

Unusual Double Palladium(II) Cyclometallation in a Tweezer-like Receptor with Stacked Arms: Synthesis, Properties and X-Ray Structure

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Double metallation of L^1 via aliphatic carbon and amide nitrogen atoms results in the formation of a tweezer-like molecule **1** with a four-membered Pd-C*-C(O)-N ring and a helical configuration around the metal.

We are interested in the synthesis and study of ligands with folding ability induced by metal binding and leading to stacked interactions with nucleic bases.¹ Linear or macrocyclic ligands L , able to act in this way, have been investigated (Scheme 1). Two planar aromatic entities R^1 and R^2 are connected by a central link through amide functions. As a potential metal ion binding site, three heteroatoms separated by ethylene groups constitute the link between the two side arms R^1 and R^2 . The complexation of metal ions by these molecules induces the coiling of the ligand L on itself and fashions a tweezer-like metalloceptor $M \subset L$.² The later inclusion of exogenous planar guests G is possible by intercalation and stacking between the arms R^1 and R^2 , and simultaneously by coordination on an available metal ion site.³ This mechanism yields 1:1:1 host ligand L -metal M -guest G complexes $(M,G) \subset L$ (Scheme 1). The guests utilized are essentially purine and pyrimidine bases.

In this paper, we report the synthesis, X-ray structure and properties of such a tweezer metalloceptor with the palladium(II) ion. It presents two unexpected and original metallations.^{4,5}

The ligands L were obtained by condensation of the appropriate aromatic amines with dicarboxylic acid chlorides. Palladium(II) and platinum(II) complexes were obtained with nitrate, acetate salts or $[Pd(MeCN)_4](BF_4)_2$ in MeCN leading to diamagnetic compounds. With Pd^{II} , the ligand L^1 , N,N' -bis(3,5-dinitrophenyl)-3,6,9-trithiaundecanediamide, $C_{20}H_{20}N_6O_{10}S_3$, gives compound **1**. Elemental analysis, and mass, 1H and ^{13}C NMR spectroscopy† identify unambiguously the reaction product **1** as $PdC_{20}H_{18}N_6O_{10}S_3$. This diamagnetic compound exhibits 1H NMR spectra in which the α -protons to the carbonyl groups are characterized by a multiplet (2 H, AA' system for C-11 protons) and a singlet (1 H, for the C-3 proton). Furthermore, the homologous protons of the two aromatic rings are inequivalent.

The molecular structure‡ of **1** (Fig. 1) reveals an unusual very distorted square-planar geometry. The palladium binds to only two sulfur atoms [S(7) and S(10)], in contrast to the

situation in (2,2'-dimercaptodiethyl sulfide)palladium(II).⁶ The ligand L^1 , which has lost two protons on N(1) and C(3), is doubly cyclometallated. Consequently, this generates a four-membered planar Pd-C*-C(O)-N metalocycle with an asymmetric metallated carbon C(3)§ and a helical winding of the ligand around the metal similar to the conformation of helixenes. The two planar aromatic arms $-NC_6H_3(NO_2)_2$ are stacked at the average distance of 3.31 Å and the molecule adopts a tweezer-like form (Fig. 1).

1H NMR studies in dimethyl sulfoxide at 293 K show that cyclopalladation is preceded by coordination of the three S

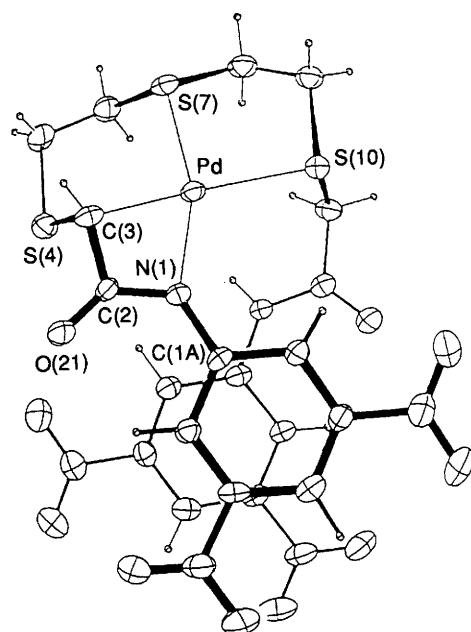
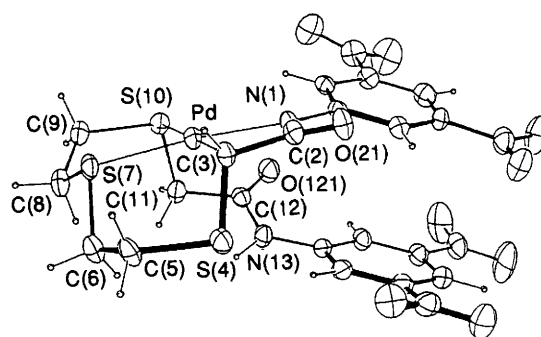
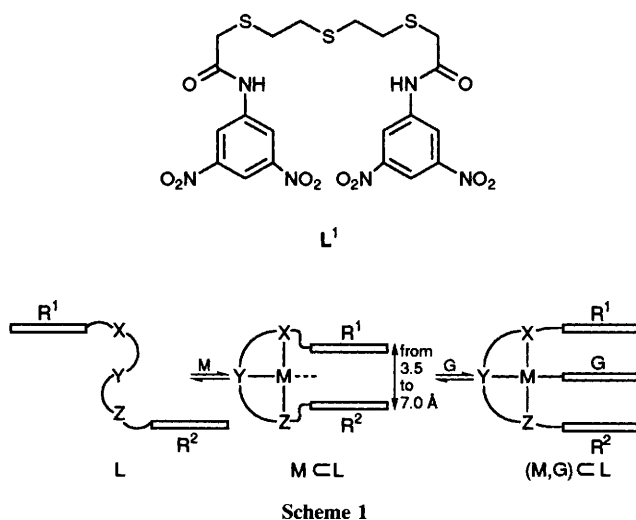


Fig. 1 Molecular structure of $PdC_{20}H_{18}N_6O_{10}S_3$, **1**, showing numbering scheme. Selected distances (Å) and angles ($^\circ$): Pd-N(1) 2.083(5), Pd-C(3) 2.033(7), Pd-S(7) 2.277(2), Pd-S(10) 2.417(2), N(1)-C(2) 1.332(8), C(2)-O(21) 1.246(8), C(2)-C(3) 1.507(9); N(1)-Pd-C(3) 66.4(2), N(1)-Pd-S(10) 112.3(1), C(3)-Pd-S(7) 92.8(2), S(7)-Pd-S(10) 88.6(1), Pd-N(1)-C(2) 95.9(3), N(1)-C(2)-C(3) 104.9(5), C(2)-C(3)-Pd 92.6(4).



heteroatoms to the metal followed by slow ligand metallation and amide nitrogen deprotonation. This process occurs without the need for special pH conditions or reductants, showing that the position of the hydrocarbon activation equilibria is determined by the strength of the final Pd–C bond and not by that of the reacting C–H bond.⁷

The whole structural work has been done in the UPR de Biologie Structurale 9004, IBMC CNRS, Strasbourg. We thank Dr D. Moras for his hospitality.

Received, 30th December 1993; Com. 3/07579F

Footnotes

† *Mass spectroscopy data* (FAB+): L¹ calc. for C₂₀H₂₀N₆O₁₀S₃: 600 (100%), 601 (28), 602 (19), 604 (1.5); found: 601 (M + H⁺, 100%), 602 (27.41), 603 (18.07), 604 (3.01); others: 585, 390, 344, 316, 284, 268, 257, 238. 1 calc. for Pd C₂₀H₁₈N₆O₁₀S₃: 704 (100%), 702 (31), 703(71), 705 (35), 706 (93), 707 (25), 708 (49), 709 (13); found: 705 (M + H⁺, 100%), 703 (34.18), 704 (72.50), 706 (47.05), 707 (91.46), 708 (35.02), 709 (49.40), 710 (18.29); others: 689, 538, 518, 482, 463, 440, 423, 391, 360, 329.

NMR (δ , J/Hz) (CD₃SOCD₃, 30 °C): L¹: ¹H: 2.70–2.96 (m, 8H) AA'BB', SCH₂CH₂SCH₂CH₂S: 3.42 (s, 4 H) SCH₂CO: 8.48 (t, 2 H) and 8.82 (d 4 H) A₂X, J = 2.08, aromatic; 10.99 (s, 2 H) NH amide; ¹³C: 169.74 (C-2, C-12 carbonyl); 148.52 (C-1A, C-1B), 141.22 (C-3A, C-5A, C-3B, C-5B), 118.56 (C-2A, C-6A, C-2B, C-6B) and 112.48 (C-4A, C-4B aromatic); 35.25 (SCH₂, C-6, C-8); 31.96 (SCH₂ C-5, C-9); 30.71 (SCH₂ C-3, C-11).

1: ¹³C{¹H} (DEPT) CH: 32.67 (C-3); 108.74 (C-4A); 112.51 (C-4B); 118.23 (C-2B, C-6B); 120.81 (C-2A, C-6A); CH₂: 32.12 (C-11); 30.10, 33.45 (C-5, C-9); 37.44, 37.80 (C-6, C-8); ¹³C: 32.21 (C-11); 32.77 (C-3); 33.29, 33.55 (C-5, C-9); 37.51, 37.82 (C-6, C-8); 108.77 (C-4A); 112.56 (C-4B); 118.30 (C-2B, C-6B); 120.86 (C-2A, C-6A); 140.23 (C-3B, C-5B); 147.95 (C-3A, C-5A); 148.06 (C-1B); 148.47 (C-1A); 167.04 (C-12); 174.48 (C-2).

¹H: 2.54–2.64 (m, 1 H) 2.80–2.89 (2t, 1 H) 3.04–3.12 (2t, 1 H) and 3.70–3.78 (2t, 1 H) H-8, H-8', H-9 and H-9'; 3.46–3.57 (m, 4 H) H-5, H-5', H-6 and H-6'; 3.17 (s, 1 H) H-3; 3.63–3.83 (q, 2 H) AB H-11, H-11' J = 13.5; 8.16 (t, 1 H) and 8.42 (d, 2 H) AX₂ H-4B and H-2B + H-6B J = 2.15; 8.41–8.47 (m, 3 H) ABC H-2A, H-4A, H-6A.

‡ *Crystal data* for 1: PdC₂₀H₁₈N₆O₁₀S₃, M = 704.99, monoclinic P2₁/c, a = 12.611(2), b = 13.344(1), c = 14.863(2) Å, β = 97.79(1)°, V = 2478.0 Å³, Z = 4, D_c = 1.89 g cm⁻³, μ = 91.4 cm⁻¹, F(000) = 1416.

Structure solution and refinement based on 3429 reflections with $F_0^2 > 3\sigma(F_0^2)$ converged at $R = 0.046$ and $R_w = 0.054$. Data were collected at room temp., in the θ range 2–72°, on an Enraf-Nonius CAD4 diffractometer using Cu–K α radiation. Nonhydrogen atoms were refined anisotropically by full-matrix least-squares methods and hydrogen atoms were included at calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Evidently, the centrosymmetric space group P2₁/c indicates that the crystal is racemic as is the compound in solution. The molecule of the crystallographic asymmetric unit in Fig. 1 is chiral: helical chirality and three asymmetric centres C(3), S(7) and S(10) are in the RRR configuration.

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