

Thiol end-capped one-dimensional platinum and palladium complexes

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Received 23 September 2005; accepted 10 October 2005

Available online 15 June 2006

Abstract

The synthesis and characterisation of acyl-thiol end-capped homobimetallic rigid-rod structured molecules of type [(MeC(O)S–4-NCN)Pt ← N≡C–C₆H₄–C≡N → Pt(NCN–4-SC(O)Me)](OTf)₂ (**6**, NCN = [C₆H₂(CH₂NMe_{2-2,6})₂][−]) and (MeC(O)S–4-C₆H₄–C₆H₄)(Ph₃P)₂Pd ← C₃H₄N–CH=CH–C₆H₄–CH=CH–C₃H₄N → Pd(PPh₃)₂(C₆H₄–C₆H₄–4-SC(O)Me)](OTf)₂ (**9**) in which the metal fragments are spanned by π-conjugated organic connecting units is reported.

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There is a wide interest in the synthesis of one-dimensional molecules [1], because they possess considerable attention in the developing field of molecular electronics [2]. The ability of such species is to transport in a very efficient way electrons across the π-delocalised bridge. If the molecules possess at both ends a thiol group as anchoring unit, the bridging of two surfaces/electrodes is possible [3]. As connecting units π-conjugated linear structured organic and/or inorganic building blocks can be used. From the literature reports, it appeared that the properties of such molecules strongly depend on the nature of the redox termini and the appropriate connecting spacer [4]. Among them, conjugated end-capped organic thiols have received a great deal of attention, because of their intrinsic semiconductor or insulator properties, and of their unique capability to form well-ordered mono-layers via the self-assembly process onto gold or other metal surfaces [5]. The use of redox-active organometallic constituents assembled with all-carbon or

heteroatomic π-spacers offer fascinating perspectives for the design and realisation of one-dimensional molecular wires [6].

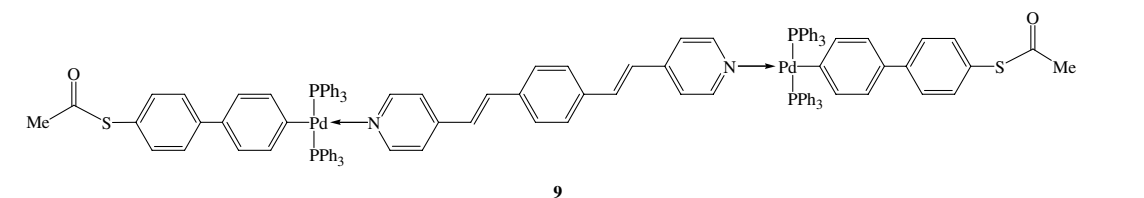
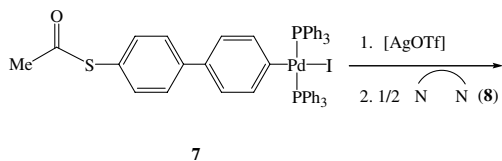
We here describe the synthesis and characterisation of MeC(O)S end-capped homobimetallic palladium and platinum complexes in which the metal atoms are bridged by π-conjugated organic nitrogen containing units.

Complex [(MeC(O)S–4-NCN)Pt ← N≡C–C₆H₄–C≡N → Pt(NCN–4-SC(O)Me)](OTf)₂ (**6**, NCN = [C₆H₂(CH₂NMe_{2-2,6})₂][−]) can be obtained in a three-step synthesis protocol as outlined in Scheme 1. The first step involves the introduction of an acyl-S functionality in the bifunctional pincer molecule NC(Br)N–I (NC(Br)N = C₆H₂(CH₂NMe_{2-3,5})₂–4-Br) (**1**) [7] by its subsequent reaction with ^tBuLi, S₈ and Me(O)CCl. Refluxing the thus obtained acyl-S-NC(Br)N pincer **2** with 0.5 equivalents of [Pt(tol)₂(SEt₂)₂] [8] (**3**, tol = tolyl) in benzene for 4 h afforded the oxidative addition product **4** (Scheme 1). In situ debromination of yellow **4** with [AgOTf] (OTf = triflate, OSO₂CF₃) produces the respective triflate functionalised species, which further reacts with the Lewis-base C₆H₄–1,4-(C≡N)₂ (**5**) in a 2:1 stoichiometry in a dichloromethane–toluene mixture

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of ratio 5:2 to give the title complex **6** in excellent yield (Scheme 1).¹

According to the synthesis protocol shown in Scheme 1, also homobimetallic acyl-thiol end-capped linear palladium complexes can be prepared (Eq. (1)).

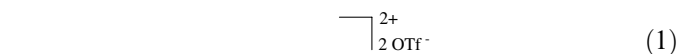


Treatment of **7** [9] with [AgOTf] followed by addition of C₅H₄N–CH=CH–C₆H₄–CH=CH–C₅H₄N (**8**) gives **9**. After appropriate work-up, rigid-rod structured **9** can be obtained as a pale yellow coloured solid in 83% yield.

Complexes **6** and **9** are stable under inert gas atmosphere for months. However, they rapidly decompose, when they are exposed to air and moisture. They nicely dis-

solve in dichloromethane, whereas in acetonitrile, dimethylformamide and dimethylsulfoxide they decompose upon formation of a black insoluble material.

Complexes **6** and **9** have been characterised by elemental analysis, IR and NMR (¹H, ³¹P{¹H}) spectroscopy.¹



Single crystals of **6** could be obtained by slow diffusion of *n*-pentane into a dichloromethane solution containing **6**. The molecular structure of **6** is shown in Fig. 1. Relevant bond distances (Å) and angles (°) are listed in the legend of Fig. 1.

In **6** the two platinum atoms are bridged by the π -conjugated organic connecting unit N≡C–C₆H₄–C≡N to form a 2:1 complex with a Pt1–Pt2 separation of 11.976 Å (Fig. 1). The nitrogen atoms of the bridging 1,4-dicyanobenzene unit are datively bonded to the d⁸-configured Pt1 and Pt2 atoms at the interchangeable coordination site of the transition metal building blocks. Interestingly to mention is that the dihedral angle between the least-square planes of Pt1–N1–N2–N3–C6 (r.m.s.d. 0.0074) and Pt2–N4–N5–N6–C28 (r.m.s.d. 0.0086) is 66.9°. These planes form an angle to the benzene ring of the 1,4-dicyanobenzene of 63.3° (Pt1) and 49.8° (Pt2), respectively. As a result of the bis-ortho chelating of the ortho(dimethylamino)methyl substituents the NCN aryl rings are slightly turned by 10.1° (Pt1) and 11.0° (Pt2), respectively, out of the platinum coordination plane.

The bond distances and angles of **6** are in agreement with those ones found for other platinum transition metal complexes featuring similar groups [10,11].

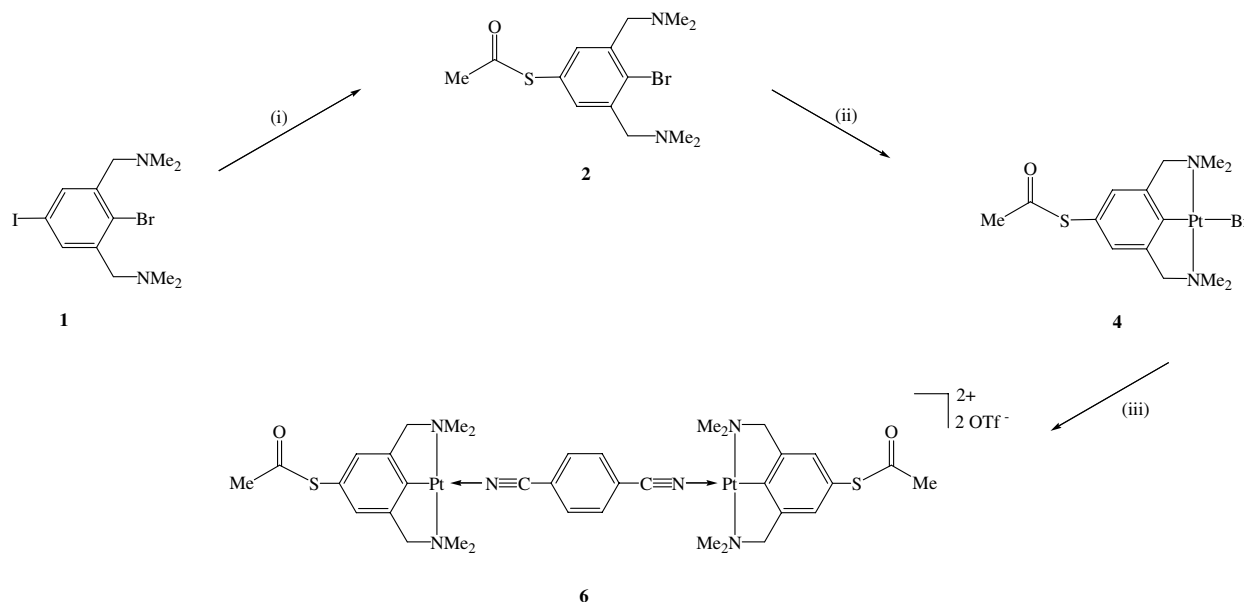
In order to gain further insight into the properties of these metallo systems, preliminary electrochemical studies were conducted with **6** and **9**. The cyclic voltammograms of **6** and **9** display, as expected, a irreversible oxidation wave at ca. 1.4 V, due the presence of the thio acetyl group [5d]. Furthermore, a irreversible oxidation wave is found at +0.71 V which is similar to that observed for [Pt(Me₄NCN)Cl] (+0.76 V) [12]. This behaviour is characteristic for the metal-centred oxidation of platinum(II)

¹ Synthesis of **6**: To **4** (172.5 mg, 0.319 mmol) dissolved in 50 ml of a toluene–dichloromethane mixture of ratio 5:2 one equivalent of [AgOTf] (82.0 mg, 0.319 mmol) is added in one portion at 25 °C. After 30 min of stirring, the reaction mixture is filtered through a pad of Celite. To the eluate, terephthalonitrile (**5**) (20.5 mg, 0.159 mmol) is added and the resulting suspension is stirred for 30 min. Addition of 60 ml of *n*-hexane produces a yellow precipitate. The supernatant solution is decanted and the obtained yellow solid is dried in *oil-pump vacuum*. Yield: 150 mg (0.11 mmol, 70% based on **4**).

C₃₈H₄₆F₆N₆O₈Pt₂S₄ (1347.21): Anal. Calcd.: C, 33.88; H, 3.44; N, 6.24. Found: C, 33.80; H, 3.89; N, 6.12. M.p.: 110 °C (dec.). IR (KBr): 3107 (m), 2996 (m), 2927 (m), 2245 (w) (ν_{CN}), 1700 (s) (ν_{CO}), 1460 (s), 1403 (s), 1263 (vs) (ν_{SO}), 1228 (sh), 1155 (s), 1094 (sh), 1030 (s) (ν_{CF}) 946 (m), 873 (w), 822 (s), 638 (s), 563 (m), 517 (m) cm⁻¹. ¹H NMR (CD₂Cl₂): δ = 2.4 (s, 6 H, CH₃), 3.0 (t, 24 H, ³J_{PH} = 36.1 Hz, N(CH₃)₂), 4.0 (t, 8H, ³J_{PH} = 49.5 Hz CH₂), 6.82 (s, 4 H, C₆H₂), 7.9 (bs, 4 H, C₆H₄). ¹³C{¹H} NMR data could not be obtained, due to the low solubility of **6** in common organic solvents.

Crystallographic data for **6**: Crystal data were collected from shock-cooled crystals on a BRUKER SMART CCD 1k diffractometer (Mo-K α radiation, λ = 71.073 pm) at 203(2) K [16]. The structure is solved by direct methods (SHELXS-97) and refined by full-matrix least-square methods against F^2 (SHELXS-97) [17]. The two triflate counter-anions are disordered and have been refined to split occupancies of 0.51/0.49 and 0.68/0.32, respectively.

C₃₈H₄₆F₆N₆O₈Pt₂S₄, M = 1347.23 g/mol, triclinic, space group $P\bar{1}$, a = 10.368(5), b = 14.010(7), c = 17.194(9) Å, α = 82.43(2), β = 87.94(2), γ = 74.83(2)°, V = 2389(2) Å³, Z = 2, ρ_{calc} = 1.873 g cm⁻³, μ = 6.100 mm⁻¹, $F(000)$ = 1308, 16617 reflections measured, 7961 unique, $R(\text{int})$ = 0.0560, $wR2$ (all data) = 0.1571, $R1$ ($I > 2\sigma(I)$) = 0.0616, 733 parameters and 586 restraints. CCDC-No. 277556. See <http://www.ccdc.cam.ac.uk> for crystallographic data in .cif or other electronic format.



Scheme 1. Synthesis of homobimetallic **6**; (i) $t\text{BuLi}$, S_8 , $\text{Me}(\text{O})\text{CCl}$, thf , $-100\text{ }^\circ\text{C}$. (ii) $[\text{Pt}(\text{tol})_2(\text{SEt}_2)_2]$, benzene, ΔT , 4 h. (iii) (a) $[\text{AgOTf}]$, toluene-dichloromethane (ratio 5:2), $25\text{ }^\circ\text{C}$, 30 min; (b) $\text{C}_6\text{H}_4\text{-1,4-(C}\equiv\text{N)}_2$ (**5**), $25\text{ }^\circ\text{C}$, toluene-dichloromethane (ratio 5:2), 1 h.

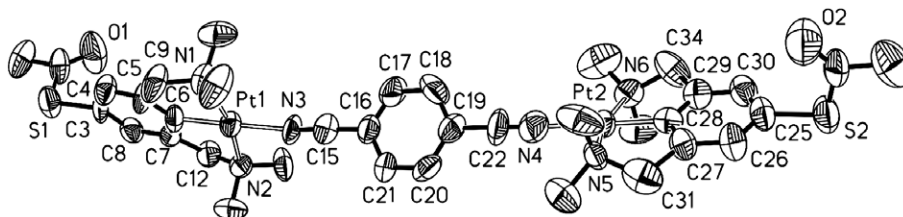


Fig. 1. XP drawing of **6** (at 50% probability level). The hydrogen atoms and the two TfO^- counter-ions are omitted for clarity. Selected distances (\AA) and angles ($^\circ$): Pt1–N1 2.08(2), Pt1–N2 2.08(1), Pt1–N3 2.08(2) Pt1–C6 1.95(2), C3–S1 1.82(2), Pt2–N4 2.10(2), Pt2–N5 2.05(2), Pt2–N6 2.09(2) Pt2–C28 1.93(2), C25–S2 1.77(2); C6–Pt1–N3 179.2(6), N3–Pt1–N2 97.6(5), N3–Pt1–N1 97.3(5), N2–Pt1–N1 165.1(5), C15–N3–Pt1 174.(2), C28–Pt2–N5 82.9(6), C28–Pt2–N6 82.1(6), N5–Pt1–N6 164.9(5), C28–Pt2–N4 179.3(5), N5–Pt2–N4 96.9(5), N6–Pt2–N4 98.2(6).

complexes [12]. Comparable irreversible waves have been reported for related complexes with NCN pincer ligands [12,13]. Moreover, complex **6** shows irreversible reductions at -1.32 and -1.58 V, attributed to the bridging Lewis-base ligand $\text{C}_6\text{H}_4\text{-1,4-(C}\equiv\text{N)}_2$ (**5**) (for comparison, the cyclic voltammogram of free terephthalonitrile measured under similar experimental conditions shows reversible reduction potentials at $E_{1/2} = -2.23$ V ($\Delta E = 350$ mV) and $E_{1/2} = -2.70$ V ($\Delta E = 350$ mV)), thus revealing a significant anodic shift of the ligand centred reduction upon coordination, which is typical in organometallic chemistry by going from free to complexed ligands [14]. The electrochemical behaviour of homobimetallic **9** is represented by two irreversible oxidation waves at 1.03 V and 1.42 V (vide supra). In addition, at -1.53 and -1.75 V two irreversible reductions are observed, which are in comparison with **8** ($E_{1/2} = -2.27$ V ($\Delta E = 350$ mV), $E_{1/2} = -2.40$ V ($\Delta E = 330$ mV) and $E_{1/2} = -2.60$ V ($\Delta E = 180$ mV)) shifted to more positive values, reflecting the donating nature of **8** [15].

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