

An in situ spectroscopic study of the ruthenium catalyzed carbonylation of piperidine starting with triruthenium dodecacarbonyl

The importance of path dependence in homogeneous catalysis[☆]

Guowei Liu, Moshen Hakimifard, Marc Garland*

*Department of Chemical and Environmental Engineering, 4 Engineering Drive 4,
National University of Singapore, Singapore 117576, Singapore*

Received 19 June 2000; accepted 18 October 2000

Abstract

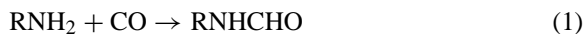
The homogeneous ruthenium catalyzed carbonylation of piperidine was studied, starting with $\text{Ru}_3(\text{CO})_{12}$ in *n*-hexane solvent, at 333 K under 0.1–1.0 MPa CO and 10 ml piperidine. The analytic method was in situ high-pressure infrared spectroscopy. It was observed that the precursor $\text{Ru}_3(\text{CO})_{12}$ (2011, 2028 and 2059 cm^{-1}) disappeared from solutions after a few hours of reaction time at 333 K and 1.0 MPa CO. The major observable organometallic species, which accounted for the majority of the ruthenium mass balance in the active system was $\text{Ru}(\text{CO})_5$ (1966, 2002 and 2037 cm^{-1}). Numerous new bands also appeared in the mid-infrared during the active catalysis. The turnover frequency based on the nominal loading of ruthenium in the system was circa 0.06 h^{-1} . The reaction is very clean but slow. A tentative catalytic cycle is suggested for this system. Particularly interesting, is the path dependence of this system. If the system is started at 0.1 MPa CO, it rapidly degrades. However, if the system is started at 1.0 MPa CO, until cluster fragmentation is complete and then the system pressure is reduced, a very active system is obtained. Finally, $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ was also used successfully as a precursor for piperidine carbonylation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Triruthenium dodecacarbonyl; Carbonylation; Piperidine; Ruthenium pentacarbonyl; Turnover frequency

1. Introduction

The homogeneous carbonylation of both primary (RNH_2) [1–3] and secondary amines (R_2NH) [4] can be catalyzed starting with a variety of ruthenium complexes, i.e. $\text{RuCl}_3\text{H}_2\text{O}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{COD})(\text{COT})$, $\text{Ru}(\text{CO})_3(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{PPh}_3)_3$. These carbony-

lations can be carried out either with or without the addition of phosphine. However, in both cases, selectivity to the formamide (Eqs. (1) and (2)) is usually considerably less than 100%. The other principle organic products are the substituted ureas.

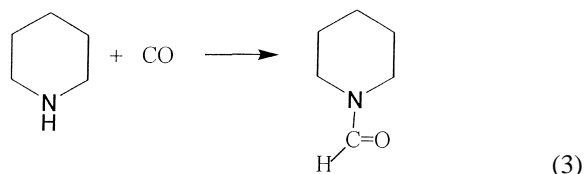


In contrast, the ruthenium catalyzed carbonylation of secondary cyclic amines results in the exclusive formation of the corresponding *N*-formyl amine [5–7].

[☆] Primary experimental research performed at ETH-Zurich 1992–1995. Analysis performed at NUS 1999.

* Corresponding author. Tel.: +65-874-6617; fax: +65-779-1936.
E-mail address: chemvg@nus.edu.sg (M. Garland).

The cyclic amines pyrrolidine (C_4H_8NH), piperidine ($C_5H_{10}NH$) and hexamethylenimine ($C_6H_{12}NH$) have been used. The overall organic reaction can be written (Eq. (3)).



Rempel et al. [5] studied reaction 3 starting with $[\text{HRu}(\text{CO})_3]_n$, $[\text{Ru}(\text{CO})_2(\text{OCOCH}_3)]_n$ and $\text{Ru}_3(\text{CO})_{12}$ as catalyst precursors at approximately $P_{\text{CO}} = 1$ atm and 75°C . Starting with these various complexes, both $[\text{Ru}]^{0.5}$ and $[\text{Ru}]^{1.0}$ rate dependencies and both $[\text{CO}]^0$ and $[\text{CO}]^1$ rate dependencies were observed. Consequently, the authors proposed more than one mechanism for the catalytic formation of *N*-formyl piperidine, depending on which ruthenium complex was used.

In a much later study [6], the organometallic clusters $\text{Ru}_3(\text{CO})_{12}$, $[\text{HRu}_3(\text{CO})_{11}]^-$ and $[\text{H}_3\text{Ru}_3(\text{CO})_{12}]^-$ were used to catalyze the carbonylation of cyclic amines under the reaction conditions $140\text{--}185^\circ\text{C}$ and $60\text{--}70$ bar CO. In the case of $\text{Ru}_3(\text{CO})_{12}$ as precursor, it was possible to isolate the species $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu_2, \eta^2\text{-OCNR}_2)$ from the reaction. This observation led the authors to suggest the existence of a catalytic cycle consisting *entirely of tri-nuclear ruthenium species as intermediates*. In the case of piperidine as cyclic amine, the isolated carbamoyl cluster shows IR absorbance maxima at $\nu_{\text{CO}} = 2100\text{w}, 2064\text{vw}, 2050\text{vs}, 2024\text{s}, 2015\text{vs}, 1998\text{vw}, 18988\text{vw}, 1981\text{w}, 1957\text{vw}, \text{br}$ in pentane solvent.

Our interest in the carbonylation of piperidine is motivated by the observations that (i) the reaction is very selective, (ii) numerous ruthenium complexes are effective precursors and (iii) the systems exhibit interesting transient effects — specifically induction and deactivation.

In the following, the carbonylation of piperidine starting with $\text{Ru}_3(\text{CO})_{12}$ as precursor is re-examined. In contrast to previous studies, high pressure in situ infrared spectroscopy is used as the analytic tool. The use of an appropriate in situ spectroscopy can reveal the possible degradation of the precursor, the forma-

tion of new complexes under reaction condition, as well as the preliminary measurements of the system activity.

2. Experimental

2.1. General information

All solution preparations were carried out under argon (99.999% Pan Gas AG, Luzern, Switzerland) using standard Schlenk techniques [8]. The argon was further purified prior to use by passage through a column containing 100 g reduced BTS-catalyst (Fluka AG Buchs, Switzerland) and 100 g of 4 \AA molecular sieve to adsorb trace oxygen and water, respectively. All reactions were carried out under carbon monoxide (99.997% Messner Griesheim GmbH, Germany) after further purification through deoxy and zeolite columns.

The precious metal complex $\text{Ru}_3(\text{CO})_{12}$, with stated purity of 98% min, was obtained from Strem Chemicals SA (Bischheim, France) and was used without further purification. The *n*-hexane solvent (stated purity $>99.6\%$, Fluka AG) was refluxed over sodium potassium alloy under argon. The piperidine 97% was obtained from Fluka and was distilled from NaOH under nitrogen [9]. *N*-formyl piperidine was obtained from Fluka and used as received.

The species $\text{Ru}_3(\text{CO})_{12}$ has absorbance maxima at $2011, 2028$ and 2059 cm^{-1} [10]. Piperidine has a large maximum at 1693 cm^{-1} and hexane has an analytical band at 1778 cm^{-1} . The absorptivities of $\text{Ru}_3(\text{CO})_{12}$, piperidine and hexane at $2059, 1693$ and 1778 cm^{-1} in *n*-hexane are $24,900, 1960$ and $0.1591 \text{ mole}^{-1} \text{ cm}^{-1}$ [11].

2.2. Equipment

In situ spectroscopic studies were performed in a 1.51 stainless steel (SS316) autoclave (Büchi-Uster, Switzerland) which was connected to a high-pressure infrared cell. The autoclave ($P_{\text{max}} = 22.5 \text{ MPa}$) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineers, Erie PA) and was constructed

with a heating/cooling mantle. A high-pressure membrane pump (Model DMK 30, Orlita AG, Geissen Germany), with a maximum rating of 32.5 MPa and a 31 h^{-1} flow rate, was used to circulate the *n*-hexane solutions from the autoclave to the high pressure IR cell and back to the autoclave via jacketed 1/8 in. (SS316) high-pressure tubing (Autoclave Engineers). The entire system, consisting of autoclave, pump, transfer lines and infrared cell, was cooled using a Lauda RX20 cryostat and could be maintained isothermal ($\Delta T \approx 0.5^\circ\text{C}$) at 298–333 K. Temperature measurements were made at the cryostat, autoclave and IR cell with PT-100 thermoresistors. The necessary connections to vacuum and gases were made with 1/4 in. (SS316) high-pressure tubing (Autoclave Engineers) and 1.0, 5.0, 10.0 piezocrystals were used for pressure measurements (Keller AG Winterthur Switzerland). The entire system was gas tight under vacuum as well as at 20.0 MPa, the maximum operating pressure [12–20].

The high-pressure infrared cell was constructed SS316 steel from at the ETH-Zürich and could be heated and cooled. The CaF_2 single crystal windows (Korth Monokristalle, Kiel Germany) had dimensions of 40 mm diameter by 15 mm thickness. Two sets of Viton and silicone gaskets provided sealing and Teflon spacers were used between the windows. The construction of the flow through cell [21], is a variation on a design due to Noack [22] and differs in some respects from other high-pressure infrared cells described in the literature (for a review, see [23]). The high-pressure cell was situated in a Perkin-Elmer 983 infrared spectrometer. The resolution was set to 4 cm^{-1} for all spectroscopic measurements. A schematic diagram of the experimental set-up can be found in [15].

2.3. *In situ* spectroscopic studies

All experiments were performed in a similar manner. First, circa 10 ml piperidine, 64 mg $\text{Ru}_3(\text{CO})_{12}$ and 200 ml hexane were transferred to a schlenk tube and mixed under argon. No reaction appeared to take place. Indeed the solution has the typical bright-orange color of $\text{Ru}_3(\text{CO})_{12}$. This solution was transferred to the autoclave and pressurized with 1.0 MPa CO. Spectra were taken in the range $1600\text{--}2200\text{ cm}^{-1}$.

3. Results and discussion

3.1. Preliminary experiment with $\text{Ru}_3(\text{CO})_{12}$ at circa 0.1 MPa CO

Since the literature indicated that the carbonylations could be carried out at low CO partial pressures, but that the systems deactivated, a preliminary experiment was performed. At 0.1 MPa CO, the metal–ligand vibrational area initially exhibited strong absorbance, however, after a relatively short reaction period, the total absorbance of the metal–ligand region decreased significantly. This indicated to us, the instability of the ruthenium system at these conditions and loss of ruthenium — either to ruthenium metal, species with multiple piperidine ligands, or insoluble complexes. The rate of formation of piperidine and, hence, system activity was minimal.

3.2. Experiments with $\text{Ru}_3(\text{CO})_{12}$ at 1.0 MPa CO

After transferring the solution to the autoclave and pressurizing the system, infrared spectra were acquired on 30 min intervals. The initial spectrum (after hexane, CO, piperidine and background subtraction) at 60°C and 1.0 MPa pressure is shown in Fig. 1 (curve A). This spectrum shows the presence of clean $\text{Ru}_3(\text{CO})_{12}$ (2011 , 2028 and 2059 cm^{-1}).

As the reaction time progressed, the degradation of $\text{Ru}_3(\text{CO})_{12}$ became apparent. After circa 12 h, no $\text{Ru}_3(\text{CO})_{12}$ was observable in solution. Instead, a whole new set of metal–ligand vibrations appeared at 1914 , 1931 , 1938 , 1946 , 1969 , 1963 , 1980 , 2001s , 2036s , 2052 , 2058 cm^{-1} (Fig. 1, curve B), as did the organic product *n*-formyl piperidine at 1693 cm^{-1} . The turnover frequency based on the nominal ruthenium loading was circa 0.059 h^{-1} . The system appeared to be stable.

First, it should be noted that the two most prominent metal–ligand vibrations at 2001s and 2036s correspond to $\text{Ru}(\text{CO})_5$ [24]. Therefore, under CO pressure, the cluster $\text{Ru}_3(\text{CO})_{12}$ was degraded. This is in accordance with the known chemistry and kinetics of $\text{Ru}_3(\text{CO})_{12}$ under CO [25]. Furthermore, it should be noted that the other new metal–ligand vibrations *do not* correspond with the tri-nuclear complex $(\mu_2\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu_2,\eta^2\text{-OCNR}_2)$ identified in [7] after release of CO and isolation. Our solution,

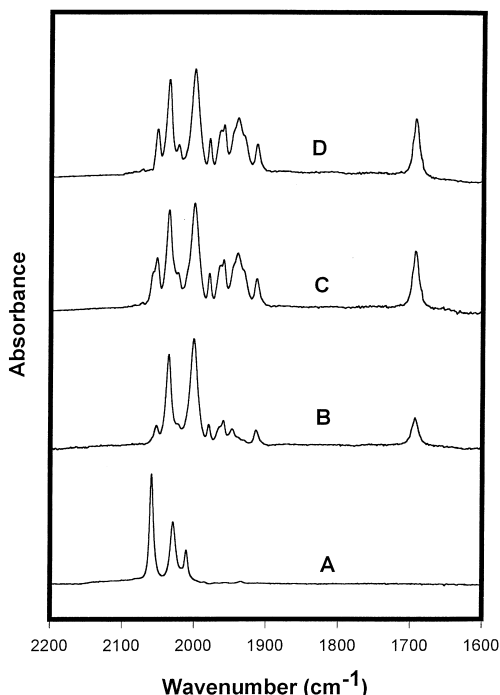


Fig. 1. In situ high-pressure infrared spectra of the reaction of $\text{Ru}_3(\text{CO})_{12}$ under CO at 333 K and in the presence of piperidine. (A) Initial spectrum of $\text{Ru}_3(\text{CO})_{12}$ (hexane, CO, piperidine, background subtraction). (B) Reaction solution after circa 6 h at 1.0 MPa CO (hexane, CO, piperidine, background subtraction). (C) Reaction solution after decreasing pressure to 0.1 MPa CO and circa 2 more hours reaction time (hexane, CO, piperidine, background subtraction). (D) Solution C after subtraction of $\text{Ru}_3(\text{CO})_{12}$ absorbance.

upon removal from the autoclave was almost colorless — in contrast to dark and highly colored solutions containing polynuclear ruthenium complexes.

3.3. After lowering pressure to 0.1 MPa

If low CO partial pressures lead to a degradation of $\text{Ru}_3(\text{CO})_{12}$ to metal or insoluble complexes (first experiment) with its associated low system activity and if CO is needed to fragment the cluster $\text{Ru}_3(\text{CO})_{12}$ to produce mononuclear, then it would be interesting to take $\text{Ru}_3(\text{CO})_{12}$ /piperidine/hexane, pressurize it to 1.0 MPa CO for a few hours and then reduce the pressure to 0.1 MPa CO. Indeed, in the first step, the precious metal catalyst precursor would be almost quantitatively transformed to mononuclear species

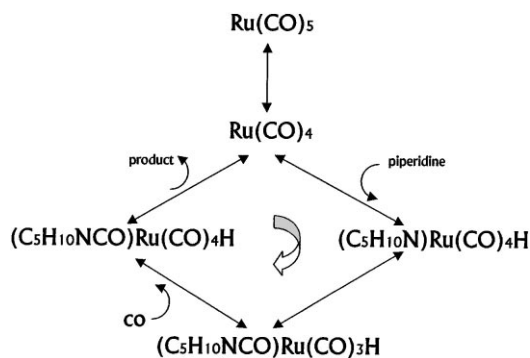
(where $\text{Ru}(\text{CO})_5$ is the primary species) and in the second step, the loss of CO partial pressure should cause the $\text{Ru}(\text{CO})_5$ to quickly transform to other mononuclear complexes due to coordinately unsaturation caused by CO dissociation. As a net effect, the concentrations of the other complexes should be increased. The primary assumption is that $\text{Ru}(\text{CO})_5$ acts as a reservoir for the active catalytic system. By taking *this path-dependent route* to the active catalytic system, little or no ruthenium will be lost and a very active system will result.

Upon lowering the CO partial pressure from 1.0 to 0.1 MPa, there was an immediate re-distribution of metal complexes in the active system. The total integrated metal–ligand absorbance remained approximately the same, but the relative intensity due to $\text{Ru}(\text{CO})_5$ was substantially reduced. After a few more hours of reaction, essentially the same metal–ligand spectrum remained, however, considerable product formation has occurred (Fig. 1, curve C). The formation of a little $\text{Ru}_3(\text{CO})_{12}$ could be verified by subtraction (Fig. 1, curve D).

3.4. Notes with $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ as precursor

A solution consisting of 200 ml hexane, 10 ml piperidine and 77 mg $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ was prepared. This solution was not homogeneous since ruthenium carbonyl chloride is only sparingly soluble in hexane. The solution was transferred to the batch reactor (333 K) and 1.0 MPa CO was added. The first spectra clearly show the characteristic bands of $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ at 2076, 2082 and 2141 [26].

Again, as the reaction proceeded, the in situ spectra show bands at 1693, 1914, 1931, 1938, 1946, 1969, 1963, 1980, 2001s, 2036s, 2052, 2058 cm^{-1} . The metal–ligand bands appear at the same wave-numbers and with approximately the same relative intensity which are shown in Fig. 1 (curve B) when $\text{Ru}_3(\text{CO})_{12}$ is used as precursor. Product formation occurs with approximately the same turnover frequency. This suggests that both $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ lead to the same active catalytic system. For completeness, it should be noted that the absolute integrated absorbance in the metal–ligand region was reduced when $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ was used as precursor. Therefore, in terms of metal utilization, $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ is not as good a precursor as $\text{Ru}_3(\text{CO})_{12}$ under these reaction



Scheme 1. A tentative catalytic cycle for the carbonylation of piperidine in the presence of ruthenium pentacarbonyl.

conditions. In other words, the yield of intermediates was lower. Finally, it should be noted that the solutions were turbid upon removal from the autoclave. This is consistent with the formation of the piperidine salts due to the presence of Cl in the precursor.

3.5. Tentative catalytic cycle

The reduction of the pressure from 1.0 to 0.1 MPa CO and the subsequent rapid concentration decrease of $\text{Ru}(\text{CO})_5$ and rapid increase in other complexes, indicates that $\text{Ru}(\text{CO})_5$ is probably a reservoir for the catalytic system. Perhaps the simplest mononuclear catalytic system consistent with these observations is shown in Scheme 1.

The reaction sequence in Scheme 1 accommodates the need for coordinately unsaturation of the mononuclear ruthenium carbonyl, the concerted addition of piperidine with cleavage of the N–H bond, CO insertion, coordinative saturation and the elimination. If the addition of piperidine and cleavage of the

N–H on $\text{Ru}(\text{CO})_4$ is not concerted, then an additional intermediate exists on the cycle.

References

- [1] D. Durand, C. Lassau, *Tetrahedron Lett.* 8 (1969) 2329.
- [2] Y. Tsuji, T. Ohsumi, T. Kono, Y. Watanabe, *J. Organomet. Chem.* 309 (1986) 333.
- [3] G. Bitsi, G. Jenner, *J. Organomet. Chem.* 330 (1987) 429.
- [4] T.J. Kealy, R.E. Benson, *J. Org. Chem.* 26 (1961) 3126.
- [5] G.L. Rempel, W.K. Teo, R.B. James, D.V. Plackett, *Adv. Chem. Ser.* 132 (1974) 166.
- [6] G. Suss-Fink, M. Langenbahn, M.T. Jenke, *J. Organomet. Chem.* 368 (1989) 103.
- [7] G. Jenner, G. Bitsi, E. Schleiffer, *J. Mol. Catal.* 39 (1987) 233.
- [8] D.F. Shriver, M.A. Drezdson, *The Manipulation of Air-Sensitive Compounds*, Wiley, New York, 1986.
- [9] D.D. Perrin, W.L.F. Armarego, *Purification of Organic Compounds*, Pergamon Press, Oxford, 1988.
- [10] W. Beck, K. Lottes, *Chem. Ber.* 94 (1961) 2578.
- [11] M. Hakimifard, *Diplomarbeit #4095*, ETH-Zurich, 1991.
- [12] M. Garland, *Dissertation #8585*, ETH-Zurich, 1988.
- [13] M. Garland, G. Bor, *Inorg. Chem.* 28 (1989) 410.
- [14] M. Garland, P. Pino, *Organometallics* 10 (1991) 1693.
- [15] Ch. Fyhr, M. Garland, *Organometallics* 12 (1993) 1753.
- [16] J. Feng, M. Garland, *Organometallics* 18 (1999) 417.
- [17] M. Garland, *Organometallics* 12 (1993) 535.
- [18] J. Feng, M. Garland, *Organometallics* 18 (1999) 1542.
- [19] G. Liu, R. Volken, M. Garland, *Organometallics* 18 (1999) 3429.
- [20] G. Liu, M. Garland, *Organometallics* 18 (1999) 3457.
- [21] U.K. Dietler, *Dissertation #5428*, ETH-Zurich, 1974.
- [22] K. Noack, *Spectrochim. Acta, Part A* 24 (1968) 1917.
- [23] R. Whyman, in: H.A. Willis, J.H. van der Maas, R.G.J. Miller (Eds.), *Laboratory Methods in Vibrational Spectroscopy*, 3rd Edition, Wiley, New York, 1987 (Chapter 12).
- [24] F. Calderazzo, F. L'Eplattenier, *Inorg. Chem.* 6 (1967) 1220.
- [25] R. Koelliker, *Dissertation #8704*, ETH-Zurich, 1988.
- [26] E. Benedetti, G. Braca, G. Sbrana, F. Salvetti, B. Grassi, *J. Organomet. Chem.* 37 (1972) 361.