The Development of Molecular Wires

PART II: ROLE OF RUTHENIUM AND OSMIUM POLYPYRIDINE COMPLEXES FOR FAST VECTORIAL ELECTRON TRANSFER

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The concluding part of this paper on the use of ruthenium(II) and osmium(II) polypyridyl complexes, as molecular sized terminal subunits that are linked together by polyyne bridges functioning as molecular girders to retain the stereochemical rigidity, deals with the process of electron transfer between the subunits and considers the benefits conferred by the use of polyyne bridges. The ruthenium and osmium complexes have properties which aid the selective promotion of an electron from the metal to the bridging ligand, together with amenable absorption and emission spectral profiles, and facile oxidation-reduction processes. This makes them promising candidates for vectorial electron transfer. Future work to extend the lengths of the linkages, to ensure unidirectional and long-range electron tunnelling, and to anchor the wires to supports is discussed. These are the necessary requirements for the development of molecular wiring made from these materials for future use with molecular-scale electronic devices.

The first part of this paper introduced the subject of molecular wires and considered the structure and chemistry of the complexes that can be used for them, and other materials currently believed to be the best for this purpose (13). Here, the topic is further illustrated by reference to light-induced electron transfer.

The selective population by an electron of the ethynyl-substituted terpyridyl ligand, followed by electron delocalisation over an extended π^*-orbital is of extreme importance for the design of effective molecular wires. It gives direction to the electron flow, since, upon excitation of the ruthenium(II) complex, an electron is pushed along the molecular axis towards the acceptor. In principle, this electron can approach close to the cation that is co-ordinated to the second terpyridyl ligand, so that the actual electron-transfer step might occur over a relatively short distance. However, there is no suggestion that the extended π^*-orbital includes the second terpyridyl ligand bound to the bridge. The corresponding hole transfer, which involves both metal centres, must occur between more widely-spaced reactants and it displays a more significant attenuation factor.

Interestingly, the insertion of a platinum(II) bis-trialkylphosphine complex into the polyyne bridge, see Figure 6 and Panel 6, has the effect of inhibiting through-bond electron-transfer reactions occurring from the terminal ruthenium(II) polypyridine complex (14). This situation arises because the platinum(II) centre donates charge to the ethynyl-substituted bipyridyl ligand, making its reduction potential more negative than that of the corresponding platinum(II)-free ligand, see Panel 6. Consequently, excitation of the ruthenium(II) complex results in selective electron donation from the metal centre to the unsubstituted ligand. The electron is localised at this ligand and is unable to migrate to an ethynyl-substituted ligand because of the unfavourable thermodynamic position; thus the photophysical properties remain virtually unchanged from those of the unsubstituted complex.

Fig. 6 Molecular structures of the trinuclear trans-Ru$^{II}_2$Pt^{II} and trans-Ru^{II}Pt^{II}Os^{II} complexes
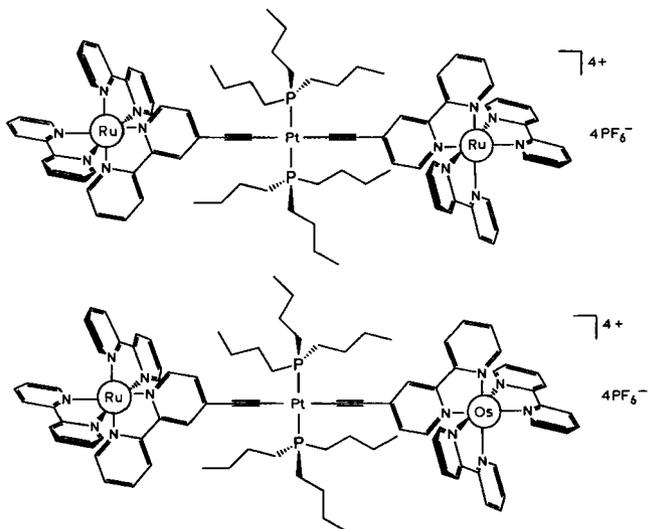
The same situation is observed for the analogous osmium(II) complexes, see Figure 6, but not for the rhenium(I) bipyridine complex shown in Figure 7. In this latter case, excitation of the rhenium(I) chromophore results in the transfer of an electron from the rhenium(I) centre to the co-ordinated bipyridine ligand.

Although the presence of a central platinum(II) complex lowers the reduction potential of the bipyridine ligand because of charge injection, the metal-to-ligand charge-transfer transition still occurs in the platinum(II)-containing rhenium(I) complexes, with the result that the promoted electron resides in an extended π^*-orbital. This causes a substantial enhancement in the triplet lifetimes of the platinum(II)-containing rhenium(I) complexes (~ 80 ns) relative to that of the unsubstituted complex (~ 40 ns), as measured in acetonitrile solution at room temperature. The stabilised triplet state arises because of decreased vibronic coupling between triplet and ground states, and is a common feature of ethynyl-substituted polypyridine ligands.

Symmetrical Binuclear Complexes

A special case can be made for binuclear complexes possessing identical ruthenium(II) polypyridine complexes at opposite ends of a polyyne wire (7), as illustrated in Figure 8. Here, excitation of one of the chromophores results in the formation of the corresponding triplet excited state of the metal complex, which is of metal-to-ligand charge-transfer character. These binuclear complexes luminesce at much longer wavelength than do the reference compounds, due to the lower energy of the charge-transfer state. Furthermore, the triplet lifetimes of the binuclear complexes are significantly longer, relative to analogous mononuclear ruthenium(II) polypyridine complexes of similar energy, at both room temperature and 77 K.

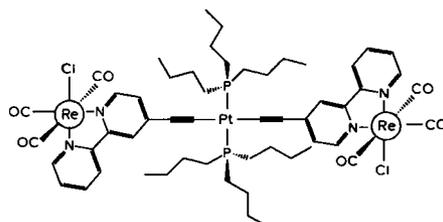In these polyyne-bridged binuclear complexes it appears that, under illumination, an

Fig. 7 Molecular structure of the trinuclear trans-Re$^I_2$Pt^{II} complex

Panel 6

The σ-alkynyl-bipyridine derivatives of platinum(II) were stereoselectively prepared from the ethynyl-substituted building blocks and trans-[Pt^{II}(P^{n}Bu$_3$)$_2$Cl$_2$], using a CuI catalysed reaction. The platinum(II)-free ligand was prepared by a catalytic homo-coupling reaction of the ethynyl-substituted bipyridine in the presence of CuCl$_2$/tetramethylethylenediamine complexes, see Chart A, below.

Chart A
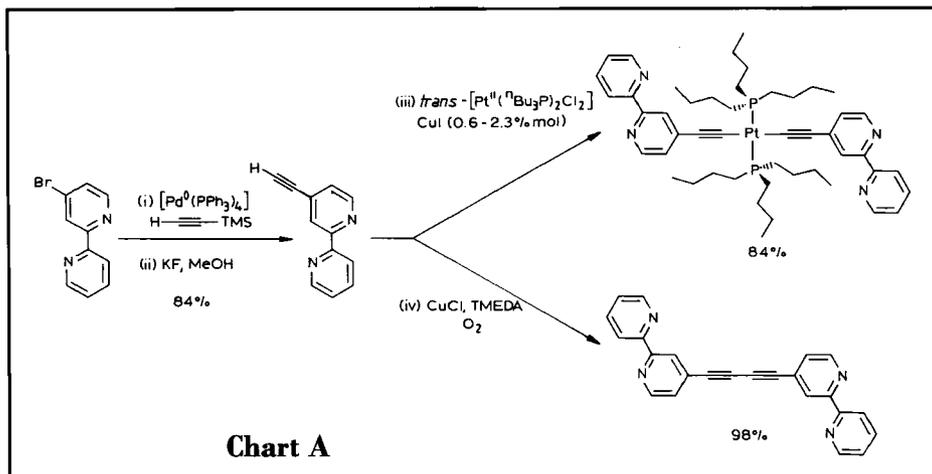
The parent cis-compound of the metallosynthon was similarly prepared (85 per cent yield) from the parent cis-[Pt^{II}(P^{n}Bu$_3$)$_2$Cl$_2$]. Selective complexation of one of the two bipyridine domains with complex cis-[Ru(bpy)$_2$Cl$_2$]. 2H$_2$O (bpy is 2,2′-bipyridine), afforded either the dinuclear Pt^{II}Ru^{II} or the trinuclear Pt^{II}Ru$^{II}_2$ complexes.

Further complexation of the free bipyridine subunit within the Pt^{II}Ru^{II} complex with the cis-[Os(bpy)$_2$Cl$_2$] afforded, in a clean reaction, the heterotrinuclear complex Ru^{II}Pt^{II}Os^{II}, see Chart B, below.
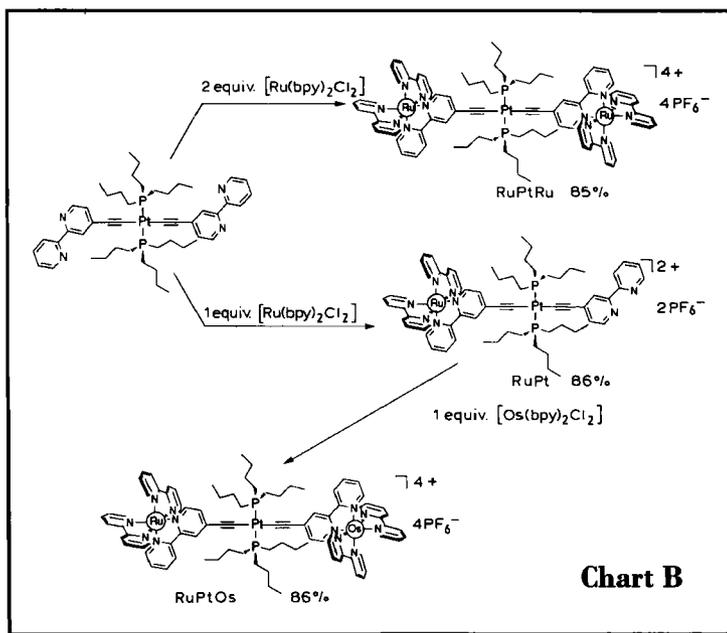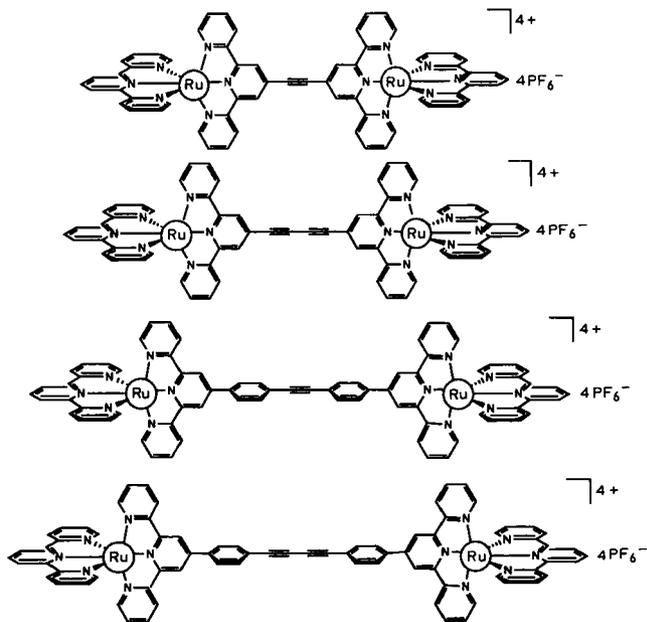

Chart B

Fig. 8 Molecular structures of the ethynyl-substituted, diethynyl-substituted, diphenyl acetylene-substituted and diphenyldiacetylene-substituted dinuclear ruthenium(II) complexes

electron is promoted from one of the ruthenium(II) centres to a π^*-orbital associated with the bridging ligand. As suggested earlier, this π^*-orbital is not restricted to the polypyridine ligand but, because of conjugation, it extends over part of the bridging polyyne chain.

Due to the similarity of the terminal groups, photon migration can take place in which simultaneous electron- and hole-transfer steps serve to alternate the photon between the two termini, see Panel 7. In this manner, the triplet state shuttles between the terminal metal complexes, each journey taking about 1 ns, and can react with a quencher molecule at either site. This is a remarkable process, made possible by the strong electronic communication provided by the polyyne bridge, and closely resembles the natural light harvesting complexes found in photosynthetic bacteria (15).

Decreasing the extent of electronic coupling between the ruthenium(II) polypyridine complexes, by inserting a bridging phenyl ring, see Figure 8, severely inhibits triplet migration and the photophysical properties of such binuclear complexes resemble the photophysical properties of the mononuclear reference compounds.

Overall, it is clear that polyynes provide several important benefits when covalently attached to transition metal polypyridine complexes of the type considered here. They can cause a marked increase in triplet lifetime, thereby favouring reactions with adventitious quenchers, and can induce a sense of directionality into intramolecular energy- or electron-transfer steps. Polyynes operate as molecular girders to retain stereochemical rigidity and, at the same time, they provide highly effective electron and hole channels.

Future Work on Molecular Wires

It is now necessary to fabricate longer polyyne bridges and to ensure that the excellent electronic conductivity is not restricted to short chain lengths. In this respect, it is important to realise that the energy of the bridge is likely to decrease with increasing length and, in terms of superexchange theory, the degree of through-bond electronic coupling will increase as the energy of the bridge approaches that of the excited triplet state. Each added ethynyl group,

Panel 7

According to superexchange theory, the electronic matrix coupling element (V_{DA}), a term that quantifies the amount of electronic communication between the terminal metal complexes, can be expressed in the following form:

$$V_{DA} = C_\alpha C_\beta / \delta E$$

where C_α and C_β are the atomic orbital coefficients describing coupling between the triplet excited state and the bridge, and between the bridge and the final acceptor, respectively; δE represents the energy gap between appropriate orbitals localised on the triplet state and on the bridge. For electron transfer, δE refers to the difference in energy between LUMOs associated with bridge and triplet while for hole transfer the appropriate energy gap would be between HOMOs associated with bridge and triplet. The magnitudes of C_α and C_β are controlled by the nature of the reactants, especially stereochemical aspects, and can be estimated by detailed molecular orbital calculations.

For an homologous series of donor-acceptor compounds, V_{DA} is predicted to decrease exponentially with increasing length (R) of the bridge according to:

$$V_{DA} = V_{DA}{}^0 \exp [-\beta R/2]$$

Here, $V_{DA}{}^0$ refers to the electronic coupling matrix element when the reactants are in orbital contact. For the polyyne-bridged molecular systems considered in this work, it appears that V_{DA} will decrease with increasing R due to the effective decreased overlap of wavefunctions associated with the reacting species.

However, the energy gap between triplet state and bridge (δE) will also decrease with increasing R (see the Chart) because of conjugation, such that V_{DA} might actually increase with increasing length of the bridge. These offsetting properties give rise to particularly small β values, at least over modest separations.
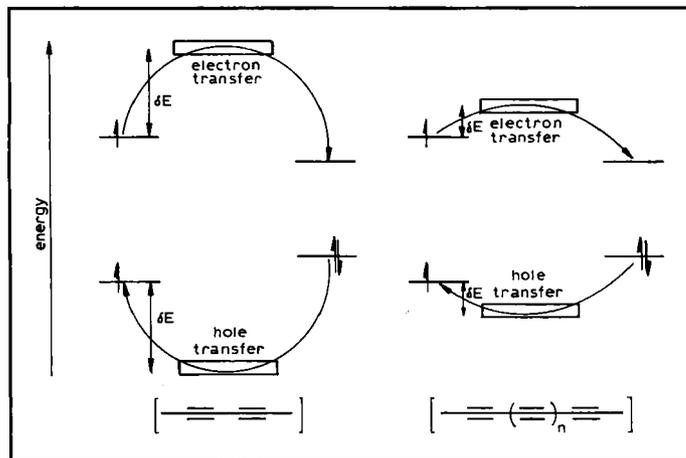
therefore, should act co-operatively to decrease the energy of the bridge and this effect might offset the decrease in the magnitude of electronic coupling that occurs upon increasing the length of the bridge, see Panel 7. Such properties might serve to minimise the attenuation factors for through-bond electron and hole transfer. As such, polyynes possess many of the requisites for good molecular wires.

It is also instructive to consider the role of the metal complex in such systems and to enquire if these complexes possess unique properties that make them particularly attractive subunits for molecular-scale electronic devices. The importance of these complexes lies in the fact that their triplet excited states, often long lived and formed in quantitative yield under visible-light illumination, are of metal-to-ligand charge-transfer character. This property facilitates selective promotion of an electron from the metal centre to the bridging ligand, thereby providing the impetus for vectorial electron transfer.

Other common types of chromophore do not provide this directionality which is inherent in ruthenium(II), osmium(II) and rhenium(I) polypyridine complexes. Of these complexes, those based on ruthenium(II) or osmium(II) look to be the more promising because of their amenable absorption and emission spectral profiles and their facile oxidation-reduction processes.

We should also consider, at this stage, the feasibility of constructing molecular-scale wires that promote unidirectional and long-range electron tunnelling. Several such systems have been described (9) and many more seem certain to emerge in the near future. Perhaps the most effective bridges are those based on polyenes (2), where charge transfer has been observed to occur over distances in excess of 30 Å. These spacer moieties are probably too unstable for practical purposes, hence our utilisation of polyynes, although there have been innovative attempts to provide both protection and inherent redundancy.

Other types of bridge, such as those formed from polycondensed aromatic residues (4–6) or DNA (16), provide a more stable environment and exhibit interesting properties.

Theoretical models, predicting very small attenuation factors for electron tunnelling through certain materials, are also beginning to appear (17) and major advances are taking place in the synthetic practices used to fabricate supramolecular entities (9). These various factors combine to ensure that appropriate molecular wires will soon be available. The next step will involve anchoring the wires to a macroscopic support and, by using scanning tunnelling electron microscopy and time-resolved reflectance spectroscopy, the means to study such interactions are in place. One might argue, therefore, that the age of molecular electronic devices is drawing ever closer.

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Preparation of Platinum/Polymer Nanocomposites

A simple method of producing metal/polymer composites, in which nanosized metal particles are homogeneously distributed throughout the polymer, would promote the development of a new generation of useful materials and devices. These devices would utilise the specific compositions and size-dependent electrical, chemical and magnetic properties of the composite. Some syntheses for specific applications have been reported, but no general synthesis for such a nanocomposite material has emerged.

Now, however, scientists at the University of Massachusetts, U.S.A., have developed a synthesis for making platinum/polymer composites (J. J. Watkins and T. J. McCarthy, "Polymer/Metal Nanocomposite Synthesis in Supercritical CO_2", *Chem. Mater.*, 1995, 7, (11), 1991–1994). Their method involves the use of a supercritical fluid, in this case carbon dioxide. As a supercritical fluid, carbon dioxide offers great control over composite composition and structure and has a high permeation rate in polymers. Carbon dioxide is also a versatile process solvent and it is clean and environmentally friendly.

The precursor, dimethyl(cyclooctadiene)platinum(II), was dissolved into the carbon dioxide, and then sequentially impregnated into, and reduced in, thick films of the polymers poly(4-methyl-1-pentene) and poly(tetrafluoroethylene). The reduction to metallic platinum was by hydrogenolysis and thermolysis. This resulted in platinum/polymer composites containing platinum clusters, of sizes from 15 to over 100 nm (depending upon preparation) being dispersed throughout the films. The sizes and distributions of the platinum clusters were measured by SEM and TEM.

In general, adjusting the permeation and reduction rates controls the size and distribution of the platinum clusters, and further work is being done to produce gradient structures.