Novel pyridyl-stabilised rigid-rod organometallic polymers and their monomeric precursors

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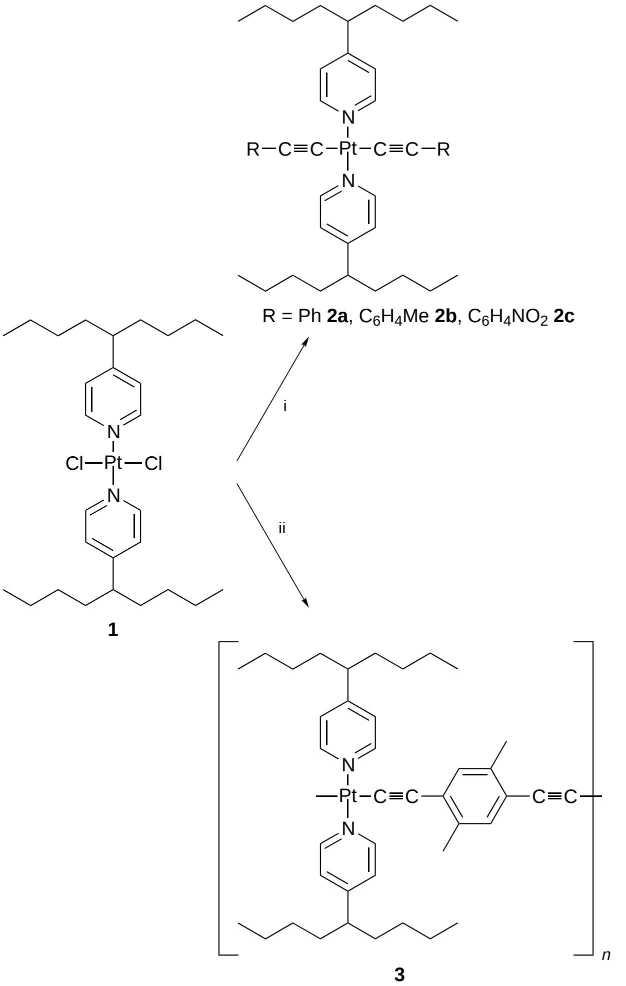
Reaction of *trans*-[Pt($NC_5H_4CHBu^n{}_2$)$_2$$Cl_2$] 1 with an excess of HC≡CR (R = Ph, C_6H_4Me, $C_6H_4NO_2$) affords the monomeric complex *trans*-[Pt($NC_5H_4CHBu^n{}_2$)$_2$(C≡CR)$_2$] (R = Ph 2a, C_6H_4Me 2b, $C_6H_4NO_2$ 2c), the *trans* arrangement of the alkynyl ligands being confirmed from spectroscopic data and by an X-ray analysis of 2c; when 1 is treated with 1 equiv. of HC≡CC_6H_2(Me)$_2$C≡CH the polymer [Pt($NC_5H_4CHBu^n{}_2$)$_2$C≡C$C_6H_2Me_2$C≡C]$_n$ is formed, which is soluble in a range of organic solvents.

There is considerable current interest in σ-alkynyl transition-metal complexes and in the polymers formed from them because of their potential for use as non-linear optical, low-dimensional conducting, luminescent or liquid-crystalline materials.[1] Within this group the 'rigid-rod' *trans*-bis(σ-alkynyl) systems with the general formula [ML_x–C≡C–R–C≡C]$_n$ (M = Fe, Ru, Os, Ni, Pd, Pt; L = phosphine, arsine, n = 2,4; R = C_6H_4, $C_6H_2Me_2$, $C_6H_2F_2$, C_4H_4S, $C_{14}H_8$)[2] have been shown to exhibit a variety of novel electronic properties.[3] The ancillary ligands, L, in these metal-containing polymers are almost always phosphines, and this derives from the overwhelming proportion of monomeric platinum-group alkynyl precursor complexes which are stabilised by phosphines.[4] Imine donors are expected to impart different properties to both monomeric and polymeric systems, particularly with regard to their optical and redox behaviour.[5] We have, therefore, embarked on the development of platinum-group alkynyl chemistry with nitrogen donor ligands, and have recently reported the preparation of the *cis*-diimine stabilised complexes [(Me_2bipy)Pt(C≡CC_6H_4R-4)$_2$] (bipy = bipyridyl; R = H, Me, NO_2).[6] We now report the synthesis of the first diimine stabilised *trans*-bis(σ-alkynyl) platinum complex [Pt($NC_5H_4CHBu^n{}_2$)$_2$(C≡CR)$_2$] (R = Ph **2a**, C_6H_4Me **2b**, $C_6H_4NO_2$ **2c**) and the formation of the novel polymer [Pt($NC_5H_4CHBu^n{}_2$)$_2$C≡C$C_6H_2Me_2$C≡C]$_n$ **3**.

A frequent problem in the synthesis of σ-alkynyl complexes and the subsequent formation of the polymers is their insolubility in common organic solvents. In order to reduce this problem *trans*-[Pt($NC_5H_4CHBu^n{}_2$)$_2$$Cl_2$] **1**, prepared by an adaption of the literature method,[7] was used as the starting material; the long hydrocarbon chains attached to the 4-position of the pyridine group greatly enhance the solubility. The reaction of **1** with 3 equiv. of HC≡CR (R = Ph, C_6H_4Me, $C_6H_4NO_2$), in the presence of catalytic amounts of CuI, in CH_2Cl_2 solution containing $Pr^i{}_2NH$, afforded [Pt($NC_5H_4CHBu^n{}_2$)$_2$(C≡CR)$_2$] (R = Ph **2a**, C_6H_4Me **2b**, $C_6H_4NO_2$ **2c**) in high yield, after stirring for 1 h (Scheme 1). The products were isolated as crystalline solids after purification by column chromatography on alumina using CH_2Cl_2–hexane (1 : 1) as eluent. The products were characterised initially by IR, ^1H and ^{13}C NMR spectroscopy, and by mass spectrometry.† The single ν(C≡C) stretching frequency in the range 2102–2098 cm^{-1} in the IR spectrum confirmed the presence of the σ-alkynyl ligands, consistent with the *trans* geometry.

In order to confirm the *trans* geometry of the products a single-crystal X-ray analysis of **2c** was undertaken. The molecular structure‡ is illustrated in Fig. 1 which includes selected bond parameters. The Pt atom sits on a crystallographic centre of symmetry, which imposes exact planarity at the metal centre, and requires the two alkynyl groups and the two substituted pyridine ligands to occupy mutually *trans* positions, respectively. The Pt–C(21)–C(22) alkynyl unit is essentially linear. The geometry is similar to that found in a number of *trans*-bis(phosphine) stabilised platinum bis(alkynyl) complexes,[8] and the Pt–C(21) distance lies within the range 1.98(1)–2.06(1) Å found in the other complexes.

The reaction of **1** with 1 equiv. of HC≡C$C_6H_2Me_2$C≡CH, under the same reaction conditions as described above, afforded, after purification, the polymer *trans*-[Pt($NC_5H_4CHBu^n{}_2$)$_2$C≡C$C_6H_2Me_2$C≡C]$_n$ **3** as a brown solid in moderate yield (Scheme 1). The polymer was characterised by spectroscopic techniques,† and the presence of the σ-alkynyl confirmed by the presence of the ν(C≡C) stretching vibration in



Scheme 1 i, 3 equiv. HC≡CR (R = Ph **2a**, C_6H_4Me **2b**, $C_6H_4NO_2$ **2c**), catalytic amount of CuI in $Pr^i{}_2NH$, CH_2Cl_2, stirred at room temp. for 1 h; ii, 1 equiv. HC≡C$C_6H_2Me_2$C≡CH, catalytic amount of CuI in $Pr^i{}_2NH$, CH_2Cl_2, stirred at room temp. for 1 h

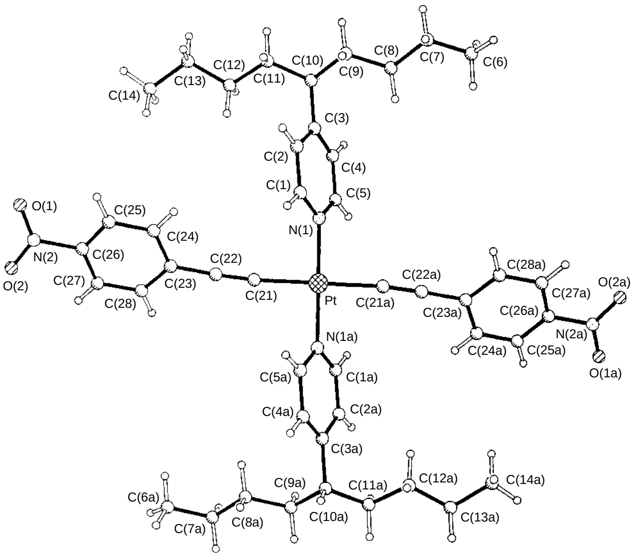


Fig. 1 Molecular structure of **2c** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Pt–N(1) 2.001(10), Pt–C(21) 2.02(2), C(21)–C(22) 1.21(2), C(22)–C(23) 1.42(2), C(26)–N(2) 1.49(2), N(2)–O(1) 1.22(2), N(2)–O(2) 1.22(2); N(1)–Pt–C(21) 88.2(4), N(1)–Pt–C(21A) 91.8(4), Pt–C(21)–C(22) 174.8(11), C(21)–C(22)–C(23) 174(2), O(1)–N(2)–C(26) 118.2(13), O(2)–N(2)–C(26) 116.1(14), O(1)–N(2)–O(2) 125.6(14).

the IR spectrum. As in other σ-alkynyl polymers[9] this ν(C≡C) stretch does not show a significant shift from the position in the precursor complex. The ^{13}C NMR spectrum confirmed the presence of both the arene spacer group and the substituted pyridine ligands, but in common with other 'rigid-rod' polymers chemical shifts corresponding to the σ-alkynyl carbons were not observed.[2,3]

Unlike many of the phosphine-stabilised 'rigid-rod' polymers **3** is soluble in a range of organic solvents. Therefore, it has been possible to run a series of electronic spectra to observe the shift in the absorption consistent with the greater delocalisation of electron density through the extended π-system along the polymer chain. In the free ligand, $HC{\equiv}CC_6H_2Me_2C{\equiv}CH$, two strong absorptions are observed at λ_{max} = 263.8 nm (ε = 1.9 × 10^4 dm^3 mol^{-1} cm^{-1}) and λ_{max} = 273.3 (2.31 × 10^4) in the UV region. For the precursor complex *trans*-$[Pt(NC_5H_4CHBu^n{}_2)_2Cl_2]$ **1** one broad absorption is observed at λ_{max} = 252.5 nm (ε = 9.39 × 10^3 dm^3 mol^{-1} cm^{-1}), while in the alkynyl-substituted monomer $[Pt(NC_5H_4CHBu^n{}_2)_2(C{\equiv}CPh)_2]$ **2a** the absorption is slightly shifted to λ_{max} = 281.0 nm (ε = 3.53 × 10^4 dm^3 mol^{-1} cm^{-1}). In contrast, for the polymer there is a considerable shift in absorption to λ_{max} = 342.2 nm (ε = 2.92 × 10^4 dm^3 mol^{-1} cm^{-1}), again a very broad band being observed. This shift in the position of the absorption is consistent with the greater delocalisation along the polymer chain. Similar shifts in the absorption spectra have been observed previously for related systems.[10]

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Footnotes and References

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† **2a**: IR ν(C≡C)/cm^{-1} (CH_2Cl_2) 2102; *m/z* 807.8 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 9.31 (d, 2 H, *J* 6.73 Hz), 7.23 (m, 5 H), 7.03 (d, 2 H, *J* 6.79 Hz), 2.50 (qnt, 1 H), 1.2 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 158.05 (py), 155.44 (py), 131.67 (arene), 127.8 (arene), 125.46 (arene), 124.6 (py), 119.2 (C≡C), 100.13 (C≡C), 45.73 (nonyl), 35.64 (nonyl), 29.59 (nonyl), 22.67 (nonyl), 13.9 (nonyl). **2b**: IR ν(C≡C)/cm^{-1} (CH_2Cl_2) 2102; *m/z* 835.7 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 9.32 (d, 2 H, *J* 6.72 Hz), 7.22 (d, 2 H, *J* 8 Hz), 7.01 (d, 2 H, *J* 6.8 Hz), 6.98 (d, 2 H, *J* 8 Hz), 2.50 (qnt, 1 H), 2.27 (s, 3 H), 1.2 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 157.92 (py), 155.5 (py), 135.14 (toluene), 131.5 (toluene), 128.6 (toluene), 124.8 (toluene), 124.5 (py), 118.2 (C≡C), 100.0 (C≡C), 45.7 (nonyl), 35.6 (nonyl), 29.5 (nonyl, 22.6 (nonyl), 21.3 (nonyl), 13.9 (nonyl). **2c**: IR ν(C≡C)/cm^{-1} (CH_2Cl_2) 2098; *m/z* 898.5 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 9.16 (d, 2 H, *J* 6.75 Hz), 7.36 (d, 2 H, *J* 5. Hz), 7.11 (d, 2 H, *J* 7 Hz), 3.05 (d, 2 H, *J* 5.Hz), 2.56 (qnt, 1 H), 1.25 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 158.9 (py), 154.9 (py), 145.0 (arene), 132.0 (arene), 127.9 (arene), 124.9 (py), 123.4 (arene), 100.12 (C≡C), 82.3 (C≡C), 45.76 (nonyl), 35.6 (nonyl), 22.6 (nonyl), 13.9 (nonyl). **3**: IR ν(C≡C)/cm^{-1} (CH_2Cl_2) 2097; ^{1}H NMR ($CDCl_3$) δ 9.29 (d, 2 H, *J* 6.98 Hz), 7.01 (s, 2 H), 6.98 (d, 2 H, *J* 6.8 Hz), 2.49 (qnt, 1 H), 2.16 (s, 6 H), 1.10 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 157.6 (py), 155.43 (py), 135.97 (arene), 132.3 (arene), 124.51 (py), 124.3 (arene), 45.65 (nonyl), 35.64 (nonyl), 29.5 (nonyl), 22.61 (nonyl), 20.4 (arene), 13.88 (nonyl). Satisfactory microanalyses were obtained on all the complexes.

‡ *Crystal data* for **2c**: $C_{44}H_{54}N_4O_4Pt$, M_r = 898.00, monoclinic, space group $P2_1/c$, a = 7.693(2), b = 22.908(5), c = 11.738(2) Å, β = 94.35(3)°, U = 2062.6(8) Å^3, Z = 2, D_c = 1.446 g cm^{-3}, μ = 3.447 mm^{-1} for Mo-Kα radiation (λ = 0.710 73 Å), F(000) = 912, T = 153(2) K. 3471 Refelctions measured on a Rigaku AFC7R diffractometer, 2696 unique absorption corrected (R_{int} = 0.082) used for structure solution (Patterson) and refinement (full-matrix least squares on F^2, anisotropic displacement parameters for non-H atoms, riding isotropic H-atoms); R_1 = 0.053 for 1670 reflections with $I > 2\sigma(I)$ and wR_2 = 0.172 for all data, goodness of fit = 1.079 for all F^2 values, 243 parameters; final difference map showed only ripples in the vicinity of the Pt atom. Programs: TeXsan, SHELXTL-PLUS and SHELXL 93. CCDC 182/614.

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