

SOME CARBONYL COMPLEXES OF RHODIUM
AND IRIIDIUM WITH TRICYCLOHEXYL
ARSINE

IN recent years a number of carbonyl and hydride complexes of the platinum group metals, wherein the metal-carbon or the metal-hydrogen bond is stabilised by the presence of tertiary arsines and phosphines, have been synthesised and their properties investigated in view of their potential importance as catalysts¹⁻³. In this context several novel carbonyl and hydride complexes of the platinum metals containing the bulky ligand tricyclohexyl phosphine have been reported³⁻⁹. The corresponding compounds containing tricyclohexyl arsine however have not been well investigated. Hieber and Heinicke¹⁰ have reported the preparation of a few nitrosyl complexes of rhodium of the formulae $[\text{Rh}(\text{NO})_2\{(\text{C}_6\text{H}_{11})_3\text{As}\}_2][(\text{NO})_2\text{RhCl}_2]$ and $\text{Rh}(\text{NO})\{(\text{C}_6\text{H}_{11})_3\text{As}\}_3$ and a simple compound of the type $\text{RhCl}_2[(\text{C}_6\text{H}_{11})_3\text{As}]_3$. We report here the preparation and characterisation of some new carbonyl and hydrido carbonyl complexes of rhodium and iridium containing tricyclohexyl arsine.

When tricyclohexyl arsine is added to the pale yellow solution obtained by passing carbon monoxide through a refluxing solution of rhodium halide in ethanol^{11,12} or methoxy ethanol, yellow crystalline compounds of the type *trans*- $\text{RhX}(\text{CO})[(\text{C}_6\text{H}_{11})_3\text{As}]_2$, where X is Cl or Br, get separated. These compounds show a νCO peak around 1945 cm^{-1} and add on the corresponding halogen to give octahedral compounds of the type $\text{RhX}_3(\text{CO})[(\text{C}_6\text{H}_{11})_3\text{As}]_2$, which show a νCO peak *ca.* 2060 cm^{-1} (Table I). Under similar conditions in

methoxy ethanol solvent iridium halides give mixtures containing two or more species. However if hydrohalic acid is added to the reaction system after the addition of the arsine, hydrido carbonyls of the type $\text{IrHX}_2(\text{CO})[(\text{C}_6\text{H}_{11})_3\text{As}]_2$ (white) may be isolated^{13,14}. These hydrido carbonyls show two peaks in the infrared region, an intense peak *ca.* 2010 cm^{-1} which we assign as due to the carbonyl stretch and a comparatively weaker peak around 2180 cm^{-1} which is due to the iridium-hydrogen stretch. They also have an iridium-hydrogen bending mode *ca.* 740 cm^{-1} . The compounds further show a resonance peak around 27τ (Table I) on the high field side of their nmr spectra confirming the presence of hydridic hydrogen¹³. A comparison of this data with that of similar compounds reported earlier¹³ suggest that the CO and the hydridic hydrogen are *trans* to the two halogens in the compounds (leaving the arsines *trans* to each other).

Attempts to dehydrohalogenate these hydrido carbonyls of iridium by treating the compounds with sodium methoxide¹³ or piperidine¹⁵ produce products whose infrared data suggest that they are probably mixtures of carbonyl compounds of iridium (I) of the type $\text{IrX}(\text{CO})[(\text{C}_6\text{H}_{11})_3\text{As}]_2$ and their oxygen adducts¹⁶ of the type $\text{IrX}(\text{CO})(\text{O}_2)[(\text{C}_6\text{H}_{11})_3\text{As}]_2$ [The solid products show two νCO peaks one around 1930 cm^{-1} probably due to the iridium (I) carbonyl compound and another one around 2000 cm^{-1} which may be ascribed as due to the oxygen adduct. There is also a peak around 840 cm^{-1} which may be assigned to $\nu\text{O-O}$ stretch]. These are being further investigated. Similarly attempts to prepare hydrido carbonyl complexes of

TABLE I

Compound*	M.P. or Dec. P. (°C)	IR bands (cm^{-1})†		$\tau\text{M-H}\ddagger$	Analytical data (%) calculated (found)		
		νCO	$\nu\text{M-H}$		Carbon	Hydrogen	Halogen
$\text{IrHCl}_2(\text{CO})\text{L}_2$	-- > 280	2012	2179 (743)**	27.32	47.23 (47.03)	7.18 (6.82)	7.54 (7.94)
$\text{IrHBr}_2(\text{CO})\text{L}_2$	-- > 280	2010	2180 (741)**	26.60	43.14 (43.17)	6.56 (6.62)	15.52 (15.11)
$\text{RhCl}(\text{CO})\text{L}_2$	-- 270-272	1943			54.51 (54.04)	8.16 (8.00)	4.35 (4.47)
$\text{RhBr}(\text{CO})\text{L}_2$.. 252-255	1947			51.28 (51.70)	7.68 (7.97)	9.22 (9.45)
$\text{RhCl}_3(\text{CO})\text{L}_2$	-- 189-193	2061			50.17 (49.52)	7.51 (7.50)	12.01 (11.61)
$\text{RhBr}_3(\text{CO})\text{L}_2$... 188-190	2053			43.32 (41.73)	6.49 (6.43)	23.36 (25.04)
RhCl_3L_2	... 226-228				50.39 (49.31)	7.75 (7.76)	

* L = $(\text{C}_6\text{H}_{11})_3\text{As}$; 10^{-3} M solutions in nitrobenzene are non-electrolytes. † Infrared spectra taken in nujol. ** M-H bending mode. ‡ nmr spectra taken in CDCl_3 using TMS as internal standard.

rhodium of the type $\text{RhHX}_2(\text{CO})[(\text{C}_6\text{H}_{11})_3\text{As}]_2$ by reacting the rhodium (I) carbonyl compounds with the corresponding hydrohalic acid produce only the rhodium (III) compounds of the type $\text{RhX}_3(\text{CO})[(\text{C}_6\text{H}_{11})_3\text{As}]_2$, suggesting that the hydrido carbonyls of rhodium are very unstable and easily get converted to the rhodium (III) carbonyl compounds. Such observations have been made earlier also¹¹⁻¹². The rhodium (I) carbonyl compounds also fail to add on molecular oxygen or nitrogen.

Rhodium trichloride however reacts with tricyclohexyl arsine in methoxy ethanol in presence of hydrochloric acid to give a five-co-ordinate reddish-brown crystalline compound of the formula $\text{RhCl}_3[(\text{C}_6\text{H}_{11})_3\text{As}]_2$. The formation of such a five-co-ordinate compound of rhodium (III) as against a six-co-ordinate compound is probably due to steric factors involving the bulky arsine. The configuration and other aspects of this compound are being investigated.

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THERMAL RESPONSES IN *CATLA CATLA* FRY

EARLIER, results have been reported on the thermal responses in *Cyprinus carpio* and *Cirrhina mrigala* fry and fingerlings¹⁻². Recently an attempt has been made to study the responses of *Catla catla* fry to temperature stress and shock under laboratory conditions. *Catla catla* constitutes an important inland fishery resource in India.

The responses of *Catla catla* fry (2.5–3.5 cm length) to thermal stress were studied by exposing the fry to various test temperatures ranging from 30.3°C to 36.0°C. The mortalities observed over 24 hr test period are given in Table I. It is seen that the Median Lethal Temperature (MLT) is 36.0°C.

TABLE I
Responses of carp fry to various water temperatures
(Exposure time 24 hr)

No. of specimens	Acclimation temperature (°C)	Test temperature (°C)	% Mortality
20	20.3	30.3 ± 0.1	10
20	21.5	33.5 ± 0.1	15
20	22.0	35.9 ± 0.1	45
20	22.5	36.0 ± 0.1	50

TABLE II
Responses of carp fry to test temperature of 38.4°C ± 0.1 for various exposure periods

No. of specimens	Duration of Exposure (min)	% Mortality	% Mortality observed on transfer to acclimated water (48 hr)
12	2	0	0
12	4	0	0
12	6	0	17
12	8	0	33

The effects of thermal shock were studied by exposing carp fry to temperatures above MLT. In first set of experiments the fry were momentarily