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CHEMISTRY OF DIRUTHENIUM COMPOUNDS HAVING METAL-METAL MULTIPLE BONDS*

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The chemistry of diruthenium compounds having Ru-Ru multiple bonds is summarized in this article. The use of tetracarboxylates of the type $Ru_2Cl(O_2CR)_4$ in the synthesis of various other diruthenium compounds has been described in detail. The reactions can be classified into three categories. The reactions with anionic ligands of the three atom bridging and unidentate types give a variety of diruthenium(III, III) and diruthenium(II, II) species. Using a melt reaction technique in which the tetraacetate is stirred in molten ligand under inert atmosphere, a variety of stable diruthenium(II, III) compounds are obtained. The most interesting result is the isolation of a series of polar molecules in which the coordination environments of two ruthenium centres are totally different. Another series of compounds which were isolated by this technique are the monochlorotetraamidato species. The compounds, $Ru_2Cl(ArCONH)_4$, undergo reactions with $P(Ar)_3$ to produce products in which one aryl group of $P(Ar)_3$ has migrated onto the metal centre with a simultaneous insertion of amidato oxygen onto the phosphorus atom. The third category of compounds are obtained by reacting tetraacetate with neutral three atom bridging ligands in boiling alcohol. The products are mixed ligands compounds which also show a polar arrangement of ligands. Mixed-ligand species can be used to prepare a moderately air stable diruthenium (II, II) compound, $[Ru_2Cl(dmpm)_2(PhNpy)_2]$-$[BPh_4]$. 1.5MeOH. The reaction between $Ru_2Cl(PhNpy)_4$ with $Li(C\equiv CPh)$ forms a stable compound $Ru_2(PhNpy)_4(C\equiv CPh)$ which has a Ru(II) Ru(III)/Ru(III) Ru(III) couple at + 0.2V *vs* SCE. The only porphyrin compounds known are $[Ru(P)]_2$. It is observed that diruthenium(II, III) complexes have bench-top stability. In general the Ru-Ru bond distances lie in the range of 2.248–2.319Å for diruthenium(II, III) compounds with Ru–Ru bond order of 2.5; in the range of 2.238–2.408Å for diruthenium(II, II) compounds having bond order 2.0; and in the range of 2.567–2.650Å for diruthenium(III, III) compounds having Ru–Ru bond order 1.0. The Ru–Ru distance is 2.311(3)Å in $Ru_2(CH_2Bu^t)_6$.

Key Words : **Ru–Ru Bonds; Migratory Process; Polar Molecules**

INTRODUCTION

AFTER the discovery[2] of the Re–Re quadruple bonds in 1964, the chemistry of metal-metal multiple bonds[3,4] has got its distinctive place in the transition metal chemistry

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as a result of the pioneering work by his group and others. In the last two decades, several new Cr_2, Mo_2, W_2, Re_2 and Rh_2 compounds have been prepared and their molecular structures have been characterized[3,4] by X-ray Crystallography. Extensive theoretical, physico-chemical and structural studies on such compounds reveal a complete picture of the nature of metal-metal interactions, their bond order, ground electronic state of the dimetal unit, the spectroscopic results and also the effect of ligands on the metal-metal bond lengths.

While previous studies include the above mentioned metals, the only diruthenium compounds investigated in detail[3,5–10] are the tetracarboxylates, $Ru_2Cl(O_2CR)_4$. During this period, a few results are also reported from other laboratories. In this article, an attempt has been made to summarize these results. Table I shows the available structural data on diruthenium compounds.

I. Diruthenium Tetracarboxylates[5a]

The X-ray structure of $Ru_2Cl(O_2CC_3H_7)_4$ was reported[5b] in 1969. In this molecule, the diruthenium unit is held by four butyrato bridges and the $Ru_2(O_2CC_3H_7)_4$ units are linked by Cl in a zig-zag way to form an infinite chain. A linear chain was observed[6] in propionato species. In $Ru_2Cl(O_2CCA_3)_4$, both the linear[7] and zig-zag[8] chains are known to exist. The Ru-Ru distances in $Ru_2Cl(O_2CR)_4$ range between 2.248Å to 2.290Å. Such a short distance indicates strong metal-metal interaction. The formal oxidation state of Ru is + 2.5. The compounds are all paramagnetic and have magnetic moments which correspond to three unpaired spin. Fig. 1 shows how the *d*-orbitals on the metal atom interacts when two ML_4 squares are brought very close to each other in an eclipsed conformation. In Re(III) Re(III) compound, $Re_2Cl_8^{4-}$, the eight electrons occupy four bonding orbitals as $\sigma^2\pi^4\delta^2$ to give

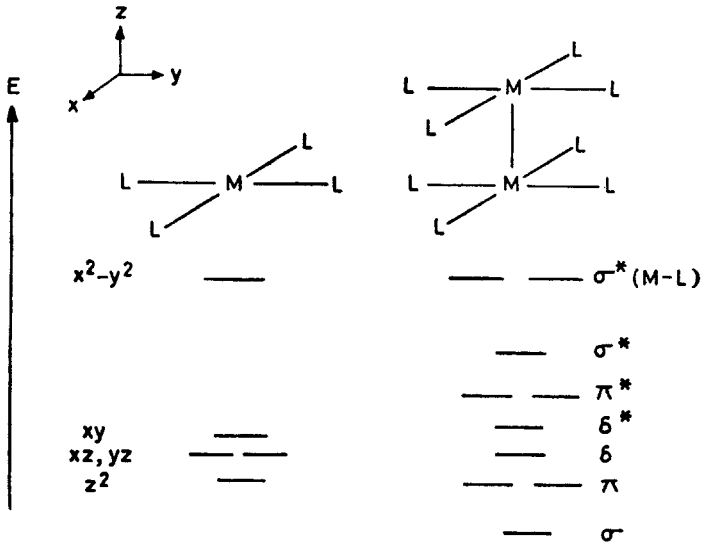


Fig 1 Qualitative energy level diagram for M_2L_8.

TABLE I

Structural data on diruthenium compounds

Compound	Ru–Ru, Å	Ru–*X*(*X* = *Cl*, Br), Å	Ref.
Ru(III)Ru(III)			
1. $Ru_2(CH_2Bu^t)_6$	2.311(3)		14
2. $Ru_2(ap)_6$ $(PMe_2Ph)_2$	2.573(2)		12
3. $[Ru_2(NH_3)_6$ $(\mu\text{-}NH_2)_2]$ $Cl_4 . 4H_2O$	2.625(1)		13
4. $Ru_2(Ph)_2$ $(PhCONH)_2$ $[Ph_2POC(Ph)N]_2$	2.566(1)		18
5. $Ru_2(Ph)_2$ $(3,5\text{-}OMe\text{-}C_6H_3CONH)_2$– $[Ph_2POC(3,5\text{-}OMe\text{-}C_6H_3)N]_2$	2.561(1)		36
6. $Ru_2(p\text{-}C_6H_4CH_3)_2$ $(PhCONH)_2$– $[(p\text{-}C_6H_4CH_3)_2$ $POC(Ph)N]_2$	2.570(2)		36
7. $Ru_2(PMe_3)_6$ $(CH_2)_3$	2.650(1)		35
Ru(III) Ru(II)			
8. $[Ru_2(OH_2)_2$ $(O_2CCH_3)_4]$ BF_4	2.248(1)		6
9. $Ru_2Cl(O_2CCH_3)_4 . 2H_2O$[a]	2.267(1)	2.556(1)	6
10. Cs $[Ru_2Cl_2(O_2CCH_3)_4]$	2.286(2)	2.521(4)	6
11. K $[Ru_2Cl_2(O_2CCH_3)_4]$	2.290(1)	2.517(2)	6
12. $Ru_2Cl(O_2CC_2H_5)_4$[a]	2.292(7)	2.566(4)	6
13. $Ru_2Cl(O_2CC_3H_7)_4$[b]	2.281(4)	2.587(5)	5
14. $Ru_2Cl(O_2CCH_3)_4$[b]	2.281(3)	2.571(1)	7
15. $Ru_2Cl(O_2CCH_3)_4$[b]	2.287(2)	2.577(1)	8
16. $Ru_2Br(O_2CH)_4$[b]	2.2899[7]	2.7242[9]	10
17. $Ru_2Cl(PhCONH)_4$[b]	2.293[2]	2.592[3]	19
18. $Ru_2Cl(4\text{–}Cl\text{–}C_6H_4CONH)_4 . MeOH$[b]	2.296[1]	2.583[2]	20
19. $Ru_2Cl(PhNpy)_4$	2.275(3)	2.437(7)	21
20. $Ru_2Cl(hp)_4$ (H*hp*)	2.286(1)	2.558(2)	21
21. $Ru_2Cl(chp)_4 . CH_2Cl_2$	2.281(1)	2.443(2)	23
22. $Ru_2Cl(fhp)_4$	2.284(1)	2.427(3)	22
23. $Ru_2Cl(O_2CCH_3)_2$ $(mhp)_2 . CH_2Cl_2$	2.278(2)	2.419(5)	30
24. $Ru_2Cl(O_2CCH_3)$ $(chp)_3 . CH_2Cl_2$	2.282(4)	2.474(9)	31
25. $Ru_2Cl(O_2CCH_3)_2$ $(PhNpy)_2$– $(PhNHpy) . CH_2Cl_2$	2.308(1)	2.560(2)	31
26. $Ru_2(C\equiv CPH)$ $(PhNpy)_4 . 2CH_2Cl_2$	2.319(2)		40
27. $[RuL]_2$ Cl . EtOH[c]	2.267(3)		3,29
Ru(II) Ru(II)			
28. $Ru_2(mhp)_4 . CH_2Cl_2$	2.238(1)		11
29. $Ru_2(O_2CCH_3)_4$ $(THF)_2$	2.260(2)		15
30. $[Ru(L)]_2$[c]	2.379(1)		3,29
31. $[Ru(OEP)]_2$[d]	2.408(1)		39
32. $[Ru_2Cl(dmpm)_2$ $(PhNpy)_2]$ $[BPh_4]$. – 1.5MeOH	2.340(2)	2.480(5)	37

[a]Linear Ru–Cl–Ru chains. [b]Zig-zag Ru–Cl–Ru chains. [c]H_2L-Protonated form of dibenzotetraaza [14] annulene. [d]Octaethylporphyrin dianion.

a quadruple bond.[2,3] In diruthenium(II, III) compounds, one would expect an arrangement of 11 electrons as $\sigma^2\pi^4\delta^2\ \delta^{*2}\pi^{*1}$ to give a one-electron magnetic moment. The SCF–Xα–SW calculations done on carboxylato species show[9] that

the δ^* and π^* levels are almost degenerate in energy, thus giving a ground electronic configuration of $\sigma^2\pi^4\delta^2(\delta^*\pi^*)$.[3] It was observed that the δ^* orbital interacts significantly with several carboxylate orbitals and thus destabilizes the δ^* level relative to π^*. The Ru–Ru bond order in tetracarboxylates is 2.5 which constitutes one net σ, one net π and a half δ-bond. The system attains additional stability due to equal population of three unpaired spins in three almost degenerate antibonding orbitals. Any addition or removal of electron to or from this level makes the system unstable.

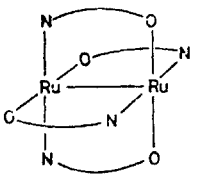
The axial Ru–Cl distances in tetracarboxylates are *ca* 2.55Å. The presence of weak Ru–Cl bond is evidenced from the electro-chemical studies. In polar solvents, it undergoes dissociation to form solvent coordinated species e.g., $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$.[6] Other known[6] complexes are $Cs[Ru_2Cl_2(O_2CCH_3)_4]$ and $K[Ru_2Cl_2(O_2CCH)_4]$. Most recent report[10] on tetracarboxylates is the preparation and structure of $Ru_2Br(O_2CH)_4$.

1. *Reactivity Studies*

In the last few years, the reactivity of the tetracarboxylates towards a variety of ligands has been explored in different laboratories. The reactivity pattern can be broadly classified into three different categories. There are some reactions of tetracarboxylates in which the products are monomeric compounds[3] are excluded from this article.

A. Reaction with Anionic Ligand—The sodiuum salt of 2-hydroxy-6-methylpyridine (Hmhp) is known[11] to react with $Ru_2Cl(O_2CCH_3)_4$ in methanol to produce a diruthenium (II, II) species, $Ru_2(mhp)_4$ in only *ca* 6 per cent yield. The molecular structure of $Ru_2(mhp)_4.CH_2Cl_2$ shows a 2 : 2 arrangement of ligands around the diruthenium core.

The Ru–Ru distance is 2.238(1)Å and is the shortest among all known diruthenium compounds. The metal-metal bond order is 2.0 with the ground electronic configuration of $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^4$ which corresponds to two unpaired spin that has been observed from the magnetic moment measurements. The compound is air-sensitive. The observed low yield of the compound indicates that the reaction proceeds in a different way than that observed in the preparation of $Mo_2(mhp)_4$ and $W_2(mhp)_4$. Here, during the reaction the Ru_2^{5+} core has been reduced to Ru_2^{4+}.



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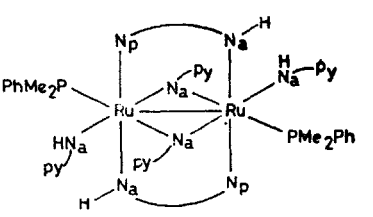
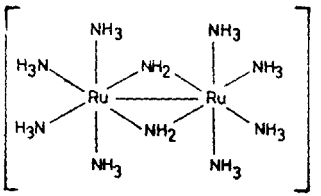


N_a = amine nitrogen, N_p = pyridine nitrogen

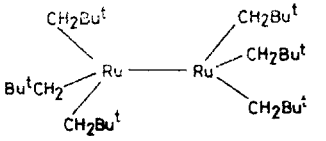
2

Similar type of reaction between the lithium salt of 2-aminopyridine (Hap) and $Ru_2Cl(O_2CCH_3)_4$ in tetrahydrofuran does not produce any clean product. But addition of PMe_2Ph into the reaction mixture and subsequent crystallization is known to form a novel diruthenium(III, III) edge-sharing bioctahedral species $Ru_2(ap)_6(PMe_2Ph)_2$ in which the *ap* ligand displays three different coordination modes.[12] Compound 2 is the first example where ap ligand is in 3-atom bridging mode across two metal centres. One amine nitrogen is in μ^2 bridging mode. The Ru–Ru distance is 2.573(2)Å. In the edge-sharing bioctahedral molecule the interaction between metal orbitals can give σ, π, δ bonding and corresponding antibonding orbitals. Ten electrons of two Ru(III) centers will be populated as $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}$, thus giving a net σ-bond between two Ru atoms. The presence of an amido bridging group in a similar type of compound $[Ru_2(NH_3)_8(\mu\text{-}NH_2)_2]Cl_4.4H_2O$ is also known.[13] The Ru–Ru distance in 3 is 2.625(Å). The presence of a three atom bridge could be responsible for shortening the Ru–Ru distance in 2.



$Cl_4 . 4H_2O$

3



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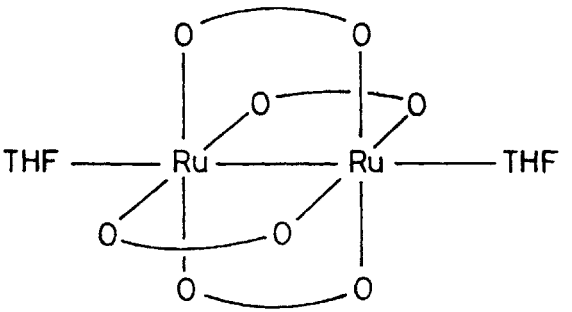
The reactivity of $Ru_2Cl(O_2CCH_3)_4$ towards Grignard reagents is different from the reaction with alkali metal salts of three atom bridging ligands. Use of excess Grignard reagent is known[14] to produce a diruthenium(III, III) species $Ru_2(CH_2Bu^t)_6$(4). X-ray structure of this compound shows that the metal atoms are bonded in absence of any supporting bridges. The Ru–Ru distance of 2.311(3)Å is considerably longer than that observed in other diruthenium compounds having Ru–Ru bond orders of 2.0 and 2.5.

When the proportion of Grignard reagent and $Ru_2Cl(O_2CCH_3)_4$ is 1 : 1, the reaction product is known[15] to be a diruthenium(II, II) compound, $(Ru_2(O_2CCH_3)_4(THF)_2$(5) (where THF = tetrahydrofuran). The Ru–Ru distance is 2.260(2)Å and the metal-metal bond order is 2.0. In $Ru_2(mhp)_4.CH_2Cl_2$, the Ru–Ru distance is shorter than that in 5. While one reason could be the absence of two axial ligands, the other reason may be due to the presence of *mhp* ligands in 2. Oxypyridine ligands are known[3] to produce compounds with short *M–M* bond lengths.

B. Reaction with Molten Ligands—The observed fact is that the use of anionic ligands exhibits strange reactivity resulting in the initial removal of the axial Cl atoms which makes the cage structure to fall apart. The observed yields in all such reactions are poor.

It was observed by Bear and his group[16,17] that use of melt reaction in which the solid acetate when reacted with molten acidamides yields the tetrasubstituted



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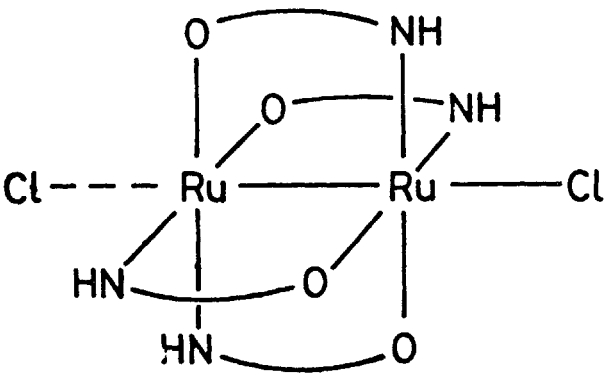
product quantitatively. Using this procedure $Ru_2Cl(CF_3CONH)_4$[16] and $Ru_2Cl(CH_3CONH)_4$[17] were prepared. No structural data are available on these compounds. Other studies[16] have shown that the compounds are polymeric in nature like tetracarboxylates and the Ru–Cl bond can be easily cleaved by using polar solvents.

Using the same technique, crystalline complexes $Ru_2Cl(PhCONH)_4$–MeOH and $Ru_2Cl(4\text{-}Cl\text{-}C_6H_4CONH)_4$.MeOH were isolated.[18–20] Structural study shows that the Ru–Ru core is bridged by four amidato ligands in 2 : 2 arrangement in the centrosymmetric molecule 6. The Ru–Ru bond order is 2.5 and the distance



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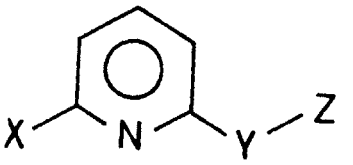
lies in the range of 2.25–2.30Å. The Ru–Cl chains are zig-zag as in $Ru_2Cl(O_2CC_3H_7)_4$. The Ru–Cl bond which is 2.592[3]Å in benzamide complex, can be cleaved by using polar solvents like Me_2SO.

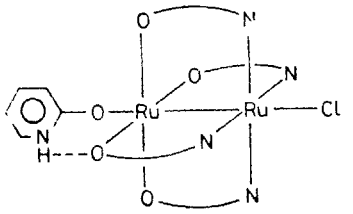
Anionic type 7 ligands are not able to substitute quantitatively all four acetato bridges in $Ru_2Cl(O_2CCH_3)_4$. However, by using the melt reaction technique it is



X	*Y*	*Z*	
H	O	H	Hhp
F	O	H	Hfhp
Cl	O	H	Hchp
Me	O	H	Hmhp
H	NH	Ph	PhNHpy

7

possible to isolate crystalline compounds $Ru_2Cl(hp)_4$ (*Hhp*) (8), $Ru_2Cl(fhp)_4$ (9a),[22] $Ru_2Cl(chp)_4.CH_2Cl_2$ (9b)[23] and $Ru_2Cl(PhNpy)_4$ (10).[21] The *Hmhp* ligand does not



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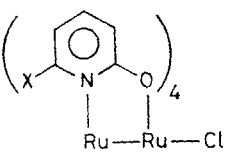
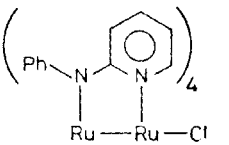


a = X = F

b = X = Cl

9



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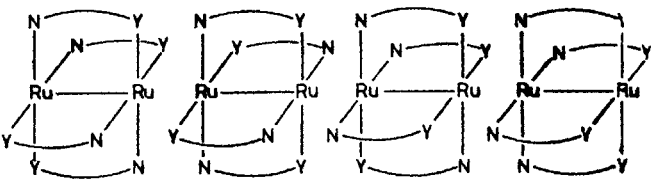
produce any clean product by this technique. Substitution of four carboxylate groups in $Ru_2Cl(O_2CCH_3)_4$ by the unsymmetric ligand like 7 can give rise to four possible geometric isomers, 11–14. The compounds 8–10 show a totally polar

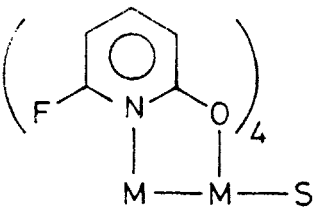


11 12 13 14

arrangement of ligands around the diruthenium center like 14. A type 11 arrangement is observed in $Ru_2Cl(PhCONH)_4$-MeOH[19] and $Ru_2Cl(4\text{-}Cl\text{-}C_6H_4CONH)_4$.

MeOH.[20] The compound $Ru_2(mph)_4.CH_2Cl_2$ displays[11] a type 12 arrangement. Type *13* is known[24,25] to occur in some dirhodium species.

The polar arrangement of ligands was first observed[26,27] in Cr_2, Mo_2, W_2 and Rh_2 complexes of H*fhp* ligand. It was thought that the presence of one strong axial M–S bond in 15 is responsible for such an arrangement. The steric bulk of F is small and it is possible to accommodate all four F atoms on one side of the M_2 unit without any steric hindrance. Axial ligation on that side is not possible because of the presence of four F atoms which screen that site. Such metals do not form any polar molecules with H*chp* and PhNH*py* ligands. Even H*hp* forms compounds having 2 : 2 arrangement of ligands in $Os_2Cl_2(hp)_4$.[28] So it is rather surprising why diruthenium compounds with these ligands are all polar. The H*mhp* ligand cannot form polar molecular because of steric reason.



S = THF; *M* = Cr, Mo, W
S = Me_2SO; *M* = Rh

15

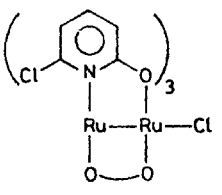
Although the steric requirement is not needed in case of *hp* ligand, but the formation of a polar arrangement of *hp* ligands in 8 is interesting. This compound is also stabilized by the formation of a N–H. .O hydrogen bond. The Ru–Ru distance is 2.286(1)Å. The presence of two axial ligands makes the axial bonds long. The Ru–Cl bond distance which is 2.558(2)Å, is similar to the Ru–Cl distances observed in carboxylato and acidamidato species.

The compound $Ru_2Cl(fhp)_4$ crystallizes in the tetragonal space group with one ligand and Ru–Ru–Cl in the asymmetric unit. There is no twist in the ligand system. The Ru–Ru and Ru–Cl distances are 2.284(1)Å and 2.427(3)Å, respectively. On changing the ligand from *fhp* to *chp*, it was observed that in $Ru_2Cl(chp)_4.CH_2Cl_2$, the ligand undergoes severe twist around the Ru_2 core in order to accommodate four bulky Cl atoms. The average torsion angle is *Ca* 18°. Although the Ru–Ru distance does not change much (2.281(1)Å in 9b) but the formation of polar arrangement of ligands has a pronounced effect on the axial bond length. The Ru–Cl distance is 2.443(2)Å in 9b. The 2-anilinopyridine ligand also forms polar arrangement of ligands in $Ru_2Cl(PhNpy)_4$ but as in the case of $Ru_2Cl(chp)_4.CH_2Cl_2$, here is also a severe twist present in the ligand system with an average value of 22°.

The polar compound $Ru_2Cl(mhp)_4$ is not known so far. Unlike *mhp* ligand, PhN*py* is slightly flexible and thus it is possible to have four pendant phenyl groups on one side of the Ru_2 unit.

C. Reaction with Neutral Ligands in Alcoholic Medium—Ligands having acidic protons e.g. dibenzotetraaza-[14]-annulene, $C_{22}H_{24}N_4 \equiv H_2L$, reacts with tetraacetate in ethanol to produce $[RuL]_2Cl.EtOH$.[29] The compound can be oxidised and reduced to $[RuL]_2^{z+}$ and $[RuL]_2$ by Cp_2Fe^+ and $NaBH_4$, respectively. In these compounds, the Ru–Ru bond is not supported by any bridging ligands. X-ray structural studies show[3] that the Ru–Ru distances in $[RuL]_2$ and $[RuL]_2^+$ are 2.379(1) and 2.267(3)Å, respectively. The Ru–Ru bond orders and ground electronic configurations are : $[RuL]_2$, 2.0, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$; $[RuL]_2^+$, 2.5, $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*1}$. In $[RuL]_2^{z+}$, the bond order is 3 0 and the ground electronic configuration is $\sigma^2\pi^4\delta^2\delta^{*2}$.

The reactions between $Ru_2Cl(O_2CCH_3)_4$ and types 7 neutral ligands in 1 : 4 molar proportions in boiling methanol produce a variety of compounds $Ru_2Cl(O_2CCH_3)_2(mhp)_2.CH_2Cl_2$ (16),[30] $Ru_2Cl(O_2CCH_3)(chp)_3.CH_2Cl_2$ (17),[31] $Ru_2Cl(fhp)_4$ (9a), and $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy).CH_2Cl_2$ (18).[31] Such mixed



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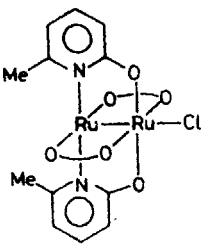

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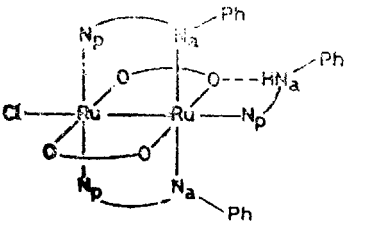
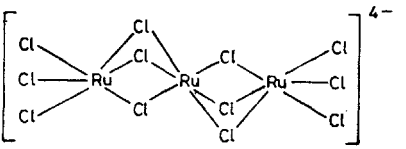


18

ligand compounds are the first in diruthenium chemistry and can be used as a starting material in the synthesis of other compounds.

The arrangements of ligands are also polar in nature. The torsion angles are *Ca* 5°. While H*fhp* is able to substitute all four acetates, H*chp* is able to displace three acetate ligands. H*mhp* ligand can only substitute two acetates because of the greater bulk of Me compared to Cl. The PhNH*py* ligand forms a compound which is similar to that of $Ru_2Cl(hp)_4(Hhp)$ (8). The Ru–Ru distances in these compounds lie in the range 2.278(2)–2.308(1)Å. The Ru–Cl distance observed in $Ru_2Cl(O_2CCH_3)_2(mhp)_2.CH_2Cl_2$ is 2.419(5)Å and is the shortest among all diruthenium species having axial Ru–Cl bond(s). As expected the Ru–Cl bond in (18) is long having a value of 2.560(2)Å.

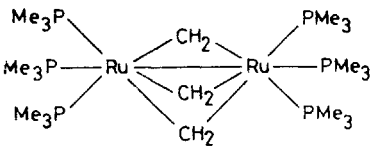
Interaction between $Ru_2Cl(O_2CCH_3)_4$ and 12M HCl in presence of NH_4Cl under argon atmosphere is known[32] to produce on slow evaporation a green product $[NEt_4]_2[H_7O_3]_4[Ru_3Cl_{12}]$. The anionic part, shown in 19, has a Ru–Ru distance of 2.805(1)Å which is short enough to have a Ru–Ru bonding interaction.



19

2. *Reactivity of Diruthenium Compounds towards Phosphines*

Reaction of acetate $Ru_2Cl(O_2CCH_3)_4$ with PPh_3 produces monomeric product. Cleavage of Ru–Ru bond is also known[33,34] to take place in several reactions of acetate with MgR_2(R = alkyl or aryl group) in presence of PMe_3. In one case, along with the major product of *cis*-$RuMe_2(PMe_3)_4$, Wilkinson and his group were able to isolate a minor product of the novel red, air sensitive, diamagnetic compound $Ru_2(PMe_3)_6(\mu\text{-}CH_2)_3$ (20) from the reaction of $Ru_2Cl(O_2CCH_3)_4$ and $MgMe_2$ in presence of PMe_3.[35] The diruthenium(III, III) compound which has a Ru–Ru

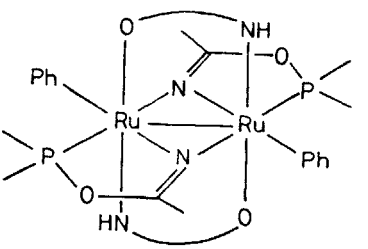


20

single bond with a distance of 2.650(1)Å, can also be prepared in higher yield by using $Ru_3O(O_2CCH_3)_6(H_2O)_3.(CH_3COO)$ instead of tetraacetate. A shorter Ru–Ru distance of 2.641(1)Å is observed in $[Ru_2(PMe_3)_6\ (\mu\text{-}CH_2)_2]\ (BF_4)_2$ which is known[35] to form on addition of 2 equivalent of HBF_4 to 20.

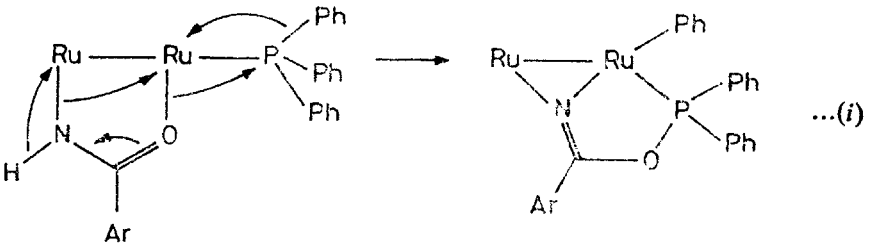
It is mentioned above that in the reaction between $Ru_2Cl(O_2CCH_3)_4$ and Li(*ap*), the product was isolated only after the addition of PMe_2Ph. The reaction product is again a Ru(III) Ru(III) compound, $Ru_2(ap)_6(PMe_2Ph)_2$, but has a different structure from that of 20.

While PPh_3 is able to cleave the Ru–Ru bond in $Ru_2Cl(O_2CCH_3)_4$, it reacts with $Ru_2Cl(ArCONH)_4$ in a different manner. The product isolated from the reaction is a diruthenium(III, III) compound, $Ru_2(Ph)_2(ArCONH)_2[Ph_2POC(Ar)N]_2$, 21.[18,36]



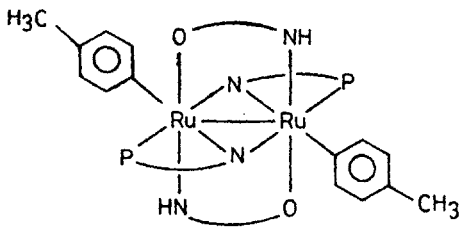
21

The molecule is an example of edge sharing bioctahedra. The Ru–Ru bond is single having a distance of 2.566 (1)Å. The interesting features in this molecule are the presence of Ru–Ph bond and the formation of a new phosphine ligand which is showing chelating mode as well as μ^2-N bridging mode. Two of the bridging ArCONH ligands in $Ru_2Cl(ArCONH)_4$ are still in the three-atom bridging mode. The migration of the phenyl group from PPh_3 onto the metal centre occurs simultaneously with the insertion of oxygen of the bridging amide to the phosphorus atom. In the whole process, the Ru_2^{5+} unit gets oxidized to Ru_2^{6+} The μ^2-N is planar since $\angle$ RuNRu + $\angle$ RuNC + $\angle$ RuNC = 360°. Mechanistically the reaction can be shown as :



...(*i*)

Although there is no experimental evidence for the Ru–PPh_3 axial bond formation, however, electrochemical studies done on $Ru_2Cl(RCONH)_4$ have shown that the Ru–Cl bond undergoes dissociation in presence of polar solvents like Me_2SO(R = CF_3, CH_3 or Ph). Reaction (*i*) proceeds in case of Ar = Ph or substituted phenyl group but dose not occur when it is an alkyl group. The reaction also proceeds on changing the phosphine from PPh_3 to P(p-Tol)$_3$.[36] The formation of the product $Ru_2(p\text{-}C_6H_4CH_3)_2(PhCONH)_2$–[$p$-$C_6H_4CH_3)_2$ POC(Ph)N]$_2$ (22) indicates that it is the P–C bond which is activated.



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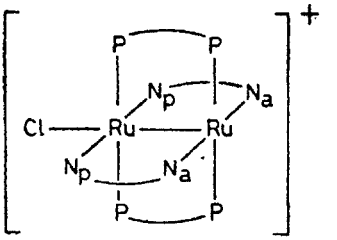


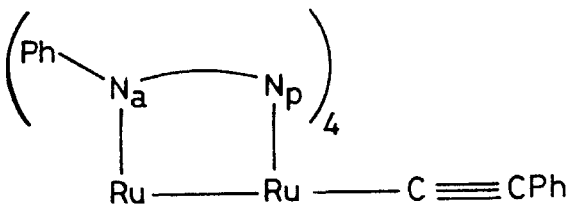
23

Reactions between $Ru_2Cl(O_2CCH_3)_4$ and diphosphines yield monomeric products. But, when a mixed ligand compound is used instead of tetraacetate, the product obtained[37,38] is a dimer. It is observed[37] that the reaction of $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2$ ($PhNHpy$) with dmpm (dimethylphosphinomethane) in presence of Me_3SiCl yields a novel Ru(II) Ru(II) compound, $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]$.

1.5 MeOH (23). Structural studies show[37] that the bridging acetates are replaced by bridging dmpm ligands. The axial PhNH*py* ligand which was hydrogen-bonded with one of the oxygen of the acetate ligands is also replaced during the reaction. This compound is moderately stable in the solid state. Cyclic voltammetric studies show that the Ru(II) Ru(II)/Ru(II) Ru(III) couple appears near +0.3V *vs.* SCE. All other known[11,15,29,39] diruthenium(II, II) complexes are air sensitive. The Ru–Ru distance in 23 is 2.340 (2)Å which is considerably longer than the same observed in $Ru_2(mhp)_4 \cdot CH_2Cl_2$ and $Ru_2(O_2CCH_3)_4(THF)_2$. Such a lengthening of the Ru–Ru bond could be due to the greater bite of the phosphine ligand.

II. Diruthenium Tetraanilinopyridinates $Ru_2Cl(PhNPy)_4$

The reactivity of acetylenes towards polar molecules has been studied. The lithium salt of phenylacetylene (LiC≡C(Ph)) reacts with $Ru_2Cl(PhNpy)_4$ to produce $Ru_2(C{\equiv}CPh)(PhNpy)_4$, 24.[40] The effect of the presence of a strong electron withdrawing group in the axial position is expected to increase the Ru–Ru bond



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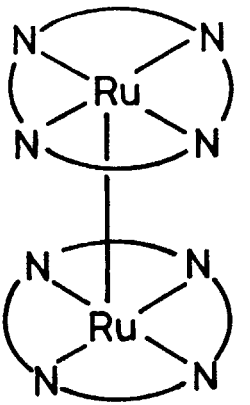

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length by withdrawing electron density from d_{z^2} orbital involved in the σ-bonding. This is true in this molecule. The Ru–Ru distance is 2.319(2)Å which is considerably longer than the Ru–Ru distance of 2.275 (3)Å observed[21] in $Ru_2Cl(PhNpy)_4$. The other reason could be that some electron density of acetylene π-system is transferred to the antibonding level of the diruthenium core. This is evidenced from the electrochemical studies. The Ru(II) Ru(III)/Ru(III) Ru(III) couple which appears near +0.5V in $Ru_2Cl(PhNpy)_4$, has been shifted to +0.2V on replacement of Cl by —C≡CPh.

III. Diruthenium Porphyrin Compounds

The only diruthenium compounds which are not obtained from starting tetracarboxylates are the porphyrin species $[Ru(P)]_2$, where *P* is octaethylporphyrinato (OEP)

or tetraphenylporphyrinato (TPP).[39] The compounds are obtained by pyrolysis as shown in Scheme I. Structural studies on

Scheme I

$$[RuCl_2(CO)_3]_2 + H_2P \xrightarrow{\Delta} RuP(CO)\ (MeOH) \xrightarrow[py]{h\nu} RuP(py)_2 \xrightarrow[\text{vacuum}]{\Delta} [Ru(P)]_2$$

$[Ru(OEP)]_2 \cdot 2C_5H_{12}$ (25).

Show that two cofacial [Ru(OEP)] groups are bonded by a Ru–Ru double bond. The Ru–Ru distance is 2.408(1)Å which is longer than the same observed in $[Ru(L)]_2$, where L is tetraazaannulene.

The ruthenium atoms in 25 are 0.30Å out of the respective porphyrin planes and are pointed towards each other. The porphyrin planes are twisted 23.8(1)° with respect to each other to form a gouch conformation. The remarkable feature of this compound is the presence of strong metal-metal interaction in absence of any bridging ligand. The compound is highly air-sensitive like most of other diruthenium(II, II) species.

Conclusion

Synthetic and structural studies on these diruthenium complexes reveal the fact that such systems behave in a completely different manner than the rest in the chemistry of metal-metal multiple bonds. One reason could be due to the presence of non-integral formal oxidation state of + 2.5 in stable compounds. This is exemplified in the formation of a series of polar molecules.

If we consider the reactivity pattern of tetracarboxylates, it is observed that the high yield melt reaction technique forms all diruthenium(II, III) compounds. When reacted with anionic ligands, in most cases the yields of the products are low and a variety of compounds are obtained with novel structural characteristics. The compounds are having either diruthenium(III, III) or diruthenium(II, II) core. When diruthenium(III, III) compounds are obtained, the cage structure containing four bridging ligands is no longer present. In most cases the products from such reactions are monomeric in nature.

The amidato compounds resemble very close to the carboxylato species. The only difference is in the reactivity of amidato compounds towards phosphines. While triarylphosphines cleave the Ru–Ru bond in tetracarbyxylates, they form novel diruthenium(III, III) species with amidato compounds. The reaction between $Ru_2Cl(ArCONH)_4$ with $P(Ar)_3$ results in the migration of aryl group from $P(Ar)_3$ onto the metal centre. Such type of aryl group migration although known in monomeric compounds having metal atom in lower oxidation state but is unknown in the chemistry of metal-metal multiple bonds.

In recent years, a number of diruthenium(II, II) compounds are reported in literature. The compounds are in general air-sensitive except the $[Ru_2Cl(PhNpy)_2(dmpm)_2][BPh_4] \cdot 1.5$ MeOH which is moderately stable in the solid state. On

changing the coordination environment around the Ru_2^{4+} core it should be possible to isolate air-stable compounds.

The remarkable feature in the diruthenium chemistry is the isolation of a series of polar molecules. Even in the mixed ligand species, the polar arrangement of ligands is the most favourable one. To understand whether only steric reason is behind this or electronic factor also plays a role, a theoretical study on such systems is needed.

The reactivity of acetylenes towards polar molecules could generate an interesting chemistry as is the reactivity of tetracarboxylates towards alkoxides, isocyanides and similar type of ligands. Already the results reported on the reaction of tetraacetates with Grignard reagents are promising to open up a new field.

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