Letter

Rhodium nitrone complexes: efficient catalyst for carbonylation of methanol

Pankaj Das [a], Monalisa Boruah [b], Nandini Kumari [a], Manab Sharma [a], Dilip Konwar [b], Dipak K. Dutta [a],*

[a] *Material Science Division, Regional Research Laboratory (CSIR), Jorhat 785 006, Assam, India*
[b] *Organic Chemistry Division, Regional Research Laboratory (CSIR), Jorhat 785 006, Assam, India*

Abstract

Newly synthesized rhodium(I) carbonyl complexes of the type $[Rh(CO)_2ClL]$ (**1**), where L = α,*N*-diphenylnitrone (**a**), α-styryl-*N*-phenylnitrone (**b**), *N*,*N'*-diphenyldinitrone (**c**) and α-(2-furyl)-*N*-phenylnitrone (**d**), act as efficient catalyst precursors (maximum turn over number (TON) 1200–1400 per 90 min) for carbonylation of methanol to produce acetic acid and its ester at temperature $150 \pm 10\,^{\circ}C$ and pressure 20 bar. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The chemistry of nitrones is well established with respect to its applications as catalysts as well as reagents for organic synthesis [1–4], but their transition metal chemistry is not much developed. Literature survey reveals [5–7] that only a few nitrone complexes of first row transition metals have so far been reported, where nitrones are coordinated to metal through oxygen donor. To the best of our knowledge, till today there is no report on the rhodium nitrone complex. Recently, rhodium metal complexes with different types of donor ligands have gained much attention because of their potential applications as cat-

alysts, particularly in carbonylation reaction [8–12]. Since the first report [8], the species $[Rh(CO)_2I_2]^-$ is used as preferred commercial catalyst for carbonylation of methanol to acetic acid. Research activities are continued to modify the catalyst either by incorporating different types of ligands in the metal complex species [9–12] or by changing the metal center [13–15]. Recently, BP Chemicals has commercialized an iridium iodide based catalyst system (Cativa process) for carbonylation of methanol to acetic acid [14].

As a part of our work [16,17], i.e. the effects of various ligands on rhodium catalyzed carbonylation of methanol, we report in the present communication the synthesis of rhodium(I) complexes containing different types of nitrones (Fig. 1) and their application as catalyst precursors for carbonylation of methanol.

* Corresponding author. Tel.: +91-376-370121x529;
fax: +91-376-370011.
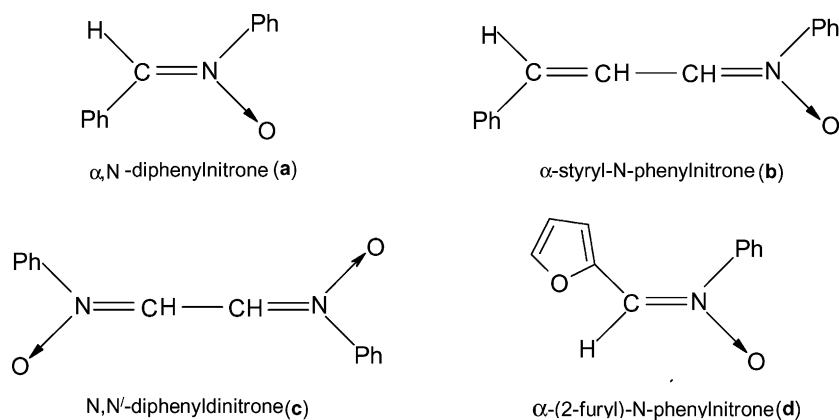*E-mail address:* dipakkrdutta@yahoo.com (D.K. Dutta).

Fig. 1. Schematic presentation of different nitrones.

2. Experimental

2.1. General methods

Elemental analyses were performed using Perkin-Elmer 2400 elemental analyzer and IR spectra were recorded in KBr disc on a Perkin-Elmer System 2000 FT IR spectrophotometer. The ^1H (300.13 MHz) NMR spectra were recorded in $CDCl_3$ solution on a Bruker DPX-300 spectrophotometer and chemical shift were reported relative to $SiMe_4$ as an internal reference. The carbonylation reaction was carried out in a 150 ml teflon-coated reactor (Laboratory High Pressure Reactor, model HR-100, Berghof, Germany) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID). Nitrones [18] and $[Rh(CO)_2Cl]_2$ [19] were prepared by literature methods.

2.1.1. Synthesis of complexes 1a–d

$[Rh(CO)_2Cl]_2$ (0.0515 mmol) was dissolved in $CHCl_3$ (40 cm^3) and to this solution, a stoichiometric quantity (Rh:L = 1:1) of the respective nitrone ligand (a–d) (0.108 mmol) was added. The reaction mixture was stirred for 2 h at room temperature under nitrogen atmosphere. The solution was then evaporated to dryness. The solid compound thus obtained was washed several times with petroleum ether and finally dried over $CaCl_2$ in a desiccator.

2.1.2. Synthesis of complexes 1d′

A red colored compound was formed on storing the orange-red complex **1d** in a desiccator for about 10 days. The product was thoroughly washed with hexane–petroleum ether mixture.

Analytical data for the complexes are as follows:

1a: color (deep red); yield (93%); anal. calcd. for $C_{15}H_{11}ClNO_3Rh$ in %: C (46.03), H (2.81), N (3.58); found: C (45.93), H (2.76), N (3.49).

1b: color (reddish yellow); yield (95%); anal. calcd. for $C_{17}H_{13}ClNO_3Rh$ in %: C (48.92), H (3.11), N (3.35); found: C (48.76), H (3.21), N (3.44).

1c: color (reddish brown); yield (91%); anal. calcd. for $C_{16}H_{12}ClN_2O_4Rh$ in %: C (44.23), H (2.76), N (6.46); found: C (44.34), H (2.65), N (6.57).

1d: color (orange-red); yield (90%); anal. calcd. for $C_{13}H_9ClNO_4Rh$ in %: C (40.94), H (2.36), N (3.67); found: C (40.73), H (2.45), N (3.71).

1d′: color (red); yield (80%); anal. calcd. for $C_{12}H_9ClNO_3Rh$ in %: C (40.73), H (2.54), N (3.96); found: C (40.81), H (2.57), N (3.93).

2.2. Carbonylation of methanol

MeOH (3.1 ml, 0.076 mol), MeI (1 ml, 0.006 mol), H_2O (1 ml, 0.055 mol) and the complex **1** (0.045 mmol) were charged into the reactor. The reactor was purged with CO gas for about 5 min and then pressurized with CO gas (6 bar, 0.036 mol at about 30 °C). The pressure in the reactor was maintained at about 20 bar

by increasing the temperature to $150 \pm 10\,°C$ (reaction time 30–90 min).

For recycling experiment, the orange colored solution obtained after carbonylation reaction (90 min run) was evaporated to dryness under reduced pressure to get a dark brown solid mass. With this solid mass as catalyst the carbonylation reaction was repeated by maintaining the same experimental conditions as described above.
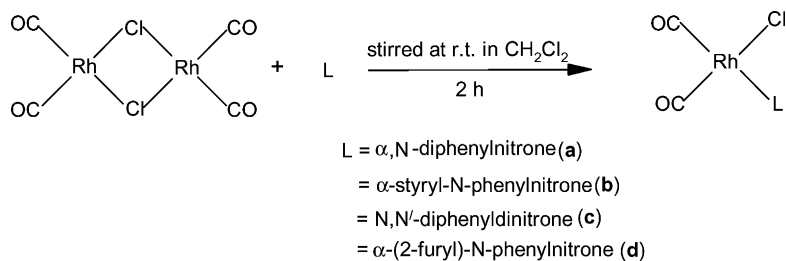
3. Results and discussion

3.1. Synthesis and characterization of complexes

The dimeric complex $[Rh(CO)_2Cl]_2$ undergoes bridge splitting reaction with two molar equivalent (Rh:L = 1:1) of nitrone ligands (**a–d**) to produce complexes of the type $[Rh(CO)_2ClL](1a–d)$ (L = nitrones) (Scheme 1). The IR spectra of the complexes **1a–d** exhibit two almost equally intense terminal $\nu(CO)$ bands in the range 2000–2080 cm^{-1} (Table 1) indicating *cis* disposition of the two carbonyl groups

[20–22]. IR spectra also show a strong $\nu(NO)$ stretching band in the range 1160–1200 cm^{-1} (Table 1), which is about 25–40 cm^{-1} lower compared to the corresponding free ligands value indicate formation of rhodium–oxygen bond. The ^{1}H NMR spectra of all the complexes show (Table 1) a set of multiplates in the range δ 6.8–7.7 ppm assigned to the aromatic proton and other characteristic resonances for different types of –CH protons. Except **1d** all the complexes are very much stable in air.

It has been observed that the dicarbonyl complex **1d** on storing in a desiccator for about 10 days undergoes a decarbonylation reaction resulting a monocarbonyl complex $[Rh(CO)Cl\{\alpha\text{-}(2\text{-furyl})\text{-}N\text{-phenylnitrone}\}]$ (**1d′**) (Scheme 2) as indicated by a single terminal $\nu(CO)$ value at 2000 cm^{-1}. The $\nu(COC)$ band occurs at 1025 cm^{-1} which is about 15 cm^{-1} lower compared to that of the complex **1d** indicating chelate formation through furyl oxygen atom. The chelation of the ligand is further substantiated by ^{1}H NMR spectroscopy (Table 1) where the signal due to the –CH proton attached to furyl oxygen atom is shifted to downfield compared to that of the non-chelated

stirred at r.t. in CH$_2$Cl$_2$
2 h

L = α,N-diphenylnitrone(**a**)

= α-styryl-N-phenylnitrone(**b**)

= N,N′-diphenyldinitrone (**c**)

= α-(2-furyl)-N-phenylnitrone (**d**)

Scheme 1.

Table 1
IR and NMR spectral data of the complexes

Complexes	IR (cm^{-1})		^{1}H NMR (δ in ppm)[b]
	$\nu(CO)$	$\nu(NO)$[a]	
1a	2000, 2070	1170	7.0–7.6 (m, 10H, C$_6$H$_5$), 8.2 (s, 1H, CH)
1b	2005, 2070	1165	6.8–7.4 (m, 10H, C$_6$H$_5$), 7.6 (d, 2H, CH), 7.8 (d, 1H, CH=N)
1c	2020, 2080	1160	7.1–7.7 (m, 10H, C$_6$H$_5$), 8.4 (s, 2H, CH)
1d	2020, 2060	1200	6.9–7.4 (m, 5H, C$_6$H$_5$), 7.9 (s, 1H, CH), 6.3 (s, 1H, C$_4$H$_3$O), 7.6 (s, 1H, C$_4$H$_3$O), 7.7 (s, 1H, C$_4$H$_3$O)
1d′	2000	1200	6.8–7.3 (m, 5H, C$_6$H$_5$),7.9 (s, 1H, CH), 6.4 (s, 1H, C$_4$H$_3$O), 7.5 (s, 1H, C$_4$H$_3$O), 8.2 (s, 1H, C$_4$H$_3$O)

[a] Free ligand $\nu(NO)$ value: 1200 (**a**); 1195 (**b**); 1185 (**c**); 1240 (**d**).

[b] m: multiplate; s: singlet; d: doublet.
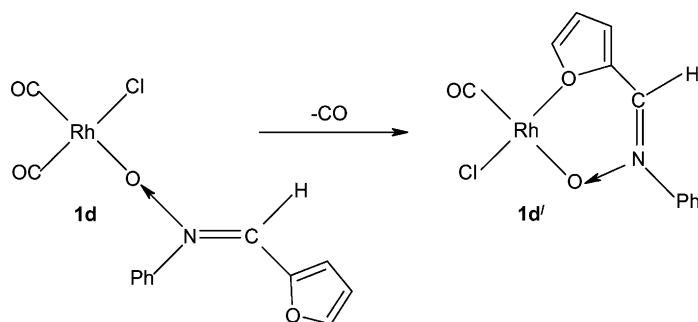
Scheme 2.

complex **1d**. In the complex **1d′** the CO is at *trans* to nitrone oxygen atom because high electron withdrawing nature of CO prefer a more electron donor group at its *trans* position [23].

3.2. Carbonylation of methanol

The results of batch carbonylation of methanol to acetic acid and its ester in presence of complexes **1a–d** as catalyst precursors are shown in Table 2. GC anal-ysis of the product reveals that when the reaction was carried out for 30 min, the precursor complex **1a–d** show 48, 51, 54 and 52% conversion of methanol, respectively, with corresponding turn over number (TON) 691, 734, 777 and 748. Under the same exper-imental condition the well-known catalyst precursor $[Rh(CO)_2I_2]^-$ generated in situ from $[Rh(CO)_2Cl]_2$ [24] show only 30% conversion with a TON 430. It can be seen from Table 2 that as the reaction time increases the TON also increases. The complexes

Table 2
Time resolved data of carbonylation reaction of methanol[a]

Complex	Time (min)	Conversion (%)	Acetic acid (%)	Methyl acetate (%)	TON[b]
$[Rh(CO)_2Cl]_2$	30	30	4	26	430
	60	43	9	34	618
	90	64	12	52	921
1a	30	48	12	36	691
	60	61	20	41	878
	90	83	43	40	1195
	90[c]	82	46	36	1180
1b	30	51	14	37	734
	60	67	28	39	964
	90	91	55	36	1310
	90[c]	89	56	33	1281
1c	30	54	14	40	777
	60	71	27	44	1022
	90	96	55	41	1382
	90[c]	95	60	35	1367
1d	30	52	12	38	748
	60	63	23	40	907
	90	87	37	50	1252
	90[c]	85	38	47	1223

[a] Temperature: $150 \pm 10\,°C$; pressure: 20 bar.
[b] TON: mole of product per mole of catalyst.
[c] Recycled.

1a–d after 90 min reaction time show a maximum conversion of 83, 91, 96 and 87% respectively with corresponding TON 1195, 1310, 1382 and 1252. After completion of carbonylation reactions (90 min run) the catalyst has been recovered. On recycling the catalyst for second time almost the same amount of conversion has been found (Table 2) indicating longer durability as well as stability of the catalyst. It has been observed that for a particular reaction time the complexes **1a–d** show higher TON over the species $[Rh(CO)_2I_2]^-$, which may be attributed to higher stability of the complexes. The higher conversion or TON shown by the complexes **1b–d** over **1a** may be attributed to the possible chelate formation in the complexes through O, C=C(**1b**) or O, O(**1c** and **1d**) donors of the ligands (Fig. 1) leading to higher stability of the intermediate complex formed during the catalytic reaction.

Acknowledgements

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