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Dodecacarbonyltriruthenium catalyzed one-to-one addition of *N*-substituted formamides to olefins

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Abstract

Dodecacarbonyltriruthenium ($Ru_3(CO)_{12}$) showed high catalytic activity for the first one-to-one addition of *N*-substituted formamides to both terminal and internal olefins at 180–200 °C under a carbon monoxide pressure of 20 kg cm^{-2}. The addition of *N*-metylformamide to cyclopentene afforded *N*-methylcyclopentanecarboxamide in 90% yield.

Introduction

Formic acid and its derivatives, which are easily derived from carbon monoxide, are important as sources of functionalized C_1 units [1]. Isnard et al. recently revealed that $RuCl_2(PPh_3)_3$ catalyzes the addition of methyl formate to ethylene at 190–200 °C [2]. However, the catalytic activity was rather low and the applicable olefin was limited to ethylene. On the other hand, free radical addition of formamide derivatives to olefins induced by photo-irradiation [3] or radical initiators [4] has been well studied, but to our knowledge, a complex catalyzed addition of formamide derivatives to olefins has not yet been reported. Here we report the first example of transition metal catalyzed addition of *N*-substituted formamides to both terminal and internal olefins, which could be regarded as the *catalytic* activation of a functionalized C–H bond. The reaction mechanism is also discussed.

Results and discussion

N-Octyl and *N*-benzylformamide reacted with 1-hexene as a terminal olefin in the presence of a catalytic amount of $Ru_3(CO)_{12}$, to give the corresponding adducts (**1** + **2**) in 63 and 45% yields, respectively (eq. 1). Results are listed in Table 1. The

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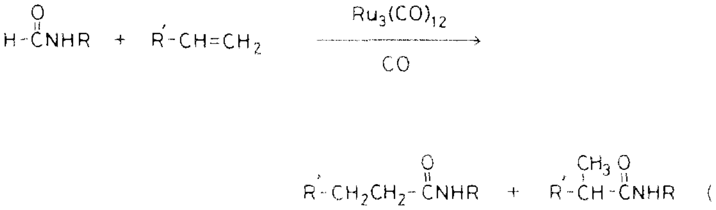


$$H\text{-}\overset{O}{\overset{\|}{C}}NHR + R'\text{-}CH{=}CH_2 \xrightarrow[CO]{Ru_3(CO)_{12}} R'\text{-}CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}NHR + R'\text{-}\overset{CH_3}{\overset{|}{C}H}\text{-}\overset{O}{\overset{\|}{C}}NHR \quad (1)$$

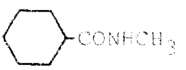
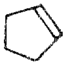
1 2

straight and branched adducts (**1**, **2**) were always produced in ca. 1.5/1 ratio (Runs 1, 2). In this catalyst system, cyclohexene and cyclopentene which are internal olefins, and thus should be less active, were also smoothly hydroamidated with *N*-substituted formamides and the corresponding adducts were obtained in excellent yields (Runs 3–5). On the other hand, formamide and *N*,*N*-dimethylformamide did not react with either 1-hexene or cyclohexene at all, partly because of their low solubility in olefins.

Effects of the reaction conditions, which were examined with *N*-octylformamide and 1-hexene, are summarized in Table 2. Carbon monoxide pressure is essential for the catalytic activity, and under an argon atmosphere, *N*-octylformamide was converted to various products and the yield of the adducts (**1** + **2**) was quite low (Run 6). However, higher carbon monoxide pressures suppressed the reaction considerably (Run 8). At 160 °C, both the conversion of *N*-substituted formamide, and the n/iso ratio of the adducts were low (Run 9), and elevation of the reaction temperature appreciably enhanced the yield and n/iso ratio of the adducts (Runs 9, 10, 1). When the reaction was quenched after 6 h, both conversion of *N*-oc-

Table 1

$Ru_3(CO)_{12}$ catalyzed one-to-one addition of *N*-substituted formamides to olefins [a]

Run	*N*-Substituted formamide	Olefin	Conv. [b] (%)	Product (%) [c]	
1	$HCONM\text{-}n\text{-}C_8H_{17}$	$n\text{-}C_4H_9CH{=}CH_2$	88	$n\text{-}C_6H_{13}CONH\text{-}n\text{-}C_8H_{17}$ $n\text{-}C_4H_9\overset{CH_3}{\overset{\vert}{C}H}\text{-}\overset{O}{\overset{\Vert}{C}}NH\text{-}n\text{-}C_8H_{17}$	38 25
2	$HCONHCH_2Ph$	$n\text{-}C_4H_9CH{=}CH_2$	100	$n\text{-}C_6H_{13}CONH\text{-}n\text{-}CH_2Ph$ $n\text{-}C_4H_9\overset{CH_3}{\overset{\vert}{C}H}\text{-}\overset{O}{\overset{\Vert}{C}}NHCH_2Ph$	29 17
3	$HCONHCH_3$		100		(87)
4	$HCONHCH_2Ph$		96		(73)
5	$HCONHCH_3$		100		(90)

[a] *N*-Substituted formamide (5 mmol), olefin (40 mmol), $Ru_3(CO)_{12}$ (0.05 mmol), CO (20 kg cm^{-2}) at 200 °C for 24 h. [b] Conversion of *N*-substituted formamide determined by GLC. [c] Determined by GLC based on the amount of *N*-substituted formamide charged and figures in parentheses are isolated yields.

Table 2

Effects of reaction conditions [a]

Run	CO pressure ($kg\ cm^{-2}$)	Temp. (°C)	Conv. [b] (%)	Yield [c] (%)	**1**/**2** [d]
6	0 [e]	180	71	16	63/37
7	10	200	93	63	68/32
1	20	200	88	63	61/39
8	40	200	50	38	48/52
9	20	160	15	6	50/50
10	20	180	58	47	52/48

[a] *N*-Octylformamide (5 mmol), 1-hexene (40 mmol), $Ru_3(CO)_{12}$ (0.05 mmol) for 24 h. [b] Conversion of *N*-octylformamide determined by GLC. [c] The yield of the adducts (**1** + **2**) determined by GLC based on the amount of *N*-octylformamide charged. [d] See eq. 1. [e] Under an argon atmosphere.

tylformamide and yield of the adducts were low (Run 11 in Table 3). When the reaction time was prolonged to 24 h, the yield of the corresponding adducts (**1** + **2**) reached 63% (Run 1 in Table 1).

Several transition-metal complexes were used as catalyst precursors in the addition of *N*-octylformamide to 1-hexene (Table 3). Although Isnard et al. reported that $RuCl_2(PPh_3)_3$ catalyzed the addition of methyl formate to ethylene [2], $RuCl_2(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$ showed no catalytic activity in the present reaction (Runs 12, 13). Other transition-metal carbonyls were also inactive in the present reaction (Runs 14–19). These results showed that this catalytic reaction was characteristic of $Ru_3(CO)_{12}$.

Although the radical chain mechanism was proposed for both previous reactions [3,4], radical initiators (1.0 mol% based on the *N*-substituted formamide), such as α,α'-azobisisobutyronitrile, benzoyl peroxide, and di-t-butyl peroxide were found not to induce the present reaction (Runs 20, 22, 24 in Table 4), and combination of $Ru_3(CO)_{12}$ with these radical initiators did not enhance the yield at all (Runs 21, 23, 25). Furthermore, addition of 2,6-di-t-butylphenol as a radical scavenger did not

Table 3

Activities of several catalyst precursors [a]

Run	Catalyst	Conv. [b] (%)	Yield [c] (%)	**1**/**2** [d]
11	$Ru_3(CO)_{12}$	56	24	69/31
12	$RuCl_2(PPh_3)_3$	0	0	–
13	$Ru(CO)_3(PPh_3)_2$	33	0	–
14	$Rh_6(CO)_{16}$	16	1	0/100
15	$Co_2(CO)_8$	2	0	–
16	$Fe(CO)_5$	10	0	–
17	$Fe_2(CO)_9$	20	0	–
18	$Fe_3(CO)_{12}$	23	0	–
19	$Re_2(CO)_{10}$	15	1	64/36

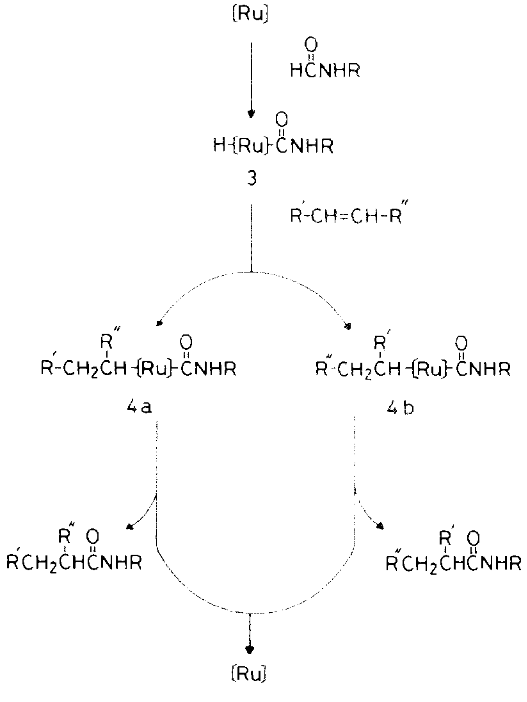
[a] *N*-Octylformamide (10 mmol), 1-hexene (80 mmol), catalyst (0.3 mmol as metal atom), CO (30 $kg\ cm^{-2}$) at 180 °C for 6 h. [b] Conversion of *N*-octylformamide determined by GLC. [c] The yield of the adducts (**1** + **2**) determined by GLC based on the amount of *N*-octylformamide charged. [d] See eq. 1.

Table 4

Reaction with radical initiator or radical scavenger [a]

Run	Catalyst	Additive	Conv. [b] (%)	Yield [c] (%)	**1**/**2** [d]
11	$Ru_3(CO)_{12}$	–	56	24	69/31
20	–	$(CH_3)_2\overset{CN}{\overset{\vert}{C}}N{=}N\overset{CN}{\overset{\vert}{C}}(CH_3)_2$	33	2	64/36
21	$Ru_3(CO)_{12}$	$(CH_3)_2\overset{CN}{\overset{\vert}{C}}N{=}N\overset{CN}{\overset{\vert}{C}}(CH_3)_2$	60	28	55/45
22	–	$(C_6H_5CO)_2O_2$	20	1	96/4
23	$Ru_3(CO)_{12}$	$(C_6H_5CO_2O_2$	61	22	81/19
24	–	$(CH_3)_3COOC(CH_3)_3$	35	2	80/20
25	$Ru_3(CO)_{12}$	$(CH_3)_3COOC(CH_3)_3$	91	13	48/52
26 [e]	$Ru_3(CO)_{12}$	2,6-di-t-butylphenol	45	23	67/33

[a] *N*-Octylformamide (10 mmol), 1-hexene (80 mmol), $Ru_3(CO)_{12}$ (0.1 mmol), additive (0.1 mmol), CO (30 kg cm^{-2}) at 180 °C for 6 h. [b] Conversion of *N*-octylformamide determined by GLC. [c] The yield of the adducts (**1** + **2**) determined by GLC based on the amount of *N*-octylformamide charged. [d] See eq. 1. [e] Additive (0.5 mmol).



Scheme 1

affect the reaction (Run 26), so a radical chain mechanism is apparently not involved in the present reaction [5*].

The most plausible route to the adducts is illustrated in Scheme 1. Oxidative addition of the *N*-substituted formamide to an active catalyst centre affords the hydridocarbamoyl intermediate (**3**) [6]. Coordination of olefin to **3** and insertion of the olefin into the hydrido–metal bond then provides the isomeric alkylcarbamoyl species (**4a**, **4b**). The adducts are then formed via a reductive elimination. A hydridocarbamoyl intermediate (**3**) has been isolated and the reaction sequences involving **3** have been outlined in a previous study [7]. Furthermore, in the present reaction, carbon monoxide pressure was essential for the catalytic activity (vide supra). It is suggested that carbon monoxide stabilizes some of the active catalyst species such as $Ru(CO)_5$ and $Ru_3(CO)_{12}$, (which were identified in the present reaction as FT-IR absorption bands at 1985 cm^{-1} [8] and at 2061, 2035, 2018 cm^{-1} [9] respectively, and/or promote the reductive elimination (last step in Scheme 1), and/or suppress the decarbonylation and decomposition of the *N*-substituted formamide (results of the run under an argon atmosphere: Run 6 in Table 2). In the course of the reaction, no decarbonylation of the *N*-substituted formamide to the corresponding amine and carbon monoxide was observed irrespective of whether olefin was present or not, showing that the present reaction proceeds via the direct addition of *N*-substituted formamides to olefins under carbon monoxide.

Experimental

Materials

The reagents used were purified by distillation under argon. *N*-Substituted formamides were prepared by a method described by Moffat [10]. Carbon monoxide (> 99.9%) was used without further purification. $RuCl_2(PPh_3)_3$ [11], $Ru(CO)_3(PPh_3)_2$ [12], $Rh_6(CO)_{16}$ [13], $Fe_2(CO)_9$ [14], $Fe_3(CO)_{12}$ [15] were prepared by published procedures. $RuCl_3 \cdot nH_2O$ (mainly $n = 3$) was purchased from Mitsuwa Chemicals and $Ru_3(CO)_{12}$, $Fe(CO)_5$, $Co_2(CO)_8$, $Re_2(CO)_{10}$ were purchased from Strem Chemicals and were used without further purification.

General procedure

A mixture of olefin (40 mmol), *N*-substituted formamide (5 mmol) and $Ru_3(CO)_{12}$ (0.05 mmol) was placed in a 50-ml stainless steel autoclave (Yuasa Giken; SUS 316) equipped with a glass liner and a magnetic stirring bar. The unit was sealed and then purged three times with 10 kg cm^{-2} pressurization-depressurization cycles of carbon monoxide. The reactor was then pressurized to 20 kg cm^{-2} with carbon monoxide (at room temperature), and the autoclave was heated to 180–200 °C within 15 min with stirring, and held at this temperature for 24 h. The reaction was terminated by rapid cooling, and gaseous products were discharged. The resulting orange solution was analyzed by GLC and FT-IR.

Analytical procedure

The products were isolated by vacuum fractional distillation and/or medium pressure column chromatography (absorbent: silica gel or aluminium oxide; eluent:

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* Reference number with asterisk indicates a note in the list of references.

a mixture of hexane and ethyl acetate). The products were identified by ^{13}C NMR, ^{1}H NMR, IR spectroscopy and from elemental analysis.

GLC analyses were performed on Shimadzu GC-4CM and GC-8A chromatographs with 3 mm i.d. × 3 m columns packed with Apiezon Grease L (5% on Neopak 1A, 60–80 mesh), Silicone OV-17 (5% on Chromosorb W(AW), 60–80 mesh), and PEG-HT (5% on Uniport HP, 60–80 mesh).

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

All products, except for *N*-benzylcyclohexanecarboxamide, whose ^{1}H NMR spectrum has been previously reported [16], are novel compounds. The spectral and analytical data of the products are shown below.

N-Octylheptanamide. White solid. m.p. 38.8–39.2 °C. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 14.1 (q, $2C\mathrm{H_3}$), 22.6 (t, $\mathrm{NH(CH_2)_6}C\mathrm{H_2CH_3}$), 22.7 (t, $\mathrm{CH_3}C\mathrm{H_2(CH_2)_4CO}$), 25.9 (t, $C\mathrm{H_2(CH_2)_3CO}$), 27.0 (t, $\mathrm{NH(CH_2)_5}C\mathrm{H_2}$), 29.1 (t, $C\mathrm{H_2(CH_2)_2CO}$), 29.3 (t, $\mathrm{NH(CH_2)_4}C\mathrm{H_2}$), 29.4 (t, $\mathrm{NH(CH_2)_3}C\mathrm{H_2}$), 29.7 (t, $\mathrm{NH(CH_2)_2}C\mathrm{H_2}$), 31.7 (t, $C\mathrm{H_2CH_2CO}$), 31.9 (t, $\mathrm{NHCH_2}C\mathrm{H_2}$), 36.8 (t, $C\mathrm{H_2CO}$), 39.6 (t, $\mathrm{NH}C\mathrm{H_2}$), 173.3 (s, $C\mathrm{{=}O}$). ^{1}H NMR($\mathrm{CDCl_3}$): δ 0.88 (t, 6H, $2\mathrm{C}H_3$), 1.27 (br, 20H, $\mathrm{C}H_2$), 1.42 (t, 2H, $\mathrm{CH_2C}H_2\mathrm{CO}$), 3.23 (m, 2H, $\mathrm{NHC}H_2$), 8.03 (br, 1H, $\mathrm{N}H$). IR (KBr): ν(N–H) 3340.9, ν(C=O) 1676.3, δ(N–H) 1539.3 cm^{-1}.

N-Octyl-2-methylhexanamide. White solid. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 14.0 (q, $C\mathrm{H_3}$), 18.0 (q, $\mathrm{CH(}C\mathrm{H_3)CO}$), 22.6 (t, $\mathrm{NH(CH_2)_6}C\mathrm{H_2}$), 22.7 (t, $\mathrm{CH_3}C\mathrm{H_2CH_2CH(CH_3)CO}$), 26.9 (t, $\mathrm{NH(CH_2)_5}C\mathrm{H_2}$), 29.1 (t, $\mathrm{NH(CH_2)_3}C\mathrm{H_2}C\mathrm{H_2}$), 29.7 (t, $C\mathrm{H_2CH_2CH(CH_3)CO}$), 29.8 (t, $\mathrm{NH(CH_2)_2}C\mathrm{H_2}$), 31.8 (t, $\mathrm{NHCH_2}C\mathrm{H_2}$), 34.1 (t, $C\mathrm{H_2CH(CH_3)CO}$), 39.3 (t, $\mathrm{NH}C\mathrm{H_2}$), 41.8 (d, $C\mathrm{H}$), 172.5 (s, $C\mathrm{{=}O}$).

N-Benzylheptanamide. White solid. m.p. 50.2–52.3 °C. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 14.0 (q, $C\mathrm{H_3}$), 22.5 (t, $\mathrm{CH_3}C\mathrm{H_2}$), 25.8 (t, $\mathrm{CH_3CH_2}C\mathrm{H_2}$), 29.0 (t, $\mathrm{CH_3(CH_2)_2}C\mathrm{H_2}$), 31.5 (t, $C\mathrm{H_2CH_2CO}$), 36.8 (t, $C\mathrm{H_2CO}$), 43.5 (t, $\mathrm{NH}C\mathrm{H_2C_6H_5}$), 127.3 (d, phenyl 4), 127.7 (d, phenyl 2, 6), 128.6 (d, phenyl 3, 5), 138.5 (s, phenyl 1), 173.1 (s, $C\mathrm{{=}O}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.87 (t, 3H, $\mathrm{C}H_3$), 1.26 (br, 4H, $\mathrm{C}H_2$), 1.60 (m, 2H, $\mathrm{C}H_2$), 2.18 (t, 2H, $\mathrm{C}H_2\mathrm{CO}$), 4.36 (d, 2H, $\mathrm{NHC}H_2\mathrm{C_6H_5}$), 6.29 (br, 1H, $\mathrm{N}H$), 7.25 (br, 5H, phenyl). IR(KBr): ν(N–H) 3292.7, ν(C=O) 1633.8, δ(N–H) 1548.9 cm^{-1}.

N-Benzyl-2-methylhexanamide. White solid. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 14.0 (q, $C\mathrm{H_3}$), 17.9 (q, $\mathrm{CH(}C\mathrm{H_3)CO}$), 22.7 (t, $\mathrm{CH_3}C\mathrm{H_2}$), 29.7 (t, $\mathrm{CH_3CH_2}C\mathrm{H_2}$), 34.0 (t, $\mathrm{CH_3(CH_2)_2}C\mathrm{H_2}$), 41.0 (d, $C\mathrm{H}$), 43.0 (t, $\mathrm{NH}C\mathrm{H_2C_6H_5}$), 127.0 (d, phenyl 4), 127.4 (d, phenyl 2, 6), 128.4 (d, phenyl 3, 5), 138.9 (s, phenyl 1), 177.0 (s, $C\mathrm{{=}O}$).

N-Methylcyclohexanecarboxamide. White crystals. m.p. 115.4–116.5 °C. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 25.8 (t, $\mathrm{CH_2(}C\mathrm{H_2)_3CH_2CHCO}$), 26.2 (q, $\mathrm{NH}C\mathrm{H_3}$), 29.7 (t, $C\mathrm{H_2(CH_2)_3}C\mathrm{H_2CHCO}$), 45.4 (d, $C\mathrm{HCO}$), 177.1 (s, $C\mathrm{{=}O}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.29–2.14 (m, 11H, $\mathrm{C}H_2\mathrm{(C}H_2\mathrm{)_4C}H\mathrm{CO}$), 2.78 (d, 3H, $\mathrm{NHC}H_3$), 6.68 (br, 1H, $\mathrm{N}H$). IR (KBr): ν(N–H) 3300.4, ν(C=O) 1643.5, δ(N–H) 1562.5 cm^{-1}. Found: C, 68.02; H, 10.93; N, 9.95; O, 11.33. $\mathrm{C_8H_{15}NO}$ calc: C, 68.05; H, 10.71; N, 9.92; O, 11.33%.

N-Benzylcyclohexanecarboxamide. White solid. Kugelrohr distillation (b.p. 80–90 °C/0.2 Torr). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 25.7 (t, $\mathrm{CH_2(}C\mathrm{H_2)_3CH_2CHCO}$), 29.7 (t, $C\mathrm{H_2(CH_2)_3}C\mathrm{H_2CHCO}$), 43.2 (t, $\mathrm{NH}C\mathrm{H_2C_6H_5}$), 45.4 (d, $C\mathrm{H}$), 127.2 (d, phenyl 4), 127.5 (d, phenyl 2, 6), 128.5 (d, phenyl 3, 5), 138.6 (s, phenyl 1), 176.0 (s, $C\mathrm{{=}O}$).

^1H NMR spectrum was consistent with it in the literature [16]. IR (KBr): ν(N–H) 3273.4, ν(C=O) 1641.5, δ(N–H) 1556.7 cm^{-1}. Found, C, 77.37; H, 9.00; N, 6.15. $C_{14}H_{19}NO$ calc: C, 77.38; H, 8.81; N, 6.45%.

N-Methylcyclopentanecarboxamide. Pale-yellow crystals. m.p. 56.0–57.5 ° C. ^{13}C NMR ($CDCl_3$): δ 26.0 (t, $CH_2(CH_2)_2CH_2CHCO$), 26.1 (q, $NHCH_3$), 30.5 (t, $CH_2(CH_2)_2CH_2CHCO$), 45.5 (d, CH), 177.2 (s, C=O). ^1H NMR ($CDCl_3$): δ 1.47–1.98 (m, 9H, $CH_2(CH_2)_3CHCO$), 2.76 (d, 3H, $NHCH_3$), 7.29 (br, 1H, NH). IR (KBr): ν(N–H) 3300.4, ν(C=O) 1639.6, δ(N–H) 1558.6 cm^{-1}. Found: C, 65.90; H, 10.43; N, 11.15; O, 12.76. $C_7H_{13}NO$ calc: C, 66.11; H, 10.30; N, 11.01; O, 12.58%.

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