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Diruthenium(I,I) Catalysts for the Formation of β- and γ-Lactams *via* Carbenoid C–H Insertion of α-Diazoacetamides

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Abstract: Intramolecular carbenoid C–H insertion of five α-diazoacetamides [N_2CH–$CONR_2$, $NR_2 = NEt_2$ (**3a**), NBu_2 (**3b**), N(*i*-Pr)$_2$ (**3c**), $N(CH_2Ph)_2$ (**3d**), N(*i*-Pr)(CH_2Ph) (**3e**)], was investigated using as catalysts dinuclear Ru(I,I) complexes of the type [$Ru_2(\mu\text{-}L^1)_2(CO)_4L^2_2$], where L^1 is a bidentate bridging acetate, calix[4]arenedicarboxylate, saccharinate, pyridin-2-olate, or triazenide ligand, as well as [$RuCl_2$(*p*-cymene)]$_2$. The Ru(I,I) complexes were found to be suitable catalysts for the carbenoid cyclization reactions, except in the case of **3a**. With diazoamides **3b–e**, [$Ru_2(\mu\text{-sac})_2(CO)_5$]$_2$ (sac = saccharinate) and [Ru_2(μ-6-chloropyridin-2-olate)$_2(CH_3CN)_2(CO)_4$] are as effective as $Rh_2(OAc)_4$ under the same conditions, although some differences in the regioselectivity and chemoselectivity of the cyclization are observed. The carbenoid cyclization reactions yield γ-lactams from diazoamides **3a** and **3b**, both a β- and a γ-lactam from **3c**, and a β-lactam as well as a 3-azabicyclo[5.3.0]deca-5,7,9-trien-2-one from **3d**. With **3e**, formation of γ-lactam **21** and of bicyclic lactam **23** prevails.

Keywords: bimetallic catalysts; C–H insertion; cyclization; diazo compounds; β- and γ-lactams; ruthenium

Introduction

Transition metal-catalyzed intramolecular carbenoid C–H insertion by decomposition of α-diazocarbonyl compounds constitutes a powerful tool for the construction of carbocyclic and heterocyclic compounds, in particular of five-membered ones.[1–5] Starting from α-diazoacetamides, this method provides an access to β- and γ-lactams. These ring systems are quite common in natural products and pharmaceuticals.[6]

After initial successes with copper catalysts in particular,[1,7] dinuclear rhodium(II) complexes have emerged as catalysts of choice for intramolecular carbenoid C–H insertion. Rhodium-catalyzed transformations of α-diazoacetamides into lactams *via* C–H insertion are popular as well and have been reviewed recently.[8,9] Currently ruthenium complexes are receiving growing attention as catalysts for carbenoid transformations.[10–13] Che and co-workers have shown that ruthenium porphyrins are effective catalysts for cyclization of tosylhydrazones *via* intramolecular carbenoid C–H insertion;[14,15] *inter alia*, β-lactams were obtained in high yields and with excellent stereoselectivity from *N*-alkyl-*N*-*tert*-butyl 3-(tosylhydrazono)acetoacetamides. They have also reported that [$RuCl_2$ (*p*-cymene)]$_2$ catalyzes the formation of lactams from diazomalonic ester amides or 2-diazo-3-ketocarboxamides.[16]

In this paper, we show that several dinuclear ruthenium complexes of the type [$Ru_2(CO)_4(\mu\text{-}L^1)_2L^2_2$], where L^1 is a bidentate bridging carboxylate, pyridin-2-olate or saccharinate ligand, are also potent catalysts for the intramolecular carbenoid C–H insertion of α-diazoacetamides.

Results and Discussion

Diazoacetamides **3a** and **b** were prepared conveniently by direct diazoacetyl transfer from succinimidyl diazoacetate (**1**)[17] in high yields after column chromatography. Under the same conditions (room temperature, 12 h), the sterically more hindered amines **2c–e** underwent no conversion with **1**. However, when a higher temperature (50 °C) and an excess of amine (up to 5 equivalents) were applied, diazoacetamides **3c–e** could be obtained in 81–85% yield, too (Table 1). Diazoacetamides **3a**,[18,19] **3c**,[20] and **3d**[19,21] have been prepared before by different approaches.

For the catalytic decomposition of diazoacetamides **3a–e**, we applied several dinuclear ruthenium(I) and rhodium(II) complexes (Figure 1). The dinuclear ruthenium(I,I) complex [$Ru_2(\mu\text{-}OAc)_2(CO)_4$]$_n$ (**5**)[22]

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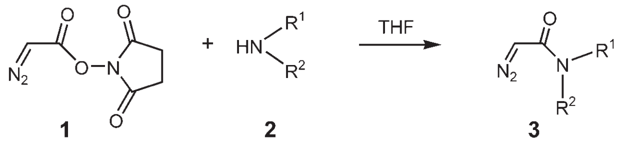
Table 1. Synthesis of diazoacetamides **3a–e** from succinimidyl diazoacetate (**1**).



Amine No.	 R^1	 R^2	Equivalents of **2**	T [°C]	Time [h]	Yield of **3** [%]
2a	Et	Et	2	20	12	98
2b	Bu	Bu	2	20	12	98
2c	*i*-Pr	*i*-Pr	5	50	50	81
2d	CH_2Ph	CH_2Ph	3.5	50	50	85
2e	*i*-Pr	CH_2Ph	3	50	24	85

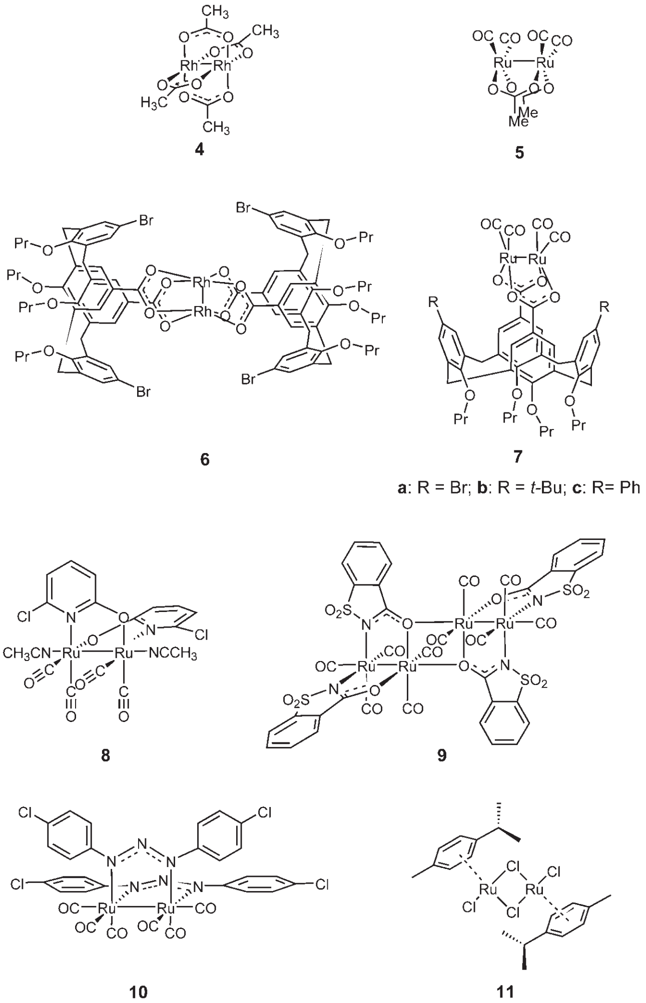


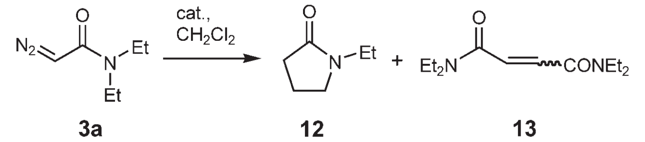
Figure 1. Rhodium and ruthenium catalysts used in this study

and the structurally analogous complexes containing calix[4]arenedicarboxylate (**7a–c**),[23] 6-chloropyridin-2-olate (**8**),[24] saccharinate (**9**),[25] or triazenide (**10**)[26] as bridging ligands had been identified in our earlier studies as suitable catalysts for olefin cyclopropanation with diazoacetates and some other diazo compounds as well. They were compared with the time-honored catalyst $Rh_2(OAc)_4$ (**4**) which served as a benchmark and source of comparison with literature reports. Furthermore, a comparison of catalysts **7a–c** with the dirhodium-bis(calix[4]arenedicarboxylate) complex **6**[27] was made in order to learn whether the additional calixarene ligand would influence the chemoselectivity of the carbenoid reaction. Finally, we included also $[RuCl_2(p\text{-cymene})]_2$ (**11**) in this investigation because of the recent report that this complex is highly active for the high-yielding transformation of 3-keto-2-diazocarboxamides into lactams.[16]

The products of decomposition of diazoacetamides **3a–e** with $Rh_2(OAc)_4$ and in selected cases with a ruthenium catalyst were isolated after chromatographic work-up. With all other catalysts, the composition of the product mixtures was established by ^1H NMR spectroscopy only.

For the carbenoid reactions, diazoacetamides **3a-e** (1 or 3 mmol) dissolved in dichloromethane were gradually added within one hour to a 25 mL volume of CH_2Cl_2 containing the catalyst. An extended addition time of 12 h did not entail a significant change in yields. They were also not affected depending on whether the reactions were carried out under an inert atmosphere (argon) or not. As can be seen in Table 2,

Table 2. Catalytic decomposition of *N,N*-diethyldiazoacetamide (**3a**).[a]



Catalyst	Catalyst loading [mol%]	T [°C]	Time [h]	Yields [%][a] **12**	 (*Z*)-**13**	 (*E*)-**13**
4	3	40	5	82 (77[b])	1	2
5	3	40	24	10	7	8
6	1	25	5	84	0	1
7a	3	40	24	28 (23[b])	23 (17[b])	18 (14[b])
7b	3	40	24	15	25	19
7c	3	40	24	18	19	18
8	3	40	48	9	10	10
9	3	40	48	23	5	7
10	3	40	72	7	16	19
11	3	40	24	5	12	12

[a] Yields were determined by ^1H NMR analysis of the reaction mixture (naphthalene as internal standard).

[b] Isolated yield after purification by column chromatography over basic alumina.

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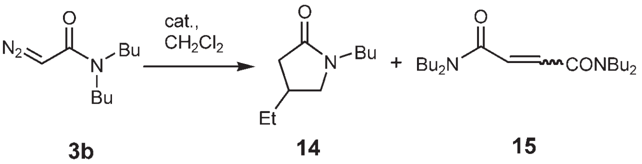
Table 3, Table 4, Table 5 and Table 6, the additional reaction time after completed addition was dependent on the catalyst and the diazoamide as well. Rhodium had consistently higher turnover frequencies, and among the ruthenium catalysts, the triazenide and calixarenedicarboxylate complexes (**10** and **7a–c**) were in general the least reactive ones. These catalysts also gave the highest yields of the formal carbene dimers, ethene-1,2-dicarboxamides **13** and **15**. We explain the lower efficiency of the ruthenium catalysts with their lower ability toward electrophilic attack at the diazo compounds, which may be attributed in part to a stronger coordination of the axial ligands at the metal centers compared to the rhodium carboxylates. (It should be noted that the calixarenedicarboxylate complexes **7a–c**, although represented in Figure 1 without axial ligands, complete their coordination sphere either by the formation of coordination polymers in the solid state or by donor molecules in solution.[23])

Table 3. Catalytic decomposition of *N,N*-dibutyldiazoacetamide (**3b**).[a]



Catalyst	Catalyst loading [mol%]	*T* [°C]	Time [h]	Yields [%][a] **14**	(*Z*)-**15**[b]	(*E*)-**15**[b]
4	3	40	1	97 (98)[c]	0	0
5	3	40	3	86	1	1
6	1	25	1	93	0	0
7a	3	40	3	72	2	2
7b	3	40	3	66	2	4
7c	3	40	3	64	2	5
8	3	40	1	92	1	2
9	3	40	1	99	0	0
10	3	40	12	47	6	8
11	3	40	24	31	5	6

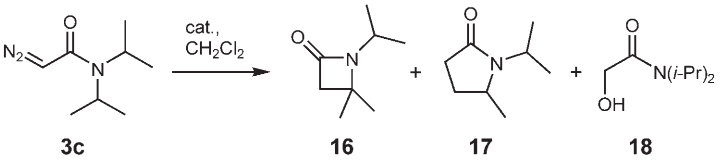
[a] Yields were determined by ^{1}H NMR analysis of the reaction mixture (naphthalene as internal standard).

[b] (*E*)- and (*Z*)-**15** were identified in the product mixture by the ^{1}H NMR signals at $\delta = 6.26$ and 7.37 ppm, respectively, which match those of (*E*)- and (*Z*)-**13**.

[c] Isolated yield after purification by column chromatography over basic alumina.

Before we discuss the individual results, it should be recalled that in spite of a general preference for the formation of five-membered rings in sterically and electronically unbiased systems, the carbenoid C–H-insertion is dependent on the kind of C–H bond, the reactivity sequence being methine > methylene ≫ methyl.[28] The appearance of β-lactams in cyclizations of diazoacetamides is caused by the activation of a C–H bond adjacent to the nitrogen atom.[20,29] In addition, the nature of the catalyst can influence the regioselectivity and chemoselectivity of the carbenoid reaction;[1,8,30] e.g., in carbenoid cyclizations of diazoacetamides, the transition from Rh$_2$(acetamide)$_4$ to Rh$_2$(acetate)$_4$ and Rh$_2$(perfluorobutyrate)$_4$ as catalyst, corresponding to a change towards a more electro-

Table 4. Catalytic decomposition of *N,N*-diisopropyldiazoacetamide (**3c**).[a]



Catalyst	Catalyst loading [mol%]	*T* [°C]	Time [h]	Yields [%][a] **16**	**17**	**18**[b]	Ratio **16**/**17**	Total yield of lactams [%]
4	3	40	1	70 (68[c])	23 (21[c])	4 (0[c])	3.00[d]	93[d] (89[d])
5	3	40	3	59	25	1	2.36	84
6	1	25	1	55	12	21	4.58	67
7a	3	40	6	41	37	4	1.11	78
7b	3	40	6	49	33	4	1.48	82
7c	3	40	6	43	36	4	1.19	79
8	3	40	1	56	35	0	1.60	91
9	3	40	1	72 (68[c])	26 (20[c])	0	2.77	98
10	3	40	10	48	29	0	1.66	77
11	3	40	24	18	20	5	0.90	38

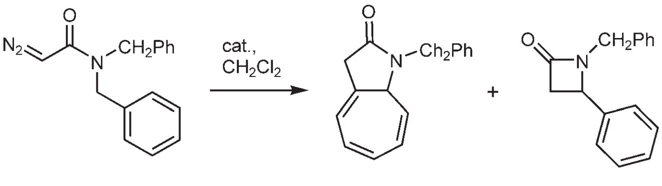
[a] Yields were determined by ^{1}H NMR analysis of the reaction mixture (naphthalene as internal standard).

[b] Identified by elemental analysis and NMR comparison with literature data.[33]

[c] Isolated yield after purification by column chromatography over basic alumina.

[d] Lit.[20]: Yield of **16**+**17**: 85%; ratio **16**/**17** = 4.26.

Table 5. Catalytic decomposition of *N,N*-dibenzyldiazoacetamide (**3d**).[a]



3d **19** **20**

Catalyst	Catalyst loading [mol%]	T [°C]	Time [h]	Yields [%][a] 19	20[b]	Total yield [%]
4	3	40	1	92 (74[c])	0 (0[c])	92 (74[c])
5	3	40	3	91	1	92
6	1	25	1	96	1	97
7a	3	40	8	70	6	76
7b	3	40	8	63	1	64
7c	3	40	8	70	6	76
8	3	40	1	96	0	96
9	3	40	1	94	1	95
10	3	40	78	57	3	60
11	3	40	12	19	1	20

[a] Yields were determined by ^{1}H NMR analysis of the reaction mixture (naphthalene as internal standard).

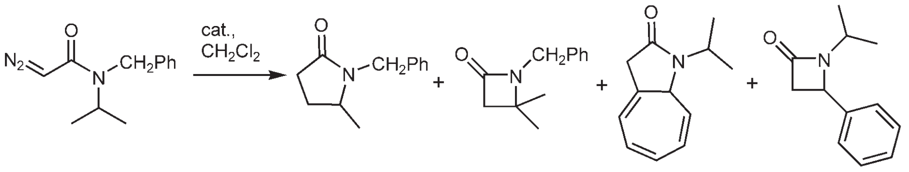
[b] Compound **20** could not be isolated in pure form but was identified by comparison with the published[34] ^{1}H chemical shifts and coupling constants.

[c] Isolated yield after purification by column chromatography over basic alumina.

philic and less selective metal-carbene intermediate, results in an increase of the ratio β-lactam/γ-lactam,[31,32] as well as a higher preference for carbenoid attack at an aromatic ring over γ-lactam forming C–H insertion.[31]

The results of Rh- and Ru-catalyzed carbenoid C–H insertion of diazoacetamides **3a–c** (Table 2, Table 3 and Table 4) are in agreement with the above-mentioned reactivity sequences. While only the γ-lactams (**12** and **14**, respectively) were formed from diethylamide **3a** and dibutylamide **3b** – the absence of an IR absorption around 1750 cm^{-1} from the crude reaction mixture indicated that no β-lactam was present –, diisopropylamide **3c** provided a mixture of β-lactam **16** and γ-lactam **17** in which the former prevailed (except with catalyst **11**). It may be annotated here that the photochemical decomposition of **3a** in dioxane gave a mixture of β- and γ-lactams in the ratio of 57:43.[18] The reluctance of the metal-carbene derived from **3a** to insert into a non-activated methyl C–H bond can be recognized from the generally lower yields and much longer reaction times as compared to **3b** and **3c**. In the case of **3a**, only the employed rhodium catalysts **4** and **6** gave high yields of lactam **12**, while the yields with none of the ruthenium catalysts surpassed 28% and consequently, the formal carbene dimers, ethene-1,2-dicarboxamides (*Z*)- and (*E*)-**13**, were formed in significant amounts. Their formation could not be suppressed by working in more dilute solution. The reproducible formation of hydroxyacetamide **18** from **3c** in various catalytic runs was some-

Table 6. Catalytic decomposition of *N*-benzyl-*N*-isopropyldiazoacetamide (**3e**).



3e **21** **22** **23** **24**

Catalyst	Catalyst loading [mol%]	T [°C]	Time [h]	Yields [%][a] 21	22	23	24[b]	Total yield [%]
4	3	40	1	37 (36[c])	15 (13[c])	43 (42[c])	0 (0[c])	95 (91[c])
5	3	40	3	23	9	42	1	75
6	1	25	1	48	18	18	4	88
7a	3	40	6	21	7	40	4	72
7b	3	40	6	30	9	27	3	69
7c	3	40	6	23	7	40	6	76
8	3	40	4	21	5	53	1	80
9	3	40	1	20	14	62	1	97
10	3	40	12	14	8	31	3	56
11	3	40	12	9	2	6	1	18

[a] Yields were determined by ^{1}H NMR analysis of the reaction mixture (naphthalene as internal standard).

[b] The product could not be isolated in pure form but was identified by comparison of ^{1}H chemical shifts and coupling constants with those of **20**[34].

[c] Isolated yield after purification by column chromatography on silica gel.

what unexpected because the usual precautions to exclude water and air from the reaction had been taken.

For the carbenoid transformations of **3b** and **3c**, almost quantitative formation of the lactams could be achieved not only with $Rh_2(OAc)_4$ as catalyst but also with the ruthenium catalysts **8** and **9**. With **3c**, where carbenoid insertion into a reactive methine C–H bond is possible, all tested ruthenium catalysts except **11** gave a high combined yield of β- and γ-lactam. The comparison of Tables 2–4 allows us to rank the ruthenium catalysts in the following order of decreasing effectiveness for lactam formation: **9**>**8**>**5** ≈ **7a–c**>**10**>**11**. This sequence may be compared with our studies on intermolecular alkene cyclopropanation with diazoacetates from which the approximate order **5**>**7a-c** ≈ **9**>**8**>**10** can be set up.[22–26]

Doyle et al. have already studied the catalyst dependence of the β:γ lactam ratio resulting from the rhodium-catalyzed decomposition of **3c**.[20] Notably, electronic ligand effects did not correlate well with the β/γ ratio, in contrast to results obtained for diazo*aceto*acetamides.[31,32] With $Rh_2(OAc)_4$ (**4**) a **16/17** ratio of 4.26 was reported. We observed a somewhat smaller ratio (3.00, Table 4), perhaps because of the higher reaction temperature (40 *vs.* 20 °C). With the rhodium-calix[4]arenedicarboxylate catalyst **6** we observed a β/γ ratio of 4.58. It is not very likely that this increased preference for the β-lactam is due simply to a change in the electronic properties of the carboxylate ligands [the β/γ lactam ratio is hardly changed when $Rh_2(OAc)_4$ (81:19) is replaced by $Rh_2(OOCPh)_4$ (80:20)[20]]. Instead, steric shielding of each metal center in **6** by two 4-bromophenyl groups may favor formation of the β-lactam because of lower steric demands in the near-metal region of the associated transition structure. The involvement of steric factors is suggested by the results with Ru-calixarenedicarboxylate catalysts **7a–c** where **7b** (R=*t*-Bu) gives a higher β/γ ratio than **7a** (R=Br) and **7c** (R=Ph). Among the ruthenium catalysts, **9** gives a **16/17** ratio of 2.77, close to the result with $Rh_2(OAc)_4$. The preference for the β-lactam decreases in the sequence **9**>**5**>**10** ≈ **8**>**7a–c**, and almost equal amounts of **16** and **17** are obtained with **11** as catalyst. The selectivity differences between the ruthenium(I,I) catalysts have a correlation with electronic and steric factors. Complex **9**, because of the electron-withdrawing sulfonamide ligands, is likely to be the most electrophilic catalyst in the series and therefore should yield a larger β/γ-lactam ratio by analogy to observations reported for rhodium catalysts (see above). On the other hand, the two catalysts which gave the highest β/γ ratio (**9** and **5**) are also those where the derived carbene unit can coordinate to a sterically less shielded metal center [two Ru–O and two Ru–C(O) bonds, for **9** achieved after cleavage of the coordination dimer] as compared to the remaining dinuclear Ru(I,I) complexes.

For the catalytic decomposition of *N,N*-dibenzyldiazoacetamide (**3d**) with $Rh_2(OAc)_4$ (**4**), Doyle et al.[21] have reported the exclusive formation of the 2-azabicyclo[5.3.0]decatrienone **19** in 93% yield, and this agrees with our results (Table 5). It is assumed that **19** arises from intramolecular cyclopropanation of the phenyl ring and subsequent norcaradiene-to-cycloheptatriene ring expansion. Rhodium calixarenedicarboxylate catalyst **6** also furnished the γ-lactam **19** almost quantitatively, together with a trace of β-lactam **20**. Ruthenium catalysts **5**, **8** and **9** were very active as well and afforded **19** in 91–96% yield. The Ru-calix[4]arenedicarboxylate catalysts **7a–c** produced **19** with yields of 63–70% and also the β-lactam **20** in up to 6% yield, but with significantly lower turnover frequencies. Catalyst **10** still gave fair yields of **19** but reacted extremely slowly.

The catalytic decomposition of *N*-benzyl-*N*-isopropyldiazoacetamide (**3e**) yielded up to four products by intramolecular carbenoid pathways (Table 6): carbenoid insertion into an isopropyl CH_3 bond (γ-lactam **21**), the isopropyl CH bond (β-lactam **22**) and a benzylic CH bond (β-lactam **24**), furthermore carbenoid reaction at the phenyl ring leading to bicyclic lactam **23**. With all catalysts, products **21** and **23** are the major ones while azetidinone **24** is formed in trace amounts only. The low amount of **24** is not surprising because it is known that carbenoid insertion in benzylic C–H bonds is less favored than insertion into more electron-rich aliphatic C–H bonds (such as isopropyl C–H).[28] Because of the partial double bond character of the amide C–N bond and the unsymmetrical *N*,*N*-disubstitution, it can be expected that the intramolecular carbenoid reactions of **3e** are under conformational control, provided that they occur faster than the rotation around the carbonyl-nitrogen bond. Results of previous investigations on diazoacetamides have been explained along these lines, assuming that the larger N-substituent prefers the *syn*-position at the C(O)–N bond.[21,29,32,35] The results given in Table 6 suggest that the carbenoid reactions of **3e** are not much governed by these conformational factors. Rather, an appreciable influence of the catalyst becomes obvious. The two rhodium catalysts (**4** and **6**) induce predominantly reactions at the *N*-isopropyl group (products **21** and **22**), and all ruthenium catalysts favor reactions at the *N*-benzyl substituent (products **23** and **24**). The highest yield of **21** was obtained using rhodium bis(calixarenedicarboxylate) catalyst **6** (48%) and the highest yield of **23** with ruthenium saccharinate complex **9** (62%). Irrespective of the catalyst, we find that γ-lactam **21** is always favored over β-lactam **22**, an obvious contrast to the behavior of *N*,*N*-diisopropyldiazoacetamide **3c** (see Table 4). This difference may be caused by the influence of the second amide substituent on the reactive conformation around the N–C(isopropyl) bond where

C–H insertion occurs; this may place the methine C–H bond in an appropriate place for interaction with the metal center in the case of **3c**, and the methyl C–H bond in the case of **3e**.

In terms of catalyst effectiveness, one notes again that ruthenium complex **9** provides an almost quantitative total yield for the intramolecular carbenoid reactions and matches $Rh_2(OAc)_4$ with respect to yield and activity. The performance of the other ruthenium catalysts agrees with the picture obtained in the preceding experiments.

Conclusions

We have found that several dinuclear ruthenium(I,I) complexes of the type $[Ru_2(CO)_4(\mu\text{-}L^1)_2L^2_2]$, where L^1 is a bidentate bridging acetate, calix[4]arenedicarboxylate, pyridin-2-olate or saccharinate ligand, catalyze intramolecular carbenoid reactions of *N,N*-dialkyldiazoacetamides efficiently and effectively. In particular, the complex $[Ru_2(\mu\text{-saccharinate})_2(CO)_5]_2$ (**9**) is as effective as $Rh_2(OAc)_4$ under the same conditions, and $[Ru_2(\mu\text{-6-chloropyridin-2-olate})_2(CH_3CN)_2(CO)_4]$ (**8**) comes very close. However, none of the ruthenium catalysts promotes an effective intramolecular insertion into C–H bonds of *N,N*-diethyldiazoacetamide. The differences between rhodium and ruthenium catalysts in terms of regioselectivity (C–H insertion leading either to β- or γ-lactams) and chemoselectivity (lactam formation *vs.* intramolecular cyclopropanation of an aromatic ring) are moderate: It appears that the ruthenium catalysts studied show a lower preference for β- *vs.* γ-lactam formation (methine *vs.* methyl C–H insertion, see experiments with **3c**) and in general a higher preference for aromatic cyclopropanation *vs.* lactam formation (see experiments with **3e**) as compared with the two rhodium catalysts **4** and **6**. Further studies must show whether such differences originate in electronic or steric properties of the catalysts. Anyway, ruthenium complexes **9** and **8**, both of which are easily prepared from $Ru_3(CO)_{12}$ and the protonated ligands (saccharin or 6-chloropyridin-2-one), are attractive alternatives to $Rh_2(OAc)_4$ and similar carboxylate or amidate complexes in catalyzing carbenoid reactions of diazoacetamides. The low effectiveness of the $RuCl_2$-*p*-cymene complex **11**, on the other hand, contrasts strongly with the report[16] that this catalyst induces high yields of lactams from 3-oxo-2-diazocarboxamides.

Experimental Section

General Remarks

All reactions were carried out in dried and distilled solvents. Column chromatography was performed on silica gel 60 (0.063–0.2 mm, Merck) or alumina (aluminum oxide 90 basic, activity I, 0.063–0.2 mm, Merck) with distilled cyclohexane and ethyl acetate as eluents. NMR spectra were recorded at 400.1 MHz (^{1}H) or 100.6 MHz (^{13}C), if not stated otherwise; $CDCl_3$ solutions with tetramethylsilane (TMS) as the internal standard; m_c = centered multiplet. Infrared spectra (ν, cm^{-1}) were recorded on a Bruker Vector 22 spectrometer. Mass spectra were obtained on a Finnigan MAT SSQ 7000 spectrometer in the CI mode. Elemental analyses were carried out with a Elementar Vario EL elemental analyzer. Succinimidyl diazoacetate (**1**) was synthesized with slight modification as described previously.[17,36] Catalysts **5**,[37] **6**,[27] **7a–c**,[23] **8**,[24] and **9**[25] were prepared as described in the literature. The activity of catalyst **8** decreases on storing; therefore, it was re-activated prior to use by dissolution in dry acetonitrile, warming at 60 °C for 10 min and evaporation of the solvent in a flow of argon.

N,N-Diethyl-α-diazoacetamide (3a)

Diethylamine (3.00 g, 40.0 mmol) was dissolved in THF (40 mL) at 20 °C. Succinimidyl diazoacetate (**1**) (3.50 g, 19.1 mmol) was added and the solution was stirred at 20 °C for 12 h. After column chromatography with cyclohexane/ethyl acetate (2:1) a yellow oil was obtained; yield: 2.67 g (99 %). ^{1}H NMR and IR: see lit.[18,20]; ^{13}C NMR: $\delta = 13.7$ (CH_3), 41.2 (CH), 46.2 (NCH_2), 164.6 (CO); anal. calcd. for $C_6H_{11}N_3O$ (141.2): C 51.05, H 7.85, N 29.77; found: C 51.17, H 7.82, N 29.83.

N,N-Dibutyl-α-diazoacetamide (3b)

The preparation from dibutylamine (4.30 g, 33.0 mmol) and **1** (2.83 g, 15.5 mmol) as described for **3a** afforded a yellow oil; yield: 3.00 g (99 %). ^{1}H NMR: $\delta = 0.86$ (t, 6H, $^3J =$ 7.3 Hz, CH_3), 1.24 (sext, 4H, $^3J = 7.6$ Hz, CH_3CH_2), 1.46 (quin, 4H, $^3J = 7.6$ Hz, NCH_2CH_2), 3.12 (very broad, 4H, NCH_2), 4.90 (s, 1H, $N_2{=}CH$); ^{13}C NMR: $\delta = 13.6$ (CH_3), 20.7 (CH_3CH_2), 29.9 (NCH_2CH_2), 41.1 (CH), 46.0 (broad, NCH_2), 164.5 (CO); IR (KBr): $\nu = 2101$ (s, CN_2), 1606 (s, CO), 1429 (br, m), 1368 cm^{-1} (m); anal. calcd. for $C_{10}H_{19}N_3O$ (197.3): C 60.88, H 9.71, N 21.30; found: C 60.84, H 9.67, N 21.06; MS (100 eV): *m/z* (%) = 198 (100), 170 (28), 156 (12).

N,N-Diisopropyl-α-diazoacetamide (3c)

Diisopropylamine (10.00 g, 98.8 mmol) was dissolved in THF (50 mL) at 20 °C. Succinimidyl diazoacetate (**1**) (4.00 g, 21.8 mmol) was added, and the solution was stirred at 50 °C for 12 h. After purification by chromatography with cyclohexane/ethyl acetate (4:1) a yellow oil was obtained; yield: 3.00 g (81 %). ^{1}H NMR: see lit.[20]; ^{13}C NMR: $\delta = 21.1$ (CH_3), 46.9 (CH), 47.9 (NCH), 164.5 (CO); IR (KBr): $\nu = 2103$ (s, CN_2), 1601 (s, CO), 1440 (s), 1368 cm^{-1} (s); anal. calcd. for

$C_8H_{15}N_3O$ (169.2): C 56.78, H 8.93, N 24.83; found: C 56.65, H 8.95; N 25.03; MS (100 eV): *m*/*z* (%) = 170 (100), 142 (11), 128 (55), 100 (35).

N,N-Dibenzyl-α-diazoacetamide (3d)

The preparation from dibenzylamine (3.55 g, 18.0 mmol) and **1** (1.00 g, 5.5 mmol) as described for **3c**, but with a reaction time of 50 h, furnished a yellow oil; yield: 1.23 g (85%). ^{1}H NMR and IR: see lit.[19]; ^{13}C NMR: $\delta = 47.0$ (CH), 49.5 (NCH_2), 127.6, 128.5, 128.8, 136.8 (all C_{Ar}), 166.6 (CO); anal. calcd. for $C_{16}H_{15}N_3O$ (265.3): C 72.43, H 5.70, N 15.84; found: C 72.28, H 5.73, N 15.90; MS (100 eV): *m*/*z* (%) = 266 (100), 237 (72), 196 (20), 104 (32), 91 (51).

N-Benzyl-*N*-isopropyl-α-diazoacetamide (3e)

The preparation from *N*-benzyl-*N*-isopropylamine (9.78 g, 65.5 mmol) and **1** (4.00 g, 21.8 mmol) as described above for **3c**, but with a reaction time of 24 h, furnished a yellow oil; yield: 4.02 g (85%). ^{1}H NMR (500.1 MHz, 325 K): $\delta = 1.13$ (d, 6H, $^3J = 6.8$ Hz, CH_3), 4.37 (s, 2H, CH_2), 4.45–4.70 (bs, 1H, CH), 4.80 (s, 1H, CH), 7.22–7.32 (m, 5 H_{Ph}); ^{13}C NMR (125.7 MHz, 325 K): $\delta = 20.7$ (CH_3), 45.6 (CH_2) 47.0 (CH), 47.3 (N_2CH), 126.4, 127.1, 128.7, 138.7 (all C_{Ar}), 166.5 (CO); IR (KBr): $\nu = 2104$ (s, CN_2), 1601 (s, CO), 1417 (br s), 1356 cm^{-1} (s); anal. calcd. for $C_{12}H_{15}N_3O$ (217.3): C 66.34, H 6.96, N 19.34; found: 66.09, H 6.93, N 19.45; MS (100 eV): *m*/*z* (%) = 218 (100), 189 (51), 176 (11), 148 (29), 104 (25), 91 (47).

C–H Insertion of Diazoacetamides 3a–e; General Procedure

The catalyst (1 or 3 mol%) was added to dry CH_2Cl_2 (25 mL). At 40 °C (25 °C with catalyst **6**), a solution of diazoamide **3a–e** (1–3 mmol) in dry CH_2Cl_2 (25 mL) was added *via* a syringe pump during a period of 1 h. After completed addition, the mixture was kept with stirring at 40 °C until the diazo compound had been consumed (IR control, see Tables 2–6 for details). The solvent was evaporated and the residue was separated by column chromatography over basic alumina (85–110 g). The desired lactams were obtained by elution with mixtures of cyclohexane/ethyl acetate. If necessary, they were purified further by vacuum distillation in a Kugelrohr apparatus. Further tractable products, in addition to those reported in Tables 2–6, could not be isolated.

For experiments without product isolation, the solvent was evaporated at 40 °C/700 mbar, and the crude product mixture was analyzed by ^{1}H NMR spectroscopy, whereby the product yields were determined by integration using naphthalene as an internal standard.

1-Ethylpyrrolidin-2-one (12)

Obtained from **3a** (424 mg, 3.0 mmol) and $Rh_2(OAc)_4$ (38.8 mg, 87.8 μmol) as a colorless oil; yield: 261 mg (77%). ^{1}H NMR: $\delta = 1.05$ (t, 3H, $^3J = 7.4$ Hz, CH_3), 1.95 (m, 2H, 4-H_2), 2.31 (t, 2H, $^3J = 8.2$ Hz, 3-H_2), 3.25 (q, 2H, $^3J = 7.6$ Hz, CH_2CH_3), 3.32 (m_c, 2H, $^3J = 16.5$ Hz, 5-H_2); ^{13}C NMR: $\delta =$ 12.3, 17.6, 31.0, 36.9, 46.4, 174.5; IR (KBr): $\nu = 2974$, 2935, 2876 (all m), 1686 (s, CO), 1462 (m), 1428 (m), 1285 cm^{-1} (m); anal. calcd. for $C_6H_{11}NO$ (113.16): C 63.68, H 9.80, N 12.38; found: C 63.99, H 9.80 N 12.19; MS (100 eV): *m*/*z* (%) = 114 (100), 100 (16), 86 (11), 72 (13).

Ruthenium-Catalyzed Carbenoid Reaction of 3a

The reaction was carried out as described in the General Procedure, with **3a** (495 mg, 3.5 mmol) and complex **7a** (123 mg, 0.11 mmol). Column chromatography (basic alumina, elution with ethyl acetate/cyclohexane/aqueous ammonia (20–30%) (3:1:0.05)) furnished: a) 1-ethylpyrrolidin-2-one (**12**) (yield: 91 mg, 23%); b) *N,N,N′,N′-tetraethylfumaramide* [(*E*)-**13**] (yield: 67 mg, 17%); c) *N,N,N′,N′-tetraethylmaleamide* [(*Z*)-**13**] (yield: 55 mg, 14%).

(*E*)-**13**: colorless oil, bp 170 °C/0.1 mbar (Kugelrohr); IR (film): $\nu = 2977$, 2935, 2876 (all s), 1622 cm^{-1} (s, CO); ^{1}H NMR: $\delta = 1.18$ (t, 6H, $^3J = 7.2$ Hz, CH_3), 1.23 (t, 6H, $^3J =$ 7.2 Hz, CH_3), 3.45 and 3.47 (2 q, each 4H, $^3J = 7.2$ Hz, NCH_2), 7.37 (s, 2H, CH); ^{13}C NMR: $\delta = 12.8$ (CH_3), 14.8 (CH_3), 40.8 (CH_2), 42.1 (CH_2), 131.1 (CH), 164.2 (CO); anal. calcd. for $C_{12}H_{22}N_2O_2$ (226.3): C 63.68, H 9.80, N 12.38; found: C 63.50, H 9.83, N 12.40.

(*Z*)-**13**: colorless oil, bp 170 °C/0.1 mbar (Kugelrohr); IR (film): $\nu = 2975$, 2935, 2875 (all s), 1634 cm^{-1} (s, CO); ^{1}H NMR: $\delta = 1.15$ (t, 6H, $^3J = 7.1$ Hz, CH_3), 1.18 (t, 6H, $^3J =$ 6.9 Hz, CH_3), 3.37 (q, 4H, $^3J = 7.2$ Hz, NCH_2), 3.42 (q, 4H, $^3J = 7.2$ Hz, NCH_2), 6.32 (s, 2H, CH); ^{13}C NMR: $\delta = 12.8$ (CH_3), 14.2 (CH_3), 39.3 (CH_2), 42.5 (CH_2), 129.2 (CH), 165.9 (CO); anal. calcd. for $C_{12}H_{22}N_2O_2$ (226.3): C 63.68, H 9.80, N 12.38; found: C 63.52, H 9.69, N 12.45.

1-Butyl-4-ethylpyrrolidin-2-one (14)

Obtained from **3b** (423 mg, 2.2 mmol) and $Rh_2(OAc)_4$ (26.4 mg, 59.7 μmol) as a colorless oil; yield: 356 mg (98%); ^{1}H NMR: $\delta = 0.89$ (t, 6H, $^3J = 7.4$ Hz, $(CH_2)_3CH_3$, CH_2CH_3), 1.28 (m, 2H, 3-H_2 Bu), 1.42 (m, 4H, CH_2CH_3, 2-H_2 Bu), 2.03 (dd, 1H, $J = 16.5$ and 7.5 Hz, 3-H^A), 2.19 (m_c, 1H, 4-H), 2.46 (dd, 1H, $J = 16.5$ and 8.7 Hz, 3-H^B), 2.96 (dd, 1H, $|^2J| = 9.6$ Hz, $^3J = 6.3$ Hz, 5-H^A), 3.21 [t, 2H, $^3J = 7.3$ Hz, NCH_2 (Bu)], 3.42 (dd, 1H, $|^2J| = 9.6$ Hz, $^3J = 7.8$ Hz, 5-H^B); ^{13}C NMR: $\delta = 11.6$ (CH_3), 13.6 (CH_3), 19.9 [CH_2 (Bu)], 27.6 [CH_2 (Et)], 29.3 [CH_2 (Bu)], 33.2 (C-4), 37.5 (C-3), 42.1 [C-1 (Bu)], 52.6 (C-5), 174.2 (CO); IR (KBr): $\nu = 2960$, 2930, 2874 (all s), 1685 (s, CO), 1457–1430 cm^{-1} (br, m); anal. calcd. for $C_{10}H_{19}NO$ (169.26): C 70.96, H 11.31, N 8.28; found: C 70.79, H 11.12, N 8.38; MS (100 eV): *m*/*z* = 170 (100%).

Ruthenium-Catalyzed Carbenoid Reaction of 3c

The reaction was carried out as described in the general procedure with **3c** (519 mg, 3.1 mmol) and ruthenium complex **9** (61.4 mg, 90 μmol). Column chromatography over basic alumina [110 g, elution with ethyl acetate/cyclohexane (4:1)] furnished first *1-isopropyl-4,4-dimethylazetidin-2-one* (**16**) (yield: 294 mg, 68%), then *1-isopropyl-5-methylpyrrolidin-2-one* (**17**) (yield: 87 mg, 20%).

16: Colorless oil; ^{1}H NMR and IR: see lit.[20]; ^{13}C NMR: $\delta = 21.7$ (CH_3), 26.1 (CH_3), 44.3 (NCH) 50.2 (C-3), 55.9 (C-4), 165.6 (CO).

17: Colorless oil; ^{1}H NMR and IR: see lit.[20]; ^{13}C NMR: $\delta = 19.5$ (CH_3), 21.7 (CH_3), 22.3 (CH_3), 27.4 (C-4), 30.4 (C-3), 44.3 (C-5), 53.0 (NCH), 174.7 (CO).

3-Benzyl-3-azabicyclo[5.3.0]deca-5,7,9-trien-2-one (19)

Obtained from **3d** (526 mg, 2.0 mmol) and $Rh_2(OAc)_4$ (26.0 mg, 58.8 μmol) as a white powder; yield: 348 mg (74%); mp 129°C; ^{1}H NMR: $\delta = 3.16$ (broad s, 1H, 1-H), 4.06 and 4.07 (AB system, 2H, $|^2J| = 17.2$ Hz, 4-H_2), 4.56 and 4.60 (AB system, 2H, $|^2J| = 14.7$ Hz, NCH_2), 5.33 (dd, 1H, $^3J = 9.3$ and 3.8 Hz, 10-H), 6.09 (s, 1H, 6-H), 6.17–6.22 (m, 1H, 9-H), 6.45–6.51 (m, 2H, 7-H, 8-H), 7.27–7.32 (m, 5 H_{Ph}); ^{13}C NMR: $\delta = 46.3$ (C-4), 46.5 (C-1), 50.5 (NCH_2), 119.5 (C-6), 120.6 (C-10), 125.8 (C-5), 127.0 (C-9), 127.8, 128.2, 129.2, 129.9 (C-7), 130.3 (C-8), 174.0 (CO); IR (KBr): $\nu = 3062$, 3029, 2924, 2849 (all m), 1682 (s, CO), 1650 (s), 1475/1455/1442/1425 cm^{-1} (all m); anal. calcd. for $C_{16}H_{15}NO$ (237.12): C 80.98, H 6.37, N 5.90; found: C 80.90, H 6.43, N 5.89; MS (100 eV): $m/z = 238$ (100%).

$Rh_2(OAc)_4$-Catalyzed Reaction of 3e

The reaction was carried out as described in the general procedure with **3e** (441 mg, 2.0 mmol) and $Rh_2(OAc)_4$ (26.2 mg, 59.3 μmol). Column chromatography over basic alumina [85 g, elution with cyclohexane/ethyl acetate (7:3)] furnished a) *3-isopropyl-3-azabicyclo[5.3.0]deca-5,7,9-trien-2-one* (**23**) (yield: 160 mg, 42%); b) *1-benzyl-4,4-dimethylazetidin-2-one* (**22**) (52 mg, 13%); c) *1-benzyl-4-methyl-pyrrolidin-2-one* (**21**) (yield: 137 mg, 36%).

21:[38] Colorless oil; ^{1}H NMR: $\delta = 1.15$ (d, 6H, $^3J = 6.3$ Hz, CH_3), 1.58–1.62 (m, 1H, 4-H^1), 2.14–2.16 (m, 1H, 4-H^2), 2.39–2.50 (m, 2H, 3-H_2), 3.54 (sext, 1H, 5-H), 3.98 (d, 1H, $^2J = 15.1$ Hz, NCH^A), 4.96 (d, 1H, $^2J = 14.9$ Hz, NCH^B), 7.22–7.32 (m, 5 H_{Ph}); ^{13}C NMR: $\delta = 19.6$ (CH_3), 26.6 (C-4), 30.2 (C-3), 43.9 (C-5), 52.8 (NCH_2), 127.3, 127.9, 128.5, 136.8, 174.9 (CO); IR (KBr): $\nu = 1734$ (s, CO), 1437 cm^{-1} (m); anal. calcd. for $C_{12}H_{15}NO$ (189.25): C 76.16, H 7.99, N 7.40; found: C 75.83, H 7.97, N 7.56; MS (100 eV): $m/z = 190$ (100%).

22:[39] Colorless oil; ^{1}H NMR: $\delta = 1.23$ (s, 6H, CH_3), 2.76 (s 2H, 3-H_2), 4.30 (s, 2H, NCH_2), 7.26–7.32 (m, 5 H_{Ph}); ^{13}C NMR: $\delta = 25.1$ (CH_3), 43.2 (C-3), 50.6 (NCH_2), 56.1 (C-4), 127.5, 128.3, 128.5, 137.0, 166.3 (CO); IR (KBr): $\nu = 2967$ (m), 1744 (s, CO), 1391 cm^{-1} (m); $C_{12}H_{15}NO$ (189.25): calcd. C 76.16, H 7.99, N 7.40; found: C 76.23, H 8.03, N 7.50; MS (100 eV): $m/z = 190$ (100%).

23: Colorless oil; ^{1}H NMR: $\delta = 1.17$ (d, 3H, $^3J = 6.8$ Hz, CH_3), 1.20 (d, 3H, $^3J = 6.6$ Hz, CH_3) 3.09 (dd, 1H, $J = 2.0$ and 1.3 Hz, 1-H), 4.17 (s, 2H, 4-H_2), 4.51 (sept, 1H, $^3J = 6.8$ Hz, NCH), 5.28 (dd, 1H, $J = 3.8$ and 9.6 Hz, 10-H), 6.15–6.19 (m, 2H, 6-H, 9-H), 6.44–6.53 (m, 2H, 7-H, 8-H);^{13}C NMR: $\delta = 19.7$ (CH_3), 42.5 (CH) 45.8 (C-4), 46.9 (C-1), 119.4 (C-6), 120.8 (C-10), 126.8 (C-9), 129.7 (C-7), 129.8 (C-8), 130.2 (C-5), 173.2 (CO); IR (KBr): $\nu = 2972$ (m), 1773 (s, CO), 1473 (m), 1427 cm^{-1} (m); anal. calcd. for $C_{12}H_{15}NO$ (189.25): C 76.16, H 7.99, N 7.40; found: C 76.00, H 8.04, N 7.43; MS (100 eV): $m/z = 190$ (100%).

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