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Gold nanoparticles assisted formation of cobalt species for intermolecular hydroaminomethylation and intramolecular cyclocarbonylation of olefins

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The intermolecular hydroaminomethylation and the intramolecular cyclocarbonylation efficiently proceeded on cobalt oxide supported gold nanoparticles. The intermolecular reaction employing terminal olefins and *N*-isopropylaniline afforded hydroaminomethylated products as a mixture of regioisomers *via* a common reaction path consisting of hydroformylation, imine formation, and hydrogenation. In contrast, indolinone derivatives were exclusively obtained in the case of 2-alkenylanilines based on the intramolecular cyclocarbonylation mechanism. Both of these reactions were catalyzed by cobalt species derived from cobalt oxide. The active cobalt species were formed *via* reduction of the oxide support promoted by deposited gold nanoparticles. Characterization of the catalysts before and after the reaction was also performed.

1. Introduction

In recent decades, gold nanoparticles (GNPs) have become one of the mainstreams in the field of catalysis. As a new era of GNPs catalysis was opened by an oxidation reaction,[1] a wide range of reactions can be carried out using GNPs.[2] Various types of GNP catalysts have been prepared by employing metal oxides, polymers, and carbon materials as supports.[3] Although the choice of support affects the performance and durability of catalysts, the catalysis is generally recognized as a function of deposited Au with the supplemental aid of the support. In contrast, we have recently reported a novel feature of cobalt oxide supported GNPs (Au/Co_3O_4) to supply cobalt active species under a syngas ($CO + H_2$) atmosphere.[4] The cobalt oxide is reduced by spillover hydrogen and the resulting Co(0) subsequently bound with CO to afford the cobalt carbonyl equivalent. In this process, the deposited GNPs just promote the reduction step by providing spillover hydrogen. A similar effect of Au was found in the literature on cobalt-catalyzed Fischer–Tropsch synthesis.[5] The *in situ* formed cobalt active species can be used as an alternative to homogeneous cobalt carbonyl to catalyze hydroformylation,[4a,b] amidocarbonylation,[4c] alkoxycarbonylation,[4d] Pauson–Khand reaction,[4d] and Fischer–Tropsch synthesis.[4e,f]

The hydroaminomethylation reaction is an elegant, atom-efficient, and clean approach to synthesize amines.[6] This tandem synthesis consists of three consecutive steps: (1) an initial hydroformylation of olefins to aldehydes; (2) reaction of resulting aldehydes with primary or secondary amines to give the corresponding intermediate imines or enamines; and (3) hydrogenation of the intermediates to the desired secondary or tertiary amine products as shown in Scheme 1. The amine product is generally obtained as a mixture of linear and branched products. The ratio of linear and branched products (l/b ratio) of the reaction obviously depends on the product distribution at the stage of the initial hydroformylation step. Homogeneous Rh-based catalysts are commonly employed for this reaction because of their high activity in the initial hydroformylation step and moderate activity in hydrogenation.[7,8] In this study, intermolecular and intramolecular hydroaminomethylation reactions were investigated to elucidate the compatibility of the Au/Co_3O_4 catalyst system with various amines. In addition, the characterization of catalysts before and after the reaction was also carried out.

2. Experimental section

2.1 General remarks

^1H NMR and ^{13}C NMR spectra were recorded on JEOL AL-400, JEOL JNM-ECS400, and Bruker DRX-600. ^1H assignment

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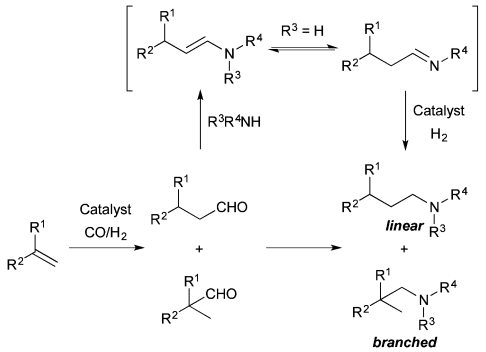


Scheme 1 Intermolecular hydroaminomethylation of olefins in the presence of primary or secondary amines.

abbreviations are the following; singlet (s), doublet (d), triplet (t), quartet (q), heptet (hept), broad singlet (brs), doublet of doublets (dd), doublet of triplets (dt), doublet of doublets of doublets (ddd), doublet of doublets of quartets (ddq), and multiplet (m). Elemental analysis was performed at the center of elemental analysis of Kyushu University. Chromatographic purification was performed on silica gel (Kanto Chemicals, Silica gel 60N, spherical, neutral). GC analysis was carried out using an Agilent GC 6850 series II equipped with a HP-1 Column (length 30 m, 0.32 mm I.D.). The recycle GPC purification was performed on a JAI LC-908. All reactions were conducted in a 50 mL stainless steel autoclave reactor (Toyo Koatsu Co. Ltd.) with a glass tube equipped inside. All commercial chemicals were used as received unless otherwise noted. Piperidine, *N*-methylaniline, and *N*-isopropylaniline were distilled under a reduced pressure prior to use. Temperature programmed reduction (TPR) profiles were measured with a BEL Japan, BELCAT equipped with a thermal conductivity detector (TCD). High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed using a JEOL JEM-ARM200F operating at 200 kV at the research laboratory for high vacuum electron microscopy (HVEM), Kyushu University. X-ray powder diffraction (XRD) measurements were performed using a Rigaku MultiFlex at a scanning rate of 2° min^{-1} and a sampling angle interval of 0.02° in the 2θ range of 10° to 80° with Cu-Kα radiation (λ = 0.151478 nm). The operating voltage and current were 40 kV and 40 mA. Crystalline phases were identified by matching the diffraction patterns to the JCPDS powder diffraction file. The content of metals in the reaction mixtures was determined using an Agilent 4100 Microwave Plasma-Atomic Emission spectrometer.

2.2 Preparation of catalysts

The 5 and 10 atom% Au/Co_3O_4 catalysts were prepared by the coprecipitation method.[4] This was performed by adding an aqueous solution containing $Co(NO_3)_2{\cdot}6H_2O$ and $HAuCl_4{\cdot}4H_2O$ to an aqueous solution of sodium carbonate at room temperature. The coprecipitates were washed with water, dried overnight at 100 °C, and calcined at 400 °C for 4 h. The gold loading was expressed by atom% = 100 × Au/(Au + Co).

2.3 Typical procedure for the intermolecular hydroaminomethylation of olefins (Table 2)

The 5 atom% Au/Co_3O_4 catalyst (20 mg, 0.75 mol% Au and 13.8 mol% Co to olefin) and heptane (2 mL) were introduced into the autoclave reactor and were then purged with hydrogen twice. The pressure was adjusted to 2 MPa at room temperature. Then, the temperature was elevated to 100 °C to pretreat the catalyst for 3 h. After pre-treatment, the catalyst and solvent were cooled to room temperature and then the olefin substrate (1.6 mmol) and *N*-isopropylaniline (2 mL, 14 mmol) were introduced into the autoclave in sequence. The autoclave was purged with syngas (CO/H_2 = 1/1) twice and then the pressure was adjusted to 4 MPa at room temperature. The temperature was elevated to 120 °C to start the reaction. After the time indicated in Table 2, the reaction mixture was analyzed by GC and purified by silica gel column chromatography to obtain hydroaminomethylation products as a mixture of regioisomers. Further isolation of the major isomer was carried out by recycle GPC. Characterization of the product was performed by GC, GC-MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

***N*-Heptyl-*N*-isopropylaniline (4a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 6.8 Hz, 3H), 1.17 (d, J = 6.6 Hz, 6H), 1.27–1.36 (m, 8H), 1.52–1.59 (m, 2H), 3.09 (t, J = 8.0 Hz, 2H), 4.03 (hept, J = 6.6 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 6.72 (d, J = 8.3 Hz, 2H), 7.20 (dd, J = 8.3, 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 20.0, 22.6, 27.3, 29.1, 29.3, 31.9, 44.0, 48.5, 113.2, 115.9, 129.1, 148.8; elemental analysis calcd (%) for $C_{16}H_{27}N$: C 82.34, H 11.66, N 6.00; found: C 82.22, H 11.74, N 5.84.

***N*-Isopropyl-*N*-nonylaniline (5).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.8 Hz, 3H), 1.16 (d, J = 6.6 Hz, 6H), 1.24–1.33 (m, 12H), 1.51–1.59 (m, 2H), 3.08 (t, J = 7.9 Hz, 2H), 4.03 (hept, J = 6.6 Hz, 1H), 6.64 (t, J = 7.2 Hz, 1H), 6.72 (d, J = 8.5 Hz, 2H), 7.20 (dd, J = 7.1, 7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 20.1, 22.7, 27.3, 29.3, 29.4, 29.5, 29.7, 31.9, 44.0, 48.5, 113.2, 115.8, 129.1, 148.8; elemental analysis calcd (%) for $C_{18}H_{31}N$: C 82.69, H 11.95, N 5.36; found: C 82.62, H 11.92, N 5.37.

***N*-Isopropyl-*N*-tridecylaniline (6).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.16 (d, J = 6.6 Hz, 6H), 1.22–1.33 (m, 20H), 1.50–1.60 (m, 2H), 3.09 (t, J = 8.0 Hz, 2H), 4.03 (hept, J = 6.6 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 6.72 (d, J = 8.4 Hz, 2H), 7.20 (dd, J = 8.4, 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 20.1, 22.7, 27.3, 29.4, 29.5, 29.62, 29.64, 29.66, 29.68, 29.69, 29.70, 31.9, 44.0, 48.5, 113.2, 115.8, 129.1, 148.8; elemental analysis calcd (%) for $C_{20}H_{35}N$: C 83.21, H 12.38, N 4.41; found: C 83.07, H 12.32, N 4.39.

***N*-(4,4-Dimethylpentyl)-*N*-isopropylaniline (7).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 9H), 1.17 (d, J = 6.6 Hz, 6H), 1.17–1.21 (m, 2H), 1.48–1.57 (m, 2H), 3.05 (t, J = 8.1 Hz, 2H), 4.05 (hept, J = 6.6 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 6.71 (d, J = 8.8 Hz, 2H), 7.21 (dd, J = 8.8, 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.0, 24.6, 29.4, 30.2, 41.4, 44.8, 48.2, 112.9, 115.8, 129.2, 148.8; elemental analysis calcd (%) for $C_{16}H_{27}N$: C 82.34, H 11.66, N 6.00; found: C 82.21, H 11.77, N 5.92.

***N*-(2-Cyclohexylethyl)-*N*-isopropylaniline (8).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92–1.03 (m, 2H), 1.11–1.37 (m, 4H), 1.16 (d, J = 6.6 Hz, 6H), 1.46 (m, 2H), 1.64–1.78 (m, 5H), 3.14 (t, J = 8.3 Hz, 2H), 4.03 (hept, J = 6.6 Hz, 1H), 6.64 (t, J = 7.2 Hz, 1H), 6.72 (d, J = 8.3 Hz, 2H), 7.20 (dd, J = 7.2, 8.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.0, 26.3, 26.6, 33.4, 36.4, 36.7, 41.9, 48.4, 113.1, 115.7, 129.1, 148.8; elemental analysis calcd (%) for $C_{17}H_{23}N$: C 83.20, H 11.09, N 5.71; found: C 83.13, H 11.02, N 5.71.

***N*-(Bicyclo[2.2.1]heptan-2-ylmethyl)-*N*-isopropylaniline (9).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02–1.13 (m, 4H), 1.10 (d, J = 6.7 Hz, 3H), 1.18 (d, J = 6.7 Hz, 3H), 1.32–1.34 (m, 1H), 1.36–1.40 (m, 1H), 1.43–1.46 (m, 2H), 1.69–1.76 (m, 1H), 2.12 (brs, 1H), 2.21 (brs, 1H), 2.74 (dd, J = 5.6, 14.5 Hz, 1H), 2.87 (dd, J = 9.0, 14.5 Hz, 1H), 3.97 (hept, J = 6.7 Hz, 1H), 6.72 (d, J = 7.2 Hz, 1H), 6.84 (dd, J = 8.8, 8.8 Hz, 2H), 7.21 (dd, J = 8.8, 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.8, 20.5, 28.9, 29.8, 35.4, 36.0, 36.3, 39.4, 40.3, 49.0, 51.5, 116.2, 117.2, 128.8, 149.6; elemental analysis calcd (%) for $C_{17}H_{25}N$: C 83.89, H 10.35, N 5.75; found: C 83.51, H 10.74, N 5.74.

2.4 Typical procedure for the intramolecular cyclocarbonylation of 2-isopropenylanilines (Table 3)

The 10 atom% Au/Co_3O_4 catalyst (20 mg, 1.4 mol% Au and 12 mol% Co to substrate) and heptane (2 mL) were introduced into the autoclave reactor and were then purged with hydrogen twice. The pressure was adjusted to 2 MPa at room temperature. Then, the temperature was elevated to 100 °C to pretreat the catalyst for 3 h. After pre-treatment, the catalyst and solvent were cooled to room temperature and then 2-isopropenylaniline substrate **11**[8a,9] (1.6 mmol) was introduced into the autoclave. The autoclave was purged with syngas or CO twice and then the pressure was adjusted to an initial pressure given in Table 3 at room temperature. The temperature was elevated to start the reaction. After 24 h, the reaction mixture was analyzed by GC and purified by silica gel column chromatography to obtain hydroaminomethylation products as a mixture of regioisomers. Further isolation of the major isomer was carried out by recycle GPC. Characterization of the products was performed by GC, GC-MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis. ^{1}H and ^{13}C NMR spectra of **12a–c** and **13a,b** were in agreement with those of the reported one.

3,3-Dimethylindolin-2-one (12a)[10]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 6H), 6.92 (d, J = 8.2 Hz, 1H), 7.04 (dd, J = 7.5, 7.5 Hz, 1H), 7.18–7.22 (m, 2H), 8.19 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4 (2C), 44.7, 109.8, 122.6, 122.8, 127.7, 136.3, 139.7, 183.7; elemental analysis calcd (%) for $C_{10}H_{11}NO$: C 74.51, H 6.88, N 8.69; found: C 74.67, H 6.97, N 8.66.

1,3,3-Trimethylindolin-2-one (12b)[11]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 6H), 3.21 (s, 3H), 6.84 (d, J = 7.8 Hz, 1H), 7.05 (ddd, J = 1.0, 7.5, 7.5 Hz, 1H), 7.20 (ddd, J = 0.5, 1.3, 7.4 Hz, 1H), 7.25 (ddd, J = 1.3, 7.7, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5 (2C), 26.3, 44.2, 108.1, 122.3, 122.5, 127.7, 135.9, 142.7, 181.4; elemental analysis calcd (%) for C11H13NO: C 75.40, H 7.48, N 7.99; found: C 75.39, H 7.67, N 7.99.

1-Benzyl-3,3-dimethylindolin-2-one (12c)[12]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 6H), 4.92 (s, 2H), 6.72 (d, J = 7.8 Hz, 1H), 7.02 (dd, J = 7.6, 7.6 Hz, 1H), 7.13 (dd, J = 7.8, 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.24–7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6 (2C), 43.6, 44.3, 109.2, 122.4, 122.6, 127.3 (2C), 127.6, 127.7, 128.9 (2C), 135.9, 136.2, 141.8, 181.5.

4-Methyl-3,4-dihydroquinolin-2(1*H*)-one (13a)[13]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (d, J = 6.9 Hz, 3H), 2.42 (dd, J = 7.2, 16.2 Hz, 1H), 2.74 (dd, J = 5.6, 16.2 Hz, 1H), 3.13 (ddq, J = 6.9, 6.9, 6.9 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 7.03 (dd, J = 7.8, 7.8 Hz, 1H), 7.16–7.21 (m, 2H), 8.07 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 30.8, 38.4, 115.5, 123.5, 126.7, 127.6, 128.9, 136.4, 171.1; elemental analysis calcd (%) for $C_{10}H_{11}NO$: C 74.51, H 6.88, N 8.69; found: C 74.68, H 6.94, N 8.66.

1,4-Dimethyl-3,4-dihydroquinolin-2(1*H*)-one (13b)[14]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (d, J = 7.0 Hz, 3H), 2.45 (dd, J = 7.6, 15.8 Hz, 1H), 2.73 (dd, J = 5.5, 15.8 Hz, 1H), 3.05 (ddq, J = 6.9, 6.9, 6.9 Hz, 1H), 3.36 (s, 3H), 6.99 (d, J = 8.1 Hz, 1H), 7.05 (dd, J = 7.5, 7.5 Hz, 1H), 7.20 (d, J = 7.0 Hz, 1H), 7.23–7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 29.5, 30.4, 39.2, 114.9, 123.1, 126.3, 127.5, 131.1, 139.9, 170.0; elemental analysis calcd (%) for $C_{11}H_{13}NO$: C 75.40, H 7.48, N 7.99; found: C 75.22, H 7.52, N 7.80.

3-Benzylindolin-2-one (15)[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (dd, J = 13.7, 9.2 Hz, 1H), 3.50 (dd, J = 13.7, 4.6 Hz, 1H), 3.75 (dd, J = 9.2, 4.6 Hz, 1H), 6.73 (d, J = 7.3 Hz, 1H), 6.85–6.91 (m, 2H), 7.14–7.27 (m, 6H), 9.15 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.7, 47.7, 109.9, 122.1, 124.9, 126.8, 128.1, 128.5, 129.1, 129.5, 137.9, 141.6, 180.1.

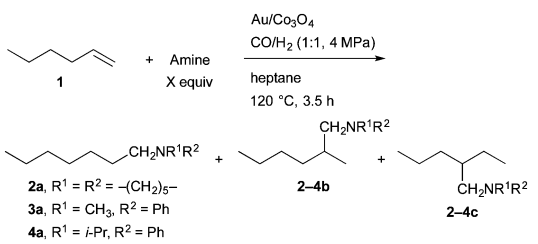
1-Phenylpyrrolidin-2-one (18)[16]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (tt, J = 7.6, 7.6 Hz, 2H), 2.61 (t, J = 8.0 Hz, 2H), 3.86 (t, J = 7.1 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.36 (dd, J = 8.0, 8.0 Hz, 2H), 7.60 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 32.9, 48.9, 120.1 (2C), 124.6, 128.9 (2C), 139.4, 174.4.

3. Results and discussion

3.1 Intermolecular hydroaminomethylation catalyzed by Au/Co_3O_4

The intermolecular hydroaminomethylation of 1-hexene (**1**) was investigated by employing piperidine, *N*-methylaniline, and *N*-isopropylaniline (Table 1). Piperidine completely suppressed the initial hydroformylation of **1** to aldehydes probably due to a strong coordination to the active cobalt site (Table 1, entry 1). Although all of **1** was converted into corresponding aldehydes in the presence of *N*-methylaniline, aldol condensation of the resulted aldehydes was dominant over the formation of imine intermediates (Table 1, entry 2). In the case of *N*-isopropylaniline, results highly depended on the amount of amine. With 1.3 equiv. of amine, a significant amount of the aldehyde intermediate remained (Table 1, entry 3). The yield of desired tertiary amines reached 89% by using 8.8 equiv. of *N*-isopropylaniline (Table 1, entry 4). When the amount of *N*-isopropylaniline was further increased from 8.8 equiv., the

Table 1 Effect of the structure and amount of amines on the intermolecular hydroaminomethylation of 1-hexene catalyzed by Au/Co_3O_4[a]



Entry	Amine (equiv.)	Conv.[b] (%)	Yield[b] (%)		
1	Piperidine (8.8)	0	0 (**2a**)	0 (**2b**)	0 (**2c**)
2[c]	*N*-Methylaniline (8.8)	100	16 (**3a**)	17 (**3b**)	6 (**3c**)
3[d]	*N*-Isopropylaniline (1.3)	85	18 (**4a**)	0 (**4b**)	0.2 (**4c**)
4	*N*-Isopropylaniline (8.8)	100	61 (**4a**)	22 (**4b**)	6 (**4c**)
5	*N*-Isopropylaniline (13.1)	84	30 (**4a**)	11 (**4b**)	2 (**4c**)
6	*N*-Isopropylaniline (17.5)	0	0 (**4a**)	0 (**4b**)	0 (**4c**)

[a] Reaction conditions: 5 atom% Au/Co_3O_4 (20 mg, 0.75 mol% Au and 13.8 mol% Co to **1**), 120 °C, 3.5 h, p(CO) = 2 MPa, $p(H_2)$ = 2 MPa, hetpane + amine = 28 mmol, 1-hexene (1.6 mmol). [b] Determined by GC. [c] Heavily branched aldehydes (57%) and heavy amines (4%) were also formed. [d] Remaining unreacted aldehyde intermediate (55%).

catalytic activity was gradually depressed till completely deactivated at the amount of 17.5 equiv. (Table 1, entries 5 and 6). After the reaction under the condition shown in entry 4, the contents of Co and Au in the reaction mixture were determined by MP-AES. Whereas a small amount of leached Co (2.1%) was found in the solution, leaching of Au was not practically observed (0.08%).

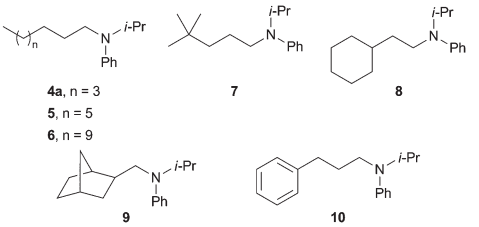
To generalize this method to the synthesis of tertiary amines, various olefins have been investigated. As shown in Table 2, most of selected olefins gave desired tertiary amines in high yields. The reactivity of olefins and the linear/branched (l/b) ratio of product amines were similar to that of the hydroformylation reaction.[4a,b] This result indicated that the amine products were afforded *via* a similar reaction sequence as shown in Scheme 1. In all cases except styrene, linear products were obtained as major products. Although

Table 2 Hydroaminomethylation of various olefins with *N*-isopropylaniline catalyzed by Au/Co_3O_4[a]

Entry	Olefin	Time (h)	Yield of amines[b] (%)	Selectivity of normal product[c] (%)
1	*cis*-2-Hexene	17	86	65 (**4a**)
2	1-Octene	3.5	89	66 (**5**)
3	1-Dodecene	4.5	94	59 (**6**)
4	3,3-Dimethyl-1-butene	4	90	94 (**7**)
5	Methylenecyclohexane	21	71	56 (**8**)
6	2-Norbornene	18	92	81 (**9**)
7	Styrene	18	11	41 (**10**)

[a] Reaction condition: 5 atom% Au/Co_3O_4 (20 mg, 0.75 mol% Au and 13.8 mol% Co to olefin), 120 °C, p(CO) = 2 MPa, $p(H_2)$ = 2 MPa, heptane (2 mL), *N*-isopropylaniline (14 mmol), olefin (1.6 mmol). [b] Determined by GC. [c] Calculated as (100× yield of normal product/total yield of products).

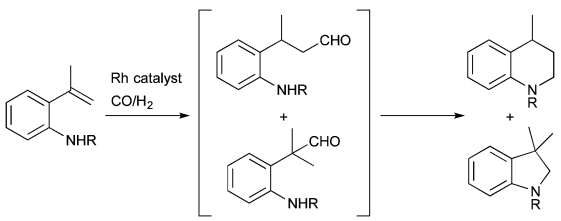
both 1-hexene and *cis*-2-hexene gave **4a** as the major product, the latter took a longer reaction time since isomerization of olefin was involved in the reaction course (Table 1, entry 4 *vs.* Table 2, entry 1). For methylenecyclohexane, the yield of amine products was slightly lower (71%, Table 2, entry 5). In the case of styrene, the hydrogenation to ethylbenzene was much faster, which therefore gave desired amines in very low yields of 11% (Table 2, entry 7). The dominance of hydrogenation over the objective reactions is often observed in cobalt-catalyzed hydroformylation of styrene derivatives.[17]



3.2 Intramolecular cyclocarbonylation catalyzed by Au/Co_3O_4

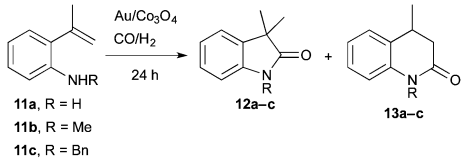
As for intramolecular hydroaminomethylation of 2-alkenylaniline derivatives, which has been demonstrated by rhodium-based catalysts[8a] (Scheme 2), the expected reaction did not occur. Instead, cyclocarbonylation to lactams proceeded in good yields and regioselectivities (Table 3). Under high H_2 partial pressure, reduction of the C–C double bond was dominant and a significant amount of 2-isopropylaniline was formed (Table 3, entry 1). Along with increasing CO partial pressure, the selectivity of lactam products was improved (Table 3, entries 2 and 3). However, a minimum amount of H_2 seemed to be essential for the *in situ* formation of cobalt active species by the hydrogenation of the cobalt oxide support (Table 3, entry 4). The product distribution also depended on the substrates. A benzyl compound **11c** exclusively gave an indolinone **12c** (Table 3, entry 6).

Under the similar conditions, the cyclocarbonylation of aniline derivatives proceeded with various substrates (Scheme 3). Due to steric reasons, the substrates having an internal multiple bond such as **14** and **16** required a longer reaction time than **11** and gave indolinone products in moderate yields. The same transformations using homogeneous Pd,[18a] $Rh_6(CO)_{16}$,[19a] and Co/Rh bimetallic nanoparticles[19b] are reported. *N*-allylaniline **17** formed the desired lactam **18** only in 30% yield even after a prolonged reaction time, suggesting



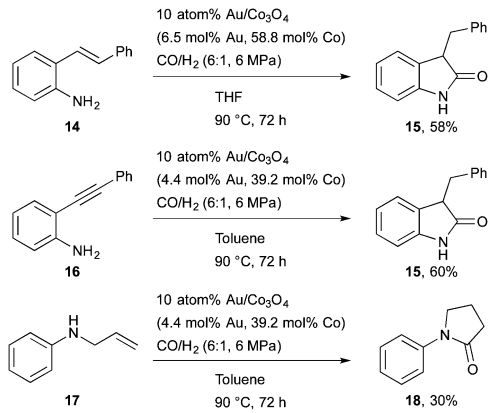
Scheme 2 Rhodium catalyzed intramolecular hydroaminomethylation of 2-isopropenylanilines to tetrahydroisoquinolines and indolines.

Table 3 Au/Co_3O_4-catalyzed intramolecular cyclocarbonylation of 2-isopropenylanilines[a]



Entry	Pressure (CO/H_2, MPa)	Temp. (°C)	Substrate	Yield[b] (%)	
1[c]	1/1, 4	120	**11a**	39 (**12a**)	13 (**13a**)
2[d]	3/1, 4.5	90	**11a**	69 (**12a**)	14 (**13a**)
3	5/1, 6	90	**11a**	92 (**12a**)	2 (**13a**)
4	CO only, 6	90	**11a**	0 (**12a**)	0 (**13a**)
5	5/1, 6	100	**11b**	64 (**12b**)	17 (**13b**)
6	5/1, 6	90	**11c**	91 (**12c**)	0 (**13c**)

[a] Reaction conditions: 10 atom% Au/Co_3O_4 (20 mg, 1.4 mol% Au and 12 mol% Co to **11**), heptane (2 mL), **11** (1.6 mmol). [b] Determined by GC. [c] 48% of 2-isopropylaniline was obtained. [d] 17% of 2-isopropylaniline was obtained.

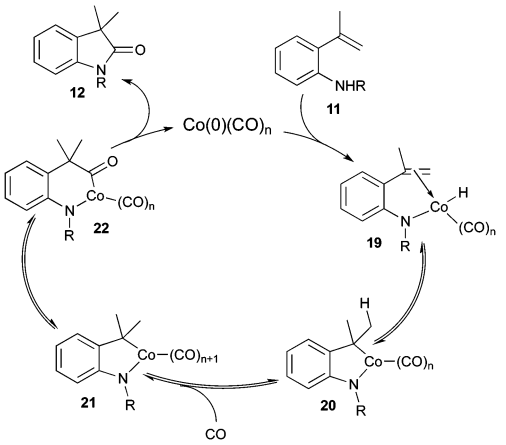


Scheme 3 Cyclocarbonylation of various aniline derivatives catalyzed by Au/Co_3O_4.

that a proximity effect was playing an important role in the efficient formation of the lactam ring. The same product **18** can be obtained from *N,N*-diallylaniline with $Co_2(CO)_8$.[20]

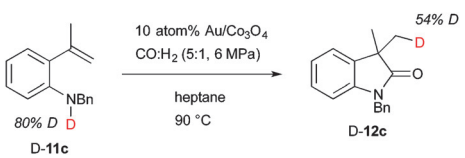
3.3 Possible mechanism for the intramolecular cyclocarbonylation of 2-isopropenylanilines catalyzed by Au/Co_3O_4

To obtain information about a reaction mechanism for the intramolecular cyclocarbonylation, a deuterized substrate **11c** was treated under similar conditions. As the result, the deuterium on the nitrogen atom of **11c** was incorporated into a geminal methyl group of **12c** (eqn (1)). Based on this result, the mechanism was presumed as shown in Scheme 4. Oxidative addition of the N–H bond to the Co site, and coordination of the olefin moiety would form **19**. A five-membered cobaltacycle **20** would be afforded by intramolecular hydrometallation. Subsequent adsorbed CO insertion into the Co–C bond forms the six-membered ring **22** followed



Scheme 4 Possible mechanism for the intramolecular cyclocarbonylation of 2-isopropenylaniline to lactams on the Au/Co_3O_4 catalyst. Co stands for the Co(0) active sites on the catalyst surface.

by reductive elimination to produce **12** with regeneration of the Co metal active site. Although CO has a chance of being inserted into the Co–N bond, the same products will be eventually obtained. Two impressive characteristics of Au/Co_3O_4-catalyzed cyclocarbonylation in Scheme 4 should be pointed out. The alkenyl group of **11** was not hydroformylated when catalyzed by Rh catalysts, which is possibly ascribed to –NHR group coordination to Co metal promoting intramolecular hydrometallation. The interaction between Co and the –NHR group may also prevent hydrogenation of the olefin moiety which was observed in the case of intermolecular hydroaminomethylation of styrene (Table 2, entry 7). When styrene is employed for the hydroformylation or hydroaminomethylation, the formation of a branched product is generally dominant. The regioselectivity can be controlled by using appropriate ligands in Rh-catalyzed intramolecular hydroaminomethylation[8] and Pd-catalyzed cyclocarbonylation.[18] In the case of Au/Co_3O_4-catalyzed intramolecular cyclocarbonylation, exclusive formation of **12c** was achieved by modification of the reaction conditions.



(1)

3.4 Characterization of catalysts

Temperature programmed reduction (TPR) profiles. In our previous report, the reduction of Co_3O_4 was clearly observed after H_2 treatment in X-ray absorption near edge structure (XANES) spectra[4e,f] and X-ray diffraction (XRD) patterns.[4b] Temperature programmed reduction (TPR) profiles of Au/Co_3O_4 and Co_3O_4 were obtained under 5% H_2/Ar flow (Fig. 1). Whereas Co_3O_4 showed two peaks at 234 and 315 °C attributed to the reduction of Co(II, III) to Co(II) and Co(II) to Co(0),

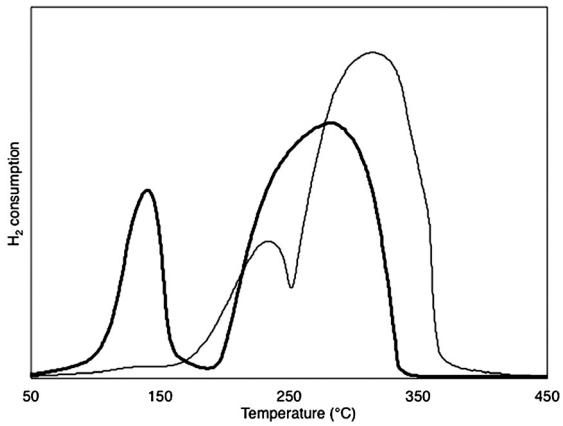


Fig. 1 TPR profiles for Au/Co_3O_4 and Co_3O_4 under 5% H_2/Ar flow (50 mL min^{-1}). Thick line, Au/Co_3O_4; thin line, Co_3O_4.

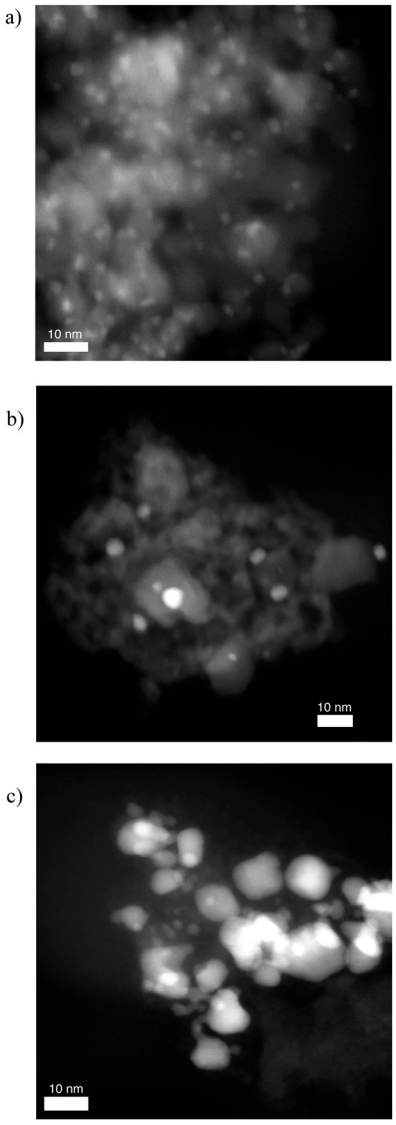


Fig. 2 HAADF-STEM images of (a) Au/Co_3O_4, after air calcination, (b) after H_2 treatment (2 MPa, 100 °C, 3 h, in heptane), (c) after intermolecular hydroaminomethylation reaction (1-hexene and *N*-isopropylaniline, 120 °C, 4 h, CO/H_2 = 1 : 1, 4 MPa, in heptane).

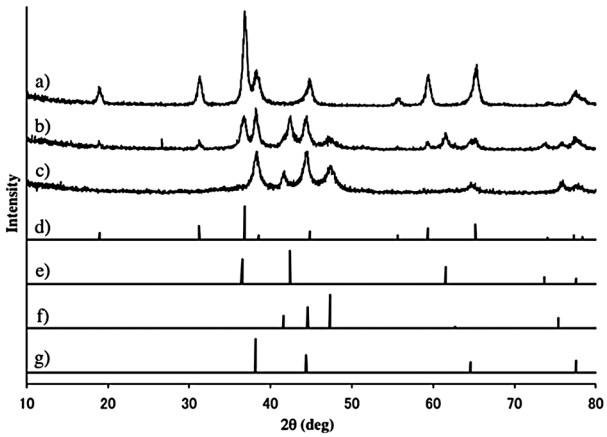


Fig. 3 XRD patterns of Au/Co_3O_4. (a) after air calcination, (b) after H_2 treatment (2 MPa, 100 °C, 3 h, in heptane), (c) after intermolecular hydroaminomethylation reaction (1-hexene and *N*-isopropylaniline, 120 °C, 4 h, CO/H_2 = 1 : 1, 4 MPa, in heptane). The patterns of (d) Co_3O_4, (e) CoO, (f) Co, and (g) Au are shown based on JCPDS data.

a drastic lowering of the reduction temperatures was observed by the deposition of GNPs on Co_3O_4. The H_2 pressurized conditions for the pretreatment of Au/Co_3O_4 may accomplish the reduction of the Co_3O_4 support even at much lower temperature.

High angle annular dark field scanning transmission electron microscopic (HAADF-STEM) images. HAADF-STEM was performed to obtain structural information of Au/Co_3O_4. GNPs having diameters of a few nanometers were well-dispersed on the surface of Co_3O_4 after air calcination (Fig. 2a). Hydrogen treatment resulted in aggregation of GNPs to some extent (Fig. 2b). After the hydroaminomethylation in the presence of 1-hexene, *N*-isopropylaniline, and CO/H_2, further aggregation of GNPs was observed (Fig. 2c). Whereas the catalytic activity of GNPs highly depends on the particle size,[1,2] the Au/Co_3O_4 system is relatively insensitive to the size of GNPs. Even with 25 atom% Au/Co_3O_4, which contained quite larger GNPs than the most effective 5 atom% catalyst, the hydroformylation of olefins still proceeded in moderate yield with high selectivity.[4b] Since the GNPs just participate in the promotion of the reduction of Co_3O_4 and are not involved in the catalysis, the catalytic activity of Au/Co_3O_4 is probably insensitive to the size of GNPs. In addition, Co_3O_4 without GNPs does not catalyze the hydroformylation around 120 °C at all because it requires a harsher temperature to be reduced to Co metal.[4b] Consequently, the hydroaminomethylation in this study will not obviously take place without GNPs under the conditions shown in Tables 1 and 2.

X-ray diffraction (XRD) patterns. The powder XRD patterns of Au/Co_3O_4 catalysts are shown in Fig. 3. The catalyst after calcination in air showed peaks attributable to Co_3O_4 and Au (Fig. 3a, d, and g). H_2 treatment at 100 °C partially reduced Co_3O_4 to CoO and Co metal. As the result, the observed pattern is a summation of Co_3O_4, CoO, Co, and Au (Fig. 3b and d–g). Since the hydroaminomethylation was conducted in a reducing environment at a slightly higher

temperature of 120 °C, the remaining Co_3O_4 and CoO after H_2 treatment were completely reduced to Co metal during the reaction (Fig. 3c, f, and g). This phenomenon could account for the necessity of H_2 in the case of intramolecular cyclocarbonylation (Table 3, entry 4).

4. Conclusions

In summary, one-pot intermolecular hydroaminomethylation and intramolecular cyclocarbonylation of olefins by Au/Co_3O_4 have been demonstrated. By employing terminal olefins and *N*-isopropylanilines as substrates, the intermolecular reactions proceeded *via* a common reaction path for hydroaminomethylation. On the other hand, the intramolecular cyclocarbonylation was observed when a C–C double bond and an amine moiety were located in appropriate positions in the same molecule under similar conditions.

The characterization of the catalyst was also performed. A TPR profile clearly showed the promotional effect of GNPs for the reduction of the cobalt oxide support and the resulting Co worked as the active catalytic species. The reduction of the oxide support and aggregation of GNPs were also revealed by XRD spectra and HAADF-STEM images.

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