Rigid Multinuclear Arrays assembled around Platinum Centres†

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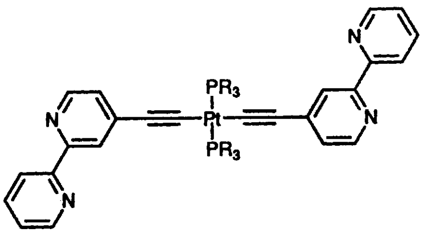
A series of *cis*- and *trans*-platinum(II) acetylide complexes of the type $[Pt^{II}(PBu^n_3)_2L_2]$ (L = 2,2′-bipyridin-4-ylethynyl or 2,2′:6′,2″-terpyridin-4′-yl-ethynyl or -butadiynyl) has been prepared and fully characterized. These metalloligands represent the first examples of oligopyridine σ-alkynyl derivatives of platinum(II). The crystal structure of the bis(terpyridin-4′-ylethynyl)platinum compound has been determined; it is centrosymmetric and confirms the *trans* arrangement of the two sets of ligands around a slightly distorted square-planar platinum(II) core. Reaction of the corresponding bis(bipyridin-4-ylethynyl)platinum compound with 1 or 2 equivalent(s) of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$, *cis*-$[Os(bipy)_2Cl_2]$ (bipy = 2,2′-bipyridine) or $[Re(CO)_5Cl]$ afforded, respectively, dinuclear MPt or trinuclear M_2Pt complexes. Homoleptic complexation of the unco-ordinated bipy moiety in the MPt complexes with iron(II) salts allows synthesis of heptanuclear M_3Pt_3Fe complexes (M = Ru^{II}, Os^{II} or Re^{I}). The photophysical properties, measured at 293 and 77 K, and half-wave potentials derived for the various multinuclear complexes remained comparable to those recorded for the corresponding unsubstituted mononuclear parent compounds. It was further shown that the spacer does not quench the excited states of the terminal photoactive subunit, but photons collected by the central platinum(II) complex are transferred quantitatively to the peripheral metal complexes.

A major goal of the emerging field of supramolecular chemistry[1] concerns the identification of molecular modules capable of interlocking together so as to form coherent arrays.[2-4] Two types of functionality are needed; namely, redox- or photo-active subunits that provide for information storage and molecular connectors that facilitate stereochemical control of the array. In turn, the molecular connectors can be divided into two main categories; namely, active components that promote long-range electronic coupling between terminal subunits (*e.g.* unsaturated hydrocarbons[5] or polyphenyls[6]) or passive connectors that serve as effective insulators (*e.g.* saturated hydrocarbons). To date, most attention has focused on the design of bridges that are good electronic conductors (*i.e.* molecular wires)[7] and, over the past few years, many elaborate molecular systems have been designed.[5-11] Polyynes, in particular, have been found to promote strong electronic communication between terminal subunits and to favour rigid, rod-like structures.[11,12] Here we describe a modified approach to the construction of multicomponent arrays in which the photoactive subunits are connected through a platinum(II) bis(σ-acetylide) moiety. The synthetic strategy can be adapted so as to produce linear or 'L-shaped' structures and can be applied readily to the fabrication of multinuclear systems. As an illustration, linear and 'L-shaped' trinuclear systems comprising terminal tris(2,2′-bipyridyl)ruthenium(II) complexes assembled around a platinum(II) centre are considered, together with several branched heptanuclear systems gathered about a central iron(II) cation.



A

A large number of metal bis(acetylide) complexes have been synthesized *via* σ co-ordination of two acetylene ligands to a metal centre.[13] Among these complexes, bis(ferrocenyl)acetylene and 1,4-bis(ferrocenyl)butadiyne have been recognized as being good model systems for investigation of intervalence charge-transfer transitions occurring through a π-conjugated spacer moiety.[14] It has also been reported that ferrocenylbutadiyne complexes exhibit interesting non-linear optical properties.[15] The corresponding σ-acetylide complexes having appended 2,2′-bipyridine (bipy) or 2,2′:6′,2″-terpyridine (terpy) subunits have been prepared only very recently.[16] Based on the availability of these compounds and stimulated by the anticipated photochemical activity of the corresponding transition-metal complexes, we have initiated a systematic study of the synthesis, structure and photophysical properties of multinuclear complexes connected by way of alkynes and polyynes. Here, we consider the use of bis(2,2′-bipyridylethynyl)bis(trialkylphosphine)platinum(II) metalloligands A to assemble multicomponent arrays. The resultant complexes are kinetically stable in solution, resistant to thermal and photochemical isomerization and facilitate exact positioning of prefabricated modules into ordered arrays. The central

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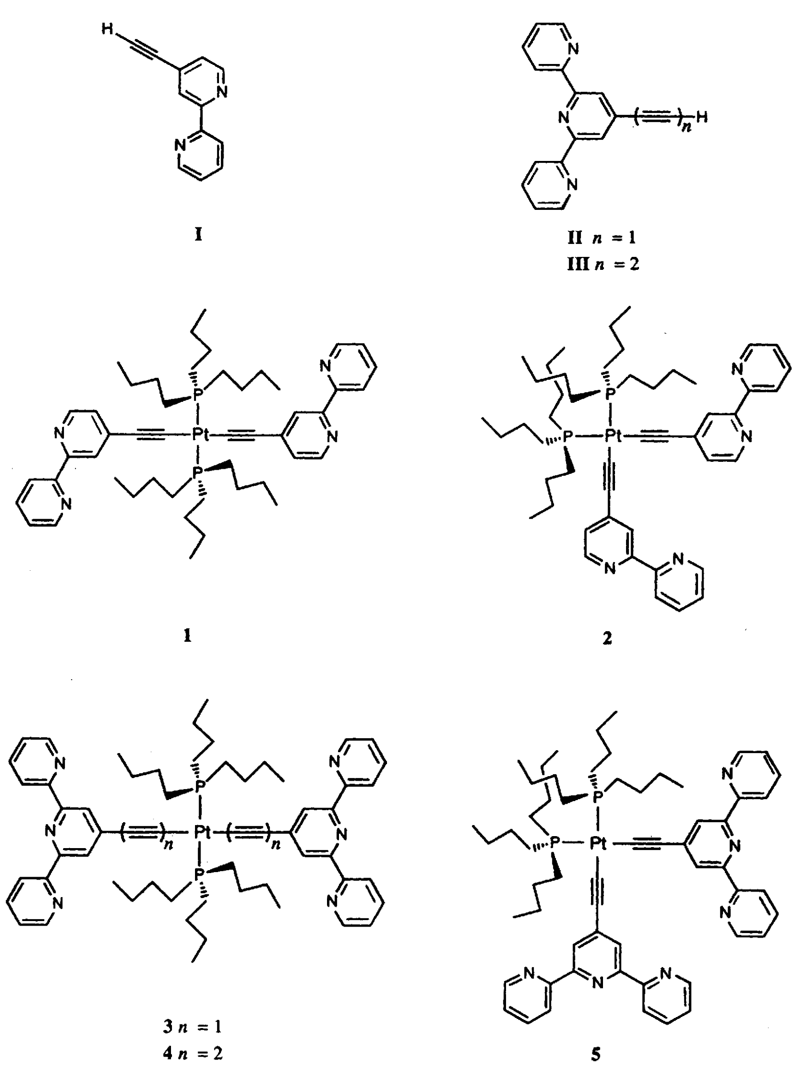
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI unit employed: eV ≈ 1.60×10^{-19} J.



Scheme 1

platinum(II) complex possesses square-planar geometry so that, by making judicious use of *cis* or *trans* isomers, elaborate stereochemical structures can be envisaged. Indeed, linear alkyne–Pt^{II}–alkyne structures have been prepared previously from alkynes bearing terminal *trans*-bis(trialkylphosphine)-platinum(II) groups[17] while bis(alkynes) gave rise to high-molecular-weight polymers containing this repeating unit. Using a similar strategy, Sanders and co-workers[18] synthesized Pt^{II}-linked cyclic porphyrin trimers capable of binding aluminium chelates inside the central cavity. By making use of the corresponding *cis* isomer it should be possible to expand on the range of structures that can be formed, each being functionalized with photo- and/or redox-active subunits.

Results and Discussion

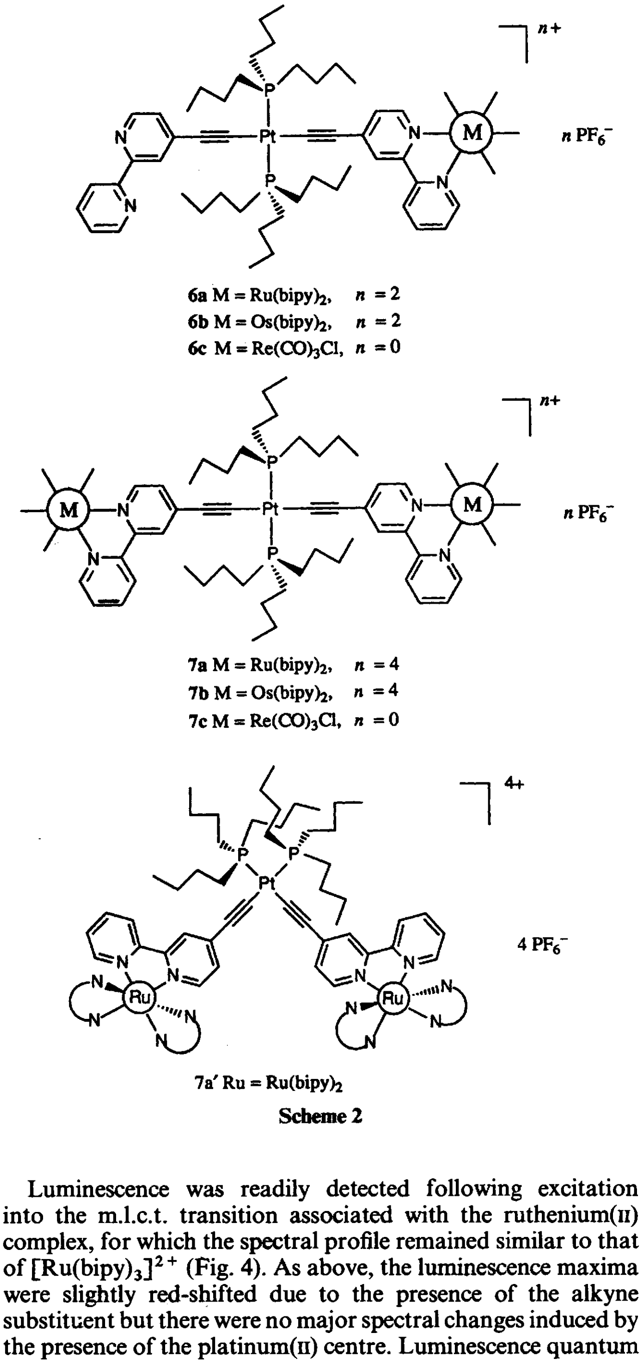
Synthetic Strategy.—Oligopyridines functionalized with alkyne substituents[19] have been used as building blocks in the synthesis of homoditopic,[20,21] heteroditopic[20] and tritopic ligands.[22] The corresponding polynuclear transition-metal complexes possess rigid and rod-like structures for which the extent of electronic coupling between the respective metal centres depends strongly on the exact nature of the spacer moiety.[7] These alkyne-substituted bipy and terpy subunits have now been used as molecular modules for the preparation of platinum(II) σ-acetylide complexes (Scheme 1). Subsequent complexation of the mononuclear platinum(II) compounds with redox- and/or photo-active metal complexes provides access to luminescent dinuclear MPt or trinuclear M_2Pt complexes, M = Ru^{II}, Os^{II} or Re^{I} (Scheme 2). The shape of the trinuclear supermolecules is easily altered between linear and L-shaped by preselection of the stereochemistry of the platinum(II) precursor. Homoleptic complexation of the dinuclear MPt compounds with iron(II) salts leads to preparation of the multicomponent heptanuclear complexes M_3Pt_3Fe (Scheme 3).

The *trans*-$[Pt^{II}(PBu^n_3)_2\{(C\equiv C)_nR'\}_2]$ compounds **1**, **3** and **4** (*n* = 1 or 2, R′ = bipyridin-4-yl or terpyridin-4′-yl) (Scheme 1) were prepared in good yield by quantitative reaction of 4-ethynyl-2,2′-bipyridine **I**, 4′-ethynyl-2,2′:6′,2″-terpyridine **II** or 4′-butadiynyl-2,2′:6′,2″-terpyridine **III** respectively, with *trans*-$[Pt^{II}(PBu^n_3)_2Cl_2]$. A CuI catalyst (0.6–2.3 mol%) was used, with diisopropylamine as base, following procedures described previously for the preparation of similar compounds.[23] The parent *cis* compounds **2** and **5** were prepared similarly, in yields of *ca.* 85%, using *cis*-$[Pt^{II}(PBu^n_3)_2Cl_2]$ as starting compound. As expected, the observed ethynyl carbons were strongly deshielded (*ca.* 20 ppm) in the ^{13}C NMR spectrum of the metalloditopic ligand **1** compared to the analogous compound without the platinum(II) centre.[20]

The dinuclear MPt and trinuclear M_2Pt complexes were prepared by selective complexation of the bipy moiety of the metalloligand **1** with 1 or 2 equivalent(s), respectively, of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$, *cis*-$[Os(bipy)_2Cl_2]$ or $[Re(CO)_5Cl]$. Based on ^{31}P NMR spectral data collected in solution and on Fourier-transform IR spectra recorded for the solid state, it appears that there is no thermal or photochemical isomerization of the starting metalloligands **1**–**5** or the resultant di- or tri-nuclear complexes in the solution or solid phases. The ^{31}P NMR chemical shifts are located at *ca.* δ +5 for the *trans* complexes, with the ^{31}P–Pt coupling constant lying in the range 2270–2300 Hz and with a ν(C≡C) stretching vibration around 2080–2095 cm^{-1}. The parent *cis* complexes exhibit a chemical shift of *ca.* δ −2, with the ^{31}P–Pt coupling constant being *ca.* 2250 Hz, and ν(C≡C) at *ca.* 2115 cm^{-1}. As expected, subsequent complexation of the ditopic metalloligands **1** and **2** with a metal cation induced minor modifications to the NMR and IR spectral patterns. Reaction of the three dinuclear complexes, MPt, with $FeSO_4 \cdot 7H_2O$ resulted in quantitative formation of the corresponding heteroheptanuclear M_3Pt_3Fe complexes (Scheme 3). These latter complexes were isolated as mixtures of diastereo- and geometrical-isomers and were characterized by ^{31}P-{^1H} NMR, Fourier-transform IR, electronic absorption and emission spectroscopy, as well as by elemental analysis. Electrospray mass spectrometry (ESMS) confirms the unique formation of these cationic polynuclear complexes. The spectra obtained are clear and readily interpreted, due to the presence of several pseudo-molecular peaks corresponding to successive loss of counter anion. Fragmentation of the complexes in solution was easily prevented by using a low acceleration potential.

Crystal Structure of Compound **3**.—An ORTEP[24] drawing of the neutral complex **3** is shown in Fig. 1; the crystallographic data, atomic coordinates and selected bond lengths and angles are listed in Tables 1–3. The crystals consist of discrete neutral centrosymmetric molecules, the platinum atom being located on a crystallographic two-fold axis. The two sets of ligands around the square-planar platinum(II) core confirm the *trans* arrangement of the molecule. An angle of 5(1)° between the planes defined by the two pyridine rings containing nitrogen atoms N(1) and N(2) and a dihedral angle of 9(1)° between the planes of the rings containing N(1) and N(3) illustrate the twist about the interannular C–C bonds, as well as the slight distortion within the terpyridine unit. As expected, all three nitrogen atoms are in a transoidal arrangement in order to minimize electronic interaction between the neighbouring nitrogens, a situation observed in other oligopyridine ligands (*e.g.* 2,2′-bipyridine,[25] 2,2′:6′,2″:6″,2‴-quaterpyridine[26] or 4′-phenyl-2,2′:6′,2″-terpyridine[27]). The metal-to-phosphorus bond length 2.317(1) Å, the metal-to-acetylide bond distance 1.998(4) and the acetylide C≡C bond 1.190(6) Å found for **3** are in agreement with other structually characterized σ-acetylide platinum(II) complexes.[28,29] The geometry of the platinum(II) centre does not exhibit any apparent deviation from that expected for regular square-planar co-ordination [P(1)–Pt–C(13) 92.9(1) and C(13)–Pt–P(1′) 87.1(1)°].

Photophysical Properties of the Ruthenium(II) *Analogues*.—Absorption spectra recorded for the RuPt **6a** and Ru_2Pt **7a** complexes in acetonitrile solution are similar to that of tris(2,2′-bipyridyl)ruthenium(II), $[Ru(bipy)_3]^{2+}$, used as reference compound [Fig. 2(*a*)]. In particular, there are no obvious spectral perturbations in the visible region caused by bonding to Pt^{II}, by attachment of the second ruthenium(II) complex, or by *cis*/*trans* isomerization at the Pt^{II} site. Relative to $[Ru(bipy)_3]^{2+}$, the spectra exhibit small red shifts in the position of the lowest-energy metal-to-ligand charge-transfer (m.l.c.t.) absorption band, λ_{max}, and small changes in absorption coefficient at the absorption maximum, ε_{max} (Table 4). Such spectral modifications are consistent with substitution of the alkyne group at the 4 position of the 2,2′-bipyridine ring.[30] Also apparent in the absorption spectra of the Pt^{II}-containing compounds are transitions around 320 nm which are attributed to charge-transfer bands associated with the Pt^{II}–alkyne–bipy groups.[33] Small changes in the position and intensity of these latter transitions appear characteristic of *cis* and *trans* isomers (Fig. 3).



6a M = Ru(bipy)₂, *n* = 2
6b M = Os(bipy)₂, *n* = 2
6c M = Re(CO)₃Cl, *n* = 0

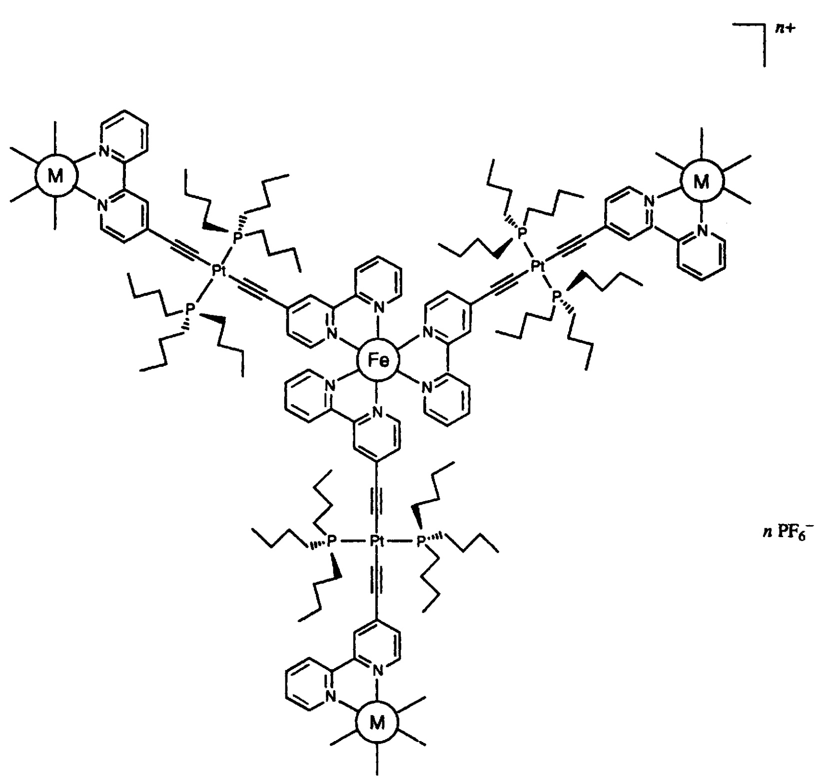
7a M = Ru(bipy)₂, *n* = 4
7b M = Os(bipy)₂, *n* = 4
7c M = Re(CO)₃Cl, *n* = 0

7a′ Ru = Ru(bipy)₂

Scheme 2

Luminescence was readily detected following excitation into the m.l.c.t. transition associated with the ruthenium(II) complex, for which the spectral profile remained similar to that of $[Ru(bipy)_3]^{2+}$ (Fig. 4). As above, the luminescence maxima were slightly red-shifted due to the presence of the alkyne substituent but there were no major spectral changes induced by the presence of the platinum(II) centre. Luminescence quantum yields (Φ_L) and lifetimes (τ_L) were measured for each complex in acetonitrile solution at 295 K and in an ethanol glass at 77 K following excitation into the m.l.c.t. absorption band. The derived values are collected in Table 5 and indicate that the platinum(II) centre does not quench the excited triplet state of the terminal ruthenium(II) complex. There is no obvious effect of adding the second ruthenium(II) complex or changing the stereochemistry at the Pt^{II} site. Compared[34,35] to $[Ru(bipy)_3]^{2+}$, however, the luminescence lifetimes and yields are slightly but significantly increased (Table 5).

It is instructive to compare the above-mentioned results with those reported earlier for mono- and di-nuclear ruthenium(II) complexes functionalized at the 5 position of one of the 2,2′-bipyridyl rings with a 1,4-bis(ethynyl)bicyclo[2.2.2]octane substituent.[10a] For these latter systems, there is a 20 nm red shift in the luminescence maxima and an enhancement in the triplet lifetimes relative to $[Ru(bipy)_3]^{2+}$, but since the triplet lifetimes were recorded in aerated acetonitrile it is difficult to make a direct comparison with our work. Even so, the



8a M = Ru(bipy)$_2$, $n = 8$
8b M = Os(bipy)$_2$, $n = 8$
8c M = Re(CO)$_3$Cl, $n = 2$

Scheme 3

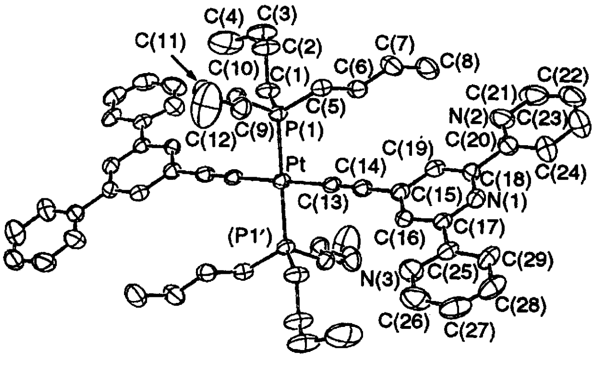


Fig. 1 An ORTEP drawing of complex **3** showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity

Table 1 Crystallographic data for complex **3**

Formula	$C_{58}H_{74}N_6P_2Pt{\cdot}C_7H_8$
M	1204.5
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	33.180(9)
b/Å	10.334(3)
c/Å	21.899(6)
β/°	125.83(2)
U/Å^3	6087.9
Z	4
D_c/g cm^{-3}	1.314
μ/cm^{-1}	24.208
Crystal dimensions/mm	0.35 × 0.22 × 0.25
F(000)	337
No. of independent reflections	7182
No. of observed reflections [$I > 3\sigma(I)$]	3842
λ (Mo-Kα)/Å	0.70926
$R(F)$*	0.030
$wR(F^2)$*	0.035

* $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)]^{\frac{1}{2}}$, with $w = \sigma(F)^{-2}$.

magnitude of both the emission shift and the enhancement in triplet lifetime observed by Vögtle *et al.*[10a] exceed those shown by the Pt^{II}-containing compounds studied here. This may indicate that the alkyne substituent is more directly involved in the triplet state (*i.e.* by way of electron delocalization over an extended π* orbital associated with the substituted bipy ligand)[37,38] in the system having the fused hydrocarbon spacer than in the analogous system assembled around the central platinum(II) complex.

The triplet excited state of each of the Pt^{II}-containing complexes was readily detected following excitation at 532 nm with a 30-ps laser pulse. In each case the triplet differential absorption spectrum was similar to that[39] of $[Ru(bipy)_3]^{2+}$ and was characterized by strong absorption in the near-UV region, bleaching of the m.l.c.t. absorption band and weak absorption stretching into the near-IR region (Fig. 5). No other transient species were detected and the triplet decayed cleanly *via* first-order kinetics to reform the corresponding ground state. Triplet lifetimes measured in deoxygenated acetonitrile solution at 20 °C were similar to those recorded by time-resolved luminescence spectroscopy (Table 5). The presence of the platinum(II) centre had no effect on the triplet absorption spectral profile or decay kinetics and there is no evidence to indicate the existence of low-lying excited states that are

Table 2 Atomic coordinates (× 10^4) for complex **3**

Atom	x	y	z	Atom	x	y	z
Pt	0.250	0.250	0.000	C(18)	0.126 2(2)	−0.212 2(4)	−0.274 6(2)
P(1)	0.208 91(4)	0.174 4(1)	0.049 46(5)	C(19)	0.155 3(1)	−0.141 4(5)	−0.208 6(2)
C(1)	0.251 0(2)	0.135 3(6)	0.149 4(2)	C(20)	0.118 2(2)	−0.353 5(5)	−0.271 5(2)
C(2)	0.227 9(2)	0.080 0(7)	0.187 6(2)	N(2)	0.138 8(2)	−0.404 6(5)	−0.203 6(2)
C(3)	0.267 1(2)	0.037 6(8)	0.269 2(2)	C(21)	0.131 4(2)	−0.530 1(7)	−0.200 1(3)
C(4)	0.295 1(3)	0.146(1)	0.318 7(3)	C(22)	0.104 7(2)	−0.608 4(6)	−0.261 3(3)
C(5)	0.170 1(1)	0.031 2(5)	0.006 6(2)	C(23)	0.084 2(3)	−0.557 0(7)	−0.330 7(4)
C(6)	0.197 8(2)	−0.092 6(5)	0.017 0(2)	C(24)	0.091 2(2)	−0.426 7(6)	−0.335 7(3)
C(7)	0.164 8(2)	−0.209 0(5)	−0.015 2(3)	C(25)	0.079 5(1)	0.024 3(5)	−0.424 6(2)
C(8)	0.191 5(2)	−0.331 3(7)	−0.007 4(3)	N(3)	0.078 0(2)	0.153 3(5)	−0.428 9(2)
C(9)	0.167 0(2)	0.295 2(5)	0.045 3(2)	C(26)	0.052 1(2)	0.204 7(7)	−0.498 7(3)
C(10)	0.123 5(2)	0.328 3(6)	−0.033 2(3)	C(27)	0.027 8(2)	0.134 5(8)	−0.563 3(2)
C(11)	0.089 0(2)	0.427 8(6)	−0.035 1(3)	C(28)	0.029 8(2)	0.005 8(7)	−0.558 8(2)
C(12)	0.047 4(3)	0.465(1)	−0.111 3(5)	C(29)	0.056 1(2)	−0.054 3(6)	−0.487 9(2)
C(13)	0.210 7(1)	0.137 2(5)	−0.091 1(2)	C(30)	0.000	0.102(1)	0.250
C(14)	0.188 5(1)	0.070 2(5)	−0.145 6(2)	C(31)	0.042 0(2)	0.046(1)	0.276 7(3)
C(15)	0.159 9(1)	−0.008 6(5)	−0.212 9(2)	C(32)	0.041 9(3)	−0.086(1)	0.277 8(3)
C(16)	0.135 0(1)	0.045 0(5)	−0.284 4(2)	C(33)	0.000	−0.151(1)	0.250
C(17)	0.106 9(1)	−0.0319(5)	−0.348 0(2)	C(34)	0.000	0.245(1)	0.250
N(1)	0.102 6(1)	−0.159 9(4)	−0.343 6(2)				

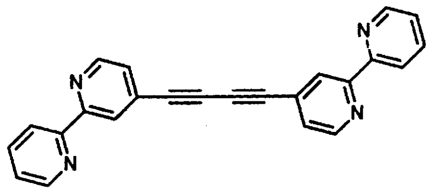
Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Pt–P(1)	2.317(1)	C(17)–C(25)	1.481(6)
Pt–C(13)	1.998(4)	P(1)–C(5)	1.820(6)
C(13)–C(14)	1.190(6)	P(1)–C(1)	1.824(5)
C(14)–C(15)	1.449(7)	P(1)–C(9)	1.830(6)
C(18)–C(20)	1.491(9)		
P(1)–Pt–C(13)	92.9(1)	C(17)–C(25)–N(3)	116.4(4)
C(13)–C(14)–C(15)	177.9(6)	C(5)–P(1)–C(9)	104.0(3)
C(14)–C(15)–C(16)	121.7(5)	C(1)–P(1)–C(9)	103.7(3)
C(14)–C(15)–C(19)	121.3(5)	C(1)–P(1)–C(5)	104.6(3)
N(1)–C(18)–C(20)	116.3(5)		
C(18)–C(20)–N(2)	116.8(6)		
N(1)–C(17)–C(25)	116.6(4)		

associated with the platinum(II) complex.[33] Similarly, laser excitation at 310 nm, where the absorption spectrum contains contributions from c.t. bands associated with the Pt^{II} site, resulted in quantitative formation of the m.l.c.t. triplet state from the ruthenium(II) complex. Thus, intramolecular triplet energy transfer must occur rapidly (*i.e.* < 50 ps) in these compounds.

Prolonged irradiation with visible light (λ > 290 nm) of the trinuclear complexes **7a** and **7a′** in deoxygenated acetonitrile solution at room temperature did not effect isomerization at the Pt site, as indicated by ^{31}P-{^{1}H} NMR studies. Thus, the similarity of the photophysical properties noted for **7a** and **7a′** does not arise because of rapid isomerization within the triplet manifold. Similarly, the complexes were found to be stable towards photodissociation, at least at room temperature.

Cyclic voltammetry studies made in acetonitrile solution indicate that the electrochemistry of the various Pt^{II}-containing compounds is similar to that of the reference compound (Table 4). Thus, the ruthenium(II) centre undergoes a quasi-reversible oxidation process with a half-wave potential ($E_{\frac{1}{2}}^{ox}$) of *ca.* 1.2 V *vs.* the saturated calomel electrode (SCE). There is no splitting of the oxidation peak for the trinuclear supramolecular species **7a** and **7a′** such that the terminal ruthenium(II) complexes remain in electronic isolation. Similarly, three separate reduction processes can be resolved, with the respective half-wave potentials ($E_{\frac{1}{2}}^{red}$) being around −1.3, −1.5 and −1.7 V *vs.* SCE (Table 4). These reduction steps are associated with addition of an electron to the 2,2′-bipyridyl ligands.[40] Finally, the potential difference for addition and removal of one electron (ΔE) remains identical for the Pt^{II}-containing complexes and is only slightly reduced with respect to [Ru(bipy)$_3$]$^{2+}$. This modest reduction in ΔE appears consistent[41] with the small red shifts in both absorption and emission spectral maxima noted for the m.l.c.t. bands of the Pt^{II}-containing complexes. The cyclic voltammograms show no obvious peaks that can be assigned to reduction or oxidation processes which involve the central platinum(II) complex.



B

There is no indication from the $E_{\frac{1}{2}}^{red}$ values observed for these heteronuclear compounds that the alkyne-substituted ligand is reduced preferentially since the values measured for the first reduction step are almost unaffected by the presence of the substituent. In fact, $E_{\frac{1}{2}}^{red}$ measured for the *trans* ligand **1** (−2.02 V *vs.* Ag) is only slightly less negative than that for bipy (−2.06 V *vs.* Ag) in dimethylformamide solution. This situation is in marked contrast to that found in the absence of the central platinum(II) complex, where the corresponding alkyne-substituted ditopic ligand (**B**) is reduced at much less negative potentials (−1.52 V *vs.* Ag) than is free bipy.

We may consider, therefore, that charge-transfer interactions between the platinum(II) donor and ethynyl-bipyridine acceptor, as evidenced by the UV/VIS absorption spectra, serve to raise the electron density resident on the substituted bipy ligand. This, in turn, would have the effect of lowering $E_{\frac{1}{2}}^{ox}$ for the ruthenium(II) centre, as is observed, and pushing $E_{\frac{1}{2}}^{red}$ for the alkyne-substituted bipy ligand to a more negative value than that for the analogous system not containing a platinum(II) centre. The compensatory effect of Pt^{II} may be enhanced by complexation of the unco-ordinated bipy sites on ligand **1** to the ruthenium(II) centre(s). In this case, the unsubstituted bipy ligands resident on the heteronuclear complexes would be reduced preferentially.

An alternative explanation is that each of the three bipy-based ligands bound to Ru^{II} in the various multinuclear complexes is reduced at much the same potential, as is the case with the free bipyridine derivatives. In the event that the electron is localized on the particular ligand to which it is promoted in the m.l.c.t. triplet excited state, this situation would give rise to a statistical distribution of triplet states

Table 4 Absorption spectral and cyclic voltammetric data recorded for various metal complexes in acetonitrile solution

Compound	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	E^{ox}/V *vs.* SCE	E^{red}/V *vs.* SCE			Δ*E*/eV
[Ru(bipy)$_3$]$^{2+}$	452	14 600[a]	1.27	−1.35	−1.54	−1.79	2.62
6a	458	15 200	1.23	−1.33	−1.54	−1.79	2.56
7a	456	31 200	1.22	−1.33	−1.52	−1.78	2.55
7a′	456	31 100	1.22	−1.33	−1.54	−1.79	2.55
[Os(bipy)$_3$]$^{2+}$	478	11 100[b]	0.83	−1.25	−1.54	—	2.08
6b	481	7 750	0.79	−1.23	−1.53	—	2.02
7b	481	15 600	0.79	−1.23	−1.53	—	2.02
[Re(bipy)(CO)$_3$Cl]	386	3 680[c]	1.32[d]	−1.35	*e*	*e*	2.67
6c	289	27 200	1.33[d]	−1.38	*e*	*e*	2.71
7c	392	36 200	1.32[d]	−1.40	*e*	*e*	2.72

[a] From ref. 30. [b] From ref. 31. [c] From ref. 32. [d] Irreversible process, refers to peak potential. [e] Irreversible.

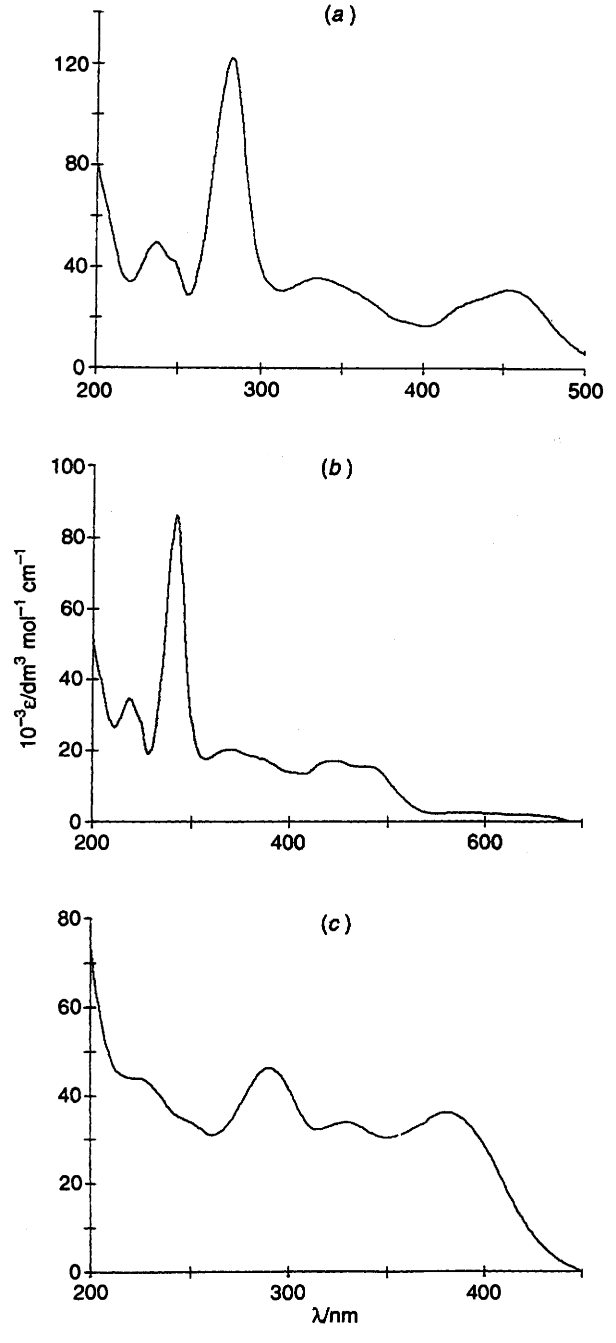


Fig. 2 Absorption spectra of the **7a** (*a*), **7b** (*b*) and **7c** (*c*) complexes in acetonitrile solution at room temperature

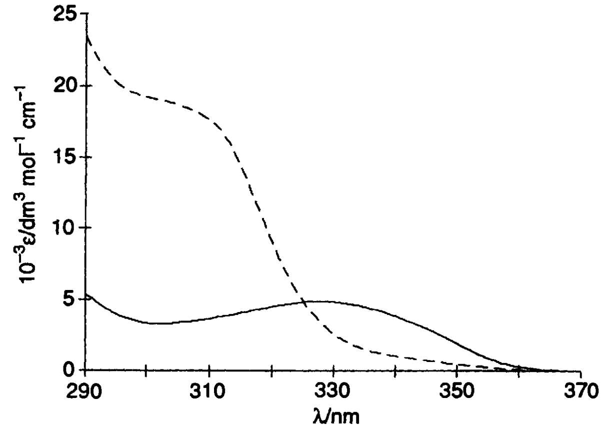


Fig. 3 Absorption spectra of metallocomplexes **4** (—) and **5** (– – –) in dichloromethane solution at room temperature

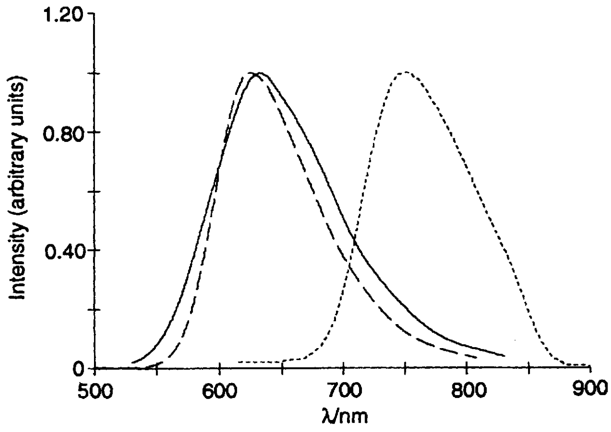


Fig. 4 Corrected luminescence spectra of complexes **7a** (– – –), **7b** (· · ·) and **7c** (—) in acetonitrile solution at room temperature

differing from each other in respect of which bipy ligand is present in a reduced state. It is difficult to estimate what influence, if any, the presence of a single ethynyl substituent might have on the overall photophysical properties but, as a rough approximation, we can use the 1,4-bis(ethynyl)bicyclo[2.2.2]octane-substituted derivative[10a] mentioned above as a model. Also, we note that binuclear ruthenium(II) complexes linked directly[38] or *via* rigid ethynyl[11] or ethenyl[39] groups exhibit (*i*) a substantial red shift in the luminescence spectrum, (*ii*) a markedly longer triplet lifetime in fluid solution, (*iii*) the appearance of an intense near-IR band in the triplet absorption spectrum and (*iv*) changes in the

Table 5 Photophysical properties measured for the various metal complexes in deoxygenated acetonitrile at 295 K or ethanol at 77 K

	Acetonitrile 295 K			Ethanol 77 K		
Compound	λ_{em}[a]/nm	τ_L[b]/ns[b]	Φ_L[c]	λ_{em}[a]/nm	τ_L[b]/μs	Φ_L[c]
$[Ru(bipy)_3]^{2+}$	620	980	0.062[d]	600	5.2	0.38[e]
6a	626	1240	0.080	610	6.4	0.44
7a	625	1300	0.084	608	6.7	0.45
7a′	625	1260	0.085	610	6.6	0.46
$[Os(bipy)_3]^{2+}$	745	60	0.0046[f]	710	0.83	0.065
6b	750	66	0.0050	715	0.88	0.066
7b	750	68	0.0048	715	0.90	0.068
$[Re(bipy)(CO)_3Cl]$[g]	622	30	0.0030	540	2.8	0.28
6c	635	83	0.0080	590	4.5	0.46
7c	633	73	0.0072	590	4.4	0.44
8a	628	570	0.038	—	—	—
8b	760	64	0.0050	—	—	—
8c	635	75	0.0065	—	—	—

[a] ± 22 nm. [b] ± 5%. [c] ± 10%. [d] From ref. 34. [e] From ref. 35. [f] From ref. 36. [g] From ref. 32.

electrochemical properties. These features, especially the characteristic red-shifted luminescence, are not observed with the Pt^{II}-containing multinuclear complexes and it is important to realize that only a single component is observed in the luminescence decay records. On this basis, we suggest that in the m.l.c.t. triplet excited states of these Pt^{II}-assembled ruthenium(II) complexes the electron is localized on one of the unsubstituted bipy ligands.

Photophysical Properties of the Osmium(II) *Analogues*.—Half-wave potentials recorded for the two Pt^{II}-containing osmium(II) complexes, **6b** and **7b**, are compiled in Table 4. Examination of the relevant data indicates that the osmium(II) centre is oxidized at slightly lower potential for the Pt^{II}-containing complexes than for $[Os(bipy)_3]^{2+}$, whereas the half-wave potential for the first reduction process is insensitive to the presence of the central platinum(II) complex. As noted above, this situation might arise if the Pt^{II} site donates charge through the alkyne group, by way of charge-transfer interactions, onto the substituted bipy ligands. As such, the first reduction process might be expected to take place at one of the unsubstituted bipy ligands. Alternatively, in the event that the compensatory effect of the platinum(II) group is to render the electron density resident on the substituted bipy ligand the same as that on an unsubstituted bipy bound to the same osmium(II) centre, reduction might be non-selective. In either case, there is no indication that the alkyne-substituted ligand is reduced preferentially.

Both complexes **6b** and **7b** absorb strongly around 480 nm, possessing low-energy absorption tails that stretch across much of the near-infrared region, and emit around 750 nm [Figs. 2(*b*) and 4]. The luminescence spectra and photophysical properties measured at 295 and at 77 K differ slightly from those recorded[35,42] for $[Os(bipy)_3]^{2+}$ but there are no obvious effects that can be attributed to the central platinum(II) complex. As noted for the corresponding ruthenium(II) complexes, the slightly red-shifted luminescence maxima observed for Pt^{II}-containing osmium(II) complexes are consistent with the somewhat smaller ΔE values noted for these compounds relative to that of $[Os(bipy)_3]^{2+}$. The luminescence lifetimes derived for **6b** and **7b** are slightly longer than those recorded for the reference compound under identical conditions (Table 5). However, by extrapolation of the comprehensive kinetic data reported by Meyer and co-workers[36] for osmium(II) 2,2′-bipyridyl complexes it is clear that the triplet lifetimes recorded for **6b** and **7b** are as might be expected on the basis of their triplet energy.

The osmium(II) complexes can be compared with related compounds having a 1,4-bicyclo[2.2.2]octane group in place of the platinum(II) bis(trialkylphosphine) spacer.[10a] The mono- and di-nuclear osmium(II) complexes based on the fused alkane spacer exhibit a red shift of 44 nm in the luminescence maximum and a 40% decrease in luminescence lifetime, as measured in aerated acetonitrile at room temperature.[10a] For these latter compounds the reduced triplet lifetime arises because of the lower triplet energy, as expected from the energy-gap law.[43] The significantly smaller red shifts and less pronounced changes in triplet lifetime observed for the Pt^{II}-containing complexes are considered to be consistent with electron localization at the unsubstituted bipy ligands within the m.l.c.t. triplet state. In this respect, it is also noteworthy that the differential triplet absorption spectra recorded for **6b** and **7b** are very similar, if not identical, to that found for $[Os(bipy)_3]^{2+}$ (Fig. 5).

Photophysical Properties of the Rhenium(I) *Analogues*.—According to cyclic voltammetry studies carried out with the various rhenium(I) complexes in acetonitrile solution, the oxidation peaks remained unaffected by substitution and were irreversible[32] (Table 4). It is likely that these processes correspond to oxidation of the chloride ligand, not the metal centre which occurs at higher potential. Reduction of the various complexes is believed to take place at the bipy ligand and the derived $E_{\frac{1}{2}}^{red}$ values are slightly more negative for **6c** and **7c** than for *fac*-$[Re(bipy)(CO)_3Cl]$ (Table 4) in acetonitrile solution. As noted above for the other Pt^{II}-containing heteronuclear complexes, the central platinum(II) complex most probably donates charge to the ethynyl-substituted bipy moiety, thereby raising its reduction potential relative to that of the corresponding Pt^{II}-free ligand. This compensatory effect causes the $E_{\frac{1}{2}}^{red}$ value for the substituted bipy ligand to appear almost equal to that of bipy, both in the free bipyridine derivatives and in the corresponding rhenium(I) complexes.

In acetonitrile solution *fac*-$[Re(bipy)(CO)_3Cl]$ exhibits a relatively weak m.l.c.t. absorption band centred at *ca.* 386 nm and luminescence centred at *ca.* 620 nm.[32] For the Pt^{II}-containing rhenium(I) complexes **6c** and **7c** these m.l.c.t. absorption bands overlap considerably with the more intense absorption transitions associated with the platinum(II) complex. Excitation into this absorption band, however, gives rise to weak luminescence centred around 635 nm at room temperature which appears characteristic of the rhenium(I) complex. The spectral shape and wavelength of this emission is consistent with its assignment as m.l.c.t. rather than being ligand- or metal-centred. Relative to the corresponding ruthenium(II) complexes, this luminescence is short-lived in fluid solution at room temperature but the lifetime is greatly enhanced upon cooling to 77 K.[44] As noted previously, there is

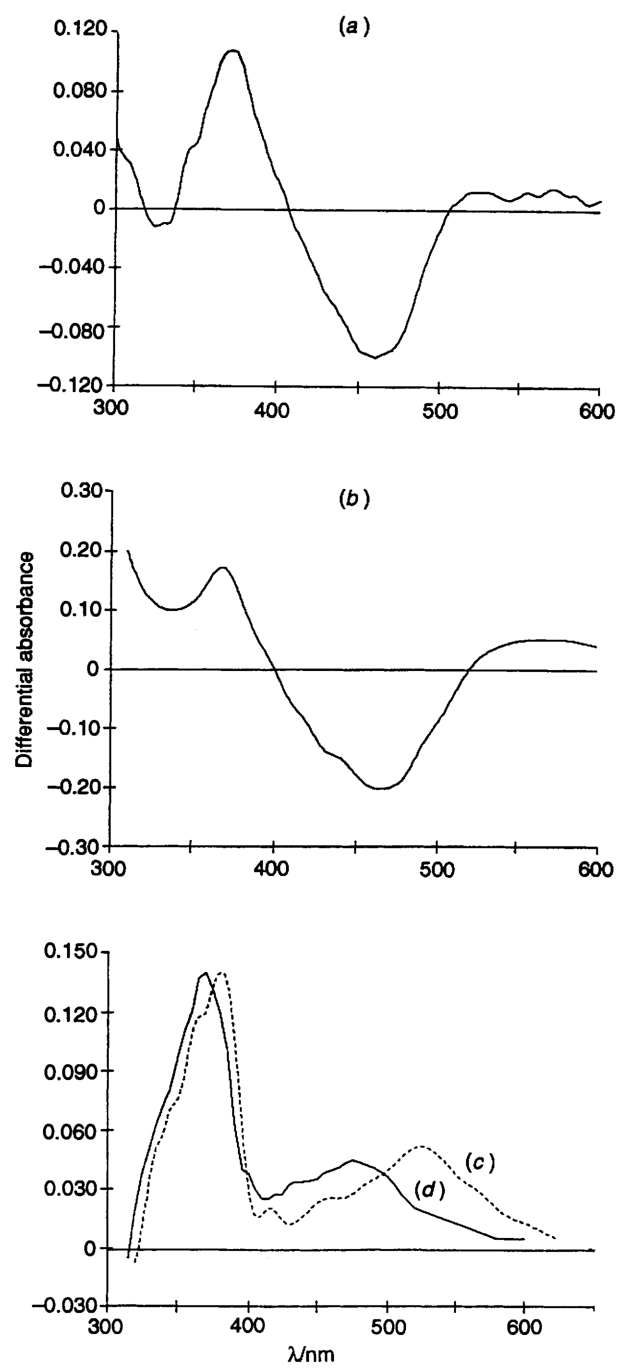


Fig. 5 Transient differential absorption spectra recorded immediately after excitation of complexes **7a** (*a*) and **7b** (*b*) with a 30-ps laser pulse at 532 nm, and transient spectrum recorded after excitation of **7c** (*c*) and *fac*-[Re(bipy)(CO)$_3$Cl] (*d*) with a 30-ps laser pulse at 355 nm, in deoxygenated acetonitrile

a substantial blue shift in the emission maxima upon moving from fluid solution to frozen glass but emission from the Pt^{II}-containing complexes still occurs at significantly lower energy than found for the reference compound. The luminescence lifetimes recorded for **6c** and **7c** are considerably longer than that found for *fac*-[Re(bipy)(CO)$_3$Cl], under the same conditions (Table 5). Previous studies[32] have shown that, to a large degree, the rates of non-radiative deactivation of the triplet states of such rhenium(I) complexes increase markedly with decreasing triplet energy, following the so-called 'energy-gap law'.[43] Clearly, this is not the case with **6c** and **7c**, where the triplet lifetimes are enhanced but the triplet energies are reduced with respect to *fac*-[Re(bipy)(CO)$_3$Cl].

The magnitudes of the enhancement in triplet lifetime and of the red shift in emission maximum observed for these Pt^{II}-containing rhenium(I) complexes exceed those found for the corresponding complexes of Ru^{I} and Os^{II} measured under identical conditions (Table 5). For both **6c** and **7c**, formation of the triplet excited state corresponds to transfer of an electron from the rhenium(I) centre to the co-ordinated ethynyl-substituted bipy ligand. Conjugation between bipy and ethynyl groups has the effect of providing an extended π^* orbital in which the promoted electron resides.[10] Previous work with ruthenium(II) complexes[5,10,37,38] has provided unambiguous evidence that the availability of this extended π^* orbital serves to both lower the triplet energy and to increase the triplet lifetime. Presumably, the same phenomenon is responsible for the differences in photophysical properties observed between the Pt^{II}-containing rhenium(I) complexes and *fac*-[Re(bipy)(CO)$_3$Cl].

Laser flash-photolysis studies are also consistent with formation of the π-radical anion of the bipy ligand within the m.l.c.t. triplet excited state. Thus, laser excitation of *fac*-[Re(bipy)(CO)$_3$Cl] in deoxygenated acetonitrile solution gives rise to a transient absorption spectrum possessing the characteristic features of the π-radical anion of the co-ordinated bipy, as formed by electron transfer from the rhenium(I) centre (Fig. 5). The corresponding transient absorption spectrum recorded for complex **7c** is similar but red-shifted (Fig. 5), as expected for an extended π system. This spectral comparison clearly shows that, in the case of the heteronuclear rhenium(I) complexes, the m.l.c.t triplet state includes a contribution from a form having the electron resident on the bipy ligand and that the ethynyl substituent is conjugated to that ligand. In contrast, the absence of any spectral perturbations in the triplet absorption spectra recorded for the heteronuclear complexes of Ru^{II} and Os^{II} is suggestive of electron localization at the unsubstituted bipy ligands.

Photophysical Properties of the Heptanuclear Complexes M$_3$Pt$_3$Fe.—Polynuclear bipyridine-containing complexes have previously been synthesized from alkane-bridged ditopic ligands. Some of these tetranuclear Ru$_3$Fe[45] or Ru$_3$Ru[46] complexes exhibit quenching of the luminescence of the peripheral ruthenium bipyridyl centres by the iron or ruthenium bipyridyl complex at the core of the cluster. More recently, Balzani and co-workers[47] have developed a simple strategy allowing the construction of multinuclear arrays starting from a central point and adding successive layers of chromophore. A similar approach has been followed to prepare clusters containing five porphyrin rings[48,49] and can be employed as a means to enlarge the size of the Pt^{II}-containing systems studied here. Thus, heptanuclear arrays, assembled around a central iron(II) cation, have been synthesized, each containing three metal complexes isolated from the core by platinum(II) alkyne bridges (complexes M$_3$Pt$_3$Fe in Scheme 3). Tris(2,2′-bipyridyl)-iron(II) does not emit, even in an ethanol glass at 77 K,[50] and its excited-state lifetime, measured by transient absorption spectroscopy, is *ca.* 0.8 ns.[51–53] Previous work[52] has allowed assignment of the lowest-energy excited state as being of ligand-field character, not m.l.c.t., and being located at an energy less than 0.9 eV. It might be expected, therefore, that the central iron(II) complex will quench the excited triplet states of the terminal metal complexes *via* Förster-type energy transfer.

Absorption spectra recorded for each of the heptanuclear complexes in acetone solution resemble superpositions of spectra recorded for the isolated components (Fig. 6). There are no obvious perturbations caused by assembling the subunits into a multicomponent array. Similarly, excitation at a wavelength corresponding to absorption by the peripheral metal complexes resulted in the appearance of luminescence characteristic of that chromophore. Luminescence lifetimes

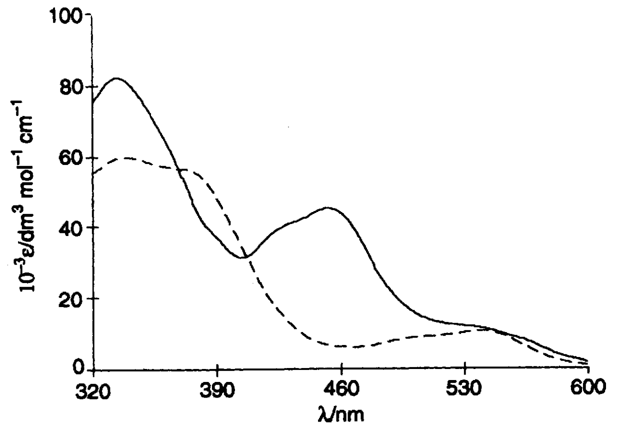


Fig. 6 Absorption spectra of the Ru_3Pt_3Fe **8a** (—) and Re_3Pt_3Fe **8c** (– – –) complexes in acetone solution at room temperature

measured in acetonitrile solution at 295 K for the Os^{II}- and Re^{I}-containing heptanuclear systems **8b** and **8c** remained very similar to those characterized for the simpler systems (Table 5). These complexes have relatively short-lived excited triplet states such that intramolecular triplet energy transfer to the central iron(II) complex is unable to compete with non-radiative deactivation of the triplet state. The inherent triplet lifetime is much longer for the terminal ruthenium(II) complex and, in this case, intramolecular triplet energy transfer appears to take place. Thus, the triplet lifetime measured for the terminal ruthenium(II) complexes in **8a** is 550 ns, which can be compared with that recorded for **7a** (τ_t = 1.3 µs) under identical conditions. On this basis, the rate constant for intramolecular triplet energy transfer can be estimated as being *ca.* $10^6\ s^{-1}$. This is a modest rate constant which is inconsistent with effective through-bond electron exchange between the reacting metal complexes[11] but seems entirely consistent with the concept of triplet localization. In this latter case, triplet energy transfer is most likely to proceed by way of a Förster dipole–dipole mechanism.

Conclusion

The peripheral metal complexes of the Pt^{II}-assembled molecular systems described herein possess relatively long-lived excited triplet states such that they could be expected to function as effective photosensitizers. It is further shown that the platinum(II) complex does not quench the excited states of these terminal photoactive subunits. This is because molecular orbitals associated with the platinum(II) centre are situated at too high energy to favour energy- or electron-transfer processes, even with the rhenium(I) complex. However, photons collected by the central Pt^{II} site are rapidly and quantitatively transferred to the terminal metal complexes. The platinum(II) centre, therefore, functions as a light-harvesting antenna, albeit for near-UV light. It is pertinent to recall that this centre is resistant towards light-induced isomerization such that the stereochemistry of the assembly remains intact under illumination. Although we have concentrated on metal complexes assembled around 2,2′-bipyridyl ligands, the corresponding 2,2′:6′,2″-terpyridyl complexes are also readily accessible. These latter ligands provide for greater stereochemical control of the array but, at least in the case of ruthenium(II) complexes at ambient temperature, do not form good photosensitizers.[30]

The synthetic methodology reported here can be easily adapted to produce higher-order oligomers, such as the heptanuclear complexes, and systems with increased spatial separation which might be suitable for use as artificial light-harvesting antennae. The heptanuclear arrays are rigid and the central iron(II) complex is a poor quencher of excited states associated with the peripheral metal complexes. Thus, this is a useful strategy for construction of well ordered and logically sited multicomponent systems. In the case of peripheral tris(2,2′-bipyridyl) complexes of Ru^{II} and Os^{II}, charge-transfer interactions within the bridging platinum(II) ethynyl-2,2′-bipyridyl metalloligands tend to localize the photon at the peripheral complex, because of preferential electron donation to the unsubstituted bipy ligands within the m.l.c.t. triplet state. This has the effect of minimizing through-bond interactions between individual chromophores such that these subunits are maintained in electronic isolation. This property of the assembly, which is much more pronounced than that observed with fused-alkane spacer moieties, serves to inhibit photon annihilation, to minimize the significance of (undesired) electron-transfer events and to favour long-range, through-space processes. The platinum(II)-alkyne connectors used here are especially appealing because of their synthetic versatility and simplicity.

Experimental

Nuclear magnetic resonance spectra were recorded on Brüker SY-200 or AC-200 instruments at 200.1 MHz for ^1H, 50.3 MHz for ^{13}C and 81.0 MHz for ^{31}P. The ^1H chemical shifts are reported in ppm relative to residual protiated solvents [δ 5.32 for CD_2Cl_2, δ 2.04 for $(CD_3)_2CO$ and δ 1.94 for CD_3CN], $^{13}C-\{^1H\}$ relative to CD_2Cl_2 (δ 53.85), $(CD_3)_2CO$ (δ 206.00, 29.80) and MeCN (δ 181.21, 1.32) and $^{31}P-\{^1H\}$ relative to external 85% H_3PO_4. Infrared spectra were obtained with an IFS 25 Brüker spectrometer, with the sample in the form of anhydrous KBr pellets. Fast atom bombardment (FAB, positive mode) spectra were recorded on a ZAB-HF-VB-analytical apparatus in *m*-nitrobenzyl alcohol matrices; Ar atoms were used for the bombardment (8 keV) and electrospray (ES) mass spectra were recorded on a Bio-Q-analytical apparatus, in acetone, using gramicidin as internal standard. Routine absorption spectra were measured in dichloromethane or acetone solutions at room temperature with Shimatzu UV-260 or Perkin-Elmer Lambda 5 spectrophotometers. Structural assignments are based on ^1H, $^{13}C-\{^1H\}$, $^{31}P-\{^1H\}$ NMR, IR, FAB^+ or ES mass spectra and elemental analysis. Solvents used for spectroscopic studies were spectral grade and were fractionally distilled before use.

For the photophysical investigations, absorption spectra were recorded in acetonitrile solution using an Hitachi U3210 spectrophotometer. Fluorescence spectra were recorded with a fully corrected Perkin-Elmer LS5 spectrofluorimeter, where necessary equipped with a red-sensitive detector. Fluorescence quantum yields were measured relative to tris(2,2′-bipyridyl)-ruthenium(II) in acetonitrile at 295 K[34] or in an ethanol glass at 77 K.[35] Absorption and fluorescence maxima were calculated by computer iteration. All luminescence studies were made with deoxygenated solutions having absorbance values less than 0.05 at the excitation wavelength. The corresponding low-temperature studies were made by slowly cooling an ethanol solution to 77 K in a quartz Dewar.

Transient absorption measurements were made with a frequency-doubled, mode-locked Quantel YG402 Nd:YAG laser (pulse duration 30 ps, maximum energy 25 mJ per pulse, 532 nm). In certain cases the output from the laser was frequency-tripled to provide excitation at 355 nm or Raman-shifted with benzene to provide excitation at 310 nm. The monitoring beam was provided with a pulsed, high-intensity xenon arc lamp and was detected with a fast-response, red-sensitive photomultiplier tube. Output was directed to a Tektronix SCD1000 transient recorder and subsequently to a microcomputer for storage and analysis. Transient differential absorption spectra were recorded point-by-point with five individual laser shots being averaged at each wavelength. Kinetic studies were made at fixed wavelength with 100 individual laser shots being computer averaged and corrected for minor changes in the profile of the baseline. Data analysis was by non-linear, least-squares iteration. Luminescence lifetimes were measured with the same instrument operated without the monitoring beam. The time resolution of the spectrometer, after deconvolution of the detector response function, was about 1 ns. All solutions were adjusted to possess an absorbance of about 0.15 at the excitation wavelength and were deoxygenated before and during the experiment by purging with Ar. For low-temperature studies the sample cell was housed in a quartz Dewar and was cooled to 77 K by slow addition of liquid N_2.

Electrochemical studies were made by cyclic voltammetry with a conventional three-electrode system using a Pine Instruments potentiostat connected to an X-Y chart recorder. The working electrode was a highly polished glassy carbon disc while the counter electrode was a platinum wire. A saturated calomel reference electrode was separated from the solution by a glass frit. Solutions contained the electrode-active substrate (2×10^{-4} mol dm^{-3}) and tetra-*n*-butylammonium tetrafluoroborate (0.2 mol dm^{-3}) as supporting electrolyte. All solutions were deoxygenated by purging with Ar prior to electrolysis. The quoted redox potentials were reproducible to within 10 mV.

X-Ray Crystallography.—Pale yellow, single crystals of complex **3** were grown by slow evaporation of dichloromethane from a dichloromethane–toluene solution at room temperature. A single crystal was cut out from a cluster of crystals and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using an Enraf-Nonius CAD4-F automatic diffractometer showed that the crystals belong to the monoclinic space group. Quantitative data were obtained at room temperature. All experimental parameters used are given in Table 1. The resulting data set was transferred to a VAX computer and the Enraf-Nonius MOLEN package[54] was used for all subsequent calculations. Three standard reflections measured every hour during the entire data collection period showed no significant change. The raw data were converted into intensities and corrected for Lorentz and polarization factors. Absorption corrections derived from the ψ scans of four reflections were applied. The structure was solved using the heavy-atom method. After refinement of the heavy atoms, a Fourier-difference map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced into structure-factor calculations by their computed coordinates (C–H 0.95 Å) and isotropic thermal parameters such as $B(H) = 1.3\ B_{eq}(C)$ Å^2 but not refined. Full least-squares refinements were calculated from $\sigma^2(F^2) = \sigma^2$ counts + $(pI)^2$. A final difference map revealed no significant maxima. The scattering-factor coefficients and anomalous-dispersion coefficients, respectively, were taken from ref. 55(*a*) and 55(*b*).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Materials.—Tri-*n*-butylphosphine, 2,2′-bipyridine, CuI and diisopropylamine were obtained from Aldrich Chemical Co. 4-Ethynyl-2,2′-bipyridine **I**,[20] 4′-ethynyl-2,2′:6′,2″-terpyridine **II**,[56] 4′-butadiynyl-2,2′:6′,2″;-terpyridine **III**,[57] *trans*-[Pt(PBu^n_3)Cl_2],[58] *cis*-[Pt(PBu^n_3)Cl_2],[58] *cis*-[Ru(bipy)$_2$$Cl_2$]·$2H_2O$,[59] *cis*-[Os(bipy)$_2$$Cl_2$][31] and [Re(CO)$_5$Cl][60] were prepared and purified according to literature procedures. All reactions were carried out under dry argon using Schlenk-tube and vacuum-line techniques. Solvents, including diisopropylamine, were dried over suitable reagents and freshly distilled under argon before use.

Preparations.—trans-*Bis*(2,2′-*bipyridin*-4-*ylethynyl*)*bis*(*tri*-n-*butylphosphine*)*platinum*(II) **1**. A solution of CuI (0.0025 mmol) in acetonitrile (2 cm^3) was added dropwise to a solution of 4-ethynyl-2,2′-bipyridine **I** (0.400 g, 2.22 mmol) and *trans*-[Pt(PBu^n_3)$_2$$Cl_2$] (0.744 g, 1.1 mmol) in anhydrous tetrahydrofuran (20 cm^3) containing diisopropylamine (5 cm^3). During the course of reaction (25 °C) a white precipitate was formed. After complete consumption of the starting material (TLC, 5 d), the suspension was filtered over paper. The filtrate was concentrated by rotary evaporation to give a crude product which was purified by column chromatography (alumina), eluting with dichloromethane. Recrystallization of the product by slow diffusion of hexane into a dichloromethane solution afforded the analytically pure compound **1**. The crystals were filtered off and dried under high vacuum (0.850 g, 81%). TLC (alumina, CH_2Cl_2) $R_f = 0.40$ (Found: C, 59.85; H, 7.00; N, 5.60. $C_{48}H_{68}N_4P_2Pt$ requires C, 60.15; H, 7.15; N, 5.85%). NMR (CD_2Cl_2): ^1H, δ 0.98 [t, 18 H, $P(CH_2)_3C\mathit{H}_3$, $^3J = 7.0$], 1.60 [m, 24 H, $PCH_2(C\mathit{H}_2)_2CH_3$], 2.17 [m, 12 H, $PC\mathit{H}_2(CH_2)_2CH_3$], 7.15 (d, 2 H, $^3J = 4.9$), 7.29 (m, 2 H), 7.81 (td, 2 H, $^3J = 7.7$, $^4J = 1.7$), 8.33 (s, 2 H), 8.42 (d, 2 H, $^3J = 7.9$), 8.50 (d, 2 H, $^3J = 4.9$) and 8.66 (d, 2 H, $^3J = 3.9$); ^{13}C-{^1H}, δ 14.08 (CH_3), 23.81–27.05 ($P\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_3$), 108.32 ($CC_{ethynyl}$), 117.43 ($CC_{ethynyl}$), 121.11 (CH), 122.91 (CH), 123.93 (CH), 125.54 (CH), 137.05 (CH), 137.77 (CC), 149.11 (CH), 149.44 (CH), 156.09 (CC) and 156.69 (CC); ^{31}P-{^1H}, δ +3.95 (pseudo t, $J_{PPt} = 2317$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 3045m, 2960s, 2867s, 2097vs ($\nu_{C\equiv C}$), 1585vs, 1456vs, 1382vs, 1093s, 988s, 900vs, 799s, 728s, 549m and 407m. FAB$^+$: *m*/*z* 958 [M + H]$^+$, 814 [$M - C_4H_9$], 756 [$M - PBu^n_3$], 598 [$M - 2C{\equiv}CC_{10}H_7N_2$] and 391 [$M - 2C{\equiv}CC_{10}H_7N_2 - PBu^n_3$]. UV/VIS ($CH_2Cl_2$): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 246 (10 500), 276 (23 700) and 334 (4900).

cis-*Bis*(2,2′-*bipyridin*-4-*ylethynyl*)*bis*(*tri*-n-*butylphosphine*)-*platinum*(II) **2**. Following the procedure described for complex **1**, reaction of **I** (0.0406 g, 0.22 mmol) and *cis*-[Pt(PBu^n_3)$_2$$Cl_2$] (0.0755 g, 0.11 mmol) afforded a white compound which was filtered off to give analytically pure **2** (0.093 g, 86%). TLC (alumina, ethyl acetate–hexane 1:4) $R_f = 0.57$ (Found: C, 59.80; H, 6.90; N, 5.60. $C_{48}H_{68}N_4P_2Pt$ requires C, 60.15; H, 7.15; N, 5.85%). NMR (CD_2Cl_2): ^1H, δ 0.95 [t, 18 H, $P(CH_2)_3C\mathit{H}_3$, $^3J = 6.7$], 1.37 [m, 24 H, $PCH_2(C\mathit{H}_2)_2CH_3$], 2.04 [m, 12 H, $PC\mathit{H}_2(CH_2)_2CH_3$], 7.25 (m, 4 H), 7.77 (td, 2 H, $^3J = 7.5$, $^4J = 1.7$), 8.34 (m, 4 H), 8.45 (d, 2 H, $^3J = 5.0$ Hz) and 8.62 (d, 2 H, $^3J = 3.9$); ^{13}C-{^1H}, δ 14.27 (CH_3), 24.12–27.18 ($P\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_3$), 113.03 ($CC_{ethynyl}$), 113.46 ($CC_{ethynyl}$), 115.86 ($CC_{ethynyl}$), 116.26 ($CC_{ethynyl}$), 121.08 (CH), 122.84 (CH), 123.80 (CH), 125.85 (CH), 136.91 (CC), 137.11 (CC), 149.01 (CH), 149.44 (CH), 156.02 (CC) and 156.63 (CC); ^{31}P-{^1H}, δ −2.87 (pseudo t, $J_{PPt} = 2252$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 3056m, 2955vs, 2926vs, 2867vs, 2115vs ($\nu_{C\equiv C}$), 1585vs, 1455s, 1382vs, 1285m, 1092s, 906m and 794s. FAB$^+$: *m*/*z* 958 [M + H]$^+$, 756 [$M - PBu^n_3$], 599 [$M - 2C{\equiv}CC_{10}H_7N_2 + H^+$], 541 [$M - 2C{\equiv}CC_{10}H_7N_2 - C_4H_9$], 485 [$M - 2\,C{\equiv}CC_{10}H_7N_2 - 2C_4H_9$], 429 [$M - 2\,C{\equiv}CC_{10}H_7N_2 - 3C_4H_9$] and 391 [$M - 2\,C{\equiv}CC_{10}H_7N_2 - PBu^n_3$]. UV/VIS ($CH_2Cl_2$): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 256 (43 900), 278 (54 500) and 316 (17 200).

trans-*Bis*(2,2′:6′,2″-*terpyridin*-4′-*ylethynyl*)*bis*(*tri*-n-*butylphosphine*)*platinum*(II) **3**. Following the procedure described for complex **1**, reaction of **II** (0.050 g, 0.194 mmol) and *trans*-[Pt(PBu^n_3)$_2$$Cl_2$] (0.065 g, 0.097 mmol) afforded a yellow compound which was filtered off. Subsequent purification gave **3** in an analytically pure form (0.091 g, 84%). TLC (alumina, ethyl acetate–hexane 1:19) $R_f = 0.60$ (Found: C, 62.65; H, 6.80; N, 7.35. $C_{58}H_{74}N_6P_2Pt$ requires C, 62.65; H, 6.70; N, 7.55%). NMR (CD_2Cl_2): ^1H, δ 0.99 [t, 18 H, $P(CH_2)_3C\mathit{H}_3$, $^3J = 7.1$), 1.62 [m, 24 H, $PCH_2(C\mathit{H}_2)_2CH_3$], 2.22 [m, 12 H, $PC\mathit{H}_2(CH_2)_2CH_3$], 7.33 (dddd, 4 H, $^3J = 7.4$, 4.8, $^4J = 1.3$), 7.86 (td, 4 H, $^3J = 7.7$, $^4J = 1.8$), 8.34 (s, 4 H), 8.59 (m, 2 H), 8.63 (m, 2 H), 8.67 (m, 2 H) and 8.70 (m, 2 H); ^{13}C-{^1H}, δ 14.09 (CH_3), 24.20–27.11 ($P\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2CH_3$), 108.81 ($CC_{ethynyl}$), 117.64 ($CC_{ethynyl}$), 121.21 (CH), 122.89 (CH), 123.97 (CH), 137.02 (CH), 138.78 (CC), 149.50 (CH), 155.50 (CC) and 156.82 (CC); ^{31}P-{^{1}H}, δ +3.92 (pseudo t, $J_{PPt} = 2317$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2924vs, 2857vs, 2104s ($\nu_{C\equiv C}$), 1581vs, 1463vs, 1385vs, 1265s, 1121s, 1039m, 899m, 794m, 737m and 621m. FAB$^+$: *m/z* 1112 $[M + H]^+$, 909 $[M - PBu^n_3]$, 709 $[M - 2PBu^n_3]$ and 452 $[M - 2PBu^n_3 - C{\equiv}CC_{15}H_{10}N_3]$. UV/VIS ($CH_2Cl_2$): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 254 (23 850), 288 (37 400) and 336 (21 400).

trans-*Bis*(2,2′:6′,2″-*terpyridin-4′-ylbutadiynyl*)*bis*(*tri*-n-*butylphosphine*)*platinum*(II) **4**. Following the procedure described for complex **1**, reaction of **III** (0.020 g, 0.071 mmol) and *trans*-$[Pt(PBu^n_3)_2Cl_2]$ (0.024 g, 0.035 mmol) afforded a yellow compound which was filtered off. Subsequent purification gave **3** (0.032 g, 78%). TLC (alumina, CH_2Cl_2) $R_f = 0.60$ (Found: C, 64.05; H, 6.60; N, 7.20. $C_{62}H_{74}N_6P_2Pt$ requires C, 64.20; H, 6.65; N, 7.25%). Fourier-transform IR (KBr pellets, cm^{-1}): 2953s, 2925s, 2866m, 2178vs ($\nu_{C\equiv C}$), 2054s, 1581s, 1563s, 1462s, 1388s, 1264m, 1088m, 1047s, 894s, 790s and 614m. FAB$^+$: *m/z* 1161 $[M + H]^+$, 958 $[M - PBu^n_3]$ and 757 $[M - 2PBu^n_3]$. UV/VIS (CH_2Cl_2): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 287 (136 500), 343 (89 300) and 360 (89 800).

cis-*Bis*(2,2′:6′,2″-*terpyridin-4′-ylethynyl*)*bis*(*tri*-n-*butylphosphine*)*platinum*(II) **5**. Following the procedure described for complex **1**, reaction of **II** (0.050 g, 0.194 mmol) and *trans*-$[Pt(PBu^n_3)_2Cl_2]$ (0.065 g, 0.097 mmol) afforded a white compound which was filtered off. Subsequent purification gave **5** (0.092 g, 85%). TLC (alumina, ethyl acetate–hexane 3:2) $R_f = 0.38$ (Found: C, 62.50; H, 6.50; N, 7.35. $C_{58}H_{74}N_6P_2Pt$ requires C, 62.65; H, 6.70; N, 7.55%). NMR (CD_2Cl_2): ^{1}H, δ 1.01 [t, 18 H, $P(CH_2)_3CH_3$, $^{3}J = 6.8$], 1.57 [m, 24 H, $PCH_2(CH_2)_2CH_3$], 2.08 [m, 12 H, $PCH_2(CH_2)_2CH_3$], 7.30 (m, 4 H), 7.83 (t, 4 H, $^{3}J = 7.4$), 8.47 (s, 4 H), 8.57 (m, 2 H), 8.61 (m, 2 H), 8.65 (m, 2 H) and 8.67 (m, 2 H); ^{13}C-{^{1}H}, δ 14.00 (CH_3), 24.44–27.23 ($PCH_2CH_2CH_2CH_3$), 113.08 ($CC_{ethynyl}$), 113.49 ($CC_{ethynyl}$), 115.90 ($CC_{ethynyl}$), 116.32 ($CC_{ethynyl}$), 121.21 (CH), 123.11 (CH), 123.83 (CH), 136.87 (CH), 138.15 (CC), 149.47 (CH), 155.48 (CC) and 156.78 (CC); ^{31}P-{^{1}H}, δ −2.95 (pseudo t, $J_{PPt} = 2246$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 3057w, 2957vs, 2927vs, 2867vs, 2117vs ($\nu_{C\equiv C}$), 1581vs, 1463vs, 1388vs, 1264m, 1120s, 1093s, 990m, 909s, 794vs, 738s, 660w and 621m. FAB$^+$: *m/z* 1112 $[M + H]^+$, 909 $[M - PBu^n_3]$, 709 $[M - 2PBu^n_3]$, 597 $[M - 2C{\equiv}CC_{15}H_{10}N_3]$, 452 $[M - 2PBu^n_3 - C{\equiv}CC_{15}H_{10}N_3]$. UV/VIS ($CH_2Cl_2$): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 256 (175 400), 280 (271 400) and 310 (89 800).

Complex **6a**. To ethanol–water (4:1, 40 cm^3) containing complex **1** (0.030 g, 0.031 mmol) was added *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.016 g, 0.031 mmol). The mixture was heated at reflux for 15 h, then concentrated to *ca.* 10 cm^3 before addition of an excess of NH_4PF_6 in distilled water. The resultant red-orange precipitate was filtered off, then dissolved in the minimum volume of methanol, followed by slow diffusion of diethyl ether. This recrystallization process was repeated twice and afforded the analytically pure complex **6a** (0.044 g, 86%) (Found: C, 48.85; H, 4.80; N, 6.50. $C_{68}H_{84}F_{12}N_8P_4PtRu$ requires C, 49.15; H, 5.10; N, 6.75%). NMR [$(CD_3)_2CO$]: ^{1}H, δ 0.91 [t, 18 H, $P(CH_2)_3CH_3$, $^{3}J = 7.4$], 1.38–1.71 [m, 24 H, $PCH_2(CH_2)_2CH_3$], 2.23 [m, 12 H, $PCH_2(CH_2)_2CH_3$] and 7.25–8.82 (aromatic protons, m, 30 H); ^{13}C-{^{1}H}, δ 14.06 (CH_3), 24.48–27.36 ($PCH_2CH_2CH_2CH_3$), 108.60 ($CC_{ethynyl}$), 109.26 ($CC_{ethynyl}$), 111.61 ($CC_{ethynyl}$), 111.83 ($CC_{ethynyl}$), 121.54 (CH), 123.12 (CH), 124.81 (CH), 125.27 (CH), 125.86 (CH), 128.65 (CH), 129.61 (CH), 138.00 (CH), 138.80 (CH), 148.61 (CC), 148.99 (CC), 150.01 (CH), 151.64 (CH), 152.44 (CH), 152.58 (CH), 155.28 (CC), 155.68 (CC), 157.41 (CC) and 158.01 (CC); ^{31}P-{^{1}H}, δ +4.96 (pseudo t, $J_{PPt} = 2294$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2927s, 2862s, 2090s ($\nu_{C\equiv C}$), 1601s, 1525w, 1463s, 1208w, 1098m, 842s, 764m, 621w and 559s. FAB$^+$: *m/z* 1517 $[M - PF_6]^+$, 1372 $[M - 2PF_6]$ and 958 $[M - Ru(bipy)_2 - 2PF_6 + H]$. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 288 (95 700), 334 (28 900) and 458 (15 200).

Complex **7a**. Following the procedure described for complex **6a**, reaction of **1** (0.030 g, 0.031 mmol) and *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.032 g, 0.062 mmol) afforded the red-orange compound **7a** (0.062 g, 85%) (Found: C, 44.45; H, 4.10; N, 6.95. $C_{88}H_{100}F_{24}N_{12}P_6PtRu_2$ requires C, 44.70; H, 4.25; N, 7.10%). NMR [$(CD_3)_2CO$]: δ 0.87 [t, 18 H, $P(CH_2)_3CH_3$, $^{3}J = 7.3$], 1.35–1.67 [m, 24 H, $PCH_2(CH_2)_2CH_3$], 2.21 [m, 12 H, $PCH_2(CH_2)_2CH_3$] and 7.26–8.81 (aromatic protons, m, 46 H); ^{13}C-{^{1}H}, δ 14.02 (CH_3), 24.08–27.01 ($PCH_2CH_2CH_2CH_3$), 108.41 ($CC_{ethynyl}$), 121.04 ($CC_{ethynyl}$), 124.53, 124.98, 125.51, 128.38, 129.29, 138.17, 138.49, 149.67, 151.36, 152.13, 152.28, 157.58 and 157.66; ^{31}P-{^{1}H}, δ +5.01 (pseudo t, $J_{PPt} = 2281$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2927m, 2082m ($\nu_{C\equiv C}$), 1603s, 1466s, 1128s, 842vs, 764s, 620m and 558s. FAB$^+$: *m/z* 2222 $[M + 2H - PF_6]$, 2076 $[M + 2H - 2PF_6]$, 1929 $[M - 3PF_6]$, 1518 $[M - 3PF_6 - Ru(bipy)_2 + H]$ and 1371 $[M - 4PF_6 - Ru(bipy)_2]$. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 248 (87 200), 256 (94 600), 286 (220 000), 334 (27 100) and 456 (31 200).

Complex **6b**. A mixture of complex **1** (0.100 g, 0.104 mmol) and *cis*-$[Os(bipy)_2Cl_2]$ (0.060 g, 0.104 mmol) in ethanol (40 cm^3) was heated at 90 °C for 3 d then concentrated to *ca.* 10 cm^3 before addition of an excess of NH_4PF_6 in distilled water. The dark green precipitate formed was purified by column chromatography (alumina), eluting with MeCN–toluene (1:1). Recrystallization by slow diffusion of ether into an acetone solution afforded the analytically pure dark green compound **6b**. The crystals were filtered off and dried under high vacuum (0.076 g, 42%). TLC (alumina, toluene–MeCN 1:1) $R_f = 0.45$ (Found: C, 46.50; H, 4.70; N, 6.35. $C_{68}H_{84}F_{12}N_8OsP_4Pt$ requires C, 46.65; H, 4.85; N, 6.40%). NMR [$(CD_3)_2CO$]: ^{1}H, δ 0.89 [t, 18 H, $P(CH_2)_3CH_3$, $^{3}J = 6.8$], 1.41–1.65 [m, 24 H, $PCH_2(CH_2)_2CH_3$], 2.18 [m, 12 H, $PCH_2(CH_2)_2CH_3$] and 7.17–8.76 (aromatic protons, m, 30 H); ^{13}C-{^{1}H}, δ 14.07 (CH_3), 24.43–27.33 ($PCH_2CH_2CH_2CH_3$), 108.19 ($CC_{ethynyl}$), 108.99 ($CC_{ethynyl}$), 121.31 ($CC_{ethynyl}$), 122.85 ($CC_{ethynyl}$), 125.02, 125.39, 125.50, 125.98, 129.14, 129.87, 137.62, 138.10, 150.71, 151.52, 151.67, 151.74, 159.27, 159.79 and 160.01; ^{31}P-{^{1}H}, δ +5.03 (pseudo t, $J_{PPt} = 2294$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2973s, 2926s, 2870s, 2083vs ($\nu_{C\equiv C}$), 1603s, 1580s, 1460vs, 1262m, 1089vs, 1048vs, 841vs and 557vs. FAB$^+$ (2,5,8,11,14-pentaoxapentadecane): *m/z* 1605 $[M - PF_6]^+$, 1460 $[M - 2PF_6]$ and 958 $[M - Os(bipy)_2 - 2PF_6 + H]$. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 284 (46 600), 336 (14 500), 481 (7750) and 627 (1800).

Complex **7b**. A mixture of complex **1** (0.042 g, 0.044 mmol) and *cis*-$[Os(bipy)_2Cl_2]$ (0.05 g, 0.088 mmol) in ethanol (40 cm^3) was heated at 90 °C for 3 weeks then concentrated to *ca.* 10 cm^3 before addition of an excess of KPF_6 (0.04 g, 0.40 mmol) in distilled water. Partial removal of the solvent by rotary evaporation gave the crude product, which was subsequently purified by column chromatography (alumina), eluting with water–MeCN–KNO_3 (15:50:1). Elimination of excess of KNO_3 and anion metathesis to the PF_6^- salt was performed by dissolving the nitrate complex and excess of KNO_3 in the minimum of water (*ca.* 10 cm^3) followed by addition of an excess of KPF_6 in water to precipitate the crude compound. Recrystallization by slow diffusion of ether into an acetone solution afforded the analytically pure dark green compound **7b**. The crystals were filtered off and dried under high vacuum (0.020 g, 18%). TLC (alumina, water–MeCN–KNO_3 15:50:1) $R_f = 0.60$ (Found: C, 41.40; H, 3.80; N, 6.55. $C_{88}H_{100}F_{24}N_{12}Os_2P_6Pt$ requires C, 41.55; H, 3.95; N, 6.60%). NMR [$(CD_3)_2CO$]: ^{1}H, δ 0.86 [t, 18 H, $P(CH_2)_3CH_3$, $^{3}J = 7.2$], 1.38–1.64 [m, 24 H, $PCH_2(CH_2)_2CH_3$], 2.17 [m, 12 H, $PCH_2(CH_2)_2CH_3$] and 7.11–7.99 (aromatic protons, m, 46 H); ^{13}C-{^{1}H}, δ 13.87 (CH_3), 24.16–26.87 ($PCH_2CH_2CH_2CH_3$), 108.24 ($CC_{ethynyl}$), 114.85 ($CC_{ethynyl}$), 125.15, 126.54, 128.31, 128.90, 129.48, 129.92, 137.86, 150.80, 151.31, 151.53, 152.05, 152.85, 153.96, 159.18 and 160.72; ^{31}P-{^{1}H}, δ +5.21 (pseudo t, $J_{PPt} = 2279$ Hz). Fourier-transform IR (KBr pellets, cm^{-1}):

2975vs, 2926vs, 2081s ($\nu_{C\equiv C}$), 1636s, 1603s, 1463s, 1262m, 1088s, 1047vs, 842vs, 765m and 557vs. FAB$^+$(2,5,8,11,14-pentaoxapentadecane): *m/z* 2398 [*M* − PF$_6$]$^+$, 2253 [*M* − 2PF$_6$], 2108 [*M* − 3PF$_6$], 1605 [*M* − Os(bipy)$_2$ − 3PF$_6$ + H] and 1458 [*M* − Os(bipy)$_2$ − 4PF$_6$ − H]. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 284 (78 100), 340 (21 400), 481 (15 600) and 626 (6800).

Complex **6c**. A solution of toluene (50 cm^3) containing [Re(CO)$_5$Cl] (0.038 g, 0.104 mmol) and complex **1** (0.100 g, 0.104 mmol) was heated progressively from 20 to 80 °C over 40 min. Then the yellow solution was concentrated by rotary evaporation to give a crude product which was purified by column chromatography (silica), eluting with MeCN–toluene (1:9). After recrystallization of the crude product from hot hexane, the yellow crystals of analytically pure **6c** were filtered off and dried under high vacuum (0.032 g, 24%). TLC (silica, MeOH–CH$_2$Cl$_2$ 1:19) R_f = 0.59 (Found: C, 48.30; H, 5.25; N, 4.30. $C_{51}H_{68}ClN_4O_3P_2PtRe$ requires C, 48.45; H, 5.40; N, 4.45%). NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 0.95 [t, 18 H, P(CH$_2$)$_3$C*H*$_3$, ^3J = 7.2], 1.42–1.74 [m, 24 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$], 2.18–2.28 [m, 12 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$], 7.19 (dd, 1 H, ^3J = 5.0, ^4J = 1.5), 7.40 (12-line multiplet, 2 H), 7.77 (m, 1 H), 7.90 (td, 1 H, ^3J = 7.7, ^4J = 1.8), 8.27 (s, 1 H), 8.33 (dd, 1 H, ^3J = 7.8, ^4J = 1.5), 8.38 (s, 1 H), 8.44–8.57 (m, 3 H), 8.66 (d, 1 H, ^3J = 4.0), 8.86 (d, 1 H, ^3J = 5.8) and 9.09 (d, 1 H, ^3J = 4.8); ^{13}C-{^{1}H}, δ 14.13 (CH$_3$), 24.55–27.43 (P*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 108.89 (CC$_{ethynyl}$), 109.08 (CC$_{ethynyl}$), 116.57 (CC$_{ethynyl}$), 116.83 (CC$_{ethynyl}$), 121.34, 122.89, 124.39, 124.66, 125.45, 125.75, 128.18, 129.12, 137.62, 140.53, 149.72, 149.97, 153.85, 156.18, 156.47, 156.80, 190.99 (CO) and 199.13 (2CO); ^{31}P-{^{1}H}, δ +5.02 (pseudo t, J_{PPt} = 2299 Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2954s, 2867s, 2095vs ($\nu_{C\equiv C}$), 2017vs (ν_{CO}), 1924vs (ν_{CO}), 1878vs (ν_{CO}), 1602s, 1454s, 1206w, 1089s, 1048s, 878w, 789s, 620w and 534w. FAB$^+$: *m/z* 1264 [*M* + H]$^+$, 1228 [*M* − Cl + H] and 958 [*M* − Re(CO)$_3$Cl + H]. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 289 (27 200) and 364 (19 700).

Complex **7c**. A solution of [Re(CO)$_5$Cl] (0.038 g, 0.104 mmol) and complex **1** (0.05 g, 0.052 mmol) in toluene (50 cm^3) was heated at 90 °C for 6 h. During the course of reaction a yellow precipitate was formed. The mixture was cooled at 0 °C overnight. Filtration through a glass frit yielded a yellow solid and a yellow-orange solution. The solid, subsequently analysed as **7c**, was washed three times with 10 cm^3 portions of ether and dried by suction. The filtrate was concentrated by rotary evaporation to give a crude product which was purified by column chromatography (silica), eluting with dichloromethane. Recrystallization of the precipitate by slow diffusion of hexane into a dichloromethane solution afforded the yellow analytically pure compound **7c** (0.061 g, in total 78%). TLC (silica, MeOH–CH$_2$Cl$_2$ 1:19) R_f = 0.18 (Found: C, 41.25; H, 4.30; N, 3.45. $C_{54}H_{68}Cl_2N_4O_6P_2PtRe_2$ requires C, 41.30; H, 4.35; N, 3.55%). NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 0.93 [t, 18 H, P(CH$_2$)$_3$C*H*$_3$, ^3J = 7.2], 1.48–1.72 [m, 24 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$], 2.24 [m, 12 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$], 7.46 (dd, 2 H, ^3J = 5.8, ^4J = 1.6), 7.76 (m, 2 H), 8.27 (m, 4 H), 8.53 (d, 2 H, ^3J = 8.1), 8.86 (d, 2 H, ^3J = 5.8) and 9.08 (d, 2 H, ^3J = 4.6); ^{13}C-{^{1}H}, δ 13.83 (CH$_3$), 24.22–27.13 (P*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 108.86 (CC$_{ethynyl}$), 119.37 (CC$_{ethynyl}$), 124.04, 125.14, 127.97, 128.85, 140.28, 132.00, 152.90, 153.60, 156.27, 156.46, 190.67 (CO) and 198.76 (2CO); ^{31}P-{^{1}H}, δ +5.24 (pseudo t, J_{PPt} = 2273 Hz). Fourier-transform (KBr pellets, cm^{-1}): 2962vs, 2931vs, 2869vs, 2085vs ($\nu_{C\equiv C}$), 2019vs (ν_{CO}), 1911vs (ν_{CO}), 1888vs (ν_{CO}), 1727vs, 1599vs, 1467vs, 1275vs, 1124vs, 1072s, 788m, 626w, 580w, 523w and 482w. FAB$^+$: *m/z* 1568 [M + H]$^+$, 1533 [*M* − Cl + H] and 1227 [*M* − Re(CO)$_3$ − 2Cl]. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 282 (111 000), 335 (43 700) and 392 (36 200).

Complex **7c′**. A solution of *cis*-[Pt(PBu$^n{}_3$)$_2$Cl$_2$] (0.020 g, 0.030 mmol) and [Ru(bipy)$_2$l][PF$_6$]$_2$ (0.052 g, 0.015 mmol) was prepared in a mixture of anhydrous tetrahydrofuran (20 cm^3), anhydrous acetonitrile (10 cm^3) and diisopropylamine (5 cm^3). A solution of CuI (0.0007 mmol) in acetonitrile (1 cm^3) was added dropwise. During the course of reaction (25 °C) the required product precipitated. After complete consumption of the starting material (TLC, 5 d) the suspension was filtered over paper. The reaction mixture was then concentrated to *ca.* 10 cm^3 before addition of an excess of NH$_4$PF$_6$ (0.0097 g, 0.059 mmol) in distilled water. A red-orange precipitate was formed which was dissolved in the minimum of acetonitrile, followed by slow diffusion of ether. This recrystallization was repeated twice and afforded the analytically pure complex **7c′** (0.055 g, 78%) (Found: C, 44.40; H, 4.00; N, 6.80. $C_{88}H_{100}F_{24}N_{12}P_6PtRu_2$ requires C, 44.70; H, 4.25; N, 7.10%). NMR [(CD$_2$)$_2$CO]: ^{1}H, δ 0.85 [t, 18 H, P(CH$_2$)$_3$C*H*$_3$, ^3J = 7.1], 1.35–1.59 [m, 24 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$], 2.08 [m, 12 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$] and 7.02–8.54 (aromatic protons, m, 46 H); ^{31}P-{^{1}H}, δ −2.08 (pseudo t, J_{PPt} = 2255 Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 3087w, 2957s, 2929s, 2869s, 2116s ($\nu_{C\equiv C}$), 1603vs, 1466vs, 1443vs, 1126vs, 848vs, 763vs, 621w, 557vs and 446w. FAB$^+$: *m/z* 2222 [*M* + 2H − PF$_6$], 2076 [*M* + 2H − 2PF$_6$], 1929 [*M* − 3PF$_6$] and 1371 [*M* − 4PF$_6{}^-$ − Ru(bipy)$_2$ + H]. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 246 (106 700), 258 (123 400), 286 (247 200) and 456 (31 100).

Complex **8a**. To a solution of complex **6a** (0.014 g, 0.008 mmol) in ethanol–water (4:1, 20 cm^3) was added FeSO$_4$·7H$_2$O (0.0008 g, 0.003 mmol). After 10 min of exposure to ultrasonic irradiation (35 Hz, 800 W, *ca.* 20 °C), the mixture was concentrated to *ca.* 10 cm^3. Addition of an excess of NH$_4$PF$_6$ in distilled water resulted in the formation of a deep red precipitate, which was washed by decantation with water (3 × 10 cm^3) and dried under high vacuum during a few hours to give analytically pure **8a** (0.011 g, 91%) (Found: C, 45.55; H, 4.40; N, 6.10. $C_{204}H_{252}F_{48}FeN_{24}P_{14}Pt_3Ru_3$ requires C, 45.95; H, 4.75; N, 6.30%). NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 0.86 [t, 54 H, P(CH$_2$)$_3$C*H*$_3$, ^3J = 6.9], 1.38–1.64 [m, 72 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$], 2.17 (m, 36 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$] and 7.26–7.84 (aromatic protons, m, 90 H); ^{31}P-{^{1}H}, δ +5.02 (pseudo t, J_{PPt} = 2278 Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2955s, 2925s, 2868s, 2080vs ($\nu_{C\equiv C}$), 1601vs, 1466s, 1048s, 840vs and 557s. ES (in acetone, pseudo-molecular peaks): *m/z* 1187.3 [*M* − 4PF$_6$], 920.8 [*M* − 5PF$_6$] and 743.1 [M − 6PF$_6$]. UV/VIS (acetone): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 460 (45 100) and 530 (15 200).

Complex **8b**. Following the procedure described for complex **8a**, reaction of **6b** (0.021 g, 0.012 mmol) and FeSO$_4$·7H$_2$O (0.001 g, 0.004 mmol) afforded the deep green compound **8b** (0.017 g, 78%) (Found: C, 43.50; H, 4.45; N, 5.85. $C_{204}H_{252}F_{48}FeN_{24}Os_3P_{14}Pt_3$ requires C, 43.75; H, 4.55; N, 6.00%). NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 0.86 [t, 54 H, P(CH$_2$)$_3$C*H*$_3$, ^3J = 7.4], 1.38–1.64 [m, 72 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$], 2.14 [m, 36 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$] and 7.18–8.82 (aromatic protons, m, 90 H); ^{31}P-{^{1}H}, δ +5.14 (pseudo t, J_{PPt} = 2277 Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2926s, 2080s ($\nu_{C\equiv C}$), 1602s, 1463s, 1262w, 1089s, 1048vs, 839vs and 557vs. UV/VIS (acetone): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 338 (41 300), 481 (23 600), 536 (8700) and 638 (4700). ES (in acetone, pseudo-molecular peaks): *m/z* 1720.2 [*M* − 3PF$_6$], 1254.1 [*M* − 4PF$_6$], 974.2 [*M* − 5PF$_6$], 784.9 [*M* − 6PF$_6$] and 654.1 [*M* − 7PF$_6$].

Complex **8c**. Following the procedure described for complex **8a**, reaction of **6c** (0.02 g, 0.016 mmol) and FeSO$_4$·7H$_2$O (0.0014 g, 0.005 mmol) afforded the deep red compound **8c** (0.018 g, 81%) (Found: C, 44.15; H, 4.70; N, 3.80. $C_{153}H_{204}Cl_3F_{12}FeN_{12}O_9P_8Pt_3Re_3$ requires C, 44.40; H, 4.95; N, 4.05%). NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 0.91 [t, 54 H, P(CH$_2$)$_3$C*H*$_3$, ^3J = 6.9], 1.42–1.68 [m, 72 H, PCH$_2$(C*H*$_2$)$_2$CH$_3$], 2.21 [m, 36 H, PC*H*$_2$(CH$_2$)$_2$CH$_3$], 7.29–7.81 (m, 16 H), 8.27–8.35 (m, 9 H), 8.47–8.55 (m, 6 H), 8.73 (d, 3 H, ^3J = 7.4), 8.86 (d, 3 H, ^3J = 5.8) and 9.10 (d, 5 H, ^3J = 5.2); ^{31}P-{^{1}H}, δ +5.14 (pseudo t, J_{PPt} = 2272 Hz). Fourier-transform IR (KBr pellets, cm^{-1}): 2925vs, 2082vs ($\nu_{C\equiv C}$), 2016vs (ν_{CO}), 1910vs (ν_{CO}), 1887vs (ν_{CO}), 1653w, 1600vs, 1520w, 1470m, 1047vs, 839vs, 787m and 557m. UV/VIS (acetone): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 333 (62 300), 364 (56 800) and 538 (11 400). ES (in acetone, pseudo-molecular peaks): *m/z* 1923.1 [*M* − 2PF$_6$] (doubly charged peak obtained by high resolution).

[Ru(bipy)$_2$I][PF$_6$]$_2$. To ethanol–water (4:1, 40 cm^3) containing **I** (0.100 g, 0.555 mmol) was added *cis*-[Ru(bipy)$_2$Cl$_2$]·2H$_2$O (0.288 g, 0.555 mmol). The mixture was heated at reflux for 15 h, then concentrated to *ca.* 10 cm^3 before addition of NH$_4$PF$_6$ (0.268 g, 1.647 mmol) in distilled water. The resultant red-orange precipitate was filtered off, then dissolved in the minimum volume of methanol, followed by slow diffusion of diethyl ether. This recrystallization process was repeated twice and afforded the analytically pure complex [Ru(bipy)$_2$I][PF$_6$]$_2$ (0.325 g, 64%). TLC (alumina, MeCN) R_f = 0.75 (Found: C, 43.40; H, 2.70; N, 9.40. C$_{32}$H$_{24}$F$_{12}$N$_6$P$_2$PtRu requires C, 43.50; H, 2.75; N, 9.50%). NMR (CD$_3$CN): ^{1}H, δ 3.99 (s, 1 H) and 7.40–8.49 (aromatic protons, m, 23 H); ^{13}C-{^{1}H}, δ 87.65 (CC$_{ethynyl}$), 87.90 (CC$_{ethynyl}$), 125.28 (CH), 125.58 (CH), 127.56 (CH), 128.62 (CH), 128.92 (CH), 130.28 (CH), 132.23 (CC), 138.84 (CH), 138.95 (CH), 152.59 (CH), 152.74 (CH), 157.14 (CC), 157.89 (CC) and 158.57 (CC). Fourier-transform IR (KBr pellets, cm^{-1}): 3271m ($\nu_{C\equiv CH}$), 3086w, 2974w, 2117s ($\nu_{C\equiv C}$), 1585vs, 1466vs, 1444vs, 1313m, 1130s and 838vs. UV/VIS (MeCN): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 241 (42 400), 286 (93 700) and 451 (12 900). ES (in acetone, pseudo-molecular peaks): *m/z* 738.2 [M − PF$_6$] and 296.6 [M − 2PF$_6$].

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References

1 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.

2 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.

3 F. L. Carter, *Molecular Electronic Devices*, eds. R. E. Siatkowsky and H. Woltijen, North Holland, Amsterdam, 1988.

4 F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1991.

5 A. C. Benniston, V. Goulle, A. Harriman, J.-M. Lehn and B. Marczinke, *J. Phys. Chem.*, 1994, **98**, 7798.

6 J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.

7 D. Gust, *Nature (London)*, 1994, **372**, 133.

8 L. R. Khundkar, A. E. Stiegman and J. W. Perry, *J. Phys. Chem.*, 1990, **94**, 1224; A. Slama-Schwok, M. Blanchard-Desce and J.-M. Lehn, *J. Phys. Chem.*, 1990, **94**, 3894; S. R. Marder, C. B. Gorman, B. G. Tiemann and L.-T. Cheng, *J. Am. Chem. Soc.*, 1993, **115**, 3006.

9 J. L. Sessler, V. L. Capuano and A. Harriman, *J. Am. Chem. Soc.*, 1993, **115**, 4618; R. W. Wagner and J. S. Lindsey, *J. Am. Chem. Soc.*, 1994, **116**, 9759; H. L. Anderson, S. J. Martin and D. D. C. Bradley, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 655.

10 (*a*) F. Vögtle, M. Frank, M. Nieger, P. Belser, A. von Zelewsky, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1643; (*b*) F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable and A. M. W. Cargill-Thompson, *J. Chem. Soc., Chem. Commun.*, 1993, 942; (*c*) J.-P. Collin, P. Lainé, J.-P. Launay, J.-P. Sauvage and A. Sour, *J. Chem. Soc., Chem. Commun.*, 1993, 434; (*d*) L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank and F. Vögtle, *Inorg. Chem.*, 1993, **32**, 5229; (*e*) F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage, A. Sour, E. C. Constable and A. M. W. Cargill-Thompson, *J. Am. Chem. Soc.*, 1994, **116**, 7692; (*f*) J.-P. Sutter, D. M. Grove, M. Beley, J.-P. Collin, N. Veldman, A. L. Spek, J.-P. Sauvage and G. van Koten, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1282.

11 A. C. Benniston, V. Grosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1884.

12 A. C. Benniston, V. Grosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1100.

13 D. Touchard, P. Haquette, N. Pirio, L. Toupet and P. H. Dixneuf, *Organometallics*, 1993, **12**, 3132; J. Lewis, M. S. Khan, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittmann, R. H. Friend and A. E. Dray, *J. Organomet. Chem.*, 1992, **425**, 165; Y. Sun, N. J. Taylor and A. Carty, *Organometallics*, 1992, **11**, 4293; L. D. Field, A. V. George, T. W. Hambley, E. Y. Malouf and D. L. Young, *J. Chem. Soc., Chem. Commun.*, 1990, 931; R. R. Tykwinski and P. J. Stang, *Organometallics*, 1994, **13**, 3203.

14 C. LeVanda, D. O. Cowan, C. Leitch and K. Bechgaard, *J. Am. Chem. Soc.*, 1974, **96**, 6788; C. LeVanda, K. Bechgaard and D. O. Cowan, *J. Org. Chem.*, 1976, **41**, 2700; J. A. Kramer and D. N. Hendrickson, *Inorg. Chem.*, 1980, **19**, 3330; E. E. Bunel, L. Valle, N. L. Jones, P. J. Carroll, M. Gonzalez, N. Munoz and J. M. Manriquez, *Organometallics*, 1988, 7, 789; R. L. Blackbourn and J. T. Hupp, *J. Phys. Chem.*, 1990, **94**, 1788.

15 M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky and R. J. Jones, *Nature (London)*, 1987, **330**, 360; L.-T. Cheng, W. Tam, G. R. Meredith and S. R. Marder, *Mol. Cryst. Liq. Cryst.*, 1990, **189**, 137; S. R. Marder, J. W. Perry, B. G. Tiemann and W. P. Schaefer, *Organometallics*, 1991, **10**, 1896; J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227; Z. Yuan, N. J. Taylor, Y. Sun, T. B. Marder, I. D. Williams and L.-T. Cheng, *J. Organomet. Chem.*, 1993, **449**, 27.

16 M. Hissler and R. Ziessel, *J. Chem. Soc., Dalton Trans.*, 1995, 893; *New J. Chem.*, 1995, **19**, 751.

17 K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 1977, 291; S. Takahashi, M. Kiraya, T. Yatake, K. Sonogashira and N. Hagihara, *Macromolecules*, 1978, **11**, 1063; B. F. G. Johnson, A. K. Kakkar, M. S. Khan, J. Lewis, A. E. Dray, R. H. Friend and F. Wittman, *J. Mater. Chem.*, 1991, 485.

18 J. G. Mackay, H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1992, 43.

19 J. Suffert and R. Ziessel, *Tetrahedron Lett.*, 1991, **32**, 757.

20 V. Grosshenny and R. Ziessel, *Tetrahedron Lett.*, 1992, **33**, 8075.

21 V. Grosshenny and R. Ziessel, *J. Chem. Soc., Dalton Trans.*, 1993, 817.

22 F. M. Romero and R. Ziessel, *Tetrahedron Lett.*, 1994, **35**, 9203.

23 K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1978, **145**, 101.

24 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

25 L. L. Merritt, jun. and E. D. Schroeder, *Acta Crystallogr.*, 1956, **9**, 801; K. Nakatsu, H. Yoshioka, M. Matsui, S. Koda and S. Ooi, *Acta Crystallogr., Sect. A*, 1972, 24; M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress and W. H. Woodruff, *J. Am. Chem. Soc.*, 1981, **103**, 4945.

26 E. C. Constable, S. M. Elder, J. A. Healy and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 1010.

27 E. C. Constable, J. Lewis, M. C. Liptrot and P. R. Raithby, *Inorg. Chim. Acta*, 1990, **178**, 47.

28 A. C. Villa, A. G. Manfredotti and C. Guastini, *Cryst. Struct. Commun.*, 1976, **5**, 139; M. Ciriano, J. A. K. Howard, J. L. Spencer, F. G. A. Stone and H. Wadepohl, *J. Chem. Soc., Dalton Trans.*, 1979, 1749; A. Sebald, B. Wrackmeyer, C. R. Theocharis and W. Jones, *J. Chem. Soc., Dalton Trans.*, 1984, 747; H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto and H. Yamazaki, *Organometallics*, 1988, **7**, 2257.

29 V. W.-W. Yam, L.-P. Chan and T.-F. Lai, *J. Chem. Soc., Dalton Trans.*, 1993, 2075; F. Diederich, R. Faust, V. Gramlich and P. Seiler, *J. Chem. Soc., Chem. Commun.*, 1994, 2045.

30 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

31 E. M. Kober, J. V. Caspar, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1988, **27**, 4587.

32 J. V. Caspar and T. J. Meyer, *J. Phys. Chem.*, 1983, **87**, 952.

33 H. Masai, K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2226.

34 E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, 1985, **24**, 2755.

35 J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, 1971, **93**, 2841.

36 J. V. Caspar, E. M. Kober, B. P. Sullivan and T. M. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 630.

37 S. Boyde, G. F. Strouse, W. E. Jones, jun. and T. J. Meyer, *J. Am. Chem. Soc.*, 1990, **112**, 7395.

38 A. J. Downad, G. E. Honey, L. F. Phillips and P. J. Steel, *Inorg. Chem.*, 1991, **30**, 2259.

39 P. Braterman, A. Harriman, G. A. Heath and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1983, 1801.

40 Y. Ohsawa, K. W. Hanck and M. K. DeArmond, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, **175**, 229.

41 S. D. Ernst and W. Kaim, *Inorg. Chem.*, 1989, **28**, 1521.

42 E. M. Kober, J. V. Caspar, R. S. Lumpkin and T. J. Meyer, *J. Phys. Chem.*, 1986, **90**, 3722.

43 R. Engelman and R. Jortner, *J. Mol. Phys.*, 1970, **18**, 145.

44 M. S. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998.

45 R. H. Schmehl, R. A. Auerbach, W. F. Wacholtz, C. M. Elliot, R. A. Freitag and J. W. Merkert, *Inorg. Chem.*, 1986, **25**, 2440.

46 W. F. Wacholtz, R. A. Auerbach and R. H. Schmehl, *Inorg. Chem.*, 1987, **26**, 2989.

47 G. Denti, S. Campagna, S. Serroni, M. Ciano and V. Balzani, *J. Am. Chem. Soc.*, 1992, **114**, 2944; S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano and V. Balzani, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1493; S. Serroni, A. Juris, S. Campagna, M. Venturi, G. Denti and V. Balzani, *J. Am. Chem. Soc.*, 1994, **116**, 9086 and refs. therein.

48 J. Davila, A. Harriman and L. R. Milgrom, *Chem. Phys. Lett.*, 1987, **136**, 427.

49 S. Prathapan, T. E. Johnson and J. S. Lindsey, *J. Am. Chem. Soc.*, 1993, **115**, 7519.

50 D. E. Lacky, B. J. Pankuch and G. A. Crosby, *J. Phys. Chem.*, 1980, **84**, 2068; B. J. Pankuch, D. E. Lacky and G. A. Crosby, *J. Phys. Chem.*, 1980, **84**, 2061.

51 A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley and M. W. Windsor, *Chem. Phys. Lett.*, 1976, **37**, 199.

52 A. J. Street, D. M. Goodall and R. C. Greenhow, *Chem. Phys. Lett.*, 1978, **56**, 326.

53 C. Creutz, M. Chou, T. L. Netzel, M. Okumura and N. Sutin, *J. Am. Chem. Soc.*, 1980, **102**, 1309.

54 MOLEN, An Interactive Structure Determination Procedure, Enraf-Nonius, Delft, 1990.

55 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, (*a*) Table 2.2b; (*b*) Table 2.3.1.

56 V. Grosshenny and R. Ziessel, *J. Organomet. Chem.*, 1993, **453**, 19.

57 J. Suffert and R. Ziessel, *J. Org. Chem.*, unpublished work.

58 G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **7**, 245.

59 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.

60 A. Juris, S. Campagna, I. Bidd, J.-M. Lehn and R. Ziessel, *Inorg. Chem.*, 1988, **27**, 4007 and refs. therein.

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