RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.4 (2009), 886-889
ISSN: 0974-1496
CODEN: RJCABP

SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES ON PALLADIUM(O) AND PLATINUM(O) COMPLEXES WITH MIXED-LIGAND.

R.N. Pandey*, Gunjan Kumari, A.K. Nag and Renu Bala.
P.G. Centre of Chemistry (M.U.), College of Commerce Patna – 800020 (India)
E-mail : rameshwarnath.pandey@yahoo.com

ABSTRACT

Mixed- ligand phosphine complexes of palladium(O) and platinum(O) with 2-mercapto-3-butyl-quinazoline-4-one have been prepared from precursors complexes $[M(P\phi_3)_4]$ (M=Pd/Pt) and their oxidative addition reactions with inorganic acids are investigated. Probable structure of all new compounds are assigned using various physico-chemical data.

Keywords: Pd(O) & Pt(O) compounds, oxidative reaction products, IR, UV-vis & ^1H NMR

INTRODUCTION

The literature survey reveals that some of the Pd(O) and Pt(O) complexes undergo reactions involving either coordinating dissociation or coordinative addition[1]. However, Cryoscopic[2] and NMR spectral data[3] indicate that the reactions of $M(P\phi_3)_4$ (M= Pt/Pt) in solution are somewhat complicated. We have reported replacement reactions without affecting the oxidation state of central metal in our previous communications[4-5]. The present study describes coordinative displacement as well as oxidative addition reactions of Pd(O) and Pt(O) complexes. All solid products isolated during reactions are characterized using IR, ^1H NMR, UV – vis and other physio-chemical investigations.

EXPERIMENTAL

All chemicals used were of AR grade or CP grade. The ligand, 2- mercapto-3-butyl-quinazoline-4-one (BQTH)[6], $[Pd(P\phi_3)_4]$[7] and $[Pt(P\phi_3)_4]$[8] were prepared by the methods described in literature. All zerovalent complexes were prepare following our method reported earlier[9-10]. Hydridophosphine complexes of platinum were prepared by oxidative addition of 15% ethanolic solution of inorganic acids to zero valent complexes by our previous method[11]. The carbon, hydrogen and nitrogen analyses, IR, UV-vis and ^1H NMR spectra, molar conductance and magnetic measurements were obtained as reported earlier[10]. The molecular weight of compounds were measured cryoscopically using highly purified benzene as solvent. Determination of oxidation states of metal in complexes were determined by iodometric and acidimetric titration described in literature[12].

RESULTS AND DISCUSSION

The analytical data of all isolated products are given in table**1** supports their stoichiometry. All the freshly prepared zerovalent complexes were soluble in benzene and chloroform but less soluble in these solvents after long standing in air. All these complexes were found to be diamagnetic suggesting d^{10} – configuration for Pd(O) and Pt(O). However, determination of oxidation state of metal was verified by iodometric and acidimetric titration[12]. The 10^{-3} M solution of all complexes in DMF were non-electrolyte and molecular weight measurement indicated them to be monomeric.

$[Pt^o(P\phi_3)(BQTH)_2]$ display oxidative reaction with ethanolic inorganic acids to form colourless and diamagnetic hydrides of Pt(II) as below:

EtOH / 65^oC

$$[Pt^{o}(P\phi_3)_2(BQTH)_2] + HX \xrightarrow{\hspace{3em}} [HPt^{II}(P\phi_3)(BQTH)_2]X + P\phi_3$$
$$(X = Cl, NO_3, HSO_4, ClO_4)$$

Molar conductance value in DMF (table**1**) is in agreement with required by a uni-univalent electrolyte[13]. The low value of molar conductance may be due to large ions. It seems that these anions have low coordinating power to form ionic hydrides and present in the outer sphere of complexes. Chatt et al(14) have suggested that ions like CN^- and SCN^- have high coordinating power and affords covalent compounds during oxidative addition to Pt^{o}-complexes. The presence of ionic chloride, nitrate, bisulphate and perchlorate was further supported by chemical analysis of sodium extract solution of complexes and infrared spectra. However, no hydride complex was formed by $[Pd^{o}(P\phi_3)_2BQTH_2]$ under similar conditions.

$$[Pd^{o}(P\phi_3)_2(BQTH)_2] + 2HX \xrightarrow{EtOH\ /\ 65^{o}C} [Pd^{II}(P\phi_3)_2(BQTH)_2]X_2 + H_2\ (g)$$

All these isolated products were 1:2 electrolyte and sodium extract of complexes produced total chlorine with $AgNO_3$ solution and supported molar conductance value.

Electronic Spectra:

Electronic spectra of Pd(O) and Pt(O) complexes display a single broad band of very high intensity at 28820 cm^{-1} and 30300 cm^{-1} respectively assigned to charge transfer band. The other d-d transition bands are obscured by charge transfer band probably due to high degree of d-p mixing in these complexes. Albano et al[15] have suggested tetrahedral configuration of $[Pt(P\phi_3)_3(CO)]$ by the study of crystal structure. Thus, in the light of previous observation[15-17], the tetrahedral structure of all zerovalent complexes may be assigned.

The electronic spectrum of Pd(II) complex (Sl. No. 3) exhibits bands at 18460 cm^{-1} ($^1A_1g \rightarrow {}^1B_1g$) and 27690 cm^{-1} ($^1A_1g \rightarrow {}^1E_1g$) confirms square planar stereochemistry[18]. The high intensity band at 31540cm^{-1} in UV region is ascribed a charge transfer band. However, hydridophosphine complexes of Platinum(II) (Sl. No. 7) exhibits one ligand field transition at ~ 23300 cm^{-1} attributed to $^1A_1g \rightarrow {}^1B_1g$ transition similar to planar complexes[19].

IR Spectra:

The υ N-H of the free ligand (BQTH) observed as medium band at 3225cm^{-1} blue shifts to higher frequency (90-115cm^{-1}) indicating presence of free imino group and absence of bonding through imino nitrogen.. The υ C = 0 band at 1680cm^{-1} in free ligand remained unaltered in the complexes suggesting that carbonyl oxygen has not taken part in the complex formation.

Thioamide band IV of ligand is mainly due to υ C ¨- S mode[20] and it is observed as medium band at 803 cm^{-1} in the spectrum of the ligand. This band red shifts (30-50 cm^{-1}) on complexation indicating bonding through thiocarbonyl sulphur[21]. Thioamide band II (1270cm^{-1}), band III (1020 cm^{-1}) of free ligand also red shifts to lower frequency and confirms coordination of ligands through thiocarbonyl sulphur[20-22]. The characteristic bands due to $P\phi_3$[23] and coordinated thio carbonyl group[24] were also present in the expected region.

All hydridophosphine complexes of platinum(II) display an infrared absorption band of medium intensity between 2215 – 2265 cm^{-1} assigned to Pt-H and another less intense one between 810 – 805 cm^{-1} to δ Pt-H are in agreement with the criteria suggested by Chatt el al[25)] considering trans effect of $P\phi_3$ group. All Pt(II) and Pd(II) complexes give rise to a doublet band[26] below 300 cm^{-1} separated by 10-15 cm^{-1} due to metal-S stretching mode supports two BQTH molecules at trans deposition in square planar structure. However, two doublet at 430 and 420 cm^{-1}(υ Pd-P) and two weak bands at 350 and 340 cm^{-1} (υ Pd-S) suggest C_{2v}-point group in tetrahedral structure of Pd(O) complex.

The absorption associated with anions in the hydridophosphine complexes of Platinum(II) are identified at 1365 and 830 cm^{-1} for ionic nitrate[27], at 1090 and 610 cm^{-1} for ionic perchlorate[28] and at 3420, 1555, 1230, 1050 and 1020 cm^{-1} for bisulphate[29].

Thus, Pd(O) and Pt(O) complexes have tetrahedral and Pd(II) and Pt(II) complexes have trans-square planar configuration maybe tentatively assigned considering aforesaid observations.

^{1}H NMR Spectra:

^{1}H NMR Spectra of ligand (BQTH), Pd(O) and Pt(O) complexes were recorded in $CDCl_3$/TMS to substantiate further metal ligand bonding. The spectra of complexes show triplet at δ1.73 for methyl protons of butyl group. The two middle CH_2 signal are complex and are centered at δ2.1 and δ2.3ppm. The CH_2 group attached to nitrogen atom of the quinazoline ring is deshielded giving a triplet at δ4.8ppm. The signal due to the aromatic protons are observed at δ7.6 – 8.3ppm. The aromatic proton at position-5 is deshielded by the carbonyl oxygen and the extreme signals at δ8.43ppm is considered to be due to this proton. The signal due to imino proton is always difficult to identify because of the quadrupole moment of nitrogen and exchange of this proton. However, a peak observed at δ3.2ppm in the ligand(BQTH) remains almost at the same position in complexes and imino proton is intact after complication. Aromatic protons of $P\phi3$ ligand resonated as broad multiplet in the region δ7.52 - 7.18 ppm in complexes[30]. These observations are consistent with the conclusions drawn from ir spectral studies.

Table-1 : Analytical and Physical data of Complexes.

Sl. No.	Complex/ Colour	Analysis % Found/(calcd.)				Molar cond. (Λ-^{1}cm^{2}mol^{-1})
		C	H	N	Metal	
1.	$[Pd^o(P\phi_3)_2(BQTH)_2]$ (Dull yellow)	66.00 (65.54)	5.38 (5.28)	5.33 (5.09)	10.11 (9.68)	nc
2.	$[Pd^o(P\phi_3)_2(CS)(BQTH)]$ (light yellow)	65.11 (64.72)	4.97 (4.84)	3.12 (3.08)	12.11 (11.71)	nc
3.	$[Pd^{11}(P\phi_3)_2(BQTH)_2]Cl_2$ (yellow)	62.10 (61.57)	5.01 (4.95)	5.01 (4.78)	9.01 (9.09)	51.21
4.	$[Pt^o(P\phi_3)_2(BQTH)_2]$ (bright yellow)	60.12 (60.65)	4.81 (4.88)	4.77 (4.71)	16.81 (16.42)	nc
5.	$[Pt^o(P\phi_3)_2(CS)(BQTH)]$ (marine grey)	59.12 (58.97)	4.51 (4.41)	3.10 (2.85)	20.11 (19.55)	nc
6.	$[HPt^{11}(P\phi_3)(BQTH)_2]Cl$ (white)	52.32 (52.41)	4.44 (4.57)	5.92 (5.82)	20.31 (20.27)	24.31
7.	$[HPt^{11}(P\phi_3)(BQTH)_2]NO_3$ (faint yellow)	51.20 (51.08)	4.43 (4.28)	7.02 (7.08)	20.01 (19.73)	25.32
8.	$[HPt^{11}(P\phi_3)(BQTH)_2]HSO_4$ (white)	49.36 (49.26)	4.40 (4.39)	5.50 (5.47)	19.11 (19.05)	22.62
9.	$[HPt^{11}(P\phi_3)(BQTH)_2]ClO_4$ (white)	49.32 (49.14)	4.22 (4.29)	5.40 (5.46)	19.22 (19.01)	20.31

REFERENCES

1. R. Ugo ,*Coord. Chem. Rev.* ,**3,** 319(1968).
2. F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.* **5**, 1128(1966).
3. C.D. Cook and G.S. Jauhal, *J. Am. Chem. soc.* **90**, 1464(1968).
4. R.N. Pandey, Arun Kumar, R.S.P. Singh, A.N. Sahay and Shashikant Kumar, *J. Indian chem. Soc.* **69**, 804(1992).
5. R.N. Pandey, Sunil Kumar, Shashikant Kumar,Rita Roy Chaudhary and A.N. Shahay, *Indian J. chem. soc.* **32A**, 987(1993).
6. G.R. Dave, G.S. Mewade and G.C. Amin, *J. Indian chem. soc.* **37**, 595 (1960)
7. D.R. Coulson, *Inorg Synth* **13**, 121(1972).
8. R.Ugo, F. Cariati and G.La. Monica, *Inorg. Synth.* **11,** 105(1987).
9. R.N. Pandey and J.N. Das, *J. Indian chem. soc.* **71**, 187(1994).
10. R.N. Pandey and Ashok Kumar, *Oriental J. chem.* ,**24**, 697(2008).
11. R.N. Pandey, Gunjan Kumari and Rajnish Kumar Singh, *Oriental J. Chem.* **25**(2009) (in press).
12. B.Singh, R.Singh and U. Agarwala, *Indian J. chem.* **9**, 73(1971).

13. F.Cariati, R. Ugo and F.Bonati, *Inorg. Chem.* **5** 1128(1966).
14. J. chatt and B.L. Shaw, *J. Chem. Soc.* 5075(1962).
15. V.G. Albano, G.M. Ricci Basso and P.L. Bellon, *Inorg. Chem.* **8,** 2109(1969).
16. L.Mallatesta and R. Ugo, *J. chem. soc.* **A**, 2080(1963).
17. R.N. Pandey, Ashok Kumar and M.P. Sinha, *J. ultra chem.* **5**, 39(2009).
18. S.Chandra and R.Singh, *Indian J. chem. Sect A*, **27** ,417(1988).
19. W.R. Mason and H.B.Gray, *J. Am. Chem. Soc.* **85**, 260(1968).
20. C.N.R. Rao, R.Venkataraghavan and T.R. Kasturi *Can. J. chem.* **42**, 36(1964).
21. R.N. Pandey, Ashok Kumar and M.P. Sinha, *J. ultra chem.* **5**, 39(2009).
22. B. Singh and R.Singh, *J. Inorg. Nucl. Chem* **34**, 3449(1972).
23. M.S. El-Shahawi and A.F. Shoir, *Spectrochim. Acta, Part A* ,**60**, 121(2004).
24. J.D. Gilbert , M.C. Baird and G.Wilkinson *J. Chem. Soc A*, 2198(1968).
25. J.Chatt and B.L. Shaw, *J. Chem. Soc.* 5075(1962).
26. D.M. Adams and J.B. Cornell, *J. Chem. Soc. A*, 884(1967).
27. C.C. Addition, R. Devis and N. Logan *J. Chem. Soc. A*, 3333(1970).
28. J.G. Bullitt, F.A. Cotton and J.J. Marks *Inorg. Chem.* **11**, 671(1972).
29. F.Cariati, R.Ugo and F.Bonati, *Inorg. Chem.* **5**,1128(1966).
30. S.Kanchanadevi, K.P.Balasubramnian, V. Chinnusamy, R. Karvembu and K.Natarajan, *Trans. Met. Chem.* ,**30**, 330(2005).

(Received: 20 October 2009 Accepted: 25 October 2009 RJC-337)