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Novel blue luminescent platinum acetylide materials with a 9-acridone or a dansyl group [dansyl = 5-(dimethylamino)-naphthalene-1-sulfonyl]

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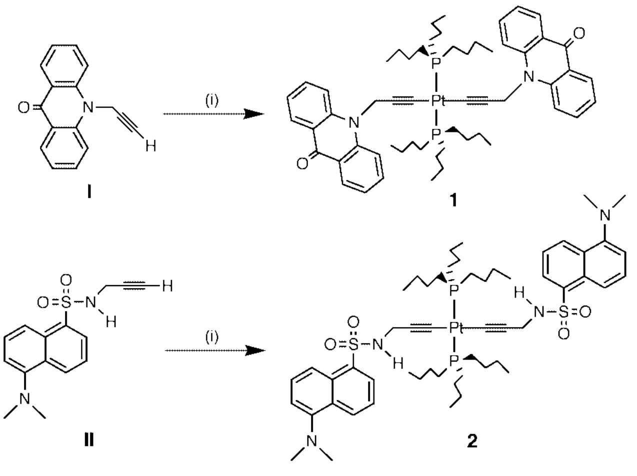
Air-stable blue luminescent platinum(II) acetylide compounds *trans*-[Pt(PBu$_3$)$_2$(L)$_2$] [LH = 10-(2-propynyl)-9-acridone 1, 5-(dimethylamino)-*N*-(2-propynyl)-1-naphthalenesulfonamide 2] are synthesised and structurally characterised.

There is an upsurge of research interest by scientists and industrialists alike in the search for new luminescent materials due to their potential use in electroluminescence (EL) display technology.[1] Specifically, research into blue luminescent compounds is receiving a great deal of current attention in both academia and industry, and the realisation of blue EL is an important step for the possible application of these materials in flat-panel colour displays.[2] Within the family of blue luminescent compounds previously used in EL devices or light-emitting diodes, most of them belong to either aromatic organic molecules or conjugated organic polymers.[3] Blue emissive organometallic complexes are, to our best knowledge, very rare.[1a,4] In line with our interests in transition metal acetylide complexes and polymers, we have discovered two interesting blue luminescent platinum acetylide compounds carrying the 9-acridone or 5-(dimethylamino)naphthalene-1-sulfonyl (dansyl) entity. In view of the well-known high luminescence quantum yields of the auxiliary 9-acridone and dansyl groups,[5] we envisioned that a properly derivatised molecule such as 10-(2-propynyl)-9-acridone **I** or 5-(dimethylamino)-*N*-(2-propynyl)-1-naphthalenesulfonamide **II** could be used to attach a fluorescent label to the metal centre through an acetylide bridge, which is likely to exhibit novel optical and photo-electronic properties. We report here the preliminary results of such a study.

An adaptation of the literature methods was used to prepare the ligand precursors **I** and **II**.[6] The off-white platinum(II) acetylide complexes **1** and **2** were synthesised by the CuI-catalysed dehydrohalogenation reaction between *trans*-[PtCl$_2$(PBu$_3$)$_2$] and two molar equivalents of **I** or **II** using NHPr$^i_2$ as a base (Scheme 1).[7] Both compounds were isolated by alumina TLC and recrystallisation from hexane–CH$_2$Cl$_2$ gave air-stable colourless crystals in 38 (**1**) and 42% (**2**) yields. Compounds **1** and **2** have been characterised by satisfactory elemental analysis, FAB mass spectrometry, IR and NMR spectroscopies.† The disappearance of IR bands at 3301 cm^{-1} due to $\nu_{C\equiv CH}$ of the free ligands indicates the formation of metal–acetylide bonds in **1** and **2**. The single $\nu_{C\equiv C}$ stretching frequency in the range 2121–2125 cm^{-1} confirmed the presence of the σ-alkynyl ligands, consistent with the *trans* geometry. A singlet signal in their ^{31}P-{^{1}H} NMR spectra is also in accord with the *trans* arrangement of the Pt(PBu$_3$)$_2$ unit.



Scheme 1 (i) *trans*-[PtCl$_2$(PBu$_3$)$_2$], CuI, NHPr$^i_2$.

Table 1 Absorption and emission data for compounds **I**, **II**, **1** and **2**

Compound	Absorption[a] λ_{max}/nm (ε/10^4 dm^3 mol^{-1} cm^{-1})	Emission, λ_{em}/nm CH$_2$Cl$_2$	Thin film	KBr
I	250 (3.6), 373 (1.9), 390 (2.4)	417	[b]	462
II	230 (1.4), 253 (1.6), 345 (0.5)	508	479	470
1	249 (1.6), 305 (0.4), 383 (0.5), 401 (0.7)	413	449	440
2	228 (2.0), 256 (1.8), 305 (0.6), 342 (0.3), 363 (0.3)	494	473	463

[a] In CH$_2$Cl$_2$. [b] Good-quality films not available.

The solid state structures of both **1** and **2** were established unambiguously by single-crystal X-ray analyses.‡ Figs. 1 and 2 depict the molecular structures of **1** and **2**, respectively, along with some pertinent bond parameters. Each of the platinum atoms in **1** and **2** sits on a crystallographic centre of symmetry, which imposes exact planarity at the metal centre, and requires the two alkynyl groups and the two PBu$_3$ ligands to occupy mutually *trans* positions. The local coordination environment around the Pt(II) ion is square planar in both cases. The Pt–C distance lies within the range 1.98–2.06 Å found in other platinum bis(alkynyl) complexes and the C≡C bond lengths of 1.178(7) and 1.21(1) Å in **1** and **2**, respectively, are characteristic of metal–acetylide σ-bonding. The Pt(1)–C(28)–C(27)–C(26) (for **1**) and Pt(1)–C(1)–C(2)–C(3) (for **2**) alkynyl fragments are essentially linear. For **2**, the sulfur atom S(1) essentially adopts a distorted tetrahedral geometry. The mean naphthalene plane is almost planar (maximum deviation 0.048 Å). There are no unusual bond parameters in the organic moieties of both molecules.

The photophysical properties of uncomplexed (**I** and **II**) and complexed (**1** and **2**) chromophores have been studied. The absorption and emission data are collected in Table 1. Both ligand precursors **I** and **II** exhibit three intense absorption bands in the near-UV region that are ascribed to π–π* (intra-

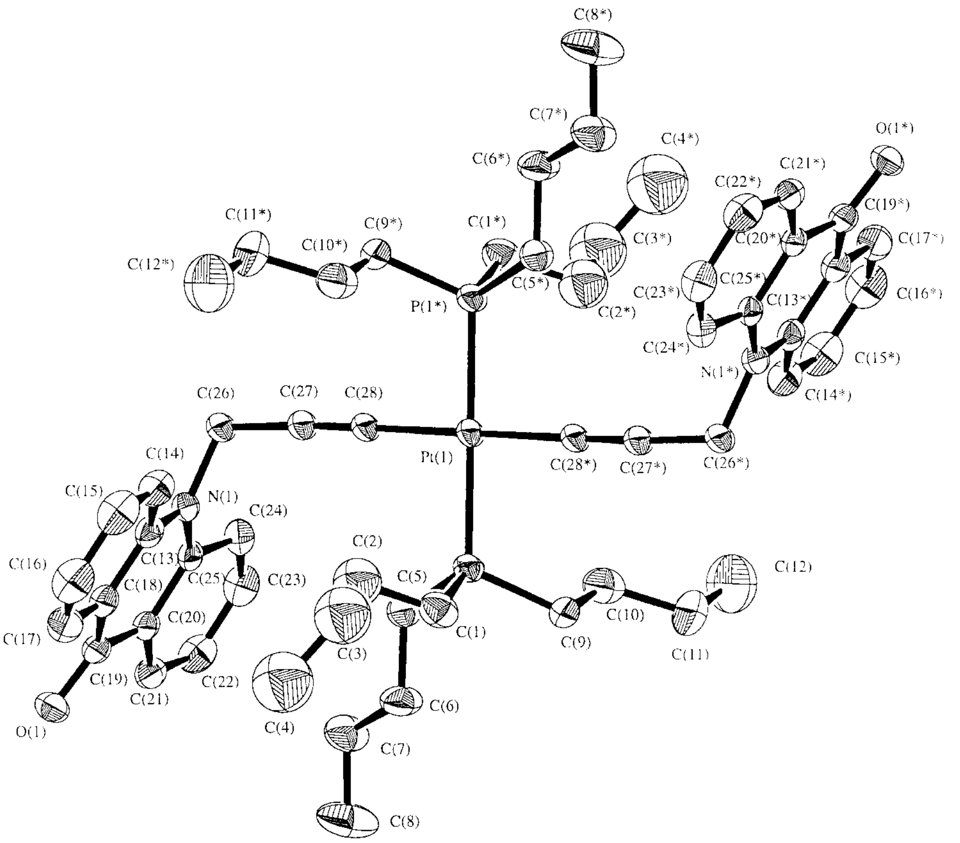


Fig. 1 The molecular structure of **1** with hydrogen atoms omitted. Thermal ellipsoids are shown at the 25% probability level. Important bond lengths (Å) and angles (°): Pt(1)–P(1) 2.298(1), Pt(1)–C(28) 2.000(5), C(27)–C(28) 1.178(7), C(26)–C(27) 1.477(7), N(1)–C(26) 1.475(6), O(1)–C(19) 1.239(6); P(1)–Pt(1)–C(28) 88.9(2), Pt(1)–C(28)–C(27) 176.9(6), C(26)–C(27)–C(28) 175.2(6), N(1)–C(26)–C(27) 112.9(4).

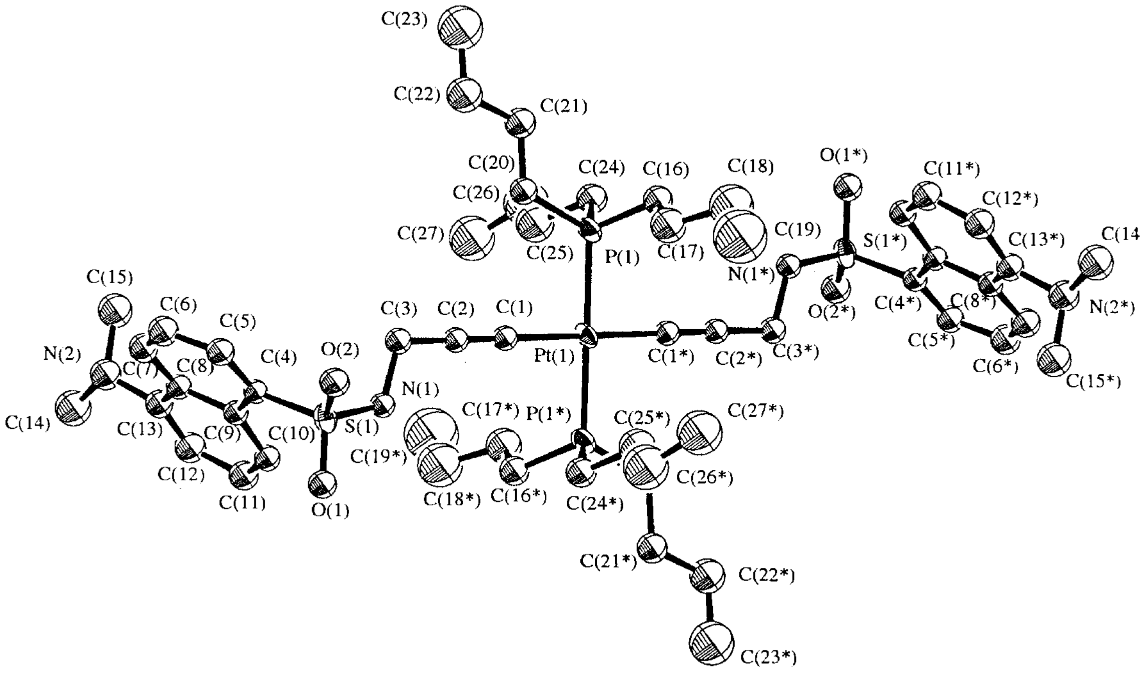


Fig. 2 The molecular structure of **2** with hydrogen atoms omitted. Thermal ellipsoids are shown at the 25% probability level. Important bond lengths (Å) and angles (°): Pt(1)–P(1) 2.301(2), Pt(1)–C(1) 2.003(8), C(1)–C(2) 1.21(1), C(2)–C(3) 1.45(1), N(1)–C(3) 1.49(1), S(1)–O(1) 1.440(7), S(1)–O(2) 1.430(7), S(1)–N(1) 1.605(7); P(1)–Pt(1)–C(1) 87.1(2), Pt(1)–C(1)–C(2) 179.6(7), C(1)–C(2)–C(3) 177.2(9), N(1)–C(3)–C(2) 110.0(7).

ligand high energy bands) transitions. Apart from the ligand-localised π–π* peaks, the electronic absorption spectra of the Pt(II) acetylide complexes **1** and **2** also display an energy band at around 305 nm, which is presumably due to an alkynyl–platinum ligand-to-metal charge transfer transitions.[8] It is found that compounds **1** and **2** both exhibit very high solubility in common organic solvents and are easily cast into thin films. Excitation of these complexes as solid films by a He–Cd laser at room temperature results in an intense blue luminescence peaking at *ca.* 449 (**1**) and 473 nm (**2**). In particular, compound **2** has a strong visible blue luminescence under UV irradiation. In CH_2Cl_2, the emission peaks appear at *ca.* 413 (**1**) and 494 nm (**2**). These results are significant in that most other platinum σ-acetylide complexes and polymers previously reported usually exhibit yellow-green and orange photoluminescence in the solid state at ambient temperatures.[9] Due to the influence of the heavy transition metal, interesting effects can be achieved by virtue of the mixing of singlet and triplet excited states as in other related platinum acetylide complexes.[9] Such a blue emissive property together with their associated high solubility and stability makes these compounds promising as a blue-emitting EL material and their EL properties are currently under investigation. Efforts to gain a better understanding of the luminescent mechanism of **1** and **2** are also being undertaken by our group.

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Notes and references

† Preparations of **1** and **2**. To a mixture of *trans*-[PtCl$_2$(PBu$^n{}_3$)$_2$] (40 mg, 0.06 mmol) and 2 equivalents of **I** (28 mg, 0.12 mmol) or **II** (35 mg, 0.12 mmol) in CH$_2$Cl$_2$–NHPr$^i{}_2$ (20 cm^3, 1 : 1 v/v) was added CuI (3 mg). The solution was stirred at room temperature over 15 h, after which all volatile components were removed. The residue was purified by preparative TLC on alumina with hexane–CH$_2$Cl$_2$ (1 : 2, v/v) as eluent, affording compounds **1** and **2** as white powders in 38 and 42% yields, respectively. **1**: IR (CH$_2$Cl$_2$): 2121 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR (CDCl$_3$): δ 0.73 (t, 18H, $J = 7.1$ Hz, Me), 1.25 (m, 24H, CH$_2$), 1.71 (m, 12H, PCH$_2$), 5.00 (s, 4H, NCH$_2$), 7.26 (m, 4H, aromatic H), 7.70 (m, 8H, aromatic H) and 8.53 (m, 4H, aromatic H). ^{31}P-{^{1}H} NMR (CDCl$_3$, H$_3$PO$_4$ as reference): δ 4.15 ($^1J_{Pt-P} = 2332$ Hz). FAB mass spectrum: *m*/*z* 1064 (M$^+$). Calc. for C$_{56}$H$_{74}$N$_2$O$_2$P$_2$Pt: C, 63.20; H, 7.01; N, 2.63. Found: C, 63.04; H, 6.89; N, 2.44%. **2**: IR (CH$_2$Cl$_2$): 3374 (ν_{N-H}), 2125 ($\nu_{C\equiv C}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.84 (t, 18H, $J = 7.0$ Hz, Me), 1.34 (m, 24H, CH$_2$), 1.81 (m, 12H, PCH$_2$), 2.88 (s, 12H, NMe$_2$), 3.71 (d, 4H, $J = 5.3$ Hz, NCH$_2$), 4.42 (t, 2H, $J = 5.3$ Hz, NH), 7.17 (d, 2H, $J = 7.6$ Hz, aromatic H), 7.51 (m, 4H, aromatic H), 8.25 (m, 4H, aromatic H) and 8.52 (d, 2H, $J = 8.6$ Hz, aromatic H). ^{31}P-{^{1}H} NMR (CDCl$_3$, H$_3$PO$_4$ as reference): δ 4.03 ($^1J_{Pt-P} = 2336$ Hz). FAB mass spectrum: *m*/*z* 1174 (M$^+$). Calc. for C$_{54}$H$_{84}$N$_4$O$_4$P$_2$S$_2$Pt: C, 55.23; H, 7.21; N, 4.77. Found: C, 55.04; H, 7.15; N, 4.49%.

‡ Crystal data for **1**: C$_{56}$H$_{74}$N$_2$O$_2$P$_2$Pt, $M = 1064.25$, monoclinic, space group $P2_1/c$, $a = 9.9213(5)$, $b = 15.3887(8)$, $c = 18.1315(9)$ Å, $\beta = 100.632(1)°$, $U = 2720.7(2)$ Å^3, $Z = 2$, Bruker Axs Smart 1000 CCD diffractometer, $T = 298$ K, μ(Mo-Kα) = 26.77 cm^{-1}, 16000 reflections measured, 6301 unique, R(int) = 0.024, final $R = 0.034$, $R_w = 0.040$ (based on F) for 3811 [$I > 1.5\sigma(I)$] observed reflections. All non-hydrogen atoms were refined anisotropically except the atoms C(2), C(3) and C(4) of one butyl group. The C(4) atom showed positional disorder and its position was refined in two sites with 50% occupancy and with restraints placed on some of the C–C distances and angles. For **2**, C$_{54}$H$_{84}$N$_4$O$_4$P$_2$S$_2$Pt, $M = 1174.44$, triclinic, space group $P\bar{1}$, $a = 9.959(1)$, $b = 12.718(1)$, $c = 13.040(2)$ Å, $\alpha = 102.72(1)$, $\beta = 102.27(1)$, $\gamma = 101.84(1)$ °, $U = 1518.3(4)$ Å^3, $Z = 1$, Mar research image plate scanner, $T = 298$ K, μ(Mo-Kα) = 24.65 cm^{-1}, 14328 reflections measured, 9335 unique, R(int) = 0.028, final $R = 0.052$, $R_w = 0.073$ (based on F) for 4011 [$I > 3.0\sigma(I)$] observed reflections. Only the Pt, P and S atoms were refined anisotropically, while the C, N and O atoms were assigned with isotropic displacement parameters. CCDC reference number 186/1757. See http://www.rsc.org/suppdata/dt/a9/a908198d/ for crystallographic files in .cif format.

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