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Synthesis, Structural Characterisation and Electrochemistry of the Tetranuclear Compound [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-Cl)$_4$] (R = C_6H_4Me-*p*): A Precursor to Triazenido-bridged Palladium(II) Complexes

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The tetranuclear complexes [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-X)$_4$] (R = C_6H_4Me-*p*, X = Cl or I), in which two triazenido-bridged dipalladium units are linked by halide bridges to give an S_4N_4-like Pd_4Cl_4 core, are novel precursors to redox-active triazenido-bridged derivatives.

Among the several co-ordination modes reported for 1,3-diaryltriazenido ligands, bidentate bridging behaviour leads to face-to-face binuclear complexes of metals with a d^8 electron configuration,[1] *e.g.* [M_2(μ-L^1)$_2$(CO)$_2$$L^2{}_2$] [M = Rh or Ir, L^1 = diaryltriazenido, $L^2{}_2$ = $(PPh_3)_2$, 2,2′-bipyridine, cycloocta-1,5-diene, *etc.*]. Such species form part of extensive electron-transfer series where complexes containing $[Rh_2]^{n+}$ (*n* = 2, 3 or 4) and $[Ir_2]^{n+}$ (*n* = 2 or 3) cores can be systematically synthesised. Variation of the ligands L allows fine-tuning of the potentials associated with each electron-transfer step.[2,3] Moreover, the variation in M–M distance with *n* is in accord with an extended-Hückel molecular orbital description of the bonding, and sequential depopulation of a σ* metal–metal orbital.[2]

In contrast, related binuclear triazenido species containing the $[Pd_2]^{4+}$ core are limited to the homoleptic complex [Pd_2(μ-PhNNNPh)$_4$],[4] the allyl-dimethyltriazenido[5] and -diaryltriazenido[6] dimers of formula [{Pd(μ-R^1NNNR^1)(η^3-$C_3H_4R^2$)}$_2$] (R^1 = Me or Ph, R^2 = H or Me), the dication [Pd_2(μ-PhNNNPh)$_2$(PEt$_3$)$_4$]$^{2+}$ [7] and [Pd_2Cl_2(μ-R^1NNNR^1)$_2$-($PR^2{}_3$)$_2$] (R^1 = Ph, C_6H_4Me-*p* or C_6H_4F-*p*, R^2 = Et or Bu).[8] Moreover, in contrast to the chemistry of the rhodium and iridium complexes, the detection by electrochemistry or the chemical isolation of complexes with other $[Pd_2]^{n+}$ cores, have not been described. We therefore report the synthesis and structural characterisation of the novel tetranuclear complex [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-Cl)$_4$] (R = C_6H_4Me-*p*), the precursor to a variety of other redox-active complexes [$Pd_2X_2L_2$(μ-RNNNR)$_2$] (X = anion, L = neutral ligand).

Treatment of a methanolic solution of $Li_2[PdCl_4]$ with an equimolar amount of 1,3-di-*p*-tolyltriazene and sodium carbonate under reflux for 2 h yields a dark green solution from which high yields of [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-Cl)$_4$] can be isolated as almost black crystals (Scheme 1). This novel tetranuclear complex was partially characterised by elemental analysis and ^{1}H NMR spectroscopy‡ but the details of its unusual structure were revealed only by a single crystal X-ray analysis of its hexane solvate.§

The molecular structure of [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-Cl)$_4$] **1** is illustrated in Fig. 1. Each palladium atom has local square-planar geometry being ligated by two *cis* bridging triazenido and two mutually *cis* bridging chloride ligands [Pd–N and Pd–Cl distances in the range 2.011(4)–2.038(4) and 2.331(1)–2.349(2) Å, respectively]. The molecule contains a Pd_4Cl_4 core in which the bridging chlorine atoms form an almost perfect square-planar arrangement and the four palladium atoms define the corners of a tetrahedron. The 'pseudocluster' therefore has D_{2d} symmetry and its structure resembles that of S_4N_4. The Pd ··· Pd distances bridged by the triazenido ligands are 2.747(1) and 2.756(1) Å while those bridged by chloride are 3.704(1), 3.711(1), 3.695 and 3.741(1) Å. Although the former are closer to those in Pd–Pd bonded systems they are formally non-bonding given the 16-electron, square-planar co-ordination environment of the Pd^{II} centres in **1**.

The cyclic voltammogram of [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-Cl)$_4$] (Fig. 2) shows two oxidation waves centred at 1.33 and 1.46 V (both apparently reversible, but insufficiently well separated to apply the standard criteria for reversibility) and one electrochemically irreversible reduction at −0.58 V. On controlled potential reduction at −0.7 V, coulometry showed the consumption of one electron (*n* = 1.0). However, the cyclic voltammogram of the reduced solution showed no oxidation or

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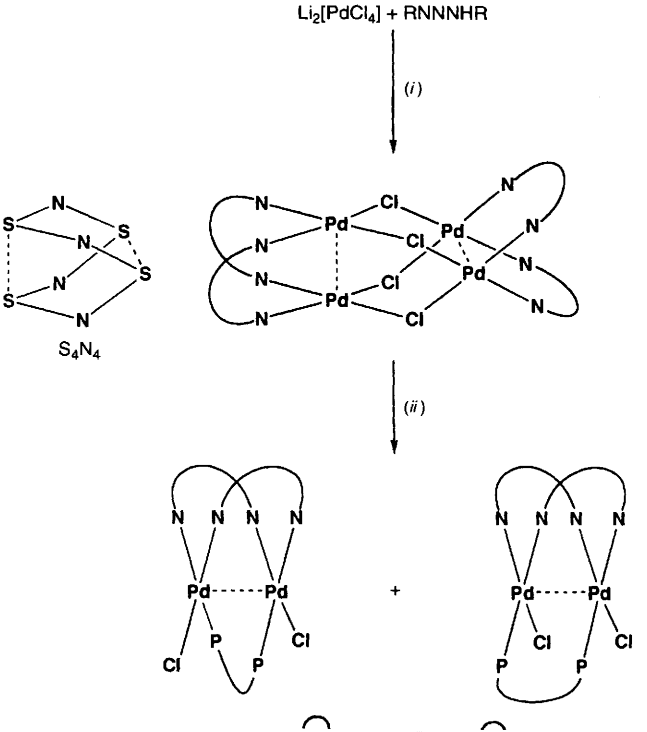
‡ Spectroscopic data for [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-Cl)$_4$]: ^{1}H NMR ($CDCl_3$, 80 MHz): δ 2.27 (s, 24 H, C_6H_4*Me*), 7.39 (m, 32 H, C_6*H_4*Me); [{Pd_2(μ-RNNNR)$_2$}$_2$(μ-I)$_4$]: ^{1}H NMR ($CDCl_3$, 80 MHz): δ 2.16 (s, 24 H, C_6H_4*Me*), 7.44 (m, 32 H, C_6H_4Me); [Pd_2Cl_2(μ-dppm)(μ-RNNNR)$_2$]: ^{1}H NMR ($CDCl_3$, 80 MHz): δ 2.16 (s, 6 H, C_6H_4*Me*), 2.24 (s, 6 H, C_6H_4*Me*), 3.57 (t, 2 H, PCH_2P, $^2J_{PH}$ 12 Hz), 6.63 (m, 4 H, C_6*H_4*Me), 7.31 (m: 12 H, C_6*H_4*Me; 20 H, Ph_2P). Satisfactory C, H and N elemental analyses were obtained for all new compounds.

§ Crystal data for complex **1**·1.33C_6H_{14}: $C_{56}H_{56}Cl_4N_{12}Pd_4$·1.33$C_6H_{14}$, crystal dimensions 0.40 × 0.20 × 0.60 mm, M_r = 1578.8, triclinic, space group $P\bar{1}$ (no. 2), *a* = 12.932(3), *b* = 15.702(6), *c* = 19.366(4) Å, α = 76.56(3), β = 81.89(2), γ = 77.48(3)°, *U* = 3717(2) Å^3, *Z* = 2, D_x = 1.411 g cm^{-3}, λ = 0.710 73 Å, μ(Mo-Kα) = 1.14 mm^{-1}, *F*(000) = 1590, *T* = 295 K. Data were collected on a Siemens R3m diffractometer for 4 < 2θ < 50°. The structure was solved by heavy atom methods and refined by least squares to *R*1 0.0378 (*wR*$_2$ = 0.1023) for 13096 unique, absorption-corrected intensity data.[8] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 R = C_6H_4Me-*p*, $\overset{\frown}{NN}$ = RNNNR, $\overset{\frown}{PP}$ = dppm; (*i*) Na_2CO_3, MeOH, reflux; (*ii*) dppm

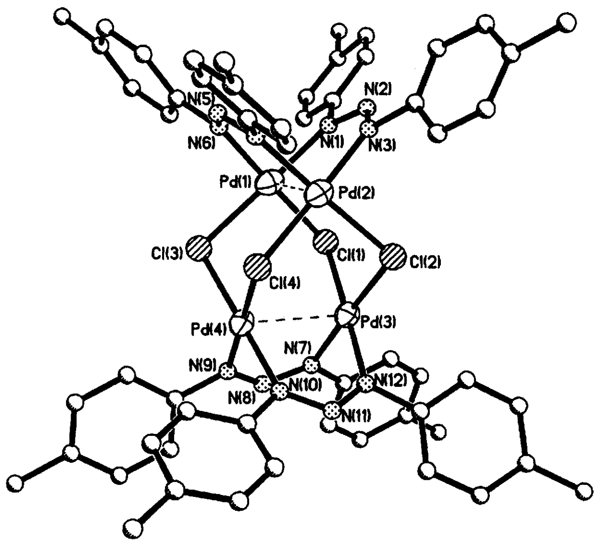


Fig. 1 Molecular structure of $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-Cl})_4]$ **1**. All hydrogen atoms have been omitted for clarity

reduction waves in the range −0.8 to +1.6 V, indicating the 1− anion to be unstable on the time-scale of the electrolysis.

Unlike the previously reported dipalladium triazenido derivatives noted above, $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-Cl})_4]$ is a useful precursor to other redox-active complexes. Thus, treatment with NaI in acetone afforded a high yield of $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-I})_4]$,‡ the cyclic voltammogram of which shows waves at −0.65, 1.22 and 1.37 V (shifted to more negative potentials by *ca.* 100 mV compared with the chloride complex). Moreover, the chloride bridges of $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-Cl})_4]$ are easily cleaved by P-donor ligands, the reaction with bis(diphenylphosphino)methane (dppm), for example, affording binuclear $[Pd_2Cl_2(\mu\text{-dppm})(\mu\text{-RNNNR})_2]$, characterised by ^1H NMR spectroscopy as a mixture of isomers with C_2 and C_s symmetries. Crystals of the two isomers can be mechanically separated (in spite of the absence of the precise assignation of its geometry), the cyclic voltammogram of the isomerically pure (C_2 or C_s isomer?) sample ‡ showing a reversible oxidation wave at +1.02 V, an irreversible oxidation wave at +1.40 V and irreversible reduction waves below −1.0 V. Preliminary results show that both $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-Cl})_4]$ and $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-I})_4]$ are readily cleaved by N-, P- or S-donor ligands, giving mixtures of isomers similar to those for dppm. Attempts to separate the pure isomers, in order to explore their structure and electrochemical behaviour, are currently in progress.

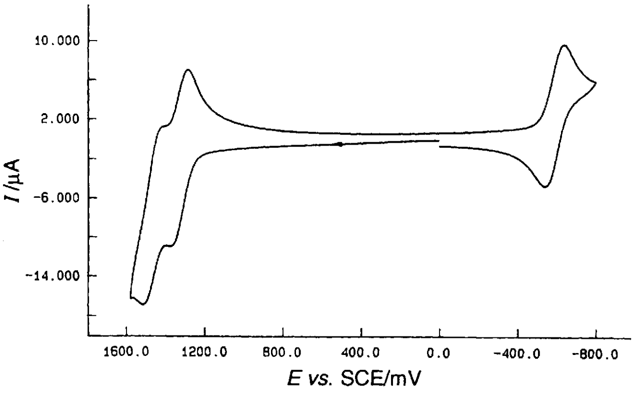


Fig. 2 Cyclic voltammogram of $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-Cl})_4]$ at a platinum bead electrode in CH_2Cl_2. Potentials are *vs.* the saturated calomel electrode; under the experimental conditions used $E^{\circ\prime}$ for the ferrocene–ferrocenium couple is 0.47 V

The synthesis, reactivity and electrochemistry of $[\{Pd_2(\mu\text{-RNNNR})_2\}_2(\mu\text{-Cl})_4]$ imply that, as for the dirhodium analogues noted above, the redox behaviour of dipalladium triazenido complexes is tunable by the systematic variation of the co-ordinated ligands.

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