Control of Regioselectivity by Chelating Substrates in Some Rhodium(I) and Rhodium(III)-catalysed Reactions of Butadiene

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Rhodium(I) catalyses the addition of butadiene to chelating substrates such as *N*-allylamides of organic acids, or alkylamides of but-3-enoic or pent-4-enoic acids, under mild conditions, to give linear products exclusively. No reaction occurs in the absence of chelation. Rhodium(III) reacts in the same way with amides of butenoic acid, but gives branched products regioselectively with *N*-allylcarboxamides or sulfonamides. Rhodium(I) and rhodium(III) complexes with chelating amides have been isolated and their reactivity has been investigated. The chelation effect causing reactivity and regioselectivity changes in rhodium(I)- and rhodium(III)-catalysed reactions is discussed.

It is well known that butadiene reacts with ethylene to give the industrially important hexa-1,4-diene in the presence of $RhCl_3$.[1] If this reaction is applied to higher olefins the product is a mixture of linear and branched diolefins, the latter being predominant. Rhodium(I) complexes appear to be unreactive in this reaction.

In the course of our studies, aimed at achieving better efficiency and regioselectivity in catalytic reactions by using chelating substrates,[2] we had previously found that butadiene reacted with but-3-enoic acid in the presence of $RhCl(PPh_3)_3$ and obtained a highly regioselective reaction[3] [eqn. (1)].

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2CO_2H \xrightarrow{RhCl(PPh_3)_3} MeCH{=}CHCH_2CH{=}CHCH_2CO_2H \quad (1)$$

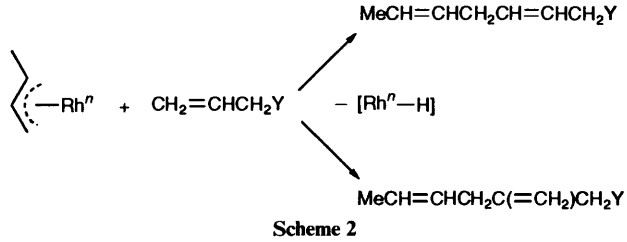
As shown by the previously described[4] Ni- or Rh-catalysed C–O bond cleavage and rearrangement of allyl but-3-enoate and by the isolation of metallacyclic carboxylates,[5] the reaction clearly involves the formation of a chelating ring (Scheme 1).

Scheme 1

Under the same conditions the corresponding methyl ester did not react appreciably.

In our search for other chelating substrates we chose *N*-allylamides or *N*-butenamides of organic acids, *N*-allylsulfonamides and *N*-alkyl-but-3-enamides or pent-4-enamides as potentially useful reagents for reaction with conjugated dienes. The amido group was reported in the literature as an efficient directing group for hydrogenations,[6] hydroformylations[7] and alkylations.[8]

Assuming a butadiene-derived crotylrhodium† group as intermediate we could expect the directing effect to lead to attack either on the internal or on the terminal carbon atom of the double bond (Scheme 2, Y = amide group-containing residue, n = I or III).



Scheme 2

Results

As briefly reported previously,[9] *N*-allylbenzamide reacted regioselectively with butadiene in the presence of $RhCl_3$ as catalyst in ethyl alcohol at 95 °C, to give the branched product (substantially in the *E* form), resulting from the reaction of the butadiene-derived crotyl group with the internal carbon atom of the allyl double bond. The reaction is quite general for *N*-allylamides according to eqn. (2). Product **1b** was obtained in

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2NR'COR \xrightarrow{Rhodium(III)} MeCH{=}CHCH_2C(=CH_2)CH_2NR'COR \quad (2)$$

1a (4*E*; R = Me, R′ = H)
1b (4*E*; R = Ph, R′ = H)
1c (4*E*; R = Ph, R′ = Me)

satisfactory yield (78% on the amide). Butadiene was used in excess (~5 mol per mol of substrate) and gave some self-addition by-products.

Curiously, when we used the rhodium(I) complex $[(\eta^4\text{-}C_4H_6)Rh]BPh_4$ as catalyst under the same conditions, linear products (mainly 1,5-unsaturated mixtures of *E* and *Z* isomers, 1*Z*,5*E* and 1*E*,5*E*, along with minor amounts of 2*E*,5*E* isomers) were obtained regioselectively (83% total yield for R = Ph) [eqn. (3)].

† Crotyl = but-2-enyl.

$$CH_2{=}CHCH{=}CH_2 + R''CH{=}CHCH_2NR'COR \xrightarrow{\text{Rhodium(I)}} MeCH{=}CHCH_2CHR''CH{=}CHNR'COR + MeCH{=}CHCH_2CR''{=}CHCH_2NR'COR \quad (3)$$

2a (1*Z*,5*E*; R = Me, R′ = R″ = H)
2b (1*E*,5*E*; R = Me, R′ = R″ = H)
2c (1*Z*,5*E*; R = Ph, R′ = R″ = H)
2d (1*E*,5*E*; R = Ph, R′ = R″ = H)
2e (1*Z*,5*E*; R = Ph, R′ = Me, R″ = H)
2f (1*E*,5*E*; R = Ph, R′ = Me, R″ = H)
2g (1*E*,5*E*; R = Ph, R′ = H, R″ = Me)

2′d (2*E*,5*E*; R = Ph, R′ = R″ = H)

When R = Me, Ph and R′ = R″ = H a small amount (yield 5–10%) of an unidentified mixture of isomeric products, derived from the addition of two molecules of butadiene and one of ethanol per molecule of allylamide, was also obtained.

The reaction took place in toluene as well under the same conditions (50% yield in 24 h). 1-Phenylbuta-1,3-diene was formed as by-product, derived from the coupling reaction of a phenyl group (from tetraphenylborate) and butadiene. Addition of palladium(0) as a complex with triphenylphosphine (0.1 mol per mol of rhodium) accelerated the reaction remarkably: after 6 h the conversion was almost complete and the yield of linear isomers reached 90%, product distribution being essentially the same as in the absence of palladium. Analogous results were obtained in toluene although after a longer time (90% conversion in 24 h with the rhodium–palladium system).

We allowed *N*-allylbenzamide to react with butadiene and bis(ethylene)rhodium chloride dimer in ethanolic HCl solution and according to what we observed with $RhCl_3$ [eqn. (2)] we isolated the corresponding branched product **1b** (71% yield). When the same reaction was carried out with $RhCl_3$, and Na_2CO_3 as neutralizing agent, in EtOH–water (85:15 v/v) only the linear products **2c**, **2d** and **2′d** (33:56:11 respectively) were found (50% yield) [eqn. (3)]. Complex $RhH(PPh_3)_4$ slowly reacted in toluene to give 10% of the mixture of linear amides, together with a large amount (35%) of prop-1-enylamide. As shown by separate experiments, phosphines adversely affected the reaction. Simple non-chelating olefins did not react with rhodium(I) complexes.

The results obtained from the reaction of butadiene with different olefins with rhodium(I) and rhodium(III) complexes as catalysts are reported in Table 1, which gives the percentage of linear and branched compounds (derived from attack of the crotyl group on the terminal and on the internal carbon of the double bond, respectively) as determined after hydrogenation of the reaction products. The relevant equations, corresponding to different types of substrates, are 2–11. It can be seen that the reaction is quite sensitive to the presence of substituents exerting steric hindrance and to the efficiency of the chelating system. The *N*-methyl derivative of *N*-allylbenzamide reacted with butadiene much more slowly but gave the linear products with rhodium(I) (14% yield, two isomers **2e** and **2f**) and the branched product **1c** with rhodium(III) (44% yield). A side-reaction is worth mentioning: with rhodium(III) the allyl was in part cleaved and *N*-methylbenzamide was formed.

A terminal methyl group on *N*-allylbenzamide (*N*-crotylbenzamide) gave a low conversion (14%) into MeCH=CHCH$_2$CH(Me)CH=CHNHCOPh (**2g**, 1*E*,5*E*) in 11% yield with rhodium(I) and no product with rhodium(III).

N-Allyltoluene-*p*-sulfonamide gave, with rhodium(III), a branched product **3a**, corresponding to the one obtained with *N*-allylamides of carboxylic acids [eqn. (2)], while no product was obtained with rhodium(I). The *N*-methyl derivative behaved analogously, although to a lesser extent, to give product **3b** [eqn. (4)].

$$CH_2{=}CHCH{=}CH_2 + p\text{-}MeC_6H_4SO_2NR'CH_2CH{=}CH_2 \xrightarrow{\text{Rhodium(III)}} p\text{-}MeC_6H_4SO_2NR'CH_2C(=CH_2)CH_2CH{=}CHMe \quad (4)$$

3a (R′ = H)
3b (R′ = Me)

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2CH_2NHCOPh \xrightarrow{\text{Rhodium(III)}} MeCH{=}CHCH_2CH_2CH{=}CHCH_2NHCOPh + MeCH{=}CHCH_2C(=CH_2)CH_2CH_2NHCOPh \quad (5)$$

4 (2*E*,6*E*)
5 (5*E*)

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2CONRR' \xrightarrow{\text{Rhodium(I or III)}} MeCH{=}CHCH_2CH_2CH{=}CHCONRR' + MeCH{=}CHCH_2CH{=}CHCH_2CONRR' + (MeCH{=}CHCH_2)_2CHCH{=}CHCONRR' \quad (6)$$

6a (2*E*,6*E*; R = H, R′ = Pr)
6b (2*E*,6*E*; R = R′ = Et)

6′a (3*E*,6*E*; R = H, R′ = Pr)
6′b (3*E*,6*E*; R = R^1 = Et)

7a (2*E*,6*E*,6′*E*; R = H, R′ = Pr)
7b (2*E*,6*E*, 6′*E*; R = R′ = Et)

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2CO_2Et \xrightarrow{\text{Rhodium(I)}} MeCH{=}CHCH_2CH_2CH{=}CHCO_2Et + MeCH{=}CHCH_2CH{=}CHCH_2CO_2Et \quad (7)$$

8 (2*E*,6*E*)
8′ (3*E*,6*E*)

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2CO_2Et \xrightarrow{\text{Rhodium(III)}} MeCH{=}CHCH_2C(=CH_2)CH_2CO_2Et + \mathbf{8}(2E,6E) + \mathbf{8'}(3E,6E) \quad (8)$$

9 (5*E*)

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2CH_2CONHPr \xrightarrow{\text{Rhodium(I)}} MeCH{=}CHCH_2CH_2CH{=}CHCH_2CONHPr \quad (9)$$

10 (3*E*,7*E*)

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CHCH_2CH_2CONHPr \xrightarrow{\text{Rhodium(III)}} MeCH{=}CHCH_2C(=CH_2)CH_2CH_2CONHPr + \mathbf{10}\,(3E,7E) \quad (10)$$

11 (6*E*)

$$CH_2{=}CHCH{=}CH_2 + CH_2{=}CH[CH_2]_nMe \xrightarrow{\text{Rhodium(III)}} MeCH{=}CHCH_2C(=CH_2)[CH_2]_nMe + \text{four linear isomers} \quad (11)$$

12 (*n* = 6; 4*E*)
13 (*n* = 10; 4*E*)

We also observed that if the distance between the double bond and the NH group is increased by only one CH_2 unit, rhodium(I) is no longer active (the substrate does not have sufficient coordinative power) and rhodium trichloride gives a 1:2 mixture of linear and branched products **4** and **5** [eqn. (5)].

In contrast with *N*-allylamides, but-3-enamides, in which the NH–CO sequence is inverted, gave exclusive formation of linear products both with rhodium(I) and rhodium(III) [eqn. (6)]. *N*,*N*-Diethylbut-3-enamide too gave the linear isomers **6b** and **6′b** both with rhodium(I) and with rhodium(III). Small amounts of products **7**, derived from further attack of butadiene (as a crotyl group) on octa-3,6-dienamides **6′**, were also found.

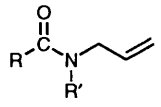
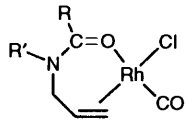
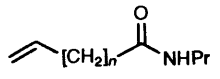
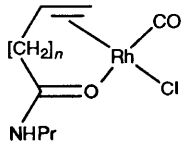
The oxygen of butenoic esters coordinates to a certain extent

Table 1 Linear *vs.* branched products of the reaction of butadiene with different chelating olefins catalysed by rhodium(I) or rhodium(III) species

	Rh^{I} species[a]				Rh^{III} species[b]				
		Linear isomers				Linear isomers		Branched isomer	
Substrate	Conv.[c] (%)	Yield[d] (%)	Selectivity[e] (%)	Yield[c] (%) of other products	Conv.[c] (%)	Yield[d] (%)	Selectivity[e] (%)	Yield[d,f] (%)	Yield[c] (%) of other products
$MeCONHCH_2CH{=}CH_2$	92	82	**2a**, 67; **2b**, 33	7[g]	67			**1a**, 59	6[h]
$PhCONHCH_2CH{=}CH_2$	92	86	**2c**, 32; **2d**, 60; **2'd**, 8	6[g]	87			**1b**, 78	7[i]
$PhCON(Me)CH_2CH{=}CH_2$	17	14	**2e**; **2f** (58:42 or *vice versa*)[j]		85			**1c**, 44	29[k], 9[l]
$p\text{-}MeC_6H_4SO_2NHCH_2CH{=}CH_2$	2				78			**3a**, 66	
$p\text{-}MeC_6H_4SO_2N(Me)CH_2CH{=}CH_2$	0				26			**3b**, 25	
$PhCONH[CH_2]_2CH{=}CH_2$	3				61	19	**4**, 100	**5**, 41	
$CH_2{=}CHCH_2CONHPr$	86	74	**6a**, 77; **6'a**, 23	**7a**, 9	87	76	**6a**, 10; **6'a**, 90		**7a**, 9
$CH_2{=}CHCH_2CONEt_2$	44	36	**6b**, 62; **6'b**, 38	**7b**, 8	49	45	**6b**, 20; **6'b**, 80		**7b**, 4
$CH_2{=}CHCH_2CO_2Et$	18	15	**8**, 63; **8'**, 37		69	26	**8**, 34; **8'**, 66	**9**, 37	5[n]
$CH_2{=}CH[CH_2]_2CONHPr$	48	43	**10**, 85; 15[m]	3[n]	61	19	**10**, 87; 13[m]	**11**, 35	4[n]
$CH_2{=}CH[CH_2]_6Me$	1				93	21	4 isomers[o]	**12**, 63	7[n]
$CH_2{=}CH[CH_2]_{10}Me$	1				61	15	4 isomers[p]	**13**, 42	3[n]

[a] Reaction conditions: $[\eta^4\text{-}(C_4H_6)Rh]BPh_4$ (0.02 mmol), substrate (2.0 mmol), butadiene (10 mmol), dry EtOH (2 cm^3), 95 °C for 24 h; similar results were obtained under the same conditions in the presence of bis(ethylene)rhodium chloride dimer and $NaBPh_4$ as catalytic system. [b] $RhCl_3{\cdot}3H_2O$ (0.02 mmol), substrate (2.0 mmol), butadiene (10 mmol), EtOH (2 cm^3), 95 °C for 36 h. [c] Based on starting substrates. [d] Based on starting substrates after hydrogenation in the presence of Pd/C (10%). [e] Calculated as percentage of one linear (or branched) isomer in respect to the total of linear (or branched) isomers. [f] Selectivity of the branched isomer is substantially complete. [g] Unidentified mixture of isomers derived from the addition of two molecules of butadiene and one of ethanol to the substrate, detected by GLC–MS; see Experimental section. [h] *N*-(Prop-1-enyl)acetamide. [i] *N*-(Prop-1-enyl)benzamide. [j] Not separated, but directly hydrogenated. [k] *N*-Methylbenzamide. [l] *N*-Methyl-*N*-(prop-1-enyl)benzamide. [m] Unidentified linear isomer, detected by GLC–MS; see Experimental section. [n] Unidentified isomer derived from the addition of two molecules of butadiene to the substrate, detected by GLC–MS; see Experimental section. [o] Hydrogenated to tridecane. [p] Hydrogenated to heptadecane.

Table 2 IR wavenumbers of carbonyl groups in rhodium(I) carbonyl complexes with *N*-allylamides and *N*-propylalkenamides

Amide	ν_{CO}/cm^{-1}	Rh^{I} complex	ν_{CO}/cm^{-1}
			
		Rh 1	
a; R = Ph, R′ = H	1640	**Rh1a** R = Ph, R′ = H	1602, 2012
b; R = Ph, R′ = Me	1633	**Rh1b** R = Ph, R′ = Me	1590, 2000
			
		Rh2	
n = 1	1653	**Rh2a**	1608, 2013
n = 2	1651	**Rh2b**	1600, 1997

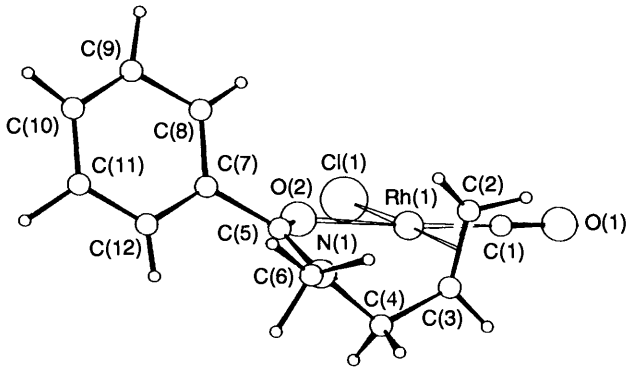


Fig. 1 X-Ray molecular structure of compound **Rh1b**

to rhodium(I)[6] and the reaction with butadiene still gave the linear products, **8** and **8′**, [eqn. (7)], although in lower yield. Rhodium trichloride gave a mixture of linear and branched products, the latter (**9**) being predominant [eqn. (8)].

If pent-4-enamides were used with rhodium(I), linear products were again obtained, while with rhodium(III) a mixture of linear (**10**) and branched (**11**) products (1:2) was formed [eqns. (9) and (10)].

The reaction of terminal alkenes such as non-1-ene and tridec-1-ene is reported in Table 1 for comparison. They did not react with rhodium(I), while with rhodium(III) they gave a mixture of linear and branched products in 1:3 ratio, identified after hydrogenation to the corresponding hydrocarbons [eqn. (11)].

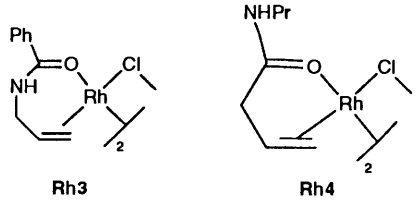
It is worth noting that the butadiene-derived moiety is found to be essentially linear in all the products.

In order to gain further information on the coordination type adopted by chelating amides we prepared new rhodium(I) complexes containing *N*-allylamides, starting from $[Rh(CO)_2Cl]_2$ in chloroform. The amides gave stable complexes, whose IR spectra show coordination through oxygen. The C=O stretching frequency decreases in respect to that of the free amide, as expected.[10,11] The structures of two complexes (**Rh1** and **Rh2**) are shown in Table 2 along with the IR CO signals in comparison with those of the free amides. ^1H NMR spectra are characterized by a shift of the NH absorption from δ 6–6.5 to δ 8–9. The double-bond protons give large shifts (up to 2 ppm) to higher fields and their multiplicity is in accord with participation in a chelate system, which differentiates their position. Analogous large upfield shifts are observed in the ^{13}C NMR spectrum for the vinylic carbons. Coupling with rhodium is of the order of 10–15 Hz. The amide carbonyl resonance shifts to lower fields.

Suitable crystals of one of these complexes (**Rh1b**, R = Ph, R′ = Me) were obtained, and analysed by X-ray methods. The structure with arbitrary numbering scheme is shown in Fig. 1. The Rh atom shows a normal square arrangement. The chloride ion is placed *trans* to the double bond which occupies a position nearly perpendicular to the square plane. The aromatic ring is tilted by 72.7(1)° with respect to the square coordination plane.

The complexes obtained from $[Rh(CO)_2Cl]_2$ and *N*-propylbut-3-enamide or *N*-propylpent-4-enamide (**Rh2a** and **Rh2b**), behave in their IR spectrum analogously to those *N*-allylamides as shown in Table 2.

The rhodium(I) complexes did not react with butadiene. We attribute this behaviour to the carbonyl group, which deactivates the catalytic intermediate, thereby blocking a coordination site as shown by inhibition of the catalytic reaction with rhodium(I) complexes in the presence of CO. To avoid the use of rhodium carbonyl complexes, we started from bis(ethylene)rhodium(I) chloride dimer and *N*-allylbenzamide or *N*-propylbut-3-enamide in $CHCl_3$ and obtained insoluble dimeric complexes (**Rh3**- or **Rh4**-dimers).



Rh3 **Rh4**

In accord with our prediction, when we started from complex **Rh3** and treated it with an excess of butadiene in ethanol at 95 °C in the presence of sodium tetraphenylborate, formation of the linear products **2** (**2c**:**2d** 2:1) occurred readily (65% yield). Complex **Rh4** behaved analogously and formed compounds **6** (**6a**:**6′a** 3:1, 68% yield).

The reaction of $RhCl_3$ with *N*-allylbenzamides was also examined. To obtain the desired complex we started from (butadiene)di-(η^3-butenyl)tetrachlorodirhodium(III) described by Cramer[1] and by Shaw.[12] Replacement of the butadiene molecule with *N*-allylbenzamide in $CHCl_3$ led to an insoluble product (**Rh5**) in which the IR absorptions of the amide were rather similar to those of the free amide. We could ascertain that two molecules of the amide were contained in the complex, corresponding to the structure **Rh5**, in which the relative positions of the crotyl and allylamide groups were not assigned.

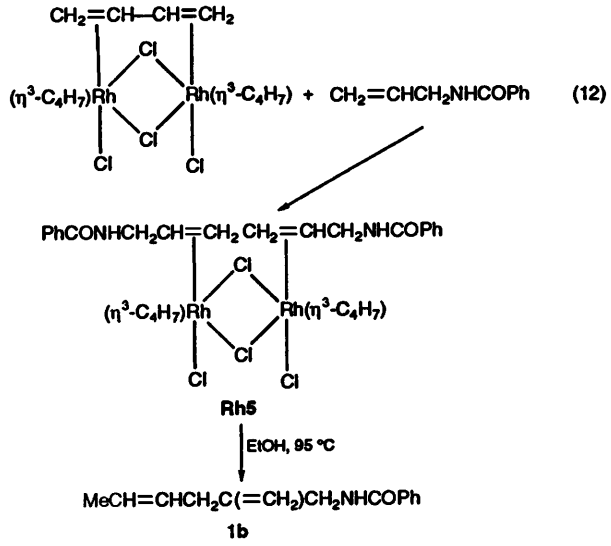
The reaction of complex **Rh5** in ethanol at 95 °C gave the expected amide **1b**, although in low yield (25%) [eqn. (12)].

Discussion

We have first to consider the opposed regioselectivity of the reaction of an allylamide such as *N*-allylbenzamide with rhodium(I) or rhodium(III) complexes.

Since we could detect phenylbutadiene in the reaction mixture of $[(\eta^4\text{-}C_4H_6)Rh]BPh_4$ with butadiene and allylamide, we argued that a rhodium hydride (although not detected spectroscopically) must be formed and that the following steps must also involve a rhodium(I) species[9] [eqn. (13)].

The process was further catalysed by palladium(0), which accelerated the phenyl migration in a sort of 'catalysis of catalysis'.



$$[(\eta^4\text{-}C_4H_6)Rh]BPh_4 \longrightarrow PhCH{=}CHCH{=}CH_2 + Rh\text{–}H + BPh_3 \quad (13)$$

Rhodium(III) hydride catalysis had previously been shown to be at work if $RhCl_3$ or bis(ethylene)rhodium chloride dimer in hydrochloric acid solution were used as catalyst for the reaction of butadiene with ethylene.[1] We confirmed this result by allowing *N*-allylbenzamide to react with butadiene and bis(ethylene)rhodium chloride dimer in hydrochloric acid solution, and according to what was observed with $RhCl_3$ [eqn. (2)] we isolated the branched product **1b** [eqn. (14)].

$$[(CH_2{=}CH_2)_2RhCl]_2 + 2HCl \longrightarrow RhCl_3 + EtOH \xrightarrow[-HCl]{} RhCl_2OEt \xrightarrow[-MeCHO]{} RhHCl_2 \quad (14)$$

$$\xrightarrow{CH_2=CHCH=CH_2} [(\eta^3\text{-}MeCH\text{–}CH\text{–}CH_2)RhCl_2] \xrightarrow{PhCONHCH_2CH=CH_2} \mathbf{1b}$$

Although the use of a neutralizing agent in conjunction with $RhCl_3$ in ethanol did not lead to reaction in the case of butadiene and simple non-chelating olefins,[1] owing to reduction to rhodium(I), we expected, on the basis of our rhodium(I) hydride hypothesis, that under the same conditions chelating substrates would lead to reaction with formation of the linear products. The isolation of linear products exclusively from the reaction of *N*-allylbenzamide and butadiene in EtOH in the presence of $RhCl_3$–Na_2CO_3 is in agreement with the formation of such a rhodium(I) hydride from ethanol[13,14] [eqn. (15)].

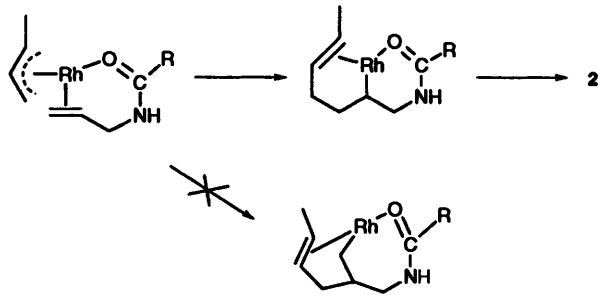
$$-Rh\text{–}Cl \xrightarrow[Na_2CO_3]{EtOH} -Rh\text{–}OEt \xrightarrow[-MeCHO,\ NaCl]{} -Rh\text{–}H \quad (15)$$

The pathway of eqn. (13), implying rhodium(I) hydride formation by hydrogen transfer from the ligand, was much more effective, however, and was operative also in toluene. As further evidence for rhodium(I) hydride catalysis, $RhH(PPh_3)_4$ proved to be active as catalyst in spite of the negative effect of the phosphine ligands.

To interpret the course of the subsequent steps we have to take into consideration the previously described behaviour of simple terminal olefins.[1] The formation of a rhodium-coordinated crotyl group is followed by double-bond insertion. For olefins higher than propylene the insertion into a crotylrhodium(III) bond is only moderately regioselective, and in any case the carbon–carbon bond formation involves the internal carbon atom of the double bond preferentially.

The tendency of the rhodium(III) complex to form a Rh–C bond with the terminal unsaturated carbon of the olefin undergoing insertion may be due to steric reasons. As previously mentioned, rhodium(I) complexes are not reactive. In our case, however, a suitably placed amide group able to form a chelate causes the reaction to occur. The regioselectivity is complete and is inverted in respect to that observed with rhodium(III). Therefore the square planar rhodium(I) complex must form a Rh–C bond with the internal unsaturated carbon of the olefin.

It is known from the literature that amides coordinate through oxygen,[6,10] unless they are deprotonated or converted into iminol tautomers.[11,15] The isolated complexes confirm this property, and we propose the following Scheme 3 for the rhodium(I)-catalysed reactions.



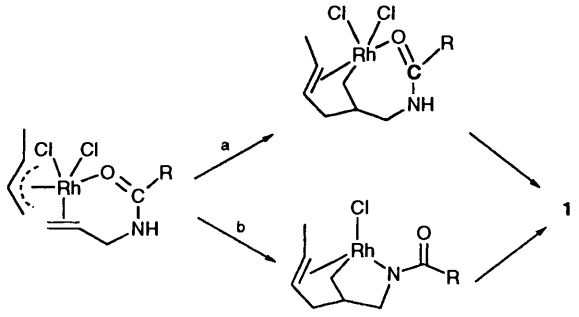
Scheme 3

According to the suggested pathway the reaction is driven by formation of a chelate. The six-membered ring must be highly preferred to the seven-membered one, which would be required for formation of the branched product. It is to be observed in this context that increasing the size of the chelate by one CH_2 leads to loss of reactivity. Actually, no interaction was observed in the ^1H NMR spectrum of but-3-enylbenzamide in the presence of $[Rh(CO)_2Cl]_2$ and no complex was obtained.

The situation is quite different with $RhCl_3$, which, as mentioned before, tends to give branched products even in the absence of an additional chelating group. Depending on the position of the latter we can observe reinforcement of the selectivity towards the preferred branched product or inversion to give the linear product as we shall see later. It should be recalled that simple olefins give a mixture of linear and branched products.

The chelation effect exerted by the amide must intervene also in the reaction of complex **Rh5** (not containing a chelated amide), which gives the branched product exclusively. We assume conversion of complex **Rh5** into a chelated monomeric structure which then reacts with the coordinated crotyl group. In this case, however, the amide ligand could also dissociate from the dimeric complex before formation of the chelated species and the crotyl group could undergo independent reactions. Scheme 4 reports the proposed pathway (a) for the rhodium(III)-catalysed reaction.

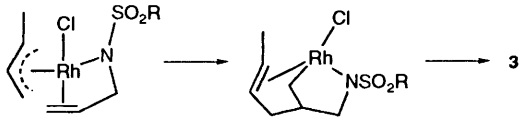
Chelation through oxygen (path a) would form a seven-membered ring which, although not very strong, could further stabilize the preferred rhodium to a primary carbon bond. We cannot exclude, however, an alternative pathway (b), based on a rhodium–nitrogen interaction at the stage of double-bond insertion to form a five-membered chelate (to stabilize the precursor of the linear product an unfavourable four-membered chelate would have to have been formed). The interaction with nitrogen could lead to deprotonation, as shown in Scheme 4. However, the fact that *N*-allyl-*N*-methylbenzamide, which does



Scheme 4

not contain the NH group, gives the branched product, at least in part, excludes the generality of a pathway involving deprotonation. In spite of this a nitrogen–rhodium interaction remains a possibility. For example, the cleavage of the nitrogen–allyl bond in *N*-allyl-*N*-methylbenzamide can also be interpreted as an indication of metal interaction with the amide group, probably occurring *via* the nitrogen atom.

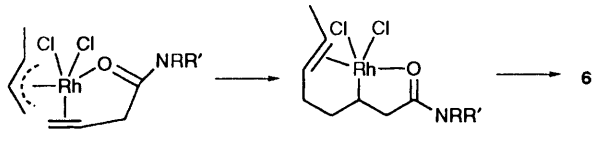
The deprotonation pathway (b) depicted in Scheme 4 could be at work in the case of *N*-allylsulfonamides.[16] The latter gave the branched product exclusively in the rhodium(III)-catalysed reaction. The complete regioselectivity obtained could be explained by a nitrogen–rhodium interaction, which, owing to the acidic character of the NH group, would readily lead to deprotonation (Scheme 5). The corresponding *N*-methyl-



Scheme 5

sulfonamide, however, also reacts to a certain extent to give the branched product exclusively, and again this behaviour points to a nitrogen–rhodium interaction.

Passing now to the *N*-propylamide of but-3-enoic acid, in which the NHCO sequence is inverted in respect to *N*-allylamides, we could expect that, again, linear products would be obtained, as were indeed observed. What is rather surprising, in view of the behaviour of rhodium(III) described so far, is the exclusive formation of linear products in the $RhCl_3$-catalysed reaction. Our interpretation is that the formation of a very stable five-membered chelate, *via* either oxygen or nitrogen, has the effect of reversing the rhodium(III) tendency to give the branched product preferentially, thus forming a stable bond with the secondary carbon resulting from the double-bond insertion (Scheme 6).



Scheme 6

Coordination through nitrogen *via* deprotonation is a possibility (formation of chelates of but-3-enamide through nitrogen and carbon, involving deprotonation at nitrogen, was observed with nickel),[17] but it has to be excluded as a general feature on the grounds that the diethylamide of but-3-enoic acid reacted as well, although to a smaller extent. The main factor determining regioselectivity towards the linear products must be chelation through the amide oxygen although a metal–nitrogen interaction cannot be discarded. It is noteworthy that with an increase in the length of the butenoic chain by one carbon unit rhodium(I) still gives the linear product, whereas with rhodium(III) the regioselectivity is lost. Apparently the larger and more flexible ring no longer is able to control the type of insertion occurring on rhodium.

Similar considerations are appropriate also for butenoic esters which exhibit a limited chelating power, sufficient to lead to the linear product with rhodium(I), although in a low yield, but not sufficient to control regioselectivity with rhodium(III).

So much for the regioselective insertion step. The final hydride elimination deserves some comment insofar as the preferred position of the double bond thus formed is different for allylamides and for butenamides. As shown in Table 1 the products derived from the former are mainly 1-unsaturated (compounds **2**), while those from the latter are mainly 3-unsaturated with rhodium(III) (compounds **6'**) and 2-unsaturated with rhodium(I) (compounds **6**). This behaviour might be traced to the different size and flexibility of the chelate ring, which could reach a favourable stereochemistry for H-elimination from the 4-position in the case of butenamides [eqn. (6), rhodium(III)] and from the 1-position in the case of allylamides [eqn. (3), rhodium(I)]. The tendency of butenoic acid amides and esters to give, with rhodium(I), more 2- than 3-unsaturated compounds could be explained by their weaker chelation in respect to rhodium(III) which might favour H-elimination from the 2-position. The larger size of the chelating ring of a pentenamide allows H-elimination from the 3-position (compound **10**) not only with rhodium(I) but also with rhodium(III) [eqns. (9) and (10)].

As to the double-bond stereochemistry we have to notice the higher propensity of *N*-allylbenzamide to give *E* rather than *Z* products in respect to the corresponding acetamide. This has probably to do with the easier enolization of the former group, but it was not investigated further.

In conclusion, regioselective additions of butadiene to allylamides of organic acids, leading to linear compounds, can be achieved by using rhodium(I) complexes, able to chelate the substrate through both oxygen and the double bond. By contrast the tendency of rhodium(III) to give branched products with non-chelating olefins is reinforced by chelation. With *N*-alkylbutenamides both rhodium(I) and rhodium(III) give linear products because of the formation of a more stable five-membered ring by chelation through oxygen. The coordination type that can be obtained with rhodium(I) and rhodium(III) and chelating ligands thus determines the regioselectivity of these reactions.

Experimental

ACS-grade reagents were used without further purification. Absolute EtOH was dried over 3 Å molecular sieves; butadiene was distilled and dried over 3 Å molecular sieves. $Pd(PPh_3)_4$,[18] [μ-dichloro(tetraethylene)dirhodium(I)],[19] $[(\eta^3\text{-}C_4H_7)Rh_2Cl_4(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_4H_7)]$,[1,13] $[(\eta^4\text{-}C_4H_6)Rh]^+$ Ph_4B^-,[20] $HRh(PPh_3)_4$,[21] *N*-but-2-enylamine,[22] *N*-but-3-enylamine,[23] ethyl but-3-enoate[24] and amides[24,25] were prepared by literature methods; tetracarbonyldi-μ-chlorodirhodium(I) and the other organic substrates were commercially available research-grade chemicals (Aldrich, Fluka and Janssen).

M.p.s were measured on a Büchi 530 apparatus and are not corrected. ^1H NMR spectra were recorded at 100, 200 or 400 MHz, and ^{13}C spectra at 25 MHz, with tetramethylsilane as internal standard (*J* values in Hz) on Bruker AC100, CXP200 or AMX400 spectrometers. Mass spectra were recorded at an ionizing voltage of 70 eV on a Finnigan/MAT SSQ 710 spectrometer. FTIR spectra were recorded using a Nicolet 5PC spectrometer. Elemental analyses were carried out with a Carlo Erba EA 1108 instrument. X-Ray fluorescence measurements were carried with a Philips PW 1400 apparatus to determine the

Rh/Cl ratio. Gas chromatographic analyses were performed on a Dani 3800HR GC instrument, equipped with a methylsilicone (OV 101) capillary column, and gas chromatographic peaks were recorded by a Millipore Waters Integrator. Quantitative GLC determinations of the products, if not otherwise specified, were carried out by using the internal-standard method. HPLC was carried out with a Perkin-Elmer Series 2 LC instrument, equipped with a UV LC75 detector. The samples were analysed and/or separated using a Spherisorb 10 ODS (25 cm × 10 mm) reversed-phase column with MeOH–water as eluent in the appropriate ratio at 5 cm^3 min^{-1} flow rate. Merck silica gel 60F sheets were used for analytical TLC, and silica gel 60F254 (Merck) was used for preparative TLC (PLC). Preparative column chromatography (PCC) was performed on SiO_2 (70–230 mesh) with elution gradients of EtOAc–hexane.

Rhodium(I) *Monomeric Carbonyl Complexes* (Table 2).—The procedure is illustrated by the following preparation.

[(N-*Allylbenzamide*)(*carbonyl*)(*chloro*)*rhodium*(I)] **Rh1a**. To a stirred solution of tetracarbonyldi-μ-chlorodirhodium(I) (40 mg, 0.2 mmol) in chloroform (3 cm^3), under nitrogen, was added a solution of allylbenzamide (80 mg, 0.5 mmol) in chloroform (2 cm^3) at 25 °C. After being stirred at 25 °C overnight, the mixture was evaporated under reduced pressure at 25 °C. The yellow solid was repeatedly washed with Et_2O to yield complex **Rh1a** (59 mg, 92%), m.p. (decomp.) 164–165 °C (Found: C, 40.3; H, 3.4; N, 4.3. $C_{11}H_{11}ClNO_2Rh$ requires C, 40.33; H, 3.38; N, 4.28%); ν_{max}(KBr)/cm^{-1} 3237, 3090, 2012, 1602, 1565, 1491, 1426, 1332 and 699; δ_H(400 MHz; CD_3COCD_3; 25 °C) 3.00 (1 H, d, *J* 13.0, =CH*H*), 3.44 (1 H, d, *J* 7.8, =C*H*H), 4.02 (1 H, d, J_{gem} 17.8, NC*H*H), 4.19 (1 H, d, J_{gem} 17.8, NCH*H*), 4.60–4.72 (1 H, m, =CH), 7.40–7.50 (2 H, m, Ph), 7.60–7.65 (1 H, m, Ph), 7.80–7.92 (2 H, m, Ph) and 9.41 (1 H, br s, NH); δ_C(25 MHz; $CDCl_3$) 43.20 (NCH_2), 48.44 (d, J_{CRh} 11.9, CH_2=), 67.05 (d, J_{CRh} 12.7, CH=), 128.45 (2 C, Ph), 129.52 (2 C, Ph), 132.05 (1 quat. C), 133.97 (1 C, Ph) and 179.50 (NCO).

[(N-*Allyl*-N-*methylbenzamide*)(*carbonyl*)(*chloro*)*rhodium*(I)] **Rh1b**. Reaction of $[Rh(CO)_2Cl]_2$ (40 mg, 0.2 mmol) with *N*-allyl-*N*-methylbenzamide (87 mg, 0.5 mmol) in $CHCl_3$ yielded a yellow solid (43 mg, 67%). Recrystallization from hexane gave gold yellow crystals of complex **Rh1b**, m.p. 154–155 °C (decomp.) (Found: C, 43.1; H, 3.9; N, 4.2. $C_{12}H_{13}ClNO_2Rh$ requires C, 43.10; H, 3.90; N, 4.19%); ν_{max}(KBr)/cm^{-1} 3058, 2000, 1590, 1571, 1503, 1478, 1443, 1434, 1411, 1100, 794, 724 and 695; δ_H(400 MHz; $CDCl_3$; 25 °C) 2.89 (1 H, d, *J* 12.7, =CH*H*), 3.23 (3 H, s, NMe), 3.44 (1 H, d, *J* 7.6, =C*H*H), 3.72 (1 H, br d, J_{gem} 16.4, NC*H*H), 4.47–4.57 (2 H, m, =CH + NCH*H*), 7.38–7.42 (2 H, m, Ph) and 7.47–7.51 (3 H, m, Ph); δ_H(400 MHz; $CDCl_3$; −55 °C) 2.95 (1 H, d, *J* 12.7, =CH*H*), 3.31 (3 H, s, NMe), 3.50 (1 H, d, *J* 7.2, =C*H*H), 3.80 (1 H, br d, J_{gem} 17.4, NC*H*H), 4.53 (1 H, d, J_{gem} 17.4, NCH*H*), 4.56–4.62 (1 H, m, =CH), 7.40–7.43 (2 H, m, Ph) and 7.48–7.54 (3 H, m, Ph); δ_C(25 MHz; $CDCl_3$) 42.56 (NMe), 47.40 (d, J_{CRh} 11.8, $=CH_2$), 52.64 (NCH_2), 64.45 (d, J_{CRh} 13.3, =CH), 128.77 (2 C, Ph), 128.93 (2 C, Ph), 131.93 (quat. C), 132.35 (1 C, Ph) and 175.10 (NCO).

[(*Carbonyl*)(*chloro*)(N-*propylbut*-3-*enamide*)*rhodium*(I)] **Rh2a**. Reaction of $[Rh(CO)_2Cl]_2$ (40 mg, 0.2 mmol) with *N*-propylbut-3-enamide (63 mg, 0.5 mmol) in $CHCl_3$ yielded complex **Rh2a** as a red-orange oil (55 mg, 90%) (Found: C, 28.7; H, 4.5; N, 4.7. $C_8H_{13}ClNO_2Rh$ requires C, 28.63; H, 4.43; N, 4.77%); ν_{max}(KBr)/cm^{-1} 3265, 3107, 2965, 2940, 2875, 2013, 1608, 1569 and 1367; δ_H(400 MHz; $CDCl_3$; 25 °C) 0.88 (3 H, t, *J* 7.4, Me), 1.54 (2 H, m, CH_2Me), 3.17 [3 H, m, NCH_2 + C(O)C*H*H], 3.36 [2 H, br d, =C*H*H + C(O)CH*H*], 3.65 (1 H, br d, *J* 6.7, =CH*H*), 4.36 (1 H, m, =CH) and 8.17 (1 H, br s, NH); δ_H(400 MHz; $CDCl_3$; −57 °C) 0.83 (3 H, t, *J* 7.4, Me), 1.51 (2 H, m, CH_2Me), 3.09 [1 H, m, C(O)C*H*H], 3.22 (2 H, m, NCH_2), 3.38 (1 H, d, *J* 12.9, C=CH*H*), 3.51 [1 H, br d, J_{gem} 14.4, C(O)CH*H*], 3.68 (1 H, br d, *J* 6.7, C=C*H*H), 4.39 (1 H, m, =CH) and 8.44 (1 H, br s, NH); δ_C(25 MHz; $CDCl_3$) 11.62 (Me), 22.33 (CH_2Me), 40.71 (CH_2), 42.85 (CH_2), 56.33 (d, J_{CRh} 15.4, CH_2), 68.73 (1 C, d, J_{CRh} 3.4, =CH) and 178.97 (NCO).

[(*Carbonyl*)(*chloro*)(N-*propylpent*-4-*enamide*)*rhodium*(I)] **Rh2b**. Reaction of $[Rh(CO)_2Cl]_2$ (40 mg, 0.2 mmol) with *N*-propylpent-4-enamide (70 mg, 0.5 mmol) in $CHCl_3$ yielded compound **Rh2b** as a yellow solid (43 mg, 72%), m.p. (decomp.) 134–135 °C (Found: C, 35.1; H, 4.8; N, 4.5. $C_9H_{15}ClNO_2Rh$ requires C, 35.13; H, 4.88; N, 4.48%); ν_{max}(KBr)/cm^{-1} 3285, 3140, 2950, 2930, 1997, 1600, 1594 and 1422; δ_H(400 MHz; $CDCl_3$; 25 °C) 0.87 (3 H, t, *J* 7.4, Me), 1.53 (2 H, m, CH_2Me), 2.16–2.86 [4 H, m, C(O)CH_2CH_2], 3.15 (2 H, dt, *J* 6.7 and 6.5, NCH_2), 3.32 (1 H, d, *J* 13.3, =CH*H*), 3.51 (1 H, d, *J* 7.8, =C*H*H), 4.55–4.70 (1 H, m, =CH) and 7.48 (1 H, br s, NH); δ_H(400 MHz; $CDCl_3$; −45 °C) 0.83 (3 H, t, *J* 7.4, Me), 1.51 (2 H, m, CH_2Me), 2.26 (1 H, br s, C*H*HCH_2), 2.55 (2 H, m, CH_2CH_2), 2.81 (1 H, br s, CH*H*CH_2), 3.10 (2 H, m, NCH_2), 3.37 (1 H, d, *J* 13.3, =CH*H*), 3.51 (1 H, d, *J* 7.8, =C*H*H), 4.70 (1 H, m, =CH) and 7.89 (1 H, br s, NH); δ_C(25 MHz; $CDCl_3$) 11.74 (Me), 22.28 (CH_2Me), 26.55 (CH_2), 29.81 (CH_2), 42.75 (NCH_2), 51.96 (d, J_{CRh} 12.26, $=CH_2$), 73.12 (d, J_{CRh} 12.55, $=CH_2$) and 175.61 (NCO).

X-Ray Structure Analysis of Compound **Rh1b**.—Intensity data were measured using an Enraf–Nonius CAD4 (Mo-Kα) diffractometer with a prismatic specimen of dimensions ~0.2 × 0.3 × 0.6 mm. Cell parameters and an orientation matrix were obtained from a least-squares refinement using the setting angles of 23 carefully centred reflections. The intensities of two check reflections measured after every 300 reflections showed only statistical variations. A total of 3155 reflections (h = 14/13, k = 0/11, l = 0/17) were measured in the 0–27° θ-range, and 2199 of them with $I \geqslant 2\sigma(I)$ were those independently observed (R_{int} 0.021). The XFPS program [26] was used to solve the structure. An absorption correction was applied using the Walker and Stuart method [27] with a program written by Gluzinski.[28] All the heavy atoms were refined anisotropically while the hydrogens, found in a ΔF map, were subjected to isotropic refinement. Final agreement factors with 206 parameters refining were R = 0.034 and R_w = 0.036 [w = $1.0/(\sigma^2F + 0.2574F^2)$]. Scattering factors were those of SHELX76.[29] All the calculations were performed using the CRYSRULER package [30] on a DELL 486 personal computer.

Crystal data. $C_{12}H_{13}ClNO_2Rh$, M = 341.6, monoclinic, a = 11.143(2), b = 8.817(2), c = 13.718(2) Å, β = 102.29(3)°, V = 1316.9 $Å^3$, Z = 4, D_c = 1.72 g cm^{-3}, μ(Mo-Kα) = 14.70 cm^{-1}, space group $P2_1/n$ (#14), λ = 0.710 69 Å. Table 3 reports bond distances and angles. Lists of atomic coordinates and thermal parameters have been deposited with the CCDC.*

Rhodium(I) *Dimeric Complexes.*—The procedure is illustrated by the following preparation.

Bis(N-*Allylbenzamide*)*bis*(μ-*chloro*)*dirhodium*(I) **Rh3**. *N*-Allylbenzamide (40 mg, 0.25 mmol) was added at 25 °C, in CH_2Cl_2 (2 cm^3), to a stirred solution of complex μ-dichloro(tetraethylene)dirhodium(I) (77 mg, 0.2 mmol) in CH_2Cl_2 (2 cm^3). After 1 h filtration yielded a light brown solid (115 mg, 96%), m.p. (decomp.) 154–155 °C (Found: C, 40.0; H, 3.6; N, 4.6. $C_{20}H_{22}Cl_2N_2O_2Rh_2$ requires C, 40.08; H, 3.67; N, 4.67%); X-ray fluorescence: Rh:Cl = 1:1; ν_{max}(KBr)/cm^{-1}

* For full details of the Cambridge Crystallographic Data Centre deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, issue 1.

Table 3 Bond distances (Å) and angles (°) in complex **Rh1b**

Rh(1)–Cl(1)	2.347(1)	C(2)–C(3)	1.383(5)
Rh(1)–O(2)	2.066(3)	C(3)–C(4)	1.493(5)
Rh(1)–C(1)	1.781(5)	C(5)–C(7)	1.502(6)
Rh(1)–C(2)	2.129(4)	C(7)–C(8)	1.379(6)
Rh(1)–C(3)	2.120(4)	C(7)–C(12)	1.363(6)
O(1)–C(1)	1.143(7)	C(8)–C(9)	1.397(8)
O(2)–C(5)	1.263(5)	C(9)–C(10)	1.357(8)
N(1)–C(4)	1.460(5)	C(10)–C(11)	1.361(9)
N(1)–C(5)	1.316(5)	C(11)–C(12)	1.394(9)
N(1)–C(6)	1.463(5)		
C(2)–Rh(1)–C(3)	38.0(1)	Rh(1)–C(3)–C(2)	71.4(2)
C(1)–Rh(1)–C(3)	96.4(1)	C(2)–C(3)–C(4)	124.0(3)
C(1)–Rh(1)–C(2)	90.8(1)	Rh(1)–C(3)–C(4)	110.1(2)
O(2)–Rh(1)–C(3)	87.9(1)	N(1)–C(4)–C(3)	115.4(3)
O(2)–Rh(1)–C(2)	91.9(1)	O(2)–C(5)–N(1)	122.1(3)
O(2)–Rh(1)–C(1)	175.6(1)	N(1)–C(5)–C(7)	121.5(3)
Cl(1)–Rh(1)–C(3)	159.9(1)	O(2)–C(5)–C(7)	116.4(3)
Cl(1)–Rh(1)–C(2)	161.9(1)	C(5)–C(7)–C(12)	120.9(3)
Cl(1)–Rh(1)–C(1)	88.6(1)	C(5)–C(7)–C(8)	117.9(3)
Cl(1)–Rh(1)–O(2)	87.8(1)	C(8)–C(7)–C(12)	121.1(4)
Rh(1)–O(2)–C(5)	129.8(2)	C(7)–C(8)–C(9)	118.4(4)
C(5)–N(1)–C(6)	123.8(3)	C(8)–C(9)–C(10)	120.6(4)
C(4)–N(1)–C(6)	116.0(2)	C(9)–C(10)–C(11)	120.3(5)
C(4)–N(1)–C(5)	120.2(3)	C(10)–C(11)–C(12)	120.3(5)
Rh(1)–C(1)–O(1)	177.9(4)	C(7)–C(12)–C(11)	119.2(4)
Rh(1)–C(2)–C(3)	70.6(2)		

3279, 3055, 2907, 1602, 1560, 1550, 1489, 1385, 1316, 1027, 713 and 693.

Bis(μ-*chloro*)*bis*(N-*propylbut*-3-*enamide*)*dirhodium*(I) **Rh4**. Reaction of *N*-propylbut-3-enamide (32 mg, 0.25 mmol) at 25 °C in CH_2Cl_2 (2 cm^3) with di-μ-dichloro(tetraethylene)dirhodium(I) (77 mg, 0.2 mmol) in CH_2Cl_2 (2 cm^3) yielded a light brown solid (100 mg, 95%), m.p. (decomp.) 144–145 °C (Found: C, 31.8; H, 4.9; N, 5.3. $C_{14}H_{26}Cl_2N_2O_2Rh_2$ requires C, 31.70; H, 4.89; N, 5.28%); X-ray fluorescence: Rh:Cl = 1:1; ν_{max}(KBr)/cm^{-1} 3270, 3100, 2968, 2935, 1603, 1563, 1411, 1368 and 1148.

Rhodium(III) *Dimeric Complexes*.—The procedure is illustrated by the following preparation.

Preparation of Bis(N-*allylbenzamide*)*bischloro bis*(μ-*chloro*)-*bis*(η^3-1-*methylallyl*)*dirhodium*(III) **Rh5**. To a stirred solution of [(η^3-C_4H_7)$_2$$Rh_2Cl_4$(η^3-$C_4H_6$)] (100 mg, 0.2 mmol) in chloroform (3 cm^3) was added a solution of *N*-allylbenzamide (105 mg, 0.65 mmol) in chloroform (2 cm^3) under nitrogen. After the mixture had been stirred at 25 °C overnight, the solvent was removed under reduced pressure at 25 °C. The brownish orange solid was repeatedly washed with Et_2O to yield complex **Rh5** (125 mg, 80% yield), m.p. (decomp.) 154–155 °C (Found: C, 43.2; H, 4.8; N, 3.6. $C_{28}H_{36}Cl_4N_2O_2Rh_2$ requires C, 43.20; H, 4.78; N, 3.59%); X-ray fluorescence: Rh:Cl = 1:2; ν_{max}(KBr)/cm^{-1} 3321, 3064, 2963, 1640, 1602, 1573, 1544, 1489, 1446 and 700.

Reactions of Complexes **Rh3** *and* **Rh5**.—Complex **Rh3** (50 mg, 0.1 mmol) was added to a mixture of EtOH (2 cm^3), $NaBPh_4$ (162 mg, 0.3 mmol) and butadiene (110 mg, 2.04 mmol) under nitrogen. After being stirred at 95 °C for 14 h the brown mixture was cooled to room temperature, the excess of butadiene was removed, and all the solvent was distilled off under reduced pressure. The residue was extracted with CH_2Cl_2 and analysed by GLC. A mixture of the linear isomers **2** (**2c**, 1*Z*,5*E* and **2d**, 1*E*,5*E*; 1:2 ratio) was found along with unchanged *N*-allylbenzamide (8 mg, 24%) and phenylbutadiene. After hydrogenation the yield of the saturated linear isomers was 28 mg (65%).

Complex **Rh5** (35.5 mg, 0.046 mmol) was added with EtOH (2 cm^3) under nitrogen and the mixture was stirred for 6 h at 95 °C. After cooling, the solvent was distilled under reduced pressure and the brown residue was extracted with CH_2Cl_2 and analysed by GLC. The branched product **1b** (8.5 mg, 25% yield) was present along with dehydrogenation and hydrogenation products of the coordinated amide and other reaction products of the crotyl group.

General Procedure for Catalytic Reactions.—In a glass autoclave (capacity 50 cm^3) equipped with a Rotaflo valve the appropriate rhodium complex (0.02 mmol) was charged under N_2 or Ar, and the substrate (2 mmol) and the solvent [EtOH, EtOH–water or toluene (2 cm^3)] was added with stirring of the mixture. The reaction mixture was cooled at −50 °C and buta-1,3-diene (10 mmol) was condensed under vacuum into the mixture by means of a three-way stopcock. The amount of butadiene introduced was determined by weighing the autoclave at room temperature before and after the diene addition. The mixture was stirred at 95 °C for the time indicated in Table 1. After cooling of the mixture at room temperature the unchanged diene was degassed from the reactor while the reaction mixture was stirred, and the autoclave was weighed again. Generally 60–65% of starting butadiene was recovered. The diene which had not reacted with the substrate gave mainly oligomers of low relative molecular mass. The residue mixture was analysed by GLC or was subjected to preparative column chromatography using, first, hexane as eluent to separate the butadiene oligomers, then an appropriate hexane–ethyl acetate mixture to separate the other polar products.

Reaction of N-*allylbenzamide with butadiene in the presence of bis*(*ethylene*)*rhodium chloride dimer and* HCl. Bis(ethylene)-rhodium chloride dimer (38.9 mg, 0.01 mmol) was added to a 0.1 mol dm^{-3} solution of HCl in EtOH (2 cm^3) at 0 °C, containing *N*-allylbenzamide (322 mg, 2.0 mmol) and butadiene (600 mg, 11 mmol) under nitrogen. The mixture was stirred for 36 h at 95 °C. Analysis by GLC showed 85% conversion of the starting amide, and yields of 71% for compound **1b** and 9% for *N*-(prop-1-enyl)benzamide.

Reaction of N-*allylbenzamide with butadiene in the presence of* $RhCl_3$·$3H_2O$ *and* Na_2CO_3. $RhCl_3$·$3H_2O$ (5.3 mg, 0.02 mmol) was added to a mixture of *N*-allylbenzamide (322 mg, 2.0 mmol), EtOH–water (85:15 v/v; 2 cm^3), Na_2CO_3 (10.6 mg, 0.1 mmol) and butadiene (650 mg, 12 mmol) under nitrogen. The mixture was stirred for 24 h at 95 °C. Analysis by GLC showed 54% conversion of the starting amide and a 50% yield of products **2c**, **2d** and **2'd** (33:56:11 respectively). $KHCO_3$ or NaOH were also effective in place of Na_2CO_3.

An analogous procedure was used in the reaction of *N*-allylbenzamide with butadiene in toluene in the presence of $RhH(PPh_3)_4$ as catalyst.

Hydrogenation Reaction.—The unsaturated C=C bonds of the amidic products were hydrogenated according to the standard procedure at room temperature in EtOH in the presence of Pd/C (10%) at atmospheric pressure of hydrogen.

N-[(E)-2-*Methylenehex*-4-*enyl*]*acetamide* **1a**. Oil; PCC (10% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3270, 3070, 2990, 2920, 2850, 1670, 1540, 1430, 1380, 1290, 980 and 890; δ_H(400 MHz; $CDCl_3$) 1.63 (3 H, d, *J* 4.3, =CMe), 1.97 (3 H, s, MeCO), 2.66 (2 H, d, *J* 4.3, CH_2), 3.77 (2 H, d, *J* 5.9, NCH_2), 4.83 and 4.88 (2 H, 2 m, $=CH_2$), 5.35–5.50 (2 H, m, MeC*H*=C*H*) and 5.82 (1 H, br s, NH); *m*/*z* 153 (M^+, 10%), 138 (10), 124 (10), 111 (20), 110 (40), 98 (65), 96 (100), 94 (70), 84 (20), 79 (95), 56 (30) and 49 (20).

N-[(E)-2-*Methylenehex*-4-*enyl*]*benzamide* **1b**. Oil; PCC (first pure hexane, then 20% EtOAc in hexane), PLC (hexane–EtOAc 90:10); ν_{max}(film)/cm^{-1} 3300, 3020, 2940, 2880, 1730, 1645, 1570, 1530, 1480, 1420, 1290, 970, 890, 725 and 680; δ_H(200 MHz; $CDCl_3$) 1.63 (3 H, d, *J* 4.6, Me), 2.72 (2 H, d, *J* 3.9, CH_2), 3.97

(2 H, d, J 6.0, NCH_2), 4.87 and 4.91 (2 H, 2 s, $=CH_2$), 4.27–5.52 (2 H, m, 2 × =CH), 6.58 (1 H, br s, NH), 7.37–7.43 (3 H, m, Ph) and 7.67 (2 H, d, J_o 6.2, Ph); m/z 215 (M^+, 42%), 200 (18), 178 (9), 160 (69), 122 (18), 110 (23), 105 (100), 94 (35), 79 (48), 77 (68) and 51 (35).

N-*Methyl*-N-[(E)-2-*methylenehex*-4-*enyl*]*benzamide* **1c**. Oil; PCC (30% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3040, 2970, 2920, 1638, 1446, 1398, 1267, 1070, 969, 900, 800, 725 and 700; ^1H NMR spectroscopy showed the presence of two geometric isomers (2:1 ratio) owing to the hindered rotation about the C(O)–NR_2. The signals were broad bands; an increase of the temperature to 50 °C gave one isomer only, also showing broad signals; δ_H(400 MHz; $CDCl_3$; 25 °C) 1.60 (3 H, br s, Me, major), 1.68 (3 H, br s, Me, minor), 2.52 (2 H, br s, CH_2, major), 2.71 (2 H, br s, CH_2, minor), 2.87 (3 H, br s, NMe, major), 3.03 (3 H, br s, NMe, minor), 3.77 (2 H, br s, CH_2, major), 4.12 (2 H, br s, CH_2, minor), 4.95 and 4.99 (2 H, 2 × br s, $=CH_2$), 5.25–5.58 (2 H, m, CH=CH) and 7.39 (5 H, br s, Ph); δ_C(25 MHz; $CDCl_3$) 17.81 (Me), 33.51 (NMe), 37.01 (CH_2), 55.84 (NCH_2), 111.69 (CH_2=), 126.70 (2 C, Ph), 127.49 (=CH), 128.29 (2 C, Ph), 130.00 (1 C, Ph + 1 C, =CH), 136.09 (1 C, quat. C, Ph) and 172.33 (CO); m/z 229 (M^+, 10%), 214 (25), 174 (100), 136 (10), 124 (20), 105 (50) and 77 (25).

N-[(1Z,5E)-*Hepta*-1,5-*dienyl*]*acetamide* **2a**. Oil; PCC (first pure hexane, then 15% EtOAc in hexane), PLC (hexane–EtOAc 70:30); ν_{max}(film)/cm^{-1} 3310, 3020, 2980, 2940, 2860, 1670, 1530, 1440, 1380, 1290, 970 and 690; δ_H(400 MHz; $CDCl_3$) 1.64 (3 H, dd, J 3.6 and 1.2, Me), 2.00–2.08 (7 H, m, MeCO + 2 × CH_2), 4.70 (1 H, dt, J 8.8 and 7.2, NCH=C*H*), 5.40–5.48 (2 H, m, 2 × =CH), 5.67 [1 H, dd, J 10.3 and 8.8, NCH=; treatment with D_2O gave δ_H 5.67 (1 H, d, J 8.8, NCH=)] and 6.99 (1 H, br s, NH); m/z 153 (M^+, 5%), 110 (4), 98 (38), 56 (100) and 55 (81). Hydrogenation gave *N*-heptylacetamide.

N-[(1E,5E)-*Hepta*-1,5-*dienyl*]*acetamide* **2b**. Deliquescent solid; PCC (first pure hexane, then 15% EtOAc in hexane), PLC (hexane–EtOAc 80:20); ν_{max}(film)/cm^{-1} 3290, 3210, 3080, 2990, 2940, 2850, 1750, 1670, 1550, 1380, 1310 and 970; δ_H(400 MHz; $CDCl_3$) 1.60 (3 H, dd, J 3.5 and 1.3, Me), 1.95–2.06 (7 H, m, MeCO + 2 × CH_2), 5.11 (1 H, dt, J 14.2 and 7.0, =CH), 5.33–5.41 (2 H, m, 2 × =CH), 6.69 (1 H, dd, J 14.2 and 10.4, =CHN) and 7.73 (1 H, br s, NH); m/z 153 (M^+, 8%), 110 (5), 98 (35), 56 (100) and 55 (80). Hydrogenation gave *N*-heptylacetamide.

By-product of production of compounds **2a** and **2b** according to eqn. (3) (from the addition of two butadiene molecules and one of ethanol to the substrate, 7%); m/z 253 (M^+, absent), 207 (7%), 152 (23), 151 (14), 110 (100), 93 (18) and 55 (13).

N-[(1Z,5E)-*Hepta*-1,5-*dienyl*]*benzamide* **2c**. Light yellow oil; PCC (15% EtOAc in hexane), PLC (hexane–EtOAc 80:20); ν_{max}(film)/cm^{-1} 3320, 3070, 3020, 2940, 2880, 1730, 1650, 1520, 1420, 1290, 980, 720 and 680; δ_H(200 MHz; $CDCl_3$) 1.61 (3 H, dd, J 3.5 and 1.2, Me), 2.00–2.17 (4 H, m, 2 × CH_2), 4.86 (1 H, dt, J 8.8 and 7.2, =CH), 5.40–5.54 (2 H, m, CH=CH), 6.90 (1 H, dd, J 8.8 and 9.7, =CH), 7.37–7.47 (3 H, m, Ph), 7.77 (2 H, dd, J 8.6 and 1.5, Ph) and 8.14 (1 H, br d, J 9.7, NH); δ_C(25 MHz; $CDCl_3$) 19.19 (Me), 31.28 (CH_2), 34.22 (CH_2), 115.28 (=CH), 124.39 (=CH), 126.75 (=CH), 128.42 (2 C, Ph), 129.39 (1 C, Ph), 131.69 (=CH), 132.93 (2 C, Ph), 135.11 (quat. C) and 165.86 (CO); m/z 215 (M^+, 7%), 160 (41), 105 (100), 77 (28) and 51 (5). Hydrogenation gave *N*-heptylbenzamide.

N-[(1E,5E)-*Hepta*-1,5-*dienyl*]*benzamide* **2d**. Deliquescent solid; PCC (15% EtOAc in hexane), PLC (hexane–EtOAc 80:20); ν_{max}(film)/cm^{-1} 3310, 3080, 3040, 2980, 2940, 2860, 1650, 1540, 1500, 1330, 970 and 710; δ_H(200 MHz; $CDCl_3$) 1.62 (3 H, dd, J 3.4 and 1.2, Me), 2.01–2.28 (4 H, m, 2 × CH_2), 5.24 (1 H, dt, J 14.4 and 6.6, =CH), 5.28–5.48 (2 H, m, CH=CH), 6.96 (1 H, dd, J 14.4 and 10.3, =CHN), 7.37–7.49 (4 H, m, Ph + NH) and 7.79 (2 H, dd, J 7.8 and 1.8, Ph *o*-H); m/z 215 (M^+, 5%), 160 (46), 105 (100), 77 (46) and 51 (11), Hydrogenation gave *N*-heptylbenzamide.

N-[(2E,5E)-*Hepta*-2,5-*dienyl*]*benzamide* **2'd**. Light yellow oil; PCC (15% EtOAc in hexane), PLC (hexane–EtOAc 80:20); ν_{max}(film)/cm^{-1} 3320, 3080, 3040, 2980, 2940, 2860, 1650, 1420, 1290, 980 and 720; δ_H(200 MHz; $CDCl_3$) 1.62 (3 H, dd, J 3.5 and 1.3, Me), 2.64–2.74 (2 H, m, CH_2), 4.01 (2 H, dd, J 4.8 and 4.6, CH_2), 5.35–5.45 (2 H, m, CH=CH), 5.50 (1 H, dt, J 15.6 and 5.8, =CH), 5.67 (1 H, dt, J 15.6 and 6.0, =CH), 6.25 (1 H, br s, NH), 7.37–7.48 (3 H, m, Ph) and 7.70–7.80 (2 H, m, Ph); m/z 215 (M^+, 6%), 160 (38), 105 (100), 77 (43) and 51 (8). Hydrogenation gave *N*-heptylbenzamide.

By-products of the preparation of compounds **2c**, **2d** and **2'd** according to eqn. (3) (from the addition of two butadiene molecules and one of ethyl alcohol to the substrate, 6%); m/z 269 (5%), 214 (43), 105 (100), 77 (42), 55 (6) and 51 (8); and m/z 269 (5%), 214 (38), 105 (100), 77 (43), 55 (9) and 51 (69). The molecular peak (316, M + 1^+) showed up in the DCI mass spectrum.

N-*Heptyl*-N-*methylbenzamide* (*hydrogenated* **2e**, **2f** *mixture*). Oil. Separation by PCC (20% EtOAc in hexane) of the reaction mixture obtained from the reaction of *N*-allyl-*N*-methylbenzamide with butadiene in the presence of Rh^1 catalyst gave a mixture of two linear isomers; m/z 229 (M^+, 3%), 228 (6), 174 (30), 105 (100), 77 (58) and 51 (21); and m/z 229 (M^+, 3%), 228 (2), 174 (42), 105 (100), 77 (58) and 51 (21). After hydrogenation only one compound was obtained, identical with the one prepared from benzoyl chloride and *N*-heptyl-*N*-methylamine.

N-[(1E,1E)-3-*Methylhepta*-1,5-*dienyl*]*benzamide* **2g**. Of the two isomers present in the reaction mixture only one was separated pure, as a light yellow oil. PCC (20% EtOAc in hexane), PLC (hexane–EtOAc 90:10); ν_{max}(film)/cm^{-1} 3300, 3090, 2990, 2920, 2890, 1720, 1650, 1530, 1490, 1420, 960 and 720; δ_H(200 MHz; $CDCl_3$) 1.03 (3 H, d, J 6.5, Me), 1.65 (3 H, d, J 5.1, Me), 1.90–2.15 (3 H, m, CH_2 + CH), 5.24 (1 H, dt, J 13.2 and 7.2, =CH), 5.31–5.51 (2 H, m, 2 × =CH), 6.94 (1 H, dd, J 13.2 and 10.6, =CHN), 7.40–7.53 (3 H, m, Ph) and 7.75–7.84 (3 H, m, 2 × HPh + NH); m/z 229 (M^+, 25%), 228 (10), 200 (7), 175 (48), 174 (12), 105 (100), 77 (40) and 55 (6).

Second eluted isomer (not isolated): m/z 229 (M^+, 30%), 228 (16), 200 (7), 175 (58), 174 (15), 105 (100), 77 (48) and 55 (8).

Hydrogenation of the mixture of the two isomers gave only one product, identical with the one obtained from compound **5** after hydrogenation [*N*-(3-methylheptyl)benzamide]; m/z 233 (M^+, 8%), 176 (13), 148 (21), 135 (42), 134 (46), 105 (100), 77 (33), 55 (5) and 51 (5).

N-[(E)-2-*Methylenehex*-4-*enyl*]*toluene*-p-*sulfonamide* **3a**. Light yellow oil; PCC (10% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3340, 3095, 3010, 2995, 2950, 1608, 1467, 1353, 1175, 1016, 985, 938, 935, 825, 780, 723, 705 and 673; δ_H(400 MHz; $CDCl_3$) 1.59 (3 H, d, J 4.7, =CMe), 2.40 (3 H, s, Ar*Me*), 2.61 (2 H, d, J 4.9, CH_2), 3.46 (2 H, d, J 6.3, NCH_2), 4.65 (1 H, br t, NH), 4.81 and 4.89 (2 H, s, $=CH_2$), 5.20–5.45 (2 H, m, 2 × =CH), 7.27 (2 H, d, J 8.3, Ph) and 7.45 (2 H, d, J 8.3, Ph); δ_C(25 MHz; $CDCl_3$) 17.79 (Me), 21.46 (Me), 37.06 (CH_2), 112.64 ($=CH_2$), 127.16 (2 C, Ph), 127.57 and 127.63 (2 C, =CH), 129.64 (2 C, Ph), 137.08 (quat. C), and 143.24 and 143.66 (2 C, quat. C, Ph); m/z 265 (M^+, 8%), 250 (3), 184 (14), 155 (38), 139 (10), 110 (90), 108 (38), 95 (72), 94 (52), 91 (100), 79 (74), 65 (61) and 55 (27).

N-*Methyl*-N-[(E)-2-*methylenehex*-4-*enyl*]*toluene*-p-*sulfonamide* **3b**. Oil; PCC (20% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3090, 3020, 2990, 2940, 2890, 1605, 1460, 1350, 1175, 1100, 1015, 980, 935, 825, 805, 780, 720, 700 and 670; δ_H(400 MHz; $CDCl_3$) 1.66 (3 H, dd, J 6.1 and 1.3, Me), 2.41 (3 H, s, Me), 2.57 (3 H, s, NMe), 2.72 (2 H, d, J 8.4, CH_2), 3.47 (3 H, s, NCH_2), 4.89 and 4.93 (2 H, 2 s, $=CH_2$), 5.40 (1 H, dtq, J 15.1, 8.4 and 1.3, =CH), 5.50 (1 H, dq, J 15.1 and 6.1, =C*H*Me), 7.31 (2 H, d,

J 8.3, Ph *p*-H) and 7.65 (2 H, d, *J* 8.3, Ph *o*-H); *m/z* 279 (M^+, 10%), 198 (10), 186 (10), 155 (40), 124 (80), 123 (20), 108 (70), 94 (60), 91 (100), 79 (50), 65 (25) and 55 (10).

N-[(2E,6E)-*Octa*-2,6-*dienyl*]*benzamide* **4**. Light yellow oil; HPLC (reversed-phase 35% water in methanol); ν_{max}(film)/cm^{-1} 3320, 3090, 3030, 2990, 2920, 1645, 1605, 1590, 1540, 1495, 1320, 975, 720 and 700; δ_H(400 MHz; $CDCl_3$) 1.62 (3 H, d, *J* 4.4, Me), 2.00–2.10 (4 H, m, CH_2CH_2), 4.00 (2 H, dt, *J* 5.6 and 5.6, NCH_2), 5.30–5.41 (2 H, m, 2 × CH=), 5.50–5.58 (1 H, m, CH=), 5.63–5.72 (1 H, m, CH=), 6.18 (1 H, br s, NH), 7.38–7.42 (2 H, m, Ph), 7.45–7.47 (1 H, m, Ph) and 7.74–7.77 (2 H, m, Ph); by decoupling of the CH_2CH_2 system: 5.53 (1 H, dt, *J* 15.3 and 6.1, NCH_2CH=), 5.67 (1 H, d, *J* 15.3, NCH_2CH=C*H*); by decoupling of the NCH_2 system: 5.53 (1 H, d, *J* 15.3, NCH_2CH=) and 5.67 (1 H, dt, *J* 15.3 and 6.2, NCH_2CH=C*H*); *m/z* 229 (M^+, 5%), 174 (10), 134 (10), 122 (12), 108 (15), 105 (100), 93 (10) and 77 (30). Hydrogenation gave *N*-octylbenzamide.

N-[(E)-3-*Methylenehept*-5-*enyl*]*benzamide* **5**. Light yellow oil; HPLC (reversed-phase 35% water in methanol); ν_{max}(film)/cm^{-1} 3320, 3080, 2995, 2945, 1650, 1610, 1590, 1550, 1495, 1450, 1325, 1085, 980, 905, 810, 725 and 700; δ_H(400 MHz; $CDCl_3$) 1.65 (3 H, dd, *J* 6.0 and 1.1, Me), 2.32 (2 H, t, *J* 6.7, NCH_2CH_2), 2.71 (2 H, d, *J* 6.4, CH_2), 3.54 (2 H, dt, *J* 6.7 and 5.5, NCH_2), 4.83 and 4.87 (2 H, 2 m, $=CH_2$), 5.35–5.55 (2 H, m, HC=CH), 6.28 (1 H, br s, NH), 7.30–7.46 (3 H, m, Ph) and 7.71–7.73 (2 H, m, Ph); *m/z* 229 (M^+, 5%), 148 (10), 134 (15), 122 (18), 108 (80), 105 (100), 93 (35), 77 (55) and 51 (10).

(2E,6E)-N-*Propylocta*-2,6-*dienamide* **6a**. Deliquescent solid; PCC (first pure hexane, then 40% EtOAc in hexane), PLC (hexane–EtOAc 70:30); ν_{max}(film)/cm^{-1} 3290, 3085, 2980, 2940, 1665, 1630, 1555, 1450, 1360 and 970; δ_H(200 MHz; $CDCl_3$) 0.86 (3 H, t, *J* 7.2, Me), 1.35–1.55 (2 H, m, MeCH_2), 1.58 (3 H, dd, *J* 4.1 and 1.2, MeC=), 2.04–2.23 (4 H, m, CH_2CH_2), 3.20 (2 H, dt, *J* 13.3 and 6.7, NCH_2), 5.32–5.44 (2 H, m, 2 × =CH), 5.79 (1 H, d, *J* 15.3, =CH), 6.34 (1 H, br s, NH) and 6.75 (1 H, dt, *J* 15.3 and 6.0, =CH); δ_C(25 MHz; $CDCl_3$) 11.39 (Me), 17.81 (Me), 22.84 (CH_2), 31.30 (CH_2), 32.05 (CH_2), 41.23 (NCH_2), 124.13 (=CH), 125.76 (=CH), 129.85 (=CH), 143.46 (=CH) and 166.24 (CO); *m/z* 181 (M^+, 3%), 166 (5), 152 (9), 138 (3), 127 (40), 121 (27), 95 (18), 84 (16), 68 (19) and 55 (100). Hydrogenation gave *N*-propyloctanamide.

(3E,6E)-N-*Propylocta*-3,6-*dienamide* **6'a**. Light yellow oil; PCC (first pure hexane, then 20% EtOAc in hexane), PLC (hexane–EtOAc 90:10); ν_{max}(film)/cm^{-1} 3290, 3085, 2970, 2940, 1650, 1550, 1440, 1360 and 965; δ_H(200 MHz; $CDCl_3$) 0.85 (3 H, t, *J* 7.0, Me), 1.31–1.52 (2 H, m, CH_2), 1.58 (3 H, dd, *J* 4.7 and 1.3, CH_2CO), 3.14 (2 H, dt, *J* 13.1 and 6.8, NCH_2), 5.33–5.58 (4 H, 2 m, 4 × CH=) and 5.89 (1 H, br s, NH); δ_C(25 MHz; $CDCl_3$) 11.25 (Me), 17.81 (Me), 22.75 (CH_2), 35.49 (CH_2), 40.45 (CH_2), 41.23 (NCH_2), 123.40 (=CH), 126.20 (=CH), 128.71 (=CH), 134.35 (=CH) and 171.09 (CO); *m/z* 181 (M^+, 27%), 166 (9), 152 (9), 138 (10), 126 (12), 97 (50), 95 (53), 86 (52), 81 (100), 79 (48), 67 (59) and 55 (46). Hydrogenation gave *N*-propyloctanamide.

(2E,6E)-N,N-*Diethylocta*-2,6-*dienamide* **6b**. Light yellow oil; PCC (10% EtOAc in hexane); ν_{max}(film)/cm^{-1} 2985, 2935, 2890, 1665, 1490, 1370, 1230 and 975; δ_H(400 MHz; $CDCl_3$) 1.12 (3 H, t, *J* 7.1, Me), 1.16 (3 H, t, *J* 7.1, Me), 1.62 (3 H, dd, *J* 4.7 and 0.7, MeC=), 2.13 (2 H, dt, *J* 7.1 and 6.6, CH_2CH=CHCO), 2.25 (2 H, dt, *J* 7.1 and 6.2, MeCH=CHCH_2), 3.34 (2 H, q, *J* 7.1, NCH_2), 3.40 (2 H, q, *J* 7.1, NCH_2), 5.39–5.44 (2 H, m, MeC*H*=C*H*), 6.17 (1 H, dt, *J* 15.0 and 1.9, =CHCO) and 6.8 (1 H, dt, *J* 15.0 and 6.6, C*H*=CHCO); *m/z* 195 (M^+, 50%), 180 (15), 166 (10), 140 (18), 100 (100), 72 (70) and 58 (20). Hydrogenation gave *N*,*N*-diethyloctanamide.

(3E,6E)-N,N-*Diethylocta*-3,6-*dienamide* **6'b**. Light yellow oil; PCC (10% EtOAc in hexane); ν_{max}(film)/cm^{-1} 2990, 2930, 2895, 1645, 1490, 1440, 1390, 1380, 1230, 1145 and 980; δ_H(400 MHz; $CDCl_3$) 1.09 (3 H, t, *J* 7.0, Me), 1.14 (3 H, t, *J* 7.1, Me), 1.63 (3 H, dd, *J* 3.8 and 1.0, MeC=), 2.65–2.75 (2 H, m, CH_2), 3.05 (2 H, dd, *J* 6.2 and 1.0, CH_2CO), 3.28 (2 H, q, *J* 7.0, NCH_2), 3.34 (2 H, q, *J* 7.1, NCH_2), 5.40–5.43 (2 H, m, MeC*H*=C*H*), 5.49 (1 H, dtt, *J* 15.2, 6.1 and 1.2, C=C*H*CH_2CO) and 5.58 (1 H, dtt, *J* 15.2, 5.9 and 1.0, C*H*=$CHCH_2CO$); *m/z* 195 (M^+, 60%), 180 (15), 152 (10), 140 (20), 100 (100) and 72 (55). Hydrogenation gave *N*,*N*-diethyloctanamide.

(2E,6E)-4-[(2'E)-*But*-2'-*enyl*]-N-*propylocta*-2,6-*dienamide* **7a**. Light yellow oil; PCC (first pure hexane, then 40% EtOAc in hexane), PLC (hexane–EtOAc 70:30); ν_{max}(film)/cm^{-1} 3285, 3080, 2980, 2940, 1670, 1635, 1555, 1450, 1365 and 970; δ_H(200 MHz; $CDCl_3$) 0.92 (3 H, t, *J* 4.5, Me), 1.52–1.58 (2 H, m, CH_2), 1.61 (6 H, d, *J* 4.5, 2 × Me), 2.02–2.11 (4 H, 2 m, 2 × CH_2), 2.12–2.13 (1 H, m, CH), 3.28 (2 H, dt, *J* 14.0 and 6.6, NCH_2), 5.34–5.44 (4 H, m, 4 × CH=), 5.62 (1 H, br s, NH), 5.68 (1 H, d, *J* 15.1, CH=) and 6.67 (1 H, dd, *J* 15.1 and 6.2, CH=); *m/z* 235 (M^+, 4%), 234 (4), 181 (22), 180 (24), 140 (8), 127 (10), 112 (11), 95 (81), 86 (32), 81 (36), 67 (23), 60 (15) and 55 (100).

(2E,6E)-4-[(2'E)-*But*-2'-*enyl*]-N,N-*diethylocta*-2,6-*dienamide* **7b**. Yellow oil; PCC (10% EtOAc in hexane); ν_{max}(film)/cm^{-1} 2990, 2940, 1670, 1485, 1380, 1230 and 970; δ_H(400 MHz; $CDCl_3$) 1.13 and 1.18 (6 H, 2 t, *J* 7.1 and 7.1, 2 × Me), 1.62 and 1.63 (6 H, 2 dd, *J* 4.7, 4.7, 0.7 and 0.7, 2 × *Me*CH=), 1.99–2.18 [4 H, m, $CH(CH_2)_2$], 2.18–2.22 (1 H, m, CH), 3.34 (2 H, q, *J* 7.1, NCH_2), 3.41 (2 H, q, *J* 7.1, NCH_2), 5.28–5.47 (1 H, m, =CH), 6.11 [1 H, d, *J* 15.1, C(O)CH=] and 6.72 [1 H, dd, *J* 15.1 and 8.2, C(O)CH=CH]; *m/z* 249 (M^+, 32%), 234 (12), 194 (47), 140 (17), 100 (17) and 72 (46).

Ethyl (2E,6E)-*octa*-2,6-*dienoate* **8**. Oil; PTLC (5% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3090, 2995, 2950, 1710, 1665, 1630, 1375, 1260, 1185 and 980; δ_H(400 MHz; $CDCl_3$) 1.24 (3 H, t, *J* 7.1, Me), 1.61 (3 H, dd, *J* 6.6 and 1.3, MeC=), 2.08–2.25 (4 H, m, CH_2CH_2), 4.12 (2 H, q, *J* 7.1, OCH_2), 5.39–5.41 (2 H, m, MeC*H*=C*H*), 5.79 (1 H, dt, *J* 15.6 and 1.6, =CHCO) and 6.93 (1 H, dt, *J* 15.6 and 6.8, C*H*=CHCO); *m/z* (CI–MS, CH_4) 169 (M^+ + 1, 100%), 141 (10), 123 (30), 114 (15), 95 (50), 55 (10) and 41 (30). Hydrogenation gave ethyl octanoate.

Ethyl (3E,6E)-*octa*-3,6-*dienoate* **8'**. Oil; PTLC (5% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3095, 2995, 2950, 1740, 1665, 1375, 1345, 1260, 1185 and 980; δ_H(400 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.1, Me), 1.65 (3 H, dd, *J* 7.2 and 1.3, MeC=), 2.67–2.73 (2 H, m, CH_2), 3.05 (2 H, d, *J* 5.7, CH_2CO), 4.11 (2 H, q, *J* 7.1, OCH_2), 5.38–5.40 (2 H, m, MeC*H*=C*H*) and 5.51–5.59 (2 H, m, CH=CH); *m/z* 168 (M^+, 5%), 139 (5), 123 (45), 122 (35), 114 (95), 95 (40), 94 (20), 86 (90), 68 (40) and 55 (100). Hydrogenation gave ethyl octanoate.

Ethyl (5E)-3-*methylenehept*-5-*enoate* **9**. Oil; PLC (5% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3100, 3000, 2950, 1740, 1650, 1370, 1350, 1260, 1180, 980 and 890; δ_H(400 MHz; $CDCl_3$) 1.26 (3 H, t, *J* 7.1, Me), 1.62 (3 H, dd, *J* 6.0 and 1.2, MeC=), 2.76 (2 H, d, *J* 6.5, CH_2), 3.00 (2 H, s, CH_2CO), 4.16 (2 H, q, *J* 7.1, OCH_2), 4.87 and 4.91 (2 H, br s, $=CH_2$) and 5.33–5.39 (2 H, m, MeC*H*=C*H*); *m/z* 169 (M^+ + 1, 40%), 168 (M^+, 15), 141 (10), 127 (12), 123 (50), 95 (100), 81 (15) and 41 (22).

By-products of the preparation of compounds **8**, **8'** and **9** according to eqn. (8) (from the addition of two butadiene molecules to the substrate, 5%); *m/z* 222 (M^+, absent), 193 (5%), 177 (7), 148 (10), 114 (52), 86 (25), 67 (51) and 55 (100); *m/z* 222 (M^+, absent), 177 (5%), 167 (21), 121 (18), 93 (100), 92 (48), 90 (23), 81 (26), 79 (52), 77 (25), 67 (21) and 55 (68).

(3E,7E)-N-*Propylnona*-3,7-*dienamide* **10**. Light yellow oil; PCC (20% EtOAc in hexane); ν_{max}(film)/cm ^{1} 3294, 3082, 2964, 2933, 1646, 1554, 1438 and 966; δ_H(400 MHz; $CDCl_3$) 0.84 (3 H, t, *J* 7.4, Me), 1.40–1.52 (2 H, m, MeCH_2), 1.58 (3 H, d, *J* 4.9, *Me*CH=), 1.95–2.05 (4 H, m, CH_2CH_2), 2.86 (2 H, d, *J* 6.7, CH_2CO), 3.13 (2 H, dt, *J* 7.5 and 6.7, NCH_2), 5.33–5.38 (2 H,

m, MeC*H*=C*H*), 5.41–5.58 (2 H, m, C*H*=C*H*CH_2CO) and 5.89 (1 H, br s, NH); after decoupling of the CH_2CH_2 system: 5.45 (1 H, dt, *J* 15.8 and 6.7, =C*H*CH_2CO) and 5.54 (1 H, d, *J* 15.8, =CH); *m/z* 196 (M^+ + 1, 10%), 195 (M^+, 60), 166 (10), 141 (20), 140 (30), 138 (60), 101 (35), 95 (20), 86 (95), 81 (25), 56 (30) and 55 (100). Hydrogenation gave *N*-propylnonanamide.

Isomer of compound **10** [from the reaction with rhodium(I), 15%]; *m/z* 196 (M^+ + 1, 8%), 195 (M^+, 42), 166 (10), 140 (30), 138 (52), 101 (38), 95 (18), 86 (98), 81 (27), 56 (36), 55 (100) and 54 (27).

Isomer of **10** [from the reaction with rhodium(III), 13%]; *m/z* 196 (M^+ + 1, 10%), 195 (M^+, 100), 137 (10), 110 (31), 109 (52), 101 (38), 95 (79), 93 (53), 86 (40), 81 (41), 67 (37) and 55 (42).

By-product from preparation of compounds **10**, **11** [from the reaction of the substrate with two butadiene molecules in the presence of rhodium(I) (3%) or rhodium(III) (4%)]; *m/z* 249 (M^+, 6%), 220 (7), 195 (16), 194 (97), 109 (100), 107 (26), 93 (42), 86 (36), 67 (32), 60 (57) and 55 (58).

(6E)-4-*Methylene*-N-*propyloct*-6-*enamide* **11**. Oil; PCC (20% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3350, 3080, 2990, 2920, 2895, 1650, 1550, 1445, 1385, 1265, 980, 920 and 895; δ_H(400 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 7.4, Me), 1.48 (2 H, m, MeCH_2), 1.64 (3 H, dd, *J* 5.8 and 1.1, *Me*CH=), 2.30 (4 H, m, CH_2CH_2CO), 2.67 (2 H, d, *J* 6.3, CH_2), 3.18 (2 H, dt, *J* 6.8 and 6.3, NCH_2), 4.72 and 4.76 (2 H, 2 br s, $=CH_2$), 5.35–5.50 (2 H, m, MeC*H*=C*H*) and 5.60 (1 H, br s, NH); *m/z* 195 (M^+, 40%), 180 (12), 152 (10), 140 (20), 137 (12), 110 (35), 109 (55), 101 (55), 95 (100), 93 (45), 86 (45), 81 (40), 79 (30), 77 (20), 73 (15), 67 (40), 60 (30) and 55 (45).

(4E)-2-*Heptylhexa*-1,4-*diene* **12**. Oil; PLC (hexane); δ_H(100 MHz; $CDCl_3$) 0.90 (3 H, t, *J* 5.3, *Me*CH_2), 1.1–1.5 (10 H, m, CH_2), 1.55–1.75 (3 H, m, =CMe), 1.7–2.1 (2 H, m, $=CCH_2$), 2.60–2.75 (2 H, m, $=CCH_2$), 4.73 (2 H, br s, $=CH_2$) and 5.3–5.5 (2 H, m, HC=CH); *m/z* 180 (M^+, 20%), 109 (10), 96 (40), 95 (20), 82 (20), 81 (100), 69 (15), 68 (22), 67 (20) and 55 (15). After hydrogenation of the reaction mixture the other four linear isomers gave tridecane.

By-product from preparation of compound **12** (from the reaction of two butadiene molecules with the substrate, 7%); *m/z* 234 (M^+, 8%), 179 (32), 149 (16), 135 (36), 109 (38), 95 (100), 94 (57), 81 (96), 79 (36), 67 (52) and 55 (50).

(4E)-2-*Undecylhexa*-1,4-*diene* **13**. Oil; PLC (hexane); δ_H(100 MHz; $CDCl_3$) 0.90 (3 H, t, *J* 5.1, *Me*CH_2), 1.2–1.4 (18 H, m, CH_2), 1.60–1.75 (3 H, m, =CMe), 1.95–2.10 (2 H, m, $=CCH_2$), 2.6–2.8 (2 H, m, $=CCH_2$), 4.72 (2 H, br s, $=CH_2$) and 5.35–5.50 (2 H, m, HC=CH); *m/z* 236 (M^+, 20%), 109 (10), 97 (15), 96 (70), 95 (25), 82 (20), 81 (100), 69 (10), 68 (20), 67 (10) and 55 (15). After hydrogenation of the reaction mixture the other four linear isomers gave heptadecane.

Hydrogenated by-product of preparation of compound **13** (from the reaction of two butadiene molecules with the substrate, 3%); *m/z* 296 (M^+, 8%), 281 (15), 183 (27), 182 (56), 140 (67), 85 (91), 71 (97) and 57 (100).

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