows:

1) With a ratio EDA/Ru 1:1 or 1:20, DEM and DEF are formed in an equimolar quantity corresponding to a statistical distribution. The absence of any effect of catalyst concentration on isomer distribution seems to rule out the occurrence of a bimolecular mechanism referred to ruthenium.[16]
2) With higher EDA/Ru ratios (10–220), the DEM/DEF ratio (3–9) increases with increasing initial EDA concentration. This can be accounted for by assuming that at higher EDA concentrations the initially formed olefins (DEM and DEF) can effectively compete with EDA for coordination at the metal centre so favouring an external attack by EDA to the coordinated carbene. This attack affords the less sterically demanding *cis* isomer DEM as fully demonstrated by Rigo and co-workers.[2]

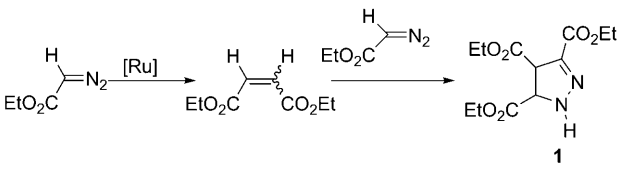
These kinetic studies fit well with the simplified mechanism shown in Scheme 1. At low concentrations of EDA (10^{-2} M) and in the absence of added olefins, the mechanism is fairly simple (pathway a) and implies COD dissociation from [RuCl(η^4-cod)(Cp)] via the {η^2-cod} intermediate **I** to give the coordinatively doubly unsaturated [RuCl(Cp)] (**II**). This undergoes successive attack by two molecules of EDA to afford the carbene and olefin intermediates **III** and **IV**. Dissociation of the olefin from **IV** affords the reaction products and the intermediate **II**, closing the catalytic cycle. The observed zero order for the rate of disappearance of EDA may be related to the fact that the rate of formation of **II**, which is the initial catalytic species in the cycle, does not



Scheme 1. Proposed catalytic cycle for the decomposition of ethyl diazoacetate catalysed by [RuCl(cod)(Cp)].

depend on the concentration of EDA itself. The slowdown effect of COD, DEF and DEM, at relatively high concentrations, implies that these olefins compete with EDA in the coordinatively unsaturated intermediates **I**–**IV**, thereby lowering the efficiency of the catalytic cycle. Furthermore, the effect on the rate of increasing the EDA concentration (2×10^{-1} versus 10^{-2} M) suggests that at higher concentrations reaction pathway b becomes important. It is possible to envisage a bimolecular attack on the ruthenium centre favoured by a variation of hapticity of COD, already observed with iridium complexes[17] and in our preliminary kinetic studies on the substitution of COD by isocyanides in [RuCl(cod)(Cp)].[18]

The presence of complex reaction pathways is confirmed by ^{1}H NMR spectroscopic studies at variable EDA concentrations. At low [EDA]/[Ru] ratios in the range of 1–10, the conversion is fast and quantitative in a few minutes at room temperature to give a mixture of DEM and DEF. Increasing the [EDA]/[Ru] ratio up to 1000, the conversion of ethyl diazoacetate needs much longer times, because of the inhibiting effect of the primary products DEM and DEF on the rate. Furthermore, in these cases, the initially formed olefin products undergo a thermal reaction with residual EDA to form a cyclic product identified as 3,4,5-triethyl-4,5-dihydro-1*H*-pyrazole-3,4,5-tricarboxylate (**1**) (Scheme 2 and Figure 2).



Scheme 2. Formation of compound **1**.

The proposed mechanism for the formation of the dihydropyrazole is a 1,3-dipolar cycloaddition of the diazo compound to an olefin, in this case, diethyl maleate or fumarate.[19]

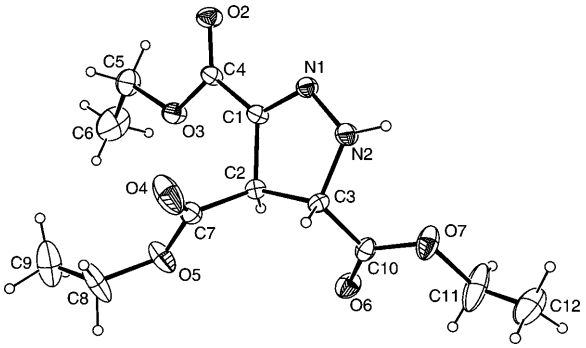


Figure 2. Molecular structure of **1** with the atom nomenclature. Selected bond lengths [Å] and angles [°]: N1–N2 1.329(6), N1–C1 1.286(6), N2–C3 1.466(6), C1–C2 1.514(7), C2–C3 1.546(7), C1–C4 1.455(7), C2–C7 1.509(7), C3–C10 1.515(7); C1-N1-N2 110.0(4), N1-N2-C3 113.4(4), N2-C3-C2 102.3, C3-C2-C1 100.7(4), C2-C1-N1 113.4(4).

To prove that the formation of **1** occurred by the proposed mechanism, we have carried out the cycloaddition of ethyl diazoacetate with DEM or DEF in a 1:1 molar ratio, in the absence of the ruthenium catalyst and **1** was obtained as the only product. Thus the synthesis of **1** from EDA is a catalytic/thermal process, in which the metal catalyst promotes the initial formation of the olefin, necessary for pyrazole formation.

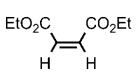
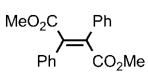
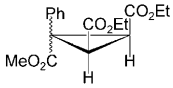
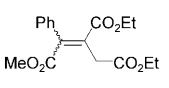
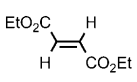
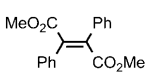
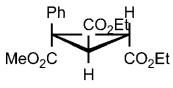
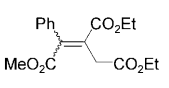
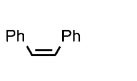
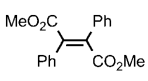
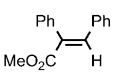
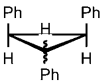
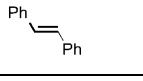
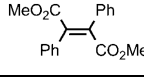
The mechanistic data obtained in the first part of this work have given important information on the characteristics of the catalyst [RuCl(cod)(Cp)] as follows: 1) albeit it is a 18-electron ruthenium(II) d^6 complex, the dissociation of COD is an easy process at room temperature, as already reported;[8] 2) the decomposition of the diazo derivative is always a fast process; 3) the addition of the second molecule of diazo to give the coupling products is also a fast process; 4) the coupling reaction is not stereoselective; and 5) the reaction products diethyl fumarate and diethyl maleate lower the decomposition rate of EDA. The reactivity of the catalytic metal centre strongly depends on the nature of the formed olefin; for example, the decomposition of methyl phenyldiazoacetate (MPDA) catalysed by [RuCl(cod)(Cp)] has been found to be fast when using MPDA alone, but becomes slower in the presence of EDA. In fact, in this last case, the coupling olefin products are less sterically hindered and compete with MPDA for the active ruthenium centre.

The formation of a highly unsaturated 14-electron species [RuCl(Cp)] with two free coordination sites, which has been clearly evidenced in our parallel kinetic study,[18] allows us to foresee a marked ability to coordinate both a carbene unit and an olefin, so leading us to evaluate the catalytic properties of [RuCl(cod)(Cp)] in cyclopropanation and/or metathesis reactions.

Decomposition of diazo derivatives in the presence of an alkene: We have chosen sets of different diazo derivatives and alkenes and used identical reaction conditions with the aim of understanding how the nature of the substituents and the geometry of the alkene direct the catalytic cycle towards the cyclopropanation or the metathesis reaction. Preliminary catalytic tests have been performed in the decomposition of MPDA in the presence of 1,2-disubstituted symmetric alkenes, like diethyl maleate, diethyl fumarate and *cis*- and *trans*-stilbene. The choice of MPDA as the diazo compound is based on its reduced tendency to form coupling products compared with the previously studied EDA. We have adopted standard reaction conditions derived from literature works (alkene (1.2 equiv), diazo compound (1 equiv), [RuCl(cod)(Cp)] (0.05 equiv), 60 °C, controlled addition of diazo compound over 6 h).[5,20] The results (Table 2) are indicated as the percentage conversion of the diazo derivative in the various products; these in turn are grouped as coupling, cyclopropanation/homologation and metathesis/2nd-cyclopropanation products.

These preliminary tests gave some important information. The complex is capable of catalysing both the cyclopropanation and metathesis reactions and the selectivity is strongly dependent on olefin substituents. In fact, MPDA reacts with diethyl fumarate or maleate to afford the cyclopropanes **2a** or **2b** and the corresponding homologation compound **3**, the

Table 2. Product distribution in the decomposition of methyl phenyldiazoacetate in presence of alkenes[a]

Diazo compound	Olefin	Product distribution[b] coupling		cyclopropanation/homologation				metathesis/2nd cyclopropanation			
			(8)		**2a**	(38)	 **3**	(17)	–		
			(36)		**2b**	(34)	 **3**	(19)	–		
			(27)		–				 **4**	(39)	 **5**[c]
			(100)		–					–	

[a] For experimental conditions see the Experimental Section. [b] Yields (in parentheses) are expressed as mol% conversion of MPDA in the various products; thermal decomposition products (methyl phenylglioxylate and methyl mandelate) complete the reaction balance. [c] The quantity of this cyclopropane of the second cycle is comparable with the one of metathesis product.

latter formally deriving from an insertion of the carbene fragment into one of the C–H bonds of the olefin.[12,21] Remarkably, catalytic cyclopropanation of electron-poor disubstituted olefins, such as diethyl fumarate or maleate, appears to be quite unprecedented in the literature; therefore, this finding highlights the potential of our complex as a cyclopropanation catalyst (see also below). By contrast, with *cis*-stilbene the preferred reaction is metathesis between the carbene fragment of MPDA and the olefin, giving product **4**. This process leaves on the metal centre the fragment =CHPh, which can react with a second molecule of alkene giving cyclopropane **5** or undergo olefin self-metathesis in a parallel catalytic cycle. The last process has been observed, in particular, when a large excess of *cis*-stilbene was used (10-fold): the unreacted stilbene at the end of the reaction was a mixture of *cis* and *trans* isomers in a 1:1 ratio.

This behaviour is accounted for by assuming the crucial formation in the catalytic cycle of a metallocyclic intermediate, which, depending on the nature of the olefin substituents, can evolve to give the cyclopropanation or metathesis/2nd-cyclopropanation products.[5,21]

Interestingly, in the reaction of MPDA with *trans*-stilbene only the diazo coupling product has been isolated, thus suggesting that coordination of this olefin to the metal centre is not occurring probably because of steric hindrance.

We performed some additional experiments aimed at maximizing the yield in cyclopropanation and/or metathesis and also at reducing catalyst loading. We repeated the experiments with *cis*-stilbene by using only 1 mol% catalyst: this causes a decrease in activity (diazo conversion 41%), which, however, could be overcome by adding the diazoacetate in 22 h (diazo conversion 70%). The yield in the coupling products could be lowered by using a large excess (10-fold) of olefin. However, since the selectivity ratio between cyclopropanation and metathesis remained unchanged upon increasing the olefin concentration, we chose to evaluate this parameter by using only a moderate excess (20%) of the olefin. The diazoacetate was added very slowly, by controlled addition over long reaction times (22 h), to minimize the coupling side reaction.

To get a better insight into the effects of steric and electronic factors on the competitive cyclopropanation/metathesis reactions, we have continued our study by investigating different couples of diazo compound/olefin (Table 3). In the first runs, 1–9, we have tried to evaluate the influence of the substituents on the diazo compound, keeping at least one phenyl group; in fact it has been verified that diazo derivatives lacking a phenyl substituent and bearing a keto or ester group (like for example EDA) gave complex intractable mixtures.

Phenyl diazomethane reacts with *cis*-stilbene to give as the metathesis product *trans*-stilbene and a cyclopropanation product (Table 3, entry 1). On the other hand, it reacts with *cis*-propenyl benzene to give a very high conversion to the cyclopropanes **6a** and **6b** (Table 3, entry 2). This is a remarkable result, given that efficient cyclopropanations with highly reactive phenyldiazomethane or its precursor phenyl tosylhydrazone have been reported very rarely and applications are generally limited to terminal olefins.[22] MPDA forms with *cis*-stilbene mainly the diazo coupling product and the metathesis product in low yield (Table 3, entry 3), with a reaction outcome similar to that reported in Table 2 under slightly different conditions. The selectivity for the metathesis/2nd-cyclopropanation product increases on moving to *cis*-propenylbenzene (Table 3, entry 4). Finally, reaction of simple styrene yields no metathesis product, but rather alkene homologation and mainly cyclopropanation products (Table 3, entry 5). Interestingly, the stereoselectivity in the formation of the cyclopropane ring favours the *Z* product, whereas when using rhodium(II) catalysts in this reaction almost exclusive *E* product formation is generally observed.[23] Diaryl diazo derivatives, such as diphenyl diazomethane or 9-diazo-9H-fluorene (DAF), do not react at all with *cis*-stilbene (Table 3, entries 6 and 8), whereas the metathesis/2nd-cyclopropanation reactions occur to some extent with *cis*-propenyl benzene (Table 3, entries 7 and 9). Clearly in this last case replacement of a methyl for a phenyl substituent on the olefin facilitates its coordination to the metal centre, which is hindered by the Cp, Cl and diaryl carbene ligands. This confirms once more the importance of steric factors in the formation of metallacyclobutane or, in general, in the interaction between the carbene fragment and the external olefin. In runs 8–17 we have used 9-diazo-9*H*-fluorene, which gives very selective reactions, and varied the olefin, to evaluate the contribution of the alkene in directing the reaction. Runs 9–11 confirm that the presence of one phenyl substituent in the alkene makes it possible for the metathesis reaction to occur; however, this is accompanied by the cyclopropanation reaction with *trans*-propenyl benzene and styrene to give **12** and **13**, respectively. This difference in behaviour with respect to *cis*-propenyl benzene is noteworthy and seems to indicate a high instability for a cyclopropane bearing three substituents on one side of the ring. Similar steric reasons can account for the lack of reactivity of DAF with diphenyl olefins (runs 8 and 12). Halogenated olefins are generally not reactive under these conditions, so that, for example, in the reaction of DAF with *cis*- and *trans*-dichloroethylene, *cis*-1,3-dichloropropene, 1-chloro-3-methyl-2-butene, 1-chloro-2-methylpropene and 1-bromo-2-methylpropene only the coupling product was observed. However, in the case of the *cis*-1-bromopropene, less-hindered and bearing a weaker electron withdrawing halogen, both metathesis and cyclopropanation products have been obtained. Remarkably, the presence of electron-withdrawing substituents in the olefin does not preclude by itself its reactivity towards diazo derivatives when using our catalyst (see also above). In fact, runs 14–19 show that a series of cyano olefins reacts very selectively with mono- and diaryl diazo compounds to give mostly cyclization products, drastically minimizing also the product of diazo coupling. It seems that the cyano group can very efficiently coordinate to the metal centre, thereby favouring the formation of the crucial metallocyclic intermediate. Therefore, the formation of a coordinatively highly unsaturated Ru com-

Table 3. Product distribution in the decomposition of diazocompounds in presence of olefins[a]

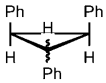
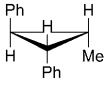
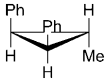
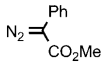
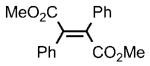
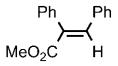
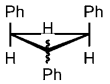
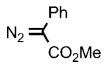
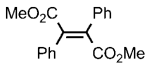
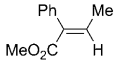
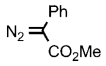
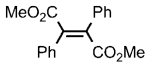
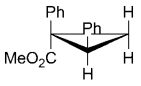
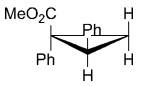
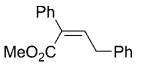
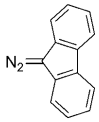
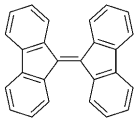
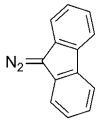
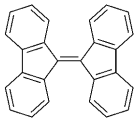
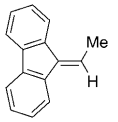
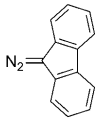
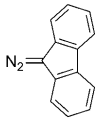
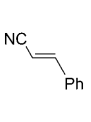
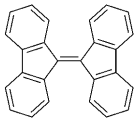
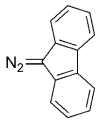
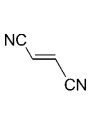
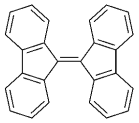
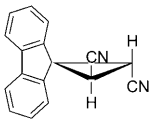
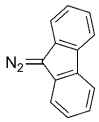
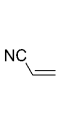
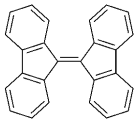
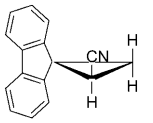
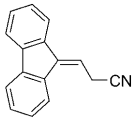
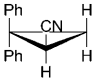
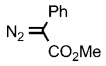
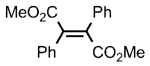
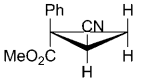
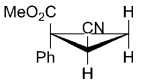
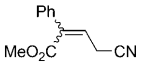
Run	Diazo compound	Olefin	Product distribution[b] coupling		cyclopropanation			metathesis			2nd cyclopropanation		
1				(5)	–					(52)		**5**	(43)
2				(2)		**6a**	(78)	–				**6b**	(10)
3				(54)	–				**4**	(25)		**5**[c]	
4				(23)	–				**7**	(41)	**6a/6b** 3.6:1[c]		
5				(5)		**8a**	(13)	–			–		
						**8b**	(47)						
						**9**	(35)						
6				(33)	–			–			–		
7				(25)	–				**10**	(10)	**6a/6b** 3.2:1[c]		
8				(100)	–			–			–		
9				(48)	–				**11**	(52)	**6a/6b** 3.7:1 [c]		
10				(43)		**12**	(32)		**11**	(22)	**6a/6b** 1:1.6[c]		
11				(30)		**13**	(59)		**14**	(11)		**15**[c]	
12				(95)	–			–			–		
13				(36)		**16**	(35)		**11**	(9)	–		
14				(11)		**17a**	(56)	–			–		
						17b	(33)						

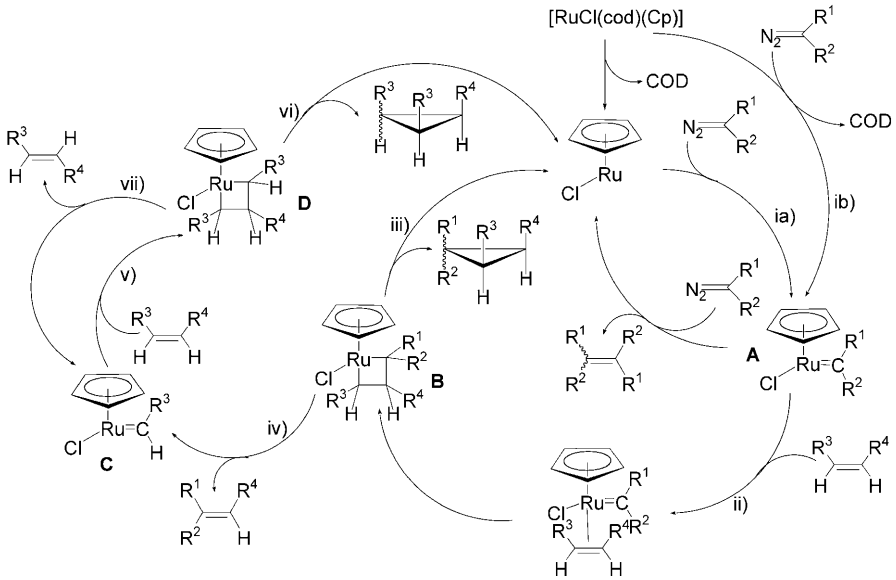
Table 3. (Continued)

Run	Diazo compound	Olefin	Product distribution[b] coupling		cyclopropanation			metathesis	2nd cyclopropanation
15				(87)	–			–	–
16				(4)		**18**	(56)[d]	–	–
17				(10)		**19**	(74)	–	–
						**20**	(16)		
18			–			**21**	(100)	–	–
19				(12)		**22a**	(12)	–	–
						**22b**	(46)		
						**23**	(22)		

[a] For experimental conditions see the Experimental Section. [b] Yields (in parentheses) are expressed as mol% conversion of the diazo compound in the various products; thermal decomposition products complete the reaction balance of the diazo derivatives. [c] The quantity of these cyclopropanes of the second cycle is comparable with the one of metathesis product. [d] The remaining 40% is an unknown product, probably the other cyclopropane isomer.

plex catalyst appears to make it possible to prepare cyclopropanes from diazocompounds and electron-poor olefins, a class of substrates that are known to be very unreactive with traditional catalytic systems. To the best of our knowledge, the only hitherto reported example of cyclopropanation of olefins of this kind (α,β-unsaturated ketones) involves the use of sulfides as mediators.[24]

The whole of these results are consistent with the catalytic cycle shown in Scheme 3. The sequence of proposed steps leads us to classify the illustrated mechanism mostly as a stoichiometric one, and not all the metal intermediates may represent minima on the potential



Scheme 3. Proposed catalytic cycle for the decomposition of diazo compounds in the presence of olefins. For the sake of clarity the homologation products are not indicated, as well as the 1,1-disubstituted- and the *trans* olefins, which are, however, discussed in the text.

energy surface. The first step (ia and ib) implies the formation of the 16-electron metal–carbene intermediate **A**; this is a rather easy process and its details have been fully illustrated in Scheme 1. The intermediate **A** can either react with a second molecule of diazo compound to give the coupling product (this reaction is always present to some extent) or (ii) coordinate the olefin, to give, subsequently, the ruthenium metallacycle **B**. Steric factors play a very important role in this step; in fact, with sterically hindered diazo/olefin couples only the diazo coupling product is obtained. In principle, cyclopropanation can occur also without coordination of the olefin to the metal centre, as observed, for example, with rhodium- and copper-metal catalysts; however, in our case we believe that this pathway is much less likely with an electron-rich, coordinatively unsaturated metal centre, which should favour the formation of the metallacyclobutane by oxidative addition.[25] In this view, the lack of any cyclopropanation product bearing four aryl substituents is attributed to steric hindrance, which does not allow the formation of the metallacycle. The geometry of the olefin also directs the reactivity, so that, for example, MPDA does not react with *trans*-stilbene, whereas it gives with the *cis* isomer the metathesis and 2nd-cyclopropanation products.

The metallacycle **B**, depending on the nature of the various substituents, can evolve to liberate in solution either the cyclopropane (iii), reforming the starting 14-electron [RuCl(Cp)] complex, or the metathesis product (iv), forming the new 16-electron carbene complex **C**. A computational analysis on a closely related system showed that the metal precursor of the cyclopropanation way was in that case thermodynamically more favoured with respect to the one giving metathesis.[7c] The prevalence of pathway iii or iv in our system can be discussed on the basis of the stability of the resulting products, by assuming that there are no kinetic limitations for the evolution of intermediate **B**. An insight into the factors determining the ability of intermediate **B** to give both cyclopropanation and metathesis can be gained from the products distributions shown in Tables 2 and 3: metathesis occurs only in the presence of olefins bearing a phenyl substituent, whereas cyclopropanation/homologation is the only reaction observed in the presence of cyano olefins. Therefore, there is a delicate thermodynamic balance between the formation of the 16-electron carbene complex/olefin and 14-electron complex/cyclopropane pairs. It appears that the metathesis reaction is driven in all cases by the formation of the intermediate [RuCl(Cp)(=C(H)Ph)] **C**, which is stabilized by the phenyl substituent in the =C(H)Ph fragment, due to its ability to delocalise electron density. This is confirmed by the reactivity exhibited by styrene and propenyl benzene, which give as unique metathesis products those resulting from the formation of **C** where $R^3 = Ph$. However, also the nature of the cyclopropane plays an important role, so that styrene and *trans*-propenyl benzene react with DAF to give both cyclopropanation and metathesis products, whereas *cis*-propenyl benzene gives only metathesis products. If one considers that generally the olefin maintains its starting geometry in the cyclopropanation products, these last observations can be accounted for on purely steric bases by assuming that three hindering substituents (for example 2 Ph + 1 Me) on the same side destabilize the cyclopropane ring.

The results obtained with cyano olefins are very interesting: the diazo coupling is drastically reduced and the reaction is very selective towards cyclopropanation. It seems that the cyano group can very efficiently coordinate to the metal centre, thereby favouring the formation of the crucial metallacyclic intermediate **B**; furthermore, the absence of any phenyl substituent drains the reaction through pathway iii.

Turning to the fate of metal intermediate **C** resulting from the metathesis process, it can react with the starting olefin to give the new metallacycle **D** (v). This, as a rule, liberates the 2nd-cyclopropanation product (vi); in fact, the metathesis and 2nd-cyclopropanation products are formed in almost equivalent quantities. Alternatively, **D** gives the *trans*-olefin isomer in a self-metathesis cycle (pathway vii)).

As a useful comment, the behaviour of [RuCl(cod)(Cp)] as the catalyst precursor can be compared with that exhibited by the Grubbs-type catalysts. In both cases a "similar" crucial ruthenium metallacyclo-butane (or -hexane)[26] complex is proposed in the catalytic cycle.[27–29] However, this similarity appears rather formal. In fact, the cyclopentadienyl intermediate is a 18-electron complex and can give either the metathesis or cyclopropane product with corresponding formation of a 16- or 14-electron complex. This second way appears disfavoured in the Grubbs system, because the cyclopropane reductive elimination step from the metallacyclobutane intermediate would afford an unlikely very high-energy 12-electron metal species.

Conclusion

[RuCl(cod)(Cp)], due to its possibility of generating a double coordinative unsaturation, appears to be a very efficient catalyst in the decomposition of diazo derivatives in the presence of olefins. Both cyclopropanation and metathesis reactions can occur: cyclopropanation is predominant with cyano olefin and in the absence of phenyl substituents on the olefin, whereas metathesis is always accompanied by a 2nd-cyclopropanation cycle, which consumes the active metal–carbene intermediate. The reactivity exhibited by our complex as a cyclopropanation catalyst with unstable aryldiazo compounds and with electron-poor olefins appears particularly noteworthy. We are currently engaged in better focussing the scope of this novel catalytic system in such challenging reactions.

Experimental Section

General comments: The reagents (Aldrich-Chemie or ABCR) were high purity products and were generally used as received. All solvents were

dried by standard procedures and distilled under nitrogen immediately prior to use. The reaction apparatus was carefully deoxygenated, and the reactions were performed under argon and all operations were carried out under an inert atmosphere. Complex [RuCl(cod)(Cp)] was prepared according to a published method.[8a] The diazo derivatives phenyldiazomethane,[30] diphenyldiazomethane,[31] MPDA[32] and DAF[33] were synthesized by literature methods. The solution ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer (300.1 for ^{1}H and 75.5 MHz for ^{13}C) at room temperature. The chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals, with tetramethylsilane as internal standard for ^{1}H and ^{13}C chemical shifts. GCMS analyses were performed with a Varian Saturn 2100T gas chromatograph/mass spectrometer (injector temperature 240 °C, column Supelco SPB 50); the temperature was programmed from 100 (1 min) to 240 °C with a gradient of 15 °C min^{-1}.

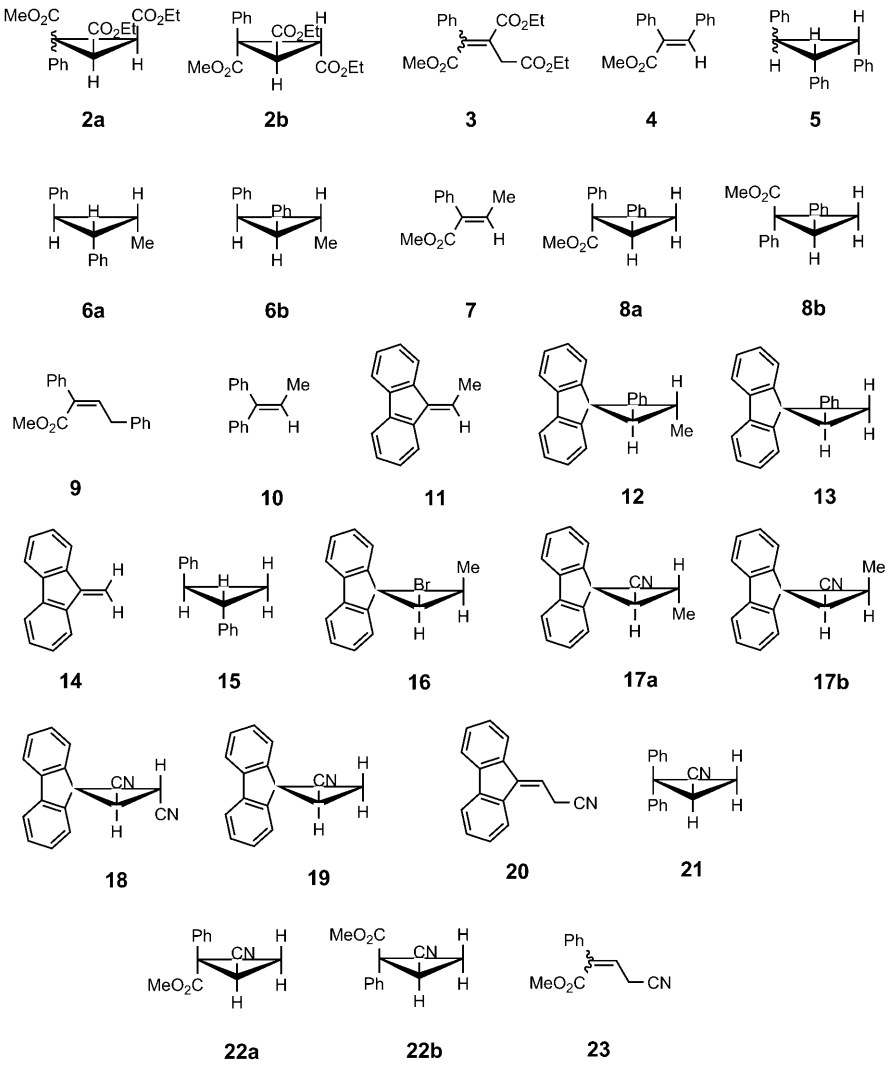
Synthesis of 3,4,5-triethyl-4,5-dihydro-1*H*-pyrazole-3,4,5-tricarboxylate (1): The required amounts of complex [RuCl(cod)(Cp)] (11 mg, 0.03 mmol) and EDA (3.2 mL, 30.0 mmol) were placed in a Schlenk tube previously evacuated and filled with argon. The resulting mixture was stirred at room temperature for 48 h and then at 40 °C for 48 h; after which a solid formed. This solid was filtered and dried in vacuum to give **1** (0.50 g, 17.5 % yield) as a tan-coloured powder. ^{1}H NMR ($CDCl_3$): δ = 1.22–1.40 (3t, 9H; CH_2CH_3), 4.15–4.38 (3q, 6H; CH_2CH_3), 4.42 (d, 1H; CH), 4.75 (d, 1H; CH), 6.77 ppm (s, 1H; NH); ^{13}C NMR ($CDCl_3$): δ = 14.0, 14.1, 14.3 (CH_2CH_3), 52.2 (CH), 61.6, 62.2, 62.6 (CH_2CH_3), 66.2 (CH), 140.0 (CN), 162.1 168.30, 171.8 ppm (COO); FTIR (KBr): $\tilde{\nu}$ = 3298 (N–H), 1695, 1738 cm^{-1} (C=O); calcd for $C_{12}H_{18}N_2O_6$ (M = 286.2): C 50.32, H 6.28, N 9.78; found: C 50.64, H 6.19, N 9.53.

The same product was obtained by reacting a mixture of ethyl diazoacetate (1.5 mL, 13.0 mmol) and DEM (1 mL, 6.0 mmol) (or DEF (1 mL, 6.0 mmol)) in a Schlenk tube. After stirring at room temperature for 16 h, the resulting suspension was filtered, giving **1** as a pale-yellow solid, which was washed with *n*-hexane (2 × 2 mL) and dried under vacuum (yield: 83 % for DEM and 73 % for DEF).

General procedure for the catalysed decomposition of diazo derivatives: The required amount of complex (5 or 1 mol %) was placed in an NMR tube and dissolved in $CDCl_3$ under an inert atmosphere. The diazo compound (1.2 mmol) was added and the reaction was followed by ^{1}H NMR spectroscopy. Yields were calculated by integration of NMR spectroscopic signals.

General procedure for the catalysed decomposition of diazo derivatives in the presence of alkenes: The required amounts of complex (5 mol % for the tests reported in Table 2, or 1 mol % for the tests reported in Table 3) and alkene (1.2 mmol) were placed in a round-bottomed flask and dissolved in dichloroethane (3 mL) under an inert atmosphere. The obtained solution was then heated at 60 °C and the diazo compound (1.2 mmol in 2 mL of dichloroethane) was added over 22 h (or 6 h for the tests reported in Table 2) by using a syringe pump. The reaction mixture was subsequently evaporated to dryness and analysed by NMR spectroscopy. Reaction products were purified by column chromatography onto silica gel 60 (eluent: *n*-hexane/diethylether 80:20). The reaction products were identified by comparison of the NMR spectra with literature data or characterized by a combination of NMR and MS techniques.

Products methyl (*E*)-2,3-diphenylpropenoate (**4**),[34] 1,2,3-triphenylcyclopropane (**5**),[35] 1-methyl-*trans*-2,3-diphenylcyclopropane (**6a**),[36] 1-methyl-*cis*-2,3-diphenylcyclopropane (**6b**),[36a,37] (*E*)-methyl 2-phenylbut-2-enoate (**7**),[38] (1*R*,2*S*)-methyl 1,2-diphenylcyclopropanecarboxylate (**8a**),[39] (1*S*,2*S*)-methyl 1,2-diphenylcyclopropanecarboxylate (**8b**),[39] (*Z*)-methyl 2,4-diphenylbut-2-enoate (**9**),[39] 1,1-diphenylpropene (**10**),[40] 9-methylmethylene-9*H*-fluorene (**11**),[41] *trans*-2-methyl-3-phenylspiro(cyclopropane-1,9′-[9*H*]fluorene) (**12**),[42] 2-phenylspiro(cyclopropane-1,9′-[9*H*]fluorene) (**13**),[43] dibenzofulvene (**14**),[44] *trans*-1,2-diphenylcyclopropane (**15**),[45] *trans*-2,3-dicyanospiro(cyclopropane-1,9′-[9*H*]fluorene) (**18**),[46] 2-cyanospiro(cyclopropane-1,9′-[9*H*]fluorene) (**19**)[46] and 2,2-diphenylcyclopropanecarbonitrile (**21**)[47] have been identified by comparison of the NMR spectra with literature data.



(2*R*,3*S*)-2,3-Diethyl-1-methyl-1-phenylcyclopropane-1,2,3-tricarboxylate (2a): ^{1}H NMR ($CDCl_3$): δ = 1.12 (t, 6H; CH_2CH_3), 2.96 (s, 2H; CH), 3.65

(s, 3H; OCH_3), 4.01 (q, 4H; CH_2CH_3), 7.26–7.39 ppm (m, 5H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 13.8$ (CH_2CH_3), 31.8 (CH), 39.7 (C(Ph)(CO_2Me)), 53.5 (OCH_3), 61.1 (CH_2CH_3), 127.3–131.9 (Ph), 166.2, 172.1 ppm (COO).

(2*R*,3*R*)-2,3-Diethyl-1-methyl-1-phenylcyclopropane-1,2,3-tricarboxylate (2b): ^1H NMR ($CDCl_3$): $\delta = 1.02$ (t, 3H; CH_2CH_3), 1.31 (t, 3H; CH_2CH_3), 3.05 (d, 1H; CH), 3.21 (d, 1H; CH), 3.65 (s, 3H; OCH_3), 3.93 (q, 2H; CH_2CH_3), 4.22 (q, 2H; CH_2CH_3), 7.26–7.35 ppm (m, 5H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 13.8$, 14.1 (CH_2CH_3), 31.3, 32.2 (CH), 44.7 (C(Ph)-(CO_2Me)), 52.9 (OCH_3), 61.1, 61.6 (CH_2CH_3), 128.4–133.7 (Ph), 167.4, 168.7 ppm (COO).

2,3-Diethyl-1-methyl-1-phenylprop-1-ene-1,2,3-tricarboxylate (3): ^1H NMR ($CDCl_3$): $\delta = 1.25$ (t, 3H; CH_2CH_3), 1.30 (t, 3H; CH_2CH_3), 3.29 (s, 2H; CH_2), 3.79 (s, 3H; OCH_3), 4.15 (q, 2H; CH_2CH_3), 4.26 (q, 2H; CH_2CH_3), 7.26–7.48 ppm (m, 5H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 13.9$, 14.1 (CH_2CH_3), 35.3 (CH_2), 52.5 (OCH_3), 61.0, 61.6 (CH_2CH_3), 127.9–134.0 (Ph), 126.9, 146.0 (C=C), 166.2, 168.5, 170.0 ppm (COO).

2-Bromo-3-methylspiro(cyclopropane-1,9′-[9*H*]fluorene) (16): ^1H NMR ($CDCl_3$): $\delta = 2.30$ (m, 1H; CHMe), 2.45 (d, 3H; CH_3), 4.10 (d, 1H; CHBr), 7.20–7.90 ppm (m, 8H; CH).

2-Cyano-3-methylspiro(cyclopropane-1,9′-[9*H*]fluorene) (17a): ^1H NMR ($CDCl_3$): $\delta = 1.52$ (d, 3H; CH_3), 2.25 (d, 1H; CH(CN)), 2.35 (m, 1H; CHMe), 6.90–7.60 ppm (m, 8H; CH).

2-Cyano-3-methylspiro(cyclopropane-1,9′-[9*H*]fluorene) (17b): ^1H NMR ($CDCl_3$): $\delta = 1.60$ (d, 3H; CH_3), 2.35 (m, 1H; CHMe), 2.59 (d, 1H; CH(CN)), 6.90–7.60 ppm (m, 8H; CH).

3-(9*H*-Fluoren-9-ylidene)propanenitrile (20): ^1H NMR ($CDCl_3$): $\delta = 3.78$ (d, 2H; CH_2), 6.50 (t, 1H; CH), 7.00–7.90 ppm (m, 8H; CH).

(1*R*,2*R*)-Methyl 2-cyano-1-phenylcyclopropanecarboxylate (22a): ^1H NMR ($CDCl_3$): $\delta = 1.85$ (dd, 1H; CH), 1.95 (dd, 1H; CH_2), 2.54 (dd, 1H; CH_2), 3.82 (s, 3H; OCH_3), 7.23–7.50 ppm (m, 5H; Ph); the proposed geometry is based on the higher values of the chemical shift of the cyclopropane protons with respect to **22b**, as observed in the cyclopropanes **8a** and **8b**.

(1*S*,2*R*)-Methyl 2-cyano-1-phenylcyclopropanecarboxylate (22b): ^1H NMR ($CDCl_3$): $\delta = 1.75$ (dd, 1H; CH), 2.05 (dd, 1H; CH_2), 2.30 (dd, 1H; CH_2), 3.75 (s, 3H; OCH_3), 7.23–7.50 ppm (m, 5H; Ph).

Methyl 4-cyano-2-phenylbut-2-enoate (23): ^1H NMR ($CDCl_3$): $\delta = 3.08$ (d, 2H; CH_2), 3.78 (s, 3H; OCH_3), 6.95 (t, 1H; CH), 7.20–7.40 ppm (m, 5H; Ph).

Kinetic experiments: Solutions of EDA and [RuCl(cod)(Cp)] ([EDA] = 10^{-2}–10^{-1} M, [Ru] = 4.4×10^{-4}–2.2×10^{-3} M) in $CHCl_3$ were carefully deoxygenated by three freeze-thaw cycles. Aliquot portions of the reacting mixture were removed, at given reaction times, through a Suba-seal rubber stopper and immediately analysed in the 2300–1700 cm^{-1} region by using a Perkin–Elmer 781 spectrophotometer (0.5 mm sodium chloride cells). The reaction rate $\Delta[EDA]/\Delta t$ was determined from the variation of the absorbance with time of the band at 2180 cm^{-1}, relative to the N–N stretching of EDA, knowing its initial concentration. When the variation was not linear, the initial velocity was determined.

X-ray structure determination for 3,4,5-triethyl-4,5-dihydro-1*H*-pyrazole-3,4,5-tricarboxylate (1): $C_{12}H_{18}N_2O_6$; $M_r = 286.28$; orthorhombic; space group = $P2_12_12_1$ (no. 19); $a = 10.504(2)$, $b = 17.737(3)$, $c = 7.875(2)$ Å; $V = 1467.2(5)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.296$ g cm^{-3}; $\mu = 0.105$ mm^{-1}; $F(000) = 608$, R_1 on F (wR_2 on F^2) = 0.068 (0.149) for 1335 observed [$I > 2\sigma(I)$] reflections. A prismatic crystal was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 diffractometer (FEBO system) with graphite-monochromated $Mo_{K\alpha}$ radiation (0.71073 Å), by following the standard procedures at room temperature. All intensities were corrected for Lorentz polarization and absorption. The structure was solved by direct methods by using reference [48]. Refinement was carried out by full-matrix least-squares procedures (based on F_o^2) by using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 U_{eq} of the parent carbon atom). The Flack parameter[49] has been refined for the structure. The calculations were performed with the SHELXL-97 program,[50] implemented in the WinGX package.[51] CCDC 684702 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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