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A practical synthetic method for dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, using ruthenium dioxide hydrate

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Abstract

Ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$) reacts with carbon monoxide at 5–20 atm to give dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, in an excellent yield. Ruthenium carboxylate complexes $[Ru_2(OCOR)_2(CO)_4]_n$ (R = H or CH_3) are almost quantitatively obtainable from the same reaction in the presence of formic or acetic acid. These isolable Ru complexes and the Ru dioxide hydrate efficiently effect a reductive carbonylation of nitrobenzene in aniline to produce *N*,*N'*-diphenylurea. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$ (**1**), is widely used as a highly efficient catalyst for many kinds of homogeneous catalyses [1] and serves as an important trinuclear framework in Ru cluster chemistry [1a,2]. For example, we have recently achieved the complex **1** catalyzed reductive carbonylation of nitrobenzene to *N*,*N'*-diphenylurea [3], which is a key intermediate of aromatic isocyanates [4]. Although the catalyst **1** has a satisfactory activity for this carbonylation in a practical sense, it is not easily obtainable at a reasonable cost because the known synthetic procedure requires very high CO pressure conditions and a complicated workup procedure [5]. An efficient synthetic method is highly desirable for the further development of the carbonylation reaction catalyzed by complex **1**. This paper discloses a practical preparative method of complex **1** from reacting a commercially available ruthenium dioxide hydrate ($RuO_2 \cdot xH_2O$) **2** with CO under mild reaction conditions and the application of **2** to a catalyst precursor for the reductive carbonylation of nitrobenzene.

2. Results and discussion

Complex **1** can be easily obtained in an 80% isolated yield from the reaction of compound **2** and 20 atm of CO at 160°C in toluene [6]. The reaction proceeds rapidly to give a clear orange solution containing complex **1** from the black suspension. On cooling the reaction mixture, an orange crystalline compound precipitates. In aniline, the reaction gave the complex **1** in a good yield under mild condition (5 atm of CO). Compound **2** reacts readily with CO in aqueous formic acid or acetic acid to give carboxylate complexes $[Ru_2(OCOR)_2(CO)_4]_n$ (R = H or CH_3) [7] in almost quantitative yields. High CO pressure is required for the reaction to take place smoothly, otherwise the atmospheric pressure of CO in refluxing mesitylene, acetic acid, or acetic anhydride gave the corresponding products in poor yields. An addition of triphenylphosphine under the standard conditions mentioned above resulted in several unidentified carbonyl triphenylphosphine complexes. Table 1 summarizes the representative results. In contrast to the reactivity of **2**, a commercially available anhydrous ruthenium(IV) dioxide, RuO_2, is completely inert under identical reaction conditions. X-ray diffraction analyses of these two Ru

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Table 1
Reaction of ruthenium dioxide hydrate, $RuO_2{\cdot}xH_2O$ and CO

Solvent	CO (atm)	Temperature (°C)	Time (h)	Product	Yield[a] (%)
$C_6H_5CH_3$	20	160	2	$Ru_3(CO)_{12}$	80
$C_6H_5NH_2$	5	160	2	$Ru_3(CO)_{12}$	70
HCOOH (aq)	3	145	1	$[Ru_2(OCOH)_2(CO)_4]_n$	96
CH_3COOH	10	160	1	$[Ru_2(OCOCH_3)_2(CO)_4]_n$	95

[a] Isolated yield.

oxides show that **2** has an amorphous structure while anhydrous RuO_2 has a crystalline structure, which might be responsible for the difference in the reactivity under mild conditions [8].

High-pressure IR spectroscopic studies [9] on the reaction of **2** with CO in aniline under 50 atm of CO at 160°C clearly indicate that a mononuclear pentacarbonyl ruthenium complex, $Ru(CO)_5$ ($\nu_{CO} = 1995$ and 2030 cm^{-1}), is the initial product of the reaction [10]. The mononuclear carbonyl complex is then converted into **1**. Although the detailed mechanism of the formation of **1** from **2** is not yet clear, CO works as a reducing agent [1b,e] of the ruthenium oxide.

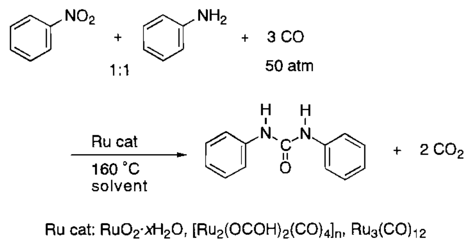
A rapid and quantitative formation of $Ru(CO)_5$ or complex **1** from **2** mentioned above should allow the utilization of compound **2** as an efficient catalyst precursor for the reductive carbonylation of nitrobenzene to *N*,*N*′-diphenylurea in aniline. As expected, the reaction of nitrobenzene (40 mmol) in aniline (40 g) under 50 atm of CO at 160°C with $RuO_2{\cdot}xH_2O$ (50 mg) proceeds rapidly to give *N*,*N*′-diphenylurea in excellent yields as shown in Scheme 1. The catalytic activity estimated by turnover frequency (TOF) is almost identical to that accessible with complex **1**, suggesting that transformation of compound **2** to the catalytically active species via pentacarbonylruthenium is almost quantitative during the carbonylation reaction (Table 2). The Ru formate complex, $[Ru_2(OCOH)_2(CO)_4]_n$, obtained above, also effects the carbonylation reaction with a similar activity to those of **1** and **2**. The formate complex decomposes possibly by releasing H_2 and CO_2 to lead an catalytically active ruthenium complex under the reaction condition. In fact, the high-pressure IR spectra of the carbonylation reaction with **1**, **2** and the formate complex showed that an identical but unidentified carbonyl complex ($\nu_{CO} = 1980$ and 2040 cm^{-1}) can be detected [9] at the initial stage of the reaction in all cases. The product, *N*,*N*′-diphenylurea, quantitatively reacts with alcohols to provide phenyl carbamic esters. The same aromatic carbamates are also obtainable from the carbonylation of nitrobenzene catalyzed by Ru or Pd complexes in alcohols solvents [1b,11].

In conclusion, we found that a commercially available compound **2** is a useful starting material for synthesis of carbonyl cluster **1** as well as an excellent catalyst precursor for the catalytic carbonylation of nitrobenzene to *N*,*N*′-diphenylurea which is a key intermediate of aromatic isocyanates [12].

3. Experimental

3.1. Synthesis of $Ru_3(CO)_{12}$ and $[Ru_2(OCOH)_2(CO)_4]_n$

$RuO_2{\cdot}xH_2O$ (Ru content 47 wt. %) purchased from Nippon Engelhard was used as a starting material without further purification. A 200 ml stainless steel autoclave, charged with 1 g of $RuO_2{\cdot}xH_2O$ and 50 ml of toluene, was pressurized with approximately 20 atm of CO at room temperature. The mixture was then heated to 160°C and stirred for 2 h. On cooling and releasing the pressure, orange compound crystallized was filtered and washed with cold toluene. Isolated yield; 80% (0.76 g) as the first crop. Orange crystalline compound was identical to authentic product, $Ru_3(CO)_{12}$: IR (KBr) 2062, 2026, 2004 cm^{-1}. Similarly, the reaction of $RuO_2{\cdot}xH_2O$ in the presence of aqueous formic acid or acetic acid was carried out to form the carbonyl formate or carbonyl acetate complex in a 96 or 95% yield, respectively. IR analysis of these complexes indicates that they are identical to the authentic compounds. $[Ru_2(OCOH)_2(CO)_4]_n$: IR (KBr) 2040, 1998, 1957 cm^{-1}. $[Ru_2(OCOCH_3)_2(CO)_4]_n$: IR (KBr) 2049, 1996, 1969, 1952 cm^{-1}.



Ru cat: $RuO_2{\cdot}xH_2O$, $[Ru_2(OCOH)_2(CO)_4]_n$, $Ru_3(CO)_{12}$
solvent: toluene, aniline

Scheme 1.

Table 2
Ru complexes catalyzed reductive carbonylation of nitrobenzene to *N*,*N*′-diphenylurea

Catalyst	Ru (mmol)	TOF[a]
$Ru_3(CO)_{12}$	0.047	120
$RuO_2 \cdot xH_2O$	0.047	130
$[Ru_2(OCOH)_2(CO)_4]_n$	0.054	110
RuO_2	0.75	0
Ru black	0.99	0

[a] TOF, mol of *N*,*N*′-diphenylurea/mol of Ru·h.

3.2. Measurement of TOF of reductive carbonylation of nitrobenzene

In a typical experiment 0.047 mmol of $RuO_2 \cdot xH_2O$, 40 mmol of nitrobenzene and 40 ml of aniline were placed in a 100-ml stainless steel autoclave. The reactor was flushed with CO and pressured to 50 atm with CO. The mixture was heated to 160°C with agitation, held at this temperature for 2 h. On cooling of the reactor and releasing the CO pressure, the reaction mixture was analyzed by LC. In some cases the reaction mixture was filtered to obtain *N*,*N*′-diphenylurea as a solid. The initial rate (TOF = mol of *N*,*N*′-diphenylurea/mol of Ru h) was determined at the initial 30% conversion of nitrobenzene, where the selectivity of *N*,*N*′-diphenylurea was over 95%.

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