



Mixed-ligand Complexes of Ruthenium(II) and Iridium(III) with Triphenylphosphine and Thiocarbohydrazide

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The ligand substitution reactions in precursor complexes $[\text{Ru}(\text{P}\Phi_3)_4\text{Cl}_2]$, $[\text{RuH}(\text{CO})(\text{P}\Phi_3)_3\text{Cl}]$ and $[\text{Ir}(\text{CO})(\text{P}\Phi_3)_2\text{Cl}]$ are reported using thiocarbohydrazide as ligand. The solid products isolated after ligand displacement reaction in $[\text{Ir}(\text{CO})(\text{P}\Phi_3)_2\text{Cl}]$ are further undergo oxidative-addition easily with ethanolic HCl leading to the formation of other iridium(III) complexes. All complexes are characterized by elemental analysis, IR, UV-VIS, ^1H NMR, molar conductivity and magnetic susceptibility data. Probable octahedral structure of ruthenium(II) and iridium(III) complexes are reasonably assigned.

Key Words: Organic derivatives, Ruthenium(II), Iridium(III) Thiocarbohydrazide.

INTRODUCTION

Survey of literature reveals that tertiary phosphine complexes of ruthenium¹⁻⁴ and iridium⁵⁻⁷ are versatile catalyst for many hydrogenation and hydroformylation reactions. They have interesting and unique insight into structure, bonding and reactivity of molecules display in solutions. The present communication comprises the study on synthesis, characterization and reactivity of mixed ligand derivatives of Vaska-Catalyst⁸, Wilkinson compound⁹ and $[\text{RuH}(\text{CO})(\text{P}\Phi_3)_3\text{Cl}]$ ¹⁰. The ligand substitution reaction as well as oxidative-addition reactions using thiocarbohydrazide is thoroughly investigated and tentative structure of new isolated products are assigned.

EXPERIMENTAL

All reagents and solvents used were of AR or CP-grade. Solvents were distilled and dried before use. Thiocarbohydrazide¹¹ (TCH) was prepared by reacting hydrazine hydrate with CS_2 (m.p.=174 °C) and precursor complexes $[\text{Ru}(\text{P}\Phi_3)_4\text{Cl}_2]$ ⁹, $[\text{RuH}(\text{CO})(\text{P}\Phi_3)_3\text{Cl}]$ ¹⁰ and $[\text{Ir}(\text{CO})(\text{P}\Phi_3)_2\text{Cl}]$ ⁸ were prepared by the methods reported in literature. The preparation of ruthenium(II) complexes were similar to earlier method¹². All iridium(III) complexes were prepared by ligand substitution in Vaska-complex followed by oxidative-addition. Benzene solution of $[\text{Ir}(\text{CO})(\text{P}\Phi_3)_2\text{Cl}]$ and ethanolic thiocarbohydrazide was stirred on magnetic stirrer for 2 h at 85 °C in covered beaker and 30 % ethanolic solution of HCl (15 mL) was added after cooling. The mixture was further reduced to -15 mL cooled and ether added. The compound obtained with different

metal ligand ratios were washed with ice-cold benzene and dried under reduced pressure.

C, H and N analyses were performed by microanalysis division, RSIC, CDRI, Lucknow. Infrared spectra of ligand and complexes were recorded on a Perkin-Elmer Model-577 spectrophotometer in the range of 4000-200 cm^{-1} as KBr pellets. The UV and visible spectra of ligand and complexes were recorded on a Beckmann and Carl Zeiss (Jenna) spectrophotometer. The magnetic measurements were made on a Gouy balance and the diamagnetic corrections for the ligand molecule were applied. The molar conductance of complexes (10^{-3} M) were measured in DMF using Wiss-werkstatter weitheim obb type LBR conductivity meter. ^1H NMR spectra of ligand and some complexes were recorded with 90 MHz, NMR Spectrophotometer using TMS as internal indicator. The complexes were dissolved in CDCl_3 for recording their ^1H NMR spectra in the range of 0-10 ppm. The number of protons were obtained with the help of internal callibrator.

Sulphur, chlorine and phosphorus were estimated gravimetrically. Metting points were determined on a Fisher-John metting point apparatus.

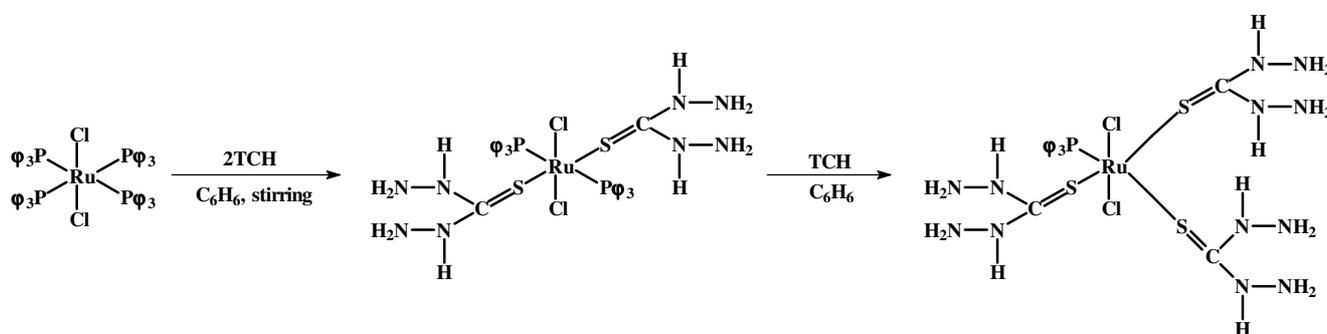
RESULTS AND DISCUSSION

The physical chemical characteristics of the synthesized complexes are given in Table-1.

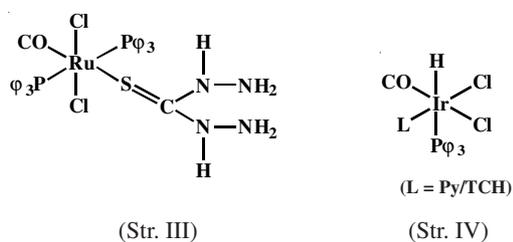
Wilkinson complex⁹ display ligand displacement reaction in benzene and three $\text{P}\Phi_3$ molecules could be easily replaced by thiocarbohydrazide (**Scheme-I**).

TABLE-I
 ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

S. No.	Complex/ Molecular formula	Colour/m.p. (°C)	Elemental analysis (%): Found (Calcd.)				Molar cond. ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
			C	H	N	Ru	
1	[RuCl ₂ (Pφ ₃) ₂ (TCH) ₂] (RuC ₃₈ I ₄₂ M ₈ P ₂ S ₂ Cl ₂)	Light yellow (115)	50.32 (50.22)	4.20 (4.18)	12.43 (12.33)	11.10 (11.12)	nc
2	[RuCl ₂ (Pφ ₃) ₂ (TCH) ₃] (RuC ₂₁ H ₃₃ N ₁₂ S ₃ Cl ₂)	Yellow (125)	33.55 (33.51)	4.40 (4.38)	22.41 (22.34)	13.50 (13.40)	nc
3	[RuH(CO)(Pφ ₃) ₂ (TCH)Cl] (RuC ₃₈ H ₃₇ N ₄ OSCl)	Gray (135)	62.11 (62.16)	5.11 (5.04)	7.75 (7.63)	13.80 (13.76)	nc
4	[RuH(CO)(Pφ ₃) ₂ (Py)Cl] (RuC ₄₂ H ₃₆ ONP ₂ Cl)	Mimosa (75)	65.56 (65.58)	4.72 (4.68)	1.92 (1.82)	13.22 (13.14)	nc
5	[IrH(CO)(Pφ ₃) ₂ (TCH)Cl ₂] (IrC ₂₄ H ₂₁ ONP ₂ Cl ₂)	Dull yellow (120)	36.30 (36.35)	3.30 (3.33)	8.50 (8.48)	29.15 (29.11)	nc
6	[IrH(CO)(Pφ ₃) ₂ (Py)Cl ₂] (IrC ₂₄ H ₂₁ ONP ₂ Cl ₂)	Dull yellow (145)	45.41 (45.48)	3.30 (3.31)	2.32 (2.21)	30.40 (30.35)	nc
7	[IrH(CO)(Pφ ₃) ₂ (TCH) ₃ Cl] ₂ (IrC ₂₂ H ₃₃ N ₁₂ OPS ₃ Cl ₃)	Yellow (130)	29.32 (29.11)	3.68 (3.63)	18.32 (18.52)	21.20 (21.19)	147.5
8	[IrH(CO)(Pφ ₃) ₂ (TCH) ₂ Cl] ₂ (IrC ₃₉ H ₄₃ N ₈ OP ₂ S ₂ Cl ₂)	Traffic yellow (180)	45.62 (45.52)	3.81 (3.79)	10.80 (10.89)	18.98 (18.67)	152.3



(Scheme-I)



(Str. III)

(Str. IV)

The pink isomer of precursor complex carbonylchlorohydridotris (triphenyl phosphine) ruthenium(II) yields [RuH(Pφ₃)₂(CO)(TCH)Cl] (str. III) under similar conditions. The Vaska complex under goes oxidative-addition with ethanolic solution of HCl in presence of thiocarbohydrazide leading to the formation of [IrH(Pφ₃)(CO)(TCH)Cl₂].

However, in presence of ethanolic pyridine [IrH(Pφ₃)(CO)(Py)Cl₂] was isolated under identical condition. (str. IV). When excess of ligand (TCH) was used then other complexes (Sl. Nos. 7 and 8) are formed on oxidative-addition to Vaska complex.

Magnetic moment and electronic spectra: The value of diamagnetism suggest Ru²⁺(d⁶) and Ir³⁺(d⁶) configuration of complexes in strong crystal field. The ligand field bands observed in iridium(III) are analogous to those observed in isoelectronic ruthenium(II) complexes of octahedrally disposed strong ligand field¹³. The electronic absorption spectra of ruthenium(II) complexes showed two spin allowed transitions

¹A_{1g} → ¹T_{1g} (500 - 510 nm) and ¹A_{1g} → ¹T_{2g} (460 - 470 nm) and one spin-forbidden transition ¹A_{1g} → ³T_{1g} (543 nm) and charge transfer (T_{2g} → π*) at 260 nm are similar to those observed for other octahedral ruthenium(II) complexes reported in literature^{12,14}.

For iridium(III) complexes two spin-forbidden transition ¹A_{1g} → ³T_{1g} and ¹A_{1g} → T_{2g} and two spin-allowed transitions ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → T_{2g} are expected in octahedral strong crystal field¹⁵. The spectral bands at 600 and 525 nm and at 426 and 335 nm confirms octahedral structure of iridium(III) complexes and these bands are due spin-forbidden and spin-allowed transitions, respectively. A charge transfer band is also observed at 260-265 nm in all complexes.

IR Spectra: Thiocarbohydrazide contains thioamide group and hydrazine residue. The normal coordinate analysis of thiocarbohydrazide¹⁶, thioamides¹⁷ and hydrazine¹⁸ is reported in literature. X-rays crystallographic studies of complexes of thiocarbohydrazide^{18,19} have also been reported and existence of dual site available for coordination is suggested. The characteristic bands of free thiocarbohydrazide NH₂ (3290s, 3205s cm⁻¹) ν(NH) (3300s cm⁻¹), thioamide band I (1530s cm⁻¹) remain almost unchanged in position indicating absence of bonding through nitrogen atom, However, thioamide bands II (1285s cm⁻¹), III (930s cm⁻¹) and IV (750m cm⁻¹) shift to lower wave number indicating bonding through thione sulphur atom which increases CN bond order and

decreases CS bond order on complexation^{20,21}. Thus metal-S bond was assumed for all complexes.

The new bands at 2240-2210 cm⁻¹ and at 820-780 cm⁻¹ in hydrido phosphine complexes of iridium(III) are assigned to $\nu(\text{Ir-H})$ and $\delta(\text{Ir-H})$ modes. These assignments are in agreement with Chatt *et al.*²² for $[\text{Ir HCl}_2(\text{CO})(\text{Et}_2\text{Ph})_2]$ and Vaska²³ for $[\text{Ir HCl}_2(\text{CO})(\text{P}\phi_3)_2]$. New band at 1990-1980 cm⁻¹ and 623-585 cm⁻¹ are assigned to $\nu(\text{C}\equiv\text{O})$ and $\nu(\text{Ir-C})$ modes. In ruthenium(II) complexes new bands at, 2050-1965 cm⁻¹ $\nu(\text{Ru-H})$, 830-810 cm⁻¹ $\delta(\text{Ru-H})$, 2000-1940 cm⁻¹, $\nu(\text{C}\equiv\text{O})$ 610-580 cm⁻¹ $\nu(\text{Ru-C})$ are in agreement previous literature. Far IR spectra contains some new bands. The $\nu(\text{Ir-Cl})$ values for $[\text{IrCl}_2(\text{CO})(\text{Py})(\text{P}\phi_3)_2]\text{Cl}$ show a reasonable agreement with those for $[\text{IrCl}_2(\text{Ph})(\text{CO})(\text{PMe}_2\text{Ph})_2]$ by Deeming and Shaw¹⁸ and Farrell and Sutton¹⁹ for $[\text{IrCl}_2\text{Ph}(\text{CO})(\text{P}\phi_3)_2]$. We assigned the bands at 335 cm⁻¹ (Cl-Ir-CO) and 275 and 265 cm⁻¹ (Cl-Ir-S=C) like wise in favour of str. IV.

For $[\text{IrH}(\text{CO})(\text{P}\phi_3)(\text{TCH})\text{Cl}_2]$ we observed Ir-Cl at 322 cm⁻¹ and also a band at 258 cm⁻¹. A value of 322 cm⁻¹ is broader line between typical Cl-Ir-Cl and Cl-Ir-CO value but the 256 band may be assigned to Cl-Ir-S=C in view of the *trans*-influencing nature of ligand (TCH). Thus, we confirmed the complex to have str. IV.

¹H NMR spectra : ¹H NMR spectra of some complexes (Sl. No. 4 & 6) are recorded to substantiate the mode of metal ligand bonding. These complexes showed signals in the range due to the aromatic protons of P ϕ_3 ²⁰. The signal for coordinated pyridine appears at 7.40, 8.0 and 8.78 ppm. Thus, ¹H NMR spectra suggest the formation of Ru-Py, Ir-Py, Ru-P and Ir-P bonds on complexation consistent with IR Spectra.

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