



Synthesis and Spectral Characterization of Organometallic Derivatives of Palladium(0), Platinum(0), Rhodium(I) and Iridium(I) with Mixed-Ligands

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Some new organometallic derivatives of Pd(0), Pt(0), Rh(I) and Ir(I) have been prepared and characterized using Wilkinson catalyst, Malatesta compounds and Vaska catalyst by the ligand substitution reaction with dibenzyl sulphide in benzene. The possible structure of all the isolated products have been assigned by elemental analyses, IR, UV-VIS, ¹H NMR spectra and other physico-chemical methods.

Key Words: Pd(0), Pt(0), Rh(I) and Ir(I), Organometallic complexes.

INTRODUCTION

Organometallic complexes of Pt-group metals are versatile catalyst¹⁻⁵ and interesting to elucidate their structure and bonding. James and Neg⁶ have reported trichlorotrans-cinnamic acid. Some complexes of dibenzyl sulphide (R₂S) have also been reported in earlier communications^{7,8}. The present communication describes some new derivatives of Wilkinson catalyst⁹, Malatesta compound¹⁰ and Vaska catalyst¹¹ with this ligand.

EXPERIMENTAL

All the chemicals used were of AR grade or CP grade. Solvents were distilled and dried before use. The dibenzyl sulphide (R₂S)¹², [Pd(Pφ₃)₄]¹³, [Pt(Pφ₃)₄]¹⁴, [Rh(Pφ₃)₃X]⁹ (X = Cl, Br, I, NCS, SnCl₃) and [Ir(CO)(Pφ₃)₂Cl]¹¹ were prepared by the methods reported in literature. All new derivatives [Pd(Pφ₃)₂(R₂S)₂], [Pt(Pφ₃)₂(R₂S)₂], [Rh(Pφ₃)₂(R₂S)X] (X = Cl⁻, Br⁻, I⁻, NCS⁻ and SnCl₃⁻) were prepared by ligand substitution reaction in benzene following previous method¹⁵⁻¹⁸.

Preparation of [Rh(Pφ₃)(Py)(R₂S)₂]X (X = BF₄ and PF₆):

A solution of [RhCl(Pφ₃)(R₂S)₂] (0.910 mmol) in methanol (20 mL) was stirred until the solid dissolved completely and it was then treated with an excess of pyridine (7.58 mmol) in methanol (10 mL) for 1 h to afford an orange solution. A solution of NH₄BF₄/NH₄PF₆ in methanol (6 mL) was added. On concentration under vacuum separated an orange solid which after filtration was washed with methanol (5 mL) before being dried under vacuum. Yield 85 %. Carbon, hydrogen

and nitrogen analyses were done at the micro analytical section of CDRI, Lucknow. The IR spectra of ligand (R₂S) and complexes were recorded with Perkin Elmer model 577 spectrophotometer in the range of 4000-200 cm⁻¹ as KBr pellets. The electronic spectra were recorded with Zeiss (Jena) model and molar conductance of complexes were measured in DMF using Wiss-Werkstatter Weithem obb type LBR conductivity meter. The ¹H and ³¹P NMR spectra were recorded on Bruker 400 MHz or varian FX 90 Q instruments using TMS and ortho-phosphoric acid as references respectively.

RESULTS AND DISCUSSION

Dibenzyl sulphide (R₂S) interacts with [M(Pφ₃)₄] (M = Pd/Pt), [IrCl(CO)(Pφ₃)₂] and [Rh(Pφ₃)₃X] (X = Cl⁻, Br⁻, I⁻, NCS⁻ and SnCl₃⁻) in benzene solution and produces solid products listed in Table-1. The stoichiometry of solid products obtained after carrying out ligand substitution reaction is assigned on the basis of elemental analysis. The addition of pyridine to methanolic solution of [Rh(Pφ₃)(R₂S)₂Cl] followed by metathetical reaction with NH₄BF₄ or NH₄PF₆ gave the corresponding derivatives [Rh(Pφ₃)(Py)(R₂S)₂]X (X = BF₄/PF₆).

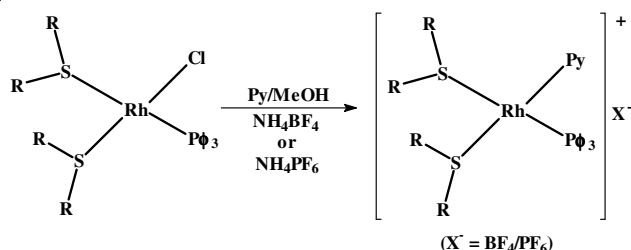


TABLE-1
 ANALYTICAL, PHYSICAL AND ELECTRONIC SPECTRAL DATA OF METAL COMPLEXES

| Complex (colour)/molecular formula | Analysis (%): found/calcd. | | | λ_{\max} (cm ⁻¹)/ (Assignment) | Molar Cond. (Λ^{-1} cm ² mol ⁻¹) |
|---|----------------------------|-------------|---------------|---|---|
| | C | H | Metal | | |
| [Pd(P ϕ_3) ₂ (R ₂ S) ₂] (Yellow) C ₆₄ H ₅₈ P ₂ S ₂ Pd | 73.01 (72.56) | 5.48 (5.47) | 10.21 (10.05) | 27370 (CT band) | 5.30 |
| [Pt(P ϕ_3) ₂ (R ₂ S) ₂] (Yellow) C ₆₄ P ₂ S ₂ Pt | 66.85 (66.95) | 5.10 (5.05) | 17.21 (17.00) | 25300 (CT band) | 6.01 |
| [Rh(P ϕ_3) ₂ (R ₂ SOCl)] (Yellow) C ₅₀ H ₄₄ P ₂ SClRh | 68.34 (68.46) | 5.10 (5.02) | 11.70 (11.74) | 27800 ($\pi \rightarrow \pi^*$) 31100 ($t_{2g} \rightarrow \pi^*$) | 5.32 |
| [Rh(P ϕ_3) ₂ (R ₂ S)Br] (Yellowish brown) C ₅₀ H ₄₄ P ₂ SBrRh | 65.21 (65.15) | 4.80 (4.77) | 11.27 (11.71) | 34400 ($\pi \rightarrow \pi^*$) 31100 ($t_{2g} \rightarrow \pi^*$) | 4.68 |
| [Rh(P ϕ_3) ₂ (R ₂ S)I] (Reddish brown) C ₅ H ₄₄ P ₂ SIRh | 62.01 (61.98) | 4.61 (4.54) | 10.75 (10.64) | 36350 ($\pi \rightarrow \pi^*$) 31400 ($t_{2g} \rightarrow \pi^*$) | 4.40 |
| [Rh(P ϕ_3) ₂ (R ₂ S)(NCS)] (Yellow) (C ₅₁ H ₄₄ P ₂ S ₂ N Rh) | 68.32 (68.07) | 4.91 (4.89) | 11.55 (11.45) | 37100 ($\pi \rightarrow \pi^*$) 32100 ($t_{2g} \rightarrow \pi^*$) | 4.28 |
| [Rh(P ϕ_3) ₂ (R ₂ S)(SnCl ₂)] (Orange) C ₅₀ H ₄₄ P ₂ SnCl ₂ Rh | 56.56 (56.27) | 4.22 (4.12) | 9.85 (9.66) | 36720 ($\pi \rightarrow \pi^*$) 32100 ($t_{2g} \rightarrow \pi^*$) | 6.34 |
| [Rh(P ϕ_3)(Py)(R ₂ S) ₂ BF ₄] (Orange) C ₅₁ H ₄₈ NPS ₂ BF ₄ Rh | 63.96 (63.83) | 5.20 (5.01) | 10.85 (10.74) | 36320 ($\pi \rightarrow \pi^*$) 32320 ($t_{2g} \rightarrow \pi^*$) | 25.34 |
| [Rh(P ϕ_3)(Py)(R ₂ S) ₂]PF ₆ (Orange) C ₅₁ H ₄₈ NP ₂ S ₂ F ₆ Rh | 60.23 (60.18) | 4.75 (4.72) | 10.32 (10.13) | 37100 ($\pi \rightarrow \pi^*$) 32320 ($t_{2g} \rightarrow \pi^*$) | 30.21 |

All solid products were diamagnetic indicating d^{10} -configuration for Pd(0) and Pt(0) and d^8 -configuration for Rh⁺ and Ir⁺ species. The suspension of these compounds were treated with iodine solution in CCl₄ and the violet colour of iodine was discharged indicating the presence of Pd⁰, Pt⁰, Rh⁺ and Ir⁺ electronic state¹⁷. However, univalent oxidation state of rhodium in complexes was further verified by titrating complexes with ceric ammonium sulphate using ferroin as indicator¹⁹. The complexes were titrated for a two electron charge. The zero oxidation state of palladium and platinum was also verified by iodometric and acidimetric titration as reported earlier¹⁷.

Analytical data of the complexes are consistent with present formulations. Conductance behavior of the complexes under study show that counter anion BF₄⁻ and PF₆⁻ are ionic nature and rest other anions are covalently bonded. Their conductances are in good agreement with those of similar electrolyte types under identical conditions. All Pd(0), Pt(0) and Rh(I) complexes display only charge transfer bands in electronic spectra. The ligand field bands are obscured by charge transfer band. However, two strong bands at 39200 and 37340 cm⁻¹ are observed in Ir(I) complex. The first band may be almost entirely of charge transfer origin and the second band presumably because of ¹A_{1g} → ¹B_{1g} transition considering molecular orbital diagram of square pyramidal (C_{4v}) configuration¹⁵.

The IR spectra of dibenzyl sulphide (R₂S) and its complexes display ν (C-H) (aromatic) and ν (C-H) (aliphatic) almost at the same position at 3000 and 3100 cm⁻¹, respectively. But ν (C-S) band of ligand (R₂S) shift from 720 cm⁻¹ to 680 ± 5 cm⁻¹ on complexation indicating bonding through sulphur^{7,8}. The non-ligand band at 1995 and 480 cm⁻¹ in [Ir(CO)(P ϕ_3)₂(R₂S)₂Cl] assigned to ν (C=O) and ν (Ir-C) modes, respectively. The presence of pyridine in Rh(I) complexes was confirmed by its characteristics vibrations. The four ν (C=C) and ν (C=N) bands due to pyridine skeletal are observed at 1590 cm⁻¹ (band I), 1560 cm⁻¹ (band II), 1450 cm⁻¹ (band III) and 1430 cm⁻¹ (band IV). On coordination these frequency vibrations are not shifted appreciably where as those 604 cm⁻¹ (in-plane-deformation) 408 cm⁻¹ (out-of-plane-deformation) shifted to higher

frequency indicating pyridine nitrogen coordination to the Rh(I) ion²⁰.

The absorption associated with counter anions²¹ are identified at 850 cm⁻¹ ν (P-F) for PF₆⁻ and at 1070 cm⁻¹ for BF₄⁻. The coordinated anions are identified by new non-ligand bands at 2085 cm⁻¹, ν (CN), 780 cm⁻¹, ν (CS), 460 cm⁻¹ for isothiocyanato group²² and at 340 and 320 cm⁻¹ for coordinated trichlorostannate(II) ion²³. The ν (Sn-Cl) of free SnCl₃⁻ ion are generally observed at 289 and 252 cm⁻¹ and shifted to higher frequencies upon coordination to metal ion²⁴.

¹H and ³¹P NMR spectra: The ligand to metal bonding is further supported by ¹H NMR spectra. The complexes (S. No. 3 and 4) showed signals in the δ 8.10-9.1 ppm range due to the aromatic protons of P ϕ_3 ²⁵ and peak at δ 7.21-7.63 ppm corresponding to aromatic protons and two peaks centred at δ 4.6 ppm and δ 3.9 ppm due to methylene (CH₂) protons of dibenzyl sulphide ligand. The shifting of CH₂ protons signals to lower field on coordination indicates coordination through sulphur²⁶. The resonances in the region δ 7.66, 8.25, 8.92 ppm assignable to the protons of coordinated pyridine.

The ³¹P NMR spectra of two complexes (3 and 4) were recorded in order to confirm the presence of P ϕ_3 groups and to determine the geometry of the complexes. The appearance of a signal around 23.74-28.80 in the spectra of complexes confirmed the presence of magnetically equivalent phosphorous atoms and thus suggesting that the two P ϕ_3 groups are trans to each other²⁷ in [Rh(P ϕ_3)₂(R₂S)Cl].

Thus, on the basis of aforesaid results, the tetrahedral structure to Pd(0) and Pt(0), square planar structure to Rh(I) and square pyramidal structure to Ir(I) complexes may be tentatively assigned.

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