Supplementary data


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Experimental

The NMR spectral assignments follow the numbering scheme shown in the following figure.

(NBu₄)₂[Pt(C≡C₆H₄)₄] 1

The synthesis of this complex has been previously reported.¹ δ_c{¹H} (CD₃COCD₃, 223 K): 133.4 [s, J(Pt-C) ~ 25, ipso-C, Ph], 132.0 (s, ortho-C, Ph), 128.2 (s, meta-C, Ph), 123.3 (s, para-C, Ph),

¹
120.9 [s, \( ^1J(Pt-C) \) 989.8, C\(_\alpha\)], 104.1 [s, \( ^2J(Pt-C) \) 287.4, C\(_\beta\)], 60.3 (s, N-CH\(_2\)), NBu\(_4\)], 25.5 (s, -CH\(_2\)), NBu\(_4\)], 20.7 (s, -CH\(_2\)), NBu\(_4\)], and 14.3 (s, -CH\(_3\)), NBu\(_4\)].

**Synthesis of \((\text{NBu}_4)_2[\text{Pt}\{C≡C(4-CF}_3\text{C}_6\text{H}_4\}_4]\) \(4\).**

This complex was prepared, as a yellow solid, following a similar procedure to that described for 2:

\[ \text{[PtCl}_2(\text{tht})_2] \text{ (0.30 g, 0.68 mmol), LiC≡C(4-CF}_3\text{C}_6\text{H}_4 \text{ (5.42 mmol), (NBu}_4)\text{Br (0.55 g, 1.70 mmol); (0.68 g, 74%)} \text{ (Found: C, 59.86; H, 6.27; N, 2.37%}. \text{ C}_{68}\text{H}_{88}\text{N}_2\text{F}_{12}\text{Pt requires: C, 60.21; H, 6.54; N, 2.07%)�max/cm}^{-1} \text{ (C≡C) 2084vs; δ_H (CD}_3\text{COCD}_3, 293 K) 7.42, 7.36 [16H, AB system, } {^1J(\text{H-H}) 7.9, (4-CF}_3\text{C}_6\text{H}_4], 3.70 (16H, m, N-CH\(_2\)), NBu\(_4\)], 1.88 (16H, m, -CH\(_2\)), NBu\(_4\)], 1.54 (16H, q, -CH\(_2\)), NBu\(_4\)], and 0.92 (24H, t, -CH\(_3\)), NBu\(_4\)]; δ\(_F\) (CD\(_3\)COCD\(_3\), 293 K) -145.72 [s, CF\(_3\)], (4-CF\(_3\))C\(_6\)H\(_4\])\; m/z = 1405 ([Pt\(_2\)(C≡CC\(_6\)H\(_4\)CF\(_3\))\(_6\)+ 1]-, 20%), 1236 ([Pt\(_2\)(C≡CC\(_6\)H\(_4\)CF\(_3\))\(_5\)+ 1]-, 22%), 872 ([Pt(C≡CC\(_6\)H\(_4\)CF\(_3\))\(_4\)+ 1]-, 8%), 703 ([Pt(C≡CC\(_6\)H\(_4\)CF\(_3\))\(_3\)+ 1]-, 100%); \(\Lambda_M\)(CH\(_3\)NO\(_2\)): 97 Ω\(^{-1}\) cm\(^2\) mol\(^{-1}\).

**Synthesis of \((\text{NBu}_4)_2[\text{Pt}\{C≡C(4-OMe)C}_6\text{H}_4\}_4]\)·2\text{H}_2\text{O 5a·2H}_2\text{O}**

This complex has been used as precursor to a cluster Pt\(_2\)Cu\(_4\) complex,\(^2\) but its synthesis and spectroscopic data have not been reported. This complex was prepared, as a pale yellow solid, following an identical procedure to complex 2, starting from \([\text{PtCl}_2(\text{tht})_2] \text{ (0.30 g, 0.68 mmol), LiC≡C(4-OMe)C}_6\text{H}_4 \text{ (3.73 mmol) and (NBu}_4)\text{Br (0.55 g, 1.70 mmol); (0.67 g, 82%) (Found: C, 66.02; H, 8.44; N, 2.02%}. \text{ C}_{68}\text{H}_{104}\text{N}_2\text{O}_6\text{Pt requires: C, 65.83; H, 8.45; N, 2.26%); υ_{max}/cm}^{-1} \text{ (C≡C) 2085vs; bands at 3455s br, 3422s br, 1651vs and 1640vs due to the presence of H}_2\text{O are also observed; δ_H (CD}_3\text{COCD}_3, 293 K) 7.16 [8H, d, J(HH) 8.5], 6.67 [8H, d, J(H-H) 8.5, C\(_6\)H\(_4\), (4-}
OMe)C₆H₄], 3.75 (16H, m, N-CH₂, NBu₄), 3.72 (12H, s, OMe, (4-OMe)C₆H₄), 1.85 (16H, m, -CH₂, NBu₄), 1.53 (16H, m, -CH₂, NBu₄) and 0.91 (24H, t, -CH₃, NBu₄); δc{¹H} (CD₃COCD₃, 223 K) 155.1 (s, C₄), 131.3 (s, C₂/₃), 123.8 (s, C₁), 115.8 [s, J(C-Pt) 990.5, C₆], 112.4 (s, C₂/₃), 101.2 [s, J(C-Pt) 286.0, C₆], 58.1 (s, N-CH₂, NBu₄), 53.9 (s, OMe, (3-OMe)C₆H₄), 23.7 (s, -CH₂, NBu₄), 19.3 (s, -CH₂, NBu₄) and 13.3 (s, -CH₃, NBu₄); m/z 1201 ([Pt(C≡C(4-CN)C₆H₄)₄]⁻). ΛM(CH₃NO₂): 91 Ω⁻¹ cm² mol⁻¹.

Synthesis of (NBu₄)₂[Pt{C≡C(3-OMe)C₆H₄}] 5b

This complex was prepared, as a very pale yellow solid, following the procedure described for 2, using [PtCl₂(tht)] (0.30 g, 0.68 mmol), LiC≡C(3-OMe)C₆H₄ (3.73 mmol) and (NBu₄)Br (0.55 g, 1.70 mmol); (0.74g, 90%) (Found: C, 67.45; H, 8.47; N, 2.38%. C₆H₈N₂O₄Pt requires: C, 67.80; H, 8.37; N, 2.33%); νmax/cm⁻¹ (C≡C) 2078 (s); δH(CD₃COCD₃, 293 K) 6.98 [4H, t, J(H-H) 8.0], 6.83 (8H, m), 6.51 [4H, dd, J(H-H) 1.7, C₆H₄, (3-OMe)C₆H₄], 3.74 (16H, m, N-CH₂, NBu₄), 3.72 (12H, s, OMe, (3-OMe)C₆H₄), 1.87 (16H, m, -CH₂, NBu₄), 1.55 (16H, m, -CH₂, NBu₄) and 0.92 (24H, t, -CH₃, NBu₄); δc{¹H} (CD₃COCD₃, 223 K) 158.5 [s, C-OMe, (3-OMe)C₆H₄], 132.5 (s), 128.0 (s), 122.8 [s, C₆H₄, (3-OMe)C₆H₄], 119.4 [s, J(C-Pt) 990.2, C₆], 114.8 (s), 108.4 [s, C₆H₄, (3-OMe)C₆H₄], 102.6 [s, J(C-Pt) 288.1, C₆], 58.2 (s, N-CH₂, NBu₄), 53.7 [s, OMe, (3-OMe)C₆H₄], 23.7 (s, -CH₂, NBu₄), 19.4 (s, -CH₂, NBu₄) and 13.3 (s, -CH₃, NBu₄); m/z 1178 ([Pt₂(C≡CC₆H₄OMe)₆]⁻ + 2], 15%), 1046 ([Pt₂(C≡CC₆H₄OMe)₅ + 1], 10%), 720 ([Pt(C≡CC₆H₄OMe)₄ + 1], 14%); ΛM(CH₃NO₂): 94 Ω⁻¹ cm² mol⁻¹.

Synthesis of (NBu₄)₂[Pt{C≡C(4-CN)C₆H₄}] 6

This complex was prepared as a lemon yellow solid following a similar procedure to that described for 2, starting from [PtCl₂(tht)] (0.20 g, 0.45 mmol), LiC≡C(4-CN)C₆H₄ (2.71 mmol) and (NBu₄)Br (0.36 g, 1.13 mmol); (0.22g, 45%) (Found: C, 68.55; H, 7.51; N, 6.90%. C₆H₈N₂O₄Pt requires: C,
68.95; H, 7.49; N, 7.10%); $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ (C$\equiv$N) 2218vs and (C$\equiv$C) 2080vs, 2041sh; $\delta_{\text{H}}$ (CDCl$_3$, 293 K) 7.41, 7.29 [16H, AB system, $J$(H-H) 7.3, (4-CN)C$_6$H$_4$], 3.47 (16H, m, N-CH$_2$, NBu$_4$), 1.64 (16H, m, -CH$_2$, NBu$_4$), 1.44 (16H, m, -CH$_2$, NBu$_4$), 0.86 (24H, t, -CH$_3$, NBu$_4$); $\delta_{\text{C}}$($^1$H) (CD$_3$COCD$_3$, 223 K) 135.8 (s), 131.1 (s, CH), 130.7 (s, CH), 128.46 [s, C$_6$H$_4$, (4-CN)C$_6$H$_4$], 119.3 (tentatively assigned to C$_\alpha$), 104.1 [s, $^2J$(C-Pt) 288.0, C$_\beta$], 58.0 (s, N-CH$_2$-, NBu$_4$), 23.4 (s, -CH$_2$-, NBu$_4$), 19.1 (s, -CH$_2$-, NBu$_4$) and 13.2 (s, -CH$_3$, NBu$_4$); m/z 696 ([Pt(C≡CC$_6$H$_4$CN)$_4$ - 3]$,^1$H$,^1$H$,^1$H$), 22%); $\Lambda_{\text{M}}$(CH$_3$NO$_2$): 93 $\Omega^{1}$/cm$^2$ mol$^{-1}$.

**Synthesis of (NBu$_4$)$_2$[Pt{C≡C(4-C≡CH)C$_6$H$_4$}]·2H$_2$O 7·2H$_2$O**

To a fresh (-78°C) solution of LiC≡C(4-C≡CH)C$_6$H$_4$ (4.35 mmol) in Et$_2$O (ca. 30 cm$^3$), [PtCl$_2$(tht)$_2$] (0.35 g, 0.80 mmol) was added, and the mixture stirred at this temperature for 2.5 hours. Then, it was slowly allowed to reach room temperature (ca. 2 h) and evaporated to dryness. The yellow residue was treated with cold deoxygenated H$_2$O (~ 40 cm$^3$) and filtered through celite. The resulting solution was treated with (NBu$_4$)Br (0.51 g, 1.6 mmol) to yield (NBu$_4$)$_2$[Pt{C≡C(4-C≡CH)C$_6$H$_4$}]·2H$_2$O 7·2H$_2$O as a yellow solid. This complex is very unstable and must be kept under Ar at low temperature (-45°C); (0.55g, 57%) (Found: C, 70.34; H, 7.93; N, 2.06%.

C$_{72}$H$_{96}$N$_2$O$_2$Pt (7·2H$_2$O) requires C, 71.08; H, 7.95; N, 2.30%, and C$_{72}$H$_{98}$N$_2$O$_3$Pt (7·3H$_2$O) requires C, 70.04; H, 8.00; N, 2.27; $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ (CH) 3200s, (C≡C) 2073vs br, bands at 3450br and 1640br due to the presence of H$_2$O are also observed; $\delta_{\text{H}}$ (CDCl$_3$, 293 K) 7.27, 7.21 [16H, AB system, $J$(H-H) 8.3, C$_6$H$_4$, (4-C≡CH)C$_6$H$_4$], 3.50 (16H, m, N-CH$_2$, NBu$_4$), 3.07 (4H, s, =CH), 2.16 (4H, br, H$_2$O), 1.63 (16H, m, -CH$_2$, NBu$_4$), 1.45 (16H, m, -CH$_2$, NBu$_4$) and 0.87 (24H, t, -CH$_3$, NBu$_4$); $\delta_{\text{C}}$($^1$H) (CD$_3$COCD$_3$, 223 K) 132.0 (s), 130.8 (s, CH), 130.2 [s, CH, C$_6$H$_4$, (4-C≡CH)C$_6$H$_4$], 124.0 [s, $^1J$(C-Pt) 993.0, C$_\alpha$], 115.1 [s, C$_6$H$_4$, (4-C≡CH)C$_6$H$_4$], 103.2 [s, $^2J$(C-Pt) 289.0, C$_\beta$], 83.9 (s, C$^6$), 78.5 (s, C$^5$), 58.0 (s, N-CH$_2$, NBu$_4$), 23.4 (s, -CH$_2$, NBu$_4$), 19.2 (s, -CH$_2$, NBu$_4$) and 13.2 (s, -CH$_3$, NBu$_4$); m/z 938 ([Pt(C≡CC$_6$H$_4$C≡CH)$_4$] (NBu$_4$) + 1, 100%); $\Lambda_{\text{M}}$(CH$_3$NO$_2$): 93 $\Omega^{1}$/cm$^2$ mol$^{-1}$.
Synthesis of (NBu₄)₂[Pt{C≡C(4-C≡CPh)C₆H₄}] 8

Complex 8 was prepared, as a yellow solid, by treating [PtCl₂(tht)] (0.25 g, 0.57 mmol) with LiC≡C(4-C≡CPh)C₆H₄ (3.39 mmol) and (NBu₄)Br (0.46 g, 1.41 mmol) in a similar way to that described above for complex 3; (0.32 g, 38%) (Found: C, 77.34; H, 7.37; N, 1.80%. C₉₆H₁₀₈N₂Pt requires: C, 77.65; H, 7.33; N, 1.89%); v_max/cm⁻¹ (C≡C) 2209m (C≡CPh), 2075s br (PtC≡C); δ_H(CDCl₃, 223 K) 132.2 (s), 131.0 (CH), 130.8 (overlapping of two CH carbons), 128.6 (s, CH), 128.1 [s, C₆H₄ and Ph, (4-CC≡CPh)C₆H₄], 124.6 [s, ¹J(C-Pt) 1003.0, C₆], 123.2 (s), 116.2 [s, C₆H₄ and Ph, (4-CC≡CPh)C₆H₄], 104.0 [s, ²J(C-Pt) 286.0, C₆], 90.3 (s), 88.9 (s, C⁵ and C⁶), 58.4 (s, N-CH₂-, NBu₄), 23.9 (s, -CH₂-, NBu₄), 19.6 (s, -CH₂-, NBu₄) and 13.6 (s, -CH₃, NBu₄); m/z 797 ([Pt(C≡CC₆H₄C₂Ph)]⁻ - 1), 83%; 598 ([Pt(C≡CC₆H₄C₂Ph)]¹, 100%) and 396 ([Pt(C≡CC₆H₄C₂Ph)]⁻, 63%); Λ₅(CH₂NO₂): 119 Ω⁻¹ cm² mol⁻¹.

Synthesis of (NBu₄)₂[Pt(C≡CC₅H₄N-2)] 9a

This complex was prepared following an identical procedure to that described for 2, but, in this case, the temperature of the LiC≡CC₅H₄N-2 ethereal solution was –50°C. In addition, the final precipitate of 9a, obtained after the addition of (NBu₄)Br, was extracted with CH₂Cl₂ and the solution dried with anhydrous MgSO₄ and evaporated to dryness. The addition of cold Et₂O (ca. 5 cm³) gives 9a as a brown solid. The following amounts of the precursors were used: 0.50 g (1.13 mmol) of [PtCl₂(tht)], 7.9 mmol of LiC≡CC₅H₄N-2 and 0.73 g (2.26 mmol) of (NBu₄)Br; (0.33 g, 27%). (Found: C, 65.93; H, 8.03; N, 7.45%. C₆₈H₉₈N₆Pt requires: C, 66.21; H, 8.15; N, 7.72%); ν_max/cm⁻¹ (C≡C) 2081vs, 2059 sh; δ_H(CDCl₃, 293 K) 8.24 [d, J(H-H) 4.2, 4H⁶], 7.34 [td, J(H-H) ~
7.6, J(H-H) ~ 1.5, 4H$^3$), 7.23 [d, J(H-H) ~ 7.9, 4H$^3$], 6.80 [t, J(H-H) ~ 5.9, 4H$^3$], 3.55 (16H, m, N-CH$_2$-, NBu$_4$), 1.66 (16H, m, -CH$_2$-, NBu$_4$), 1.42 (16H, m, -CH$_2$-, NBu$_4$) and 0.83 (24H, t, -CH$_3$, NBu$_4$), assignment based on a $^1$H-$^1$H COSY. $\delta_C$($^1$H) (CDCl$_3$, 223 K) 148.8 [s, $^3$J(Pt-C) 25.8, C$^2$], 147.9 (s, C$^6$), 134.3 (s, C$^4$), 126.1 (C$^3$), 120.5 [s, $^1$J(C-Pt) 991.7, C$\alpha$], 117.6 (C$^5$), 105.2 [s, $^2$J(C-Pt) 287.0, C$\beta$], 58.8 (s, N-CH$_2$-, NBu$_4$), 24.1 (s, -CH$_2$-, NBu$_4$), 19.4 (s, -CH$_2$-, NBu$_4$) and 13.5 (s, -CH$_3$, NBu$_4$), assignment based on a $^{13}$C-$^1$H correlation NMR spectrum; m/z = 846 ([Pt(C≡CC$_5$H$_4$N-2)$_4$](NBu$_4$) + 1], 100%), 604 ([Pt(C≡CC$_5$H$_4$N-2)$_4$]+ 1], 81%); $\Lambda_m$(CH$_3$NO$_2$): 123 $\Omega$ cm$^{-1}$ mol$^{-1}$.

**Synthesis of (NBu$_4$)$_2$[Pt(C≡CC$_5$H$_4$N-4)$_4$]·2H$_2$O 9b·2H$_2$O**

This complex has been prepared following a similar procedure to that used for complex 2, using THF as the solvent and a reaction temperature of $-50^\circ$C. The yellow solid thus obtained, which contains amounts of para-ethynylpyridine (~ 15 %), is washed with hexane (2 x 5 cm$^3$) to give 9b as a yellow solid. The following amounts of the starting materials were used: [PtCl$_2$(tht)$_2$] (0.30 g, 0.68 mmol), LiC≡CC$_5$H$_4$N-4 (4.75 mmol) and (NBu$_4$)Br (0.55 g, 1.71 mmol) (0.22g, 29% ) (Found: C, 63.84; H, 7.89; N, 7.28.%). C$_{60}$H$_{92}$N$_6$PtO$_2$ requires: C, 64.09; H, 8.25; N, 7.47%); $\nu_{max}$/cm$^{-1}$ (C≡C) 2086s and 2039sh; $\delta_H$ (CD$_3$COCD$_3$, 293 K) 8.22 [8H, d, J(H-H) 5.5, C$_5$H$_4$N-4], 7.04 [8H, d, J(H-H) 5.5, C$_5$H$_4$N-4], 3.66 (16H, m, N-CH$_2$-, NBu$_4$), 1.88 (16H, m, -CH$_2$-, NBu$_4$), 1.51 (16H, m, -CH$_2$-, NBu$_4$) and 0.93 (24H, t, -CH$_3$, NBu$_4$); $\delta_C$($^1$H) (CDCl$_3$, 223 K) 148.4 (s, C$^2$); 139.1 (s, C$^4$); 126.0 (s, C$^3$), 123.3 [s, $^1$J(C-Pt) 995.7, C$\alpha$], 102.6 [s, $^2$J(C-Pt) = 297.7, C$\beta$], 58.6 (s, N-CH$_2$-, NBu$_4$), 23.9 (s, -CH$_2$-, NBu$_4$), 19.5 (s, -CH$_2$-, NBu$_4$) and 13.8 (s, -CH$_3$, NBu$_4$); m/z 845 ([Pt(C≡CC$_5$H$_4$N-2)$_4$](NBu$_4$) + 1], 100%); $\Lambda_m$(CH$_3$NO$_2$): 79 $\Omega$ cm$^{-1}$ mol$^{-1}$.


Figure S1 Molecular structure of the anion [Pt{C≡C(4-CN)C₆H₄}₄]²⁻ 6. Ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Symmetry transformation used to generate equivalent atoms: 2-x, -y, -z.
Figure S2 Emission spectra of complex 7 in CH$_2$Cl$_2$ at 77K by exciting at different λ (nm) (concentration 10$^{-3}$ M).
Figure S3 Excitation (a) and emission (b) spectra of complex 3 in KBr pellets at room temperature by exciting at different $\lambda$ (nm).
Figure S4. Emission spectra of complex 6 in KBr pellets at room temperature by exciting at different $\lambda$ (nm).
**Table S1.** Population analysis (%) for the anion \([\text{Pt}\{\text{C≡C}(4-\text{CN})\text{C}_6\text{H}_4\}_4]^{2-}\) of complex 6

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Table S2. Emission and excitation spectral data for complexes 1, 2, 3, 4 and 6 in $10^{-3}$ M solutions of different solvents

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<td>acetonitrile(298) 394, 423, 437</td>
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<td>acetonitrile(77) 345, 365</td>
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<td>toluene(77) 358, 382, 400</td>
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<td>toluene(77) 355, 377, 402</td>
<td>500, 525, 541, 555</td>
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a) $\lambda_{\text{em}} = 450$ nm; b) $\lambda_{\text{exc}} = 350$ nm; c) $\lambda_{\text{em}} = 500$ nm; d) $\lambda_{\text{exc}} = 397$ nm;
<table>
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<th>Transition</th>
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<th>( \lambda_{\text{exc}} ) (calc)/nm</th>
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