

Dichloro(diphenylarsino)ruthenium(III) & Its Reactions with Some Nitrogen Donors

A. GARG, K. NATARAJAN & U. AGARWALA

Department of Chemistry, Indian Institute of Technology, Kanpur 208016

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Preparation and characterization of dichloro(diphenylarsino)ruthenium(III), $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ and its reactions with various nitrogen donors have been studied. Probable structures have been proposed on the basis of analytical, spectral (IR and visible) and magnetic susceptibility data.

MANY binuclear transition metal complexes with carbon, sulphur and halogen bridges are known. However, comparatively less work has been done on the complexes containing phosphorus and arsenic as bridging atoms¹⁻⁵. Hayter¹ while investigating the reactions of metal carbonyls and their cyclopentadienyl derivatives with tetra-substituted biphosphines and biarsines (R_4M_2 ; $\text{M} = \text{P}$ or As ; $\text{R} = \text{CH}_3$ or C_6H_5), observed that the M-M bond of the ligand cleaved to give R_2M radical which could act as bridging group in linking two metal atoms. Chatt and Thornton² have also reported the reactions of a number of diphosphines $[\text{R}_2\text{P}(\text{PR})_2$; $\text{R} = \text{CH}_3$, C_2H_5 or C_6H_5] and some analogous diarsines with the carbonyls of iron, chromium, molybdenum and tungsten. They have assigned phosphorus and arsenic bridged structures to these complexes. No work has been done on the reaction of ruthenium(III) compounds with tetraphenyldiarsine.

In this paper we report the preparation, properties and characterization of dichloro(diphenylarsino)ruthenium(III), $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ and its reactions with ligands containing nitrogen donor atoms.

Materials and Methods

The chemicals used were of AR or CP grade. Tetraphenyldiarsine was prepared as described in literature⁶.

(i) *Dichloro(diphenylarsino)ruthenium(III)*, $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ — To a solution of 0.1 g (~0.25 mmole) of RuCl_3 in 15 ml of *t*-butyl alcohol, 0.5 g (~1.09 mmole) of ligand was added. The mixture was refluxed for 1 hr. A brown compound separated out which was centrifuged, washed repeatedly with ethanol and ether and dried *in vacuo* (Found: C, 35.32; H, 2.86; Cl, 18.4; Ru, 26.3. $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ requires: C, 35.91; H, 2.49; Cl, 17.6; Ru, 25.7%).

(ii) *Chloro(diphenylarsino)bis(pyridine)ruthenium(II)*, $[\text{RuClAs}(\text{C}_6\text{H}_5)_2(\text{Py})_2]$ — A solution of 0.1 g (~0.25 mmole) of $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ was prepared in 10 ml of pyridine. It was refluxed for 10 min, when a green solution was obtained. The solution was concentrated to 3 ml and ether was added when green complex precipitated out. It was centrifuged, washed with ether and dried *in vacuo* (Found: C, 50.38; H, 3.7; N, 5.34; Cl, 6.92. $[\text{RuClAs}(\text{C}_6\text{H}_5)_2(\text{Py})_2]$ requires: C, 49.88; H, 4.37; N, 5.02; Cl, 7.97%).

(iii) *Dichlorotetrakis(quinoline)ruthenium(II)*, $[\text{RuCl}_2(\text{C}_7\text{H}_9\text{N})_4]$ — Following a similar procedure as (ii) $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ (0.1 g) in 10 ml of quinoline, gave a reddish brown compound [Found: C, 55.04; H, 5.02; N, 8.72; Cl, 12.78. $[\text{RuCl}_2(\text{C}_7\text{H}_9\text{N})_4]$ requires: C, 55.98; H, 6.01; N, 9.33; Cl, 11.83%].

(iv) *Trichloro(diphenylarsino)(2,2'-bipyridyl)diruthenium(II)*, $[\text{Ru}_2\text{Cl}_3\text{As}(\text{C}_6\text{H}_5)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$ — To a solution of 0.25 g (~1.6 mmole) of 2,2'-bipyridyl in 10 ml of benzene, 0.1 g (~0.25 mmole) of $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ was added. The mixture was refluxed for 4 hr when a dark brown compound separated out. It was centrifuged, washed successively with benzene and ether and dried *in vacuo* [Found: C, 38.5; H, 3.0; N, 3.9; Cl, 14.8. $[\text{Ru}_2\text{Cl}_3\text{As}(\text{C}_6\text{H}_5)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$ requires: C, 38.1; H, 2.6; N, 4.0; Cl, 15.3%].

(v) *Dichlorobis(diphenylarsino)(o-phenanthroline)diruthenium(II)*, $[\text{Ru}_2\text{Cl}_2[\text{As}(\text{C}_6\text{H}_5)_2]_2(\text{C}_{12}\text{H}_8\text{N}_2)]$ — To a solution of 0.25 g (~1.38 mmole) of *o*-phenanthroline in 10 ml of benzene was added, 0.1 g (~0.25 mmole) of $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$. The mixture was refluxed for 4 hr when a dark-brown compound separated out. It was washed repeatedly with benzene and ether and dried *in vacuo* [Found: C, 46.8; H, 3.1; N, 3.0; Cl, 8.2. $[\text{Ru}_2\text{Cl}_2[\text{As}(\text{C}_6\text{H}_5)_2]_2(\text{C}_{12}\text{H}_8\text{N}_2)]$ requires: C, 47.5; H, 3.0; N, 3.0; Cl 7.8%].

(vi) *Trichloro(diphenylarsino)tetrakis(o-chloroaniline)diruthenium(II)*, $[\text{Ru}_2\text{Cl}_3\text{As}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{NCl})_4]$ — $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ (0.1 g) in 10 ml of *o*-chloroaniline gave by a similar procedure as (ii) a violet compound [Found: C, 42.53; H, 4.09; N, 5.81. $[\text{Ru}_2\text{Cl}_3\text{As}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{NCl})_4]$ requires: C, 41.53; H, 3.27; N, 5.47%].

(vii) *Dichlorotetrakis(2-methoxyaniline)ruthenium(II)*, $[\text{RuCl}_2(\text{C}_7\text{H}_9\text{ON})_4]$ — Following a similar procedure as (ii), $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ (0.1 g) in 10 ml of 2-methoxyaniline gave a blue compound [Found: C, 51.6; H, 5.63; N, 9.36; Cl, 12.59. $[\text{RuCl}_2(\text{C}_7\text{H}_9\text{ON})_4]$ requires: C, 50.6; H, 5.41; N, 8.73; Cl, 11.6%].

(viii) *Heptachloro(diphenylarsino)dodeca(acetonitrile)tetraruthenium(II)*, $[\text{Ru}_4\text{Cl}_7\text{As}(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{CN})_{12}]$ — A solution of 0.1 g (0.25 mmole) of $[\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2]$ was prepared in 10 ml of acetonitrile. It was refluxed for 2 hr when a yellow solution was obtained. The solution was concentrated to 3 ml and *n*-butyl alcohol added whereupon a yellow compound precipitated out. It was centrifuged, washed with *n*-butyl alcohol and dried *in vacuo* [Found: C, 32.0;

H, 4.39; N, 12.36; Cl, 18.53. $\text{Ru}_4\text{Cl}_7\text{As}(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{CN})_{12}$ requires: C, 31.2; H, 3.5; N, 12.17; Cl, 18.53%].

Results and Discussion

$[\text{RuAs}(\text{C}_6\text{H}_5)_2\text{Cl}_2]$ — The magnetic moment of the complex determined by the Gouy method was found to be 1.73 BM which corresponds to one unpaired electron. For octahedral complexes of Ru(III) with ${}^2T_{2g}$ ground state, the value of the magnetic moment should be around 2.0 BM. The lower experimental value may be due to the departure from the O_h symmetry, so that the ground state is either A , B or E instead of T thus quenching the orbital contribution to the magnetic moment leading to the spin-only value. However, the value of the magnetic moment indicates that oxidation state of ruthenium in the complex is +3, and the symmetry of the ligand around ruthenium ion is distorted octahedral.

The ground state of the spin-paired Ru(III) complex is ${}^2T_{2g}$ and the first excited doublet levels are ${}^2A_{2g}$ and ${}^2T_{2g}$ (ref. 9). The energy gap between the ground and the first excited state, ${}^2A_{2g}$, is $10Dq - 3F_2 - 20F_4$. In the electronic spectrum of the complex (mull) a moderately weak band appears at 20000 cm^{-1} which may be assigned to the transition ${}^2T_{2g} \rightarrow {}^2A_{2g}$ (Table 1). Assuming $F_2 = 10F_4 = 1000\text{ cm}^{-1}$, one gets the value of Dq to be equal to 2500 cm^{-1} which agrees with those found for other octahedral Ru(III) complexes⁹.

Except for three new bands at 280, 300 and 350 cm^{-1} in the IR spectrum (KBr) of the complex rest

of the IR bands appear at the similar positions as in the free ligand. The new bands have been assigned to bridging $\nu\text{Ru-Cl}$ and $\nu\text{Ru-As}$ modes of vibrations. These may not be due to pure stretching vibration of any one particular bond but may arise from the normal coordinates having contributions from $\nu\text{Ru-Cl}$ and $\nu\text{Ru-As}$ modes of vibrations.

Thus, from the above studies it appears that the symmetry of the ligand around metal ion is distorted octahedral and Ru(III) is linked with Cl and As in agreement with the general tendency of Ru(III) to form low-spin octahedral complexes with π -donor acids and σ -donor ligands¹⁰. The octahedral symmetry of the ligand around Ru(III) requires both chloride ion and $\text{As}(\text{C}_6\text{H}_5)_2$ to act as bridging ligands forming three-dimensional polymer. The complete insolubility of the complex in water and most of the non-coordinating organic solvents further suggests its polymeric nature.

Other complexes — In order to get more evidence regarding the polymeric nature of $[\text{RuAs}(\text{C}_6\text{H}_5)_2\text{Cl}_2]$, its reactions with a number of coordinating organic solvents and with other σ -donor ligands in non-coordinating solvents have been carried out under refluxing conditions, so that the bridges may be completely or partially cleaved to form either a six-coordinated monomer or a partial polymer. As a result of these reactions, Ru(III) gets reduced to Ru(II) but complete depolymerization of the complex does not take place in any of the reactions except in the case of reactions with *o*-methoxyaniline and quinoline. It is also to be noted that both the halide and the arsenic ligands are removed simultaneously and, therefore, in all the new complexes except that formed with *o*-methoxyaniline and quinoline, both halide ion and arsenic ligand are present.

The reduction of Ru(III) to Ru(II) is not unusual because the Ru(II) complexes may be easily prepared from the reactions of unsaturated amines and Ru(III) without recourse to reducing agents, due to the stabilization of Ru(II) by unsaturated amines¹¹.

All the complexes are found to be diamagnetic which corroborates oxidation state +2 for ruthenium and further suggests that the arrangement of the ligand molecules around ruthenium is octahedral.

The ground state of Ru(II) in octahedral geometry is ${}^1A_{1g}$. The other four excited states in order of their increasing energies are ${}^3T_{1g}$, ${}^3T_{2g}$, ${}^1T_{1g}$, and ${}^1T_{2g}$. Accordingly four bands (two spin-allowed and two spin-forbidden) can be expected corresponding to the transitions ${}^1A_{1g} \rightarrow {}^3T_{1g}$, $\rightarrow {}^3T_{2g}$, $\rightarrow {}^1T_{1g}$ and $\rightarrow {}^1T_{2g}$. Bands corresponding to charge-transfer from ligand to metal ($L \rightarrow M$) do not appear in the visible region in the case low spin d^6 systems^{11,12}. However, complexes of ruthenium(II) with unsaturated amines exhibit intense charge-transfer (metal to ligand) bands in the visible region¹¹. These intense charge-transfer bands might mask the usual weak $d-d$ bands.

In the electronic spectra of these complexes a few weak to moderately intense bands appear in the visible region (Table 1). In the absence of the extinction coefficient values it is very difficult to assign these bands as due to $d-d$ transition. These may arise due to metal \rightarrow ligand charge-transfer.

TABLE 1 — ELECTRONIC SPECTRAL BANDS WITH THEIR ASSIGNMENTS

Compound	Band position (cm ⁻¹)	Assignments
$\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2$	20000	${}^2T_{2g} \rightarrow {}^2A_{2g}$
	15625	${}^1A_{1g} \rightarrow {}^3T_{1g}$
$\text{RuCl}_2\text{As}(\text{C}_6\text{H}_5)_2(\text{Py})_2$	20833	Charge-transfer
	23804	
	25640	
	31250	
	16593	
$\text{RuCl}_2(\text{C}_7\text{H}_9\text{N})_4$	18867	Charge-transfer
	20833	
	25640	
	31250	
$\text{Ru}_2\text{Cl}_3\text{As}(\text{C}_6\text{H}_5)_2(\text{C}_{10}\text{H}_8\text{N}_2)$	15625	Charge-transfer
	19230	
	23805	
	25640	
$\text{Ru}_2\text{Cl}_2[\text{As}(\text{C}_6\text{H}_5)_2]_2(\text{C}_{12}\text{H}_8\text{N}_2)$	31250	Charge-transfer
	14925	
	18867	
	24390	
	25640	
$\text{RuCl}_2(\text{C}_7\text{H}_9\text{ON})_4$	31250	Charge-transfer
	23805	
	25640	
$\text{Ru}_2\text{Cl}_3\text{As}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_5\text{NCl})$	15625	Charge-transfer
	19230	
	26315	
$\text{Ru}_4\text{Cl}_7\text{As}(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{CN})_{12}$	32258	Charge-transfer
	20833	
	23805	
	25640	
$\text{Ru}_4\text{Cl}_7\text{As}(\text{C}_6\text{H}_5)_2(\text{CH}_3\text{CN})_{12}$	31250	${}^1A_{1g} - {}^1T_{2g}$
	31250	

The latter assignments are also suggested by the shifts of the position of 20000 cm^{-1} band towards higher wavenumber side with the increase in the conjugation of the ligand. However, the relative values of the absorption of the different bands in the complex indicate that these bands arise possibly, both due to charge-transfer band as well as due to $d-d$ transition. The positions of the bands due to $d-d$ transition shown in Table 1 indicate the octahedral geometry of the complexes¹².

The IR spectra (KBr) of all the complexes show bands due to tetraphenyldiarsine, amines and other ligands with slight shifts in the band positions in the spectra of complexes as compared to their positions in free ligands or the solvents. This indicates the interaction of the metal ion with tetraphenyldiarsine, ligands and/or amines in the complexes.

Thus, it can be concluded from the above studies that the structure of the complex $[\text{RuAs}(\text{C}_6\text{H}_5)_2\text{Cl}_2]$ is distorted octahedral and it is polymeric in nature.

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