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Dinuclear ruthenium(I) complexes of the type $[Ru_2(CO)_4L_2]$ with carboxylate or 2-pyridonate ligands: Evaluation as catalysts for olefin cyclopropanation with diazoacetates

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Dedicated to Manfred Regitz on the occasion of his 70th birthday.

Abstract

Dinuclear ruthenium(I,I) carboxylate complexes $[Ru_2(CO)_4(\mu\text{-}OOCR)_2]_n$ (R = CH_3 (**1a**), C_3H_7 (**1b**), H (**1c**), CF_3 (**1d**)) and 2-pyridonate complex $[Ru_2(CO)_4(\mu\text{-}2\text{-pyridonate})_2]_n$ (**3**) catalyze efficiently the cyclopropanation of alkenes with methyl diazoacetate. High yields are obtained with terminal nucleophilic alkenes (styrene, ethyl vinyl ether, α-methylstyrene), medium yields with 1-hexene, cyclohexene, 4,5-dihydrofuran and 2-methyl-2-butene. The *E*-selectivity of the cyclopropanes obtained from the monosubstituted alkenes and the cycloalkenes decreases in the order **1b** > **1a** > **1d** > **1c**. The cyclopropanation of 2-methyl-2-butene is highly *syn*-selective. Several complexes of the type $[Ru_2(CO)_4(\mu\text{-}L^1)_2]_2$ (**4**) and (**5**), $[Ru_2(CO)_4(\mu\text{-}L^1)_2L^2]$ ($L^2 = CH_3OH$, PPh_3) (**6**)–(**9**) and $[Ru_2(CO)_4(CH_3CN)_2(\mu\text{-}L^1)_2]$ (**10**) and (**11**), where L^1 is a 6-chloro- or 6-bromo-2-pyridonate ligand, are also efficient catalysts. Compared with catalyst **3**, a halogen substituent at the pyridonate ligand affects the diastereoselectivity of cyclopropanation only slightly.

Keywords: Ruthenium complexes; Catalysis; Cyclopropanation; Diazo compounds; Metal–carbene intermediates

1. Introduction

A variety of rhodium and copper catalysts are widely used for several different carbene transfer reactions involving aliphatic diazo compounds, e.g., cyclopropanation, cyclopropenation, C–H and X–H insertion, and ylide formation [1]. Since the catalytic transformations proceed through short-lived transition metal–carbene intermediates, the variation of ligands at the metal is expected to have an impact on the reactivity and selectivity of those intermediates. For example, most of the currently used rhodium catalysts are dinuclear rhodium(II,II) complexes of the type $[Rh_2(\mu\text{-}L)_4]$, where L represents bidentate carboxylate, amidate, or phosphate ligands, and it is well known that ligand tuning, without changing the coordination motif of the complex, can be used to influence, e.g., the chemoselectivity and enantioselectivity of several types of carbene transfer reactions [1–5]. For the catalytic cyclopropanation of olefins with diazo compounds, the diastereoselectivity is an important aspect. Systematic comparisons [1,6] have shown that this particular selectivity issue can be controlled only to a limited extent by the catalytically active metal and its ligands, and those catalysts are rare which promote a highly *trans*- or (even more difficult) *cis*-selectivity in the cyclopropanation of a simple olefin such as styrene with (m)ethyl diazoacetate.

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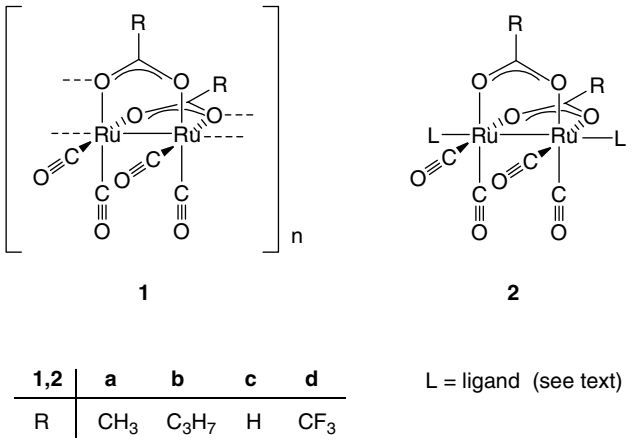
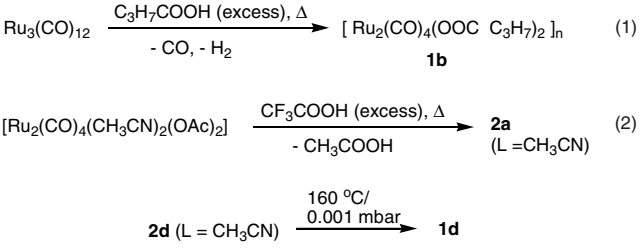
Recently, ruthenium complexes have emerged as novel catalysts for olefin cyclopropanation with diazo compounds [7] and it appears that the rich coordination chemistry of ruthenium may offer a larger range of potentially useful catalysts than in the case of rhodium. However, dimeric ruthenium(II) acetate, $[Ru_2(OOCMe)_4]$, which represents the immediate structural relative of the highly useful rhodium(II) acetate dimer but is electronically different (presence of a Ru–Ru double bond, two unpaired electrons), appears to be a less effective cyclopropanation catalyst due to the competing metathetical activity of the ruthenium–carbene intermediate [8]. In contrast, cyclopropanation of cyclooctene with ethyl diazoacetate was quantitative when catalyzed by the trifluoroacetate complex $[Ru_2(OOCCF_3)_4]$ [9].

We have identified the dinuclear ruthenium(I,I) acetate complexes $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$, which is a coordination polymer, and the related bis(acetonitrile) complex $[Ru_2(CO)_4(CH_3CN)_2(\mu\text{-}OAc)_2]$ as well suited catalysts for cyclopropanation of olefins with alkyl diazoacetates [10,11], α-silyl-α-diazoacetates [10,12] and aryl- or silyl-diazomethane derivatives [13]. The structurally similar triazenide complexes $[Ru_2(CO)_6(\mu\text{-}ArNNNAr)_2]$ were also found to catalyze efficiently and effectively the cyclopropanation of nucleophilic terminal alkenes, but were less suited for the cyclopropanation of internal alkenes [14].

Encouraged by the good performance of $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ in catalytic olefin cyclopropanation with diazoacetate, we decided to investigate the effect of ligand variation on the effectiveness and diastereoselectivity of these cyclopropanation reactions. To this end, we examined several catalysts of the type $[Ru_2(CO)_4(\mu\text{-}L)_2]$, where L is a bidentate carboxylate or 2-pyridonate (pyridin-2-olate) ligand.



Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Catalysts

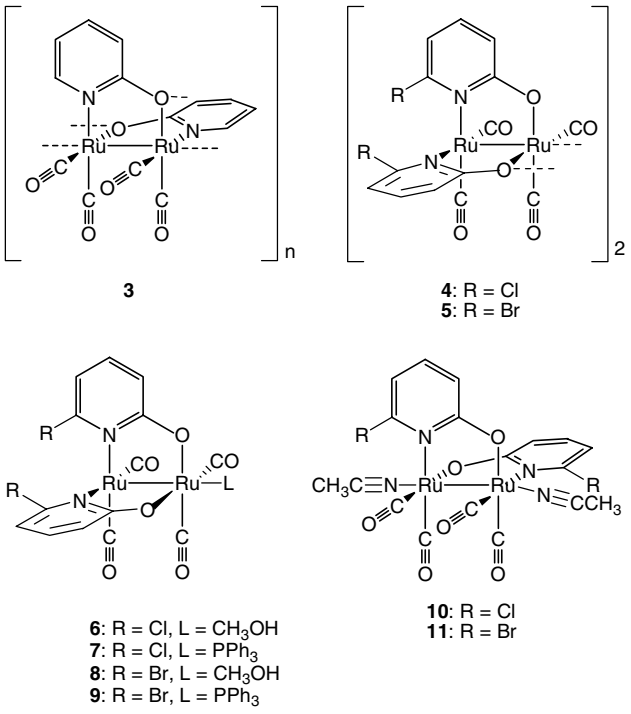
In this study, two series of dinuclear ruthenium(I) complexes are investigated as cyclopropanation catalysts: the di(μ-carboxylato)-tetracarbonyl-diruthenium complexes **1a**–**d** (Scheme 1) and the di-(μ-pyridin-2-olato)-tetracarbonyl complexes **3**–**11** (Scheme 3).

The carboxylato complexes **1a** and **1c** are already known [15]. We have prepared butyrato complex **1b** analogously by heating of $Ru_3(CO)_{12}$ in an excess of butyric acid (Scheme 2, Eq. (1)). In a related published procedure, **1b** was not isolated but directly converted into its bis(triphenylphosphane) adduct (**2b**, $L = PPh_3$) [16].

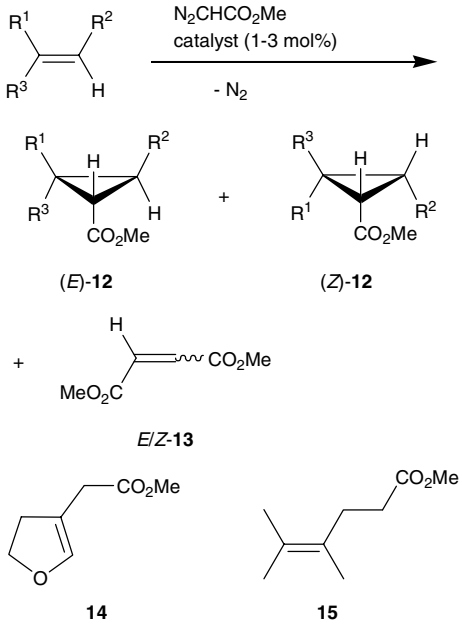
The orange-red trifluoroacetato complex **1d** was obtained from bis(acetonitrile) complex $[Ru_2(CO)_4(CH_3CN)_2(\mu\text{-}OAc)_2]$ (**2a**, $L = CH_3CN$) by ligand exchange with trifluoroacetic acid, followed by thermal decomplexation of the acetonitrile ligands from the initially formed **2d** ($L = CH_3CN$) [17] (Scheme 2, Eq. (2)). It has been reported [18] that **1d** is obtained as a "white polymer" from the reaction of $Ru_3(CO)_{12}$ with excess trifluoroacetic acid in toluene at 90 °C. This product was characterized by IR spectroscopy only and was directly converted into the bis(triphenylphosphane) adduct **2d** ($L = PPh_3$). The color of the "white polymer", its solubility in diethyl ether, and an IR absorption at 2153 cm^{-1}, which is typical for axial carbonyl ligands in complexes of type **2** [15], are not in accord with the properties of **1d** prepared by us, and we assume that these authors had prepared the hexacarbonyl complex **2d** ($L = CO$). In fact, we found that heating of $Ru_3(CO)_{12}$ with trifluoroacetic acid at reflux temperature yields **2d** ($L = CO$) which even after prolonged treatment at 180 °C/0.001 mbar does not completely release the two axial CO ligands.

Like **1a** and **1c**, the new complexes **1b** and **1d** are coordination polymers which dissolve with depolymerization only in solvents with good donor properties, e.g., acetonitrile and DMSO, yielding complexes of type **2**. Therefore, the NMR data reported in Section 4 are in fact those of **2b** and **2d** ($L = CD_3CN$).

Di-(μ-pyridin-2-olato)-tetracarbonyl-diruthenium (**3**) can be prepared from $Ru_3(CO)_{12}$ and 2-hydroxypyridine in hot toluene; like the carboxylato complexes, it exists as a coordination polymer which is depolymerized by



Scheme 3.



Scheme 4.

good donor solvents and other Lewis bases [19]. For the current investigation, we have prepared and structurally characterized a series of new 6-halopyridin-2-olato complexes **4**–**11** (Scheme 3) [20]. It should be noted that these complexes can exist with a head–head as well as a head–tail arrangement of the two bridging pyridonate ligands. While complex **3**, containing the parent pyridin-2-olate ligand, exists in the head–tail form, the 6-chloro- and 6-bromopyridin-2-olato complexes **4** and **5** show a head–head arrangement and exist as centrosymmetric coordination dimers in the solid state. Treatment of **4** and **5**, respectively, with Lewis bases such as methanol and PPh_3 generates the "monomeric" dinuclear complexes **6**–**9**. In all head–head complexes **4**–**9**, only one ruthenium atom assumes the complete octahedral coordination while a free coordination site remains at the ruthenium atom that is shielded by the two neighboring halogen atoms. Interestingly, the head–tail arrangement of 6-halopyridin-2-olato complexes can be achieved when sterically little demanding acetonitrile ligands occupy the axial site at each ruthenium atom (**10** and **11**).

2.2. Cyclopropanation studies

The cyclopropanation of a series of representative olefins with methyl diazoacetate catalyzed by ruthenium carboxylate complexes **1b**–**d** or pyridonate complex **3** was investigated and compared with the published [10] results obtained with ruthenium acetate **1a** as catalyst (Scheme 4 and Table 1). These experiments were conducted on a preparative scale (20 mmol of diazoacetate) so that reliable yields of isolated products could be obtained. In spite of the very slow addition of the diazo ester to an excess of liquid alkene (10 molar equivalents) that contained the catalyst, formation of the formal carbene dimers, dimethyl fumarate and maleate (*E*- and *Z*-**13**) was a competitive pathway which accounted almost for the complete remaining material balance in most cases. In specific cases, small amounts of other products were also identified, such as the (dihydrofuranyl)acetate **14** in the carbene transfer reaction with 4,5-dihydrofuran and the C/H insertion product **15** in the case of 2,3-dimethyl-2-butene.

The polymeric complexes **1a**–**d** and **3**, which are not soluble in the liquid alkene, are obviously depolymerized by the diazoester, as indicated by the formation of a homogeneous solution after addition of small amounts of the diazoester. Thus, all catalyses reported here occur under homogeneous conditions.

Cyclopropanation reactions with catalysts **4**–**11** (3 mol%) were performed on an analytical scale, and the alkene was diluted with dichloromethane. For comparison, catalyst **3** was also applied under these conditions (Table 2). While complexes **7** and **9** were well soluble in CH_2Cl_2, all other complexes went into solution after addition of a small amount of the diazoester. Since we were mainly interested to see the influence of the halogen substituent of the pyridonate ligands on the diastereoselectivity of cyclopropanation, the experiments were focussed on three olefins with different degree of substitution (styrene, cyclohexene and 2-methyl-2-butene).

In terms of cyclopropane yields, Tables 1 and 2 show that $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ (**1a**) is the most effective of all investigated catalysts. For the carboxylato-ruthenium

Table 1
Cyclopropanation of alkenes with methyl diazoacetate catalyzed by **1a**–**d** or **3** (see Scheme 4)[a]

Entry	Alkene and cyclopropane **12**				Yield of cyclopropanes **12**, % (*E*/*Z* ratio[b])[c]				
	R^1	R^2	R^3	R^4	Catalyst **1a**[d]	Catalyst **1b**	Catalyst **1c**	Catalyst **1d**	Catalyst **3**
1	Ph	H	H	H	95 (1.6)	78 (1.9)	70 (1.1)	72 (1.5)	78 (1.8)
2	Bu	H	H	H	67 (2.0)	55 (2.8)	32 (1.4)	54 (1.8)	52 (1.4)
3	OEt	H	H	H	89 (4.5)	80 (2.3)	62 (0.83)	71 (2.0)	72 (1.4)
4	$-(CH_2)_4-$		H	H	68 (3.7)	45 (3.6)	36 (1.8)	43 (2.2)	23 (3.1)
5	$-(CH_2)_2O-$		H	H	56 (>97:3)	50 (6.9)	37 (>97:3)	41 (>97:3)	52 (5.3)
6	Ph	H	Me	H	91 (0.67)	82 (1.0)	82 (0.59)	81 (0.77)	89 (0.91)
7	Me	Me	Me	H	61 (0.16)	38 (0.12)	31 (0.19)	36 (0.28)	33 (0.14)
8	Me	Me	Me	Me	47	28	23	27	18

[a] In neat alkene, $T = 20$ °C; catalyst:diazoacetate:alkene = 0.01:1:10 (Section 4.3.1).
[b] *Anti*/*syn* for cycloalkenes.
[c] Additional products: Dimers *Z*- and *E*-**13** were formed in all cases; in the following cases, *E*/*Z*-**13** constituted the major reaction product (catalyst, yield of *Z*-**13** (%), yield of *E*-**13** (%)): entry 2: **1c**, 41, 16; entry 4: **1b**, 35, 14; **1c**, 28, 17; **1d**, 35, 13; **3**, 49, 21; entry 5: **1c**, 22, 15; **1d**, 29, 12; entry 7: **1b**, 41, 16; **1c**, 45, 13; **1d**, 44, 18; **3**, 49, 17; entry 8: **1a**, 36, 15; **1b**, 42, 16; **1c**, 44, 16; **1d**, 48, 19; **3**, 50, 28. Entry 5: Methyl (2,3-dihydro-4-furyl)acetate (**14**) was also formed in 6–10% yield. Entry 8: Methyl 4,5-dimethylhex-4-enoate (**15**) was also formed in 4 (**1b**, **1d**), 8 (**3**), and 10% (**1c**) yield.
[d] Taken from lit. [10].

Table 2
Cyclopropanation of alkenes with methyl diazoacetate catalyzed by **3**–**11**[a]

Catalyst	Yield of cyclopropanes,[b] % (*E*/*Z* or *anti*/*syn* ratio[b])		
	From styrene	From cyclohexene	From 2-methyl-2-butene
$[Ru_2(CO)_4(pyO)_2]_n$ (**3**)	73 (1.74)	24 (2.44)	33 (0.14)
$[Ru_2(CO)_4(2\text{-Cl-pyO})_2]_2$ (**4**)	63 (1.52)	54 (1.99)	51 (0.15)
$[Ru_2(CO)_4(2\text{-Br-pyO})_2]_2$ (**5**)	70 (1.41)	49 (2.12)	73 (0.16)
$[Ru_2(CO)_4(2\text{-Cl-pyO})_2(MeOH)]$ (**6**)	63 (1.66)	52 (2.01)	64 (0.15)
$[Ru_2(CO)_4(2\text{-Cl-pyO})_2(PPh_3)]$ (**7**)	66 (1.94)	18 (2.91)	15 (0.18)
$[Ru_2(CO)_4(2\text{-Br-pyO})_2(MeOH)]$ (**8**)	75 (1.44)	56 (1.96)	69 (0.15)
$[Ru_2(CO)_4(2\text{-Br-pyO})_2(PPh_3)]$ (**9**)	38 (1.96)	15 (3.04)	11 (0.19)
$[Ru_2(CO)_4(2\text{-Cl-pyO})_2(CH_3CN)_2]$ (**10**)	69 (1.66)	44 (2.02)	34 (0.14)
$[Ru_2(CO)_4(2\text{-Br-pyO})_2(CH_3CN)_2]$ (**11**)	70 (1.39)	35 (2.00)	64 (0.16)

[a] In CH_2Cl_2, catalyst:diazoacetate:alkene = 0.03:1:10, $T = 22$ °C (Section 4.3.2).
[b] Determined by GC.

catalysts, the yields decrease in general in the order acetate (**1a**) > butyrate (**1b**) ≈ trifluoroacetate (**1d**) > formate (**1c**). With the (2-pyridonato)-ruthenium complex **3**, yields are similar to **1b**, except for the distinctly lower yields in the case of cyclohexene and 2,3-dimethyl-2-butene. Among the complexes with 6-halopyridonate ligands (**4**–**11**), the 6-bromopyridonate complexes **5**, **8** and **11** in general provide somewhat higher yields than their 6-chloropyridonate counterparts; in particular, the trisubstituted double bond of 2-methyl-2-butene is cyclopropanated in higher yields (65–73%) with these catalysts than even with acetato complex **1a**.

The effectiveness of cyclopropanation also depends on the nature of the olefin. In this respect, the same qualitative results are obtained with all ruthenium catalysts used in this study: The highest yields are obtained uniformly with nucleophilic mono- and 1,1-disubstituted alkenes, in the sequence α-methylstyrene > styrene > ethyl vinyl ether > 1-hexene. The cyclic olefins cyclohexene and 4,5-dihydrofuran give intermediate yields. With tri- and tetrasubstituted alkenes (2-methyl-2-butene and 2,3-dimethyl-2-butene), yields are lower than expected with a view to the increased electron density of the olefinic bond as compared to, e.g., 1-hexene. It is likely that for the more highly substituted C=C bonds, increased steric hindrance overrides the favorable aspect of higher nucleophilic character of these olefins. A comparison with the literature values [6] suggests that the metal carbene intermediates derived from $Rh_2(OOCR)_4$ catalysts are less sensitive and those derived from common copper catalysts are more sensitive to these steric effects than the ruthenium carbenes derived from **1a**–**d** and **3**.

For the diastereoselectivity of the cyclopropanation reactions, the dependence on the nature of the olefin is the same with all ruthenium carboxylate or pyridonate complexes investigated here. With the exception of 4,5-dihydrofuran, where the *syn*-cyclopropane may not be stable to the catalyst (*syn* → *anti* isomerization as well as ring-opening leading to **14** [21]), the thermodynamically favored *E* (or *anti*) isomer is formed preferentially from the monosubstituted and 1,2-*cis*-substituted

alkenes. While this is the common result with most cyclopropanation catalysts and the *E*/*Z* ratios are in typical ranges [1,6], the high preference for the *syn*-cyclopropane formed from 2-methyl-2-butene (up to 88:12) as well as other trisubstituted alkenes [11,14] is a unique feature of the $[Ru_2(CO)_4(\mu\text{-}L)_2]$ catalysts.

As Table 1 shows, the diastereoselectivity of cyclopropanation is only modestly dependent on the bridging ligands of the dinuclear ruthenium complexes. Leaving aside the cases of ethyl vinyl ether and 4,5-dihydrofuran (where the formed cyclopropanes may be subject to subsequent reaction with the catalyst, see above), the *E*-selectivity observed with the terminal alkenes and cyclohexene in general decreases in the sequence **1b** > **1a** > **1d** > **1c** (i.e., butyrate > acetate > trifluoroacetate > formate ligands). For 2-methyl-2-butene, the *Z*-selectivity decreases in the series **1b** > **1a** > **1c** > **1d**. The stereoselectivities observed with (2-pyridonate)-ruthenium catalyst **3** are found somewhere between those of **1b** and **1c**.

An often used working hypothesis for the ligand-dependent chemoselectivity of carbenoid reactions using dirhodium tetracarboxylate catalysts emphasizes the influence of electron-withdrawing ligands on the electrophilic character of the rhodium–carbene intermediate [2]. Considering the resonance structures $L_nM{=}CR^1R^2 \leftrightarrow L_nM^{-}\text{–}{}^{+}CR^1R^2$, it can be argued that electron-withdrawing ligands enhance the weight of the polar resonance structure due to delocalization of the negative charge, thereby rendering the metal–carbene more reactive and less selective. This hypothesis also seems to work for the diastereoselectivity of rhodium-catalyzed cyclopropanation reactions; e.g., the *E* (*anti*) selectivity for cyclopropanation of styrene, ethyl vinyl ether and cyclohexene decreases in the order Rh_2(acetamide)$_4$ > Rh_2(acetate)$_4$ > Rh_2(trifluoroacetate) > Rh_2(perfluorobutyrate)$_4$ [6c].

Within the series of carboxylato-ruthenium catalysts **1a**–**d**, however, the formato complex **1c** does not fit into the simple correlation between decreasing diastereoselectivity and increasing electron-withdrawing power of the carboxylate ligand, i.e. lower pK_a value of the corresponding carboxylic acid. Although we do not wish to speculate on the special behavior of **1c**, we consider it likely that the ligand effects on the electrophilic character and the stabilization of a metal-bound carbene intermediate are different when the carbene is bound to a $[Rh_2(OOCR)_4]$ or a $[Ru_2(CO)_4(OOCR)_2]$ unit. It has been shown that in rhodium-catalyzed carbenoid reactions, the chemoselectivity is not only correlated with the electron-withdrawing properties of the carboxylate ligands but also with their polarizability, and the relevance of metal-to-ligand backbonding (ligand = axial carbene or carbonyl) has been discussed [5]. In the D_{4h}-symmetric rhodium case, effects from all four ligands uniformly act on the axially coordinated carbene moiety. In the ruthenium case, the ligand effects and backbonding affect not only the axial carbene ligand but also the carbonyl ligands at the dinuclear metal core.

The diastereoselectivities of cyclopropanation achieved with the pyridonate complexes **3**–**11** vary only in a narrow range (Table 2); e.g., for styrene cyclopropanation, the *E*:*Z* ratio is between 66.2:33.8 (=1.96) and 58.2:41.8 (=1.39). Thus, the introduction and variation of the halogen substituent at the pyridonate ligand as well as the structure of the complex (head–head as in **3**, **10**, **11** vs. head–tail as in **4**–**9**) have only a minor influence. X-ray crystal structure determination of most of the head–head complexes **4**–**9** have shown [20] that the ruthenium atom which is close to the halogen substituents (see Scheme 3) keeps a vacant coordination site even if a small ligand such as methanol would have been available during the synthesis. Therefore, it could be argued that steric shielding by the two neighboring halogen atoms also prevents the coordination of the diazoacetate or the derived methoxycarbonylcarbene moiety at this ruthenium atom. Coordination of the carbene would take place, after displacement of the axial ligand, at the ruthenium atom surrounded by two oxygen and two carbonyl ligands (compare formulae **6**–**9** in Scheme 3, L = carbene), and no steric influence of the halogen substituents on the diastereoselectivity of cyclopropanation would exist. Whether the halogen substituents modulate the electronic ligand effects of the pyridonate groups and thus the diastereoselectivity of cyclopropanation, as discussed above, cannot be concluded firmly from the data of Table 2. For styrene in particular, there are small but significant differences depending on whether the chloropyridonate complexes (**4**) and (**6**) or bromopyridonate (**5**) and (**8**) complexes were used.

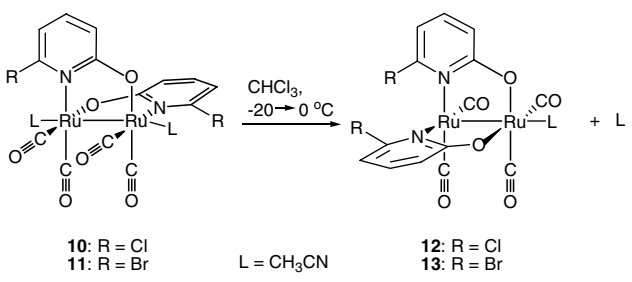
The results obtained with catalysts **7** and **9** suggest that additional or different sources of diastereoselection are present. If the preceding assumption about the constitution of the metal–carbene intermediate was correct, the same intermediate should result from all precursor complexes with a given pyridonate ligand, e.g., **4**, **6** and **7** (i.e., coordination dimer, methanol and PPh_3 complex), and identical diastereomer ratios of the formed cyclopropanes should result. However, the PPh_3 complexes **7** and **9** give rise to significantly higher *E*/*Z* (*anti*/*syn*) ratios with styrene and cyclohexene than the related MeOH complexes **6** and **8**. Currently, we can only speculate about the reasons. Perhaps, the carbene ligand does not replace the axial PPh_3 ligand in complexes **7** and **9** but coordinates at the free axial position of the second ruthenium atom; the in most cases exceptionally low cyclopropane yields with the halopyridonate/PPh_3 complexes **7** and **9** could then be attributed to the hindered access of the diazoester to this ruthenium atom which is sterically shielded by two halogen atoms. A contribution

of an uncatalyzed cyclopropanation pathway can also not be excluded [5].

For the head–tail complexes **10** and **11**, which have a C_2-symmetric molecular topology, no ambiguity concerning the coordination site of the carbene moiety exists because the axial sites at both ruthenium atoms are symmetry-equivalent. However, we have NMR-spectroscopic evidence [20b] that complexes **10** and **11** rearrange irreversibly to the head–head isomers **12** and **13**, respectively, in chloroform solution between −20 and 0 °C (Scheme 5). Thus, we encounter the same situation as with the related head–head complexes discussed above, and we would expect about the same cyclopropanation diastereoselectivities for the chloropyridonate complexes **4**, **6** and **10** on one hand, and for the bromopyridonate complexes **5**, **8** and **11** on the other. This is indeed the case for cyclopropanation of styrene (d.r. = 1.52–1.66 in the chloro series, and 1.39–1.44 in the bromo series). For the reactions with cyclohexene and 2-methyl-2-butene, the two series of complexes give rise to diastereoselectivities in the same very narrow range (d.r. = 2.00–2.12 for cyclohexene, 0.14–0.16 for 2-methyl-2-butene).

3. Conclusion

This study has shown that several ruthenium complexes with the $[Ru_2(CO)_4]^{2+}$ core and bridging carboxylate or 2-pyridonate ligands are efficient and effective catalysts for cyclopropanation of nucleophilic alkenes with methyl diazoacetate. In terms of yields, the acetate complex $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ is generally superior to the related propionate, trifluoroacetate and formate complexes (in this sequence). Among the pyridonate complexes, those with 6-bromopyridonate ligands ($[Ru_2(CO)_4(2\text{-}Br\text{-}pyO)_2]_2$ (**5**), $[Ru_2(CO)_4(2\text{-}Br\text{-}pyO)_2(MeOH)]$ (**8**) and $[Ru_2(CO)_4(2\text{-}Br\text{-}pyO)_2(CH_3CN)_2]$ (**11**)) are in general a little more effective than their relatives with 6-chloropyridonate ligands or with the parent pyridonate ligand and represent good alternatives to the acetate complex mentioned before. The diastereoselectivities of cyclopropanation of a given alkene are found in a rather limited range for all investigated catalysts. This is not unexpected, because effective control of diastereoselectivity by ligand tuning is a long-standing challenge of catalytic carbenoid cyclopropanation reactions. Nevertheless, several correlations between the ligands in the catalytically active complex and the diastereoselectivity can be extracted from the obtained data. Unfortunately, the fast rearrangement of the head–tail complexes **10** and **11** into head–head complexes **12** and **13**, respectively, under the reaction conditions did not allow us to observe the influence of this structural change on yields and diastereoselectivities of the cyclopropanation reactions. Recently, it has been shown for carbenoid C—H insertion reactions catalyzed by rhodium complexes of the type $[Rh_2(OOCR)_2L_2]$, where L is a bridging *ortho*-metallated diphenylphosphanyl-(het)aryl ligand, that the head–head and the head–tail arrangement of these unsymmetrical ligands causes indeed distinctly different results [22].



Scheme 5.

4. Experimental

4.1. Materials

$Ru_3(CO)_{12}$ was prepared as published [23] or purchased. The following complexes were prepared by published methods: $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ [15], $[Ru_2(CO)_4(CH_3CN)_2(\mu\text{-}OAc)_2]$ [15], $[Ru_2(CO)_4(\mu\text{-}OOCH)_2]_n$ [15], **4**–**9** [20a], **10** [20b], **11** [20b] and methyl diazoacetate [24].

4.2. Ruthenium complexes

4.2.1. Di-(μ-butyrato)-tetracarbonyl-diruthenium(I,I) (*1b*)

A suspension of $Ru_3(CO)_{12}$ (1.28 g, 2 mmol) in butyric acid (100 ml) was heated at reflux (130 °C) until gas evolution had ceased (7 h). The initially red solution gradually turned to yellow. The excess of butyric acid was removed by distillation at ambient pressure, remaining traces were evaporated at 100 °C/0.001 mbar. The solid residue was washed with methanol (2 × 30 ml) and ether (2 × 30 ml). After drying at 100 °C/0.001 mbar, a yellow solid was obtained which decomposed at 228 °C; yield: 1.27 g (87%). ^{1}H NMR (400.1 MHz, CD_3CN): $\delta = 0.86$ (t, $J = 7.3$ Hz, 3H, CH_3), 1.53 (mc, 2H, CH_2CH_3), 2.17 (t, $J = 7.3$ Hz, 2H, $CH_3CH_2CH_2$). ^{13}C NMR (100.6 MHz, CD_3CN): $\delta = 14.0$ (CH_3), 20.2 (CH_2), 39.4 (CH_2), 187.8 (COO), 203.3 (C≡O). IR (KBr): $\nu = 2050$ (vs, CO), 1990 (vs, CO), 1955 (vs, CO), 1945 (vs, CO), 1545 (s, br, OCO), 1390 cm^{-1} (vs, OCO). MS (EI, 70 eV): *m*/*z* (%) = 488.9/489.9 (15), 460.9/461.9 (17), 432.9/433.9 (33), 404.9/405.9 (35), 376.9/377.9 (100). Anal. Calc. for $C_{12}H_{14}O_8Ru_2$ (488.38): C 29.51, H 2.89. Found C 29.8, H 2.9.

4.2.2. Di-(μ-trifluoroacetato)-tetracarbonyl-diruthenium(I,I) (**1d**)

A solution of $[Ru_2(CO)_4(CH_3CN)_2(\mu\text{-}OAc)_2]$ (1.03 g, 2 mmol) in trifluoroacetic acid (10 ml) and acetic anhydride (1 ml) was heated at 50 °C for 2 h. The carboxylic acids are evaporated at 40 °C/0.003 mbar, last traces at 100 °C/0.001 mbar. The residue was then kept at 165 °C/0.001 mbar until its weight was constant (ca. 6 h). An orange-red solid was obtained which decomposed at 205 °C; yield: 0.96 g (89%). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN): $\delta = 115.9$ (q, $^1J(C,F) = 286$ Hz, CF_3), 170.2 (q, $^2J(C,F) = 39$ Hz, COO), 201.4 (s, C≡O). IR (KBr): $\nu = 2095$ (sh, CO), 2045 (vs, CO), 1990 (vs, CO), 1960 (vs, br, CO), 1640 (vs, br, OCO), 1460 cm^{-1} (vs, OCO). MS (EI, 70 eV): m/z (%) = 540.8/541.8 (34), 512.8/513.8 (12), 484.8/485.8 (23), 456.8/457.8 (15), 428.6 (100). Anal. Calc. for $C_8F_6O_8Ru_2$ (540.21): C 17.79. Found C 17.8.

4.3. Catalytic cyclopropanations

4.3.1. Method A

A solution of methyl diazoacetate (2.00 g, 20 mmol) in liquid alkene (20 mmol) was added during 12 h, by means of a syringe pump, to a magnetically stirred solution of the same alkene (180 mmol) in dichloromethane (25 ml) containing 1 mol% of catalyst (**1b–d**). Stirring of the reaction mixture was continued until the evolution of N_2 had ceased (3–8 h). The solvent and low-boiling alkenes were removed by distillation at 60 °C/800 mbar. The residue was separated by column chromatography (silica gel, Macherey & Nagel, 0.063–0.2 mm; water-cooled column). The alkene was eluted first with pentane, the cyclopropanes (E/Z mixture) with ether/pentane mixtures and diethyl fumarate and diethyl maleate with ether. All products reported in Table 1 are known; the stereochemistry of cyclopropanes **12** was assigned based on ^1H and ^{13}C NMR data.

4.3.2. Method B

The catalyst (**4–11**; 3.0 mol% based on diazoacetate) was dissolved in a mixture of alkene (10 mmol) and dichloromethane (4 ml). By means of a syringe pump, a solution of methyl diazoacetate (0.100 g, 1 mmol) in dichloromethane (0.9 ml) was added at a rate that was adjusted to the reactivity of the alkene (ca. 4 h for styrene, ca. 10 h for cyclohexene and 2-methyl-2-butene). The complete consumption of the diazo compound was monitored by IR spectroscopy. A defined amount of naphthalene (for experiments with styrene and cyclohexene) or mesitylene (for 2-methyl-2-butene) was added as an internal standard, and the yields and diastereomer ratios of cyclopropanes **12** were determined by gas chromatography, using a Varian CP-WAX 52 column (30 m × 0.32 mm, film thickness 0.25 μm) fitted with a retention gap. The response factor of each cyclopropane was determined using an authentic sample prepared according to Section 4.3.1.

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