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Ruthenium(I) complexes containing bridging N-donor ligands: structure, synthesis and reactivity patterns

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CONTENTS

ABSTRACT

The article reviews the chemistry of binuclear ruthenium(I) complexes containing bridging N-donor ligands. The introduction is followed by a survey of compounds, which is classified in alphabetical order according to the type of organic molecule that gives rise to each particular bridging ligand (amides, diamines, imidazoles, oximes, pyrazoles, pyridines, thiazoles, triazenes, triazoles), and covers the literature

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published up to the end of 1992. The article finishes with some comments on structural, synthetic and reactivity aspects of this class of compound.

ABBREVIATIONS

ape-R	1,2-bis(alkylamido)-1,2-bis(2-pyridyl)ethane
bipy	2,2′-bipyridine
bipyr	orthometallated 2,2′-bipyridine
cyclop	(1S,2S)-(+)-1,2-bis(diphenylphosphinomethyl)cyclohexane
dazab-R	1,4-diaza-1,3-butadienes, *N*-substituents R
dppb	1,4-bis(diphenylphosphino)butane
dppbz	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
dppen	1,2-bis(diphenylphosphino)ethylene
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
Hbtz	benzotriazole
HCp	cyclopentadiene
H_2dab	1,2-diaminobenzene
H_2dabMe_2	1,2-diamino-4,5-dimethylbenzene
H_2dan	1,8-diaminonaphthalene
Hidz	indazole
HN_3R_2	triazenes, N^1,N^3-substituents R
HOpy	2-hydroxypyridine
$HoxR^1R^2$	oxime, *C*-substituents R
Hpz	pyrazole
HpzMe	3-methylpyrazole
$HpzMe_2$	3,5-dimethylpyrazole
HSbtz	2-mercaptobenzothiazole
HSpy	2-mercaptopyridine
py	pyridine
pyca-R	pyridine-2-carbaldehyde imines, *N*-substituents R
pyr	orthometallated pyridine
tht	tetrahydrothiophene

1. INTRODUCTION

If one looks at any of the many inorganic chemistry textbooks which are now available, one finds very little information about ruthenium(I) complexes. This does not mean that such compounds are rare, but simply that most of them have been prepared very recently. In fact, before 1980 only the synthesis and derivative chemistry of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ [1], $[Ru_2Cp_2(CO)_4]$ [2] and the carboxylato complexes $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4(L)_2]$ [3] were well established, while most of the other known ruthenium(I) compounds were either just by-products of reactions of $[Ru_3(CO)_{12}]$ or other polynuclear clusters (see, for example, ref. 4), or their synthesis required the use of sophisticated ligands, as for the complexes $[Ru_2(\mu\text{-}Cl)_2(CO)_4(PR_3)_2]$ which can be obtained only by using phosphines containing at least two *t*-butyl groups [5].

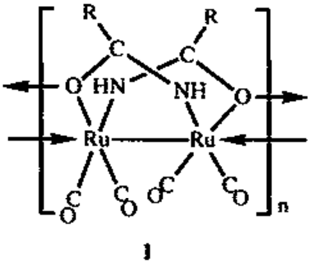
Apart from $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ and its derivatives, all the other ruthenium(I) compounds are binuclear diamagnetic metal–metal bonded complexes, or polymers made up of binuclear units, which obey the 18-electron rule. In most of these binuclear compounds, the metal–metal bonds are supported by bridging ligands, whereas compounds without bridging ligands are rare, examples of the latter being the complexes $[Ru_2(MR_3)_2(CO)_8]$ (M = Si, Ge, Sn; R = alkyl) [6], $[Ru_2Cp_2(CO)_4]$ [2] and $[Ru_2(pz_3BH)_2(CO)_4]$ [7].

It is the purpose of this article to review the chemistry of ruthenium(I) complexes containing bridging N-donor ligands, since such complexes are the most recently prepared ruthenium(I) compounds. The survey, which is classified in alphabetical order according to the type of organic molecule that gives rise to each particular bridging ligand, covers the literature published up to the end of 1992 and is followed by a summary of structural, synthetic and reactivity aspects of this class of compound. The fact that nearly all the references are from 1986 or later testifies to the current strong interest in this field.

2. SURVEY OF COMPLEXES ARRANGED BY BRIDGING LIGAND TYPE

2.1 *Amides*

The reaction of $[Ru_3(CO)_{12}]$ with organic amides (acetamide, propionamide, isobutiramide, benzamide) affords the insoluble polymeric complexes **1**. These substances are soluble only under depolymerization in solvents having good coordination properties (dimethyl sulphoxide, acetonitrile) or in the presence of suitable ligands (PPh_3), giving the binuclear tetracarbonyls **2**, in which the added ligands occupy axial positions and the bridging ligands are in a head-to-tail arrangement [8]. The reaction of **2** (L = MeCN) with acetic or trifluoroacetic acid [8] gives the well-known [3] carboxylato derivatives $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4(MeCN)_2]$.



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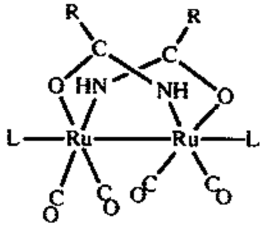

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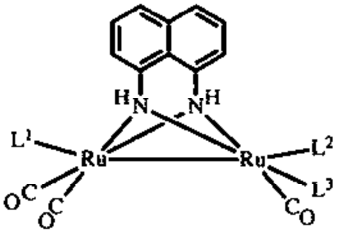
2.2 Aza- and 1,4-diaza-1,3-dienes

The reactions of aza- and diazabutadienes with [$Ru_3(CO)_{12}$] give a variety of binuclear ruthenium(I) complexes. This chemistry has been extensively studied by the groups led by Vrieze and van Koten, and has been reviewed several times [4,9–13], so this topic will not be surveyed here.

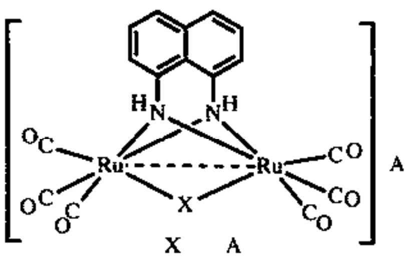
2.3 Diamines

The binuclear hexacarbonyl **3** can be made efficiently by reaction of 1,8-diaminonaphthalene with [$Ru_3(CO)_{12}$] in refluxing toluene, under an atmosphere of carbon monoxide [14,15]. This compound reacts readily with excess P-donor ligands to give di- (**4**–**7**) and trisubstituted derivatives (**8**), while its reaction with pyridine affords only the monosubstituted derivative **9** [15]. An alternative route to **5** involves the reaction of 1,8-diaminonaphthalene with [$Ru_3(CO)_9(PPh_3)_3$] [16]. When complex **3** is treated with one equivalent of dppm, a mixture of oligomers containing bridging and monocoordinated dppm ligands is obtained; aggregation of these oligomers takes place in refluxing tetrahydrofuran, giving the polymer [{Ru_2(μ-dan)$(CO)_4$}(μ-dppm)]$_n$ [15].

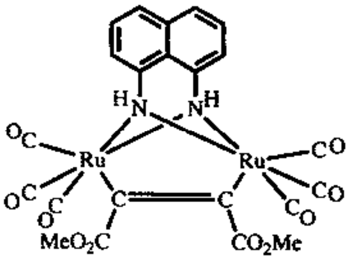


	L^1	L^2	L^3
3	CO	CO	CO
4	PPr^i_3	PPr^i_3	CO
5	PPh_3	PPh_3	CO
6	$P(OPh)_3$	$P(OPh)_3$	CO
7	dppm	dppm	CO
8	$P(OMe)_3$	$P(OMe)_3$	$P(OMe)_3$
9	CO	py	CO

Complex **3** reacts with halogens (Cl_2, Br_2, I_2) to give the cationic halogen-bridged ruthenium(II) complexes **10**–**12**. These results suggest a heterolytic cleavage of the halogen molecule X_2 to give the electrophile X^+, which then attacks the



	X	A
10	Cl	Cl
11	Br	Br
12	I	I_3
13	H	BF_4



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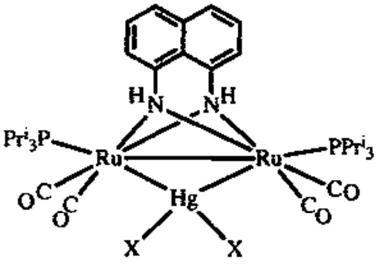
Ru—Ru bond. Similarly, complex **3** can be reversibly protonated with HBF_4 to give **13**. Complex **3** also reacts with dimethylacetylendicarboxylate to give the adduct **14** [15].

The Ru—Ru bond of 3 is not basic enough to react with metallic electrophiles. However, the presence of triisopropylphosphine in **4** increases the nucleophilic character of its Ru—Ru bond, making it susceptible to electrophilic attack by metallic fragments. Thus, complex **4** reacts with $[MPPh_3]^+$ (M = Ag, Au) to give the cationic adducts $[Ru_2(\mu\text{-}MPPh_3)(\mu\text{-dan})(CO)_4(PPr^i_3)_2]^+$ and with [AuCl(tht)], AgO_2CCF_3 or $SnCl_2$ to give $[Ru_2(\mu\text{-}ML_n)(\mu\text{-dan})(CO)_4(PPr^i_3)_2]$ (ML_n = AuCl, AgO_2CCF_3 or $SnCl_2$) [17]. Complex **4** also reacts with one equivalent of mercury(II) salts HgX_2 (X = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl, O_2CCF_3, SCN, ONC) to give the adducts $[(\mathbf{4})HgX_2]$ (**15**). Correlations between the $^2J(^{31}P\text{–}^{199}Hg)$ coupling constants of their ^{31}P NMR spectra and the corresponding halogen electronegativities or pK_a values have been observed. With the exception of $[(\mathbf{4})Hg(O_2CCF_3)_2]$, which does not react with any other mercury(II) salt, the compounds $[(\mathbf{4})HgX_2]$ (**15**) react with HgX'_2 (X′ = Cl, Br, I, O_2CCH_3, O_2CPh, O_2CCH_2Cl) to give the insertion products $[(\mathbf{4})Hg(\mu\text{-}X')_2HgX_2]$ (**16**) only when X′ is more electron-withdrawing than X, otherwise the addition products $[(\mathbf{4})Hg(\mu\text{-}X)_2HgX'_2]$ are formed [18,19].



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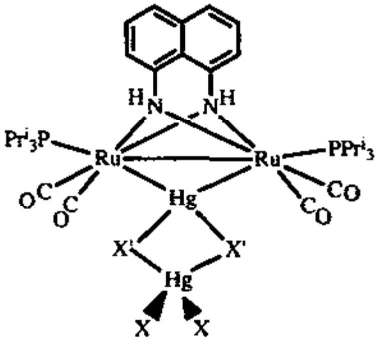

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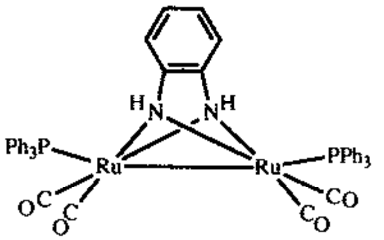
The binuclear compound **17** can be made efficiently by treatment of $[Ru(CO)_3(PPh_3)_2]$ with 1,2-diaminobenzene in refluxing mesitylene [20]. Alternative routes to **17** involve the reaction of 1,2-diaminobenzene with $[Ru_3(CO)_9(PPh_3)_3]$ [21] or the reaction of $[Ru(dab)(PPh_3)_3]$ with CO [22]. It should be noted that, when this compound was first published, it was erroneously formulated as the dicarbonyl $[Ru_2(\mu\text{-dab})(CO)_2(PPh_3)_2]$ [22]. Curiously, unlike with 1,8-diaminonaphthalene, the reactions of $[Ru_3(CO)_{12}]$ with 1,2-diaminobenzene or with 1,2-diamino-4,5-dimethylbenzene do not give the expected binuclear compounds $[Ru_2(\mu\text{-dab})(CO)_6]$ or $[Ru_2(\mu\text{-dabMe}_2)(CO)_6]$, but the trinuclear clusters **18** (R = H, Me) [14].

Complex **17** reacts with cationic (H^+, NO^+, $[AgPPh_3]^+$, $[AuPPh_3]^+$) or neutral (CuCl, [AuCl(tht)], AgO_2CCF_3) Lewis acids to give **19**. The pentanuclear

AuRu$_4$ cluster **20** has been prepared by reaction of **17** with **19** (X = AuCl) in the presence of TlPF$_6$ [23].



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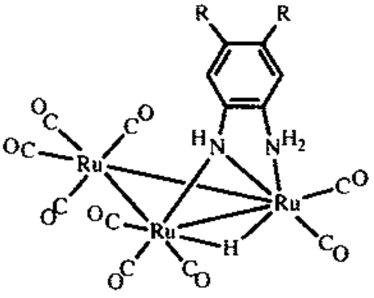

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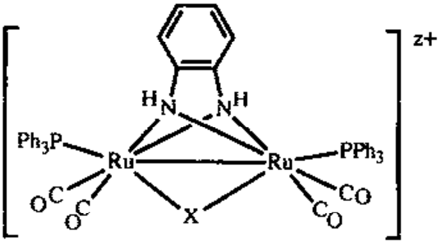

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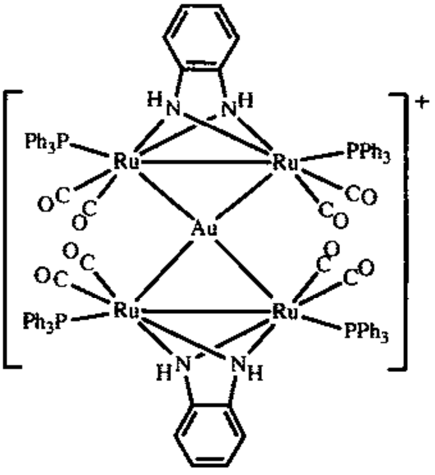
X	z
H	1
NO	1
AuPPh$_3$	1
AgPPh$_3$	1
CuCl	0
AuCl	0
AgO$_2$CCF$_3$	0



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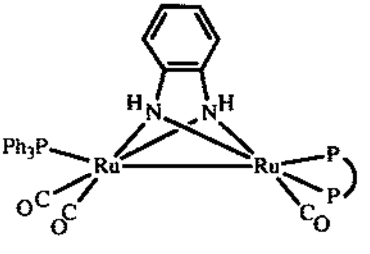
The reaction of **17** with one equivalent of diphosphine (dppe, dppen, dppbz, dppp, dppb) in boiling toluene gives purple solutions from which the yellow compounds **21** can be isolated. The use of an excess of diphosphine results in a mixture of the mononuclear complexes [Ru(dab)(CO)(η^2-diphosphine)] and [Ru(CO)$_2$(PPh$_3$)(η^2-diphosphine)] and, in the case of dppb, in a mixture of [Ru$_2$(μ-dab)(CO)$_3$(η^1-dppb)(η^2-dppb)], [Ru$_2$(μ-dab)(μ-dppb)(CO)$_2$(PPh$_3$)$_2$], [Ru$_2$(μ-dab)(CO)$_2$(η^2-dppb)$_2$] and [Ru(CO)$_2$(η^1-dppb)(η^2-dppb)]. However, the reaction of **17** with an excess of dppm affords **22** as the unique product. The binuclear compounds **21** and **22** can also be obtained by reaction of [Ru(dab)(PPh$_3$)(η^2-diphosphine)] with [Ru(CO)$_3$(PPh$_3$)$_2$] in boiling mesitylene [24].

Compound **23**, which contains two different bridging ligands, has been prepared by reaction of the trinuclear cluster **18** (R = Me) with diphenylacetylene [25].



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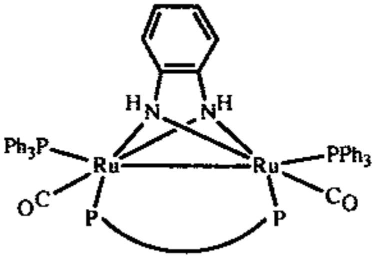

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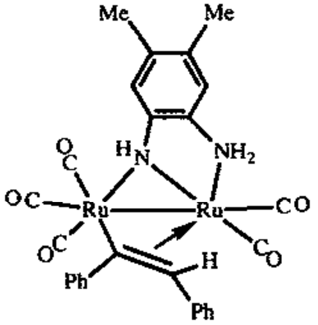

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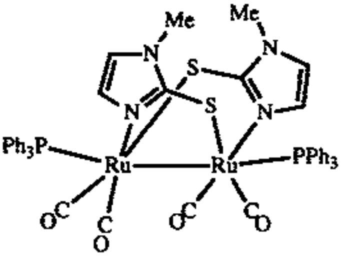

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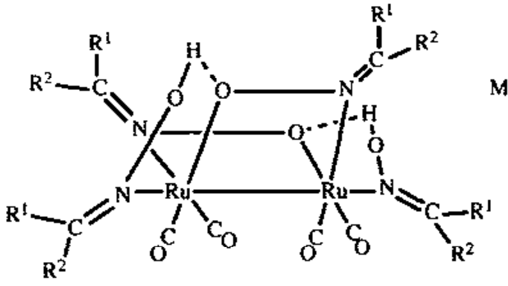
2.4 Imidazoles

The reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with *N*-methyl-2-mercaptoimidazole gives **24**, in which the bridging ligands are in a head-to-tail arrangement [16].

2.5 Oximes

The thermal reaction of $[Ru_3(CO)_{12}]$ with oximes leads to fragmentation of the trinuclear framework, giving binuclear complexes of the type $[Ru_2(\mu\text{-}oxR^1R^2)_2(CO)_4(HoxR^1R^2)_2]$ (**25**), in which the bridging ligands are in a head-to-tail arrangement. Intramolecular hydrogen bonds have been observed between the bridging oximato and the terminal oxime ligands. With oximes containing sterically demanding substituents, only complexes in which the axial oxime ligands are replaced by PPh_3 can be isolated. The complex $[Ru_2(\mu\text{-}oxMe_2)_2(CO)_4(HoxMe_2)_2]$ undergoes reactions in which the axial oxime ligands can be replaced by a variety of two-electron donor ligands (PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, acetylacetone dioxime, $S(CH_2Ph)_2$, $Se(CH_2Ph)_2$) [26].

In the presence of catalytic amounts of $[Ru_2(\mu\text{-}oxMe_2)_2(CO)_4(HoxMe_2)_2]$, acetone oxime reacts with carbon monoxide to give 2,3,4,5-tetrahydro-2,2,4,4,6-pentamethylpyrimidine ("acetonine"), CO_2 and NH_3. The reaction presumably proceeds



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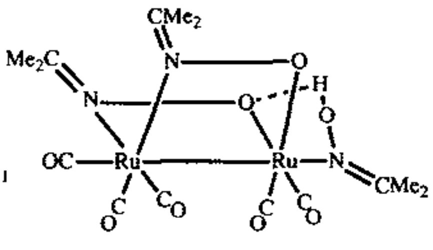

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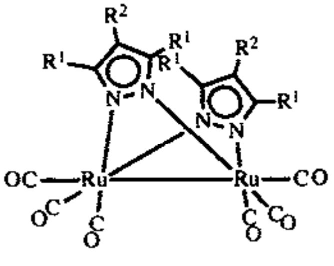
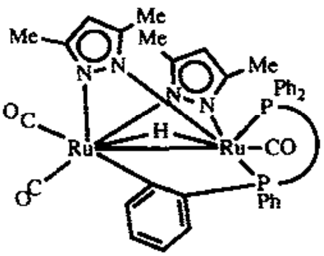
via carbonylation of the bridging acetone oximato ligand to the unstable intermediate $Me_2C{=}N{-}OCHO$, which undergoes decarboxylation to give the corresponding imine $Me_2C{=}NH$; the final product is assumed to result from the cyclotrimerisation of $Me_2C{=}NH$ with the elimination of NH_3. Evidence for the intermediacy of the imine comes from the analogous reaction with acetophenone oxime, which gives the corresponding inime $PhMeC{=}NH$ as a stable product. The complex $[Ru_2(\mu\text{-}oxMe_2)_2(CO)_5(HoxMe_2)]$ (**26**), which contains the bridging ligands in a head-to-head arrangement, has been isolated from the catalytic reaction [27].

2.6 *Pyrazoles*

The reaction of $RuCl_3{\cdot}nH_2O$ with carbon monoxide in boiling 2-methoxyethanol gives a yellow solution which, after treatment with pyrazole or 3,5-dimethylpyrazole in the presence of zinc, yields the complexes **27** and **28**. Similarly, mixtures of head-to-head and head-to-tail isomers of $[Ru_2(\mu\text{-}pzMe)_2(CO)_6]$ or $[Ru_2(\mu\text{-}idz)_2(CO)_6]$ are obtained when 3-methylpyrazole or indazole are used as ligands [28,29]. The compounds **27–29** are also accessible from the reaction of $[Ru_3(CO)_{12}]$ with the appropriate pyrazole ligand [30].



	R¹	R²
27	H	H
28	Me	H
29	H	Me



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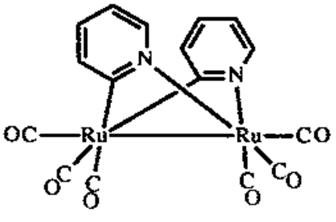
Compound **27** undergoes substitution of the axial CO ligands upon reaction with PPh_3 or dppf to give the tetracarbonyls $[Ru_2(\mu\text{-pz})_2(CO)_4(L)_2]$ ($L = PPh_3$, dppf) [30]; however, and probably owing to steric reasons, similar reactions with the 3,5-dimethylpyrazolate complex **28** only lead to the monosubstituted derivatives $[Ru_2(\mu\text{-pzMe}_2)_2(CO)_5(L)]$ ($L = MeCN$, py, PPh_3, $P(C_6C_{11})_3$, dppm) [29]. The compound $[Ru_2(\mu\text{-pz})_2(CO)_4(PPh_3)_2]$ can also be prepared by reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with pyrazole [16] or by treatment of $[Ru_2(\mu\text{-}O_2CMe)_2(CO)_4(MeCN)_2]$ with sodium pyrazolate followed by addition of PPh_3 [31]. Steric arguments may also explain the different reactivities of **27** and **28** with the diphosphines dppe or cyclop: **27** gives tetracarbonyl compounds in which the diphosphine ligands bridge the two ruthenium atoms, whereas **28** gives the hydrido derivatives **30**, which arise from the orthometallation of one of the phenyl groups of the diphosphines, which in this case act as chelating ligands [32].

Compound **28** oxidatively adds one equivalent of iodine to give two isomers of $[Ru_2I_2(\mu\text{-pzMe}_2)_2(CO)_6]$; however, the cationic complex $[Ru_2(\mu\text{-I})(\mu\text{-pzMe}_2)_2(CO)_6]I_3$ is formed when two equivalents of iodine are used [29]. Complex **28** does not react with hydrogen or with the metallic electrophiles Ag^+, $[AgPPh_3]^+$ and $[AuPPh_3]^+$ [29], but reacts with carboxylic acids to give the carboxylato-bridged derivatives $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4(HpzMe_2)_2]$. In the latter reaction, the heterocyclic bridging ligand is transformed into an η^1-substituent upon protonation of one nitrogen atom, while the unity of the binuclear system is maintained by the carboxylato bridges formed [30].

2.7 Pyridines

$[Ru_3(CO)_{12}]$ reacts with pyridine in *n*-heptane at 120°C to give a complex product mixture from which the only isolated species are the head-to-head (**31**) and head-to-tail isomers of $[Ru_2(\mu\text{-pyr})_2(CO)_6]$. In neat pyridine at 180°C, $[Ru_3(CO)_{12}]$ gives a 12% yield of compound **32**, which contains an orthometallated 2,2′-bipyridine ligand [33].



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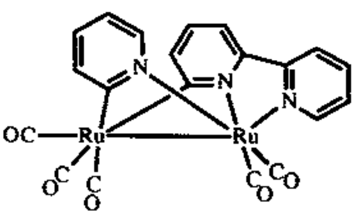

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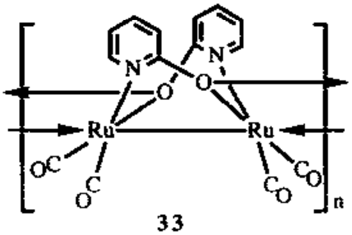
The thermal reaction of 2-hydroxypyridine with $[Ru_3(CO)_{12}]$ affords the polymer **33** or the dimer **34**, depending on the ratio of the reactants. In both cases, the bridging ligands are in a head-to-tail arrangement. The polymeric structure of **33** can be broken by reaction with two-electron donor ligands to give the binuclear derivatives **34**–**39** [34]. Alternative routes to **35** involve the reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with 2-hydroxypyridine [16] or the reaction of $[Ru_2(\mu\text{-}O_2CMe)_2(CO)_4(PPh_3)_2]$ with the sodium salt of 2-hydroxypyridine [31].



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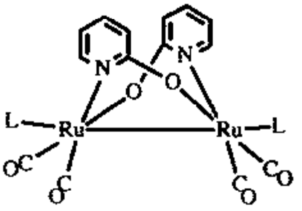


	L
34	HOpy
35	PPh_3
36	PPr^i_3
37	$P(OPh)_3$
38	CO
39	MeCN

The compounds **34**–**36** have been chemically and electrochemically oxidized to the cations $[Ru_2(\mu\text{-}Opy)_2(CO)_4(L)_2]^+$ ($L = HOpy$, PPh_3, PPr^i_3). These paramagnetic species are only stable below 0°C, undergoing disproportionation into a mixture of $[Ru_2(\mu\text{-}Opy)_2(CO)_4(L)_2]$ and $[Ru(Opy)(CO)_2(L)]^+$ (1:2 ratio) at higher temperatures [35].

In contrast to the results stated above for the thermal reaction of $[Ru_3(CO)_{12}]$ with 2-hydroxypyridine, a similar reaction with 2-mercaptopyridine gives, initially, the trinuclear complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Spy)(CO)_9]$, which is subsequently converted into the polymer $[Ru_2(\mu\text{-}Spy)_2(CO)_4]_n$ (analogous to **33**). Further reaction of this polymer with 2-mercaptopyridine gives the monomeric compound $[Ru(Spy)_2(CO)_2]$, which contains chelating Spy ligands [36].

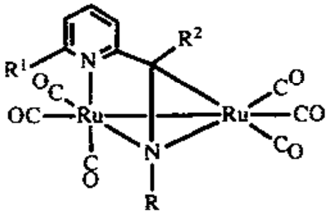
Pyridine-2-carbaldehyde imines (pyca-R) react with $[Ru_3(CO)_{12}]$ to give **40**; further reaction with more pyca-R affords $[Ru_2(\mu\text{-}ape\text{-}R)(CO)_5]$ (**41**), in which ape-R consists of two C–C coupled pyca-R ligands [37,38]. Thermolysis of the latter gives **42** or **43**. It should be noted that CO addition to **43** ($R^1 = H$, Me) results in C–C bond formation to give $[Ru_2(\mu\text{-}ape\text{-}R)(CO)_5]$ (**41**) ($R = Pr^i$) [38]. The reactivity of **40** with alkynes parallels that of $[Ru_2(\mu\text{-}dazab\text{-}R)(CO)_6]$ in that C–C coupling reactions of the coordinated imine ligand with the alkyne are observed [39].

2.8 *Thiazoles*

The thermal reaction of $[Ru_3(CO)_{12}]$ with mercaptobenzothiazole (1:3 mole ratio) affords an incompletely characterized material which upon recrystallization from pyridine gives crystals of $[Ru_2(\mu\text{-}Sbtz)_2(CO)_4(py)_2]$ (**44**) [40]. A related complex (**45**) has been prepared by reaction of sodium 2-mercaptothiazolinate with $[Ru_2(\mu\text{-}O_2CMe)_2(CO)_4(PPh_3)_2]$ [31].

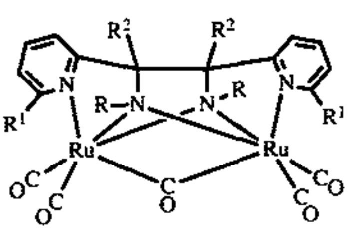
2.9 *Triazenes*

The triazenido complexes $[Ru_2(\mu\text{-}N_3R_2)_2(CO)_6]$ (**46**) have been prepared by heating $[Ru_3(CO)_{12}]$ with free triazenes in benzene under a carbon monoxide



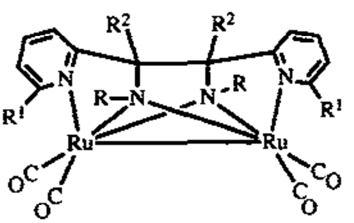
40

R = Bu^t, Pr^i; R^1 = H, Me; R^2 = H
R = C_6H_{11}; R^1 = R^2 = H
R = C_6H_{11}; R^1 = H; R^2 = Me
R = C_6H_{11}; R^1 = Me; R^2 = H



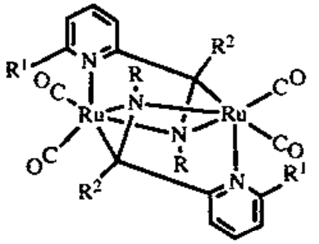
41

R = Bu^t, Pr^i; R^1 = H, Me; R^2 = H
R = C_6H_{11}; R^1 = R^2 = H



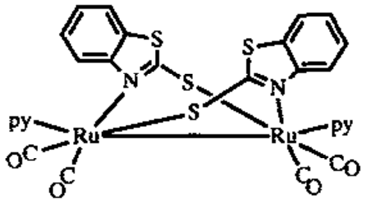
42

R = Bu^t, Pr^i, C_6H_{11}; R^1 = Me; R^2 = H

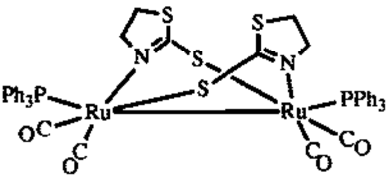


43

R = Bu^t, Pr^i; R^1 = H, Me; R^2 = H
R = C_6H_{11}; R^1 = R^2 = H

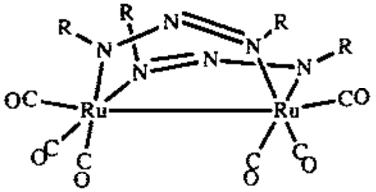


44



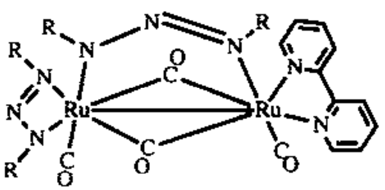
45

atmosphere, and by heating $[Ru_2(\mu\text{-}O_2CMe)_2(CO)_4]_n$ with the triazenes and triethylamine in acetonitrile under carbon monoxide. Without a carbon monoxide atmosphere, cleavage of the triazene occurs during the reaction of $[Ru_3(CO)_{12}]$ with $HN_3(p\text{-}C_6H_4Me)_2$ to give the derivative $[Ru_2(\mu\text{-}N_3R_2)_2(CO)_4(H_2NR)_2]$ ($R = p\text{-}C_6H_4Me$), while the axial-substituted tetracarbonyls $[Ru_2(\mu\text{-}N_3R_2)_2(CO)_4(NN_3R_2)_2]$ ($R = p\text{-}C_6H_5Cl$, Ph) are obtained with other triazenes. Reactions of **46** with PPh_3, $P(OMe)_3$ or $HN_3(p\text{-}C_6H_4Cl)_2$ also afford axial-disubstituted compounds [41,42]. When **46** ($R = p\text{-}C_6H_4Me$) is treated with bipy, the asymmetric product **47** is obtained [43].



46

R = Ph, p-C_6H_4Me, p-C_6H_4Cl



47

R = p-C_6H_4Me

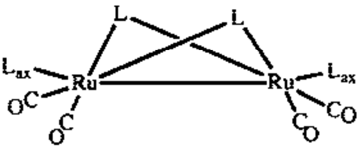
2.10 *Triazoles*

The binuclear hexacarbonyl [Ru_2(μ-btz)$_2$(CO)$_6$] has been reported as the product of the reaction of [Ru_3(CO)$_{12}$] with benzotriazole [44].

3. STRUCTURAL ASPECTS

Without exception, all compounds described in this review are diamagnetic binuclear carbonyl derivatives or polymers made of binuclear units connected by bridging ligands. The electronic configuration of ruthenium(I) is d^7, therefore the diamagnetism presented by these binuclear compounds requires the presence of a single metal–metal bond. However, no molecular orbital studies have been published.

From the X-ray diffraction data available to date, it can be concluded that in these compounds each ruthenium atom has a distorted octahedral coordination, with the equatorial plane determined by the donor atoms of the bridging ligands and (most frequently) by two CO ligands, and with the other ruthenium atom and another ligand in the axial positions. The equatorial terminal ligands are always approximately trans to the donor atoms of the bridging ligands, whereas the Ru–Ru–L_{ax} angles are always smaller than 180°, being related to the Ru–Ru–(μ-L) angles in such a way that narrow Ru–Ru–(μ-L) angles induce narrow Ru–Ru–L_{ax} angles.



The Ru–Ru bond lengths (Table 1) vary from 2.558(1) Å in [Ru_2(μ-dab)(CO)$_4$(PPh$_3$)$_2$] [20] to 2.827(2) Å in [Ru_2(μ-Hg_2Cl_4)(μ-dan)(CO)$_4$(PPr$^i_3$)$_2$] [19]. The longest Ru–Ru distances correspond to complexes in which the electron density of the Ru–Ru bond of the original binuclear complex is now shared by three metal atoms, therefore reducing the Ru–Ru bond order. The short Ru–Ru distances found in the binuclear compounds derived from 1,2-diaminobenzene and 1,8-diaminonaph-

TABLE 1

X-ray diffraction data of ruthenium(I) compounds containing bridging N-donor ligands

Compound	Ru–Ru (Å)	Ru–N (Å)	Ref.
$[\mathrm{Ru}_2(\mu\text{-HNOCPh})_2(\mathrm{CO})_4(\mathrm{MeCN})_2]$	2.668(1)	2.096(5) 2.101(5)	8
$[\mathrm{Ru}_2(\mu\text{-dan})(\mathrm{CO})_4\{\mathrm{P(OPh)_3}\}_2]$	2.571(1)	2.112(7) 2.138(8)	15
$[\mathrm{Ru}_2(\mu\text{-dan})(\mathrm{CO})_4(\mathrm{PPh}_3)_2]$	2.5788(3)	2.151(3) 2.132(3) 2.163(3) 2.144(3)	16
$[\mathrm{Ru}_2(\mu\text{-AgPPh}_3)(\mu\text{-dan})(\mathrm{CO})_4(\mathrm{PPr}^i_3)_2]\mathrm{BF}_4$	2.698(2)	2.10(1) 2.120(1) 2.130(1) 2.140(1)	17
$[\mathrm{Ru}_2(\mu\text{-Hg}_2\mathrm{Cl}_4)(\mu\text{-dan})(\mathrm{CO})_4(\mathrm{PPr}^i_3)_2]$	2.827(2)	2.10(1) 2.15(1) 2.15(1) 2.14(1) 2.14(1)	19
$[\mathrm{Ru}_2(\mu\text{-HgO}_2\mathrm{CCF}_3)(\mu\text{-dan})(\mathrm{CO})_4(\mathrm{PPr}^i_3)_2]$	2.808(1)	2.124(6)	19
$[\mathrm{Ru}_2(\mu\text{-dab})(\mathrm{CO})_4(\mathrm{PPh}_3)_2]$	2.558(1)	2.167(8) 2.101(5)	20
$[\mathrm{Ru}_2(\mu\text{-dab})(\mathrm{CO})_2(\mu\text{-dppm})(\mathrm{PPh}_3)_2]$	2.562(1)	2.186(7) 2.159(7) 2.195(6) 2.128(6)	24
$[\mathrm{Ru}_2(\mu\text{-oxMe}_2)_2(\mathrm{CO})_4(\mathrm{HoxMe}_2)_2]$	2.635(1)	2.140(3)	26
$[\mathrm{Ru}_2(\mu\text{-oxMe}_2)_2(\mathrm{CO})_4\{\mathrm{S(CH_2Ph)_2}\}_2]$	2.6352(4)	2.155(2)	26
$[\mathrm{Ru}_2(\mu\text{-oxMe}_2)_2(\mathrm{CO})_5(\mathrm{HoxMe}_2)]$	2.6378(4)	2.134(2) 2.142(2)	27
$[\mathrm{Ru}_2(\mu\text{-pzMe}_2)_2(\mathrm{CO})_6]$	2.705(2)	2.07(1) 2.09(1) 2.08(1) 2.09(1)	28
$[\mathrm{Ru}_2(\mu\text{-pz})_2(\mathrm{CO})_4(\mathrm{PPh}_3)_2]$	2.808(1)	2.124(6)	31
$[\mathrm{Ru}_2(\mu\text{-pyr})(\mu\text{-bipyr})(\mathrm{CO})_5]$	2.715(2)	2.040(1) 2.130(1)	33
$[\mathrm{Ru}_2(\mu\text{-Opy})_2(\mathrm{CO})_4(\mathrm{PPh}_3)_2]$	2.7108(4)	2.175(3) 2.166(3)	31
$[\mathrm{Ru}_2(\mu\text{-Opy})_2(\mathrm{CO})_4(\mathrm{HOpy})_2]$	2.670(1)	2.161(2) 2.177(2)	35
$[\mathrm{Ru}_2(\mu\text{-Sbtz})_2(\mathrm{CO})_4(\mathrm{py})_2]$	2.759(4)	2.198(6) 2.177(6)	40
$[\mathrm{Ru}_2(\mu\text{-N}_3\mathrm{R}_2)_2(\mathrm{CO})_4(\mathrm{H}_2\mathrm{NR})_2]$ $(\mathrm{R} = p\text{-C}_6\mathrm{H}_4\mathrm{Me})$	2.665(2)	2.150(5) 2.159(6) 2.162(6) 2.143(5)	42
$[\mathrm{Ru}_2(\mu\text{-N}_3\mathrm{R}_2)(\mathrm{N}_3\mathrm{R}_2)(\mu\text{-CO})_2(\mathrm{CO})_2(\mathrm{bipy})]$ $(\mathrm{R} = p\text{-C}_6\mathrm{H}_4\mathrm{Me})$	2.707(3)	2.19(2) 2.13(2)	43

thalene are due to the fact that the short bite of these particular ligands forces the metal atoms to be closer to each other than when other bridging ligands are used [15,16,20,24]. As commented below, the Ru—Ru bond distance has serious implications in the reactivity of these ruthenium(I) dimers with electrophilic reagents. In all cases, the distances between the Ru atoms and the N atoms of the bridging ligands are very close to 2.1 Å (Table 1).

4. COMMENTS ON SYNTHETIC METHODS

There are three different synthetic approaches that lead to ruthenium(I) compounds: (a) starting from higher oxidation state ruthenium compounds, (b) starting from lower oxidation state ruthenium compounds, and (c) transforming a ruthenium(I) compound into a different one. This last will be discussed in the section dealing with reactivity patterns.

4.1 Reduction of higher oxidation state rutheniun compounds

The complexes $[Ru_2(\mu\text{-}L)_2(CO)_6]$ (HL = Hpz, HpzMe, $HpzMe_2$, Hidz) have been prepared in high yields by bubbling CO through a solution of $RuCl_3 \cdot nH_2O$ and subsequent reduction of the obtained species with zinc in the presence of CO and the appropriate pyrazole-type ligand [28,29]. It is curious that this is the only published work which uses $RuCl_3 \cdot nH_2O$ as starting material for making ruthenium(I) complexes, in spite of being the cheapest ruthenium compound available.

4.2 Oxidation of lower oxidation state ruthenium compounds

Three ruthenium(0) complexes have been used to prepare ruthenium(I) compounds containing bridging N-donor ligands: $[Ru_3(CO)_{12}]$, $[Ru_3(CO)_9(PPh_3)_3]$ and $[Ru(CO)_3(PPh_3)_2]$. The three complexes react with ligands containing acidic hydrogen atoms (HL), under thermal conditions, releasing molecular hydrogen, as shown in the equations

$$2/3[Ru_3(CO)_{12}] + 2HL \rightarrow [Ru_2(\mu\text{-}L)_2(CO)_6] + 2CO + H_2 \quad (1)$$

$$2/3[Ru_3(CO)_9(PPh_3)_3] + 2HL \rightarrow [Ru_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2] + 2CO + H_2 \quad (2)$$

$$2[Ru(CO)_3(PPh_3)_2] + 2HL \rightarrow [Ru_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2] + 2CO + 2PPh_3 + H_2 \quad (3)$$

In the reactions involving $[Ru_3(CO)_{12}]$, an excess of HL ligand may give rise to tetracarbonyl products that contain axial HL ligands instead of CO ligands, as observed with oximes (**25**) [26]. Polymeric compounds are obtained when the bridging ligands L still contain lone pairs available for further coordination, as in the reaction of $[Ru_3(CO)_{12}]$ with 2-hydroxypyridine, which gives $[Ru_2(\mu\text{-}Opy)_2(CO)_4]_n$ (**33**) [34].

5. REACTIVITY PATTERNS

When the bridging ligands contain C-donor as well as N-donor atoms (i.e. pyr, pyca-R), they may couple to each other [33,37,38] or to other C-donor ligands [39]. However, apart from these particular reactions, ruthenium(I) complexes undergo three typical reactions: (a) substitution of terminal ligands, (b) substitution of the bridging ligands, and (c) reactions which modify the Ru—Ru bond order.

5.1 Substitution of terminal ligands

The hexacarbonyl compounds $[Ru_2(\mu\text{-}L)_2(CO)_6]$ react with a variety of two-electron donor ligands (phosphines, amines, nitriles, etc.), undergoing selective substitution of both axial CO ligands. The very mild conditions required by these reactions are responsible for the low number of known pentacarbonyl derivatives [15,27,29] and for the production of polymeric compounds from the reactions of $[Ru_3(CO)_{12}]$ with amides [8], 2-hydroxypyridine [34] and 2-mercaptopyridine [36] (as bridging ligands, the deprotonated forms of these organic molecules may act as five-electron donors). The nitrile ligands of the complexes $[Ru_2(\mu\text{-}L)_2(CO)_4(MeCN)_2]$ are also very easily substituted by other ligands [34]. The lability of the axial ligands in these compounds has to be related to the trans-labilizing effect of the metal—metal bond, as well as to the cis-labilizing effect of the bridging ligands (N-donor ligands are hard, and therefore, cis-labilizers [45,46]).

Compounds containing fewer than four CO ligands are rare; they have been prepared by reaction of hexa- [15] or tetracarbonyl [26] complexes with trimethylphosphite, or by reaction of tetracarbonyl complexes with diphosphines at high temperatures [24].

5.2 Substitution of the bridging ligands

The carboxylato complexes $[Ru_2(\mu\text{-}O_2CR)_2(CO)_2(L)_2]$ have proven to be useful starting materials to prepare ruthenium(I) compounds containing N-donor ligands. Thus, the reaction of $[Ru_2(\mu\text{-}O_2CMe)_2(CO)_4(PPh_3)_2]$ with the sodium salt of 2-hydroxypyridine and the reaction of $[Ru_2(\mu\text{-}O_2CMe)_2(CO)_4(MeCN)_2]$ with sodium pyrazolate afford the complexes $[Ru_2(\mu\text{-}Opy)_2(CO)_4(PPh_3)_2]$ and $[Ru_2(\mu\text{-}pz)_2(CO)_4(MeCN)_2]$, respectively [31]. Similarly, the reaction of the polymer $[Ru_2(\mu\text{-}O_2CMe)_2(CO)_4]_n$ with triazenes and triethylamine under carbon monoxide gives the triazenido derivatives $[Ru_2(\mu\text{-}N_3R_2)_2(CO)_6]$ [42]. The driving force for these reactions has to be related to the fact that ruthenium(I) is a soft metal and that the anionic N-donor ligands are softer than carboxylates.

When the compounds $[Ru_2(\mu\text{-}HNOR)_2(CO)_4(MeCN)_2]$ or $[Ru_2(\mu\text{-}pzMe_2)_2(CO)_6]$ are treated with acetic or trifluoroacetic acids, the complexes $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4(MeCN)_2]$ [8] or $[Ru_2(\mu\text{-}O_2CR)_2(CO)_4(HpzMe_2)_2]$ [30], respectively, are obtained. In these reactions, the protonation of the bridging N-donor ligands by the carboxylic acid reduces their hapticity, transforming them into monodentate ligands, which are either released from the complexes or moved to terminal positions.

5.3 Reactions which modify the Ru—Ru bond order

Although there are only a few reports dealing with reactions of ruthenium(I) complexes with electrophilic reagents, it can be concluded that the nucleophilic character of the Ru—Ru bond depends not only upon the basicity of the ligands but also upon the Ru—Ru bond distance. Thus, the complex $[Ru_2(\mu\text{-pzMe}_2)_2(CO)_6]$ (Ru—Ru = 2.705 Å) does not react with acids or with the metallic electrophiles $[AgPPh_3]^+$ and $[AuPPh_3]^+$ [29], whereas $[Ru_2(\mu\text{-dan})(CO)_6]$ (Ru—Ru distance in $[Ru_2(\mu\text{-dan})(CO)_4(PPh_3)_2]$ = 2.579 Å [16]) undergoes protonation with HBF_4 to give $[Ru_2(\mu\text{-dan})(\mu\text{-H})(CO)_6]^+$, but does not react with metallic electrophiles [15]. Interestingly, the complex $[Ru_2(\mu\text{-dan})(CO)_4(PPr^i_3)_2]$, which contains the basic triisopropylphosphine ligand, reacts with the electrophiles H^+, $[AgPPh_3]^+$, $[AuPPh_3]^+$, AuCl, AgO_2CCF_3, $SnCl_2$ and HgX_2 to give the corresponding adducts [17–19]. The complex $[Ru_2(\mu\text{-dab})(CO)_4(PPh_3)_2]$ (Ru—Ru = 2.558 Å) also forms adducts with H^+, NO^+, $[AgPPh_3]^+$, $[AuPPh_3]^+$, CuCl, AuCl and AgO_2CCF_3 [23].

The oxidative addition of halogens has only been studied with the compounds $[Ru_2(\mu\text{-pzMe}_2)_2(CO)_6]$ [29] and $[Ru_2(\mu\text{-dan})(CO)_6]$ [15]. In both cases, halogen-bridged binuclear ruthenium(II) complexes are formed.

Only one electrochemical study has been reported, namely the oxidation of $[Ru_2(\mu\text{-Opy})_2(CO)_4(L)_2]$ (L = PPh_3, PPr^i_3, HOpy), which gives the paramagnetic cations $[Ru_2(\mu\text{-Opy})_2(CO)_4(L)_2]^+$ [35].

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