

Synthesis, characterization, electrochemistry and luminescence studies of heterometallic gold(I)–rhenium(I) alkynyl complexes

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Abstract

The present work provides a brief summary review of the chemistry of luminescent gold(I) alkynyls and their ability to form heterometallic complexes. A series of luminescent heterometallic gold(I)–rhenium(I) alkynyl complexes has been synthesized and characterized. Their electrochemical and photophysical properties have been studied and their emission origins elucidated.

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1. Introduction

During the last decade, there has been a growing interest in the study of carbon-rich metal alkynyl complexes, owing to their potential applications in molecular electronics and materials science [1]. One class of such compounds that has attracted much attention is the gold(I) alkynyls. The reason partly stems from the recent interest in the rich luminescence properties reported of this class of compounds and the ability of gold(I) to build supramolecular architectures based on its tendency to form two-coordinate linear geometry and its aurophilic properties [2,3].

The research on gold(I) alkynyl chemistry has been initiated by Berthelot who discovered the explosive gold alkynyl Au_2C_2 in 1866 [4]. Coates and Parkin [5] reported the synthesis of alkynylgold(I) phosphine complexes in 1962. Cross reported the synthesis of mononuclear alkynylgold(I) phosphine complexes,

$[\text{Au}(\text{C}\equiv\text{CR})\text{L}]$ ($\text{L} = \text{PPh}_3$, $\text{R} = \text{Me}$, Et , Ph , CF_3 ; $\text{L} = \text{P}(\text{C}_6\text{H}_4\text{Me-}i>p)_3$, $\text{R} = \text{Ph}$) by reacting the terminal acetylene with phosphinegold chlorides in the presence of sodium ethoxide [6]. The dinuclear gold(I) complexes $[\text{LAu}(\text{C}\equiv\text{CAu})\text{L}]$ were afforded by a second reaction of $[\text{Au}(\text{C}\equiv\text{CH})\text{L}]$. Bruce et al. [7] then extended the synthesis of an extensive series of $\text{R}_3\text{PAu}(\text{C}\equiv\text{CR})$ following previous studies. Vicente et al. [8] reported the synthesis of a series of neutral and anionic gold(I) alkynyl complexes. The neutral gold(I) alkynyl complexes, $[\text{Au}(\text{C}\equiv\text{CR})(\text{NHEt}_2)]$, $[\text{Au}(\text{C}\equiv\text{CR})(\text{PR}'_3)]$, $[\text{Au}(\text{C}\equiv\text{CR})(\text{CN}'\text{Bu})]$, $[\text{Au}(\text{C}\equiv\text{CR})\{\text{C}(\text{NH}'\text{Bu})(\text{NEt}_2)\}]$ and dinuclear $[(\text{AuL})_2\{\mu\text{-C}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{C}\}]$ have been prepared by a variety of synthetic methods: (i) reaction between $[\text{PPN}][\text{Au}(\text{C}\equiv\text{CH})_2]$ and $[\text{Au}(\text{PR}_3)_2]\text{ClO}_4$, (ii) reaction of terminal alkynes with $[\text{Au}(\text{acac})(\text{L})]$, (iii) reaction of $[\text{Au}(\text{CIL})]$ complexes with terminal alkynes in diethylamine, (iv) substitution reactions; (v) reaction of diethylamine with alkynyl isocyanide derivatives to give alkynylcarbene complexes. The anionic gold(I) alkynyl complexes, $[\text{PPN}][\text{Au}(\text{C}\equiv\text{CR})_2]$ were afforded by employing the reaction of $[\text{PPN}][\text{Au}(\text{acac})_2]$ with the terminal alkynes $\text{RC}\equiv\text{CH}$.

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Recent reports on the utilization of gold(I) alkynyls in the construction of supramolecular architectures such as catenanes and macrocycles [3] have also been made. Mingos et al. [3a] reported the novel gold(I) alkynyl complex $[\{\text{Au}(\text{C}\equiv\text{C}'\text{Bu})\}_6]_2$ in the form of two catenated hexanuclear rings. From the X-ray crystal structure, it was found that the gold atom is π -coordinated in a mutually perpendicular manner to the alkynyl group in a η^2 – η^2 coordination mode. Puddephatt and co-workers [9] reported the self-assembly of rings, catenanes, and a doubly braided catenane $[\{\mu\text{-X}(4\text{-C}_6\text{H}_4\text{OCH}_2\text{CCAu})_2[\mu\text{-}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]_n\}]_n$ by reaction of the flexible dialkynyldigold(I) precursors $\text{X}(4\text{-C}_6\text{H}_4\text{OCH}_2\text{CCAu})_2$ with 1,4-bis(diphenylphosphino)butane. The complexes were formed readily and selectively as 25-membered ring compounds with $n = 1$, $\text{X} = \text{O}$ or S ; as [2]catenanes with $n = 2$, $\text{X} = \text{CH}_2$ or CMe_2 , and as a unique doubly braided [2]catenane, containing interlocked 50-membered rings with $n = 4$, $\text{X} = \text{cyclohexylidene}$ by self-assembly.

Reaction of the carbonyl derivatized bis(alkyne) $\text{O}=\text{C}(4\text{-C}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{CH})_2$, imine derivatives $\text{RN}=\text{C}(4\text{-C}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{CH})_2$ [$\text{R} = \text{OH}$, $\text{NHC}(\text{O})\text{NH}_2$, $\text{NH-C}_6\text{H}_3\text{-2,4-(NO}_2)_2$] and 4-bromomethyl-1,3-dioxolane derivative $\text{BrCH}_2\text{C}_2\text{H}_3\text{O}_2\text{C}(4\text{-C}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{CH})_2$ with $[\text{AuCl}(\text{SMe}_2)]$ in the presence of base afforded the corresponding insoluble digold(I) dialkynyl oligomers or polymers [3e]. By reacting the diphosphines $\text{Ph}_2\text{PZPPH}_2$ [$\text{Z} = \text{CC}$, *trans*- $\text{HC}\equiv\text{CH}$ and $(\text{CH}_2)_n$, $n = 3\text{--}5$] with gold(I) dialkynyl oligomers or polymers, macrocyclic gold(I) complexes $[\text{Au}_2(\mu\text{-LL})(\mu\text{-PP})]$, where LL is the dialkynyl and PP the diphosphine ligand, were produced. These macrocyclic gold(I) complexes have been studied for the ability to self-assemble to [2]catenanes. It was found that the ketone and imine derivatives did not form [2]catenanes because the orientation of the aryl groups was unfavorable, while the 1,3-dioxolane derivatives might catenate if the ring size was optimum.

Mohr and Puddephatt [10] recently reported macrocyclic digold(I) complexes of the type $[\text{Au}_2(\mu\text{-CC})(\mu\text{-PP})]$, where CC is the dialkynyl and PP is a diphosphine ligand by reacting $(\text{AuCCCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CCAu})_n$ and $(\text{AuCCCH}_2\text{OC}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_4\text{O-CH}_2\text{CCAu})_n$. The binding properties of these gold(I) alkynyl macrocyclic complexes towards alkali metal ions (Li^+ , Na^+ , K^+ , Cs^+) have been studied by electrospray-ionization mass spectrometry.

Ethynylcrown ether containing di- and tetranuclear gold(I) crown ether complexes, $[\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}_2\text{B15C5-4,5}]$ and $[\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}_4\text{DB18C6-4,4',5,5'}]$ have been reported by Yam and co-workers [11]. Both complexes exhibit intense absorptions at ca. 268–335 nm with tails extending to ca. 400 nm for the dinuclear complex and ca. 500 nm for the tetranuclear complex. The high-energy absorptions have been tentatively assigned as intraligand transitions characteristic of triphe-

nylphosphine, whereas the low-energy absorptions were assigned as $[\pi \rightarrow \pi^*]$ intraligand transitions of the alkynyl ligands. Both complexes show emission bands at 530–560 nm in dichloromethane and in the solid state at both room temperature and 77 K, which are suggested to arise from $[\pi(\text{Au-P}) \rightarrow \pi^*(\text{C}\equiv\text{C})]$ or metal-perturbed intraligand $[\pi \rightarrow \pi^*(\text{C}\equiv\text{C})]$ excited states. Both of them show electronic absorption changes upon addition of alkali metal ion. The dinuclear gold(I) complex with benzo-15-crown-5 has binding ability towards sodium ion, whereas the tetranuclear gold(I) complex with benzo-18-crown-6 ether show a preferential binding towards potassium ion.

A series of gold(I) alkynylcalix[4]crown-5 complexes, $[(\text{R}_n\text{R}'_{3-n}\text{P})\text{Au}]_2\text{L}$ ($n = 0\text{--}3$) ($\text{R} = \text{Ph}$, $\text{R}' = o\text{-Tol}$, $p\text{-Tol}$; $\text{H}_2\text{L} = 5,17\text{-diethynyl-25,27-dimethoxycalix[4]crown-5}$) have been synthesized [12]. The photophysical properties of these complexes have been studied. In general, they show high-energy absorptions at 270–300 nm which were assigned as intraligand transitions of the phosphine and ethynylcalixcrown ligand and low-energy absorptions at ca. 342 nm which were characteristic of the gold(I) alkynyl system. All the complexes show an emission band at 578–585 nm in dichloromethane which has been suggested to be derived from a triplet state of metal-perturbed intraligand or $[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{R}_n\text{R}'_{3-n}\text{P})]$ character. The binding properties of these complexes towards alkali metal ion, Na^+ and K^+ have been studied. It was found that the binding properties of the complexes could be fine-tuned with a change in the different steric effect of the auxiliary phosphine ligands.

Owing to the rich luminescence properties of gold(I) alkynyl complexes, research on this field has grown rapidly. The luminescence properties of gold(I) alkynyl complexes were first reported in 1993 in which the spectroscopic and photophysical properties of $[\text{Au}_2(\text{dppe})(\text{C}\equiv\text{CPh})_2]$ were described [13]. From the X-ray crystal structure, the intramolecular $\text{Au}\cdots\text{Au}$ separation was found to be 3.153(2) Å. The complex showed a ligand-centred emission at 420 nm in dichloromethane solution at 298 K, and a solid-state emission at 550 nm at 298 K. It was suggested that the lower energy emission originated from the $(d_{8\sigma})^1(p_{\sigma})^1$ triplet excited state. Reaction of $[\text{Au}(\text{C}\equiv\text{CPh})]_{\infty}$ with dppm gave the trinuclear complex $[\text{Au}_3(\text{dppm})_2(\text{C}\equiv\text{CPh})_2]$ $[\text{Au}(\text{C}\equiv\text{CPh})_2]$ [14]. The X-ray crystal structure showed a trinuclear $[\text{Au}_3(\text{dppm})_2(\text{C}\equiv\text{CPh})_2]^+$ cation with the three gold atoms adopting an isosceles triangle with intramolecular $\text{Au}\cdots\text{Au}$ distances of 3.083(2) and 3.167(2) Å. The complex showed a high-energy emission at 425 nm ($\tau_o = 0.45 \mu\text{s}$) and a low-energy emission at 600 nm ($\tau_o = 0.45 \mu\text{s}$) in degassed acetonitrile at 298 K. It was suggested that the high-energy emission originated from a ligand-centred emission and the low-energy band originated from a $^3[(d_{8\sigma})^1(p_{\sigma})^1]$ excited state.

The photophysical properties of a series of dinuclear gold(I) alkynyl complexes, $[(\text{Ph})_n(\text{Np})_{3-n}\text{PAuC}\equiv\text{CAuP}(\text{Ph})_n(\text{Np})_{3-n}]$ ($n = 0-3$) and $[\text{Fc}_2\text{PPhAuC}\equiv\text{CAuPPhFc}_2]$ have been studied by Mingos and Yam [2a]. The complexes showed vibronically structured absorption bands at 296 nm, which were assigned as $^1[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{Np})]$ transitions. The solid-state emission energies of the former complexes at 77 K decreased with increasing substitution of Np on the phosphine ligands. This was proposed to be in line with the increasing electron-richness around the Au–P bonds and the presence of a $^3[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{Np})]$ excited state. The presence of the ferrocene moiety in the latter complex resulted in effective intramolecular reductive electron transfer quenching, and thus the complex was found to be weakly emissive.

The complex $[(\text{C}_6\text{H}_4\text{OMe-}p)_3\text{PAu-C}\equiv\text{C-AuP}(\text{C}_6\text{H}_4\text{OMe-}p)_3]$ was reported to have a well-resolved vibronic structured emission ranging from 400 to 600 nm with progressional spacings of 2100 cm^{-1} [15]. The emission bands have been assigned to arise from the intraligand $^3[\pi-\pi^*]$ excited state of C_2^{2-} .

The photophysical properties of a series of dinuclear gold(I) complexes with bridging dialkynyl ligands $[(\text{Cy}_3\text{-P})\text{Au}-(\text{C}\equiv\text{C})_n-\text{Au}(\text{PCy}_3)]$ ($n = 1-4$) have been reported by Che et al. [2b,16] recently. The complexes with $n = 1$ and 2 showed a well-defined absorption band extending to more than 260 nm which was assigned to $[5d(\text{Au}) \rightarrow 6p(\text{Au}), \pi^*(\text{phosphine})]$ transition. The complex with $n = 4$ showed a highly vibronic electronic absorption at 274–290 nm with vibrational progressional spacings of 2010 cm^{-1} , which was assigned as dipole-allowed $[\pi \rightarrow \pi^*]$ transition of the $[(\text{C}\equiv\text{C})_4]^{2-}$. Although the complex with $n = 1$ was nonemissive in dichloromethane solution at 298 K, incorporation of the butadiyne ligand resulted in a long-lived $^3[\pi-\pi^*(\text{alkynyl})]$ emission at 417 nm at 298 K. In most media, the complex with ethynyl ligand showed two broad emissions centred at λ_{max} 415 and 530 nm, which were dominant both in the solid and alcoholic glass at 298 K. The lowest-energy $^3[\pi-\pi^*(\text{alkynyl})]$ excited states were found to acquire sufficient allowedness via Au spin-orbit coupling to appear prominently both in the electronic absorption and emission spectra. The complexes with $n = 3$ and 4 in alkynyl ligands showed sharp vibronically structured emission with λ_{0-0} lines at 498 and 575 nm in dichloromethane solutions, with vibronic progressions of ca. 2120 cm^{-1} . This was assigned as the $^3[\pi-\pi^*(\text{C}\equiv\text{C})_n]^{2-}$ emission.

A series of alkynylgold(I) with bridging phosphine or alkynyl ligands $[(\text{ToI})_3\text{PAu}-(\text{BL})-\text{AuP}(\text{ToI})_3]$ ($\text{H}_2\text{BL} = 1,4\text{-diethynylbenzene}$, $9,10\text{-diethynyl-anthracene}$), $[\text{Au}_2(\text{P-P})(\text{C}\equiv\text{CR})_2]$ ($\text{P-P} = 1,8\text{-bis}(\text{diphenylphosphino})\text{naphthalene}$ (dppn), $\text{R} = \text{C}_6\text{H}_4\text{Ph-4}$, $\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$, ${}^n\text{C}_6\text{H}_{13}$; $\text{P-P} = \text{bis}(\text{dimethylphosphino})\text{methane}$ (dmpm), $\text{R} = \text{Ph}$, $\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$) and $[\text{Au}_3(\text{dmmp})(\text{C}\equiv\text{CR})_3]$ bis (dime-

thylphosphinomethyl)methylphosphine (dmmp), $\text{R} = \text{Ph}$, $\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$) have been reported by Yam [17]. The complexes with a bridging 1,4-diethynylbenzene and 9,10-diethynylanthracene showed absorption bands at ca. 294–328 and 410–464 nm with vibrational progressional spacings of 1980 and 1400 cm^{-1} , respectively. The absorption was proposed to arise from intraligand $[\pi-\pi^*(\text{alkynyl})]$ or $^1[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{alkynyl})]$ transitions. For the complexes incorporating dppn as the bridging phosphine, absorption bands were observed at ca. 290–310 nm with a weaker absorption at ca. 400 nm tailing to ca. 500 nm. It was suggested that these absorption bands arose from $^1[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{dppn})]$ transition. The dinuclear complexes with dmpm ligand and trinuclear complexes with dmmp ligand showed strong absorption bands at ca. 252–290 nm, which were suggested to arise from $[\pi-\pi^*(\text{alkynyl})]$ or $[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{alkynyl})]$ transitions, with shoulders at ca. 320–332 nm, which were absent in the mononuclear analogues. These low-energy absorption bands have been assigned to originate from a $^1[d_{\sigma^*} \rightarrow p_{\sigma}]$ transition. However, a red shift in the absorption energy was observed from the mononuclear to the trinuclear species, thus it was possible to assign the transition as a metal–metal-to-ligand and charge-transfer MMLCT $^1[d_{\sigma^*}(\text{Au-Au}) \rightarrow \pi^*(\text{C}\equiv\text{CR})]$ transition. The complexes $[(\text{ToI})_3\text{PAu}-(\text{BL})-\text{AuP}(\text{ToI})_3]$ ($\text{H}_2\text{BL} = 1,4\text{-diethynylbenzene}$) showed solid-state emission with a vibronically structured band at ca. 533 nm, which has been assigned to arise from a ligand-centred $[\pi-\pi^*(\text{alkynyl})]$ or $[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{alkynyl})]$ triplet state. Similarly, the complex $[(\text{ToI})_3\text{PAu}-(\text{BL})-\text{AuP}(\text{ToI})_3]$ ($\text{H}_2\text{BL} = 9,10\text{-diethynylanthracene}$) showed solid-state emission at 580 nm, which was assigned to be intraligand $[\pi \rightarrow \pi^*(\text{anthryl})]$ or $[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{anthryl})]$ in origin. Complexes with dppn ligands display solid-state emissions at ca. 571–655 nm, which were suggested to originate from $^3[\sigma(\text{Au-P}) \rightarrow \pi^*(\text{naphthyl})]$ transition. The complex incorporating dcpn as bridging ligand showed a much lower energy emission peak at 707 nm, since the presence of the electron-donating cyclohexyl rings of dcpn increases the electron density of the phosphorus atoms and therefore render the $\sigma(\text{Au-P})$ electron-pair to be more donating in nature. The dinuclear gold(I) dmpm-containing alkynyl complexes with phenyl and methoxyphenyl substituted alkynyl ligands showed solid-state emission bands at 490 and 521, respectively, while the corresponding trinuclear gold(I) dmmp-containing alkynyl complexes with the same alkynyl ligands display emission bands at 538 and 539 nm, respectively. It was suggested the emission originated from metal-centred $^3[(d_{\delta^*})^1(p_{\sigma})^1]$ state. The emission energy, which seemed to be insensitive to the substituent on the alkynyl ligand showed a red shift from the dimer to the trimer. The photochemical properties of these alkynylgold(I) have also been studied. For example, it was found that the phosphorescent state of

$[\text{Au}_3(\text{dmmp})(\text{C}\equiv\text{CPh})_3]$ was quenched by the electron acceptor, 4-methoxycarbonyl-*N*-methylpyridinium ion, with a bimolecular quenching rate constant of $4.98 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The electron-transfer mechanism of this photoinduced reaction, as well as that between $[\text{Au}_2(\text{dppn})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{OCH}_3-4)_2]$ and MV^{2+} , have been studied by nanosecond transient absorption spectroscopy.

A series of dinuclear and tetranuclear gold(I) alkynyl complexes have been synthesized by us recently by reaction of $[\text{Au}(\text{C}\equiv\text{CR})]_\infty$ with 1,4-bis(diphenylphosphino)benzene (dppb) and 1,2,4,5-tetrakis(diphenylphosphino)benzene (tppb) in dichloromethane to give $[\text{Au}_2(\text{dppb})(\text{C}\equiv\text{CR})_2]$ ($\text{R} = \text{C}_6\text{H}_{13}, \text{Ph}, \text{C}_6\text{H}_4\text{OCH}_3-4$) and $[\text{Au}_4(\text{tppb})(\text{C}\equiv\text{CR})_4]$ ($\text{R} = \text{C}_6\text{H}_{13}, \text{Ph}, \text{C}_6\text{H}_4\text{OCH}_3-4$), respectively [18]. The X-ray crystallographic studies on $[\text{Au}_4(\text{tppb})(\text{C}\equiv\text{CPh})_4]$ revealed an intramolecular Au··Au separation of 3.1541(4) Å with two adjacent Au(C≡CPh) units in a crossed geometry. The electronic absorption bands of these complexes at ca. 250–300 nm have been assigned to be $^1[\sigma(\text{Au}-\text{P}) \rightarrow \pi^*(\text{Ph}_{\text{bridge}})]$ transitions. Complexes with dppb have higher absorption energies than those with tppb, due to the more electron-deficient nature of the bridging phenyl ring of tppb relative to that of the dppb. In general, the complexes with methoxyphenylalkynyl have lower energy emission than those with phenylalkynyl. The more electron-rich methoxy moiety on the alkynyl would reduce the extent of metal-to-ligand back- π -donation to the alkynyl $[\text{d}\pi(\text{Au}) \rightarrow \pi^*(\text{alkynyl})]$. This leads to an increased $\text{d}\pi(\text{Au})-3\text{d}(\text{P})$ overlap and therefore a higher $\sigma(\text{Au}-\text{P})$ orbital energy. The complex, $[\text{Au}_4(\text{tppb})(\text{C}\equiv\text{CC}_6\text{H}_4\text{OCH}_3-4)_4]$ has been studied for the photoreaction with methyl viologen by nanosecond transient absorption spectroscopy. The transient absorption difference spectrum showed a sharp absorption band at ca. 400 nm and another broad one at ca. 600 nm, typical of the $\text{MV}^{\cdot+}$ radical absorptions that indicates the strongly reducing properties of the phosphorescent state of $[\text{Au}_4(\text{tppb})(\text{C}\equiv\text{CC}_6\text{H}_4\text{OCH}_3-4)_4]$. A back electron-transfer rate constant k_b of $1.94 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ has also been estimated from a plot of $1/\Delta A$ versus time for the decay trace.

The photophysical and photochemical properties of dinuclear gold(I) alkynyl complexes with a bridging diphosphinoferrocene ligand $[\text{Au}_2(\text{dppf})(\text{C}\equiv\text{CR})_2]$ ($\text{R} = \text{Ph}$ and tBu) have also been studied [19]. The complexes showed an intense vibronically structured electronic absorption at ca. 270–295 nm with progression spacings of ca. 1825 cm^{-1} , typical of $\mu(\text{C}\equiv\text{C})$ stretching frequencies in the excited state. The absorptions have been assigned to be intraligand $[\pi-\pi^*(\text{alkynyl})]$ transitions. The complexes were non-emissive in the solid state even at 77 K. However, they showed emission bands at 410 nm in dichloromethane solution. The photoreactivities of $[\text{Au}_2(\text{dppf})(\text{C}\equiv\text{CPh})_2]$

have also been studied and the complex was found to react with the solvent leading to the formation of the C–C coupled product, $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ in dichloromethane.

The photophysical properties of luminescent phenylethynylgold(I) with isocyanide ligands, $[\text{Au}\{\text{CNC}_6\text{H}_3(\text{CH}_3)_{2-2,6}\}(\text{C}\equiv\text{CPh})]$ and $[\text{Au}_2(\text{L})(\text{C}\equiv\text{CPh})_2]$ [$\text{L} = \text{tmb}, \text{dmb}$] have been reported [20]. From X-ray crystallographic studies, it was shown that the crystal structure of $[\text{Au}\{\text{CNC}_6\text{H}_3(\text{CH}_3)_{2-2,6}\}(\text{C}\equiv\text{CPh})]$ contained two weakly interacting molecules, paired up in an *anti*-configuration with an intermolecular Au··Au contact of 3.329(4) Å. The dinuclear gold(I) complex with tmb adopted an *anti*-configuration, with an intermolecular non-bonding Au··Au separation of 3.565(2) Å. The complex with dmb was found to have an intramolecular Au··Au interaction of 3.485(3) Å. Both complexes showed an intense high-energy absorption band around 240 nm, which was assigned as MLCT $^1[\text{d}_{z^2} \rightarrow \pi^*(\text{isocyanide})]$ transition, and a lower energy absorption at ca. 273 and 278 nm, which was assigned as typical intraligand $[\pi-\pi^*(\text{alkynyl})]$ transitions. Degassed dichloromethane solutions of the complexes showed a ligand-centred $[\pi-\pi^*(\text{alkynyl})]$ emission at around 420 nm. The complexes in the solid state showed a broad emission band at ca. 550 nm, which was suggested to be derived from a metal-centred $^3[(\text{d}_{z^2})^1(\text{p}_\sigma)^1]$ excited state.

A series of polymeric gold(I) conjugated arylalkynyl complexes $[\{-\text{Au}-\text{C}\equiv\text{C}-\text{Ar}-\text{C}\equiv\text{C}-\text{Au}-\text{L}-\}_n]$ where L = diphosphine or bis(isocyanide) were reported by Puddephatt and co-workers [21]. The complexes $[(\text{CH}_3)_3\text{PAu}-\text{C}\equiv\text{C}-(\text{C}_6\text{H}_2-\text{R}_2-2,5)-\text{C}\equiv\text{C}-\text{Au}-\text{P}(\text{CH}_3)_3]$ ($\text{R} = \text{H}, \text{CH}_3$) showed emission at ca. 415 nm in dichloromethane, which was suggested to arise from an excited state of $[\pi-\pi^*(\text{alkynyl})]/[\sigma(\text{Au}-\text{P}) \rightarrow \pi^*(\text{alkynyl})]$ origin. These complexes showed solid-state emission at ca. 540 nm. With reference to the short intermolecular Au··Au separation of 3.1361(9) Å in $[(\text{CH}_3)_3\text{PAu}-\text{C}\equiv\text{C}-(\text{C}_6\text{H}_2-(\text{CH}_3)_{2-2,5})-\text{C}\equiv\text{C}-\text{Au}-\text{P}(\text{CH}_3)_3]$ in the crystal structure, it was suggested that the red shift in emission energy arose from a metal-centred $^3[(\text{d}_{z^2})^1(\text{p}_\sigma)^1]$ excited state.

The complex $[\{\text{C}_6\text{H}_3-(\text{CH}_3)_{2-2,6}\}-\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{C}-(\text{C}_6\text{H}_4-\text{NO}_2-4)]$ showed an emission at 633 nm in the solid state and at 503 nm in dichloromethane solution [21]. The low-energy emission has been ascribed to the electron-withdrawing NO_2 group, which stabilizes the π^* orbital of the alkynyl. It was believed that the stacking interactions between the phenyl rings of the alkynyl and the isocyanide of two closest molecules in the crystal structure gave rise to the exceptionally low solid-state emission energy.

A series of mono- and binuclear gold(I) complexes with arylalkynyl moieties coordinated to $[\text{Au}(\text{PCy}_3)]^+$ have been prepared by Che and co-workers [22]. Complexes with short arylalkynyl chains, $[\text{Cy}_3\text{PAu}-\text{R}^1]$ ($\text{R}^1 = \text{C}\equiv\text{C}-\text{C}_6\text{H}_5$; $\text{C}\equiv\text{C}-1,4-\text{C}_6\text{H}_4-\text{X}$, ($\text{X} = \text{F}, \text{Cl}, \text{Me}$); $(\text{C}\equiv\text{C})_2-\text{C}_6\text{H}_5$; $\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}$) and $[\text{Cy}_3\text{PAu}-\text{R}^2-$

AuPCy₃] (R² = C≡C-1,4-C₆H₄-C≡C) showed emission bands at 408–488 nm in dichloromethane solution. In the solid state, the complexes showed a well-resolved vibronic structured emission band at 420–493 nm with three types of progression spacings of ca. 1100, 1600 and 2100 cm⁻¹ that were assigned to the ³[π-π*(aryl-alkynyl)]. Complexes with long arylalkynyl chains, [Cy₃-PAu-R¹] (R¹ = C≡C-1,4-C₆H₄-C₆H₅; (C≡C-1,4-C₆H₄)_nC≡C-C₆H₅ (n = 1–3)) and [Cy₃PAu-R²-AuPCy₃] (R² = (C≡C-1,4-C₆H₄)_n-C≡C (n = 2–4); C≡C-(1,4-C₆H₄)₂-C≡C) displayed dual emissions with high-energy bands at 330–407 nm and low-energy bands located at 495–558 nm. The high energy emission was suggested to be delayed fluorescence proposed to occur via a triplet–triplet annihilation mechanism.

The photophysical properties of [TEE][Au(PCy₃)₄] and [TEB][Au(PCy₃)₃] ([TEE]H₄ = tetraethynylethene; [TEB]H₃ = 1,3,5-triethynylbenzene) was studied [23]. [TEE][Au(PCy₃)₄] was found to show ¹[π-π*(TEE)] fluorescence emission at 428 nm, and [TEB][Au(PCy₃)₃] displayed ³[π-π*(TEB)] phosphorescence emission at 479 nm in dichloromethane at 298 K.

Another series of gold(I) arylalkynyl complexes [(R₃P)Au(C≡CAr)] (R = Cy, Ar = C₆H₄-4-NO₂, C₆H₄-4-CF₃, C₆F₅; R = Ph, Ar = C₆H₄-4-NO₂) have been reported by Che and co-workers [24]. From the X-ray structure of the complex, [(Cy₃P)Au(C≡CC₆H₄-4-NO₂)], two forms namely *E*- and *N*-forms exist and are polymorphs with molecular dipoles in different orientations and with different dihedral angles between the neighboring 4-nitro-phenyl moieties. The photophysical properties of these complexes have been studied. It was found that all complexes, except the *N*-form of [(Cy₃P)Au(C≡CC₆H₄-4-NO₂)] showed an emission bands at 425–521 nm at 298 K. The *N*-form [(Cy₃P)Au(C≡CC₆H₄-4-NO₂)] is nonemissive at 298 K, but it showed an emission band at 486 nm at 77 K.

The photophysical properties of a series of luminescent gold(I) phosphine mono- and diynyl complexes with nuclearity ranging from one to three [(R₃P)Au(C≡C)₂R'] (R = Ph, R' = C₃H₇, C₆H₁₃, Ph; R = Tol, R' = Ph), [Au₂(P-P)(C≡CR)₂] (P-P = dppe, R = C≡CC₆H₁₃, C(=CH₂)Me; P-P = dppf, R = C₄H₃S, C₄H₂SC₄H₃S) and [Au₃(P-P)₂(C≡CR)₂] [Au(C≡CR)₂] (P-P = C₆H₁₁, R = C≡CC₆H₁₃, C(=CH₂)Me, C₄H₃S, C₄H₂SC₄H₃S; P-P = Ph, R = C≡CC₆H₁₃, C(=CH₂)Me, C₄H₃S, C₄H₂SC₄H₃S; P-P = Tol, R = C(=CH₂)Me, C₄H₃S; P-P = Me, R = C(=CH₂)Me, C₄H₃S) have been reported by Yam et al. recently [25]. In general, the high-energy absorption bands were suggested to arise from intraligand phosphine-centered and [π → π*(C≡C)] transitions, whereas the low-energy absorption bands were assigned as [σ(Au-P) → π*(C≡C)] or metal-perturbed intraligand [π → π*(C≡C)] mixed with metal-to-alkynyl MLCT transitions. Both the electronic absorption and emission energies were found to be

dependent on the nature of the alkynyl ligands. The nuclearity of the metal complexes was also found to influence the electronic absorption as well as emission behavior. The trinuclear complexes were found that to be lowest in emission energy, attributed to the presence of weak Au···Au interactions that would raise the energy of the metal-centered dσ* orbital. Thus, a red shift in the ³[σ(Au-P) → π*(C≡C)] or the metal-perturbed ³IL [π → π*(C≡C)] mixed with metal-to-alkynyl ³MLCT modified by metal–metal interactions, or the metal–metal-to-ligand charge transfer (³MMLCT) emission energy were observed relative to that of the mononuclear complexes.

Gold(I) alkynyl complexes have also been utilized to synthesize mixed-metal alkynyl complexes. Abu Salah reported a number of complexes using the gold(I) alkynyl unit to coordinate with copper and silver atoms in η²-alkynyl mode [26]. The pentanuclear cluster [Au₃Cu₂(C₂Ph)₆]⁻ was afforded from the reaction between [{Au(C₂Ph)}_n] and a mixture of [Au(C₂Ph)₂]⁻ and [Cu(C₂Ph)}_n]. The synthesis of the gold–silver cluster [Au₃Ag₂(C₂Ph)₆]⁻ was achieved by a slightly modified method [26a]. From the X-ray crystal structure, each gold(I) atom was σ-bonded to two alkynyl groups and the copper/silver was π-bonded to three alkynyl groups. Mixed gold–silver and gold–copper phenylalkynyl polymers [{AuM(C₂Ph)₂}_n] (M = Ag, Cu) were achieved by reaction of [Au(C₂Ph)L] (L = AsPh₃, P(OPh)₃) with [{Ag(C₂Ph)}_n] and [{Cu(C₂Ph)}_n] [26b]. The pentanuclear trimetallic cluster [Au₃AgCu(C₂Ph)₆]⁻ has been prepared by the reaction of [Au₃Cu₂(C₂Ph)₆]⁻ with a mixture of gold phenylalkynyl and silver phenylalkynyl, or reaction of [Au₃Ag₂(C₂Ph)₆]⁻ with [AuCu(C₂Ph)_{2n}], or [Au₂Cu(C₂Ph)₄]⁻ with [AuAg(C₂Ph)_{2n}] [26c]. The high nuclearity trimetallic cluster [AuAg₆Cu₆(C₂Ph)₁₄]⁻ was prepared by conversion of the [Au₃Cu₂(C₂Ph)₆]⁻ and [Au₃Ag₂(C₂Ph)₆]⁻ [26c].

Bruce et al. [27] reported a gold(I) alkynyl complex capped by a Cu₃(μ-dppm)₃ triangle [{Cu₃(μ-dppm)₃}(μ₃-I)(μ₃-η¹-C≡CC≡C-Au-C≡CC≡CH)], which was characterized by X-ray crystallography and the [{Cu₃(μ-dppm)₃}(μ₃-I)₂}(μ₃;μ₃-C≡CC≡C-Au-C≡CC≡C)]I, which was synthesized by reaction of [Cu₃(μ-dppm)₃(μ₃-I)₂]I with [PPN][Au(C≡CC≡CH)₂].

Recently, we reported the utilization of gold(I) alkynyls as η²-metallo-ligands in the construction of mixed-metal gold(I)–copper(I) and silver(I) complexes, [η²-(R₃P)Au{C≡CC(=CH₂)Me}₂Cu]PF₆ (R = Ph, *p*-Tol) and [(dppf)Au₂{η²-C≡CC(=CH₂)Me}₂M]X (M = Cu, X = PF₆; M = Ag, X = OTf) [28]. It was found that these complexes showed ion-induced luminescence switching behavior. The complexes [(R₃P)Au{C≡CC(=CH₂)Me}] (R = Ph, *p*-Tol) showed luminescence at 454 and 463 nm in the solid state, which were assigned as derived from metal-perturbed ³[π → π*(C≡C)] IL and ³[σ(Au-P) → π*(C≡C)] MLCT states. Upon

π -coordination to the copper(I) metal centre, the $\pi^*(\text{C}\equiv\text{C})$ orbital energy was lowered, giving rise a lower energy emission at ca. 606–664 nm. The complex $[(\text{dppf})\text{Au}_2\{\eta^2\text{-C}\equiv\text{CC}(\text{=CH}_2)\text{Me}\}_2]$, was nonemissive in the solid state, probably due to efficient quenching by the ferrocenyl unit. However, $[(\text{dppf})\text{Au}_2\{\eta^2\text{-C}\equiv\text{CC}(\text{=CH}_2)\text{Me}\}_2]$ gave emission at ca. 565–583 nm, which may be originated from copper(I)/silver(I) π -alkynyl core.

As an extension of our previous works on gold(I) alkynyls [2a,17–19,25] and mixed-metal alkynyl complexes of gold(I) [28] as well as rhenium(I) [29], attempts have been made to synthesize novel heterobimetallic alkynyl complexes of gold(I) and rhenium(I) by employing the metalloligand approach. Herein are reported the synthesis, electronic absorption, electrochemistry, and luminescence properties of a series of mixed-metal gold(I)–rhenium(I) alkynyl complexes and their precursor 4-ethynylpyridine gold(I) complexes.

2. Experimental

2.1. Materials

Potassium tetrachloroaurate(III), *trans*-dichlorobis(triphenylphosphine)-palladium(II) and rhenium(I) pentacarbonyl chloride were obtained from Strem Chemicals Inc. 2,2'-Bipyridine (bpy), copper(I) oxide, hexafluorophosphoric acid, sodium, 2,2'-thiodiethanol, silver trifluoromethanesulfonate, tri-*p*-tolylphosphine and triphenylphosphine were purchased from Aldrich Chemical Company. Trimethylsilylacetylene, copper(I) iodide, triethylamine and 4-bromopyridine hydrochloride were obtained from Lancaster Synthesis Ltd. 4-Ethynylpyridine [30], chlorogold(I) phosphine precursor complexes, $\text{Au}(\text{PPh}_3)\text{Cl}$, $\text{Au}(\text{P}(p\text{-Tol})_3)\text{Cl}$ [31] and $[\text{Re}(\text{L-L})(\text{CO})_3(\text{MeCN})]\text{OTf}$ (L-L = bpy or ${}^t\text{Bu}_2\text{bpy}$) [32] were prepared according to the literature procedures.

Dichloromethane (Lab Scan, AR) were purified and distilled over CaH_2 using standard procedures before use [33]. Tetra-*n*-butylammonium hexafluorophosphate (${}^n\text{Bu}_4\text{NPF}_6$) for electrochemical studies was obtained from Aldrich Chemical Company. All other solvents and reagents were of analytical grade and were used as received.

2.2. Physical measurements and instrumentation

${}^1\text{H}$ NMR spectra were recorded on a 300 MHz Bruker DPX300 FT-NMR spectrometer. Chemical shifts (ppm) were reported relative to tetramethylsilane (Me_4Si). Positive ion FAB mass spectra were collected on a Finnigan MAT95 mass spectrometer, and positive ion and negative ion ESI mass spectra on a Finnigan

LCQ mass spectrometer. IR spectra were obtained as KBr pellets on a Bio-Rad FTS-7 fourier-transform infrared spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$). UV-Vis spectra were obtained on a Hewlett–Packard 8452A diode array spectrophotometer. Steady-state excitation and emission spectra were recorded on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay signals were recorded on a Tektronix model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope, and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a 10-cm^3 round-bottom flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze-pump-thaw cycles.

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. Model CHI 620 electrochemical analyzer interfaced to a personal computer. The electrolytic cell used was a conventional two-compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a Vycor glass. A Ag/AgNO_3 (0.1 M in CH_3CN) reference electrode was used. The ferrocenium–ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 M ${}^n\text{Bu}_4\text{NPF}_6$) [34]. The working electrode was a glassy-carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode.

2.3. Syntheses

All the reactions were carried out under anhydrous and anaerobic conditions under an inert atmosphere of nitrogen using standard Schlenk technique.

2.3.1. Syntheses of gold(I) alkynyl phosphine complexes

2.3.1.1. $[(\text{PPh}_3)\text{Au}(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})]$ (**1**). An ethanolic solution (5 ml) of 4-ethynylpyridine (22 mg, 0.21 mmol) and sodium ethoxide (0.30 mmol, prepared in situ from Na in EtOH) was added to a solution of $[(\text{PPh}_3)\text{AuCl}]$ (100 mg, 0.2 mmol) in EtOH/THF (10 ml, 1:1 v/v) and stirred at room temperature. The colorless solution changed to pale yellow after 30 min. After stirring for 5 h, the solvent was evaporated to dryness and the

resulting solid was recrystallized from dichloromethane/*n*-hexane to give air-stable pale yellow crystals of **1** (82 mg, 73% yield). ^1H NMR (300 MHz, CDCl_3 , 298 K, relative to Me_4Si): δ 7.33 (d, 2H, $J = 4.9$ Hz, pyridyl protons *meta* to N), 7.48–7.55 (m, 15H, PPh_3), 8.47 (d, 2H, $J = 4.9$ Hz, pyridyl protons *ortho* to N). Positive-ion FAB-MS: m/z 562 $[\text{M}]^+$. IR (KBr disc, v/cm^{-1}): 2117 (w, $\text{C}\equiv\text{C}$). Elemental analysis: Found (%): C 53.24, H 3.29, N 2.30. Calc. for $\text{C}_{25}\text{H}_{19}\text{AuPN}$ (%): C 53.49, H 3.41, N 2.50.

2.3.1.2. $[(P(p\text{-Tol})_3)\text{Au}(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})]$ (**2**). The procedure was similar to that for **1** except $[(P(p\text{-Tol})_3)\text{AuCl}]$ (107 mg, 0.2 mmol) was used in place of $[(\text{PPh}_3)\text{AuCl}]$ to give air-stable pale yellow crystals of **2** (86 mg, 71% yield). ^1H NMR (300 MHz, CDCl_3 , 298 K, relative to Me_4Si): δ 2.40 (s, 9H, $-\text{CH}_3$), 7.21 (d, 2H, $J = 4.9$ Hz, pyridyl protons *meta* to N), 7.21–7.25 (m, 6H, $-\text{C}_6\text{H}_4-$), 7.40–7.45 (m, 6H, $-\text{C}_6\text{H}_4-$), 7.78 (d, 2H, $J = 4.9$ Hz, pyridyl protons *ortho* to N). Positive-ion FAB-MS: m/z 604 $[\text{M}]^+$. IR (KBr disc, v/cm^{-1}): 2121 (w, $\text{C}\equiv\text{C}$). Elemental analysis: Found (%): C 55.96, H 4.21, N 1.93. Calc. for $\text{C}_{28}\text{H}_{25}\text{AuPN}$ (%): C 55.73, H 4.18, N 2.32.

2.3.2. Syntheses of heterometallic gold(I)–rhenium(I) alkynyl complexes

2.3.2.1. $[(PPh_3)\text{Au}(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})\text{Re}(\text{bpy})(\text{CO})_3]\text{OTf}$ (**3**). To a THF solution (20 ml) of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{MeCN})]\text{OTf}$ (62 mg, 0.10 mmol) was added **1** (56 mg, 0.10 mmol). The mixture was warmed at ca. 42 °C for 24 h. The resulting solution was evaporated to dryness under vacuum and orange crystals of **3** (73 mg, 64% yield) were obtained after slow diffusion of *n*-hexane into a concentrated CH_2Cl_2 solution of the product. ^1H NMR (300 MHz, CDCl_3 , 298 K, relative to Me_4Si): δ 7.25 (d, 2H, $J = 6.4$ Hz, pyridyl protons *meta* to N), 7.42–7.55 (m, 15H, PPh_3), 7.78 (t, 2H, $J = 6.2$ Hz, 4- and 4'-bipyridyl protons), 7.96 (d, 2H, $J = 6.4$ Hz, pyridyl protons *ortho* to N), 8.41 (t, 2H, $J = 7.5$ Hz, 5- and 5'-bipyridyl protons), 8.98 (d, 2H, $J = 7.5$ Hz, 3- and 3'-bipyridyl protons), 9.09 (d, 2H, $J = 5.1$ Hz, 6- and 6'-bipyridyl protons). Positive-ion FAB-MS: m/z 988 $[\text{M} - \text{OTf}]^+$. IR (KBr disc, v/cm^{-1}): 2120 (w, $\text{C}\equiv\text{C}$). Elemental analysis: Found (%): C 40.93, H 2.61, N 3.48. Calc. for $\text{AuReC}_{39}\text{H}_{27}\text{N}_3\text{F}_3\text{O}_6\text{PS}$ (%): C 41.20, H 2.39, N 3.70.

2.3.2.2. $[(P(p\text{-Tol})_3)\text{Au}(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})\text{Re}(\text{bpy})(\text{CO})_3]\text{OTf}$ (**4**). The procedure was similar to that for **3** except **2** (60 mg, 0.10 mmol) was used in place of **1** to give air-stable orange crystals of **4** (77 mg, 65% yield). ^1H NMR (300 MHz, CDCl_3 , 298 K, relative to Me_4Si): δ 2.39 (s, 9H, $-\text{CH}_3$), 7.13–7.21 (m, 2H, pyridyl protons *meta* to N; 2H, 4- and 4'-bipyridyl protons; 6H, $-\text{C}_6\text{H}_4-$), 7.37 (m, 6H, $-\text{C}_6\text{H}_4-$), 7.70 (t, 2H, $J = 7.5$

Hz, 5- and 5'-bipyridyl protons), 7.88 (d, 2H, $J = 6.4$ Hz, pyridyl protons *ortho* to N), 8.38 (t, 2H, $J = 7.5$ Hz, 3- and 3'-bipyridyl protons), 9.00 (d, 2H, $J = 5.1$ Hz, 6- and 6'-bipyridyl protons). Positive-ion FAB-MS: m/z 1030 $[\text{M} - \text{OTf}]^+$. IR (KBr disc, v/cm^{-1}): 2120 (w, $\text{C}\equiv\text{C}$). Elemental analysis: Found (%): C 42.10, H 2.94, N 3.14. Calc. for $\text{AuReC}_{42}\text{H}_{33}\text{N}_3\text{F}_3\text{O}_6\text{PS} \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ (%): C 41.79, H 2.81, N 3.44.

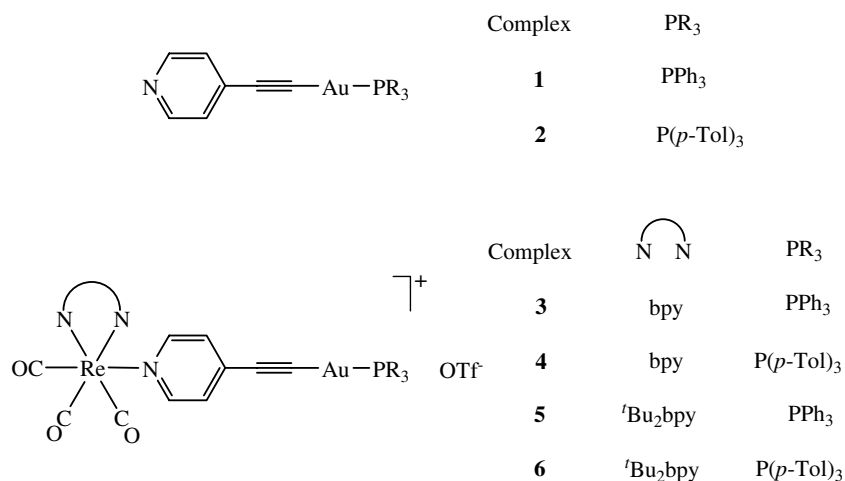
2.3.2.3. $[(PPh_3)\text{Au}(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})\text{Re}(t\text{-Bu}_2\text{bpy})(\text{CO})_3]\text{OTf}$ (**5**). The procedure was similar to that for **3** except $[\text{Re}(t\text{-Bu}_2\text{bpy})(\text{CO})_3(\text{MeCN})]\text{OTf}$ (73 mg, 0.10 mmol) was used in place of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{MeCN})]\text{OTf}$ to give air-stable orange crystals of **5** (60 mg, 48% yield). ^1H NMR (300 MHz, CDCl_3 , 298 K, relative to Me_4Si): δ 1.59 (s, 18H, $t\text{-Bu}$), 7.50–7.67 (m, 2H, pyridyl protons *meta* to N; 15H, PPh_3), 8.08 (dd, 2H, $J = 2.1$ and 5.8 Hz, 5- and 5'-bipyridyl protons), 8.58 (d, 2H, $J = 6.4$ Hz, pyridyl protons *ortho* to N), 8.89 (d, 2H, $J = 2.1$ Hz, 3- and 3'-bipyridyl protons), 8.96 (d, 2H, $J = 6.4$ Hz, 6- and 6'-bipyridyl protons). Positive-ion FAB-MS: m/z 1100 $[\text{M} - \text{OTf}]^+$. IR (KBr disc, v/cm^{-1}): 2115 (w, $\text{C}\equiv\text{C}$). Elemental analysis: Found (%): C 41.56, H 3.42, N 2.68. Calc. for $\text{AuReC}_{47}\text{H}_{43}\text{N}_3\text{F}_3\text{O}_6\text{PS} \cdot 2\text{CH}_2\text{Cl}_2$ (%): C 41.48, H 3.34, N 2.96.

2.3.2.4. $[(P(p\text{-Tol})_3)\text{Au}(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})\text{Re}(t\text{-Bu}_2\text{bpy})(\text{CO})_3]\text{OTf}$ (**6**). The procedure was similar to that for **5** except **2** (60 mg, 0.10 mmol) was used in place of **1** to give air-stable orange crystals of **6** (62 mg, 48% yield). ^1H NMR (300 MHz, CDCl_3 , 298 K, relative to Me_4Si): δ 1.46 (s, 18H, $t\text{-Bu}$), 2.46 (s, 9H, $-\text{CH}_3$), 7.34–7.40 (m, 2H, pyridyl protons *meta* to N; 12H, $-\text{C}_6\text{H}_4-$), 7.55 (d, 2H, $J = 6.4$ Hz, pyridyl protons *ortho* to N), 7.68 (dd, 2H, $J = 2.1$ and 5.9 Hz, 5- and 5'-bipyridyl protons), 8.09 (d, 2H, $J = 2.1$ Hz, 3- and 3'-bipyridyl protons), 8.96 (d, 2H, $J = 5.9$ Hz, 6- and 6'-bipyridyl protons). Positive-ion FAB-MS: m/z 1142 $[\text{M} - \text{OTf}]^+$. IR (KBr disc, v/cm^{-1}): 2115 (w, $\text{C}\equiv\text{C}$). Elemental analysis: Found (%): C 43.43, H 3.87, N 2.58. Calc. for $\text{AuReC}_{50}\text{H}_{49}\text{N}_3\text{F}_3\text{O}_6\text{PS} \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ (%): C 43.60, H 3.70, N 2.96 (see Scheme 1).

3. Results and discussion

3.1. Syntheses and characterization

The 4-ethynylpyridine gold(I) complexes were prepared by modification of the literature procedure 6b,17–19. The gold(I)–rhenium(I) complexes were prepared by heating the corresponding $[\text{Re}(\text{L-L})(\text{CO})_3(\text{MeCN})]\text{OTf}$ complexes with the 4-ethynylpyridine gold(I) complexes in dry THF under an inert atmosphere of nitrogen. After allowing the reaction mixture to heat at ca. 42 °C for 24 h, the solvent was removed



Scheme 1. Schematic drawings of 1–6.

under vacuum, and the solid residue was recrystallized from dichloromethane-*n*-hexane to obtain the analytically pure complexes. In view of the ready decomposition of gold(I) complexes at high temperature, the reaction was carried out at moderate temperature, taking advantage of the easy detachment of the neutral and weakly bound acetonitrile group of the rhenium(I) starting materials.

All the newly synthesized gold(I) alkynyl and mixed-metal gold(I)–rhenium(I) complexes gave satisfactory elemental analyses and were characterized by ¹H NMR and IR spectroscopy. The identities of all the complexes were further confirmed by positive-ion FAB mass spectrometry.

3.2. Electrochemical properties

The cyclic voltammograms of complexes 3–6 showed a characteristic irreversible oxidation wave at ca. +1.66 to +1.79 V vs. SCE. Cyclic voltammetric data for the mixed-metal gold(I)–rhenium(I) complexes were collected in Table 1 and a typical cyclic voltammogram

Table 1
Electrochemical data^a for 3–5 in acetonitrile solution (0.1 mol dm⁻³ ⁿBu₄NPF₆) at 298 K

Complex	Oxidation	Reduction
	<i>E</i> _{pa} ^b /V vs. SCE	<i>E</i> _{1/2} ^c (<i>E</i> _{pc}) ^d /V vs. SCE
3	+1.78	-1.23 (-1.49)
4	+1.79	-1.23 (-1.47)
5	+1.67	-1.36 (-1.58)
6	+1.66	-1.36 (-1.60)

^a Working electrode, glassy carbon; scan rate, 100 mV s⁻¹.

^b *E*_{pa} is the anodic peak potential of the irreversible oxidation wave.

^c *E*_{1/2} is the average of the cathodic and anodic peaks for the reversible reduction couples.

^d *E*_{pc} is the cathodic peak potential of the irreversible reduction wave.

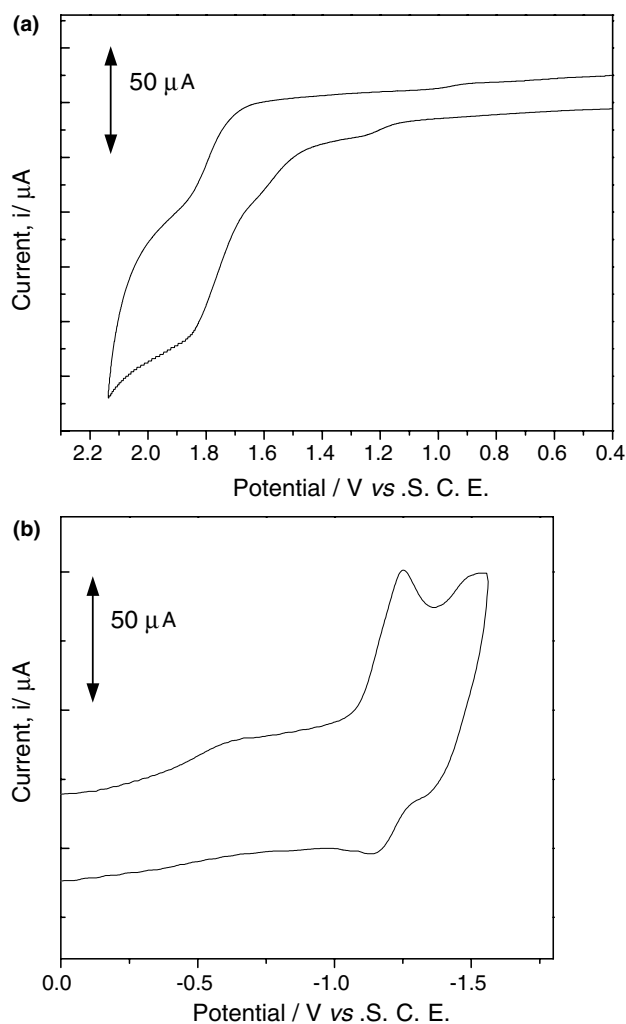


Fig. 1. Cyclic voltammogram showing (a) the oxidation and (b) the reduction of 3 in acetonitrile (0.1 mol dm⁻³ ⁿBu₄NPF₆). Scan rate = 100 mV s⁻¹.

of **4** is shown in Fig. 1. The oxidation wave was found to be insensitive to the nature of the phosphine ligands present but was found to vary with the nature of the diimine ligand. Given the electro-inactive nature of Au(I), the oxidation was tentatively assigned as a Re(I)/Re(II) oxidation, as similar observations have also been reported in other related rhenium(I) diimine systems [35,36], such as the related $[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$ which showed an oxidation wave at +1.74 V vs. SCE [40]. The assignment of the oxidation as ligand-centered oxidation was unlikely since both the diimine ligand and complexes **1** and **2** did not show any appreciable oxidation in the region. The less positive potential observed for the complexes with $^t\text{Bu}_2\text{bpy}$ ligand was in line with the poorer π -accepting ability and the greater electron richness of the $^t\text{Bu}_2\text{bpy}$, which render the rhenium(I) metal center more easily to be oxidized.

For the reductive scan, a reversible reduction wave at ca. 1.23–1.36 V vs. SCE and an irreversible wave at ca. 1.47–1.60 V vs. SCE were observed. Based on previous electrochemical work on the related rhenium(I) system [36,37] and gold(I) system [17,19], the first reduction couple was assigned as the diimine ligand-centered reduction. Similar potentials have also been observed for a related bipyridyl complex, $[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$, with the reduction couples occurring at ca. 1.09 and 1.39 V vs. SCE [40]. The more negative reduction potential observed for the $^t\text{Bu}_2\text{bpy}$ -containing complexes when compared to the bpy analogues could be readily

rationalized by the presence of electron-donating *tert*-butyl groups on the bipyridine ligand, which would make it more electron-rich and poorer π -accepting, and hence reduced its ease of reduction.

3.3. Photophysical properties

3.3.1. Electronic absorption spectroscopy

The electronic absorption spectra of the 4-ethynylpyridine gold(I) complexes, **1** and **2** in dichloromethane show intense absorptions at ca. 250–270 nm, which are also present in the free phosphines and are tentatively assigned as phosphine-centered intraligand transitions. With reference to previous spectroscopic works on gold(I) alkynyl systems [17–19,25], the intense absorptions at ca. 285 nm, which appear to depend on the alkynyl ligands present, are assigned to originate from intraligand $[\pi \rightarrow \pi^*(\text{C}\equiv\text{C})]$ transition. The electronic absorption spectral data of the 4-ethynylpyridine gold(I) and gold(I)–rhenium(I) complexes in dichloromethane at room temperature are tabulated in Table 2.

The electronic absorption spectra of the mixed-metal gold(I)–rhenium(I) complexes **3–6** show, in addition to the high-energy absorptions, a low-energy absorption shoulder at ca. 354–380 nm, which tailed off to ca. 500 nm. With reference to previous spectroscopic work on related rhenium(I) diimine systems [38,39], this absorption band, which is absent in complexes **1** and **2**, is most likely assigned as the $[\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{diimine})]$

Table 2
Photophysical data for **1–6**

Complex	Absorption ^a	Emission	
	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	Medium (T/K)	$\lambda_{\text{em}}/\text{nm}$ ($\tau_o/\mu\text{s}$)
1	254 (23,760), 268 (29,060), 284 (31,450)	Solid (298)	484 (12.3)
		Solid (77)	510
		CH ₂ Cl ₂ (298)	487 (4.7)
2	254 (36,140), 270 (32,590), 284 (34,610)	Solid (298)	514 (14.6)
		Solid (77)	535
		CH ₂ Cl ₂ (298)	494 (3.0)
3	270 (21,600), 288 (27,350), 312 (30,860), 322sh (25,450), 380sh (5670)	Solid (298)	545 (0.17)
		Solid (77)	531
		CH ₂ Cl ₂ (298)	550 (0.80)
4	270 (29,310), 288 (26,440), 312 (32,890), 318sh (26,080), 380sh (3790)	Solid (298)	548 (0.23)
		Solid (77)	528
		CH ₂ Cl ₂ (298)	550 (0.67)
5	270 (34,700), 288 (34,960), 308 (33,280), 322sh (31,300), 354sh (12,080)	Solid (298)	521 (0.37)
		Solid (77)	512
		CH ₂ Cl ₂ (298)	539 (0.73)
6	270 (21,930), 288 (27,450), 310 (27,570), 318sh (19,680), 354sh (9660)	Solid (298)	524 (0.56)
		Solid (77)	525
		CH ₂ Cl ₂ (298)	539 (1.36)

^a In dichloromethane at 298 K.

metal-to-ligand charge transfer (MLCT) transition, characteristic of the rhenium(I) diimine moiety. The electronic absorption spectra of the gold(I)–rhenium(I) complexes are shown in Figs. 2 and 3.

Although the bands appear as shoulders and are usually very broad, a dependence of the energy of the low-energy absorption on the nature of the diimine ligands is still readily observed. The slightly higher absorption energies observed for the ^tBu₂bpy-containing complexes are consistent with the higher π^* orbital energy of ^tBu₂bpy than bpy, as a result of its poorer π -accepting abilities derived from the presence of the more electron-rich *tert*-butyl groups on the bipyridine ligand. The high-energy absorptions at ca. 270–288 nm, which

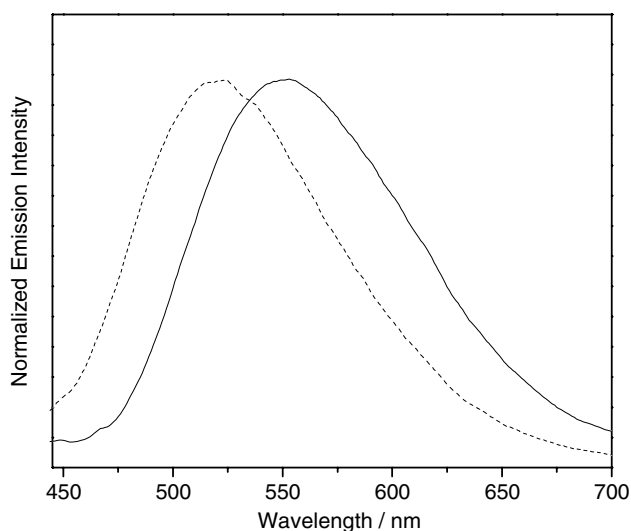


Fig. 2. Normalized solid state emission spectra of **3** (—) and **5** (----) at 298 K.

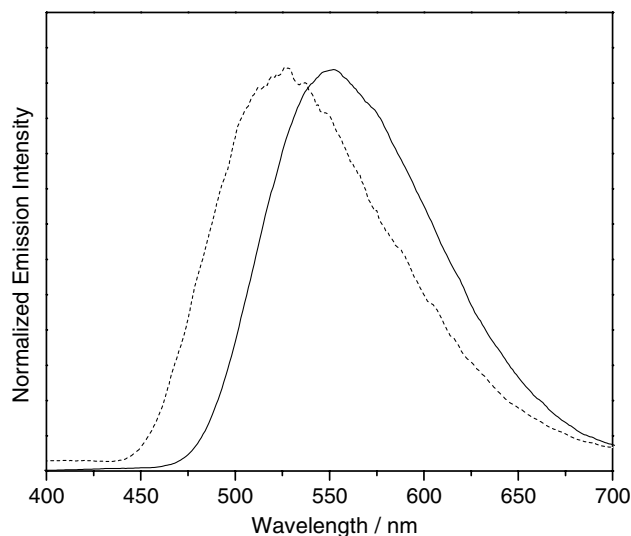


Fig. 3. Normalized emission spectra of **4** (—) and **6** (----) in CH₂Cl₂ at 298 K.

are also found in the complexes **1** and **2**, are assigned as phosphine-centered intraligand transition. The absorption bands centered at ca. 300–322 nm are likely assigned as mixtures of intraligand [$\pi \rightarrow \pi^*(C\equiv C)$], intraligand [$\pi \rightarrow \pi^*$ (bpy or ^tBu₂bpy)] and [$d\pi(\text{Re}) \rightarrow \pi^*(\text{pyridine})$] MLCT transitions, as similar transitions also occur in their precursor complexes [38–40].

3.3.2. Steady-state emission spectroscopy

The 4-ethynylpyridine gold(I) complexes **1** and **2** gave intense emission bands at room temperature at 484 and 514 nm, respectively, in the solid state upon photoexcitation with $\lambda > 350$ nm. Their luminescence lifetimes in the microsecond range suggested that the emissions are phosphorescence in nature. The photophysical data of the 4-ethynylpyridine gold(I) and gold(I)–rhenium(I) complexes are summarized in Table 2. With reference to previous spectroscopic work on gold(I) alkynyl systems [17–19,25], the emission is tentatively assigned as derived from an excited state of $^3[\sigma(\text{Au}-\text{P}) \rightarrow \pi^*(C\equiv C)]$ origin. The slight red shift in emission energy on going from PPh₃ in **1** to PTol₃ in **2** is consistent with an assignment of the emissive state as derived from a $^3[\sigma \rightarrow \pi^*]$ transition associated with the [Au(C \equiv CC₅-H₄N)] group, since PTol₃, being a better electron donor than PPh₃, would render the gold(I) center more electron rich, and hence leading to the $^3[\sigma(\text{Au}-\text{P}) \rightarrow \pi^*(C\equiv \text{CR})]$ excited state lower-lying in energy.

In solution, complexes **1** and **2** emit at 487 and 494 nm, respectively. The relatively lower emission energy of **1** than that of the related [(PPh₃)Au(C \equiv CPh)] [13,21] is in line with the lower π^* orbital energies of C \equiv CC₅H₄N than C \equiv CPh and the assignment of an excited state of $^3[(\text{Au}-\text{P}) \rightarrow \pi^*(C\equiv \text{CR})]$ origin.

Excitation of the mixed-metal gold(I)–rhenium(I) complexes **3–6** at $\lambda \geq 350$ nm both in the solid state and in dichloromethane solution at room temperature resulted in a yellowish green luminescence centered at ca. 510–580 nm. The emission spectra of complexes **3–6** are shown in Figs. 2 and 3. The difference in the emission energy as well as the large discrepancy in the luminescence lifetime observed for the mixed-metal complexes and the gold(I) precursor complexes may suggest that their emissions are of different origins. The dependence of the emission energy on the π^* orbital energy of the bipyridine ligands on the rhenium(I) center, in which the emission energies of the ^tBu₂bpy complexes are higher than that of their bpy analogues, is suggestive of an emission origin of predominantly $^3\text{MLCT}$ [$d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$] character. The lack of an alkynyl-gold(I)-based emission in the mixed-metal complexes is suggestive of an efficient intramolecular energy transfer process from the $^3[\sigma(\text{Au}-\text{P}) \rightarrow \pi^*(C\equiv \text{CR})]$ to the lower-lying $^3\text{MLCT}$ [$d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$] excited state that give rise to the emission. The slightly higher emission energy of **3** and **4** relative to their [Re(bpy)-

(CO)₃(py)]⁺ counterparts [40] is suggestive of the perturbation brought about by the presence of the alkynyl-gold(I) moiety. It is likely that the alkynylgold(I) moiety upon attachment to the pyridyl unit would reduce the σ -donor strength of the pyridyl ligand, stabilizing the $d\pi(\text{Re})$ orbital, leading to a slightly larger MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$] energy gap. Such an assignment is also in line with the electrochemical studies, in which the HOMO has substantial rhenium metal-centered character while the LUMO is mainly bipyridine ligand-based in character. The relatively long radiative lifetimes observed are suggestive of an emissive origin of triplet parentage, possibly derived from the ³MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$] state, modified by the attachment of the alkynylgold(I) moiety.

4. Conclusion

A series of mixed-metal gold(I)–rhenium(I) alkynyl complexes and their precursor 4-ethynylpyridine gold(I) complexes have been synthesized and structurally characterized. The electrochemistry of mixed-metal gold(I)–rhenium(I) complexes has also been studied. Both the gold(I) precursor complexes and the mixed-metal gold(I)–rhenium(I) alkynyl complexes are found to be emissive both in the solid state and in dichloromethane solution. An assignment of the emission of the mixed-metal gold(I)–rhenium(I) alkynyl complexes as derived from a ³MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{bpy})$] origin that has been modified by the presence of the alkynylgold(I) moiety is suggested, and supported by electrochemical studies.

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References

- [1] (a) V.W.W. Yam, *J. Organomet. Chem.* 689 (2004) 1393;
(b) N.J. Long, C.K. Williams, *Angew. Chem. Int. Ed.* 42 (2003) 2586;
(c) F. Paul, C. Lapinte, *Coord. Chem. Rev.* 431 (1998) 178;
(d) C. Bruneau, P.H. Dixneuf, *Acc. Chem. Res.* 32 (1999) 311;
(e) M.I. Bruce, M. Ke, P.J. Low, B.W. Skelton, A.H. White, *Organometallics* 17 (1998) 3539;
- (f) V. Cadierno, M.P. Gamasa, J. Gimeno, *Organometallics* 17 (1998) 697;
- (g) G. Roidl, V. Enkelmann, R.D. Adams, U.H.F. Bunz, *J. Organomet. Chem.* 578 (1999) 144.
- [2] (a) T. Müller, S.W.K. Choi, D.M.P. Mingos, D. Murphy, D.J. Williams, V.W.W. Yam, *J. Organomet. Chem.* 484 (1994) 209;
(b) C.M. Che, H.Y. Chao, V.M. Miskowski, Y. Li, K.K. Cheung, *J. Am. Chem. Soc.* 123 (2001) 4985;
(c) W. Lu, H.F. Xiang, N. Zhu, C.M. Che, *Organometallics* 21 (2002) 2343.
- [3] (a) D.M.P. Mingos, J. Yau, S. Menzer, D.J. Williams, *Angew. Chem. Int. Ed.* 34 (1995) 1894;
(b) F. Mohr, M.C. Jennings, R.J. Puddephatt, *Eur. J. Inorg. Chem.* (2003) 217;
(c) R.J. Puddephatt, *Coord. Chem. Rev.* 216–217 (2001) 313;
(d) C.P. McArdle, S. Van, M.C. Jennings, R.J. Puddephatt, *J. Am. Chem. Soc.* 124 (2002) 3959;
(e) F. Mohr, D.J. Eisler, C.P. McArdle, K. Atieh, M.C. Jennings, R.J. Puddephatt, *J. Organomet. Chem.* 670 (2003) 27.
- [4] M.P. Berthelot, *Liebigs Ann. Chem.* 139 (1866) 150.
- [5] G.E. Coates, C. Parkin, *J. Chem. Soc.* (1962) 3220.
- [6] (a) R.J. Cross, M.F. Davidson, A.J. McLennan, *J. Organomet. Chem.* 265 (1984) C37;
(b) R.J. Cross, M.F. Davidson, *J. Chem. Soc., Dalton Trans.* (1986) 411.
- [7] (a) M.I. Bruce, E. Horn, J.G. Matisons, M.R. Snow, *Aust. J. Chem.* 37 (1984) 1163;
(b) M.I. Bruce, D.N. Duffy, *Aust. J. Chem.* 39 (1986) 1697;
(c) M.I. Bruce, K.R. Grundy, M.J. Lidell, M.R. Snow, R.T. Tiekink, *J. Organomet. Chem.* 344 (1988) C49.
- [8] (a) J. Vicente, M.T. Chicote, M.D. Abrisqueta, *J. Chem. Soc., Dalton Trans.* (1995) 497;
(b) J. Vicente, M.T. Chicote, M.D. Abrisqueta, *Organometallics* 16 (1997) 5628.
- [9] C.P. McArdle, M.C. Jennings, J.J. Vittal, R.J. Puddephatt, *Chem. Eur. J.* 7 (2001) 3572.
- [10] F. Mohr, R.J. Puddephatt, *J. Organomet. Chem.* 689 (2004) 374.
- [11] X.X. Lu, C.K. Li, E.C.C. Cheng, N. Zhu, V.W.W. Yam, *Inorg. Chem.* 43 (2004) 2225.
- [12] (a) V.W.W. Yam, K.L. Cheung, L.H. Yuan, K.M.C. Wong, K.K. Cheung, *Chem. Commun.* 16 (2000) 1513;
(b) V.W.W. Yam, S.K. Yip, L.H. Yuan, K.L. Cheung, N. Zhu, K.K. Cheung, *Organometallics* 22 (2003) 2630.
- [13] D. Li, X. Hong, C.M. Che, W.C. Lo, S.M. Peng, *J. Chem. Soc., Dalton Trans.* (1993) 2929.
- [14] C.M. Che, H.K. Yip, W.C. Lo, S.M. Peng, *Polyhedron* 13 (1994) 887.
- [15] X. Hong, K.K. Cheung, C.X. Guo, C.M. Che, *J. Chem. Soc., Dalton Trans.* (1994) 1867.
- [16] W. Lu, H.F. Xiang, N. Zhu, C.M. Che, *Organometallics* 21 (2002) 2343.
- [17] V.W.W. Yam, S.W.K. Choi, *J. Chem. Soc., Dalton Trans.* (1996) 4227.
- [18] V.W.W. Yam, S.W.K. Choi, K.K. Cheung, *Organometallics* 15 (1996) 1734.
- [19] V.W.W. Yam, S.W.K. Choi, K.K. Cheung, *J. Chem. Soc., Dalton Trans.* (1996) 3411.
- [20] H. Xiao, K.K. Cheung, C.M. Che, *J. Chem. Soc., Dalton Trans.* (1996) 3699.
- [21] M.J. Irwin, J.J. Vittal, R.J. Puddephatt, *Organometallics* 16 (1997) 3541.
- [22] H.Y. Chao, W. Lu, Y. Li, M.C.W. Chan, C.M. Che, K.K. Cheung, N. Zhu, *J. Am. Chem. Soc.* 124 (2002) 14696.
- [23] W. Lu, N. Zhu, C.M. Che, *J. Organomet. Chem.* 607 (2003) 11.
- [24] W. Lu, N. Zhu, C.M. Che, *J. Am. Chem. Soc.* 125 (2003) 16081.

- [25] V.W.W. Yam, K.L. Cheung, S.K. Yip, K.K. Cheung, *J. Organomet. Chem.* 681 (2003) 196.
- [26] (a) O.M. Abu-Salah, A. Al-Ohaly, A. Razzak, *J. Chem. Soc., Dalton Trans.* (1988) 2297;
(b) O.M. Abu-Salah, *J. Organomet. Chem.* 387 (1990) 123;
(c) O.M. Abu-Salah, A. Razzak, A. Al-Ohaly, Z.F. Mutter, *J. Organomet. Chem.* 391 (1990) 267;
(d) O.M. Abu-Salah, A. Al-Ohaly, A. Razzak, Z.F. Mutter, *J. Organomet. Chem.* 389 (1990) 427.
- [27] M.I. Bruce, B.C. Hall, B.W. Skelton, M.E. Smith, A.H. White, *J. Chem. Soc., Dalton Trans.* (2002) 995.
- [28] V.W.W. Yam, K.L. Cheung, E.C.C. Cheng, N. Zhu, K.K. Cheung, *J. Chem. Soc., Dalton Trans.* (2003) 1830.
- [29] (a) K.M.C. Wong, S.C.F. Lam, C.C. Ko, N. Zhu, V.W.W. Yam, S. Roue, C. Lapinte, S. Fathallah, K. Costuas, S. Kahlal, J.F. Halet, *Inorg. Chem.* 42 (2003) 7086;
(b) V.W.W. Yam, W.Y. Lo, C.H. Lam, W.K.M. Fung, K.M.C. Wong, V.C.Y. Lau, N. Zhu, *Coord. Chem. Rev.* 245 (2003) 39;
(c) V.W.W. Yam, W.Y. Lo, N. Zhu, *Chem. Commun.* (2003) 2446;
(d) V.W.W. Yam, S.H.F. Chong, K.M.C. Wong, K.K. Cheung, *Chem. Commun.* (1999) 1013;
(e) V.W.W. Yam, W.K.M. Fung, K.M.C. Wong, V.C.Y. Lau, K.K. Cheung, *Chem. Commun.* (1998) 777.
- [30] T.B. Hadda, H.L. Bozec, *Polyhedron* 7 (1988) 575.
- [31] M.I. Bruce, B.K. Nicholson, O.B. Shawkataly, *Inorg. Synth.* 26 (1989) 324.
- [32] S.M. Fredericks, J.C. Luong, M.S. Wrighton, *J. Am. Chem. Soc.* 101 (1979) 7415.
- [33] D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemical*, third ed., Pergamon Press, Oxford, 1988.
- [34] (a) R.R. Gagne, C.A. Koval, G.C. Lisensky, *Inorg. Chem.* 19 (1980) 2854;
(b) C.M. Che, K.Y. Wong, F.C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.* 226 (1987) 211.
- [35] K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans. 2* (82) (1986) 2401.
- [36] J.K. Hino, L.D. Ciana, W.J. Dressick, B.P. Sullivan, *Inorg. Chem.* 31 (1992) 1072.
- [37] (a) S.A. Moya, J. Guerrero, R. Pastene, R. Schmidt, R. Sariego, R. Sartori, J. Sanz-Aparocop, I. Fomseca, M. Martinez-Ripoll, *Inorg. Chem.* 33 (1994) 2341;
(b) S.A. Moya, R. Pastene, R. Schmidt, J. Cuerrero, R. Sartori, *Polyhedron* 11 (1992) 1665;
(c) R. Lin, Y. Fu, C.P. Brock, T.F. Guarr, *Inorg. Chem.* 31 (1992) 4336;
(d) M.K. DeArmond, K.W. Hanck, D.W. Wertz, *Coord. Chem. Rev.* 65 (1985) 65;
(e) J.B. Cooper, D.B. MacQueen, J.D. Peterson, D.W. Wertz, *Inorg. Chem.* 29 (1990) 3701.
- [38] (a) V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, *Organometallics* 14 (1995) 2749;
(b) V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, *Organometallics* 15 (1996) 1740;
(c) V.W.W. Yam, S.H.F. Chong, K.K. Cheung, *Chem. Commun.* (1998) 2121;
(d) V.W.W. Yam, S.H.F. Chong, K.M.C. Wong, K.K. Cheung, *Chem. Commun.* (1999) 1013;
(e) V.W.W. Yam, K.K.W. Lo, K.M.C. Wong, *J. Organomet. Chem.* 578 (1999) 3.
- [39] (a) M.S. Wrighton, D.L. Morse, *J. Am. Chem. Soc.* 96 (1974) 998;
(b) M.S. Wrighton, D.L. Morse, L. Pdungsap, *J. Am. Chem. Soc.* 97 (1975) 2073;
(c) G. Tapolsy, R. Duesing, T.J. Meyer, *Inorg. Chem.* 29 (1990) 2285;
(d) J.K. Hino, L.D. Ciana, W.J. Dressick, B.P. Sullivan, *Inorg. Chem.* 31 (1992) 1072.
- [40] L. Sacksteder, A.P. Zipp, E.A. Brown, J. Sreich, J.N. Demas, B.A. DeGraff, *Inorg. Chem.* 29 (1990) 4335.