

STUDIES ON PHOSPHINE AND ARSINE COMPLEXES OF PLATINUM GROUP METALS AND THEIR INTERACTION WITH ACETYLACETONE

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Complexes of Ru(III), Rh(III), Pd(II), Ir(IV) and Pt(II) is synthesised by mixing the ethanolic solutions of their chlorides with triphenylphosphine and triphenylarsene and their mixed ligand complexes are prepared by mixing triphenylphosphine or triphenylarsine complexes with acetylacetonone. These complexes have been characterised with elemental analyses, m.p. molar-conductance and infrared spectra. The acetylacetonone in these complexes is in crystal lattice.

Keywords: Metals; Triphenylphosphine; Triphenylarsene; Complexation; Acetylacetonone.

Literature abounds in the triphenylphosphine and triphenylarsine complexes of platinum group metals. Grinberg and Razumova (1945) obtained $\text{Pt}(\text{Ph}_3\text{P})_2\text{Cl}_2$ by the interaction of K_2PtCl_4 with Ph_3P in 1 : 2 molar ratio in ethanolic medium. Vaska and Saloana (1960) obtained $\text{RuCl}(\text{Ph}_3\text{P})_3$ as yellow crystals by the reaction of RuCl_3 with excess triphenylphosphine in boiling $\text{MeOC}_2\text{H}_4\text{OH}$. They also reported the formation of $\text{RuCl}_2(\text{PH}_3\text{P})_3$ and $\text{RuCl}_3(\text{Ph}_3\text{As})_3$. Osborn and Wilkinson (1967) refluxed hot ethanolic solutions of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and Ph_3P and obtained $\text{RhCl}(\text{PR}_3\text{P})_3$. Recently, the complexes of ruthenium chloride with triphenylphosphine, triphenylarsine and acetylacetonone have been reported viz., $\text{RuCl}(\text{Ph}_3\text{P})_2$ acac and $\text{RuCl}(\text{Ph}_3\text{As})_2$ acac (Natrajan *et al.*, 1977). Very recently, Queiros and Robinson (1978) reported the complexes of β -diketones and presented i.r. evidence to show the presence of 0,0'-coordination. The products of interaction of triphenylphosphine and triphenylarsine with RuCl_3 , RhCl_3 , Na_2PdCl_4 , Na_2IrCl_6 and Na_2PtCl_4 by the simple process of mixing their ethanolic solutions in cold find little mention in the existing chemical literature although many triphenyl phosphine and triphenylarsine complexes of platinum metals containing hydrido, carbonyl and nitrosyl ligands are being reported in literature using different preparative techniques. The simple triphenylphosphine and triphenylarsine complexes of Ru(III), Rh(III), Pd(II), Ir(IV) and Pt(II) form adducts with acetylacetonone which are also being presented in this communication.

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EXPERIMENTAL

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Na_2PdCl_4 , Na_2IrCl_6 and Na_2PtCl_4 (J. M. Products), triphenylphosphine, triphenylarsine and acetylacetonone (B.D.H. products) were used without further purification for the preparation of complexes.

The metal salt solution in ethanol and the solution of the ligand (triphenylphosphine, or triphenylarsine) in the same solvent were mixed with each other and a little warmed to give a crystalline product. It was washed with hexane and dried *in vacuo*.

The mixed ligand complexes were prepared by mixing the triphenylphosphine or triphenylarsine complexes with acetylacetonone.

RESULTS AND DISCUSSION

The elemental analyses for carbon, hydrogen and chlorine give the compositions of the complexes recorded in Table I. The compounds $\text{RuCl}_3 \cdot (\text{Ph}_3\text{P})$ and $\text{RhCl}_3 \cdot (\text{Ph}_3\text{P})$ are different from the compounds $\text{RuCl}_2(\text{Ph}_3\text{P})$, $\text{RuCl}_2(\text{Ph}_3\text{P})_3$ and $\text{RuCl}_3 \cdot (\text{Ph}_3\text{As})_3$ reported by Osborn and Wilkinson (1967). This of course is possible because of the different methods of preparation used by these authors. The products of interaction of Na_2PtCl_4 with triphenylphosphine in ethanol is the same, $\text{PtCl}_2(\text{Ph}_3\text{P})_2$, as reported by Grinberg and Razumova but our product is sparingly soluble in common organic solvents and melts at 291°C whereas theirs is insoluble in common organic solvents and decomposes at 308°C .

The acetylacetonone containing mixed ligand complexes possess the same number of chlorides as present in the simple complexes. The method of preparation of the mixed complexes is such that the oxidation of the metal ions is not possible. The acetylacetonone may, therefore, be present as a non-functional molecule. The molar conductances at 10^{-3}M concentration in dimethyl sulphoxide are in the range $65\text{--}90\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ for 1 : 1 electrolytes (Broomhead & Kane-Maguire, 1967; Greenwood *et al.*, 1968; and Ames & Sears, 1955). All the complexes reported in the table are, therefore, non-electrolytes.

The i.r. bands of triphenylphosphine are retained in its complexes with platinum group metals with no major changes on complex formation. For instance, in dichloro bis (triphenylphosphine) palladium(II), two new bands at $1570(\text{s})$ and $1478(\text{vs})\text{ cm}^{-1}$ appear and a medium intensity band of triphenylphosphine at 1278 cm^{-1} disappears. This new band does not appear in the complexes of ruthenium, rhodium, iridium and platinum. The i.r. spectra of the compound of acetylacetonone with dichloro-bis (triphenylphosphine) palladium(II) shows all the bands of dichloro-bis(triphenylphosphine) palladium(II) and the acetylacetonone and a few more. Very little changes occur when acetylacetonone associates with dichloro-bis (triphenylphosphine) palladium(II). The bands occurring at 748, 746, 701, 448, 431 in the simple complex change to 751, 743, 707, 452 and 433 cm^{-1} respectively on interaction with acetylacetonone.

The β -diketonone chelate complexes have been studied by Lacomte and Morgan (cf. Bellamy, 1958). Lacomte found a strong band between 1562 and 1550 cm^{-1} which he attributes to the carbonyl group weakened by resonance between the

TABLE I
Results of analyses and other characterizing data

S. No.	Compound	Colour	m.p.	%C	%H	%Cl	Molar conduc- tance in ohm ⁻¹ cm ² mole ⁻¹
1.	RuCl ₃ . Ph ₃ P	dark grey	220 °C	46.79 (45.90)	3.28 (3.10)	22.3 (22.6)	17.9
2.	RuCl ₃ Ph ₃ P . (acac) ₂	dark grey	210 °C	50.05 (50.17)	4.38 (4.40)	15.5 (15.7)	26.4
3.	RuCl ₃ Ph ₃ As	dark violet	185 °C	42.16 (42.20)	2.89 (2.92)	20.4 (20.6)	8.5
4.	RuCl ₃ . Ph ₃ As(acac) ₂	„ „	189 °C	47.01 (47.12)	4.31 (4.34)	14.79 (14.86)	33.5
5.	RhCl ₃ . (Ph ₃ P) ₂	Yellowish brown	165 °C	58.82 (59.00)	4.05 (4.09)	14.41 (14.46)	9.1
6.	RhCl ₃ (Ph ₃ P) (acac) ₂	greyish brown	170 °C	49.95 (50.09)	4.58 (4.62)	15.58 (15.79)	20.5
7.	RhCl ₃ (Ph ₃ As) ₂	light brown	315 °C	51.95 (52.59)	3.56 (3.61)	12.55 (12.90)	11.1
8.	RhCl ₃ (Ph ₃ As) (acac) ₂	greyish brown	310 °C	45.50 (46.00)	3.91 (4.33)	14.5 (14.8)	6.7
9.	PdCl ₂ (Ph ₃ P) ₂	yellow	263 °C	61.46 (61.50)	4.28 (4.27)	9.08 (10.00)	7.6
10.	PdCl ₂ (Ph ₃ P) ₂ (acac) ₂	yellow	255 °C	61.06 (61.20)	4.68 (5.10)	8.00 (7.80)	8.3
11.	PdCl ₂ (Ph ₃ As) ₂	light yellow	246°	54.72 (54.80)	3.74 (3.80)	8.82 (8.90)	6.0
12.	PdCl ₂ (Ph ₃ As) ₂ (acac) ₂	dark yellow	250 °C	53.44 (55.30)	3.59 (3.90)	7.30 (7.10)	4.3
13.	IrCl ₄ (Ph ₃ P) ₃	light grey	185 °C	55.05 (56.90)	4.02 (4.01)	12.4 (12.6)	10.2
14.	IrCl ₄ (Ph ₃ P) ₃ (acac)	dark grey	190 °C	57.91 (57.91)	4.29 (4.34)	11.50 (11.60)	14.9
15.	IrCl ₄ (Ph ₂ As) ₃	light yellow	212 °C	51.50 (51.70)	3.58 (3.60)	11.20 (11.10)	19.6
16.	IrCl ₄ (Ph ₂ As) ₃ (acac)	light yellow	160 °C	51.64 (52.30)	3.31 (3.32)	14.60 (14.80)	17.9
17.	PtCl ₂ (Ph ₃ P) ₂	white	291 °C	52.80 (54.62)	3.86 (3.80)	8.08 (8.81)	6.3
18.	PtCl ₂ (Ph ₃ P) ₂ (acac) ₂	white	298 °C	53.98 (55.73)	4.42 (4.60)	7.10 (7.06)	6.1
19.	PtCl ₂ (Ph ₃ As) ₂	light grey	292 °C	50.03 (49.18)	3.58 (3.41)	7.40 (8.09)	6.3
20.	PtCl ₂ (Ph ₃ As) ₂ (acac) ₂	dark	295 °C	49.72 (50.26)	4.17 (4.00)	7.00 (7.26)	3.9

(Calculated values are given in parentheses)

Ph₃P = triphenylphosphine, Ph₃As = triphenylarsine

acac = acetylacetonate.

C—O — M and C = O—M links. In all these substances, there is a band near 1515 cm^{-1} which is attributed to the C = C link (cf. Bellamy, 1958; and Nakamoto, 1963). Nakamoto and Martell (*loc. cit.*) made normal coordinate analysis of the chelate ring of $\text{Cu}(\text{acac})_2$ and drew three conclusions: (1) The highest frequency band in the carbonyl region is a C \cdots C stretching and not a C \cdots O stretching band as previously concluded, (2) the bands found between 700 and 590 cm^{-1} are sensitive to change in the metal and (3) the newly found bands at 500 – 400 cm^{-1} are M—O stretching vibrations coupled slightly with the C—CH₃ stretching vibration.

The i.r. spectra of our complexes of triphenylphosphine and triphenylarsine with acetylacetonone do not show any new bands in the region of 500 – 400 cm^{-1} . Hence it is concluded that there is no metal acetylacetonone bond in these complexes. The complexes do not show a band near 1515 cm^{-1} which is due to the C = C link and the band at 1550 – 1562 does not appear in the $\text{PdCl}_2(\text{Ph}_3\text{As})_2(\text{acac})_2$, $\text{RuCl}_3\text{Ph}_3\text{P}(\text{acac})_2$, $\text{RuCl}_3\text{Ph}_3\text{As}(\text{acac})_2$, $\text{IrCl}_4(\text{Ph}_3\text{P})_3(\text{acac})$ and wherever it occurs it is a very weak band. These observations confirm that these complexes have acetylacetonone in the crystal lattices.

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