Heteropolynuclear Complexes containing Multiple Redox and Chromophoric Moieties: σ-Alkynyl-bipyridine or -terpyridine Derivatives of Platinum(II)

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The *cis*- and *trans*-platinum(II) acetylide complexes of the type $[Pt^{II}(PBu^n_3)_2L_2]$ [L = 4-ethynyl-2,2′-bipyridine or 4′-R-2,2′:6′,2″-terpyridine (R = ethynyl or butadiynyl)] have been selectively synthesized and their use as ligands in the synthesis of heterotrinuclear M_2Pt complexes (M = Ru^{II}, Os^{II} or Re^{I}) has been investigated.

One of the most active research subjects being pursued over the last decade concerns the design and construction of molecular-scale devices for information storage and transfer.[1] Such systems need a logical signal generation upon external photon- or electron-stimulation and long-range vectorial energy- or electron-transfer. Conjugated organic[2] or organometallic[3,4] polymers containing σ-acetylide bonds display extended π-electron conjugation. Oligopyridines functionalized with alkyne substituents[5] have been used as building blocks in the synthesis of homoditopic,[6,7] heteroditopic[6] or tritopic ligands.[8] Their rigid-rod-like polynuclear transition-metal complexes behave as aggregated chromophores displaying outstanding delocalization properties in their excited states.[9] Our approach is now to use these alkyne-substituted 2,2′-bipyridine (bipy) and 2,2′:6′,2″-terpyridine (terpy) subunits as building blocks for the preparation of σ-acetylide complexes (*e.g.* with Pt^{II}). Subsequent complexation of these mononuclear platinum compounds with redox- and/or photo-active metals should give luminescent monomeric or polymeric heteronuclear complexes. In these materials an optical or electric excitation might be followed by a spatially directed energy- or electron-transfer along the backbone. This could in principle be tuned by the nature and/or the geometric environment of the central metal. We report here the synthesis, characterization and preliminary properties of the hitherto unreported *cis*- and *trans*-$[Pt^{II}(PBu^n_3)_2L_2]$ (L = alkynyl-substituted bipy or terpy), as well as the preparation of novel redox- and photo-active heterotrinuclear M_2Pt (M = Ru^{II}, Os^{II} or Re^{I}) complexes.

The *trans* compounds **4**, **6** and **7** were prepared in good yield (70–84%), equation (1), respectively by quantitative reaction

$$2L + cis\text{- or } trans\text{-}[Pt(PBu^n_3)_2Cl_2] \longrightarrow cis\text{- or } trans\text{-}[Pt^{II}(PBu^n_3)_2L_2] \quad (1)$$

of 4-ethynyl-2,2′-bipyridine (**1**),[6] 4′-ethynyl-2,2′:6′,2″-terpyridine (**2**)[10] or 4′-butadiynyl-2,2′:6′,2″-terpyridine (**3**)† with *trans*-$[Pt^{II}(PBu^n_3)_2Cl_2]$,[12] using a CuI catalyst (0.6–2.3 mol %), and diisopropylamine as base;‡ this has been previously described for similar compounds.[13] The parent *cis* compounds **5** and **8** were prepared similarly (85%) from *cis*-$[Pt^{II}(PBu^n_3)_2Cl_2]$.

The trinuclear Ru_2Pt complexes **10** and **13** are prepared either by treating, respectively, the monoethynyl ruthenium complex **9**§ with *trans*- or *cis*-$[Pt^{II}(PBu^n_3)_2Cl_2]$ as described above [copper(I) catalysis], or by selective complexation of the bipyridine moiety with $[Ru(bipy)_2Cl_2]\cdot 2H_2O$[14] using a 'complex as ligand/complex as metal' methodology. The *trans*-Os_2Pt and -Re_2Pt complexes **11** and **12** were synthesized by reacting precursor **4** with, respectively, two equivalents of $[Os(bipy)_2Cl_2]$[15] or $[Re(CO)_5Cl]$.[16] All complexes were obtained as crystalline materials and characterized as shown in Table 1. The observed carbon chemical shifts are in good agreement with those reported for the ethynyl precursors.[6] For the *cis* isomers (**5** and **8**), four signals were observed for the ethynyl carbons, while only two could be detected in the parent *trans* isomers (**4** and **6**). This is likely due to steric hindrance of the oligopyridine subunit which induces asymmetry in the square planar complex. The $\nu_{C \equiv C}$ stretching vibrations in Table 1 are close to values reported for other *cis*- and *trans*-dialkynylated complexes of platinum(II).[4c,13] Ruthenium, osmium or rhenium complexation of the key complexes **4** and **5** showed, as expected, little change in the NMR and IR spectra (see Table 1). Furthermore, all the new complexes exhibited a molecular peak in their FAB^+ mass spectra with the expected isotopomer distributions and no significant peaks at higher mass. Based on the ^{31}P NMR spectra, no thermal or photochemical isomerization of either the mono- or tri-nuclear compounds has been observed, as seen previously in metal–alkynyl complexes.[1] The use of π-acidic ethynyloligopyridine and tributylphosphine ligands favours such a stabilization.

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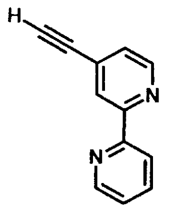
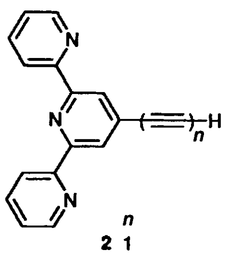
† Synthesized from **2** coupled with (triethylsilyl)acetylene bromide using the Cadiot–Chodkiewicz reaction[11] (56% yield), and subsequent deprotection with NaOH (5 mol dm^{-3}) in $MeOH-CH_2Cl_2$ (93% yield): *m/z*(nba) 282 $[M + H]^+$, 256 $[M - C{\equiv}CH]$, 232 $[M - C{\equiv}C{-}C{\equiv}CH]$ (Found: C, 81.00; H, 3.85; N, 14.75. Calc. for $C_{19}H_{11}N_3$: C, 81.10; H, 3.95; N, 14.95%).

‡ In a typical experiment compound **4** was prepared by treating **1** (0.40 g, 2.22 mmol) at room temperature for 5 d with *trans*-$[Pt^{II}(PBu^n_3)_2Cl_2]$ (0.744 g, 1.11 mmol) in anhydrous tetrahydrofuran (20 cm^3) and anhydrous diisopropylamine (5 cm^3), in the presence of CuI (2 cm^3, 0.0025 mmol in MeCN), as catalyst. The crude product was purified through a chromatography column packed with alumina and eluted with CH_2Cl_2. Recrystallization of the precipitate by slow diffusion of hexane into a CH_2Cl_2 solution afforded the analytically pure compound **4** (0.85 g, 81%).

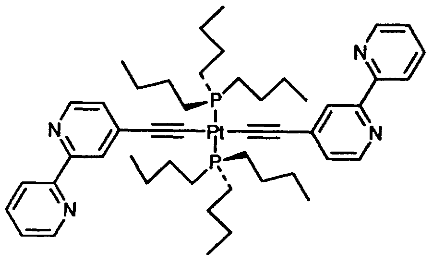
§ Synthesized in 64% yield from **1** and $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ in $EtOH-H_2O$ at 60 °C.



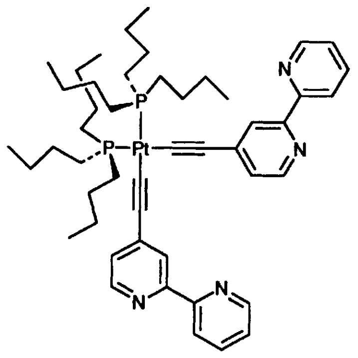
1



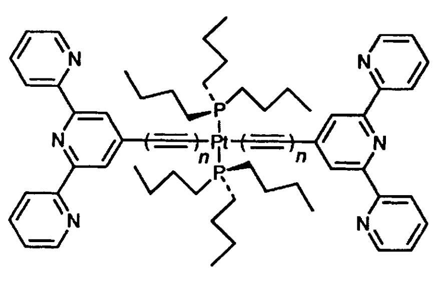
	n
2	1
3	2



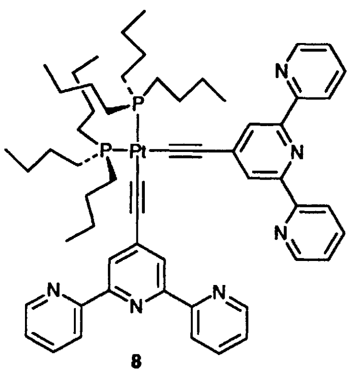
4



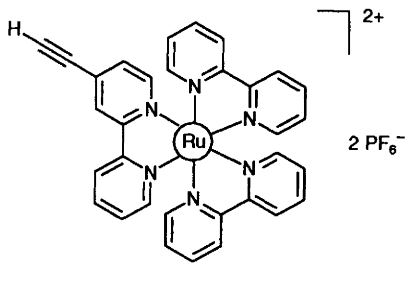
5



	n
6	1
7	2

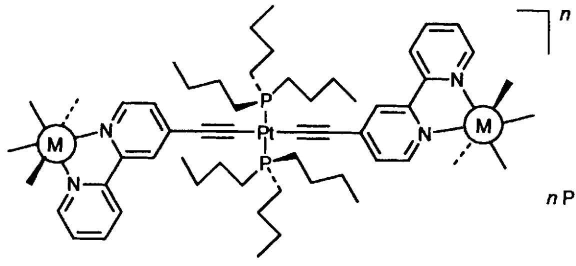


8



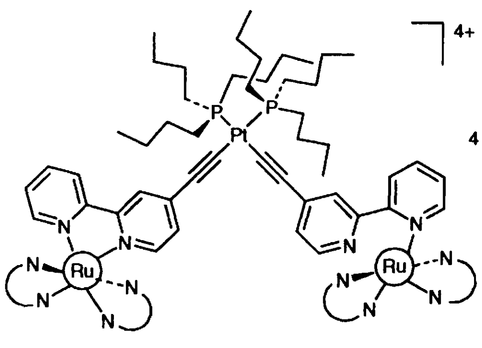
2 PF_6^-

9



n PF_6^-

	M	*n*
10	Ru(bipy)$_2$	4
11	Os(bipy)$_2$	4
12	Re(CO)$_3$Cl	0



4 PF_6^-

13

Table 1 Selected data for the mono- and tri-nuclear complexes **4–13**

Compound	Isolated yield (%)	^{31}P-{^{1}H} NMR[a] (δ) (J_{PPt}/Hz)	^{13}C-{^{1}H} NMR[b] (δ)	$\nu_{\mathrm{C\equiv C}}$[c] (cm^{-1})	FAB$^+$[d] (nature of the cluster)	λ_{max}[e]/nm (ε/dm^3 mol^{-1} cm^{-1})	Elemental analysis[f] (%)
4	81	3.95 (2317)	117.4, 108.3	2097	958 ([**4** + H]$^+$)	334 (4900)	C, 59.85 (60.15); H, 7.00 (7.15); N, 5.60 (5.85)
5	86	−2.87 (2252)	116.3, 115.9, 113.5, 113.1	2115	958 ([**5** + H]$^+$)	316 (17 200)	C, 59.80 (60.15); H, 6.90 (7.15); N, 5.65 (5.85)
6	84	3.92 (2317)	117.6, 108.8	2104	1112 ([**6** + H]$^+$)	336 (21 400)	C, 62.65 (62.65); H, 6.80 (6.70); N, 7.35 (7.55)
7	78	—	—	2179 2055	1160 ([**7** + H]$^+$)	343 (89 300) 360 (89 800)	C, 64.05 (64.20); H, 6.60 (6.65); N, 7.20 (7.25)
8	85	−2.95 (2246)	116.3, 115.9, 113.5, 113.1	2117	1112 ([**8** + H]$^+$)	310 (89 800)	C, 62.50 (62.65); H, 6.50 (6.70); N, 7.35 (7.55)
9	64	—	87.9, 87.6	3271 2116	738 {[**1** + Ru(bipy)$_2$]$^{2+}$ + PF$_6^-$}	453 (12 900)	C, 43.40 (43.50); H, 2.70 (2.75); N, 9.40 (9.50)
10	85	5.01 (2281)	121.0, 108.4	2082	2222 {[**4** + Ru$_2$(bipy)$_4$]$^{4+}$ + 3PF$_6^-$ + 2H}	456 (31 200)	C, 44.45 (44.70); H, 4.10 (4.25); N, 6.95 (7.10)
11	18	5.21 (2279)	114.8, 108.2	2081	2399 {[**4** + Os$_2$(bipy)$_4$]$^{4+}$ + 3PF$_6^-$ − H}	340 (21 400) 481 (15 600)	C, 41.40 (41.55); H, 3.80 (3.95); N, 6.55 (6.60)
12	78	5.24 (2273)	119.4, 108.9	2085	1568/1570 {[**4** + Re$_2$Cl$_2$(CO)$_6$ + H]$^+$}	335 (43 700) 393 (36 200)	C, 41.25 (41.30); H, 4.30 (4.35); N, 3.45 (3.55)
13	78	−2.08 (2255)	—	2116	2222 {[**4** + Ru$_2$(bipy)$_4$]$^{4+}$ + 3PF$_6^-$ + 2H}	456 (31 100)	C, 44.40 (44.70); H, 4.00 (4.25); N, 6.80 (7.10)

[a] Measured in CD$_2$Cl$_2$ for **4–6**, **8** or in (CD$_3$)$_2$CO for **10–13**. [b] Chemical shifts for C≡C and C≡CH (**9**), measured in CD$_2$Cl$_2$ for **4–6**, **8**, in CD$_3$CN for **9**, and in (CD$_3$)$_2$CO for **10–13**. [c] KBr pellets. [d] *m*-Nitrobenzyl alcohol (nba) matrix, except for **11** where tetraglyme (2,5,8,11,14-pentaoxapentadecane) was used. [e] In CH$_2$Cl$_2$ for **4–6**, **8** or MeCN for **9–13**. [f] Calculated values in parentheses.

The electronic absorption and luminescence spectra show a number of general trends and features. All complexes exhibit absorption bands that are ascribed to π–π* (intraligand high energy band) and charge-transfer transitions (low energy bands). In the mononuclear Pt$^{\mathrm{II}}$ complexes **4–8** the lowest absorption band (two bands being observed in the diyne complex **7**) is presumably due to an alkynyl–platinum transition [ligand-to-metal charge transfer (l.m.c.t.) in nature].[17] In the bipy case the *trans* isomer **4** (λ_{lmct} 334 nm) displays a significant bathochromic shift relative to that of the *cis* isomer **5** (λ_{lmct} 316 nm) due to a better conjugation in the *trans* form than in the *cis* isomer. In the trinuclear complexes the lowest energy absorption band was assigned to the metal-to-ligand charge transfer (m.l.c.t.) transition $\mathrm{M} \longrightarrow \pi^*(\mathrm{bipy})$. The energy required to reach those transitions compared well with that found in authentic samples of [M(bipy)$_3$]$^{2+}$ (M = Ru or Os) and [Re(bipy)(CO)$_3$Cl]. All complexes exhibit luminescence when excited in their m.l.c.t. absorption bands: λ_{em} = 618, 733, 603 and 618 ± 2 nm for **10**, **11**, **12** and **13**, respectively, in acetonitrile solution [(1.1–4.2) × 10^{-5} mol dm^{-3}], at room temperature.

In summary, some novel σ-alkynyl-bipyridine or -terpyridine complexes of platinum(II) have been synthesized and characterized. These multinucleating materials have been used in the synthesis of polymetallic assemblies, which exhibit m.l.c.t. emitting states. Further studies are clearly deserved to define fully the scope and limitation of this methodology. The photochemical and electrochemical properties are currently under investigation and will be the subject of future reports.

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