

# THE CATALYTIC DECOMPOSITION OF SECONDARY CARBOXAMIDES BY TRANSITION-METAL COMPLEXES

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**Abstract**—High-boiling secondary amides of monocarboxylic acids decompose under the influence of  $\text{RhCl}(\text{PPh}_3)_3$ ,  $\text{HRhCl}_2(\text{PPh}_3)_3$ , and some other organometallic catalysts in homogeneous phases into nitriles and carbinols. The latter are further transformed into aldehydes and hydrocarbons. N-Benzyl- (and N-substituted benzyl-) aromatic amides from nitriles generated both from the aroyl and the benzyl moieties. Amides carrying Cl, Br or I atoms in the aromatic ring are partially or completely dehalogenated during the catalysis. Malonamides are decarbonylated and form acetamides.

Both mono- and di-amides give amido-complexes with the catalysis employed. The complexes derived from  $\text{RhCl}(\text{PPh}_3)_3$  are extremely labile, while those from  $\text{RuCl}_2(\text{PPh}_3)_3$  can be isolated.

In a preliminary communication<sup>1</sup> we reported the  $\text{RhCl}(\text{PPh}_3)_3$ -catalysed transformation of some primary and secondary aromatic carboxamides into nitriles. We have now extended this study, exploring the scope of the reaction and the possible use of other transition-metal complexes as catalysts. Particular attention has been paid to the catalytic transformation of malonamides, as they lose carbon monoxide rather than water or alcohols.

In Table 1 the results obtained with N-benzylbenzamide and several catalysts are summarized.

The results indicate that  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{HRhCl}_2(\text{PPh}_3)_3$  are the most efficient catalysts and lead in this case to a similar mixture of products (80–90% benzonitrile, 35–40% toluene, 1–2% benzaldehyde and traces of benzene) though the reaction conditions and, therefore, probably the mechanisms are different (*vide infra*). The other complexes listed in Table 1 act as active catalysts only for a short period, after which the formation of the nitrile almost comes to a standstill. The

metal carbonyls  $\text{Mo}(\text{CO})_6$ ,  $\text{Fe}_2(\text{CO})_9$  and  $\text{Co}(\text{CO})_2(\text{PPh}_3)_2$  give only stoichiometric amounts of  $\text{C}_6\text{H}_5\text{CN}$ .  $\text{HRh}(\text{PPh}_3)_3$ ,  $\text{Rh}(\text{PPh}_3)_4$ , as well as powdered Rh, Pd and Pt are completely inactive.

The  $\text{RhCl}(\text{PPh}_3)_3$ -catalysed reaction can be carried out in high-boiling solvents such as  $\alpha$ -chloronaphthalene while the application of solvents with the other catalysts studied gives unsatisfactory results.

Since the more active catalysts listed in Table 1 dissociate in solution into  $\text{PPh}_3$ ,<sup>2,3</sup> which by itself converts primary amides (in  $\text{CCl}_4$ ) into nitriles,<sup>4</sup> it was necessary to show—and it has indeed been shown—that the free ligand is completely inactive in our catalysis. It effects, however, two side reactions that often accompany the primary process, *viz* the catalytic isomerization and dehalogenation. The examples mentioned in Ref 1, and those listed in Tables 2 and 3 in this paper, show that N-benzyl- (or substituted benzyl-) arylamides,  $\text{ArCONHCH}_2\text{Ar}'$ , give both the nitriles derived (formally) from the acid residue  $\text{ArCONH}$ - and from the N-benzyl group  $\text{Ar}'\text{CH}_2\text{NH}$ -. The formation of two nitriles is explained by a metal-catalysed 1,3-hydrogen shift in the amidoyl form of the amides:  $\text{Ar}-\text{C}(\text{OH})=\text{N}-\text{CH}_2-\text{Ar}' \rightleftharpoons \text{Ar}-\text{CH}(\text{OH})-\text{N}=\text{CH}-\text{Ar}'$ . This shift is (as in the case of e.g., Rh(I)-catalysed isomerization of allylbenzene)<sup>5</sup> markedly suppressed by free  $\text{PPh}_3$ . N-(*p*-Methylbenzyl)-*m*-toluamide, e.g., is converted by  $10^{-2}$  mol of  $\text{RhCl}(\text{PPh}_3)_3$  (at  $260^\circ$  and 7 hr) to 61% *p*- and 7.5% *m*-tolunitrile, while in the presence of additional  $10^{-1}$  mol of  $\text{PPh}_3$ , *m*-tolunitrile (65%) is the only cyanocompound formed.

The N-alkylated carboxamides,  $\text{ArCONHR}$  (R = alkyl) give only the acid derived nitrile  $\text{ArCN}$ . This reaction is, of course, not affected by the addition of triphenylphosphine.

Table 1. Conversion of N-benzylbenzamide into benzonitrile by various catalysts ( $2 \times 10^{-2}$  mol amide,  $2.5 \times 10^{-4}$  mol catalyst, 7 hr at  $250^\circ$ )

Catalyst	Yield of benzonitrile (%)	Catalyst	Yield of benzonitrile (%)
$\text{RhCl}(\text{PPh}_3)_3$	90	$\text{HfCl}_2(\text{PPh}_3)_3$	20
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	28	$\text{PdCl}_2$	8
$\text{RhCl}_3(\text{AsPh}_3)_3$	6	$\text{CuCl}(\text{PPh}_3)_3$	8
$\text{RuCl}_2(\text{PPh}_3)_3$	31	$\text{HRhCl}_2(\text{PPh}_3)_3^a$	82
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	11		

<sup>a</sup>Yield of benzonitrile obtained by slow distillation (30 min) of the amide over the catalyst.

Table 2. Conversion of secondary amides into nitriles by  $\text{RhCl}(\text{PPh}_3)_3$  (0.02 mol amid,  $2.5 \times 10^{-4}$  mol catalyst)

Exp.	Amide	Reaction		Nitriles formed (yield, %)
		Time, hr	Temp, °C	
1	N-Methylbenzamide	5	250	$\text{C}_6\text{H}_5\text{CN}$ (70)
2	N-Cyclohexylbenzamide	8	260	$\text{C}_6\text{H}_5\text{CN}$ (59)
3	N- <i>t</i> -Butylbenzamide	5	240	$\text{C}_6\text{H}_5\text{CN}$ (27)
4	N-( <i>p</i> -Methoxybenzyl)benzamide	9	260	$\text{C}_6\text{H}_5\text{CN}$ (25); <i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4\text{CN}$ (3)
5	N,N'-Dibenzoylthylenediamine	10	310	$\text{C}_6\text{H}_5\text{CN}$ (7)
6	N-( <i>p</i> -Chlorobenzyl)- <i>p</i> -toluamide	5	250	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (71); <i>p</i> - $\text{ClC}_6\text{H}_4\text{CN}$ (traces)
7	N-( <i>p</i> -Chlorobenzyl)- <i>m</i> -toluamide	5	250	$\text{C}_6\text{H}_5\text{CN}$ (25); <i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (72); <i>p</i> - $\text{ClC}_6\text{H}_4\text{CN}$ (traces)
8	N-( $\alpha$ -Methylbenzyl)- <i>m</i> -toluamide	16	240	<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (36)
9	N-( <i>o</i> -Chlorobenzyl)- <i>p</i> -toluamide	7	250	$\text{C}_6\text{H}_5\text{CN}$ (3); <i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (39)
10	N-( <i>m</i> -Chlorobenzyl)- <i>p</i> -toluamide	7	250	$\text{C}_6\text{H}_5\text{CN}$ (3); <i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (46)
11	N-( <i>p</i> -Chlorobenzyl)- <i>p</i> -toluamide	7	250	$\text{C}_6\text{H}_5\text{CN}$ (3); <i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (46)
12	N-Methyl- <i>p</i> -methoxybenzamide	10	250	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4\text{CN}$ (30)
13	N-Methyl- <i>m</i> -trifluoromethylbenzamide	13	240	<i>m</i> - $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$ (40)
14	N-Ethyl- <i>p</i> -fluorobenzamide	6	238	<i>p</i> - $\text{FC}_6\text{H}_4\text{CN}$ (11)
15	N-( <i>p</i> -Methylbenzyl)- <i>o</i> -chlorobenzamide	7	250	$\text{C}_6\text{H}_5\text{CN}$ (15); <i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (6)
16	N-( <i>p</i> -Methylbenzyl)- <i>m</i> -chlorobenzamide	7	250	$\text{C}_6\text{H}_5\text{CN}$ (16); <i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (7); <i>m</i> - $\text{ClC}_6\text{H}_4\text{CN}$ (25)
17	N-( <i>p</i> -Methylbenzyl)- <i>p</i> -chlorobenzamide	7	250	$\text{C}_6\text{H}_5\text{CN}$ (20); <i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ (8); <i>p</i> - $\text{ClC}_6\text{H}_4\text{CN}$ (28)
18	N-Ethyl- <i>p</i> -chlorobenzamide	10	260	$\text{C}_6\text{H}_5\text{CN}$ (58); <i>p</i> - $\text{ClC}_6\text{H}_4\text{CN}$ (25)
19	N-Methyl- <i>p</i> -bromobenzamide <sup>a</sup>	7	270	$\text{C}_6\text{H}_5\text{CN}$ (60); <i>p</i> - $\text{BrC}_6\text{H}_4\text{CN}$ (0, 7)
20	N-Ethyl- <i>o</i> -iodobenzamide	6	240	$\text{C}_6\text{H}_5\text{CN}$ (22)
21	N-Benzyl- <i>p</i> -cyanobenzamide	10	270	<i>p</i> - $\text{C}_6\text{H}_4(\text{CN})_2$ (1)
22	N-Benzyl- <i>p</i> -nitrobenzamide	12	270	—
23	N,N'-Dibenzylisophthalamide	11	260	$\text{C}_6\text{H}_5\text{CN}$ (25); <i>m</i> - $\text{C}_6\text{H}_4(\text{CN})_2$ (19); <i>m</i> -( $\text{CN})\text{C}_6\text{H}_4\text{CONHCH}_2\text{C}_6\text{H}_5$ (1)
24	N,N'-Dibenzylterephthalamide	8	310	$\text{C}_6\text{H}_5\text{CN}$ (20); <i>p</i> - $\text{C}_6\text{H}_4(\text{CN})_2$ (7); <i>p</i> -( $\text{CN})\text{C}_6\text{H}_4\text{CONHCH}_2\text{C}_6\text{H}_5$ (2)
25	N-Methyl- $\alpha$ -naphthamide	8	250	$\alpha$ - $\text{C}_{10}\text{H}_7\text{CN}$ (58)
26	N-Methyl- <i>n</i> -undecanamide	8	240	$\text{CH}_3(\text{CH}_2)_9\text{CN}$ (21)

<sup>a</sup>In the presence of a four-fold amount of  $\text{C}_6\text{Cl}_6$  52% *p*-bromobenzonitrile, 0.3% *p*-chlorobenzonitrile and 5% benzonitrile were formed.

The isomerization (and the concomitant formation of two nitriles) is inhibited also by the introduction of substituents at an *ortho* position to the CO function. Thus, N-benzyl-*o*-toluamide, N-(*p*-chlorobenzyl)-*o*-toluamide and N-(*p*-methylbenzyl)-*o*-chlorobenzamide give at most 6% of the N-benzyl derived nitriles.

In analogy to the  $\text{Rh}(\text{I})$ -catalysed desulfonylation of halogenated arenesulfonyl chlorides<sup>6</sup> and  $\text{Ru}(\text{II})$ -catalysed dehydrocarbonylation of halogenated benzaldehydes,<sup>7</sup> the halogen atoms are partially or completely eliminated—as hydrogen halide—from chlorine, bromine and iodine containing amides, independently of the place of halogen in any position in the N-benzyl or the aroyl moiety (Table 2, exps 6, 7, 9–11, 15–20). Fluorine is not eliminated in this process (exp. 14). While hexachlorobenzene suppresses practically the halogen

abstraction,<sup>1</sup> triphenylphosphine generally promotes it. N-(*p*-Methylbenzyl)-*p*-chlorobenzamide, e.g., is converted by  $10^{-2}$  mol  $\text{RhCl}(\text{PPh}_3)_3$  and  $10^{-1}$   $\text{PPh}_3$  into 63% benzonitrile and only 10% *p*-chlorobenzonitrile, while under the same conditions, but in the absence of the phosphine, a mixture of 38% *p*-chlorobenzonitrile, 20% benzonitrile and 8% *p*-tolunitrile has been obtained (Table 2, exp. 17).

The electronic nature of substituents attached to either the aroyl residue or the benzyl group has only a small effect on the reaction rates. For example, *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{CONHCH}_3$  and *m*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CONHCH}_3$  decompose in the presence of  $\text{RhCl}(\text{PPh}_3)_3$  (at 260°) at exactly the same rate. It seems that the complexing power of the substituents is the main factor controlling the reaction rates. Nitro- and cyanobenzamides react extremely

Table 3. Conversion of some secondary heterocyclic carboxamides into nitriles by  $\text{RhCl}(\text{PPh}_3)_3$  (0.02 mol amid and  $2.5 \times 10^{-4}$  mol catalyst)

Exp.	Amide	Reaction		Nitriles formed (yield, %)
		Time, hr	Temp, °C	
1	N-Methylnicotinamide	12	240	3-cyanopyridine (3)
2	N-Benzylnicotinamide	12	240	benzoxynitrile (16); 3-cyanopyridine (40)
3	N-( $\alpha$ -Methylbenzyl)nicotinamide	12	240	3-cyanopyridine (45)
4	N-Methyl-2-thiophenamide	13	250	2-cyanothiophene (9)
5	N-Benzyl-2-thiophenamide	13	250	benzoxynitrile (6); 2-cyanothiophene (20)

slowly and give only traces of the expected nitriles even after prolonged heating with the catalyst. Iso- and terephthalamides, however, give fair yields of the corresponding dinitriles which shows that the degradation of both amido groups may occur simultaneously. Mono-cyanobenzamides could be detected in these reactions only in very small amounts (Table 2, exps. 23 and 24).

The experiments listed in Table 3 indicate that secondary aromatic heterocyclic carboxamides are transformed into nitriles in an analogous manner to the carbocyclic compounds. In this series, the differences between N-alkyl- and N-benzylamides are more pronounced than in the homocyclic series.

High boiling N-substituted aliphatic amides are equally degraded. The formation of 1-cyanodecene from N-methylundecanamide (Table 3, exp. 26) is a typical example.

The carbinols initially formed in the catalysis ( $\text{ArCONHCH}_2\text{Ar}' \rightarrow \text{ArCN} + \text{Ar}'\text{CN} + \text{ArCH}_2\text{OH} + \text{Ar}'\text{CH}_2\text{OH}$ ) do not generally accumulate. They are oxidized to aldehydes when an external hydrogen acceptor is added to the reaction mixture,<sup>9</sup> or disproportionated to aldehydes and hydrocarbons in the absence of such an acceptor.<sup>9</sup>

Thus, the addition of 1-octadecene to a boiling mixture of N-benzylbenzamide and  $\text{RhCl}(\text{PPh}_3)_3$  (followed by TLC separation) yielded octadecane and isomeric octadecenes. Slow distillation of benzyl alcohol over the same Rh-catalyst gave benzaldehyde toluene, benzene, carbon monoxide and traces of water. However, kinetic measurements prove that disproportionation of the carbinol alone cannot be responsible for all the aldehyde and hydrocarbons formed in the catalysis. At least part of the amide itself must serve as an internal hydrogen acceptor and the hydrocarbons isolated are derived from both the aroyl and the N-benzyl moieties. As a typical example, the non-nitrilic products obtained from N-(*p*-methylbenzyl)-*m*-toluamide are 17.3% *p*-xylene, 5.2% *m*-xylene, 6% toluene, 1.5% *p*-tolualdehyde; 1.0% *m*-tolualdehyde, and traces of *p*-methylbenzyl alcohol and water.

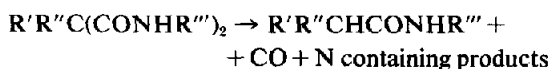
In the presence of  $\text{PPh}_3$  (molar ratio catalyst: phosphine 1:10), the nitrogen-free products are

derived entirely from the substituted N-benzyl group, and the above amide gives only *p*-xylene (22%), *p*-tolualdehyde (8%), *p*-methylbenzyl alcohol (3%) and toluene (12%). Bibenzyls are formed in some experiments in small amounts (< 1%).

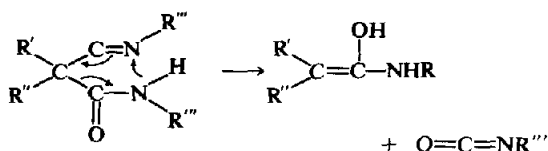
Several halogenated benzamides give halogen-free hydrocarbons together with the expected aryl halides: N-(*p*-chlorobenzyl)phenylacetamide gives benzene (2.5%) in addition to (the expected) toluene (8%) ethylbenzene (4%) and *p*-chlorotoluene (7%). Some halogenated benzamides do not lead to any aryl halides at all. N-Methyl-*p*-bromobenzamide (Table 1, exp. 19) e.g., gives only benzene and toluene.

When carbinols carrying  $\alpha$ -H atoms are expected to be formed, partial dehydration occurs. In exp. 3 of Table 3, the cyanopyridine is accompanied by 24% styrene (together with 22% acetophenone and 10% pyridine). In exp. 2 of Table 2, the cyclohexyl group is transformed into cyclohexene (73%), cyclohexanone (3%) and only 1% cyclohexanol.

Malonamides do not form malonitriles. They are, however, decomposed by several homogeneous catalysts of the platinum group into derivatives of acetamide, carbon monoxide and transformation products of the residual  $\text{R}''\text{N}$  species:



The reaction is the first case of decarbonylation of a diamide catalyzed by soluble transition-metal complexes. It is, however, most likely that the CO is not extruded directly from the amide, but from a primary degradation product. A plausible intermediate is an isocyanate, which is decarbonylated by  $\text{RhCl}(\text{PPh}_3)_3$  under our experimental conditions.



The malonamides degrade considerably faster than the aromatic monoamides—10 min being the average reaction time required.

Some typical decarbonylation experiment with primary and secondary malonamides are summarized in Table 4.

While malonamide and C-substituted malonamides degrade smoothly to the corresponding acetamides, disubstitution at the central C atom (exp. 15) permits only very slow decarbonylation (probably due to steric effects). Likewise substitution at both N atoms by long aliphatic chains leads to poor results: N,N'-dibutylmalonamide yields only 4% N-butylacetamide and diamides with even longer chains hardly decarbonylate at all.

The monoamides of relatively low b.ps distil from the reaction mixture unchanged; those of higher molecular weight (e.g., phenylacetamide, exp. 14) decompose partly into the corresponding nitrile.

The second N atom of the primary malonamides, which is not incorporated in the formation of the acetamides, appears partly as NH<sub>3</sub>. In secondary N-alkylmalonamides this type of hydrogen transfer is less pronounced, and only traces of the corresponding alkyl-amines could be detected. N-Phenyl- and N-benzylmalonamide are exceptional as they yield aniline (61%) and benzylamine (9%), respectively. The balance of the nitrogen (from the R''N residue) is recovered in polymeric form. No elementary nitrogen has ever been observed to be liberated from the reaction mixture.

Gas chromatography showed that in most cases 0.5–1 mol of carbon monoxide is formed. The CO expelled in exps. 6, 10 and 11 of Table 4, e.g., was 0.98, 0.71 and 0.67 mol, respectively. Dimethylmalonamide (exp. 15) gives only a low amount of CO, equivalent to the methylpropionamide formed.

Phenylmalonamide undergoes more extensive decomposition at its boiling point and gives 1.4–1.5 mol of CO per mol of diamide.

The gaseous products of C- and N-methylated malonamides contain always some methane. In analogy the N-Benzyl derivative (exp. 9) gives up to 2% toluene and bibenzyl.

The experiment with the ester amide, EtOCOCH<sub>2</sub>CONH(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub> (exp. 6) is remarkable, in so far as ethanol is formed in addition to N-octylacetamide, ethyl acetate and CO. To the best of our knowledge no decarbonylation of an ester amide, by homogeneous catalysis, has been observed before.

Apart from RhCl(PPh<sub>3</sub>)<sub>3</sub> and HRhCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, other decarbonylation catalysts, such as RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, promote the degradation of the malonamides as well, albeit in low yields (Table 4). The low reactivity of RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> should be noted, since this complex has been thought to be the active species in some RhCl(PPh<sub>3</sub>)<sub>3</sub>-catalysed decarbonylation reactions.<sup>10</sup>

Some qualitative experiments on the correlation between the dissociation of the product-catalyst complex and the activity of the catalyst are notable. While RhCl<sub>3</sub>·3H<sub>2</sub>O which forms stable *mer*-RhCl<sub>3</sub>(ArCN)<sub>3</sub><sup>11</sup> cannot be used in the catalytic degradation, RhCl(PPh<sub>3</sub>)<sub>3</sub>, that forms an extremely labile complex with benzonitrile (see Experimental) is our best catalyst. RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, which gives mono- and bis-nitrile complexes of type RuCl<sub>2</sub>L(PPh<sub>3</sub>)<sub>2</sub><sup>12</sup> and RuCl<sub>2</sub>L<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>,<sup>13</sup> that dissociate fairly rapidly above 200°,<sup>12</sup> has an intermediary catalytic activity.

Substrate-catalyst complexes should also be taken into consideration. None of the amido-complexes formed from the substrates is stable at

Table 4. Catalytic decarbonylation of malonamides ( $3 \times 10^{-2}$  mol diamide,  $3 \times 10^{-4}$  mol catalyst)

Exp.	Starting diamide	Catalyst	Monoamide formed (yield, %)
1	CH <sub>2</sub> (CONH <sub>2</sub> ) <sub>2</sub>	HRhCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONH <sub>2</sub> (31.2)
2	CH <sub>2</sub> (CONH <sub>2</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONH <sub>2</sub> (30.0)
3	CH <sub>2</sub> (CONH <sub>2</sub> ) <sub>2</sub>	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONH <sub>2</sub> (18.7)
4	CH <sub>2</sub> (CONH <sub>2</sub> ) <sub>2</sub>	IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> CONH <sub>2</sub> (10.7)
5	CH <sub>2</sub> (CONH <sub>2</sub> ) <sub>2</sub>	RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> CONH <sub>2</sub> (5.6)
6	CH <sub>2</sub> (CONHCH <sub>3</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONHCH <sub>3</sub> (24.5)
7	CH <sub>2</sub> [CONH(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONH(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> (4.0)
8	CH <sub>2</sub> (CONHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONHC <sub>6</sub> H <sub>5</sub> (26.4)
9	CH <sub>2</sub> (CONHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (10.8)
10	CH <sub>3</sub> CH(CONH <sub>2</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> CONH <sub>2</sub> (38.5)
11	CH <sub>3</sub> CH(CONH <sub>2</sub> ) <sub>2</sub>	RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> CONH <sub>2</sub> (15.0)
12	CH <sub>3</sub> CH(CONHCH <sub>3</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> CONHCH <sub>3</sub> (47.7)
13	CH <sub>3</sub> CH(CONHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> CONHC <sub>6</sub> H <sub>5</sub> (21.0)
14	C <sub>6</sub> H <sub>5</sub> CH(CONH <sub>2</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONH <sub>2</sub> (7.6 <sup>a</sup> )
15	(CH <sub>3</sub> ) <sub>2</sub> C(CONH <sub>2</sub> ) <sub>2</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCONH <sub>2</sub> (7.7)
16	H <sub>5</sub> C <sub>2</sub> O·OC·CH <sub>2</sub> ·CONH(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CONH(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> <sup>b</sup>

<sup>a</sup>And 11.9% C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CN.

<sup>b</sup>Varying yields up to 50% were obtained.

the reaction temperature of 240°. In this series of compounds, again, the least stable complexes are those derived from  $\text{RhCl}(\text{PPh}_3)_3$ . Somewhat more stable are the amido-complexes derived from the ruthenium catalyst,  $\text{RuCl}_2(\text{PPh}_3)_3$ . The various benzamides give two types of complexes: (a)  $\text{RuCl}_2\text{L}(\text{PPh}_3)_2$  (b)  $\text{RuCl}_2\text{L}_2(\text{PPh}_3)$ . The former are diamagnetic and their carbonyl band in their infrared spectra is shifted to a lower wavelength (as compared with the free amide); the latter are paramagnetic and exhibit a small bathochromic shift in the carbonyl absorptions.

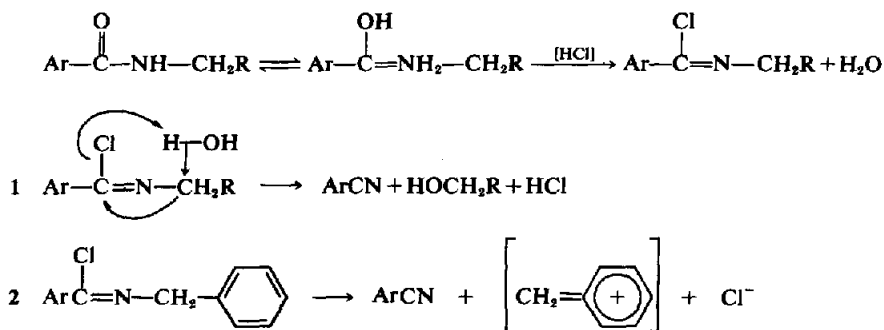
Analytically pure complexes of type (a) or (b) have been isolated only in few cases (Table 5). Many amides give mixtures of both types of complexes as shown by the elementary analyses, IR spectra and the amount of  $\text{PPh}_3$ , isolated from the reaction mixtures.

The malonamides behave analogously and give mixtures of amido-complexes. *N,N'*-Diphenylmalonamide forms a pure compound of type (b)  $[\text{CH}_2(\text{CONHPh})_2]\text{RuCl}_2(\text{PPh}_3)$  in which the diamide fills both L functions. (ESR  $g = 2.36$ ).  $\text{RhCl}(\text{CO}(\text{PPh}_3)_2)$  gives a simple addition complex  $[\text{CH}_2(\text{CONHPh})_2]\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  with the same diamide.

As these amido-metal-complexes degrade the corresponding amides at a rate similar to that by the starting metal complexes, they may be intermediates in the catalytic degradation reactions.

It is, however, difficult to describe their exact role, if any, in the very complicated mechanism which includes hydrogen transfer, bond fission, redox and elimination reactions. A further difficulty arises from the fact that the same carboxamides degrade often by different pathways when different catalysts are applied. While, e.g.,  $\text{RhCl}(\text{PPh}_3)_3$  can widely be applied, the hydride-complex  $\text{HRhCl}_2(\text{PPh}_3)_3$  (in the  $\alpha$  or  $\beta$  form) is more selective in its action; (in spite of the fact that the hydride decomposes to  $\text{RhCl}(\text{PPh}_3)_3$ , when heated in the absence of a free amide<sup>14</sup>), it does not affect *N*-methylnicotinamide, *N*-methyl-*m*-trifluorobenzamide and *N*-methylundecanamide which are degraded by the former catalyst. On the other hand the rhodium hydride converts *N*-benzylbenzamide (and other amides listed in Table 6) to nitriles 10<sup>3</sup> times faster than  $\text{RhCl}(\text{PPh}_3)_3$ . Furthermore, the catalysis by  $\text{HRhCl}_2(\text{PPh}_3)_3$  can be carried out in the absence of air, while  $\text{RhCl}(\text{PPh}_3)_3$  requires at least one equivalent of oxygen for each mol of amide.

Since  $\text{HRhCl}_2(\text{PPh}_3)_3$  dissociates to  $\text{HCl}$  and  $\text{RhCl}(\text{PPh}_3)_3$  at 150° in a reversible reaction,<sup>14</sup> it is reasonable to conclude that the  $\text{HRhCl}_2(\text{PPh}_3)_3$ -promoted (but not  $\text{RhCl}(\text{PPh}_3)_3$ -catalysed) degradation is actually a catalytic von Braun reaction. The two pathways proposed for the (non-catalytic) reaction,<sup>15</sup> that include an imidoyl chloride as intermediate, could well apply to our catalysis, provided the  $\text{HCl}$  being recycled by the catalyst:



\*It may be of interest to refer briefly to experiments we made with  $\text{RhCl}(\text{PPh}_3)_3$  and Schiff bases: When either *N*-benzyl-*p*-methylbenzalimine,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{C}_6\text{H}_5$ , or *N*-*p*-methylbenzylbenzalimine,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{N}=\text{CHC}_6\text{H}_5$ , was heated at ambient atmosphere at 230–260° with 10<sup>-2</sup> mol catalyst for 14 h, the distillable products were benzonitrile (22–23%), *p*-tolunitrile (15–18%), *p*-xylene (22%), benzaldehyde, toluene and benzene (6–8% of each). The halogen containing *N*-(*p*-methylbenzyl)-*p*-chlorobenzalimine,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{N}=\text{CH}(p\text{-ClC}_6\text{H}_4)$ , gave, under similar conditions, 28% halogen-free benzonitrile, 12% *p*-tolunitrile, 24% *p*-xylene and 4% *p*-chlorotoluene. Other Schiff bases, including the unsubstituted benzylbenzalimine, gave very low yields of nitriles or none at all.

This assumption is supported by the fact that Schiff bases (that have no OH function) are not degraded by  $\text{HRhCl}_2(\text{PPh}_3)_3$ .\*

On the other hand the  $\text{RhCl}(\text{PPh}_3)_3$ -catalysed transformation of monoamides to nitriles seems to include a free radical chain mechanism (as in the allylic oxidation by the same complex<sup>16</sup>). This assumption is supported by the following facts:

(a) Traces of  $\alpha,\alpha'$ -azoisobutyronitrile cause a 5-fold increase in the initial reaction rate in the decomposition of *N*-benzylbenzamide. In the absence of an external free radical initiator the air present could act as such directly or through peroxide formation.

Table 5. Analytical data and properties for some amido- and nitrile-complexes of Ru and Rh

Compound	Ligand L	M.p. (dec.) °C	$\nu_{\text{CO}}$ or $\nu_{\text{CN}}$ , Coordin- ated	$\nu_{\text{CO}}$ or $\nu_{\text{CN}}$ , Free ligand	Formula	C (%)		H (%)		Cl (%)		N (%)		P (%)	
						Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
RuCl <sub>2</sub> L(PPPh) <sub>2</sub>	N-Benzylbenzamide	103-105	1655 <sup>a</sup>	1644 <sup>a</sup>	C <sub>30</sub> H <sub>30</sub> Cl <sub>2</sub> NOP <sub>2</sub> Ru	66.1	66.1	4.8	4.7	8.3	7.8			7.3	6.8
RuCl <sub>2</sub> L(PPPh) <sub>2</sub>	N-methyl- <i>p</i> -bromobenzamide	126-130	1655 <sup>b</sup>	1648 <sup>b</sup>	C <sub>24</sub> H <sub>20</sub> BrCl <sub>2</sub> NOP <sub>2</sub> Ru	58.2	58.0	4.4	4.2			1.0	1.5	6.3	6.8
RuCl <sub>2</sub> L <sub>1</sub> (PPPh) <sub>2</sub>	N-( <i>p</i> -methylbenzyl)- <i>p</i> -chlorobenzamide	155-160	1644 <sup>a</sup>	1648 <sup>a</sup>	C <sub>28</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> PRu	60.8	60.4	4.6	4.5	14.9	14.9	2.3	2.9	3.3	3.3
RuCl <sub>2</sub> L(PPPh) <sub>2</sub>	N,N'-diphenylmalonamide	192	1670 <sup>b</sup>	1650 <sup>b</sup>	C <sub>28</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> PRu	58.1	57.6	4.3	4.2	10.3	10.3	4.1	4.3	4.7	4.5
RhClL(CO)(PPPh) <sub>2</sub>	N,N'-diphenylmalonamide	197-203	1660 <sup>b</sup>	1650 <sup>b</sup>	C <sub>28</sub> H <sub>28</sub> ClN <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Rh	65.6	66.1	4.7	4.7	4.3	3.8	2.7	3.0	7.0	6.6
[RhCl(PPPh) <sub>2</sub> ]O <sub>2</sub> h	benzonitrile	300	2280 <sup>ac</sup>	2231 <sup>c</sup>	C <sub>10</sub> H <sub>8</sub> ClNO <sub>2</sub> PRh	56.0	56.0	3.7	3.7			2.6			
RuCl <sub>2</sub> L(PPPh) <sub>2</sub>	isophthalonitrile	212-216	2333 <sup>b</sup>	2250 <sup>b</sup>	C <sub>14</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> P <sub>2</sub> Ru	64.1	64.1	4.4	4.1	8.3	8.6				

<sup>a</sup>In KBr.<sup>b</sup>Nujol mull.<sup>c</sup> $\nu_{\text{C}}(\text{O})$ , 852 cm<sup>-1</sup>.

Table 6. Conversion of some secondary amides into nitriles by  $\text{HRhCl}_2(\text{PPh}_3)_3$  (distillation of  $2 \times 10^{-2}$  mol amide over  $2.5 \times 10^{-4}$  mol catalyst during 20–30 min)

Exp.	Amide	Nitriles formed (yield, %)
1	N-Benzylnicotinamide	3-cyanopyridine (67); benzonitrile (11)
2	N-( $\alpha$ -Methylbenzyl)-nicotinamide	3-cyanopyridine (80)
3	N-Benzyl-2-thiophenamide	2-cyanothiophene (45)
4	N- <i>tert</i> -Butylbenzamide	benzonitrile (10)
5	N-( <i>p</i> -Methoxyphenyl)-benzamide	benzonitrile (45); <i>p</i> -methoxybenzonitrile (6)
6	N-Methyl- <i>p</i> -toluamide	<i>p</i> -tolunitrile (25)
7	N-( <i>p</i> -Chlorobenzyl)- <i>p</i> -toluamide	<i>p</i> -tolunitrile (44); benzonitrile (5); <i>p</i> -chlorobenzonitrile (< 1)
8	N,N'-Dibenzyl-ethylenediamine	benzonitrile (5)

(b) Traces of the free radical scavenger 2,5-di-*t*-butylhydroquinone considerably inhibit the accumulation of benzonitrile. Similarly, a stream of oxygen provides an inhibitory effect on the catalysis.

(c) The formation of small amounts of bibenzyls accompanies many of the  $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed, but not the  $\text{HRhCl}_2(\text{PPh}_3)_3$ -promoted reactions.

(d) The application of hexachlorobenzene as solvent in the catalytic decomposition of brominated and iodinated benzamides leads to the formation of some chlorinated benzonitrile.

It must be noted that the secondary transformations of the carbinols as they appear in our catalyses, have proven to be a purely metal-ion promoted process,<sup>17</sup> but, as already pointed out by Walborsky and Allen,<sup>18</sup> the statement does not exclude the possibility that free radical pairs may also play a part, perhaps a minor part, in such systems.

#### EXPERIMENTAL

The aromatic carboxamides were prepared in 82–98% yield by standard methods from the aroyl chlorides and excess amine. The new amides are listed in Table 7. The malonamides were obtained in the usual manner from the diethyl malonates and the appropriate amines.

**N-Octylcarboxyacetamide.** A stirred mixture of 640 g of diethyl malonate and 120 g of *n*-octylamine was heated at 125° for 3 hr, and then at 180° for 1 hr. Excess of the diester was removed under reduced pressure [93–98° (17 mm)] and the oily residue was stirred with KOH aq, at 4° for 16 hr. The N,N'-dioctylmalonamide was filtered off and washed with water. Upon acidification of the filtrate (HCl) in the cold, an orange oil separated which solidified. Repeated recrystallizations from water yielded 3.5 g of the colorless monoamide, m.p. 77–78°,  $\nu_{\text{max}}^{\text{Nujol}}$  1710 (acid C=O), 1650  $\text{cm}^{-1}$  (amide C=O). (Found: C, 61.2; H, 9.7; N, 6.6. Calc. for  $\text{C}_{11}\text{H}_{21}\text{NO}_2$ : C, 61.4; H, 9.8; N, 6.5%).

The ethyl ester of m.p. 92–94° was obtained by prolonged treatment (48 hr) of the acid with abs EtOH saturated with HCl.

The Schiff bases were prepared in 74–90% yield by azeotropic condensation of the appropriate aromatic aldehydes and benzylamines in benzene, toluene or xylene.

**N-Benzyl-*p*-methylbenzalimine.** Colorless oil, b.p. 123–124° (0.3 mm),  $\nu_{\text{max}}$  1640  $\text{cm}^{-1}$  (C=N). (Found: C, 85.7; H, 7.4; N, 6.7. Calc. for  $\text{C}_{15}\text{H}_{15}\text{N}$ : C, 86.1; H, 7.2; N, 6.7%).

**N-(*p*-Methylbenzyl)benzalimine.** Colorless oil, b.p. 120–125° (0.2 mm),  $\nu_{\text{max}}$  1635  $\text{cm}^{-1}$  (C=N). (Found: C, 85.9; H, 7.5; N, 6.5. Calc. for  $\text{C}_{15}\text{H}_{15}\text{N}$ : C, 86.1; H, 7.2; N, 6.7%).

**N-(*p*-Methylbenzyl)-*p*-chlorobenzalimine.** Colorless crystals, m.p. 93–95° (from benzene),  $\nu_{\text{max}}^{\text{KBr}}$  1630  $\text{cm}^{-1}$  (C=N). (Found: C, 73.8; H, 6.0; Cl, 14.8; N, 5.5. Calc. for  $\text{C}_{15}\text{H}_{14}\text{ClN}$ : C, 73.8; H, 5.7; Cl, 14.6; N, 5.7%).

**N-(*p*-Methoxybenzyl)-*p*-methylbenzalimine.** Colorless crystals, m.p. 54° (from cyclohexane),  $\nu_{\text{max}}^{\text{KBr}}$  1656  $\text{cm}^{-1}$  (C=N). (Found: C, 80.1; H, 7.2; N, 6.0. Calc. for  $\text{C}_{16}\text{H}_{17}\text{NO}$ : C, 80.3; H, 7.1; N, 5.8%).

**N-(*p*-Methylbenzyl)-*p*-methoxybenzalimine.** Colorless crystals, m.p. 56° (from benzene),  $\nu_{\text{max}}^{\text{KBr}}$  1650  $\text{cm}^{-1}$  (C=N). (Found: C, 80.4; H, 7.0; N, 6.1. Calc. for  $\text{C}_{16}\text{H}_{17}\text{NO}$ : C, 80.3; H, 7.1; N, 5.8%).

**N-Benzyl- $\beta$ -naphthalimine.** Pale yellow crystals, m.p. 77–78° (from cyclohexane),  $\nu_{\text{max}}^{\text{Nujol}}$  1640  $\text{cm}^{-1}$  (C=N). (Found: C, 88.5; H, 6.3; N, 5.6; Calc. for  $\text{C}_{18}\text{H}_{18}\text{N}$ : C, 88.2; H, 6.1; N, 5.7%).

The different techniques used for the degradation reactions summarized in Tables 1, 2, 3, 4 and 6 are illustrated by the following examples.

**Degradation of N-benzyl-*m*-toluamide by  $\text{RhCl}(\text{PPh}_3)_3$ .** A mixture of 5.5 g N-benzyl-*m*-toluamide and 225 mg of the catalyst was heated for 2 min at 285° and then for 8 hr at 270°. The mixture was distilled under reduced pressure (20 mm), and the distillate separated on a 1.5 m long GLC column (packed with 20% Carbowax 20 M on Chromosorb P at 80–200°). There was collected 1.17 g (50%) *m*-tolunitrile, 0.53 g (26%) benzonitrile, 0.28 g (15%) toluene, 0.01 g (0.5%) *m*-xylene, 0.02 (0.5%) bibenzyl, 0.06 g (3%) benzaldehyde and some water.

**Degradation of N-benzylbenzamide in solution.** A soln of 8.45 g N-benzylbenzamide and 450 mg  $\text{RhCl}(\text{PPh}_3)_3$  in 50 ml  $\alpha$ -chloronaphthalene was refluxed (257°) for 14 hr. Upon fractionation of the mixture, 2.55 g (62%) of benzonitrile (b.p. 185°) was obtained.

**Degradation of N-benzylnicotinamide by  $\text{HRhCl}_2(\text{PPh}_3)_3$ .** A mixture of 3.00 g N-benzylnicotinamide and 200 mg  $\text{HRhCl}_2(\text{PPh}_3)_3$ <sup>14</sup> was heated in a Claisen flask equipped with a short column, so as to permit distillation of the products below 200° within 25 min. The yellow distillate (1.9 g) was separated on a preparative GLC column packed with 10% Carbowax 20 M on Chromosorb P to yield 736 mg 3-cyanopyridine, 305 mg benzonitrile, 240 mg benzaldehyde, 310 mg pyridine, 105 mg toluene, 80 mg benzene and some water.

**Degradation of a Schiff base.** A mixture of 3.00 g N-benzyl-*p*-methylbenzalimine and 225 mg  $\text{RhCl}(\text{PPh}_3)_3$  was heated on a wax bath for 15 hr at 245°. The mixture was distilled at 70–150° (20 mm) and separated by GLC (20% Carbowax 20 M on Chromosorb P at 110–150°) to yield 0.33 g (22%) benzonitrile, 0.31 g (18%) *p*-tolunitrile, 0.35 g (23%) *p*-xylene, 0.05 g (3%) benzaldehyde, 0.11 g (8%) toluene and 0.08 g (7%) benzene.

Table 7. Analytical data and physical properties for new aromatic carboxamides

Compound	M.p., °C <sup>a</sup>	$\nu_{\text{NH}}$ , cm <sup>-1b</sup>	$\nu_{\text{CO}}$ , cm <sup>-1b</sup>	Formula	C, %		H, %		N, %		Halogen, %	
					Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub>	162	3305	1648	C <sub>8</sub> H <sub>8</sub> BrNO	44.9	44.9	3.9	3.7	6.7	6.5	37.7	37.4
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub>	71-73	3300 <sup>c</sup>	1650 <sup>c</sup>	C <sub>9</sub> H <sub>8</sub> F <sub>3</sub> NO	53.5	53.2	4.2	3.9	6.9	6.9	27.7	28.1
<i>o</i> -IC <sub>6</sub> H <sub>4</sub> CONHC <sub>2</sub> H <sub>5</sub>	113.5	3295 <sup>c</sup>	1635 <sup>c</sup>	C <sub>9</sub> H <sub>10</sub> INO	39.5	39.3	3.6	3.6	5.1	5.1	46.5	46.2
2-C <sub>4</sub> H <sub>9</sub> S(CONHCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	119-120	3290	1650	C <sub>12</sub> H <sub>11</sub> NOS	66.3	66.4	5.2	5.1	6.2	6.4	14.2 <sup>d</sup>	14.7 <sup>d</sup>
<i>m</i> -FC <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	84-85	3327	1644	C <sub>14</sub> H <sub>12</sub> FNO	73.6	73.4	5.3	5.2	6.2	6.1	8.0	8.3
<i>p</i> -C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub>	168	3336	1650	C <sub>14</sub> H <sub>12</sub> NO	80.0	79.6	6.1	6.2	6.6	6.6		
3-C <sub>2</sub> H <sub>5</sub> N(CONHCH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	140-141	3295	1645	C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O	74.2	74.3	6.5	6.2	12.3	12.4		
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONHCH <sub>3</sub> ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )	131-132	3310	1631	C <sub>15</sub> H <sub>14</sub> CINO	69.3	69.4	5.1	5.4	5.0	5.4	13.7	13.7
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )	124-125	3300 <sup>c</sup>	1650 <sup>c</sup>	C <sub>15</sub> H <sub>14</sub> CINO	69.4	69.4	5.5	5.4	5.2	5.4	13.5	13.7
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )	132-134	3285	1645	C <sub>15</sub> H <sub>14</sub> CINO	69.4	69.4	5.5	5.4	5.4	5.4	14.0	13.7
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )	195-197	3305	1648	C <sub>15</sub> H <sub>14</sub> CINO	69.4	69.4	5.7	5.4	5.3	5.4	14.0	13.7
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )	134-136	3280 <sup>c</sup>	1645 <sup>c</sup>	C <sub>15</sub> H <sub>14</sub> CINO	69.1	69.4	5.7	5.4	5.5	5.4	13.8	13.7
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )	148	3330	1640	C <sub>15</sub> H <sub>14</sub> CINO	69.1	69.4	5.4	5.4	5.5	5.4	13.8	13.7
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>o</i> -ClC <sub>6</sub> H <sub>4</sub> )	128-129	3295 <sup>c</sup>	1640	C <sub>15</sub> H <sub>14</sub> CINO	69.1	69.4	5.7	5.4	5.3	5.4	14.0	13.7
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> )	149-150	3300	1645	C <sub>15</sub> H <sub>14</sub> CINO	69.6	69.4	5.6	5.4	5.3	5.4	13.6	13.7
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> ( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )	194-195	3270	1650	C <sub>15</sub> H <sub>14</sub> CINO	69.1	69.4	5.1	5.4	5.3	5.4	13.9	13.7
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	102-103	3320	1640	C <sub>15</sub> H <sub>15</sub> NO	79.8	80.0	6.8	6.7	6.2	6.2		
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CONHCH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	102-103	3320	1638	C <sub>16</sub> H <sub>17</sub> NO	79.8	80.1	7.2	7.1	5.9	5.9		
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CON(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	173-175	3270	1645 <sup>c</sup>	C <sub>16</sub> H <sub>17</sub> NO	80.4	80.1	6.8	7.1	5.6	5.9		
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CONHCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	118-119	3370	1640	C <sub>16</sub> H <sub>15</sub> NO	81.5	81.8	5.7	5.8	5.6	5.9		
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (CONHCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	156-158 <sup>e</sup>	3300 <sup>c</sup>	1645 <sup>c</sup>	C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	76.9	76.7	5.0	5.8	8.1	8.1		

<sup>a</sup>Except for the last compound all the amides were recrystallized from EtOH or EtOH aq.<sup>b</sup>Unless otherwise stated, in KBr.<sup>c</sup>Nujol mull.<sup>d</sup>Analysis of sulfur.<sup>e</sup>From ethanol, water and acetone in the ratio 3:2:1.



**Decarbonylation of malonamide.** In a typical experiment a mixture of 3.070 g malonamide (purified and well dried) and 325 mg  $\text{RhCl}(\text{PPh}_3)_3$  was heated gently in a Claisen flask until a homogeneous soln has been formed. When the temp was now raised, a rapid evolution of gases set in. The products that distilled over (below 220°) during 7–10 min were separated by GLC (on 20% Carbowax 20 M on Chromosorb W) to yield 342 mg (30%) acetamide.

In order to measure the CO evolved, the reaction was carried out in the presence of a known volume of air, in a closed system. The gases were collected in a burette over silicon or mineral oil and analyzed by VPC<sup>19</sup> on a 200 × 0.64 cm copper column packed with Molecular Sieve 5A, operated at 35° and 50 ml/min helium. While repeated analyses by this method led to essentially the same results, the application of an alternative method based on the reduction of iodine pentoxide,<sup>20</sup> often gave erratic results.

The amononia formed was determined in separate runs in which the gases were passed through a standard HCl soln.

**N-Benzylbenzamidodichlorobis(triphenylphosphine)ruthenium**,  $(\text{C}_6\text{H}_5\text{CONHCH}_2\text{C}_6\text{H}_5)_2\text{RuCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_3$ . To a stirred soln of 240 mg  $\text{RuCl}_2(\text{PPh}_3)_3$  in 50 ml dry benzene a hot soln of 58 mg N-benzylbenzamide in 5 ml chlorobenzene was added, under argon. The mixture was refluxed for 1 hr and a small amount of black crystals formed was removed by filtration. The green soln was treated with 100 ml n-hexane to yield 180 mg (77%) of the bright green complex, m.p. 103–105° (dec).

**Dichloro-(N-methyl-p-bromobenzamido)bis(triphenylphosphine)ruthenium**,  $(\text{p-BrC}_6\text{H}_4\text{CONHCH}_3)_2\text{RuCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_3$  was prepared in 73% yield by the same procedure, except for the use of bromobenzene instead of chlorobenzene as solvent.

**Dichlorobis[N-(p-methylbenzyl)-p-chlorobenzamido](triphenylphosphine)ruthenium**,  $\text{p-ClC}_6\text{H}_4\text{CONHCH}_2(\text{p-CH}_3\text{C}_6\text{H}_4)_2\text{RuCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_3$ . A soln of 63 mg of N-(p-methylbenzyl)-p-chlorobenzamide in 3 ml 1,2,4-trichlorobenzene was added, under argon, to a boiling soln of 230 mg  $\text{RuCl}_2(\text{PPh}_3)_3$ . After 30 min 25 mg of dark crystals of m.p. 215–220° (dec.) was filtered off, and the filtrate was concentrated and treated with 100 ml light petroleum. The olive-green ppt was thoroughly washed with light petroleum to yield 125 mg (53%) amido-complex, m.p. 155–160° (dec starts at ~ 130° when heated slowly).

**Dichloro(N,N'-diphenylmalonamido)(triphenylphosphine)ruthenium**,  $[\text{CH}_2(\text{CONHC}_6\text{H}_5)_2]_2\text{RuCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_3$  was obtained in 80% yield when a soln of 275 mg of the diamide and 250 mg  $\text{RuCl}_2(\text{PPh}_3)_3$  was refluxed for 2 hr, m.p. 192° (dec) from benzene-hexane.

**Chlorocarbonyl(N,N'-diphenylmalonamido)bis(triphenylphosphine)rhodium**,  $[\text{CH}_2(\text{CONHC}_6\text{H}_5)_2]\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ . To a stirred soln of 178 mg  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  in 50 ml  $\text{CH}_2\text{Cl}_2$  a soln of 67.3 mg N,N'-diphenylmalonamide in 20 ml of the same solvent was added, under  $\text{N}_2$ . The solvent was removed after 90 min of refluxing and the yellow residue was washed with

hexane. The yellow complex (187 mg) decomposes below its m.p. at 197–203°.

**Dichloro(isophthalonitrile)bis(triphenylphosphine)ruthenium**,  $[\text{m-C}_6\text{H}_4(\text{CN})_2]_2\text{RuCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_3$ . A soln of 250 mg  $\text{RuCl}_2(\text{PPh}_3)_3$  and 50 mg isophthalonitrile in 150 ml acetone was refluxed, under argon, for 15 hr during which the soln turned deep yellow. Concentration and addition of light petroleum ether gave 180 mg (81%) yellow crystals of m.p. 212–216° (dec) from acetone.

**Chloro(benzonitrile)oxo(ruthenium)bis(triphenylphosphine)rhodium**,  $\text{O}_2\text{RhCl}(\text{C}_6\text{H}_5\text{CN})[(\text{C}_6\text{H}_5)_3\text{P}]_3$ . A soln of 150 mg  $\text{RhCl}(\text{PPh}_3)_3$  was dissolved in 10 ml degassed benzonitrile under exclusion of air. After 2 hr at room temp the soln became almost colorless. When 100 ml of degassed heptane was added, a pale yellow ppt (60 mg) was obtained. On exposure to air it turned immediately into the orange dioxygen-complex that does not melt but decomposes below 300°.  $\nu_{\text{max}}^{\text{N}} 2280$  (C=N),  $852 \text{ cm}^{-1}$  (Rh-O<sub>2</sub>).

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