© *Proc. Indian natn. Sci. Acad.*, **52**, A, No. 4, 1986, pp. 1013–1019
Printed in India.

SOME COMPLEXES OF RHODIUM AND IRIDIUM WITH NITROGEN DONOR LIGANDS*

G K N REDDY, R HALESHA, E G LEELAMANI *and* N M N GOWDA

Department of Chemistry, Central College, Bangalore University, Bangalore-560 001, India

(*Received 7 March 1986*)

Synthesis and characterisation of several mono, bi and poly nuclear complexes of rhodium and iridium containing nitrogen donor heterocycles are discussed. Studies on the catalytic activity of a few of these complexes are described.

Key Words : Rhodium; Iridium; Nitrogen Heterocycles; Catalytic Activity; Polynuclear Complexes

INTRODUCTION

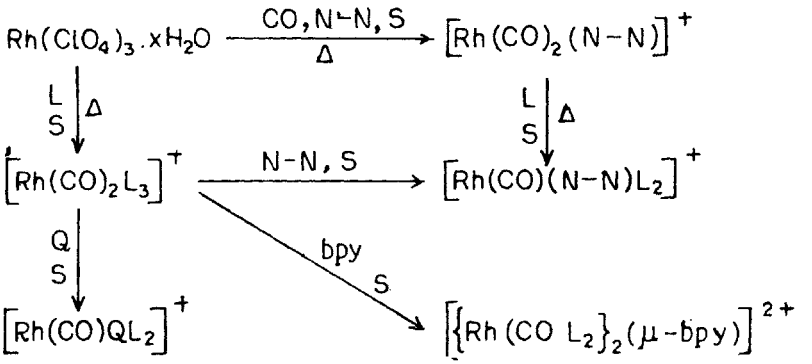
A wide variety of complexes of rhodium and iridium with nitrogen donor heterocycles have been investigated in recent years for their catalytic activity under homogeneous conditions towards hydrogenation, hydroformylation, water gas shift and related reactions.[1–7] There have also been several attempts to examine the possibility of some of these complexes behaving as one-dimensional conductors.[8,9] In view of the possibility of such applications the synthesis and characterisation of complexes of this type is of considerable interest.

SYNTHESIS AND STRUCTURE

Over the last several years a number of complexes of rhodium and iridium with nitrogen donor ligands have been isolated and reported from these laboratories. Thus a series of four- and five-coordinate cationic rhodium(I) complexes of the formulae $[Rh(CO)_2(N—N)]^+$, $[Rh(CO)(N–N)(o\text{-tolyl}_3P)]^+$, $[Rh(CO)(N–N)L_2]^+$, $[Rh(CO)QL_2]$ $[\{Rh(CO)L_2\}_2(\mu\text{-bpy})]^{2+}$ where N–N is an endobidentate nitrogen donor ligand-bipy, phen, biq, or α-pyBzlH; L is tertiary phosphine or arsine and Q is a monodentate nitrogen heterocycle, were reported as their perchlorate salts as early as 1970 and during the following years.[10–12] The reactions used to isolate these complexes are summarised in Scheme I. Binuclear cationic complexes of the type referred in the case of exobidentate ligand bpy have also been isolated with other similar ligands like bpe, bpel and phz.[13]

A list of abbreviations used appears at the end of the paper.

*Presented at the INSA Golden Jubilee Symposium on *Recent Trends in Inorganic Chemistry* held in Calcutta in December 1985.



S = alcohol; N–N = bipy, phen, biq, α-pyBzlH

L = Ph_3P, *p*-tolyl$_3$P, Ph_3As, Cy_3As, Ph_2RAs (*R* = alkyl)

Q = py, pyz, pic, qn, iqn, bfqn, Izl, BzlH

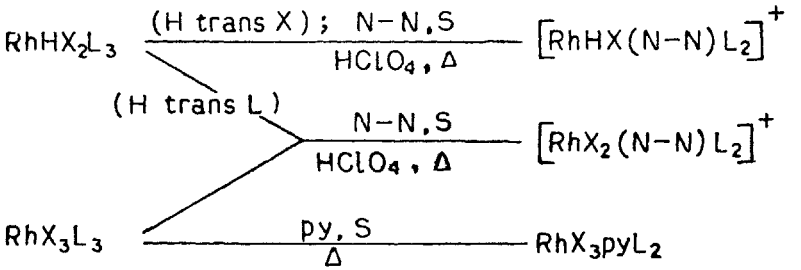
Scheme I

It may be seen from Scheme I that while the exobidentate ligand bpy reacts with $[Rh(CO)_2L_3]^+$ to given binuclear cationic complexes, pyz which can also act as a bidentate bringing ligand fails to yield such species. During these investigations we have examined the factors, such as steric and electronic, that may influence the metal ion of a d^8 electron configuration to achieve five coordination as against four coordination.

A number of six coordinate cationic and neutral rhodium(III) complexes, involving nitrogen donor heterocycles, of the types

$[RhX_2(N\text{-}N)_2]\,X$(*X* = Cl or Br; N–N = biq, α-pyBzlH),

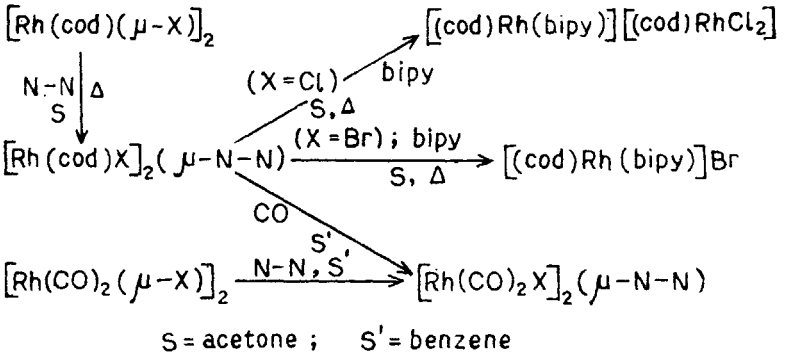
$[RhX_2(N\text{-}N)\,L_2]$,$^+$ $[RhHX(N\text{-}N)_2]^+$ (N–N = bipy or phen; *L* = Ph_2Etp or Ph_2RAs; *R* = Me, Et, *n*-pr, *n*-Bu) and $RhX_3py(Ph_2RAs)_2$ were also reported from these laboratories.[14,15] Reactions involved in the synthesis of some of these complexes are described in Scheme II.



S = alcohol

Scheme II

We have extended the above studies in the recent past to isolate neutral binuclear complexes of rhodium(I) of the type [Rh(diene) X]$_2$ (μ-N–N) where X is Cl or Br; diene is cod or nbd; N–N is bpy, bpe, bpel, phz, Pyz or qux. The binuclear nature of these compounds has been confirmed by the crystal structure analysis of the pyz complex [Rh(cod) Cl]$_2$ (μ-pyrazine).[16] In these binuclear complexes, the diene can be displaced by carbon monoxide to get carbonyl complexes of the formula [Rh(CO)$_2$$X$]$_2$ (μ-N–N). The latter compounds may also be obtained by the reaction of dihalobridged binuclear carbonyl complexes of rhodium, [Rh(CO)$_2$ μ-X)]$_2$ with the corresponding nitrogen heterocycle. It may be noted that pyz while fails to bridge two rhodium atoms in a cationic complex is able to do so in neutral species. Treatment of some of these binuclear complexes with the endobidentate ligand bipy results in the cleavage of the N–N bridge to produce ionic species.[16,17] Some of these reactions are depicted in Scheme III. The iridium (I) analogues of the composition



Scheme III

[Ir(cod) Cl]$_2$ (μ–N–N) where N–N is pyz, bpy, bpel have also been isolated and characterised.[13]

In the aforesaid reactions involving the preparation of binuclear rhodium complexes, if the exobidentate nitrogen donor ligand is replaced with BZ1H or 2–C–substituted Bz1H (R-Bz1H) and the reactions are carried out in presence of triethylamine (to facilitate deprotonation of BZ1H at the pyrrole nitrogen) trinuclear complexes of the composition [Rh(cod) (μ-R-Bzl)]$_3$ (I) where R is H, Me, Et, or n-pr, may be isolated. The BZ1 containing species (R = H) has however, been briefly reported earlier in a patent and has been obtain from a different route.[18] Carbon monoxide displaces the diene in these trinuclear complexes to produce tetranuclear carbonyl species of the type [Rh(CO)$_2$ (μ-R-Bzl)]$_4$ (II). Such a change in the nuclearity of the polynuclear species when cod is displaced by CO has been reported earlier for a few similar complexes.[19,20] It has been suggested that replacement of diene with CO modifies the electron density at the metal atom requiring significant changes in molecular geometry to stabilise the system.[19] A few iridium

analogues have also been synthesised. Structures for these polynuclear complexes have been assigned on the basis of nmr spectral data and molecular weight measurements.[13] IR and ^1H nmr spectral data of some of these complexes are compiled in Table I.

TABLE I

IR (in nujol) and PMR (in $CDCl_3$) spectral data of rhodium and iridium complexes

Complex	νCO(cm^{-1})/ CH_2	δ cod CH	δ2-*R*-Bzl *R*	(*R* = H or Me) $CH(C_6H_4)$
$[Rh(cod)\ Cl]_2$	1.75m, 2.52m	4.22s		
$[Rh(cod)\ (\mu\text{-Bzl})]_3$	1.92m, 2.50m	4.28s	6.70s	6.95m, 7.79m
$[Rh(CO)_2\ (\mu\text{-Bzl})]_4$	2020, 2080		6.53s	7.20m, 7.72m
$[Rh(cod)\ (\mu\text{-MeBzl})]_3$	1.0–3.0m	3.85–4.43m	0.96s,	6.80m, 7.20m
			1.97s,	7.90m, 8.10m,
			2.15s	8.44m
$[Rh(CO)_2\ (\mu\text{-MeBzl})]_4$	2010, 2080		0.42s,	7.00m, 7.18m,
			1.56s,	7.31m, 7.48m,
			1.91s	7.70m, 7.88m
$[Ir(cod)\ (\mu\text{-MeBzl})]_3$	1.2–2.7m	3.58–4.40m	0.90s,	6.87m, 7.25m,
			1.87s,	7.82m, 8.00m,
			2.17s	8.30m

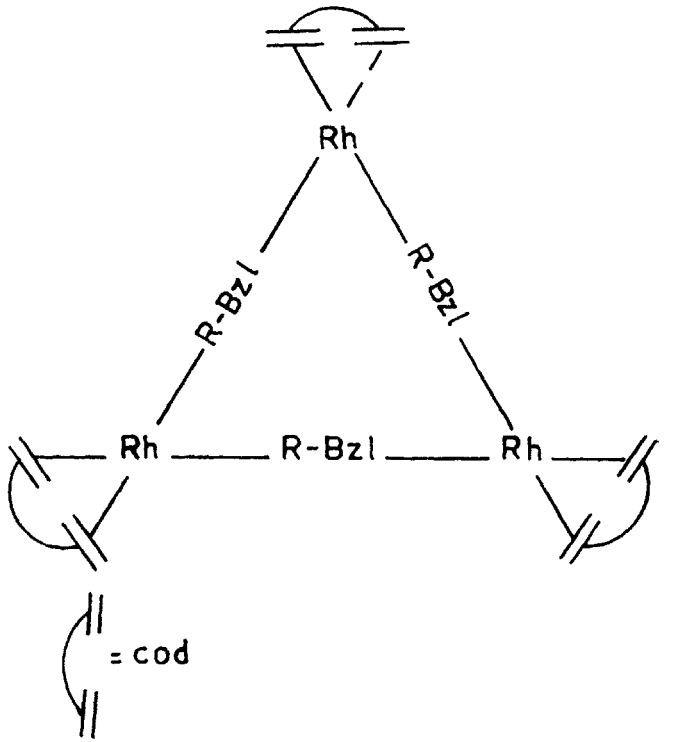
s – singlet; m – multiplet

We have furthur extended the work to attempt the isolation of rhodium and iridium complexes with mulitdentate nitrogen donor ligands derived from benzimidazole. Thus 2,6-*bis*(2-benzimidazolyl)-pyridine[21] reacts with hydrated rhodium and iridium trihalides to yield complexes of the formula $MX_3(bBzlH_2py)$ (M = Rh, Ir; X = Cl, Br) wherein the heterocycle functions as a tridentate ligand and the complexes are expected to have an octahedral configuration. An octahedral structure for a nickel complex containing this ligand and a few other complexes with similar ligands has been proposed earlier.[22–24] Addition of this ligand to carbonylated solutions of rhodium halide in alcohol or to an ethanolic solution of $[Rh(CO)_2\ (\mu\text{-}X)]_2$ gives carbonyl complexes as green solids, which analyse for the formula $Rh(CO)_2\ X(bBzlH_2py)^{3/2}H_2O$. The ligand presumably functions as a mono or bidentate ligand in these complexes.[24] Similar carbonyl complexes of iridium have also been isolated, but these appear to be mixtures and are being further investigated.[25]

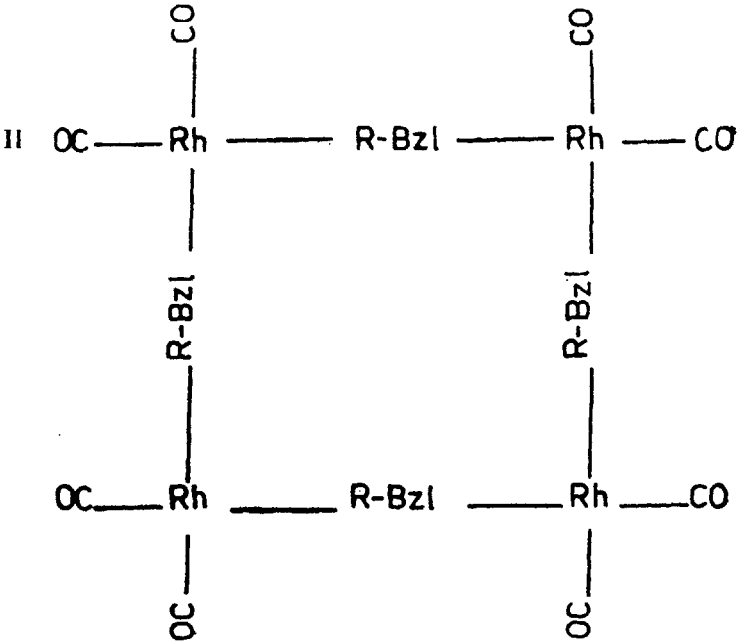
CATALYTIC ACTIVITY

Several of the complexes described above are potential homogeneous catalysts. The cation, $[Rh(CO)_2\ bipy]^+$ or its salts have been investigated as homogeneous catalysts for carbonylation or water gas shift reactions by other workers.[2,7] We have studied the catalytic activity of $[Rh(biq)_2\ Cl_2]Cl$, and the dinuclear complexes $[Rh(cod)\ Cl]_2$

I


Rh
R-Bzl
R-Bzl
Rh
R-Bzl
Rh
= cod

II


CO
CO
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(μ-N–N) (N–N = bpy, pyz, phz) towards hydrogenation of some organic substrates.

[Rh(biq)$_2$ Cl$_2$] Cl reacts reversibly with hydrogn in alkaline methanolic medium and catalyses the hydrogenation of olefins to saturated hydrocarbons. The catalytic behaviour of the complex is akin to that of its bipy analogue reported by Mestroni *et al.*[26] The complex, however, is inactive towards reduction of aromatic nitro compounds to the corresponding amines.[27]

The dinuclear complexes [Rh(cod)Cl]$_2$ (μ-bpy/pyz) catalyse the reduction of nitrophenols and nitrobenzoic acids to the corresponding amino derivatives in methanol. The catalytic cycle for the added substrate may be repeated two to three times.[28] [Rh(cod) Cl]$_2$(μ-phz) in presence of sodium borohydride in dimethyl formamide is active towards hydrogenation of olefins and towards reduction of nitro compounds to the corresponding amines.[29] The kinetics of hydrogenation of olefins by this catalyst has been investigated and the reaction is found to be first order with respect to the substrate as well as the catalyst and the rate law

$$\frac{-d(1\text{ – hexene})}{dt} = k_2\,[1\text{–hexene}]\,[\{Rh(cod)\,Cl\}_2\,(\mu\text{–phz})]$$

is applicable.[30]

The green dicarbonyl complex RhCl(CO)$_2$ (bBzlH$_2$py) reversibly loses carbon monoxide to turn yellow in alcoholic medium and is found to catalyse the oxidation of CO to CO$_2$ in hot methoxyethanol in presence of oxygen.[25] This reaction is being further investigated.

Abbreviations

bBzlH$_2$py	2,6-*bis*(2-benzimidazolyl) pyridine
bfqu	benzo(f)quinoline
bipy	2,2′-bipyridine
biq	2,2′-biquinoline
bpe	1,2-*bis*(4-pyridyl) ethane
bpel	1,2-*bis*(4-pyridyl) ethylene
bpy	4,4′-bipyridine
Bu	butyl
BzlH	benzimidazole
cod	cycloocta-1,5-diene
Cy	cyclohexyl
Et	ethyl
iqn	isoquinoline
Izl	imidazole
Me	methyl
nbd	norborna-2,5-diene
phen	1,10-phenanthroline
phz	phenazine
pic	picoline (α, β or γ)
Pr	propyl
py	pyridine

pyBzlH	pyridyl benzimidazole (α or β)
pyz	pyrazine
qn	quinoline
qux	quinoxaline

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