Journal of Organometallic Chemistry, 309 (1986) 333–344
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DODECACARBONYLTRIRUTHENIUM CATALYSED CARBONYLATION OF AMINES AND HYDROAMIDATION OF OLEFINS

YASUSHI TSUJI, TATSUYA OHSUMI, TERUYUKI KONDO and YOSHIHISA WATANABE*

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606 (Japan)

(Received November 15th, 1985; in revised form January 31st, 1986)

Summary

Dodecacarbonyltriruthenium ($Ru_3(CO)_{12}$) is an effective homogeneous catalyst precursor for the carbonylation of amines and hydroamidation of olefins under a carbon monoxide pressure of 40 kg cm^{-2} at 120–180°C. By the carbonylation of benzylamine, *N*-benzylformamide was obtained in 77% yield. 1-Octene was hydroamidated with benzylamine to *N*-benzylnonanamide in 67% yield (the selectivity to its linear isomer was 81%). These reactions appear to include ruthenium carbamoyl complex as the common key intermediate.

Introduction

The carbonylations of amines catalysed by transition metal complexes have been well studied [1]. Generally, the products obtained are *N*-substituted formamides, ureas and oxamides, depending on the nature of the catalyst employed and the reaction conditions.

In the catalytic carbonylation of amines to *N*-substituted formamides, $Co_2(CO)_8$ [2], $Ni(CO)_4$ [3] and $Fe(CO)_5$ [4] showed catalytic activities under rather severe reaction conditions, i.e. temperature over 200°C and carbon monoxide pressure between 95 and 200 atm. $[RhCl(CO)_2]_2$ was also used as a catalyst precursor with a large excess of phosphine [5]. As for ruthenium carbonyls, Kealy and Benson [6] found the formation of *N*-cyclohexylformamide from cyclohexylamine in the presence of allene using $Ru_3(CO)_{12}$ under an extremely high carbon monoxide pressure (1000 atm). Rempel et al. [7] reported that ruthenium acetate carbonyl complexes and $Ru_3(CO)_{12}$ were active catalysts for the carbonylation of secondary cyclic amines.

On the other hand, several attempts have been made to prepare *N*-substituted alkanamides from amines, olefins and carbon monoxide; so-called hydroamidation. Cobalt carbonyl complexes [8] or nickel cyanide [9] were mainly used as catalysts. Iron carbonyl [10] and ruthenium chloride [6] also showed some catalytic activity.

0022-328X/86/$03.50

However, all these reactions were carried out under very severe conditions. More recently, a patent literature [11] claimed the cobalt carbonyl catalyzed synthesis of *N*-substituted alkanamides from aliphatic amines, olefins and carbon monoxide (with primary amines as substrates at 200°C under a carbon monoxide pressure of 150 atm and with secondary amines under a carbon monoxide pressure of 110 atm).

In this paper, we report that $Ru_3(CO)_{12}$ is a highly active catalyst precursor for the carbonylation of amines to *N*-substituted formamides and hydroamidation of olefins under rather mild reaction conditions. The reaction mechanism is also discussed and the ruthenium carbamoyl species is postulated as the common key intermediate for the above two reactions.

Results

The carbonylation of amines to N-substituted formamides

Primary amines reacted with carbon monoxide in the presence of a catalytic amount of $Ru_3(CO)_{12}$ to give the corresponding *N*-substituted formamides (eq. 1).

$$RNH_2 + CO \xrightarrow{Ru_3(CO)_{12}} RNHCH \quad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

Several ruthenium as well as rhodium complexes were used as catalyst precursors in the carbonylation of benzylamine to *N*-benzylformamide. As shown in Table 1, $Ru_3(CO)_{12}$ showed the best catalytic activity among the complexes employed. *N*-Benzylformamide was obtained with 93% selectivity and 83% conversion (Run 2). A mononuclear zero-valent (η^6-1,3,5-cyclooctatriene)(η^4-1,5-cyclooctadiene)ruthenium (Ru(COD)(COT)) also showed some catalytic activity (Run 3). However, with $RuCl_2(PPh_3)_3$ as the catalyst, no carbonylation occurred, and dibenzylamine and tribenzylamine were obtained by an alkyl transfer reaction (Run 4). Similar alkyl transfer reactions were reported with ruthenium [12], palladium [13] and platinum [14] catalysts. When the rhodium catalyst was employed, the selectivity to *N*-benzylformamide was reduced owing to the considerable formation of dibenzylurea (Runs 5 and 6).

TABLE 1

CARBONYLATION OF BENZYLAMINE TO *N*-BENZYLFORMAMIDE. ACTIVITIES OF SEVERAL CATALYST PRECURSORS [a]

Run	Catalyst (mmol)	CO press. (kg cm^{-2})	T (°C)	Conv. [b] (%)	Selectivity (%) *N*-Benzylformamide
1	$Ru_3(CO)_{12}$ (0.067)	40	120	81	74
2	$Ru_3(CO)_{12}$ (0.133)	40	120	83	93
3	Ru(COD)(COT) (0.2)	40	120	66	61
4 [c]	$RuCl_2(PPh_3)_3$ (0.4)	50	200	87	0
5	$[RhCl(CO_2)]_2$ (0.4)	50	200	82	45
6	$Rh_6(CO)_{16}$ (0.068)	40	120	44	25
7 [d]	$Ru_3(CO)_{12}$ (0.067)	20	120	55	78

[a] Benzylamine (40 mmol), benzene (10 ml) for 6 h. [b] Conversion of benzylamine determined by GLC. [c] For 5 h. [d] Benzylamine (20 mmol).

TABLE 2

CARBONYLATION OF AMINES TO *N*-SUBSTITUTED FORMAMIDES [a]

Run	Amine	*T* (°C)	Conv. [b] (%)	Selectivity (%) *N*-Substituted formamide
8	Octylamine	120	61	71
9	Octylamine	180	100	91
10	Isobutylamine	120	65	24
11	Isobutylamine	180	100	71
12	1-Phenethylamine	120	58	71
13	1-Phenethylamine	180	85	85
14	Aniline	120	0	0
15 [c]	Piperidine	120	89	52

[a] Amine (40 mmol), $Ru_3(CO)_{12}$ (0.067 mmol), benzene (10 ml), CO (40 kg cm^{-2}) for 6 h. [b] Conversion of amine determined by GLC. [c] $Ru_3(CO)_{12}$ (0.133 mmol).

Rempel et al. have reported that $[Ru(CO)_2(OCOCH_3)]_n$, $[HRu(CO)_3]_n$ and $Ru_3(CO)_{12}$ are effective catalysts for the carbonylation of amines to formamide derivatives under quite mild conditions (CO 1 atm, at 75°C) [7]. However, under such reaction conditions, the carbonylation was very sluggish (reaction time 20–200 h) and the product yields were low to moderate (6–45%). Furthermore, they reported that the substrates were limited only to secondary cyclic amines. Acyclic secondary and primary amines were not substantially carbonylated under such reaction conditions. We expected that the scope of the reaction would be improved with the ruthenium catalysts under more forcing reaction conditions. As shown in Table 2, primary amines other than aniline were successfully carbonylated (Runs 1,2 and 8–13), while the carbonylation of piperidine gave *N*-formylpiperidine in moderate yield because of the corresponding urea formation (Run 15). Thus, $Ru_3(CO)_{12}$ is an effective catalyst for the carbonylation of basic primary amines ($pK_a > 9.6$) to the corresponding formamides.

The hydroamidation of olefins with primary amines and carbon monoxide

In the presence of olefins, $Ru_3(CO)_{12}$ is an effective catalyst for the carbonylation of amines to *N*-substituted alkanamides (eq. 2).

$$RNH_2 + R'CH{=}CH_2 + CO \xrightarrow{Ru_3(CO)_{12}} RNHC(=O)CH_2CH_2R' + RNHC(=O)-CH(CH_3)R' + RNHCHO \quad (2)$$

The activities of several ruthenium as well as rhodium complexes were examined, employing 1-octene and benzylamine as substrates ([1-octene]/[benzylamine] = 3.2 in molar ratio). The results are listed in Table 3. With $Ru_3(CO)_{12}$ as the catalyst, *N*-benzyl C_9-amides (*N*-benzylnonanamide and *N*-benzyl-2-methyloctanamide) were obtained with high selectivity and good conversion (Run 16). The percentage of the linear isomer, *N*-benzylnonanamide, in the C_9-amides was 81%. Ru(COD)(COT) showed some catalytic activity and $Ru(CO)_3(PPh_3)_2$ was less active in this hydro-

TABLE 3

HYDROAMIDATION OF 1-OCTENE WITH BENZYLAMINE AND CARBON MONOXIDE. ACTIVITIES OF SEVERAL CATALYST PRECURSORS [a]

Run	Catalyst (mmol)		Added ligand	Conv. [b] (%)	Selectivity (%)	
					N-Benzyl C_9-amide [c]	*N*-Benzyl formamide
16	$Ru_3(CO)_{12}$	(0.067)	–	76	88 (81)	7
17	Ru(COD)(COT)	(0.076)	–	56	68 (79)	4
18	$Ru(CO)_3(PPh_3)_2$	(0.2)	–	11	64 (86)	27
19	$Ru_3(CO)_{12}$	(0.067)	$P(OPh)_3$	24	42 (80)	8
20	$Ru_3(CO)_{12}$	(0.067)	PPh_3	0	0	0
21	$Ru_3(CO)_{12}$	(0.067)	$P(n\text{-}Bu)_3$	0	0	0
22	$[RhCl(CO)_2]_2$	(0.10)	–	66	83 (95)	12
23	$Rh_6(CO)_{16}$	(0.032)	–	73	64 (94)	7

[a] Benzylamine (40 mmol), 1-octene (126 mmol; 20 ml), phosphorus compound (0.4 mmol), CO (40 kg cm^{-2}) at 120 °C for 6 h. [b] Conversion of benzylamine determined by GLC. [c] Figures in parentheses are the percentages of the linear isomer in the N-benzyl C_9-amides.

amidation reaction (Runs 17 and 18). It is well known that phosphorus(III) ligands modify or improve the activities of transition-metal catalysts [15], but in this catalyst system, the addition of phosphorus compounds of various basicities reduced the catalytic activity drastically (Runs 19–21). The phosphorus ligands might saturate the coordination sites of the ruthenium catalyst centre. Rhodium complexes showed good catalytic activities, although they could not surpass $Ru_3(CO)_{12}$ in terms of conversion of the amine and selectivity to the *N*-substituted C_9-amides. However, it is noteworthy that the selectivity to the linear amide is exceedingly high with these rhodium catalysts (Runs 22 and 23).

The selectivity to *N*-benzyl C_9-amides was greatly affected by the molar ratio of the olefin to the amine charged (Table 4). *N*-Benzylformamide was the main product when the molar ratio of 1-octene to benzylamine was less than 2 (Runs 24 and 25). As the molar ratio increased, the formation of *N*-benzylformamide was reduced and the selectivity to *N*-benzyl C_9-amides increased. The *N*-benzyl C_9-amide

TABLE 4

HYDROAMIDATION OF 1-OCTENE WITH BENZYLAMINE AND CARBON MONOXIDE. EFFECT OF MOLAR RATIO OF OLEFIN TO AMINE [a]

Run	[1-Octene]/ $[PhCH_2NH_2]$	$PhCH_2NH_2$ (mmol)	Conv. [b] (%)	Selectivity (%)	
				N-Benzyl C_9-amide [c]	*N*-Benzyl formamide
24 [d]	1.0	40	100	14 (79)	84
25	1.6	40	78	24 (74)	58
16	3.2	40	76	88 (81)	7
26	6.3	20	77	91 (81)	trace

[a] $Ru_3(CO)_{12}$ (0.17 mol% based on amine charged), CO (40 kg cm^{-2}) at 120 °C for 6 h. [b] Conversion of benzylamine determined by GLC. [c] Figures in parentheses are the percentages of the linear isomer in the *N*-benzyl C_9-amides. [d] Benzene (20 ml) at 180 °C for 8 h.

TABLE 5

HYDROAMIDATION OF 1-OCTENE WITH BENZYLAMINE AND CARBON MONOXIDE. EFFECT OF SOLVENT [a]

Run	Solvent	Conv. [b] (%)	Selectivity(%)	
			N-Benzyl C_9-amide [c]	*N*-Benzyl formamide
26 [d]	–	77	91 (81)	Trace
16 [e]	–	76	88 (81)	7
27	DMF	93	9 (75)	84
28	Ethanol	86	42 (78)	33
29	Benzene	82	63 (79)	26

[a] Benzylamine (20 mmol), 1-octene (63 mmol), solvent (5.0 ml), $Ru_3(CO)_{12}$ (0.033 mmol), CO (40 kg cm^{-2}) at 120°C for 6 h. [b] Conversion of benzylamine determined by GLC. [c] Figures in parentheses are the percentages of the linear isomer in the *N*-benzyl C_9-amides. [d] 1-Octene (20 ml; 126 mmol). [e] Benzylamine (40 mmol), 1-octene (20 ml; 126 mmol).

derivatives were the main products at a molar ratio greater than 3 (Run 16), and at 6.3 almost no *N*-benzylformamide was detected (Run 26).

The selectivity to the products was also influenced by the nature of the solvents (Table 5). With dimethylformamide (DMF), which has a high coordination ability to the metal centre [16], the yield of *N*-benzyl C_9-amides decreased drastically and *N*-benzylformamide was obtained as the main product, maintaining the high conversion of benzylamine (Run 27). Apparently the yield of the C_9-amides increased in order of reducing coordination ability of the solvent employed (see below).

As shown in Table 6, other aliphatic primary amines were also carbonylated in the presence of 1-octene, although the selectivities to *N*-substituted C_9-amides were somewhat low compared with benzylamine. In all cases, *N*-substituted formamides were obtained as by-products. In several cases where the conversions of amines at

TABLE 6

HYDROAMIDATION OF 1-OCTENE WITH VARIOUS AMINES AND CARBON MONOXIDE [a]

Run	Amine	*T* (°C)	Conv. [b] (%)	Selectivity (%)	
				N-Substituted C_9-amide [c]	*N*-Substituted formamide
30	Octylamine	120	30	43 (69)	23
31	Octylamine	150	100	40 (75)	53
32	Octylamine	180	100	21 (76)	68
33	Butylamine	120	22	86 (77)	14
34	Butylamine	180	100	24 (75)	62
35	Isobutylamine	120	20	15 (73)	23
36	Isobutylamine	180	100	15 (67)	72
37	1-Phenetylamine	120	47	62 (79)	36
38	1-Phenetylamine	180	88	16 (71)	84
39	Aniline	120	0	0	0
40	Piperidine	120	53	4 (87)	15
41	Piperidine	180	77	1 (–)	55

[a] Amine (40 mmol), 1-octene (126 mmol), $Ru_3(CO)_{12}$ (0.067 mmol), CO (40 kg cm^{-2}) for 6 h. [b] Conversion of amine determined by GLC. [c] Figures in parentheses are the percentages of linear isomers in the *N*-substituted C_9-amides.

TABLE 7

HYDROAMIDATION OF ETHYLENE AND STYRENE [a]

Run	Olefin	Amine	Time (h)	T (°C)	Conv. [b] (%)	Selectivity (%)		
						N-Substituted Propanamide	*N*-Substituted Phenylpropanamide [c]	*N*-Substituted Formamide
42	Ethylene	Benzylamine	4	150	100	51	–	28
43	Ethylene	Octylamine	4	150	100	62	–	24
44	Styrene	Benzylamine	6	120	53	–	6 (23)	78
45	Styrene	Octylamine	6	120	100	–	9 (44)	90

[a] Ethylene (17 kg cm^{-2}; 60 mmol), styrene (60 mmol), amine (20 mmol), $Ru_3(CO)_{12}$ (0.03 mmol), benzene (10 ml), CO (40 kg cm^{-2}, initial). [b] Conversion of amine determined by GLC. [c] Figures in parentheses are the percentages of linear isomers in *N*-substituted phenylpropanamides.

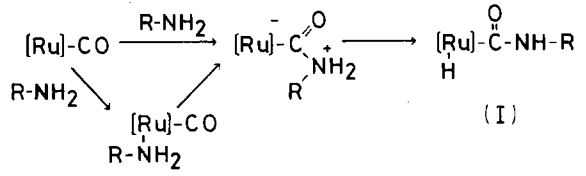
120°C were low, elevating the reaction temperature did not improve the selectivity to *N*-substituted C_9-amides and only resulted in increasing the formation of *N*-substituted formamides. Aniline was not carbonylated at all under the present hydroamidation conditions (Run 39). With piperidine, the selectivity to *N*-substituted C_9-amides was very low (Runs 40 and 41). This observation is totally distinct from that when a cobalt catalyst is used [11], in which case secondary amines such as piperidine react much more easily.

Ethylene also reacted with amines and carbon monoxide to give *N*-substituted propanamides in moderate selectivities (Table 7; Runs 42 and 43). On the other hand, with styrene, *N*-substituted phenylpropanamides were obtained in only low yields, while *N*-benzyl- and *N*-octylformamides were offered as the main products (Runs 44 and 45).

Discussion

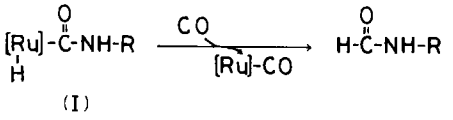
Carbamoyl species as the key intermediate

The reaction of metal carbonyl complexes with amines represents the most general method of preparing carbamoyl complexes [17]. Szostak et al. have reported that $Ru_3(CO)_{12}$ reacts with dimethylamine to produce a carbamoyl cluster complex [18]. In the present reaction, an analogous carbamoyl complex (I) seems to be the key intermediate, which is generated by intermolecular nucleophilic attack of the amine on the metal carbonyl ligands or by an intramolecular 1,2-shift reaction between coordinated carbon monoxide and amine (Scheme 1) [17,19]. We isolated a yellow complex from the reaction of $Ru_3(CO)_{12}$ with benzylamine (see Experimental section). This complex could not be characterized fully because of its low solubility,



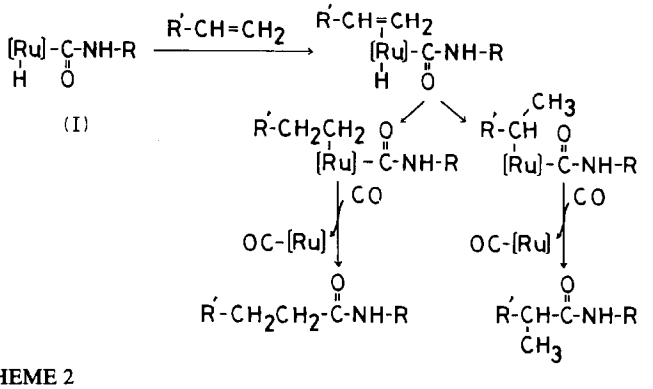
SCHEME 1

Path A



(I)

Path B



(I)

SCHEME 2

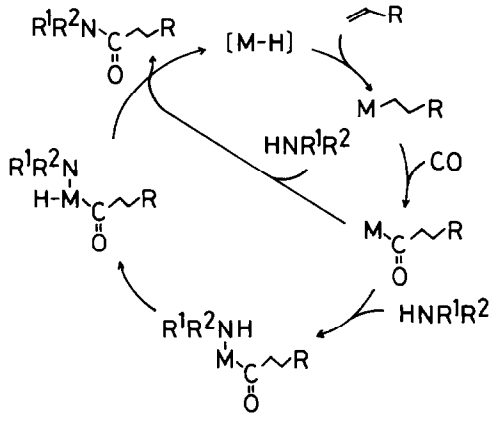
but the carbamoyl moiety in the complex was confirmed by the FT-IR absorption at 1570 cm^{-1} [20]. In the present reaction, *N*-substituted formamides would be afforded by the reductive elimination of the hydridocarbamoyl complex (I), as indicated by path A in Scheme 2.

The carbonylation of aniline did not occur at all (see above). Although primary and secondary alkylamines react smoothly with metal carbonyls to give the carbamoyl complexes, aniline and other aromatic amines have not yet been found to undergo a similar reaction with any metal carbonyl complex [17]. These less basic aromatic amines do not have enough nucleophilicity towards the coordinated carbon monoxide.

The hydroamidation of olefins

In the reaction to the *N*-substituted alkanamides from olefins, amines, and carbon monoxide, two reaction features were apparent which seem to be characteristic of the present $Ru_3(CO)_{12}$ catalysis. Firstly, *N*-substituted formamides were always formed as by-products. Secondly, the selectivities to *N*-substituted alkanamides and formamides were greatly affected by the molar ratio of the olefin to the amine. *N*-Substituted alkanamides were obtained in high selectivities only at a high molar ratio of the olefin to the amine.

The most probable route to the *N*-substituted alkanamide consistent with the above features seems to be path B in Scheme 2. The hydridocarbamoyl intermediate I is generated by the reaction between amines and coordinated carbonyl ligands (Scheme 1). Subsequently, the olefin coordinates to I and insertion of the olefin into the hydrido–metal bond occurs [22], and finally the *N*-substituted alkanamide is afforded by reductive elimination. *N*-Substituted formamides were obtained in considerable amounts especially when the molar ratio of the olefins to amines was



SCHEME 3

low. With such low concentrations of the olefins, the *N*-substituted formamides tend to be formed via the reductive elimination of I (path A, Scheme 2) prior to olefin insertion. A solvent of high coordination ability such as DMF reduced the formation of *N*-substituted alkanamide and increased the yield of *N*-substituted formamide. Such solvents interfered with the olefin coordination and insertion, and the *N*-substituted formamides were also produced via path A in Scheme 2.

There may be another route involving the formation of an acylmetal complex followed by nucleophilic attack of the amine on the acyl moiety (Scheme 3). This route has been proposed for the precedented transition metal catalysed hydroamidation of olefins by analogy of the hydroformylation reaction [21]. However, this mechanism cannot explain the reaction features observed in the present $Ru_3(CO)_{12}$ catalysis. With ethanol (20 mmol) or ethanol (20 mmol)/sodium ethoxide (3 mmol), instead of benzylamine, the hydroesterification of 1-octene did not proceed at all under similar reaction conditions (63 mmol 1-octene, 0.033 mmol $Ru_3(CO)_{12}$ under a carbon monoxide pressure of 40 kg cm^{-2} at 180°C for 4 h).

Experimental

Materials

The reagents employed in this study were commercial materials and were purified by distillation under an argon atmosphere. Carbon monoxide (> 99.9%) and ethylene were used without further purification. $Ru_3(CO)_{12}$ [23], Ru(COD)(COT) [24], $Ru(CO)_3(PPh_3)_2$ [25], $RuCl_2(PPh_3)_3$ [26], $[RhCl(CO)_2]_2$ [27] and $Rh_6(CO)_{16}$ [28] were prepared according to procedures in the literature. $RuCl_3 \cdot nH_2O$ (mainly $n = 3$) was purchased from Mitsuwa Chemicals and was used without further purification.

The carbonylation of amines

A 100 ml stainless-steel autoclave (Nitto Koatsu; SUS 316) equipped with a magnetic stirrer was used in the reactions. A glass liner was set in the autoclave and the inside was heated by a heat gun (400 W) for 2 min. The reactor was cooled in an

Ar stream and was charged with benzene (10 ml), amine (40 mmol) and $Ru_3(CO)_{12}$ (43 mg, 0.067 mmol; 0.17 mol% based on amine charged) in this order. After the reactor was sealed and purged with three 20 kg cm^{-2} pressurization-depressurization cycles of carbon monoxide, it was pressurized to 40 kg cm^{-2} with carbon monoxide (at room temperature). Then the autoclave was heated to 120°C in 15 min with stirring (500 rpm) and held at this temperature for 6 h. The reaction was terminated by rapid cooling, and the gaseous product was discharged. The resulting brown solution was analysed by GLC.

The hydroamidation of olefins

A mixture of 1-octene (20 ml, 126 mmol), amine (40 mmol) and $Ru_3(CO)_{12}$ (43 mg, 0.067 mmol; 0.17 mol% based on amine charged) was placed in the autoclave. The reaction was carried out in a similar manner to that described above.

Analytical procedure

The products were isolated by vacuum fractional distillation and/or medium pressure column chromatography (absorbent: silica gel or aluminium oxide; eluant: a mixture of hexane and ethyl acetate). The identity of the products was established by ^{13}C NMR, ^1H NMR, IR and elemental analyses.

GLC analyses were performed on a Shimadzu GC-8A chromatograph with columns (3 mm i.d. ×3 m) packed with PEG-HT (5% on Uniport HP, 60–80 mesh), Silicone OV-17 (5% on Chromosorb W(AW), 60–80 mesh), Gaskuropack 54 (60–80 mesh), and Thermon 3000 A (60–80 mesh).

^1H NMR spectra were obtained at 100 MHz and ^{13}C NMR spectra at 25.05 MHz with a JEOL JNM FX-100 spectrometer, using $CDCl_3$ and tetramethylsilane as the internal standard. IR spectra were measured on a Nicolet 5MX Fourier transform infrared spectrophotometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

The analytical data of the products are discribed below. The phenyl carbon resonances in the ^{13}C NMR spectra were tentatively assigned by calculating their chemical shifts with additive parameters [29].

N-Benzylformamide. White solid. ^{13}C NMR ($CDCl_3$): δ 42.1 (t, PhCH_2), 127.5 (d, phenyl 4), 127.6 (d, phenyl 2,6), 128.6 (d, phenyl 3,5), 137.6 (s, phenyl 1), 161.0 (d, *C*=O). The other spectral data were consistent with those of the authentic sample.

N-Octylformamide. Colourless oil. ^{13}C NMR ($CDCl_3$): δ 14.1 (q, CH_3), 22.7 (t, CH_2CH_3), 26.9 (t, $NH(CH_2)_2CH_2$), 29.2 (t, $NH(CH_2)_3(CH_2)_2$), 29.5 (t, $CH_2CH_2CH_3$), 31.8 (t, $NHCH_2CH_2$), 38.3 (t, $NHCH_2$), 161.4 (d, *C*=O). ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H, CH_3), 1.27 (br, 12H, $NHCH_2(CH_2)_6CH_3$), 3.22 (q, 2H, $NHCH_2$), 6.61 (br, 1H, N*H*), 8.12 (s, 1H, C*H*O). IR (neat): ν(N–H) 3275.4, ν(C=O) 1674.3, δ(N–H) 1543.2 cm^{-1}. Found: C, 68.99; H, 12.35; N, 9.03; O, 10.19. $C_9H_{19}NO$ calcd.: C, 68.74; H, 12.18; N, 8.91; O, 10.17%.

N-Formylpiperidine. Colourless oil. ^{13}C NMR ($CDCl_3$): δ 24.7 (t, $\overline{N(CH_2)_2CH_2(CH_2)_2}$), 25.1 and 26.2 (t, $\overline{NCH_2CH_2CH_2CH_2CH_2}$), 40.4 and 46.6 (t, $\overline{NCH_2(CH_2)_3CH_2}$), 160.5 (d, *C*=O). ^1H NMR ($CDCl_3$): δ 1.61 (br, 6H, $\overline{NCH_2(CH_2)_3CH_2}$), 2.97–3.57 (m, 4H, $\overline{NCH_2(CH_2)_3CH_2}$), 7.88 (s, 1H, C*H*O). IR (neat); ν(C=O) 1684.0 cm^{-1}.

N-Benzylnonanamide. White solid. ^{13}C NMR ($CDCl_3$): δ 14.1 (q, CH_3), 22.7 (t, CH_2CH_3), 25.9 (t, $COCH_2CH_2$), 29.4 (t, $CO(CH_2)_2(CH_2)_3$), 31.8 (t, $CO(CH_2)_5CH_2$), 36.4 (t, $COCH_2$), 43.2 (t, CH_2NH), 127.0 (d, phenyl 4), 127.4 (d, phenyl 2, 6), 128.3 (d, phenyl 3,5), 138.7 (s, phenyl 1), 173.6 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3), 1.27 (br, 10H, $(CH_2)_5CH_3$), 1.60 (m, 2H, $COCH_2CH_2$), 2.19 (t, 2H, $COCH_2$), 4.40 (d, 2H, CH_2NH), 6.14 (br, 1H, NH), 7.27 (br, 5H, phenyl). IR (KBr): ν(N–H) 3300.4, ν(C=O) 1639.6, δ(N–H) 1552.8 cm^{-1}. Found: C, 77.60; H, 10.28; N, 5.59; O, 6.22. $C_{16}H_{25}NO$ calcd.: C, 77.68; H, 10.19; N, 5.66; O, 6.47%.

N-Benzyl-2-methyloctanamide. White solid. ^{13}C NMR ($CDCl_3$): δ 14.1 (q, CH_2CH_3), 17.9 (q, $COCH(CH_3)$), 22.7 (t, CH_2CH_3), 27.5 (t, $COCH(CH_3)CH_2CH_2$), 29.4 (t, $COCH(CH_3)(CH_2)_2CH_2$), 31.8 (t, $COCH(CH_3)(CH_2)_3CH_2$), 34.4 (t, $COCH(CH_3)CH_2$), 41.1 (d, $COCH(CH_3)$), 43.9 (t, $NHCH_2$), 126.7 (d, phenyl 4), 127.1 (d, phenyl 2,6), 128.3 (d, phenyl 3,5), 140.0 (s, phenyl 1), 177.0 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, CH_2CH_3), 1.08 (d, 3H, $COCH(CH_3)$), 1.23 (br, 10H, $COCH(CH_3)(CH_2)_5$), 2.21 (m, 1H, $COCH(CH_3)$), 4.32 (d, 2H, $NHCH_2$), 6.79 (br, 1H, NH), 7.21 (br, 5H, phenyl). IR (KBr): ν(N–H) 3285.0, ν(C=O) 1651.2, δ(N–H) 1548.9 cm^{-1}.

N-(1-Phenylethyl)nonanamide. Yellow oil. ^{13}C NMR ($CDCl_3$): δ 14.1 (q, CH_2CH_3), 22.0 (q, $CH(CH_3)$), 22.6 (t, CH_2CH_3), 25.9 (t, $COCH_2CH_2$), 29.2 (t, $CO(CH_2)_4CH_2$), 29.3 (t, $CO(CH_2)_2(CH_2)_2$), 31.8 (t, $CO(CH_2)_5CH_2$), 36.5 (t, $COCH_2$), 47.4 (d, NHCH), 126.0 (d, phenyl 2,6), 126.8 (d, phenyl 4), 128.3 (d, phenyl 3,5), 143.9 (s, phenyl 1), 172.7 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, CH_2CH_3), 1.22 (br, 10H, $(CH_2)_5CH_3$), 1.35 (d, 3H, $NHCH(CH_3)$), 1.41 (br, 2H, $COCH_2CH_2$), 2.10 (t, 2H, $COCH_2$), 4.99 (m, 1H, $NHCH(CH_3)$), 7.12 (br, 5H, phenyl), 7.74 (d, 1H, NH). IR (neat): ν(N–H) 3277.3, ν(C=O) 1645.4, δ (N–H) 1543.2 cm^{-1}.

N-Benzylpropanamide. Pale yellow oil. ^{13}C NMR ($CDCl_3$): δ 9.9 (q, CH_3), 29.4 (t, $COCH_2$), 43.3 (t, $NHCH_2$), 127.1 (d, phenyl 4), 127.5 (d, phenyl 2,6), 128.4 (d, phenyl 3,5), 138.6 (s, phenyl 1), 174.0 (s, C=O). ^1H NMR ($CDCl_3$): δ 1.07 (t, 3H, CH_3), 2.09 (q, 2H, CH_2CH_3), 4.22 (m, 3H, $NHCH_2$), 7.11 (br, 5H, phenyl). IR (neat); ν(N–H) 3288.9, ν(C=O) 1647.3, δ (N–H) 1545.1 cm^{-1}.

N-Benzyl-3-phenylpropanamide. Pale yellow oil. ^{13}C NMR ($CDCl_3$): δ 31.6 (t, $COCH_2CH_2$), 38.1 (t, $COCH_2$), 43.3 (t, $NHCH_2$), 126.1, 127.1, 127.5, 128.4, and 128.7 (d, phenyl 2–6 and 2′–6′), 138.3 (s, phenyl 1), 140.8 (s, phenyl 1′), 172.1 (s, C=O). ^1H NMR ($CDCl_3$): δ 2.43 (t, 2H, $COCH_2CH_2$), 2.89 (t, 2H, $COCH_2$), 4.28 (d, 2H, $NHCH_2$), 6.29 (d, 1H, NH), 7.0–7.3 (m, 10H, phenyl). IR (neat): ν(N–H) 3296.6, ν(C=O) 1649.3, δ (N–H) 1548.9 cm^{-1}.

N-Benzyl-2-phenylpropanamide. Pale yellow oil. ^{13}C NMR ($CDCl_3$): δ 18.5 (q, CH_3), 43.3 (t, $NHCH_2$), 46.9 (d, $COCH(CH_3)$), 126.1, 127.1, 127.5, 128.4 and 128.7 (d, phenyl 2–6 and 2′–6′), 138.3 (s, phenyl 1), 141.3 (s, phenyl 1′), 174.1 (s, C=O). ^1H NMR ($CDCl_3$): δ 1.47 (d, 3H, CH_3), 3.56 (q, 1H, $COCH(CH_3)$), 4.28 (d, 2H, $NHCH_2$), 6.29 (d, 1H, NH), 7.0–7.3 (m, 10H, phenyl). IR (neat): ν(N–H) 3296.6, ν(C=O) 1649.3, δ(N–H) 1548.9 cm^{-1}.

Reaction of $Ru_3(CO)_{12}$ with benzylamine

To a hexane solution (30 ml) of $Ru_3(CO)_{12}$ (128 mg, 0.2 mmol), benzylamine (2.4 mmol) was added dropwise and the solution was stirred for 6 d at 40°C under an

Ar atmosphere. The reaction was monitored by FT-IR spectroscopy (1570 cm^{-1} absorption). The resulting red-brown solution was evaporated to dryness in vacuo. The residue was purified by column chromatography (absorbent: aluminium oxide; Merck Art 1077). Gradient elution was performed with n-hexane, ethyl acetate and methanol. On evaporation of the methanol fraction, yellow crystals (130 mg) were obtained. IR: 3427.7br. sh, 2926.2m, 2037.0m, 1967.5m, 1570.2sh, 1413.0sh cm^{-1}. Found: C, 33.50; H, 3.40; N, 2.69%.

References

1 (a) I. Tkatchenko, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon Press, Oxford, 1982, p. 173; (b) A. Rosenthal and I. Wender, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 1, Wiley-Interscience, New York, 1968, p. 405; (c) A. Mullen, in J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer Verlag, Berlin, 1980, p. 243; (d) G.W. Bird, Transition Metal Intermediates in Organic Synthesis, Academic Press, New York, 1967, p. 205; (e) P. Pino, F. Piacenti, and M. Bianchi, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley-Interscience, New York, 1977, p. 233.

2 H.W. Sternberg, I. Wender, R.A. Fiedel and M. Orchin, J. Am. Chem. Soc., 75 (1953) 3148.

3 Ya. Yu. Aliev, I.B. Romanova and L. Kh. Freidlin, Uzbeksk. Khim. Zh., No. 5 (1960) 72; Chem. Abstr., 55 (1961) 10444.

4 B.D. Dombek and R.J. Angelici, J. Catal., 48 (1977) 433.

5 D.D. Durad and C. Lassau, Tetrahedron Lett., (1969) 2329.

6 T.J. Kealy and R.E. Benson, J. Org. Chem., 26 (1961) 3126.

7 G.L. Rempel, W.K. Teo, B.R. James and D.V. Plackett, in D. Forster and J.F. Roth (Eds.), Homogeneous Catalysis II, Advances in Chemistry Series 132, Am. Chem. Soc., Washington, D.C., 1974, p. 166. J.J. Byerly, G.L. Rempel, N. Takebe and B.R. James, J. Chem. Soc., Chem. Commun., (1971) 1482.

8 N.S. Imyanitov and D.M. Rudkvsku, Zu. Pribl. Khim., 39 (1966) 2335; Chem. Abstr., 66 (1967) 10530. B.F. Crowe and O.C. Elmer, U.S. Pat. 2, 742, 502 (1956); Chem. Abstr., 50 (1956) 16849. B.K. Nefedov, N.S. Sergeeva and Ya. T. Eidus, Izu. Akad. Nauk. SSSR, Ser. Khim., 8 (1975) 1792; Chem. Abstr., 83 (1975) 205731.

9 W. Reppe and H. Kroper, Ger. Pat., 868, 149 (1951) and W. Reppe and H. Main, Brit. Pat., 672, 379 (1952); Chem. Abstr., 47 (1953) 5428.

10 A. Striegler and J. Weber, J. Prakt. Chem., 29 (1965) 281.

11 H. Isa, T. Inagaki and I. Kadoya, Japan Kokai, 75–129, 509.

12 Q. Arcelli, B.T. Khai and G. Prozi, J. Organomet. Chem., 231 (1982) C31. B.T. Khai, C. Concilio and G. Prozi, J. Organomet. Chem., 208 (1981) 249; idem, J. Org. Chem., 46 (1981) 1759. C.W. Jung, J.D. Fellmann and P.E. Garrou, Organometallics, 2 (1983) 1042. L. Shvo and R.M. Laine, J. Chem. Soc., Chem. Commun., (1980) 753. R.M. Laine, D.W. Thomas, and L.W. Cary, J. Am. Chem. Soc., 104 (1982) 1763.

13 S. Murahashi, N. Yoshimura, T. Tsumiyama and T. Kojima, J. Am. Chem. Soc., 105 (1983) 5002.

14 Y. Tsuji, J. Shida, R. Takeuchi and Y. Watanabe, Chem. Lett., (1984) 889.

15 J. Emsley and D. Hall, The Chemistry of Phosphorus, Harper & Row, London, Chapter 5, 1976.

16 T. Dunn and S. Buffagni, Nature, 188 (1960) 937; idem, J. Chem. Soc., (1961) 5105. C.L. Rollinson and R.C. White, Inorg. Chem., 1 (1962) 281. W.E. Bell, S.K. Madan, and J.E. Wills, Inorg. Chem., 2 (1963) 303.

17 R.J. Angelici, Acc. Chem. Res., 5 (1972) 335.

18 R. Szostak, C.E. Strouse and H.D. Kaesz, J. Organomet. Chem., 191 (1980) 243.

19 See Ref. 1(a), p. 177.

20 R.B. King, J. Am. Chem. Soc., 85 (1963) 1918. R.J. Angelici and D.L. Denton, Inorg. Chim. Acta, 2 (1968) 3. L. Busetto and R.J. Angelici, ibid., 2 (1968) 391. H. Behrens, E. Lindner and P. Passler, Z. Anorg. Allg. Chem., 365 (1969) 137. J. Palagyi and L. Marko, J. Organomet. Chem., 17 (1969) 453. S. Fukuoka, M. Ryang and S. Tsutsumi, J. Org. Chem., 33 (1968) 2973; idem, ibid., 36 (1971) 2721. S. Cenini, M. Pizzotti, F. Porta and La Monica, J. Organomet. Chem., 125 (1977) 95.

21 See Ref. 1(a), p. 176 and 1(e), p. 287.
22 D. Evans, J.A. Osborn and G. Wilkinson, J. Chem. Soc. (A), (1968) 3133. R.A. Sánchez-Delgado, J.S. Bradley and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1976) 399.
23 J.L. Dawes and J.D. Holmes, Inorg. Nucl. Chem. Lett., 7 (1971) 847. A. Mantovani and S. Cenini, Inorg. Synth., 16 (1976) 47.
24 K. Itoh, H. Nagashima, T. Ohshima, N. Ohshima and H. Nishiyama, J. Organomet. Chem., 272 (1984) 179.
25 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
26 T.A. Stephenson and G. Wilkinson, J. Nucl. Chem., 28 (1966) 945. P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12 (1970) 237.
27 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.
28 G.L. Rempel, P. Legzdins, H. Smith, and G. Wilkinson, Inorg. Synth., 13 (1978) 90. B.R. James and G.L. Rempel, Chem. Ind., (1971) 1036. G.L. Rempel and W.K. Teo, Inorg. Synth., 16 (1976) 49.
29 J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, p. 197.