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MIXED-LIGAND ORGANOMETALLIC COMPLEXES OF RUTHENIUM (II) PALLADIUM (II) AND PLATINUM (II) WITH TRIPHENYL PHOSPHINE AND 2-MERCAPTOBENZOTHIAZOLE.

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ABSTRACT

Some new mixed –ligand organomettalic derivatives of Ru(II), Pd(II) and Pt(II) with triphenyl phosphine and 2-mercaptobenzothiazole have been prepared and characterized by elemental, spectroscopic (IR and electronic), molar conductivity and magnetic susceptibility measurements. The Pd(II) and Pt(II) compounds are trans-square planar and Ru(II) compounds have trans-octahedral configuration. Metal-ligand vibrations in far-IR have also been tentatively assigned.

Key Words: Mixed-ligand, Triphenylphosphine, 2-mercaptobenzothiazole, Ru(II), Pd(II) and Pt(II).

INTRODUCTION

The tertiary phosphines are the ligands of one of the largest use in organometallic chemistry and homogeneous catalysis, especially in conjunction with late transition metals[1-4]. They are extensively investigated with regard to their numerous applications[5-8]. The present study elucidate structure and bonding of some new organometallics of ruthenium(II), palladium(II) and platinum(II) with mixed ligand, triphenyl phosphine($P\Phi_3$) and 2-mercaptobenzothiazole(MBTH)presented in Str-I(Figure-1).

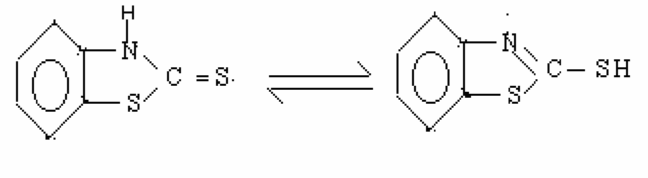

Fig.-1: Str.I

EXPERIMENTAL

All chemicals used were of CP- grade. The ligands, triphenyl phosphine(Albright and Wilson Ltd.) and 2-mercaptobenzothiazole (Central Drug house, P Ltd. Delhi, India) were used after crystallization and solvents were distilled and dried before use.

Preparation of Complexes:

The precursor complexes [Ru(H)(CO) ($P\Phi_3$)Cl][9], [Pd($P\Phi_3$)$_2$(MBTH)$_2$][10] and [Pt($P\Phi_3$)$_2$(MBTH)$_2$][11] were prepared by the methods reported in literature. The palladium (II) and platinum(II) complexes were prepared by oxidative addition to precursor complexes with 30-40 % ethanolic solution of inorganic acids with stirring until the solution became colourless or complete colour changed on magnetic stirrer at 60°C. The solution mixture was evaporated to half-volume and then ether was added. The solid products obtained after cooling are given in Table 1.All the Ruthenium(II) complexes were prepared by our earlier methods reported in literature[12].

Infra red spectra of ligands and complexes were recorded on a Perkin –Elmer 577 spectrophotometer in the range of 4000-200 cm-1 and electronic spectra on a Beckmann DU-6 spectrophotometer. The molar conductance (10^{-3}M) of complexes were measured in DMF using Wiss-Werkstatter Weithein obb type LBR conductivity meter . Magnetic measurements were made on a Gouy balance using Hg $[Co(SCN)_4]$ as calibrant.

RESULTS AND DISCUSSION

The reaction of inorganic acids with zerovalent $[Pt^0(P\Phi_3)_2(MBTH)_2]$ complex yields a clean hydridophosphine complexes of platinum (II) having general formulae $[Pt(H)(P\Phi_3)(MBTH)_2]X$ (X = Cl, NO_3, ClO_4, HSO_4, BF_4). However, under identical conditions isostructural complex $[Pd^0(P\Phi_3)_2(MBTH)_2]$ behaves differently and no hybridophosphine complexes were obtained.

$$[Pd^0(P\Phi_3)_2(MBTH)_2] + 2HX \xrightarrow{EtOH/\ 60^0C} [Pd^{II}(P\Phi_3)_2(MBTH)_2]X_2 + H_2(g)$$

(X = Cl)

$$[Pt^0(P\Phi_3)_2(MBTH)_2] + HX \xrightarrow{EtOH/\ 60^0C} [Pt^{II}(H)(P\Phi_3)(MBTH)_2]X + P\Phi_3$$

(X = Cl, NO_3, ClO_4, HSO_4, BF_4).

The brown isomer[9] (Str.II) of $[Ru(H)(CO)(P\Phi_3)_3Cl]$ undergoes ligand substitution reaction in benzene leading to the formation of

$[Ru(H)(CO)(P\Phi_3)(MBTH)_2Cl]$ (Str.III). However, brown isomer of $[Ru(H)(CO)(P\Phi_3)_3Cl]$ and ligand MBTH yields $[Ru(CO)(P\Phi_3)_2(MBT)_2Cl]$ in 1:1 molar ratio in benzene and increasing reflux time to six hours.

$$[Ru\ H\ (CO)(P\Phi_3)_3Cl] + MBTH \xrightarrow{C_6H_6\ /\ reflux,\ 6hrs.} [Ru(CO)(P\Phi_3)_2(MBT)Cl] + H_2(g) + P\Phi_3$$

The analytical data obtained for the new complexes (Table I) agree very well the proposed molecular formulae. The ligand MBTH behaves as monodentate neutral ligand with Ru(II), Pd(II) and Pt(II) but behaves as mononegative bidentate ligand with Ru(II) in vigorous conditions.

The iso-structural $[RuH(CS)(P\Phi_3)(MBTH)_2Cl]$ was obtained if molar ratio1:2 were used with MBTH and stirring the mixture for half an hour on magnetic stirrer at 60^0C.

The molar conductance value (Table1) in DMF is in agreement with the required uni-univalent electrolyte[13] for hydridocomplexes of platinum(II) and uni-bivalent electrolyte for Pd(II) complexes. However, ruthenium (II) complexes were almost non-electrolyte. These observations were further supported by the chemical analysis of Na_2CO_3 extract solution of complexes. All anions were present in the outer sphere of Pt(II) and Pd(II) complexes and were uncoordinated nature. All isolated products were diamagnetic as expected for four coordinated square planar d^8- complexes of Pd(II) and Pt(II) and six-coordinated octahedral ruthenium(II) complexes of d^6 – configuration.

Elecronic Spectra

Three to four bands appeared in the region 15625-40000 cm^{-1} . The two spin-allowed transitions $^1A_1g \rightarrow {}^1T_1g$ (20450 cm^{-1}) and $^1A_1g \rightarrow {}^1T_2g$ (18800 cm^{-1}) and weak spin – forbidden transition $^1A_1g \rightarrow {}^3T_1g$ (15625 cm^{-1}) are assigned to octahedral configuration of ruthenium(II) – complexes[14] . A strong intensity band at 37700 cm^{-1} is probably due to charge transfer transition ($T_2g \rightarrow \pi^*$). The nature of the electronic spectra are similar to those observed for other octahederal ruthenium(II) complexes reported by Natrajan et al.[15] and Balasubramian and co-workers[16]. The hydridophosphine complexes of platinum (II) exhibit one ligand field transition at 23250 cm^{-1} attributed to $^1A_1g \rightarrow {}^1B_1g$ transition similar to square planar complexes[17]. A very strong intensity band at 38025 cm^{-1} assigned to charge transfer band. The electronic spectra of palladium (II) complex is indicative of square planar geometry. The two electronic spectral bands at 18460 cm^{-1} ($^1A_1g \rightarrow {}^1B_1g$) and 27650 cm^{-1} (^1A_1g

$\longrightarrow {}^1E_1g$) and 37550 cm^{-1} in ultra violet region is ascribed to charge transfer transition. Hence, a square planar geometry may be assigned for Pd(II) complex[18].

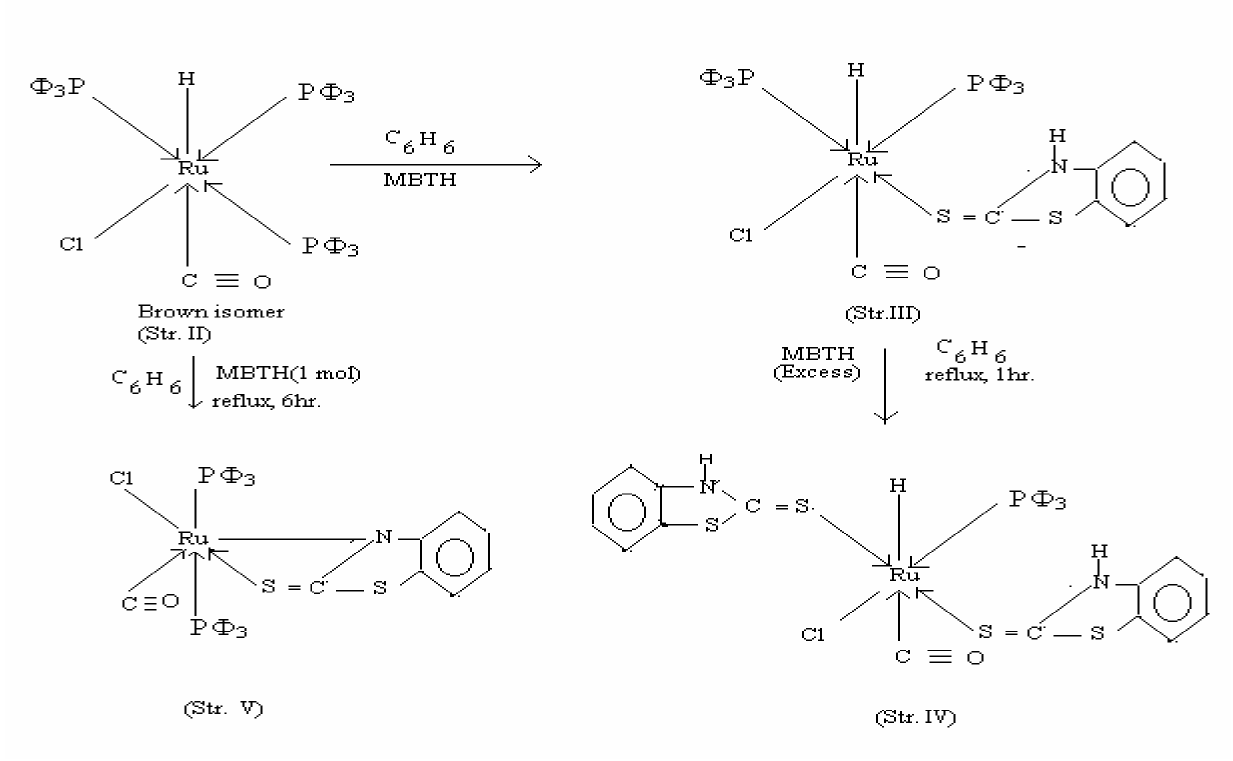

Fig.-2

Infrared Spectra

A comparison of IR spectra of complexes with those of ligands MBTH and PΦ_3 indicate the formation of metal – S and metal – P bond which results red shift of thioamide band II (1270 cm^{-1}), band III (1060 cm^{-1}) and Band IV (830 cm^{-1}) of free MBTH about 10-15 cm^{-1}, 20-30 cm^{-1} and 20-40 cm^{-1} respectively on complexation[19-23]. The ν N - H (3050 cm^{-1}) and thioamide band I[24] (1480m, 1450m, 1410s cm^{-1}) of free MBTH remain unchanged in position and intensity on coordination suggesting the non-involvement of imino nitrogen on coordination. However, deprotonation of imino nitrogen occuring in [Ru(CO)(PΦ_3)$_2$ (MBT)Cl] is clearly indicated by red shift of thioamide band I and absence of N-H stretching mode of MBTH. New bands at 1550,1540,1140,680 and 560 cm^{-1} in complexes indicate the presence of coordinated PΦ_3 molecules[25].

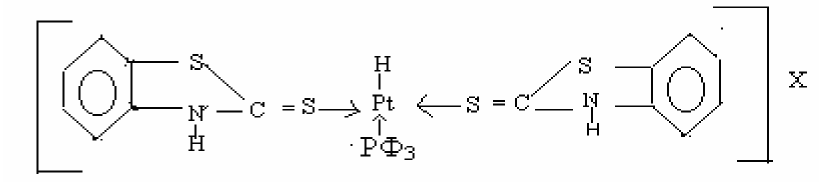

Fig.-3: Str. VI
(X = Cl, NO_3, ClO_4, HSO_4, BF_4).

Table-1: Analytical and Physical and Electronic Spectral Data of Complexes

$[Ru(H)(CS)(P\Phi_3)(MBT)_2Cl]$ (Black, 178)	nc	51.01 (50.88)	3.35 (3.34)	4.21 (3.59)	13.08 (13.06)	38460 (CT Band) 20408 ($^1A_1g \longrightarrow {}^1T_1g$) 18690 ($^1A_1g \longrightarrow {}^1T_2g$) 15576 ($^1A_1g \longrightarrow {}^3T_1g$)
$[Ru(CO)(P\Phi_3)_2(MBT)Cl]$ (Yellow – brown, 195)	nc	52.3 (52.65)	3.10 (3.20)	2.32 (2.36)	17.00 (17.04)	38465 (CT Band) 20830 ($^1A_1g \longrightarrow {}^1T_1g$) 18520 ($^1A_1g \longrightarrow {}^1T_2g$) 15620 ($^1A_1g \longrightarrow {}^3T_1g$)
$[Pd(P\Phi_3)_2(MBTH)_2]Cl_2$ (Yellow, 185d)	nc	58.01 (57.44)	3.85 (3.86)	3.11 (2.70)	10.51 (10.27)	37550 (CT Band) 27650 ($^1A_1g \longrightarrow {}^1E_1g$) 18460 ($^1A_1g \longrightarrow {}^1B_1g$)
$[Pt(H)(P\Phi_3)(MBTH)_2]BF_4$ (White, >250)	26.06	44.12 (43.93)	3.01 (2.97)	3.33 (3.20)	22.51 (22.31)	37740 (CT Band) 24040 ($^1A_1g \longrightarrow {}^1B_1g$)
$[Pt(H)(P\Phi_3)(MBTH)_2]HSO_4$ (White, >250)	22.62	43.25 (43.19)	3.81 (3.71)	3.32 (3.14)	21.45 (21.33)	37735 (CT Band) 24100 ($^1A_1g \longrightarrow {}^1B_1g$)
$[Pt(H)(P\Phi_3)(MBTH)_2]ClO_4$ (White> 250)	18.92	43.01 (43.07)	3.68 (3.58)	3.14 (3.24)	22.21 (21.88)	38022(CT Band) 22700 ($^1A_1g \longrightarrow {}^1B_1g$)
$[Pt(H)(P\Phi_3)(MBTH)_2]NO_3$ (Faint yellow , 179)	19.82	45.01 (44.96)	3.75 (3.74)	5.01 (4.91)	22.92 (22.83)	37050 (CT Band) 23800 ($^1A_1g \longrightarrow {}^1B_1g$)
$[Pt(H)(P\Phi_3)(MBTH)_2]Cl$ (Pale Cream, 185)	16.62	46.56 (46.48)	3.24 (3.14)	3.65 (3.38)	23.66 (23.56)	37735(CT Band) 23250 ($^1A_1g \longrightarrow {}^1B_1g$)

The metal –H stretching mode and bending mode of ruthenium (II) complexes at 2135 cm^{-1} and 720 cm^{-1} and at 1900-2130 amd 710-725 cm^{-1} for platinum (II) complexes are in agreement with our earlier observations[26], Robinson et al.[27] and others[28-29] . The presence of coordinated thiocabonyl group in ruthenium (II) complexes is indicated by new bands at 1380(s) 1160(m) and 1085(m) cm^{-1}. However, non-ligand bands at 1950-1945 $cm^{-1}$and at 510and 480 cm^{-1} are assigned to ν C ≡ O and ν Ru –C modes of coordinated carbonyl group[30] . The absorption associated with anions in Pt(II) complexes are identified at 1105 $cm^{-1}$and 610 cm^{-1} for perchlorate[31], 1360 and 820 cm^{-1} for nitrate[32] and at 3410, 1250, 1050 and 1020 for bisulphate[33] and at 1064 cm^{-1} for ionic tetra fluoroborate ion[34].

Triphenyl phosphine displays a number of bands in far infra red spectra[35]. However, the presence of single ν Ru –S (340 cm^{-1}) and single ν Ru –P (410 cm^{-1}) band suggest trans positions of two MBTH molecules (Str. IV) or two $P\Phi_3$ molecules (Str.V) in octahedral configuration. A single Pt-S stretching mode at 310 cm^{-1} in hydridophosphine complexes of platinum (II) indicate Trans- disposition of two MBTH molecules (Str. VI) in square planar structure.

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