

The Development of Molecular Wires

RUTHENIUM AND OSMIUM POLYPYRIDINE COMPLEX TERMINALS FOR FAST ELECTRON MOVEMENT ALONG POLYIYNE BRIDGES

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The growth in research in molecular sized electronic devices in the very recent past, for functions such as optical switches, fast recording devices, miniaturised sensors and molecular computers, has created a need for equally small connectors which comply with the stringent requirements of such structures to link them to the surrounding assembly. Among materials that are suitable for the terminal subunits are polypyridyl complexes of ruthenium(II), osmium(II) and rhenium(I), linked together by bridging polyynes. The triplet excited states of these complexes have long lives and are formed under visible-light illumination. Their metal-to-ligand charge-transfer character allows electron promotion from the metal centre to the bridging ligand, giving directional electron transfer. Complexes based on ruthenium(II) or osmium(II) seem more promising due to their amenable absorption and emission spectral profiles and their facile oxidation-reduction processes. This paper looks at the development of the molecular materials and structures that are required to act as molecular-scale connectors enabling molecular-scale electronic devices to function successfully.

The advent of molecular-scale electronic devices demands the availability of suitable molecular components that can be integrated into a supramolecular assembly and subsequently connected to a macroscopic support. Among the various components needed for fabrication of effective devices are molecular wires (1), whose purpose is to provide strong electronic communication between spatially-remote, redox-active subunits. Such wires are intended to fulfil several critical roles, including (i) maintaining strict stereochemical integrity of the final assembly and (ii) promoting unidirectional electron flow along the molecular axis under appropriate external stimulation. The latter impetus may be initiated by absorption of a photon, by application of a potential at an attached electrode, or by chemical means – the fastest response being attained by photochemical triggering of the system.

Transition metal complexes, especially those based on photoactive complexes of ruthenium(II) polypyridine complexes, appear to be promising materials for use as the redox-active terminal subunits, while polyenes (2), polyynes (3), and poly-aromatics (4–6) may be considered as potential bridging units. It is necessary, however, to determine the capability of such bridges to function as electron carriers, and this is the subject of intense current research.

Due to the rigidity, relative chemical inertness, resistance to isomerisation, and synthetic adaptability of polyynes, we have concentrated our efforts on exploring their potential application as molecular wires. Such functionalities are ideal for the construction of linear, rod-like molecules with transition metal complexes as termini.

The terminal complexes, which are formed from oligopyridine ligands, may be identical – giving rise to symmetrical systems (7), or dissimilar – resulting in asymmetrical systems (8). By careful selection of the central metal cation and the overall ligand field, it becomes possible

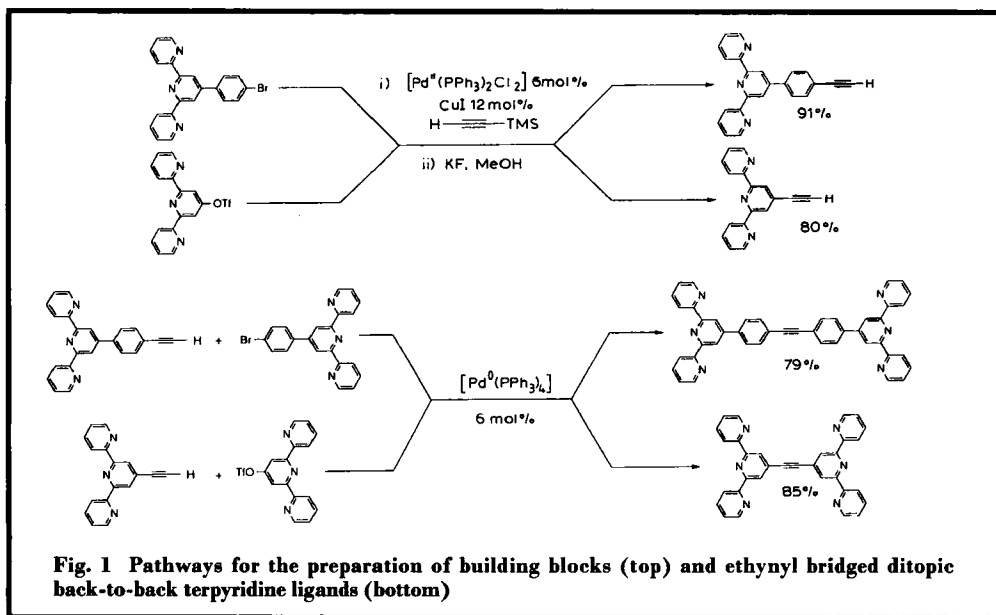


Fig. 1 Pathways for the preparation of building blocks (top) and ethynyl bridged ditopic back-to-back terpyridine ligands (bottom)

to ensure that the complexes are photo- and/or redox-active, while, by incorporating several complexes into a single molecular array, a redox gradient can be established along the chain.

For such multicomponent molecular systems, it is necessary to find out the exact role played by the polyene bridge and, in particular, to quantify its ability to promote electronic coupling between the terminal complexes. Since one of the ultimate objectives of such research (9) is to design systems comprising insulating lipid bilayer membranes capable of allowing light-induced electron flow, see Panel 1, it is especially important to establish the magnitude of any attenuation in the degree of electronic coupling

between the termini that occurs when the length of the polyene bridge is increased. This latter effect may be studied experimentally by measuring rates of intramolecular electron- or energy-transfer processes that take place via bonding or antibonding molecular orbitals localised on the bridging polyene, see Panel 2.

Measurement of Attenuation in Electronic Coupling

In order to perform such experiments, a series of multidentate ligands was first prepared (10) by a palladium(0)-catalysed cross-coupling reaction (a Heck-type reaction for the synthesis of the ethynyl-bridged compounds, see Figure 1)

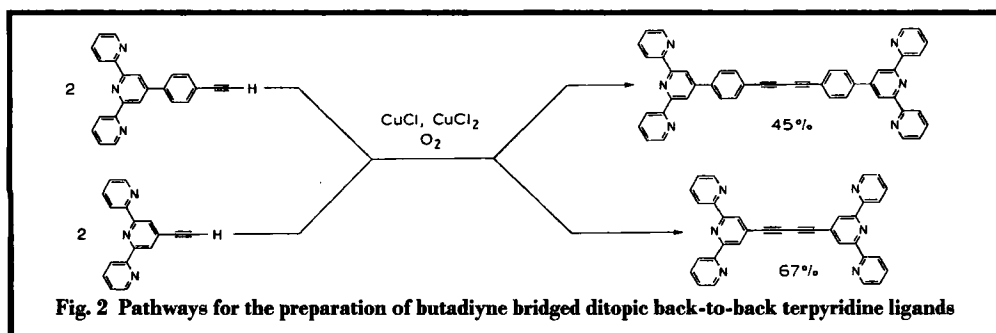


Fig. 2 Pathways for the preparation of butadiyne bridged ditopic back-to-back terpyridine ligands

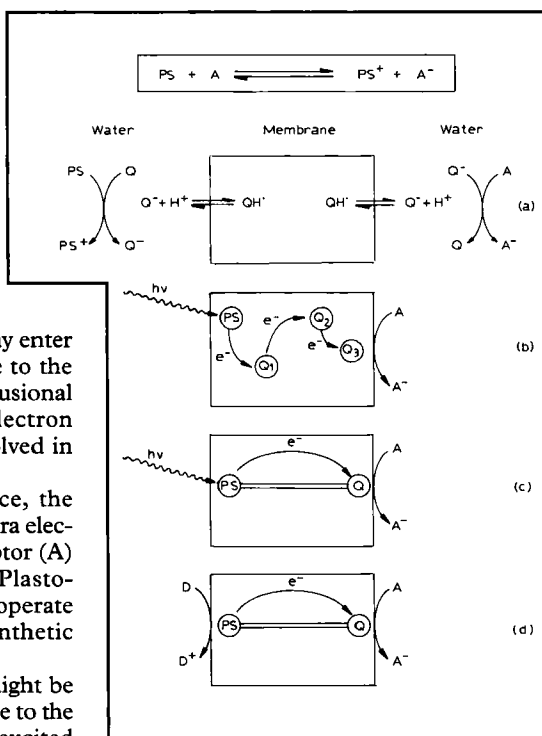
Panel 1

Photoinduced electron transfer across an insulating membrane might take place in one of three ways: First, see Diagram at (a), a photosensitiser (PS) dissolved in the aqueous phase may initiate an electron-transfer reaction with an appropriate redox-active quencher (Q) present in the aqueous phase or at the membrane-water interface. The reduced form of the quencher (Q^-), together with its complementary protonated form (QH^-), may enter the membrane and thereby migrate to the opposite interface by a random diffusional process. Migration may involve electron exchange with similar species dissolved in the membrane.

Upon reaching the other interface, the reduced quencher may transfer its extra electron to a water-bound electron acceptor (A) or enter the aqueous phase itself. Plastoquinone molecules are believed to operate in this way in green plant photosynthetic organisms.

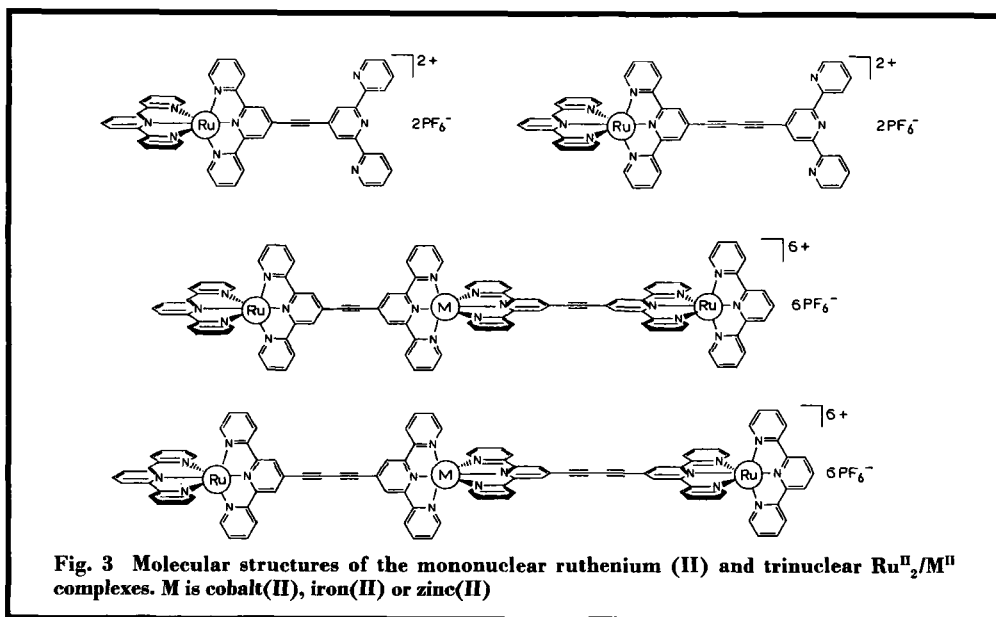
Second, see Diagram at (b), PS might be located inside the membrane but close to the interface. Under illumination, the excited state of PS may transfer an electron to an appropriate electron acceptor (Q_1) held at a fixed site deeper inside the membrane. In competition to charge recombination, the reduced form of the acceptor may transfer its extra electron to a different acceptor (Q_2) positioned further across the membrane, providing the reaction is energetically downhill. In this way, a cascade of electron-transfer steps, each event occurring over a fixed distance and being driven by a certain thermodynamic driving force, provides a means for achieving charge separation across the membrane. Subsequent reactions of the oxidised form of the donor (PS^+) and the reduced form of the ultimate acceptor (Q_3^-) with species dissolved in the aqueous phase result in transmembrane charge separation. This is the basic mechanism whereby bacterial photosynthetic reaction centres operate.

Third, see Diagram at (c), PS might be held inside the membrane but close to the aqueous surface. Rather than use a series of exactly-positioned electron relays to shuttle



the electron across the membrane it might be possible to use a highly conductive electron channel to ferry the electron to an acceptor (Q) sited at the opposite side of the membrane. Thus, upon illumination of PS a giant dipole is created comprising PS^+ and Q^- . These species might undergo secondary electron transfer processes with appropriate redox-active species dissolved in the aqueous phase on either side of the membrane. Alternately, see Diagram at (d), the excited state of the PS might abstract an electron from a donor (D) in the aqueous phase, forming PS^- . This extra electron can be transferred across the membrane to Q, and subsequently to A. Such long-range electron transfer has been demonstrated in certain modified enzymes, but the reactions are relatively slow.

Whether or not it will become possible to design artificial systems capable of rapid, long-range electron transfer remains an unanswered question. The solution depends critically on the development of molecular wires.



or a copper(II)-catalysed oxidative self-coupling reaction (Glaser-type homocoupling for the synthesis of the butadiyne-bridged compounds, see Figure 2).

The preparation of mononuclear ruthenium(II) complexes, by the selective complexation of one appended terpyridine with $[\text{Ru}(\text{terpy})(\text{DMSO})\text{Cl}_2]$ (where terpy is 2,2':6',2''-terpyridine and DMSO is dimethylsulphoxide), allows a series of trinuclear complexes to be isolated. These have terminal ruthenium(II) bis-terpyridyl complexes connected to a central metal (such as cobalt(II), iron(II) or zinc(II)) bis-terpyridyl complex by one or two ethynyl groups, see Figure 3. The corresponding mononuclear ruthenium(II) complexes lacking the central metal complex were used as reference compounds.

Electron Transfer in Trinuclear Systems

Laser excitation of these mononuclear complexes (11) gave rise to the triplet excited state of the chromophoric $\text{Ru}(\text{II})$ bis-terpyridyl complex, which allowed its lifetime to be measured by transient spectroscopy, see Panel 3. The lifetimes of these triplet excited states were found

to be in the region of 175 ns in deoxygenated acetonitrile solution at room temperature.

Systems with a Central Cobalt Complex

In contrast, the triplet lifetimes of the ruthenium(II) chromophores in the trinuclear complexes assembled around a central cobalt(II) bis-terpyridyl complex were observed to be about 7 ps. These vastly decreased triplet lifetimes can be attributed to intramolecular electron transfer from the central cobalt(II) complex to the triplet state of a terminal ruthenium(II) complex; the rate constants for these reactions being of the order of 10^{11} /s. Such reactions can be considered to involve transfer of an electron from a *d*-orbital localised on the cobalt(II) centre to a *d*-orbital localised on the ruthenium(III) centre, the latter species arising by way of a metal-to-ligand charge-transfer process associated with population of the triplet excited state of the ruthenium(II) complex, see Panel 4. Consequently, the reaction can be formally described as a hole-transfer process, and it is important to note that no such reaction occurs in the dark, see Scheme I.

By comparing the measured rate constants for hole transfer over one and two ethynyl groups,

Panel 2

The rate constant (k_{obs}) for light-induced electron transfer or for triplet energy transfer can be determined by measuring the triplet lifetime (τ_t) of the appropriate multicomponent compound and comparing it with that of the reference compound (τ_0) in deoxygenated solution:

$$k_{\text{obs}} = (1/\tau_t) - (1/\tau_0)$$

This method assumes that the difference in triplet lifetimes between the two compounds arises solely from the quenching process of interest, that is by electron or energy transfer.

Providing that this quenching process involves through-bond electron and/or hole transfer (in the case of triplet energy transfer this requires that the reaction occurs by electron exchange rather than by dipole-dipole transfer), the derived rate constant, k_{obs} , can be related to the distance (R), sep-

arating the two reactants, by the expression:

$$k_{\text{obs}} = k_0 \exp [-\beta R]$$

Here, k_0 refers to the rate constant when the reactants are within orbital contact (that is $R = 0$) and β is an attenuation factor (in \AA^{-1}) that describes the electronic resistivity of the intervening medium. When the bridge can be considered as a single chemical entity (for example: an acetylenic function) or an homologous series of identical groups (for example: a polyyne chain), β is representative of the individual molecular functions that combine to form the bridge and can be expressed in terms of groups, atoms, or bonds rather than distance. If the bridge is formed by combination of several different functionalities, as is the case with protein matrices, β cannot be assigned to individual molecular segments but must be considered as representative of the whole structure.

it becomes possible to estimate the attenuation factor for hole transfer ($\beta\{h\}$) as being about 0.12 /\AA . This is a rather small attenuation factor when compared to other bridging units, and

suggests that it may be possible to engineer molecular systems based on polyyne wires which are capable of long-range hole transfer. In fact, given that the inherent triplet lifetime of a

Panel 3

Excitation by a short duration laser pulse of the various compounds, at a wavelength corresponding to a reasonably strong absorption transition, results in rapid establishment of the lowest-energy excited triplet state. This metastable species may luminesce in solution, as is the case with most ruthenium(II) and osmium(II) polypyridine complexes, and, if so, the triplet lifetime is conveniently measured by time-resolving the luminescence decay.

This technique works very well provided the triplet lifetime is not too short (that is $\tau > 100 \text{ ps}$) and that the luminescence can be properly resolved from background light. In other cases, the triplet state can be detected by transient absorption spectroscopy. Here, a second photon, delivered by a delayed laser pulse or from a continuous light source, is

absorbed by the triplet state, giving rise to a triplet-triplet absorption transition. The absorption spectrum can be recorded in the same way as ground-state absorption spectra are measured, while kinetic measurements can be made at fixed wavelength.

This technique is also appropriate for recording absorption spectra of other reaction intermediates and for determining their lifetime under particular conditions. Such measurements can be made on time scales as short as 100 fs, and other detection modes (for example, resonance Raman, infrared, circular dichroism, or EPR) can be used. In this manner, it becomes possible to follow the course of a photochemical reaction, to monitor kinetic parameters for important intermediates, and to identify major reaction pathways.

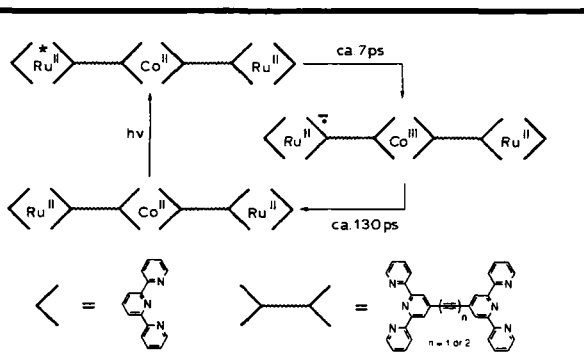
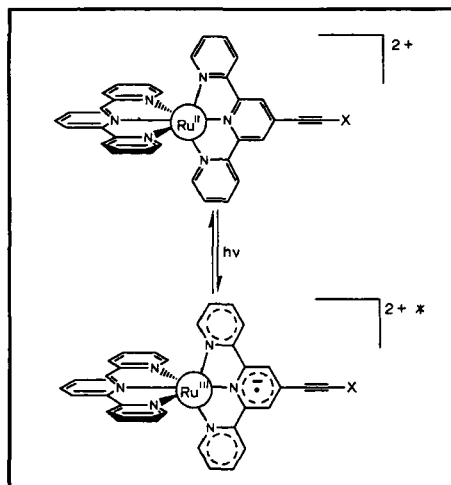
Panel 4

The primary reason for using transition metal complexes such as ruthenium(II) bis-terpyridyl as photosensitisers in these systems concerns the realisation that their lowest energy excited states are of metal-to-ligand charge-transfer (MLCT) character. In fact, the singlet excited states tend to be extremely short lived and photochemistry is restricted to the triplet manifold. Under illumination with visible light, an electron is transferred from the metal centre to one of the co-ordinated ligands, resulting in the transient formation of a ruthenium(III) centre and the π -radical anion of the ligand, see Diagram.

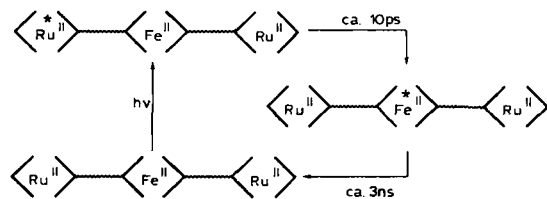
For symmetrical complexes, there is no preference as to which ligand becomes reduced and the electron may be delocalised over the entire ligand field. However, for asymmetrical complexes there will be preferential reduction of the most-easily reduced ligand and the electron will be localised at this ligand.

This is the case with ethynyl-substituted terpyridyl ligands, which are reduced preferentially to the corresponding unsubstituted

ligand. Furthermore, conjugation between the aromatic residues and the bridging polyene provides an extended π^* -orbital in which the electron can reside. In this respect, the MLCT transition can be considered to be vectorial.



Scheme 1



Scheme 2

terminal ruthenium(II) complex is about 175 ns and that $\beta\{h\} \sim 0.12/\text{\AA}$, we can calculate that light-induced hole transfer could occur over a distance of 85 \AA with an efficiency of 50 per cent, in such systems.

The redox products formed during this reaction have been detected by transient absorption spectroscopy and their lifetimes were found to be around 130 ps (11). Decay of these species occurs by way of intramolecular charge recombination in which the electron, resident in a π^* -orbital on the terpyridyl ligand of the ruthenium(II) complex, is transferred to the cobalt(III) centre, see Scheme 1. Formally, such reactions can be described as electron-transfer processes taking place via LUMOs

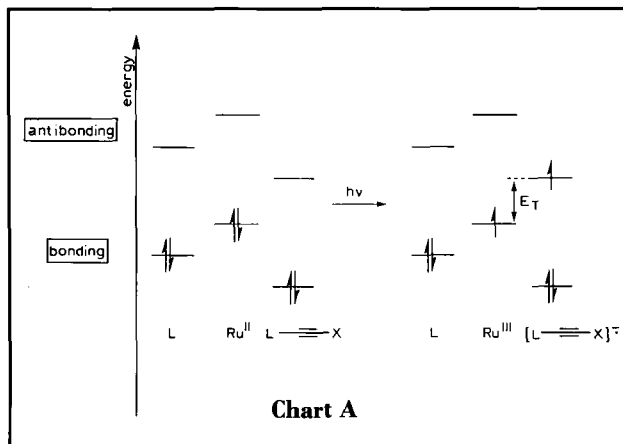
Panel 5

It is convenient to consider the various reactions in terms of frontier molecular orbital (MO) diagrams. The energy levels of the LUMO (lowest unoccupied) and HOMO (highest occupied) states for each of the metal complexes, together with those of the polyene bridge, can be derived for the ground-state subunits by electrochemistry.

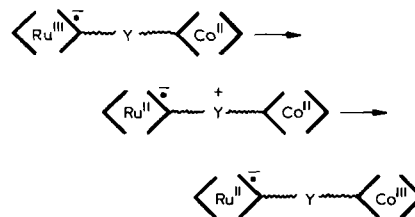
Selective excitation of the ruthenium(II) complex, see Chart A, adjacent, generates the corresponding triplet excited state, the energy levels of which differ from those of the ground-state complex by the amount of the excitation energy (E_T). Since the triplet state possesses MLCT character, it is useful to describe the triplet as consisting of a ruthenium(III) centre and with the displaced electron residing in a π^* -orbital localised on the ethynyl-substituted terpyridyl ligand.

In the cobalt(II)-containing molecular system, it is energetically favourable for an electron to move from the HOMO localised on the cobalt(II) centre, thereby forming a cobalt(III) site, to the ruthenium(III) centre, hence restoring the starting ruthenium(II) species, see Chart B. This electron-transfer step takes place via HOMOs situated on the bridge and, consequently, may be termed as "hole transfer".

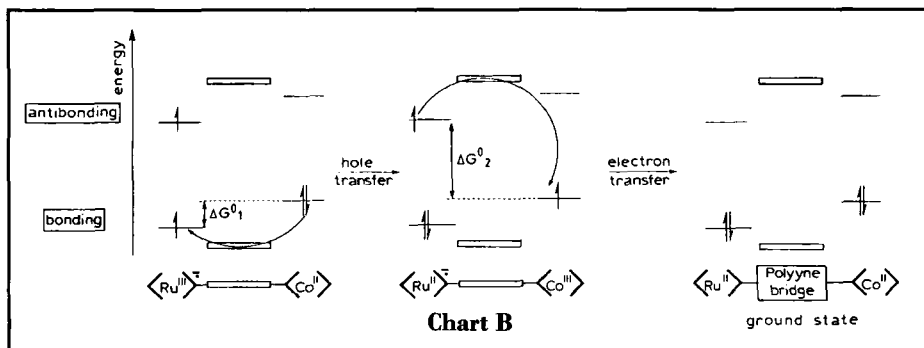
The reaction can be written in terms of the following (hypothetical) intermediate state,



usually referred to as a "virtual state":



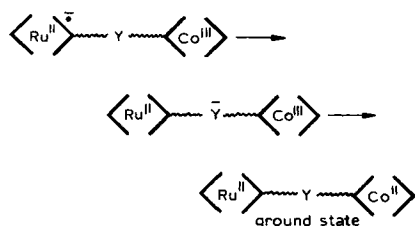
Here, we consider that the ruthenium(III) centre abstracts an electron from the bridge (Y). The resultant positive charge can migrate along HOMOs localised on the bridge by way of individual ethynyl groups. Electron abstraction from the cobalt(II) centre gives rise to the final state. For this "superexchange" mechanism to operate, it is important that the energy of the bridge is less than that of the metal-centred reactants, so that



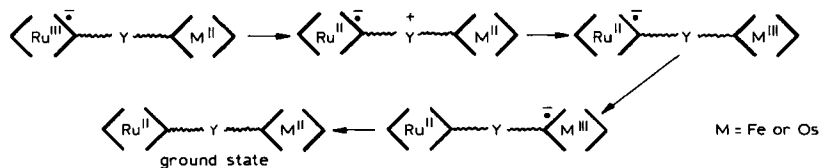
Panel 5, continued

the proposed Y^+ species does not appear as a real redox intermediate. In the systems described, the overall thermodynamic driving force (ΔG_1^0) for light-induced electron transfer from the ruthenium(II) complex to the cobalt(II) centre is about -0.37 eV.

Subsequent electron transfer from the π -radical anion of the ethynyl-substituted terpyridyl ligand co-ordinated at the ruthenium(II) centre to the cobalt(III) site is thermodynamically very favourable ($\Delta G_2^0 = -1.75$ eV). This reaction takes place by way of LUMOs localised on the bridge and can be formally described as "electron transfer". As an extreme approximation, we can express the mechanism as involving the following virtual state:



Here, the π -radical anion of the ruthenium(II) bis-terpyridyl complex can donate its extra electron, located in a ligand-centred π^* -orbital, to the LUMO associated with the



(lowest unoccupied molecular orbitals) on the bridge and, as outlined above, the attenuation factor for electron transfer ($\beta\{e\}$) was estimated to be about $0.04/\text{\AA}$. This is a particularly small value, indicating that there is a very low barrier for electron tunnelling through the bridge in these systems. In fact, this is the smallest attenuation factor reported for electron tunnelling through any organic medium; for example, the protein matrix that surrounds the bacterial photosynthetic reaction centre complex is characterised by $\beta\{e\} \sim 1.4/\text{\AA}$ (12). Clearly,

therefore, such electron-transfer reactions might be expected to occur over very large distances.

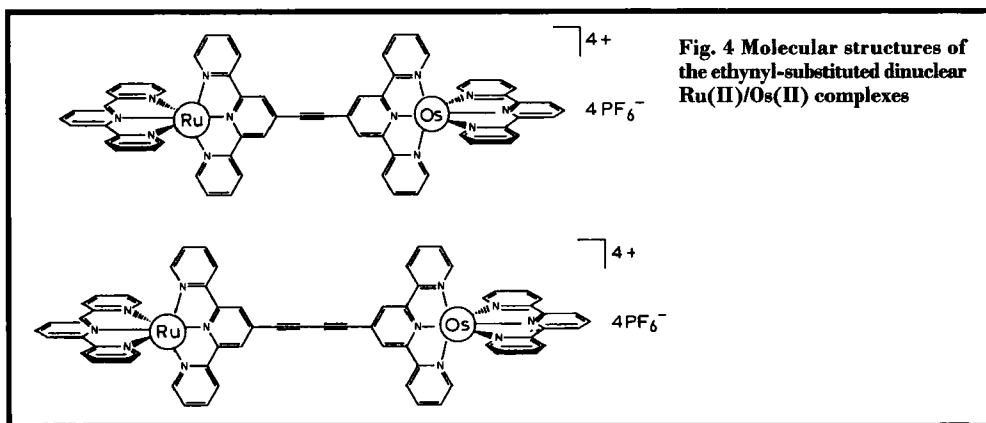
bridge. The electron can migrate along the bridge until it is transferred irreversibly to the cobalt(III) centre. As for the hole-transfer process, LUMOs situated on the bridge must be at higher energy than those on the metal complexes, such that Y^+ does not figure as a real redox intermediate.

In the corresponding osmium(II)- and iron(II)-containing molecular systems, light-induced electron transfer between the metal complexes does not take place because of unfavourable positioning of the various energy levels. However, the triplet energy gaps for the osmium(II) and iron(II) bis-terpyridyl complexes are significantly smaller than that for ruthenium(II) bis-terpyridyl, allowing triplet energy transfer to take place. In this latter process, an electron moves from the osmium(II) or iron(II) centre to the ruthenium(III) cation present in the MLCT triplet state by way of hole transfer through HOMOs localised on the bridge. Simultaneously, the electron resident in the π^* -orbital localised on the ethynyl-substituted terpyridyl ligand is transferred along the bridge to the second (covalently-linked) terpyridyl ligand. This process occurs by way of LUMOs localised on the bridge, see below.

The net result is the formation of the triplet excited state of the osmium(II) or iron(II) bis-terpyridyl complex.

Systems with a Central Iron Complex

In the corresponding trinuclear systems that have a central iron(II) bis-terpyridyl complex (Figure 3) the triplet lifetimes of the terminal ruthenium(II) complexes were found to be about 10 ps, see Scheme 2. Here, light-induced electron transfer does not take place, instead the triplet state of the chromophoric ruthenium(II) bis-terpyridyl complex transfers its excitation



energy to the appended iron(II) complex. This intramolecular triplet energy-transfer process takes place via electron exchange and may be considered to involve molecular orbitals localised on the polyyne bridge. Formally, electron exchange corresponds to simultaneous transfer of both an electron and a hole, see Panel 5. It is interesting to note that the measured attenuation factor for triplet energy transfer ($\beta\{t\} \sim 0.17/\text{\AA}$) corresponds almost exactly to the sum of attenuation factors for electron and hole transfers.

The resultant triplet state of the central iron(II) bis-terpyridyl complex survives for about 3 ns at room temperature but does not luminesce.

Ethynyl Group Connections

Similar studies (8) were made with asymmetrical binuclear complexes having terminal ruthenium(II) and osmium(II) bis-terpyridyl complexes connected via ethynyl groups, see Figure 4. In this case, very fast intramolecular triplet energy transfer occurs from the ruthenium(II) bis-terpyridyl complex to the covalently-linked osmium(II) bis-terpyridyl complex. Triplet lifetimes, measured for the ruthenium(II) and osmium(II) bis-terpyridyl subunits in acetonitrile solution at room temperature are about 20 ps and 75 ns, respectively.

The observed rates of energy transfer ($k \sim 5 \times 10^{10}/\text{s}$) are approximately 5,000-fold faster than the rates calculated for a through-space process and are therefore most likely due to

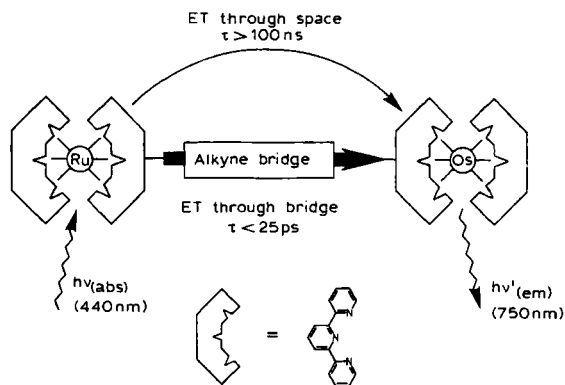
through-bond electron exchange, see Figure 5.

As mentioned above for the iron(II)-containing trinuclear complexes, the attenuation factor for triplet energy transfer ($\beta\{t\}$) was estimated to be about $0.17/\text{\AA}$. These reactions are among the fastest yet reported for triplet energy transfer between spatially-remote reactants. Identical processes take place in an ethanol glass at 77 K and, at both temperatures, triplet energy transfer is quantitative. At room temperature, the magnitude of the electronic coupling matrix element (V_{DA}) that quantifies the level of electronic coupling between the terminal metal complexes, was calculated to be about $7/\text{cm}$ for the case when a single ethynyl group was the bridge. This is a reasonable value, given that the separation distance between metals is about 14\AA , being only a fraction of the available thermal energy at 25°C ($210/\text{cm}$). This value is clearly sufficient to promote very fast intramolecular electron exchange.

These various experiments serve to indicate that polyyne bridges are very effective for the promotion of through-bond electron-transfer and hole-transfer processes between terminal metal complexes. In particular, the attenuation factor for electron transfer ($0.04/\text{\AA}$) is remarkably small, even when compared to polyenes and polyphenyls (8).

The reason for such efficient electron tunnelling becomes apparent when the photo-physical properties of the corresponding zinc(II)-containing trinuclear complexes are examined

Fig. 5 Schematic representation of energy transfer, ET, across one ($k = 7.1 \times 10^{10}/s$) and two ($k = 5 \times 10^{10}/s$) alkyne subunits at room temperature. The rate of energy transfer through space ($k = 1 \times 10^7/s$) is calculated from the Förster expression for a single ethynyl spacer



(Figure 3). In this case, the energy levels of the various components are situated such that energy- and electron-transfer reactions are thermodynamically unfavourable. Instead, the triplet lifetimes of the terminal ruthenium(II) bis-terpyridyl complexes ($\tau \sim 175 \text{ ns}$) are seen to be markedly enhanced relative to that of the mononuclear complexes ($\tau \sim 0.56 \text{ ns}$) in deoxygenated acetonitrile solution. There is also a substantial lowering of the triplet energy and an increase in the luminescence yield upon incorporation of an ethynyl substituent into one of the co-ordinated terpyridyl ligands.

Such effects are entirely consistent with selective promotion of an electron from the ruthenium(II) centre to the ethynyl-substituted terpyridyl ligand within the metal-to-ligand charge-transfer triplet manifold. Conjugation between the ethynyl substituent and the terpyridyl ligand might enable this electron to reside in an extended π^* -orbital that encompasses both the ethynyl-substituted terpyridyl ligand co-ordinated to the ruthenium centre, and the bridging alkyne.

The concluding part of this paper is scheduled to appear in the April 1996 issue of this journal.

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Small-Particle Platinum Catalysts

The highly uniform mesoporous aluminosilicate (MCM-41) has excellent catalytic properties but has only recently been studied as a support material.

Now, however, researchers from Germany have synthesised platinum-containing MCM-41 catalysts via different techniques and tested their catalytic performance during the oxidation of carbon monoxide in air (*J. Chem. Soc., Chem. Commun.*, 1995, (22), 2283-2284).

Catalyst performance depended on the preparation method. The best performance was achieved over platinum-MCM-41 prepared by incipient wetness, giving platinum particles of size around 2 nm, and 50 per cent carbon monoxide conversion at temperatures as low as 360 K.