CHEMCOMM
Feature Article
www.rsc.org/chemcomm

Luminescent carbon-rich rhenium(I) complexes

Vivian Wing-Wah Yam

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China.
E-mail: wwyam@hku.hk

Received (in Cambridge, UK) 16th August 2000, Accepted 16th February 2001
First published as an Advance Article on the web 16th March 2001

The synthesis and luminescence behaviour of carbon-rich rhenium(I) complexes containing rigid-rod sp carbon chains are reported. Perturbation of the luminescence properties through structural variation of the ancillary ligands and the carbon chain length has been achieved. Utilization of the alkynylrhenium(I) system for mixed-metal complex formation is also described.

Introduction

The constant search for new advanced materials with new and improved properties has led to a variety of investigations into inorganic/organometallic molecular materials.[1] It is well known that the properties of materials may be modified dramatically by seemingly subtle changes in chemical structure, thus the possibility of using organometallic or metal-containing structural moieties to prepare molecular materials with interesting and possibly useful characteristics is an attractive option. With metal-containing materials, a wide variety of transition metals with different nature, coordination geometry, coordination number, and oxidation states, and hence the number of d electrons, can be employed. These together with the wide diversity of ligand systems and variation would provide an extremely important and rich area of research in the field of materials science. Recently, there has been a growing interest in the chemistry of carbon-rich metal-containing systems, in particlar those with long sp carbon chains.[1d–f] The alkynyl group, with its linear geometry, the rigidity of its structure, its extended π-electron delocalization and its ability to interact with metal centres *via* p_π–d_π overlap which can effectively strengthen the metal–carbon bonds, would render it an attractive building block for the construction of carbon-rich metal-containing materials which may possess potential applications as nonlinear optical materials, molecular wires, and molecular electronics. Despite the growing interest and extensive studies in metal acetylides, relatively less attention was focused on the luminescence behaviour of this class of compounds. In this context, we have directed our research efforts specifically to the design and synthesis of luminescent metal acetylides which we believe, with a careful design and judicious choice of metal and ligand systems, can be employed as versatile building blocks for the construction of luminescent molecular and oligomeric materials.

Vivian W. W. Yam was born in Hong Kong in 1963. She graduated with her first class honours BSc degree in 1985 from The University of Hong Kong. After this she obtained her PhD degree under the supervision of Professor Chi-Ming Che on high-valent metal–oxo chemistry from the same university in 1988. After spending two years as a lecturer in the Department of Applied Science at the City Polytechnic of Hong Kong (now City University of Hong Kong), she moved back to The University of Hong Kong as a lecturer in 1990. She was appointed to a Senior Lectureship in 1995, Readership in 1997, and the Chair of Chemistry in 1999. She is now also the Head of the Chemistry Department. Her research interests include inorganic/organometallic photophysics and photochemistry, polynuclear metal complexes and clusters with special emphasis on metal acetylides, chalcogenides and chalcogenolates, supramolecular chemistry, inorganic/organometallic molecular functional materials for spectrochemical and luminescence sensing and molecular recognition, optoelectronics, photoswitching and molecular devices.

Early work on metal acetylides dated back to as early as 1960 when copper and mercury acetylides in polymeric form were reported and were proposed to have a linear geometry.[2] However, these materials were found to be intractable which precluded their purification and characterization. In the late 1970s, Hagihara and coworkers reported the first soluble polyynes containing platinum and palladium metal atoms in the main chain.[3a,b] Subsequent work by the same group had resulted in general synthetic routes to group 10 metal-containing one-dimensional polyynes.[3] Recent works by the groups of Lewis[4] and Marder[5] and others[6] have developed new routes to incorporate group 8, 9 and 10 metals into the polyyne backbone. Despite all these important contributions, studies on these polymeric systems present several difficulties, such as the exact arrangement of the structure, the molecular weight distribution, linear chains *vs.* side chains, heterogeneity of the samples, reproducibility and many others, which would render a direct understanding of the structure–property relationship and the fundamental understanding on the spectroscopic origin of these chromophores less straightforward and less amenable to study.

In order to provide a more thorough and fundamental understanding on the structure–property relationship and the spectroscopic origin of these carbon-rich metal-containing materials, it is therefore crucial to design and synthesize discrete C_n-containing and C_n-bridged metal-based molecular materials and to study their chemical and physical properties.[7]

In this article, the focus will be directed towards the rhenium(I) acetylide system and our recent efforts to design luminescent carbon-rich rhenium(I) complexes with extended carbon chains. Application of these rhenium(I) acetylides as metalloligands to generate mixed-metal luminescent molecular materials will also be described.

Mononuclear rhenium(I) acetylides

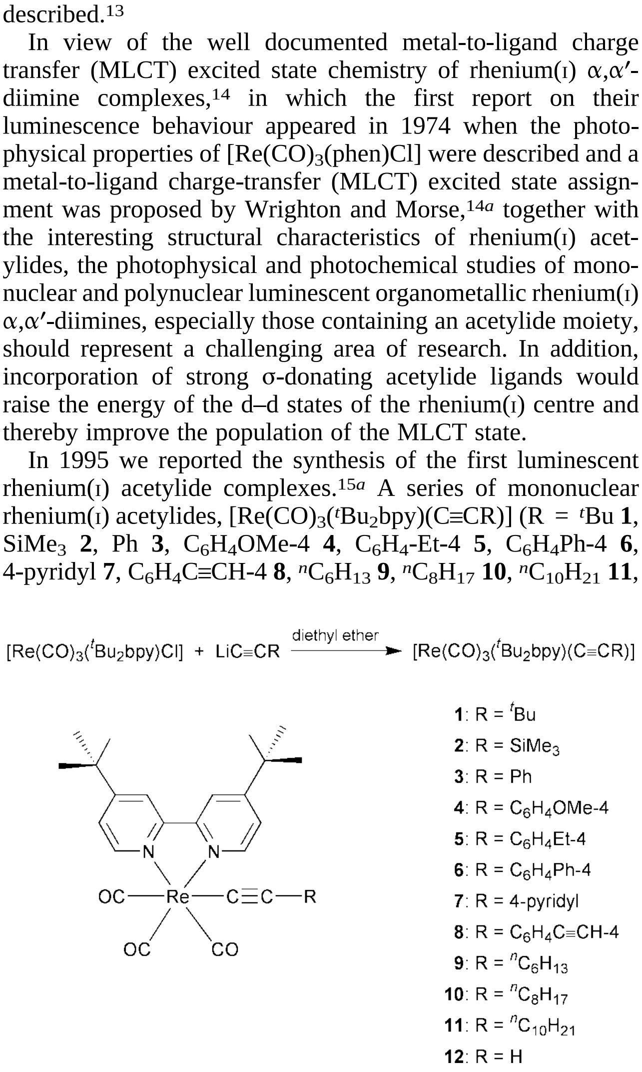
The first report on the synthesis, molecular structures and chemistry of rhenium(I) acetylide complexes dates back to 1968 when Bruce *et al.* reported the synthesis of $[Re(CO)_5(C{\equiv}CR)]$ (R = Ph or C_6F_5)[8] from the reaction of $[Re(CO)_5Cl]$ and the corresponding lithiated acetylide. Later on, Beck and coworkers reported the synthesis, molecular and electronic structures of a series of mononuclear and dinuclear pentacarbonylrhenium(I) acetylide complexes $[Re(CO)_5(C{\equiv}CR)]$ (R = CH_3, $SiMe_3$, H)

DOI: 10.1039/b006694j

and [(CO)$_5$Re–C≡C–Re(CO)$_5$].[9] Reactions of these complexes with other transition metal centres with different coordination geometry have also been studied.[10] Recently, the syntheses of rhenium(I) polyyne complexes such as [ReCp(NO)(PPh$_3$){(C≡C)$_n$R}] (R = Me, SiMe$_3$, H, Ph, 1-naphthyl, n = 1–5) and [Cp(NO)(PPh$_3$)Re(C≡C)$_n$ReCp(NO)(PPh$_3$)] (n = 2, 4, 6, 8, 10), have been reported by Gladysz and coworkers.[11] The chemical properties and the electrochemical behaviour of these complexes and the mixed-metal systems prepared from such complexes with terminal acetylides have also been studied.[11f,g,i,12] The synthesis and molecular structures of metal clusters containing rhenium(I) acetylide units have also been described.[13]

In view of the well documented metal-to-ligand charge transfer (MLCT) excited state chemistry of rhenium(I) α,α′-diimine complexes,[14] in which the first report on their luminescence behaviour appeared in 1974 when the photophysical properties of [Re(CO)$_3$(phen)Cl] were described and a metal-to-ligand charge-transfer (MLCT) excited state assignment was proposed by Wrighton and Morse,[14a] together with the interesting structural characteristics of rhenium(I) acetylides, the photophysical and photochemical studies of mononuclear and polynuclear luminescent organometallic rhenium(I) α,α′-diimines, especially those containing an acetylide moiety, should represent a challenging area of research. In addition, incorporation of strong σ-donating acetylide ligands would raise the energy of the d–d states of the rhenium(I) centre and thereby improve the population of the MLCT state.

In 1995 we reported the synthesis of the first luminescent rhenium(I) acetylide complexes.[15a] A series of mononuclear rhenium(I) acetylides, [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡CR)] (R = ^{t}Bu **1**, SiMe$_3$ **2**, Ph **3**, C$_6$H$_4$OMe-4 **4**, C$_6$H$_4$-Et-4 **5**, C$_6$H$_4$Ph-4 **6**, 4-pyridyl **7**, C$_6$H$_4$C≡CH-4 **8**, ^{n}C$_6$H$_{13}$ **9**, ^{n}C$_8$H$_{17}$ **10**, ^{n}C$_{10}$H$_{21}$ **11**, H **12**), have been synthesized (Scheme 1) by the reaction of [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl] with LiC≡CR in diethyl ether (prepared *in situ* by the reaction of ^{n}BuLi with the corresponding RC≡CH), which were subsequently characterized and their photophysical properties studied.[15,16] Fig. 1 shows the perspective drawing of **1**. In general, the electronic absorption spectra of these complexes in acetone show an intense low energy absorption band at *ca.* 391–440 nm, attributable to a MLCT [d$_\pi$(Re) → π*(^{t}Bu$_2$bpy)] transition.



Scheme 1

A red shift of this MLCT absorption band relative to that of the chloro counterpart [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl] has been observed. This finding has been ascribed to the presence of a more electron-rich rhenium(I) centre in the acetylide complexes as a result of the stronger σ-donating ability of the acetylides than the chloro ligand. The MLCT absorption energies have also been found to follow the order: **11** ≈ **10** ≈ **9** < **1** ≈ **4** ≈ **5** ≈ **3** < **2** < **12**, in line with the σ-donating ability of the acetylides: –C≡C^{n}C$_{10}$H$_{21}$ ≈ –C≡C^{n}C$_8$H$_{17}$ ≈ –C≡C^{n}C$_6$H$_{13}$ > –C≡C^{t}Bu ⩾ –C≡CC$_6$H$_4$OMe-4 ≈ –C≡CC$_6$H$_4$Et-4 > –C≡CPh > –C≡CSiMe$_3$ > –C≡CH. This is also in agreement with the fact that a more electron-donating acetylide would render the rhenium(I) centre more electron rich and thereby decrease the MLCT transition energy. Similar observations have also been reported in the photoelectron spectroscopic studies of the [FeCp(CO)$_2$(C≡CR)] (R = H, Ph, ^{t}Bu)[17] and in the [W(≡CH)(dmpe)$_2$X] (X = C≡CPh, C≡CSiMe$_3$, C≡CH) systems.[18] This low energy absorption of the rhenium(I) acetylides is also found to be sensitive to the polarity of the solvent. For example, the absorption maximum of **1** in MeOH at 391 nm is red-shifted to 464 nm in *n*-hexane. This further supports the MLCT assignment of the low energy absorption as similar solvatochromic shifts are commonly observed for rhenium(I) α,α′-diimine complexes.[14i,l,19]

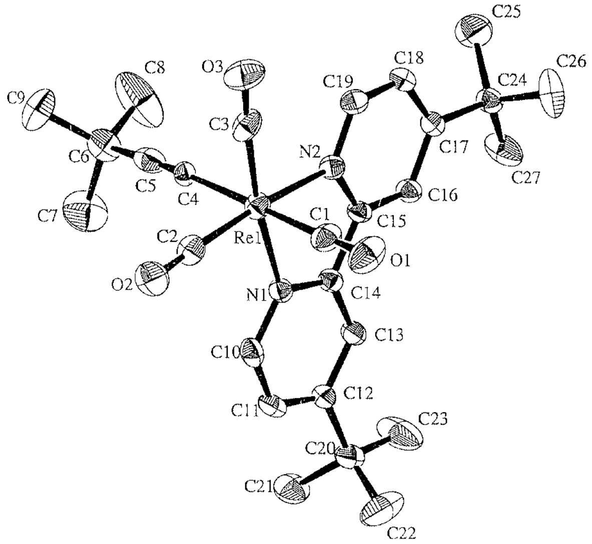
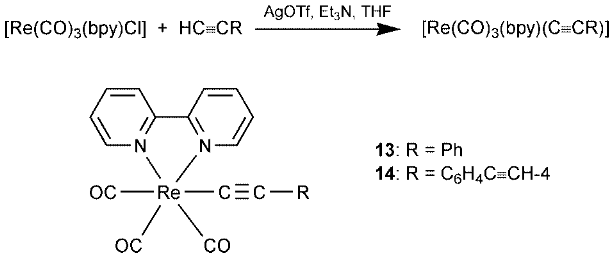


Fig. 1 The perspective drawing of **1**. Hydrogen atoms have been omitted for clarity. Reproduced with permission from ref. 15(*a*).

Attempts to synthesize rhenium(I) acetylide complexes with α,α′-diimine ligands other than that of 4,4′-di-*tert*-butyl-2,2′-bipyridine using the method described above were unsuccessful, yielding intractable solids in all cases. The use of LiC≡CR has limited the choice of the solvents employed, and in most cases the starting precursor complexes [Re(CO)$_3$(N-N)Cl], unlike the 4,4′-di-*tert*-butyl-2,2′-bipyridine analogue [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl], are insoluble or very sparingly soluble in the solvents used. Thus an improved route was developed which precluded the necessity of employing lithiated reagents. By refluxing a mixture of [Re(CO)$_3$(bpy)Cl], RC≡CH, AgOTf and Et$_3$N in THF (Scheme 2), a series of [Re(CO)$_3$(bpy)(C≡CR)] were obtained in reasonable yield (R = Ph **13**, C$_6$H$_4$C≡CH-4 **14**).[20] It has been found that both the absorption and emission of the 2,2′-bipyridine counterparts occur at a lower energy than the ^{t}Bu$_2$bpy analogues with the same acetylide ligand. This



Scheme 2

observation further supports the involvement of the π* orbital of the α,α′-diimine ligands in the MLCT excited state of the complexes while the possibility of a MLCT [d$_π$(Re) → π*(C≡C)] excited state has been ruled out as an opposite trend in the absorption energies would be observed.

Upon excitation at λ > 350 nm, these mononuclear rhenium(I) acetylide complexes all show intense and long-lived orange–red luminescence in the solid state and in solutions, with lifetimes in the microsecond to sub-microsecond range. Unlike other rhenium(I)–alkyl or –aryl complexes which only emit at low temperature and undergo photodissociation reactions readily upon excitation into their σ(M–C) → π*(N–N) transition bands,[19,21] these rhenium(I) acetylide complexes are emissive in solutions at room temperature and are fairly photostable. With reference to other luminescent rhenium(I) α,α′-diimine systems,[14] the origin of the emission has been ascribed to a ^{3}MLCT [d$_π$(Re) → π*(N–N)] excited state; the lifetimes of which are also in the range typically found for this class of excited states.[14] The emission of the rhenium(I) acetylide complexes has also been found to occur at a lower energy relative to that of [Re(CO)$_3$(N–N)Cl]. Besides, the MLCT emission energies of the rhenium(I) α,α′-diimine complexes with different acetylide ligands also show a similar trend as observed in the electronic absorption spectra. In general, more electron-donating acetylides give a lower energy MLCT emission band and this is consistent with the σ- and π-donating ability of the acetylide moieties. The emission spectra of the starting material, [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl], **1** and **12** are shown in Fig. 2. However, unlike other rhenium(I) α,α′-diimine complexes whose luminescence properties are strongly dependent on the solvent,[14i,l,19] the emission energies of these rhenium(I) acetylides are not very sensitive to the solvent polarity. On the other hand, these luminescent rhenium(I) acetylides have also been found to exhibit interesting rigidochromism. For example, the orange–red emissions of **9** (λ_{em} = 690 nm) and **12** (λ_{em} = 660 nm) in a EtOH–MeOH (4 : 1, v/v) solution at 298 K are blue-shifted to λ_{em} = 560 and 545 nm for **9** and **12**, respectively, in a 77 K glass of the same solvent mixture. Such luminescence rigidochromism has also been reported in other Re(I) α,α′-diimine systems.[14a,i,19]

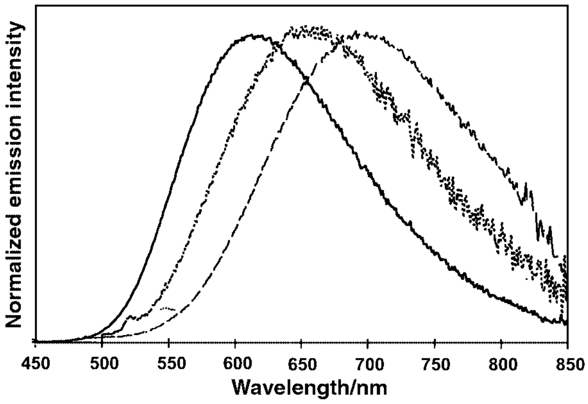


Fig. 2 The emission spectra of [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl] (—), **1** (----) and **12** (·····) in degassed THF at 298 K.

Recently, we have extended our work to the use of the diynyl and triynyl units as ligands for the extension of the carbon chain. A series of mononuclear luminescent rhenium(I) α,α′-diimine complexes containing a diynyl moiety, [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡CH)] **15** and [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡CPh)] **16**, and triynyl moiety, [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡C–C≡CPh)] **17**, [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡C–C≡CSiMe$_3$)] **18** and [Re(CO)$_3$(Me$_2$bpy)(C≡C–C≡C–C≡CSiMe$_3$)] **19**, have been synthesized (Scheme 3) and characterized in our laboratory.[22] Reaction of [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl],[14a] KF, AgOTf and Me$_3$SiC≡C–C≡CSiMe$_3$ in MeOH under reflux conditions afforded [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡CH)] **15**, while reaction of [Re(CO)$_3$(^{t}Bu$_2$bpy)Cl], AgOTf, NEt$_3$ and PhC≡C–C≡CH in refluxing THF gave [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡CPh)] **16**. The perspective drawing of **15** is shown in Fig. 3.

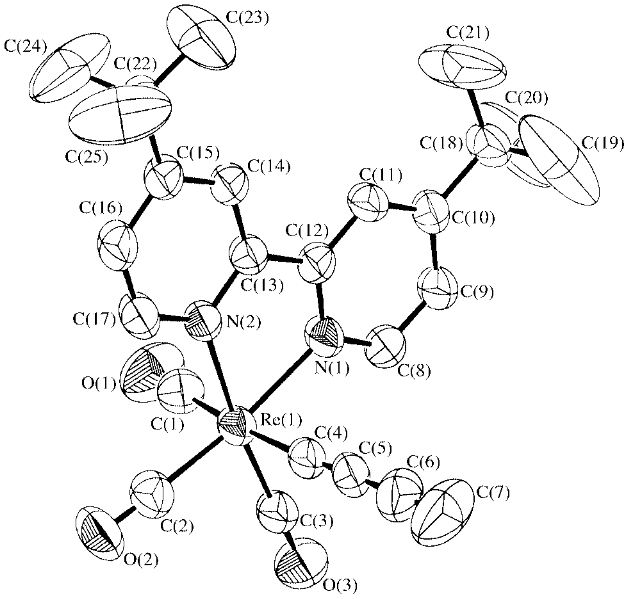


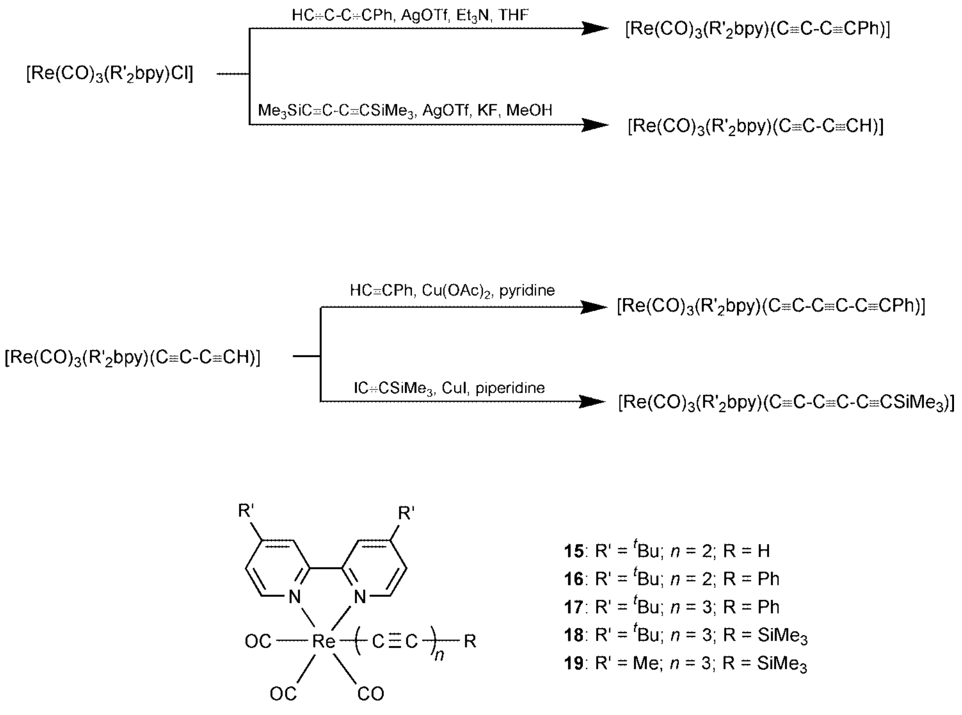
Fig. 3 The perspective drawing of **15**. Hydrogen atoms have been omitted for clarity. Reproduced with permission from ref. 22(*a*).

The triynyl complexes were synthesized by the heterocoupling reactions of [Re(CO)$_3$(N–N)(C≡C–C≡CH)] with the corresponding RC≡CH in the presence of a copper(I) catalyst and a base.[22b] Reaction of [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡CH)] **15**,[22a] PhC≡CH and Cu(OAc)$_2$ in pyridine under reflux conditions afforded [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡C–C≡CPh)] **17**, while reaction of [Re(CO)$_3$(N–N)(C≡C–C≡CH)], IC≡C-SiMe$_3$, piperidine and CuI in THF at room temperature gave [Re(CO)$_3$(N-N)(C≡C–C≡C–C≡CSiMe$_3$)] (N–N = ^{t}Bu$_2$bpy **18**; N–N = Me$_2$bpy **19**).

In THF, complexes **15** and **16** show intense absorption bands at *ca.* 404 and 416 nm, respectively, similarly assigned as the spin-allowed MLCT [d$_π$(Re) → π*(^{t}Bu$_2$bpy)] transition. The lower MLCT absorption energy for **16** than **15** is consistent with the better σ- and π- donating abilities of PhC≡C–C≡C than HC≡C–C≡C,[17,18,23] which render the Re(I) centre more electron-rich, and raise the Re d$_π$ orbital energy, similar to that observed in the related mono-alkynyl system [Re(CO)$_3$(^{t}Bu$_2$bpy)X],[15] in which the MLCT absorption band occurs at higher energy for X = HC≡C than for X = PhC≡C.

Similarly, in the triynyl series, the intense absorption bands of **17** (426 nm), **18** (412 nm) and **19** (420 nm), in THF have been tentatively assigned as the d$_π$(Re) → π*(^{t}Bu$_2$bpy or Me$_2$bpy) MLCT transition. Similar to the monoynyl and diynyl systems, the lower MLCT absorption energy for **17** than **18** is again consistent with the better π-donating abilities of PhC≡C–C≡C–C≡C than Me$_3$SiC≡C–C≡C–C≡C, which render the Re(I) centre more electron-rich, and raise the Re d$_π$ orbital energy.

Excitation of **15** and **16** both in the solid state and in solutions at room temperature at λ > 400 nm resulted in strong orange luminescence, attributed to the ^{3}MLCT phosphorescence. The excitation spectra of **15** and **16** in THF show an excitation band at *ca.* 400 and 410 nm, respectively, which closely resembles that of the MLCT absorption maxima. The slightly lower MLCT emission energy of **16** than **15** in THF is in line with the stronger σ- and π-donating abilities of the phenyldiynyl unit than the butadiynyl ligand, *i.e.* PhC≡C–C≡C **16** (625 nm) < HC≡C–C≡C **15** (620 nm). Similar trends have been observed in



Scheme 3

the monoacetylide analogues [PhC≡C **3** (688 nm) < HC≡C **12** (670 nm)].[15]

Similarly, excitation of the triynyl complexes **17**–**19** both in the solid state and in solutions at room temperature at $\lambda > 400$ nm resulted in strong orange luminescence, attributed to the ^{3}MLCT phosphorescence. All the lifetimes of the diynyl and triynyl complexes were in the microsecond to sub-microsecond range; as are typically found for ^{3}MLCT states of rhenium(I) systems.[14] The lower MLCT emission energy of **17** than **18** in THF is again in line with the stronger π-donating abilities of the phenyltriynyl unit than the trimethylsilyltriynyl ligand, *i.e.* PhC≡C–C≡C–C≡C **17** (620 nm) < Me$_3$SiC≡C–C≡C–C≡C **18** (596 nm). Both **17** and **18** emit at higher energies than their respective monoynyl and diynyl counterparts, *i.e.* in the [Re(CO)$_3$(^{t}Bu$_2$bpy)X] system, the emission energies in THF follow the order: PhC≡C–C≡C–C≡C **17** (620 nm) > PhC≡C–C≡C **16** (625 nm) > PhC≡C **3** (688 nm); Me$_3$SiC≡C–C≡C–C≡C **18** (596 nm) > Me$_3$SiC≡C **2** (670 nm). Fig. 4 shows the emission spectral trend of the complexes as a function of the acetylenic carbon chain length. The observation of a blue shift in emission energies upon increasing the number of the C≡C units disfavours an assignment of a ^{3}MLCT {d$_\pi$(Re) → π*[(C≡C)$_n$R]} or a metal-perturbed ^{3}IL {π[(C≡C)$_n$R] → π*[(C≡C)$_n$R]} origin (n = 1, 2, 3) and is suggestive of an assignment of a ^{3}MLCT [d$_\pi$(Re) → π*(^{t}Bu$_2$bpy)] origin. Preliminary molecular orbital studies using Extended Hückel molecular orbital (EHMO) theory on **17** and its diynyl analogue [Re(CO)$_3$(^{t}Bu$_2$bpy)(C≡C–C≡CPh)] **16** show that in both the diynyl and triynyl systems, the LUMO mainly consists of π*(^{t}Bu$_2$bpy) character while the HOMO is mainly dominated by the antibonding character of the Re–(C≡C)$_n$Ph (n = 2, 3) moiety resulted from the overlap of the d$_\pi$(Re) and π[(C≡C)$_n$Ph] orbitals, which is supportive of a d$_\pi$(Re) → π*(^{t}Bu$_2$bpy) MLCT character for the electronic transition. An increase in the HOMO–LUMO energy gap has also been observed on extending the C≡C unit from the diynyl to the triynyl species, in which the LUMO energies remain more or less the same while the HOMO energies decrease with an increasing number of C≡C units. The observed trend of a higher MLCT emission energy in the triynyl system than the diynyl and hence the monoynyl systems, in line with EHMO studies, may originate from a decreased overlap integral between the d$_\pi$(Re) and the triynyl π(RC≡CC≡CC≡C) orbitals than that of d$_\pi$(Re) and the π(RC≡CC≡C) and π(RC≡C) orbitals resulting from the delocalization of electron density across the C$_n$ unit, despite the better energy match between π(RC≡CC≡CC≡C) and the d$_\pi$(Re) orbital, *i.e.* the overlap of the more closely energy-matched d$_\pi$(Re) and π(RC≡CC≡CC≡C) orbitals does not necessarily raise the d$_\pi$(Re) orbital to an energy higher than that for the diynyl and monoynyl cases, and may give rise to the anomalous energy trend in which the MLCT emission energy is in the order: PhC≡C–C≡C–C≡C > PhC≡C–C≡C > PhC≡C. An alternative rationale for the increased MLCT energies upon increasing the number of the C≡C units is that given the similar σ-donating properties of the monoynyl, diynyl and triynyl unit,[17,23] the much better π-accepting ability of RC≡C–C≡C–C≡C than RC≡C–C≡C which in turn is better than RC≡C may become the dominating factor, stabilizing the Re d$_\pi$ orbitals to a greater extent, and hence gives rise to a higher energy ^{3}MLCT [d$_\pi$(Re) → π*(^{t}Bu$_2$bpy or Me$_2$bpy)] emission. However, in view of the much less importance of the d$_\pi$(Re)–π*[(C≡C)$_n$R] interaction, as reflected from EHMO studies, such possibilities are not favoured.

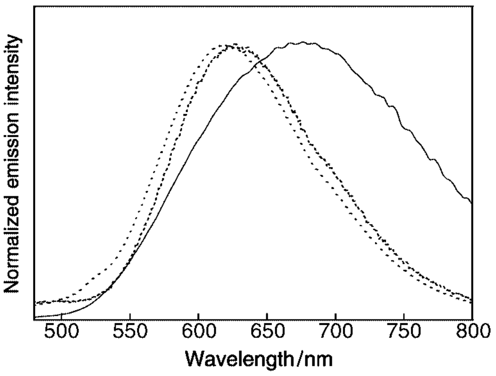
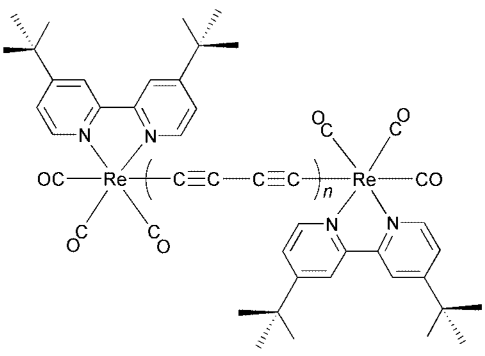
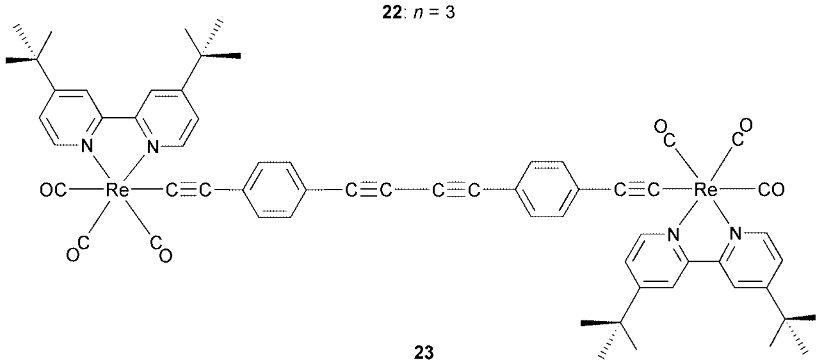


Fig. 4 The emission spectra of **3** (—), **16** (----) and **17** (·····) in THF solution at 298 K.



20: $n = 1$
21: $n = 2$
22: $n = 3$



23

Dinuclear rhenium(I) acetylides

Besides mononuclear complexes, dinuclear rhenium(I) α,α'-diimine complexes with a bridging acetylide ligand, $[(^t\mathrm{Bu_2bpy})(\mathrm{CO})_3\mathrm{Re{-}C{\equiv}C{-}C{\equiv}C{-}Re(CO)_3}(^t\mathrm{Bu_2bpy})]$ **20**,[15b] $[(^t\mathrm{Bu_2bpy})(\mathrm{CO})_3\mathrm{Re{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}Re(CO)_3}(^t\mathrm{Bu_2bpy})]$ **21**, $[(^t\mathrm{Bu_2bpy})(\mathrm{CO})_3\mathrm{Re{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}Re(CO)_3}(^t\mathrm{Bu_2bpy})]$ **22** and $[(^t\mathrm{Bu_2bpy})(\mathrm{CO})_3\mathrm{Re{-}C{\equiv}C{-}C_6H_4{-}(C{\equiv}C\text{-}4){-}C{\equiv}C{-}C_6H_4{-}(C{\equiv}C\text{-}4){-}Re(CO)_3}(^t\mathrm{Bu_2bpy})]$ **23**, have also been synthesized by homo-coupling reactions involving the respective $[(^t\mathrm{Bu_2bpy})(\mathrm{CO})_3\mathrm{Re{-}(C{\equiv}C)}_n\mathrm{H}]$ complexes in the presence of $\mathrm{Cu(OAc)_2}$ and pyridine. The perspective view of **20** is depicted in Fig. 5. Upon photoexcitation, complex **20** exhibits long-lived luminescence at *ca.* 660–690 nm which has been proposed to originate from a ^{3}MLCT $[\mathrm{d}_\pi(\mathrm{Re}) \rightarrow \pi^*(^t\mathrm{Bu_2bpy})]$ excited state. Upon excitation at $\lambda > 430$ nm, complex **23** emits at *ca.* 640 nm which is at a slightly higher energy than that of the mononuclear counterpart **8** ($\lambda_{\mathrm{em}} = 670$ nm). The solid-state emission spectra of **23** at 298 and 77 K show vibronically structured emission band with vibrational progressional spacings of *ca.* 1500 and 2000 cm^{-1}, typical of ground-state aromatic $\nu(\mathrm{C{\overset{\cdots}{-}}C})$ and acetylide $\nu(\mathrm{C{\equiv}C})$ stretching frequencies, respectively.

Mixed-metal acetylides

In order to further explore the possibility of utilizing the rhenium(I) acetylides as versatile building blocks in molecular architecture, we have successfully synthesized mixed-metal acetylide complexes using the 'metal complex as ligand' or the so-called metalloligand approach. The first approach we employed was to utilize the $[\mathrm{Re(CO)_3(bpy)(C{\equiv}CPh)}]$ **13** complex as an η^2-ligand towards Cu(I) and Ag(I) ions.[24] Reaction of $[\mathrm{Re(CO)_3(bpy)(C{\equiv}CPh)}]$ **13** with $[\mathrm{Cu(MeCN)_4}]\mathrm{PF_6}$ in THF at room temperature afforded $[\{\eta^2\text{-}\mathrm{Re(CO)_3(bpy)(C{\equiv}CPh)}\}_2\mathrm{Cu}]\mathrm{PF_6}$ **24**. Similarly, reaction of $[\mathrm{Re(CO)_3(bpy)(C{\equiv}CPh)}]$ with $[\mathrm{Ag(MeCN)_4}]\mathrm{PF_6}$ under similar conditions gave the analogue, $[\{\eta^2\text{-}\mathrm{Re(CO)_3(bpy)(C{\equiv}CPh)}\}_2\mathrm{Ag}]\mathrm{PF_6}$ **25**. The perspective drawings of the complete cations of **24** and **25** are shown in Figs. 6 and 7, respectively. The slightly longer C≡C bond distances in **24** [1.20(1)–1.23(1) Å] and **25** [1.199(8)–1.203(8) Å] relative to the $[\mathrm{Re(CO)_3(bpy)(C{\equiv}CPh)}]$ **13** precursor [1.199(9) Å], together with the bond weakening observed in IR spectroscopy where lower $\nu(\mathrm{C{\equiv}C})$ values have been observed for **24** (2029 cm^{-1}) and **25** (2033 cm^{-1}) than $[\mathrm{Re(CO)_3(bpy)(C{\equiv}CPh)}]$ **13** (2083 cm^{-1}), are consistent with the π-coordination mode of the alkynyl group to the d^{10} metal centres.

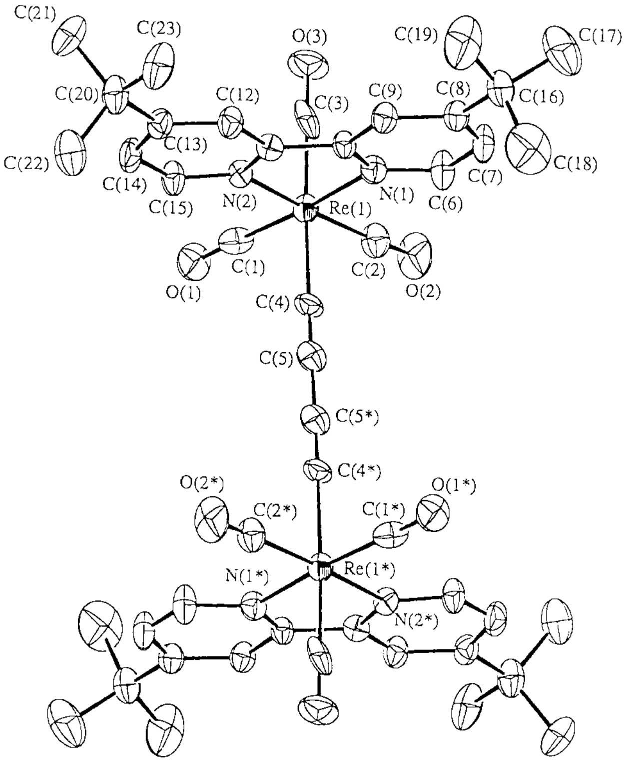


Fig. 5 The perspective drawing of **20**. Hydrogen atoms have been omitted for clarity. Reproduced with permission from ref. 15(*b*).

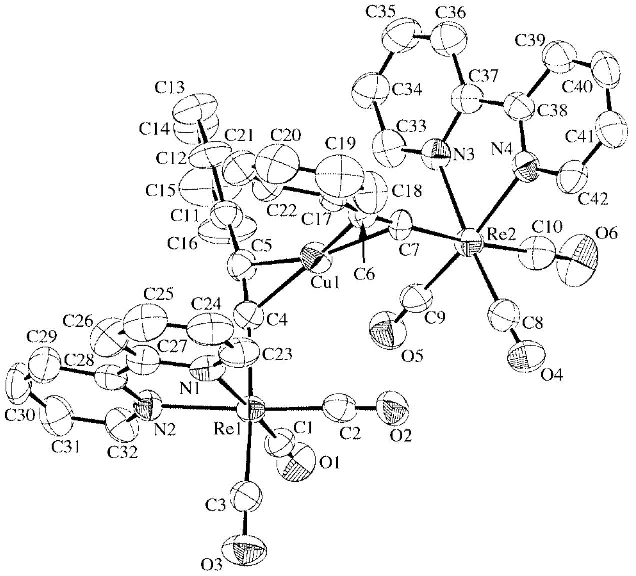
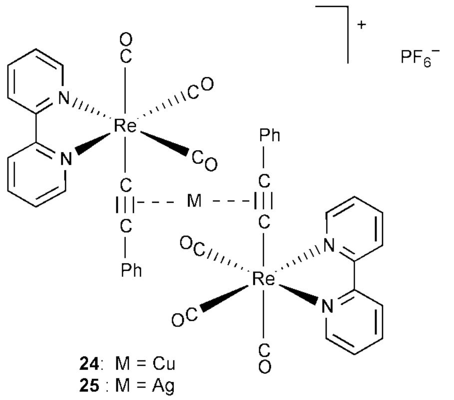


Fig. 6 The perspective drawing of the complex cation of **24**. Hydrogen atoms have been omitted for clarity. Reproduced with permission from ref. 24.



24: M = Cu
25 : M = Ag

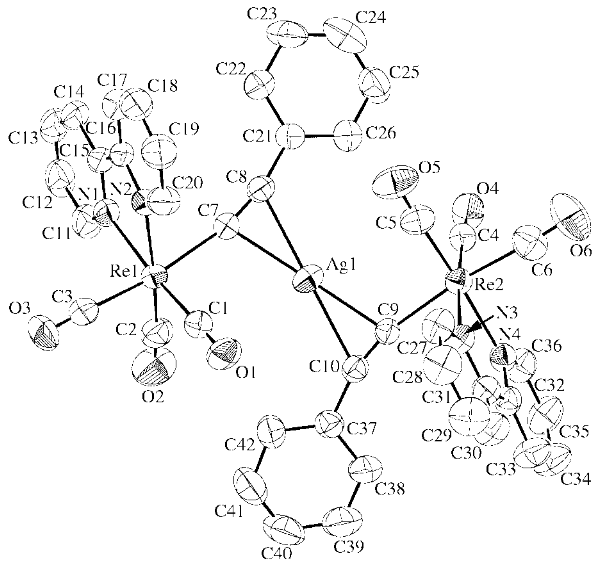


Fig. 7 The perspective drawing of the complex cation of **25**. Hydrogen atoms have been omitted for clarity. Reproduced with permission from ref. 24.

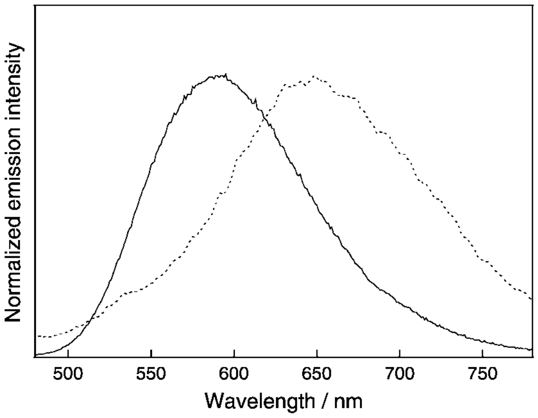
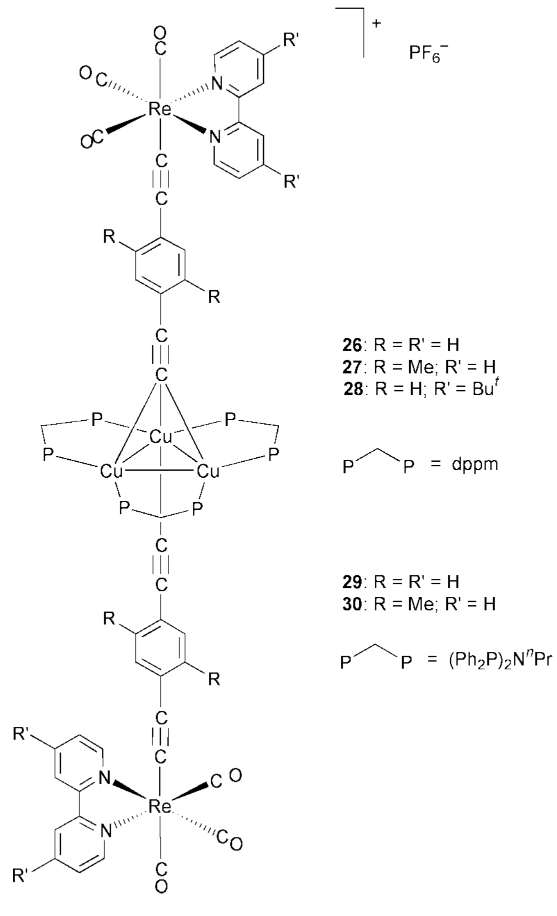


Fig. 8 The emission spectra of **13** (·····) and **24** (—) in degassed CH_2Cl_2 at 298 K.

The electronic absorption spectra of **24** and **25** show an intense MLCT absorption band at *ca.* 396 nm in dichloromethane solution. The shift of the MLCT absorption to the blue relative to that of $[Re(CO)_3(bpy)(C{\equiv}CPh)]$ **13** (420 nm) is in line with the lower-lying $d_\pi(Re)$ orbital in **24** (396 nm) and **25** (396 nm), resulted from the reduced π-donating ability of the acetylide ligand upon π-coordination to the d^{10} metal ions.

Excitation of **24** and **25** also resulted in orange ^3MLCT phosphorescence. Similar to the absorption studies, the emissions of **24** (590 nm) and **25** (600 nm) in CH_2Cl_2 are shifted to higher energies compared to that of $[Re(CO)_3(bpy)(C{\equiv}CPh)]$ **13** (654 nm). Fig. 8 shows the emission spectra of **13** and **24** in degassed CH_2Cl_2 at 298 K. Such a trend is consistent with an assignment of a ^3MLCT $[d_\pi(Re) \rightarrow \pi^*(bpy)]$ emission origin and disfavours the assignment of a ^3MLCT $[d_\pi(Re) \rightarrow \pi^*(C{\equiv}CPh)]$ origin, since the acetylide becomes a poorer π-donor upon coordination to Cu(I) and Ag(I), lowering the energy



26: R = R' = H
27: R = Me; R' = H
28: R = H; R' = Bu^t

P⌒P = dppm

29: R = R' = H
30: R = Me; R' = H

P⌒P = $(Ph_2P)_2N^nPr$

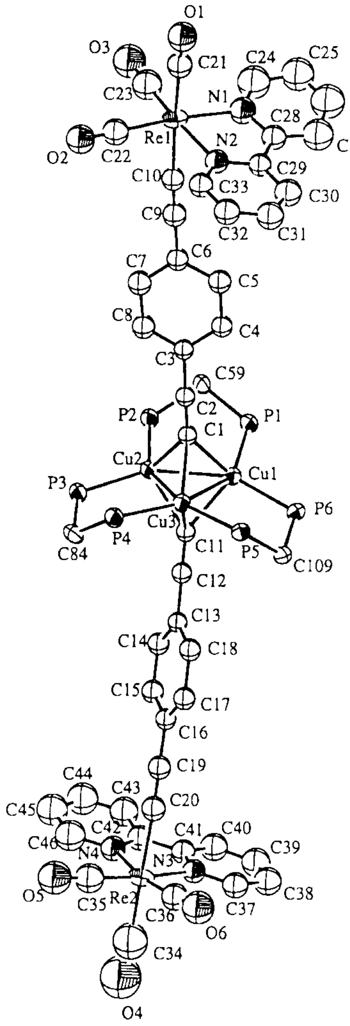


Fig. 9 The perspective drawing of the complex cation of **26**. Hydrogen atoms have been omitted for clarity. Reproduced with permission from ref. 26.

of the Re d_π orbitals, and hence leading to a higher energy ^{3}MLCT [d_π(Re) $\rightarrow$ π^*(bpy)] emission.

A second approach was to utilize the rhenium(I) acetylides with terminal –C≡CH groups as the metalloligand. Recent works by us have shown that luminescent copper(I) acetylides are also promising building blocks for the construction of rigid-rod oligomeric and polymeric materials.[25] As a further step towards this goal, a series of pentanuclear mixed-metal copper(I)–rhenium(I) acetylide complexes $[Cu_3(\mu\text{-P–P})_3\{\mu_3\text{-}\eta^1\text{-C≡C–C}_6H_2R_2\text{-2,5-C≡C-4–Re(N–N)(CO)}_3\}_2]^+$ [P–P = dppm, N–N = bpy, R = H **26**, Me **27**; P–P = dppm, N–N = ^{t}Bu$_2$bpy, R = H **28**; P–P = $(Ph_2P)_2N^nPr$, N–N = bpy, R = H **29**, Me **30**] have been synthesized and their luminescence properties studied.[26] The perspective view of the complex cation of **26** is displayed in Fig. 9. The electronic absorption spectra of these complexes reveal, in addition to the high energy intraligand (IL) absorption bands at *ca.* 250–300 nm and the vibronically structured bands at *ca.* 348–378 nm, a lower-energy absorption at *ca.* 440 nm, which is assigned to a MLCT [d_π(Re) $\rightarrow$ π^*(N–N)] transition. All the complexes display strong orange luminescence upon photoexcitation. The low energy emission bands at *ca.* 600–660 nm have been suggested to arise from a ^{3}MLCT [(d_π(Re) $\rightarrow$ π^*(N–N)] excited state. The energy trend of this low energy emission is in line with the π^* orbital energies of the diimine ligands. The complexes with more electron-rich $(Ph_2P)_2N^nPr$ phosphine ligands are found to emit at slightly lower energy than that of the dppm counterparts. This can be rationalized by the fact that the more electron-donating $(Ph_2P)_2N^nPr$ phosphines would render the copper(I) centres more electron rich, and in turn destablilize the Re(I) d_π orbitals and therefore the ^{3}MLCT [d_π(Re) $\rightarrow$ π^*(N–N)] emission occurs at lower energy.

Conclusion

It is interesting to realize that the rhenium(I) acetylide system offers, indeed, a very versatile and powerful building block for the construction of various luminescent rigid-rod and mixed-metal carbon-rich complexes. By careful planning and the judicious choice of the diimine ligands, the acetylide ligands, the extension of the C≡C units, the nature of the heterometals in the mixed-metal complexes, and the spectator ligands on the heterometal centres, one could readily tune the spectroscopic and emission properties of the systems. An interesting observation is the blue shift in the emission energy upon extending the carbon chain in these complexes, which differs from the common concept of tuning the emission energy to the red by extending the number of acetylenic units in organic polyynes. Besides, the tuning of emission energies by π-coordination of the rhenium–acetylide moiety to d^{10} metal ions or σ-coordination of the acetylide to the trinuclear copper(I) diphosphine units using the metalloligand approach would represent a new concept in the design of luminescent molecular materials. All these examples demonstrate the importance and versatility of systematic structural variation in elucidating the spectroscopic origins of these systems and the flexibility of emission energies tuning simply by changing the nature of the excited state through perturbations on the metal and ligand orbital energies.

Acknowledgements

Financial support from the Research Grants Council and The University of Hong Kong is gratefully acknowledged. The author is also indebted to her students and coworkers, whose names appear in the references. Special thanks are due to Dr K. M. C. Wong for his help in the preparation of the manuscript and to Dr K. K. Cheung for his help in solving the X-ray crystal structures.

References

1 See, for recent reviews: (*a*) *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, London, 1992; (*b*) R. J. Puddephatt, *Chem. Commun.*, 1998, 1055; (*c*) P. F. H. Schwab, M. D. Levin and J. Michl, *Chem. Rev.*, 1999, **99**, 1863; (*d*) H. Lang, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 547; (*e*) U. H. F. Bunz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 969; (*f*) M. I. Bruce, *Coord. Chem. Rev.*, 1997, **166**, 91.

2 V. V. Korshak, A. M. Sladkov and Y. P. Kurdryavtsev, *Vysokomol. Soedin.*, 1960, **2**, 1824; A. S. Hay, *J. Org. Chem.*, 1960, **25**, 1275.

3 (*a*) K. Sonogashira, S. Takahashi and N. Hagihara, *Macromolecules*, 1977, **10**, 879; (*b*) S. Takahashi, M. Kariya, T. Yakate, K. Sonogashira and N. Hagihara, *Macromolecules*, 1978, **11**, 1063; (*c*) K. Sonogashira, S. Kataoka, S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1978, **160**, 319; (*d*) S. Takahashi, E. Murata, M. Kariya, K. Sonogashira and N. Hagihara, *Macromolecules*, 1979, **12**, 1016; (*e*) K. Sonogashira, K. Ohga, S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1980, **188**, 237.

4 S. J. Davies, B. F. G. Johnson, M. S. Khan and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1991, 187; B. F. G. Johnson, A. K. Kakkar, M. S. Khan and J. Lewis, *J. Organomet. Chem.*, 1991, **409**, C12; M. S. Khan, N. A. Pasha, A. K. Kakkar, P. R. Raithby, J. Lewis, K. Fuhrmann and R. H. Friend, *J. Mater. Chem.*, 1992, **2**, 759; M. S. Khan, A. K. Kakkar, N. J. Long, J. Lewis, P. R. Raithby, P. Nguyen, T. B. Marder, F. Wittmann and R. H. Friend, *J. Mater. Chem.*, 1994, **4**, 1227; R. D. Markwell, I. S. Butler, A. K. Kakkar, M. S. Khan, Z. H. Al-Zakwani and J. Lewis, *Organometallics*, 1996, **15**, 2331; N. Chawdhury, A. Köhler, R. H. Friend, M. Younus, N. J. Long, P. R. Raithby and J. Lewis, *Macromolecules*, 1998, **31**, 722.

5 H. B. Fyfe, M. Mlekuz, D. Zargarian, N. J. Taylor and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1991, 188; H. B. Fyfe, M. Mlekuz, G. Stringer, N. J. Taylor and T. B. Marder, *Inorganic and Organometallic Polymers with Special Properties*, ed. R. M. Laine, NATO ASI Series, Kluwer Acad. Publ., Dordrecht, The Netherlands, 1992, vol. 206, p. 331.

6 K. C. Sturge, A. D. Hunter, R. McDonald and B. D. Santarsiero, *Organometallics*, 1992, **11**, 3056; H. Nishihara, T. Shimura, A. Ohkubo, N. Matsuda and K. Aramaki, *Adv. Mater.*, 1993, **5**, 752.

7 R. Nast, *Coord. Chem. Rev.*, 1982, **47**, 89; M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; H. Lang, K. Köhler and S. Blau, *Coord. Chem. Rev.*, 1995, **143**, 113; F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178**–**180**, 431; R. Ziessel, M. Hissler, A. El-ghayoury and A. Harriman, *Coord. Chem. Rev.*, 1998, **178**–**180**, 1251.

8 M. I. Bruce, D. A. Harbourne, F. Waugh and F. G. A. Stone, *J. Chem. Soc. A*, 1968, 356.

9 M. Appel, J. Heidrich and W. Beck, *Chem. Ber.*, 1987, **120**, 1087; W. Beck, B. Niemer, J. Breimair and J. Heidrich, *J. Organomet. Chem.*, 1989, **372**, 79; J. Heidrich, M. Steimann, M. Appel, W. Beck, J. R. Phillips and W. C. Trogler, *Organometallics*, 1990, **9**, 1296.

10 T. Weidmann, V. Weinrich, B. Wagner, C. Robl and W. Beck, *Chem. Ber.*, 1991, **124**, 1363; S. Mihan, T. Weidmann, V. Weinrich, D. Fenske and W. Beck, *J. Organomet. Chem.*, 1997, **541**, 423; S. Mihan, K. Sünkel and W. Beck, *Chem. Eur. J.*, 1999, **5**, 745.

11 (*a*) A. Wong and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 4948; (*b*) J. J. Kowalczyk, A. M. Arif and J. A. Gladysz, *Organometallics*, 1991, **10**, 1079; (*c*) D. R. Senn, A. Wong, A. T. Patton, M. Marsi, C. E. Strouse and J. A. Gladysz, *J. Am. Chem. Soc.*, 1988, **110**, 6096; (*d*) J. A. Ramsden, F. Agbossou, D. R. Senn and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, 1991, 1360; (*e*) Y. Zhou, J. W. Seyler, W. Weng, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1993, **115**, 8509; (*f*) J. W. Seyler, W. Weng, Y. Zhou and J. A. Gladysz, *Organometallics*, 1993, **12**, 3802; (*g*) M. Brady, W. Weng and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, 1994, 2655; (*h*) T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 414; (*i*) M. Brady, W. Weng, Y. Zhou, J. W. Seyler, A. J. Amoroso, A. M. Arif, M. Böhme, G. Frenking and J. A. Gladysz, *J. Am. Chem. Soc.*, 1997, **119**, 775.

12 W. Weng, T. Bartik and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2199; W. Weng, T. Bartik, M. Brady, B. Bartik, J. A. Ramsden, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1995, **117**, 11922.

13 A. A. Koridze, O. A. Kizas, N. E. Kolobova, V. N. Vinogradova, N. A. Ustynyuk, P. V. Petrovskii, A. I. Yanovsky and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1984, 1158; A. D. Shaposhnikova, R. A. Stadnichenko, G. L. Kamalov, A. A. Pasynskii, I. L. Eremenko, S. E. Nefedov, Y. T. Struchkov and A. I. Yanovsky, *J. Organomet. Chem.*, 1993, **453**, 279.

14 (*a*) M. S. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998; (*b*) V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis-Horwood, Chichester, 1991; (*c*) K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992; (*d*) O. Horváth and K. L. Stevenson, *Charge Transfer Photochemistry of Coordination Compounds*, VCH, New York, 1993; (*e*) S. M. Fredericks, J. C. Luong and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 7415; (*f*) J. V. Caspar, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 2104; (*g*) B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1414; (*h*) G. T. Tapolsky, R. Duesing and T. J. Meyer, *J. Phys. Chem.*, 1989, **93**, 3885; (*i*) A. J. Lees, *Chem. Rev.*, 1987, **87**, 711; (*j*) S. V. Wallendael, R. J. Shaver, D. P. Rillema, B. J. Yoblinski, M. Stathis and T. F. Guarr, *Inorg. Chem.*, 1990, **29**, 1761; (*k*) T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163; (*l*) B. P. Sullivan, *J. Phys. Chem.*, 1989, **93**, 24.

15 (*a*) V. W. W. Yam, V. C. Y. Lau and K. K. Cheung, *Organometallics*, 1995, **14**, 2749; (*b*) V. W. W. Yam, V. C. Y. Lau and K. K. Cheung, *Organometallics*, 1996, **15**, 1740.

16 V. C. Y. Lau, Ph.D Thesis, The University of Hong Kong, 1997.

17 D. L. Lichtenberger, S. K. Renshaw and R. M. Bullock, *J. Am. Chem. Soc.*, 1993, **115**, 3276; D. L. Lichtenberger, S. K. Renshaw, A. Wong and C. D. Tagge, *Organometallics*, 1993, **12**, 3522.

18 J. Manna, S. J. Geib and M. D. Hopkins, *J. Am. Chem. Soc.*, 1992, **114**, 9199.

19 D. J. Stufkens, *Comments Inorg. Chem.*, 1992, **13**, 359.

20 K. M. C. Wong, Ph.D Thesis, The University of Hong Kong, 1998.

21 J. C. Luong, R. A. Faltynek and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 1597; L. A. Lucia, R. D. Burton and K. S. Schanze, *Inorg. Chim. Acta*, 1993, **208**, 103.

22 (*a*) V. W. W. Yam, S. H. F. Chong and K. K. Cheung, *Chem. Commun.*, 1998, 2121; (*b*) V. W. W. Yam and S. H. F. Chong, *Organometallics*, 2000, **19**, 5092.

23 J. Manna, K. D. John and M. D. Hopkins, *Adv. Organomet. Chem.*, 1995, **38**, 79.

24 V. W. W. Yam, S. H. F. Chong, K. M. C. Wong and K. K. Cheung, *Chem. Commun.*, 1999, 1013.

25 V. W. W. Yam, K. K. W. Lo, W. K. M. Fung and C. R. Wang, *Coord. Chem. Rev.*, 1998, **171**, 17; V. W. W. Yam and K. K. W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323.

26 V. W. W. Yam, W. K. M. Fung, K. M. C. Wong, V. C. Y. Lau and K. K. Cheung, *Chem. Commun.*, 1998, 777.