

Ruthenium: “A Dance to the Music of Time”

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This short review was written to celebrate simultaneously the one hundred and fiftieth anniversary of the discovery of ruthenium by K. K. Klaus, and the bicentenary of his birth. A personal and (necessarily) selective overview of the highlights of the past decade of ruthenium chemistry is presented, and an attempt is made to place these in an historical perspective.

The year 1994 marked the one hundred and fiftieth anniversary of the isolation of ruthenium by Karl Karlovitch Klaus (1796–1864). K. K. Klaus (Carl Ernst Claus is the Germanic form of his name) was born and died in Dorpat (now Tartu, in Estonia), and 1996 is the bicentenary of his birth. A number of excellent accounts of his life and scientific work already exist (1, 2), and an article, soon to be published here, will carry a new perspective of his work (3). The purpose of this review, therefore, is to mark these anniversaries by selecting some of the advances in ruthenium chemistry over the last ten years, and placing them in an historical perspective.

They are waiting on the shingle

‘They are waiting on the shingle – will you come and join the dance?
Will you, wo’n’t you, will you, wo’n’t you, will you join the dance?
Will you, wo’n’t you, will you, wo’n’t you, wo’n’t you join the dance?’

Lewis Carroll, “Alice’s Adventures in Wonderland”

Between 1951 and 1975, Anthony Powell published a sequence of twelve related novels under the title “A Dance to the Music of Time”(4), from the Poussin painting, Figure 1. These novels, which can only be read as a whole, represent a unique view of British twentieth century life. The characters pursue an intricate temporal Terpsichorean path, with characters of initial colossal importance disappearing, while others, some of whom dominate the sequence, appear initially insignificant. The novels rep-

resent the personal impressions of a narrator of selective events and their complex temporal interrelation. In his view the characters perform a dance to the music of time, reminiscent of

‘Poussin’s scene, in which the Seasons, hand in hand, facing outward, tread in rhythm to the notes of the lyre that the winged and naked greybeard plays’.

The chemistry of ruthenium also seems to be dominated by this mythical being; some compounds reported in the original accounts of the discovery of ruthenium (5) still are of prime importance today, others attract only passing interest. Some of the developments reported in the following pages were unimaginable in 1844, others are a natural consequence of the observations made by Klaus. Some complexes, such as $[\text{Ru}(\text{bipy})_3]^{2+}$ (bipy = 2,2’-bipyridine), appear as mildly interesting upon their discovery in 1936 (6), but blossom into supreme importance much later, in 1976 (7).

Where shall I begin?

‘Where shall I begin, please your Majesty?’ he asked. ‘Begin at the beginning,’ the King said, very gravely, ‘and go on till you come to the end: then stop.’

Lewis Carroll, “Alice’s Adventures in Wonderland”

Georges Franju: ‘Movies should have a beginning, a middle and an end.’

Jean-Luc Goddard: ‘Certainly. But not necessarily in that order’

Time, 14th September, 1981

So, whose advice to follow? I’ll opt for Powell

Fig. 1 “Dance to the Music of Time”, by N. Poussin, 1594–1665; (reproduced with permission from the Wallace Collection)



and Goddard, ignore Carroll, and begin in 1984, when I co-authored a monograph entitled “The Chemistry of Ruthenium” (8). This was supplemented by a series of annual reviews in *Coordination Chemistry Reviews* (9–16). Later, the text was complemented by the appearance of articles in “Comprehensive Coordination Chemistry” (17), “Comprehensive Organometallic Chemistry” (18–26), and entries in the “Dictionary of Inorganic Compounds” (27–29).

If this wealth of published review material is combined with the now routine and cheap online access to *Chemical Abstracts* and *Science Citation Index*, it will be appreciated that a short review of the chemistry of ruthenium, even restricted to the past decade, will add little of value to the literature, as it cannot hope to be either comprehensive or even cover all the major highlights.

The magnitude of the problem will be seen by examining the trend in published papers concerning the chemistry of ruthenium, see Figure 2. In 1967, Griffith published an essentially comprehensive review of the chemistry of ruthenium, from its discovery up to 1966 (30): the coverage included 408 citations. In 1984, my book appeared, giving comprehensive coverage of the ruthenium literature from 1804 to 1978

(8): it cited 3254 references. Between 1981 and 1995, *Science Citation Index* (via the Bath Information and Data Services) lists 11,100 references citing ruthenium: there were 1407 papers in 1995 alone (more than three times the total number published from 1844 to 1966). The annual review of only the co-ordination chemistry of ruthenium (no organometallic compounds included) for 1993 lists 405 references (16). The literature concerning, and interest in, ruthenium is burgeoning. If this rate of publication continues (and with increasing pressures to publish in academia, it will), we should anticipate over 25,000 papers by the year 2005. It

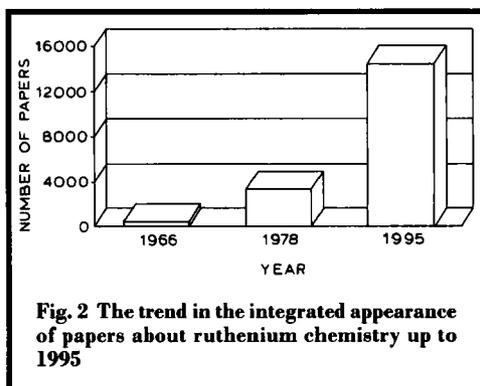
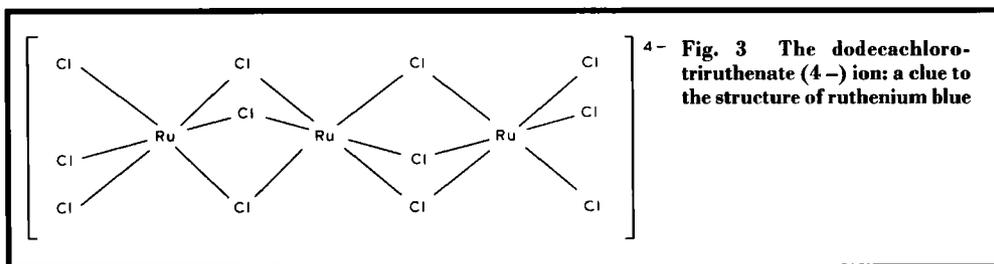


Fig. 2 The trend in the integrated appearance of papers about ruthenium chemistry up to 1995



should be remembered, however, that there is no established link between quantity and quality; it is also evident that ruthenium is no longer considered to be an expensive metal! (The average Johnson Matthey base price for ruthenium for May 1996 was \$1.77/g). It would not be a daring prediction to suggest that the percentage of handle-turning pot-boilers will be increasing at a rate proportional to the publication rate.

So, where *do* I begin? Let us this time listen to Lewis Carroll.

The beginning

'The characters of this metal [ruthenium] are so distinct, that no doubt can be entertained as to its being different from all previously known. Its highest chloride has a fine orange colour; and when ammonia is added to its aqueous solution, a black oxide is precipitated, whereas the solutions of the other platina metals are not precipitated at all by ammonia at common temperatures. The solution of the chloride is not altered by hydrosulphuric acid (H²S) till the action has been long continued, and then a brown precipitate is at first obtained, which afterwards becomes a black sulphuret, and the solution assumes a magnificent azure-blue colour. These changes depend upon the precipitation of a small portion of metallic sulphuret and the conversion of the chloride into a higher one, which has a blue colour, and which is not decomposed by the hydrosulphuric acid. If a plate of zinc be put into the solution of the

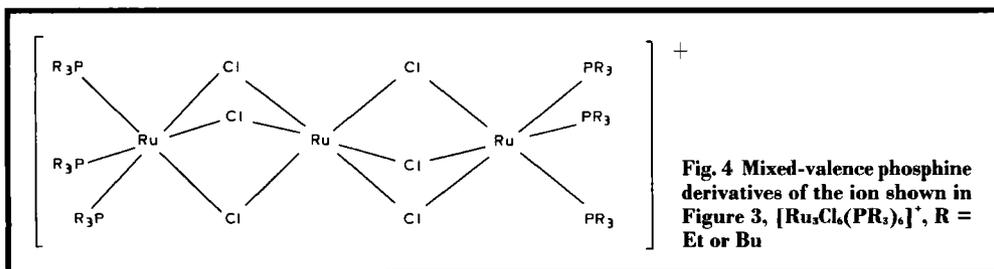
orange chloride, acidified by a little hydrochloric acid, a black metallic powder is precipitated after some time, and the solution becomes of a deep indigo-blue colour; eventually the whole of the metal is precipitated, and the solution becomes colourless.'

C. Claus, 1845 (5)

One of the abiding mysteries of ruthenium chemistry is the nature of ruthenium blue (ascribed to ruthenium for the first time, in English, in the above quote). Forty years before Klaus discovered ruthenium, Fourcroy and Vauquelin noted that the action of zinc upon certain solutions of the platinum metals generated an azure-blue solution (31–33). Ten years later, Vauquelin attributed this blue colour to iridium (34, 35). In 1846, Claus demonstrated that this blue colour was characteristic of ruthenium chemistry, suggesting that it was due to the presence of RuCl₂ in solution (36).

In 1996, we are little further forward in identifying the complex responsible for this colour, despite the extensive use of ruthenium blue as a synthetic reagent (8). The closest clue to the identity of ruthenium blue is a mixed-valence salt isolated by Bino and Cotton (37), containing the [Ru₃Cl₁₂]⁺ anion, see Figure 3.

Recently, see Figure 4, mixed-valence phosphine derivatives of this anion, [Ru₃Cl₆(PR₃)₆]⁺



(where R = Et or Bu) have also been isolated, and characterised (38–40).

The past ten years have also seen many simple halide complexes redefined, or observed in a pure form for the first time.

The anion $[\text{Ru}_2\text{OBr}_{10}]^+$, analogous to the well established $[\text{Ru}_2\text{OCl}_{10}]^+$ (11), has been shown not to exist (41); salts of this anion which have been reported in the literature (42, 43) were demonstrated to be salts of $[\text{Ru}_2\text{Br}_7]^{3-}$, an anion with an almost idealised confacial bioctahedral structure, see Figure 5, but containing a significant metal-metal interaction $\{r(\text{Ru-Ru}) = 0.2880 \text{ nm}\}$.

The hexachlororuthenate(III) anion has been generated in solution in ambient-temperature chloroaluminate(III) ionic liquids by electrochemical reduction of hexachlororuthenate(IV) (44), and the electrochemistry of the $[\text{RuCl}_6]^{2-3-}$ couple has also been recently investigated in conventional molecular solvents (45).

Twelve years ago, an important paper appeared (46) describing the formation of the novel salts $\text{A}[\text{RuO}_2\text{Cl}_3]$ ($\text{A} = [\text{PPh}_4]$ or $[\text{AsPh}_4]$), which now have a widespread utility as organic oxidants (converting alcohols to aldehydes and ketones, without attacking $\text{C}=\text{C}$ double bonds) (47–50). The green anion in these salts was tentatively described as a dimeric species, $[\text{Ru}_2\text{O}_4\text{Cl}_6]^{2-}$, in the solid state, but as a monomer, $[\text{RuO}_2\text{Cl}_3]^-$, in solution (46). It is now known to be five-co-ordinate in both solution and the solid-state, although its precise geometry is cation dependent (51).

'The metal [ruthenium] thus obtained, and all its combinations, when mixed with a large quantity of nitre and heated strongly to redness, give a blackish-green mass, which, when dissolved in water, yields a solution of a fine orange-red colour. This solution of the potash salt of the metallic acid blackens organic bodies, and is decomposed by the addition of organic substances, such as alcohol, and also by the action of acids, &c.; and there is precipitated a velvet-black compound of the oxide and potash; this is soluble in boiling hydrochloric acid, and yields an orange-coloured solution of the chloride.'

C. Claus, 1845 (5)

Continuing on our intricate temporal Terpsichorean path, the above quote returns us again

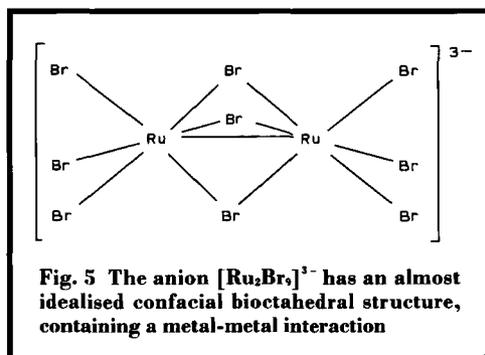


Fig. 5 The anion $[\text{Ru}_2\text{Br}_7]^{3-}$ has an almost idealised confacial bioctahedral structure, containing a metal-metal interaction

to Klaus, in the first report of the discovery of ruthenium. Connoisseurs of ruthenium chemistry will recognise the blackish-green mass described above as potassium ruthenate(VI), $\text{K}_2[\text{RuO}_4] \cdot \text{H}_2\text{O}$ (52), which dissolves in water to give an orange solution.

The barium analogue of this salt was reported in 1888 (53), however, it was almost one hundred years before it was recognised that the barium salt contained not the expected tetrahedral (T_d) tetraoxoruthenate(VI) anion, but the five-co-ordinate trigonal bipyramidal (D_{3h}) dihydroxytrioxoruthenate(VI) species, see Figure 6 (54).

Klaus noted that potassium ruthenate(VI)

'blackens organic bodies, and is decomposed by the addition of organic substances, such as alcohol, and also by the action of acids, &c.' (5).

This astute observation predates by nearly 150 years the use of ruthenium(VI) as an important oxidising agent in organic chemistry, chemistry

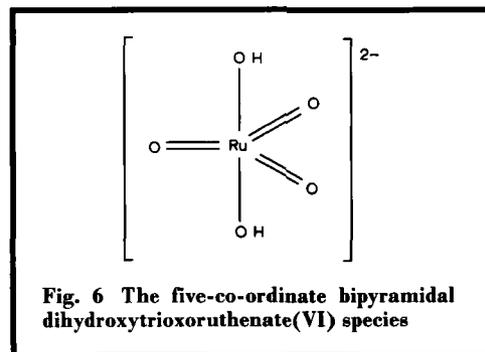


Fig. 6 The five-co-ordinate bipyramidal dihydroxytrioxoruthenate(VI) species

that has been dominated by the excellent work of Griffith (46, 47, 49, 55, 56), although other scientists have been active too (57, 58).

Will you come and join the dance?

Of course, some of the most interesting chemistry which has appeared in the last decade was not even suspected in the nineteenth century. Some (but by no means all) of the most notable examples of exciting new chemistry have included:

- The reaction between $[\text{Ru}(\text{CO})_5]$ and buckminsterfullerene, C_{60} , in toluene produces the complex $[\text{Ru}(\text{CO})_4(\eta^2\text{-C}_{60})]$ (59).
- Molecular wires with directional photoinduced electron transfer, based on alkyne-substituted terpyridine ligands, such as (terpy- C_4 -terpy, see Figure 7), have been developed (60–63): complexes include such species as $[(\text{terpy})\text{Ru}(\mu\text{-terpy-}\text{C}_4\text{-terpy})\text{M}(\mu\text{-terpy-}\text{C}_4\text{-terpy})\text{Ru}(\text{terpy})]^{6+}$. ($\text{M} = \text{Fe}, \text{Co}$ or Zn ; terpy = 2,2':6',2''-terpyridine).
- A perfluorinated ruthenium(II) phthalocyanine complex, $[\text{Ru}(\text{F}_{16}\text{Pc})]$ has been encapsulated in zeolite NaX, and used (in the presence of *tert*-butyl hydroperoxide) to oxidise cyclohexane at room temperature (64–66), whereas a simple water-soluble ruthenium(II) phthalocyanine complex, $\text{K}_2[\text{Ru}(\text{Pc})\text{L}_2]$ {LH = diphenyl(phenyl-3-sulfonic acid)phosphine, see Figure 8} is an exceptionally active agent for photodynamic cancer therapy (67).
- $[\text{Ru}(\text{CO})_6]^{2+}$ has been prepared for the first

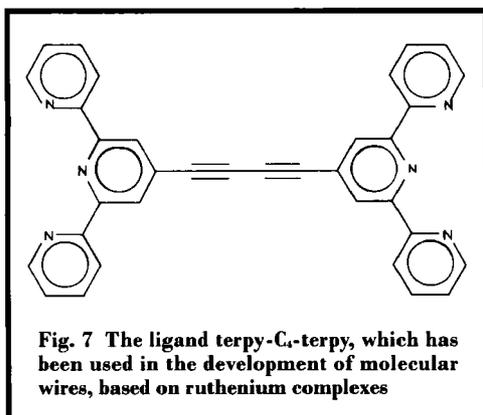


Fig. 7 The ligand terpy- C_4 -terpy, which has been used in the development of molecular wires, based on ruthenium complexes

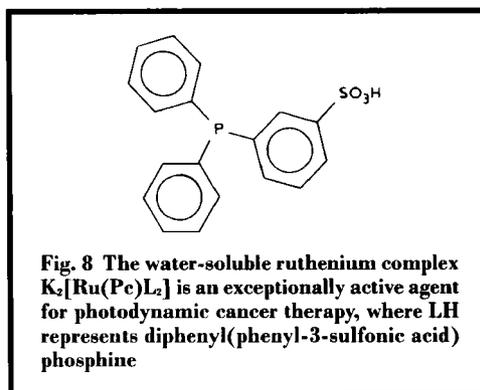


Fig. 8 The water-soluble ruthenium complex $\text{K}_2[\text{Ru}(\text{Pc})\text{L}_2]$ is an exceptionally active agent for photodynamic cancer therapy, where LH represents diphenyl(phenyl-3-sulfonic acid)phosphine

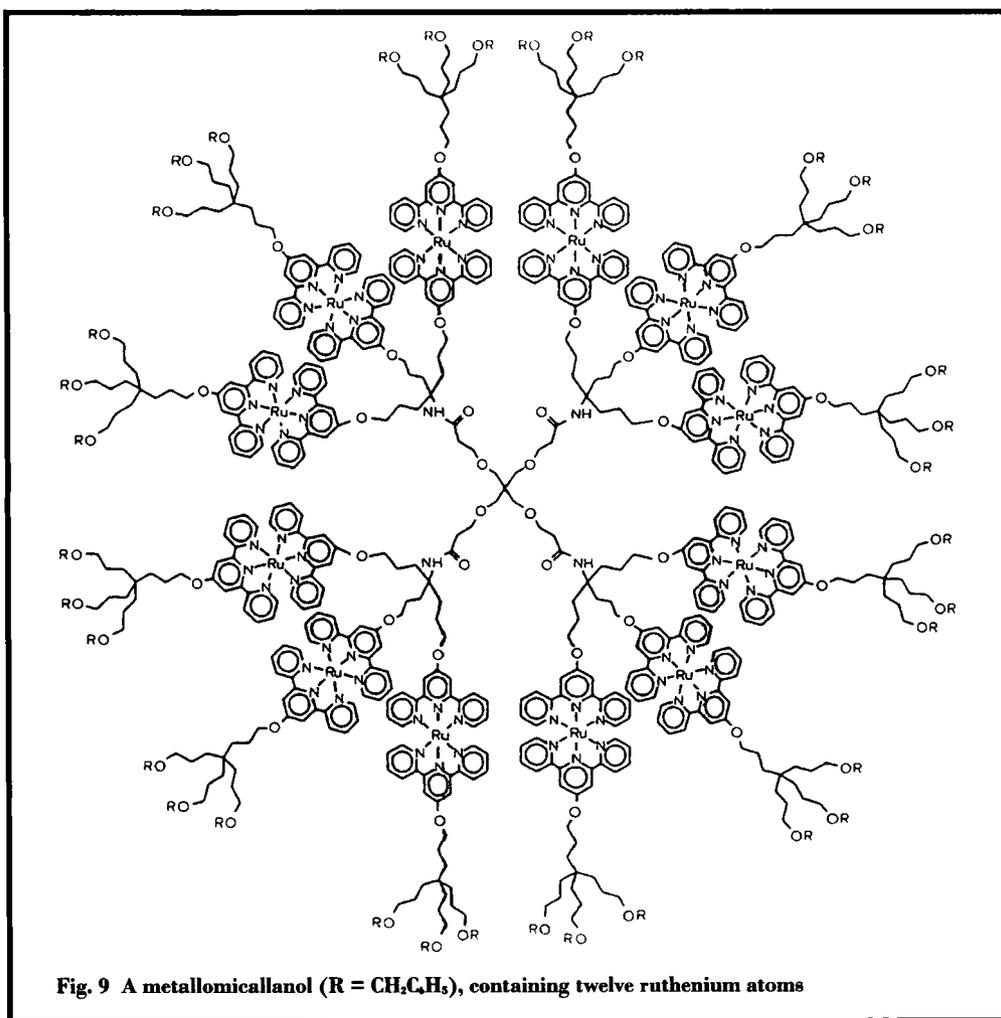
time, as a thermally-stable $[\text{Sb}_2\text{F}_{11}]^-$ salt, by the reductive carbonylation of $\text{Ru}(\text{SO}_3\text{F})_3$ under one atmosphere of carbon monoxide at 60 to 90°C (68).

- Sr_2RuO_4 has been shown to be a copper-free superconductor (69, 70).
- Grätzel has developed an efficient nanocrystalline photovoltaic device, using *cis*-di(thiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylato) ruthenate(II) as the sensitizer (71).
- In perhaps one of the most elegant synthetic studies in ruthenium chemistry of this century, Newkome and his co-workers have prepared ruthenium-containing dendrimers, as illustrated in Figure 9, containing twelve ruthenium atoms (72–74). The isolated salts are red, crystalline materials.

Come to the end: then stop

As is evident from the flavour of the papers discussed above, ruthenium continues to deliver some of the most exciting chemistry to be found today. Perhaps this is not surprising in the element which exhibits the most oxidation states in the Periodic Table. The number of papers published is growing at a phenomenal rate, as is the amount of tedious trivia, but the quality of the best work is quite outstanding. No chemist could read the highlights of the past few years, presented here, without feeling a thrill of excitement, a debt of gratitude to Klaus, and without wanting to join the dance. And so:

'On with the dance! let joy be unconfined'
Lord Byron, "Childe Harold", 1812–1817.



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