

The X-ray Structure, Electrochemistry and Catalytic Reactivity of $\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PPh}_3)$ towards the Oxidative Carbonylation of Aniline

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The reaction of the anion $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}]^-$ with one equivalent of $\text{Au}(\text{PPh}_3)\text{Cl}$ affords $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PPh}_3)]$ (1), the structure of which was established by single crystal X-ray analysis. Its electrochemical behavior and catalytic properties are also reported. This bimetallic cluster catalyses the oxidative carbonylation of aniline to give methyl phenylcarbamate in methanol with good conversion and selectivity compared to the homometallic $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ cluster.

KEY WORDS: Osmium-gold; electrochemistry; oxidative carbonylation; aniline.

INTRODUCTION

The chemistry of osmium-gold mixed metal cluster has been well established in the past decade [1–11]. These compounds are important not only because of their novel structural properties, but also for their great potential as homogeneous bimetallic catalysts. The introduction of heterometallic metal-metal bonding into these clusters leads to an increase in the polarity of the molecule, which in turn can result in enhanced the catalytic activity. Some examples of differentiated heterosite activity, which indicate that the catalytic activity may be modified in heterometallic clusters under

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homogeneous conditions, have been reported [12, 13]. The activation of a tetraruthenium cluster by a gold center has also been observed [14]. The catalytic synthesis of carbamate is an area with high potential synthetic and industrial interest. Carbamates are important as precursors for preparing isocyanates, which are intermediates for the manufacture of high performance plastics, polyurethanes, elastomers and adhesives. Bimetallic clusters that act as a catalyst in the reductive carbonylation of nitro compounds for carbamate formation have been reported [15]. However, to our knowledge, this is the first example of the oxidative carbonylation of aniline for the synthesis of methyl phenylcarbamate by bimetallic cluster. Moreover, the comparison with $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ (2) and $[\text{N}(\text{PPh}_3)_2][\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}]$ (3) is also included.

EXPERIMENTAL

All reactions and manipulations were carried out under argon using standard Schlenk techniques, except for the chromatographic separations. Solvents were purified by standard procedures and distilled prior to use [16]. Reactions were monitored by analytical thin-layer chromatography (Merck Kieselgel 60 F₂₅₄) and the products were separated by thin-layer chromatography on plates coated with silica (Merck Kieselgel 60 F₂₅₄). All chemicals, unless otherwise stated, were purchased commercially and used as received. $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ [17, 18] and $[\text{N}(\text{PPh}_3)_2][\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}]$ [18] were prepared by the literature methods. Infrared spectra were recorded on a Bio-Rad FTS-135 IR spectrometer, using 0.5 mm calcium fluoride solution cells, ¹H and ³¹P NMR spectra on a Bruker DPX300 spectrometer using CD₂Cl₂ and referenced to internal SiMe₄ and external 85% H₃PO₄ respectively. Positive ionization fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer, using *m*-nitrobenzyl alcohol as the matrix solvent. Micro-analysis was performed by Butterworth Laboratories, UK.

Preparation of $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PPh}_3)]$ (1)

The $[\text{N}(\text{PPh}_3)_2][\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}]$ (100 mg, 0.06 mmol) in dichloromethane (30 cm³) was stirred with one equivalent of Au(PPh₃)Cl (29.7 mg, 0.06 mmol) under an argon atmosphere for half an hour. The solvent was then removed under reduced pressure. The residue was chromatographed on silica using *n*-hexane/dichloromethane (1:1, v/v) as the eluent. A yellow complex $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\text{AuPPh}_3)]$ (1, *R*_f = 0.7, 42.5 mg, 0.027 mmol, 45%) was isolated.

Spectral Data of 1. MS (FAB): m/z 1559 (M^+). IR (*n*-hexane): ν (CO), 2095(w), 2070(s), 2035 (s), 2010 (w), 1976 (s), 1958 (w) cm^{-1} . ^1H NMR (CD_2Cl_2 , 298 K): δ 7.51 (m, 15H, phenyl), -20.29 (s, 1H, hydride), -20.45 (s, 2H, hydride). ^{31}P NMR (CD_2Cl_2 , 298K): 74.07 (s, PPh_3). *Anal.* Calcd. for $\text{C}_{30}\text{H}_{18}\text{O}_{12}\text{POs}_4\text{Au}$: C, 23.11; H, 1.16. Found: C, 23.1; H 1.2.

Catalytic Reactions

The reactions were performed inside a stainless steel autoclave with magnetic stirring. Dissolve clusters (**1**, 23 mg, 0.015 mmol; **2**, 22 mg, 0.02 mmol; **3**, 20 mg, 0.012 mmol) in 10 ml CH_2Cl_2 . For each reaction, pipette 1 ml of the cluster solution into the solution of aniline (110 mg, 1.18 mmol) and methanol at room temperature. The air in the autoclave was replaced with dinitrogen by 3 freeze-pump-thaw cycles. Carbon monoxide (4 MPa) and oxygen (2 MPa) were then introduced into the reactor respectively. The autoclave was heated to 180°C using a thermoregulated oven for 3 h. At the end of the reactions, the autoclave was cooled with an ice bath, and then it was blown off. The resulting liquid mixture was analyzed with a HP G1800C GCD Series II.

Electrochemical Studies

Electrochemical measurements were performed with an EG&G Princeton Applied Research (PAR) Model 273A potentiostat, connected to an interfaced computer employing PAR 270 electrochemical software. Cyclic voltammograms were obtained using a gas (argon) sealed two-compartment cell equipped with a glassy carbon working electrode (Bioanalytical), a platinum wire auxiliary electrode (Aldrich), and an Ag/AgNO_3 reference electrode (Bioanalytical) at room temperature. 0.1 mol dm^{-3} *n*-tetrabutylammonium hexafluorophosphate (TBAHFP) in anhydrous deoxygenated acetonitrile was used as a supporting electrolyte. Ferrocene was added at the end of each experiment as an internal standard. Potential data (vs. Ag/AgNO_3) were checked against the ferrocene (0/ +1) couple; under the actual experimental conditions the ferrocene/ferrocenium couple is located at +0.06 V. Bulk electrolyses were carried out in a gas-tight cell consisting of three chambers separated at the bottom by fine frits, with a carbon cloth (80 mm^2) working electrode in the middle, and Ag/AgNO_3 reference and Pt gauze auxiliary electrodes in the lateral chambers. The working potential (E_w) for oxidation processes was ca. 0.15 V more positive than the corresponding electrode potential (E_p), respectively; the coulometric experiment was performed in duplicate.

Crystallography

Crystals suitable for X-ray analyses were glued on glass fibres with epoxy resin or sealed in a 0.3 mm glass capillary. Intensity data were collected at ambient temperature using a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo-K α radiation using ω scan type. Details of the intensity data collection and crystal data are given in Table I. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [19] and expanded using Fourier technique [20]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan [21] crystallographic software package of the Molecular Structure Corporation.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 176839. Copies of this information may be obtained free from the Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK.

Table I. Crystal Data and Data Collection Parameters for
[Os₄Au(μ -H)₃(CO)₁₂(PPh₃)] **1**

1	
Empirical formula	Os ₄ AuO ₁₂ C ₃₀ PH ₁₈
Formula weight	1559.21
Crystal color, habit	Yellow, block
Crystal dimensions/mm	0.28 × 0.18 × 0.24
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (#2)
<i>a</i> (Å)	9.432(2)
<i>b</i> (Å)	11.691(3)
<i>c</i> (Å)	17.391(2)
α (Å)	108.08(1)
β (Å)	105.44(1)
γ (Å)	90.02(2)
<i>U</i> (Å) ³	1750.0(6)
<i>Z</i>	2
<i>D</i> _c (g/cm ⁻³)	2.959
μ (Mo-K α) (cm ⁻¹)	187.55
Reflections collected	10969
Unique reflections	7571
Observed reflections [<i>I</i> > 1.5 σ (<i>I</i>)]	5899
<i>R</i>	0.042
<i>R</i> _w	0.047
Goodness of fit, <i>S</i>	1.21

RESULTS AND DISCUSSION

Treatment of $[\text{N}(\text{PPh}_3)_2][\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}]$ with one equivalent of $\text{Au}(\text{PPh}_3)\text{Cl}$ affords $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\text{AuPPh}_3)]$ (**1**), which was isolated as an air stable solid in high yield. The complex was fully characterized by conventional spectroscopic techniques. The infrared spectrum of **1** reveals that only terminal carbonyl ligands are present and the mass spectrum exhibits a molecular ion envelope which agrees with the formulae of the complex, with ion peaks corresponding to stepwise losses of carbonyl ligands. The ^1H and ^{31}P NMR spectra exhibit one set of multiplets at δ 7.65–7.70 and one singlet at δ 74.07 respectively, which are assigned to the coordinated triphenylphosphine. Two singlet peaks at δ –20.29 and –20.45 with integral ratio 2:1 in ^1H NMR spectrum are attributed to the three μ_2 -bridging hydrides in tetraosmium core. The solid state structure of **1** was established by X-ray crystallography.

Solid State Structure

The molecular structure of **1** is shown in Fig. 1 and some selected important bond parameters are collected in Table II. The structure closely

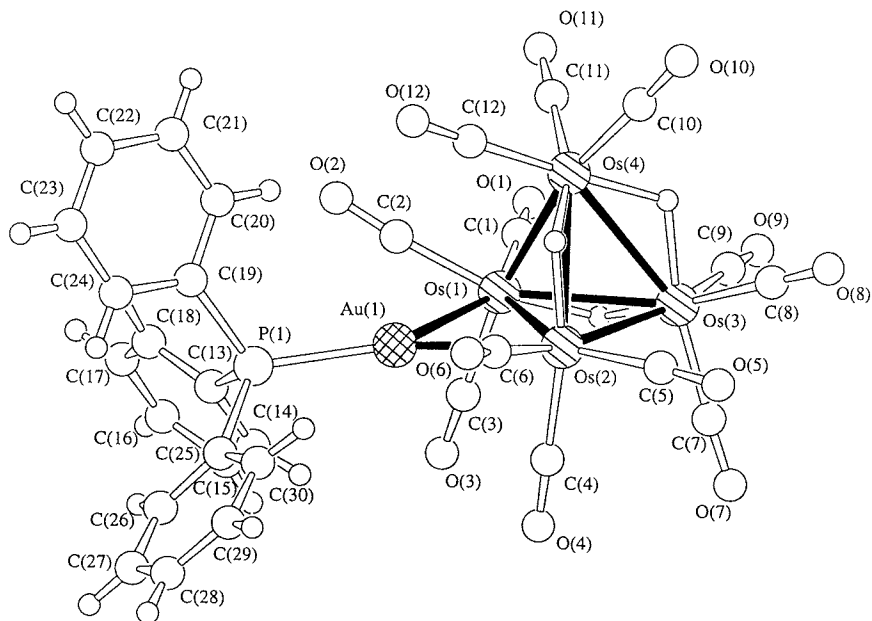


Fig. 1. Molecular Structure of $[\text{Os}_4(\mu\text{-H})_3(\text{CO})_{12}(\text{AuPPh}_3)]$ (**1**).

Table II. Selected Bond Lengths [\AA] and Angles [$^\circ$] for $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PPh}_3)] \mathbf{1}$

Bond lengths [\AA]			
Os(1)–Os(2)	2.934(1)	Os(1)–Os(3)	2.951(1)
Os(1)–Os(4)	2.806(1)	Os(2)–Os(3)	2.820(1)
Os(2)–Os(4)	2.947(1)	Os(3)–Os(4)	2.964(1)
Au(1)–Os(1)	2.872(1)	Au(1)–Os(2)	2.743(1)
Au(1)–P(1)	2.301(3)		
Bond angle [$^\circ$]			
Os(1)–Au(1)–Os(2)	63.0(1)	Os(1)–Au(1)–P(1)	133.5(1)
Os(2)–Au(1)–P(1)	163.1(1)	Au(1)–Os(1)–Os(2)	56.4(1)
Au(1)–Os(1)–Os(3)	113.6(1)	Au(1)–Os(1)–Os(4)	89.0(1)
Au(1)–Os(1)–C(1)	152.3(4)	Au(1)–Os(1)–C(2)	65.3(4)
Au(1)–Os(1)–C(3)	83.2(4)	Au(1)–Os(2)–Os(1)	60.7(1)
Au(1)–Os(2)–Os(3)	122.3(1)	Au(1)–Os(2)–Os(4)	88.7(1)

resembles those of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ [22] and $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PEt}_3)]$ [23]. Four osmium atoms define a distorted tetrahedron with twelve carbonyl ligands terminally bonded to the metal centres. The Au atom bridges the Os(1)–Os(2) bond, the average Os–Au distance [$2.807(1) \text{\AA}$] and Au–P distance [$2.302(3) \text{\AA}$] are comparable to the corresponding values observed in $[\text{Os}_4\text{Au}(\mu\text{-H})_3(\text{CO})_{12}(\text{PEt}_3)]$ and $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{AuPPh}_3)]$ [24]. The dihedral angle between the planes Au(1)–Os(1)–Os(2)–Os(3) and Os(1)–Os(2)–Os(4) is 108.1° . The Au atom may be considered as sp hybridized; it donates one electron to the midpoint of the Os(1)–Os(2) bond to form a delocalised three-center Os–Au–Os bond. Four bridging Os–Os bonds are significantly elongated, within the range [$2.934(1)$ – $2.964(1) \text{\AA}$], which is similar to the above tetraosmium carbonyl systems.

Electrochemistry

The electrochemistry of compound **1–3** has been examined and the result of the voltammetric experiment is summarized in Table III. The cyclic voltammograms of **1** contain two irreversible anodic waves at $E_{\text{pa}} = 1.11$ and $0.12 \text{ V vs Ag/AgNO}_3$, along with small return reduction peaks at -1.05 and -1.53 V . The region where the weak reduction waves appear was initially empty, with the waves appearing after the anodic waves were traversed. This indicates that the species giving rise to these small reduction peaks is derived from the species produced upon oxidation. An increased scan rate did not lead to any noticeable reversibility of the redox couple. The irreversible nature of oxidation is presumably derived from an irreversible chemical reaction that follows the redox reaction; it

Table III. The Electrochemical Data of 1–3

Clusters	Oxidation		Reduction
	E_{pa2} (V)	E_{pa1} (V)	E_{pc1} (V)
1	1.11	0.12	–
2	–	0.71	–1.99
3	1.01	0.13	–

conforms to ECEC process. No cathodic wave was located within the solvent limit. Controlled potential coulometry was performed at 0.27 V for **1**, showing that two electrons are removed for each molecule. Based on the relative peak heights, another anodic wave is tentatively assigned to have consumed two electrons too. The large potential difference between the first and second oxidation peaks (around 1V) shows that as compound **1** loses two electrons, it becomes more electron deficient which makes the second oxidation much more difficult. As expected, the electrochemical behavior of **3** is very similar to **1**. Two irreversible anodic waves at $E_{pa} = 1.01$ and 0.13 V vs Ag/AgNO₃ with small reduction peaks at –1.51 and –1.99 V were observed in the cyclic voltammograms of **3**. The oxidation potential of **3** is also comparable to corresponding values observed in **1**. Controlled potential coulometry indicated that two faraday per mole of **3** is involved in each oxidation step. Parent cluster **2** shows different redox behavior to **1** and **3**. The cyclic voltammogram of **2** contains an irreversible cathodic wave at $E_{pc} = -1.99$ V and an irreversible anodic wave at $E_{pa} = 0.71$ V respectively. The cathodic peak of **2** is located within the solvent limit, which suggested that the reduction is more feasible to occur in **2** compared to **1** and **3**. Moreover, there is a negative shift (600 mV) in oxidation potential of **2** compared to **1** and **3**, hence the oxidation of **2** is more difficult. As **2** is believed to be more electron deficient than **1** and **3**. The substitution of Au(PPh₃) for hydrogen in **2** seems activate the tetraosmium cluster by lowering the oxidation potential.

Catalytic Properties

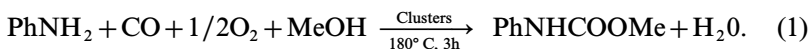
Carbamates as intermediates for the synthesis of isocyanates by non-phosgene routes have been well studied in the past two decades. [25, 26] Nevertheless, studies on the oxidative carbonylation of amines are relatively limited, in contrast to the reductive carbonylation of nitro compounds. Recently, Deng and co-workers have showed that the mononuclear gold complexes exhibited a good performance towards the oxidative carbonylation of aromatic amines. [27] However, the cluster system remains relatively

Table IV. The Catalytic Results of Clusters 1–3 towards the Oxidative Carbonylation of Aniline^a

Entry	Catalyst	Aniline/ catalyst	MeOH (ml)	Conversion (%)	Selectivity (%)					TOF ^b
					Carbamate	N-methyl aniline	Quinazoline	Formaniline	Azobenzene	
1	1	800	3	93	82	0	10	0	0	248
2	1	800	10	100	51	0	16	0	17	267
3	1	800	15	100	0	0	52	0	0	267
4	1	800	20	100	0	0	37	0	39	267
5	2	600	3	21	41	30	4	8	5	42
6	2	600	10	48	20	11	31	0	31	96
7	2	600	15	65	5	7	0	5	4	130
8	2	600	20	63	0	12	0	0	28	126
9	3	1000	3	10	43	37	8	7	5	33
10	3	1000	10	31	22	19	17	17	0	103
11	3	1000	15	32	17	37	15	10	0	27
12	3	1000	20	35	0	22	0	0	78	333

^a Aniline = 110 mg, 4 MPa CO, 2 MPa O₂, 180°C, 3 h.^b Mole substrate converted per mole cluster per hour.

unexplored. In this paper, the studies of clusters 1–3 towards the oxidative carbonylation of aniline in the presence of methanol yielding methyl phenylcarbamate, as shown in Eq. (1), were reported



The catalytic results are presented in Table IV. It is noteworthy that 93% conversion and 82% selectivity towards methyl phenylcarbamate were achieved by **1** in the absence of a co-catalyst, which is comparable to the recently reported results of the use of Au(I) mononuclear complexes as catalysts [27]. The turnover frequency of entry 1 is 248, which is much higher than the value obtained by using Au (I) complex as a catalyst. The major byproduct obtained was quinazoline. For cluster **2** and **3**, the highest selectivity towards methyl phenylcarbamate is around 40%, however, the conversion is only about 10 and 20% respectively. Moreover, more byproducts were obtained, including N-methylaniline, quinazoline, formaniline and azobenzene. The bimetallic cluster **3** is believed to be a more active and selective catalyst compared to **2** and **3**. It suggested that the substitution of Au(PPh₃) for hydrogen in [Os₄(μ-H)₄(CO)₁₂] significantly enhanced the catalytic activity owing to the synergetic effect of the bimetallic cluster.

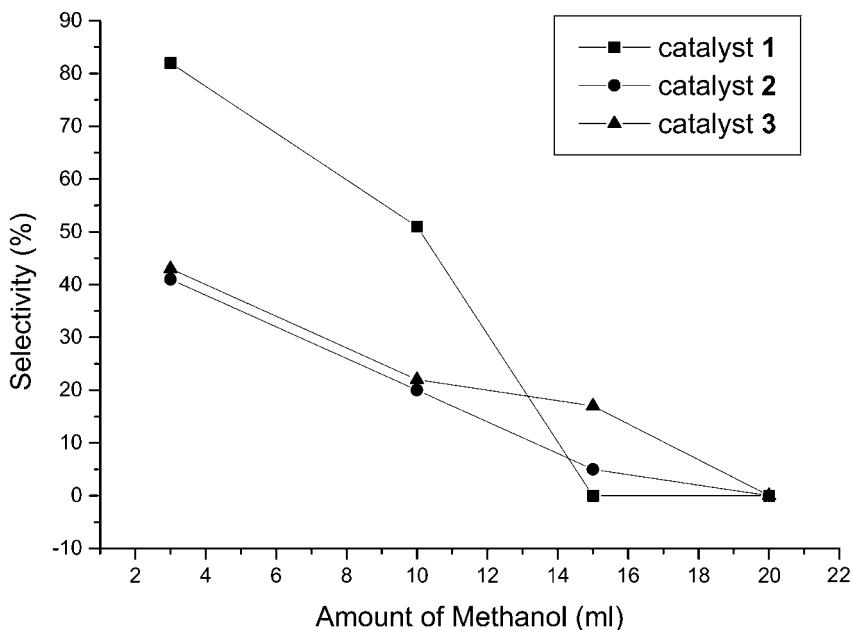


Fig. 2. The effect of amount of methanol used on the selectivity to methyl phenylcarbamate.

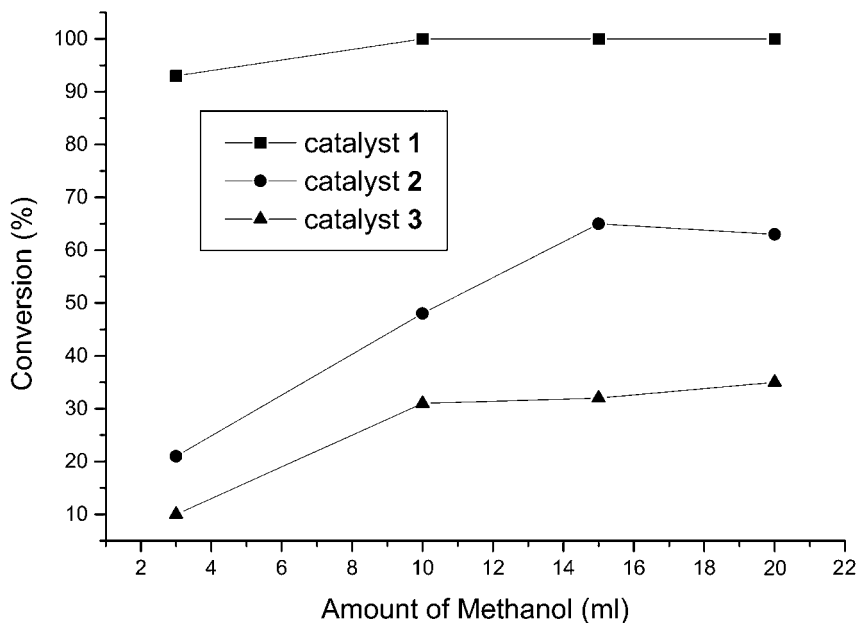


Fig. 3. The effect of amount of methanol used on the conversion of products.

Methanol plays an important role in this catalytic reaction, which acts both as a solvent and substrate. The effect of the amount of methanol on conversion and selectivity is studied and the results are presented in Figs. 2 and 3. For all the three catalysts, the more methanol used the higher the conversion but lower the selectivity to methyl phenylcarbamate. This demonstrates shows that the excess methanol is favorable for the formation of byproducts, instead of carbamate. However, the main byproducts N-methylaniline and formaniline resulting from the catalysts 2 and 3 were not detected over the bimetallic catalyst 1. This implies that the catalytic mechanism for a bimetallic catalyst is different from its monometallic analogue. The detailed mechanism and conditions are still under investigation.

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