

Organometallic polymers: an infinite organoplatinum chain in the solid state formed by (C≡CH...ClPt) hydrogen bonds

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The new platinum complex [PtCl{C₆H₂(CH₂NMe₂)₂-2,6-(C≡CH)-4}] exhibits a polymeric linear -C≡CH...ClPt- hydrogen-bonded structure in the solid state.

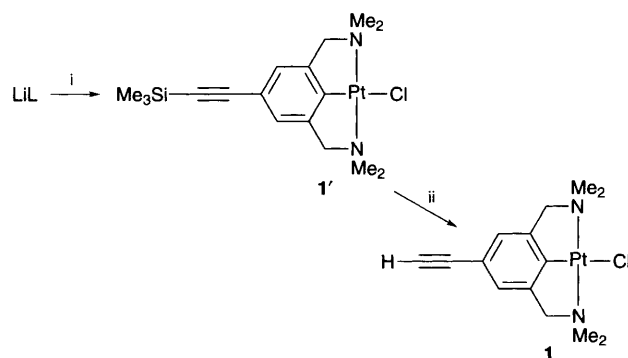
Conjugated organometallic polymers are interesting materials which may exhibit liquid-crystalline and non-linear optical behaviour.¹ Examples include polymetallaalkynes, in which the polymer backbone consists of metal atoms bridged by alkyne-diyl ligands. We have become interested in the use of aryldiamines related to C₆H₃(CH₂NMe₂)₂-2,6 (abbreviated NCN, Scheme 1) as bridging ligands for the preparation of rigid multimetallic and polymeric complexes.² Such species may achieve high stability due to the presence of chelating ligand groups, and offer intriguing possibilities for derivatisation by metal oxidation or interruption of extended conjugation through the reversible formation of arenonium species.³ In a recent article on *para*-functionalised NCN ligands we reported on the synthesis of the alkynyl-NCN ligand precursor C₆H₃(CH₂NMe₂)₂-1,3-(C≡SiMe₃)-5, HL, its organolithium complex [Li{C₆H₂(CH₂NMe₂)₂-2,6-(C≡SiMe₃)-4}]₂ (LiL)₂ (see Scheme 1), and the subsequent use of (LiL)₂ to prepare organoruthenium complexes.⁴ We have now turned to an investigation of the organoplatinum chemistry of ligand L. We report here the alkynyl functionalised NCN organoplatinum complex [PtCl{C₆H₂(CH₂NMe₂)₂-2,6-(C≡CH)-4}] **1**, which adopts an infinite zigzag chain structure in the solid state due to attractive {-C≡CH...ClPt-} interactions, and its acetonitrile solvento derivative [Pt{C₆H₂(CH₂NMe₂)₂-2,6-(C≡CH)-4}-(NCMe)][OSO₂CF₃] **2** which undergoes condensation dimerisation on the addition of a base.

Compound (LiL)₂ reacts with [PtCl₂(SEt₂)₂] in diethyl ether to give the expected³ organoplatinum complex **1'**,[†] from which the trimethylsilyl protecting group could be removed with tetrabutylammonium fluoride trihydrate to give the terminal alkyne species **1** (Scheme 2). An X-ray crystal structure determination[‡] of **1** confirmed the expected molecular structure of the complex (Fig. 1). In addition, it revealed close intermolecular contact [2.60(17) Å] between H(14) of the terminal alkyne and the chloride ligand, much shorter than their combined contact radii [H(1.20) + Cl(1.75) = 2.95 Å⁵]. The

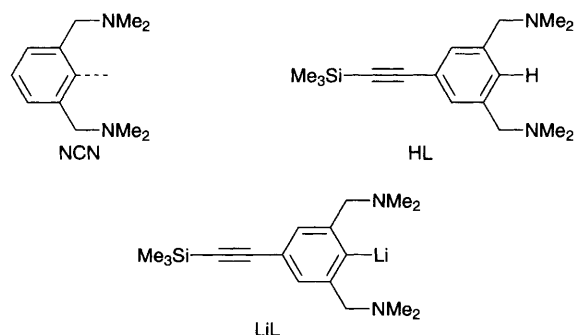
individual units of **1** are thus linked end-to-end to form infinite zigzag chains.

The exact nature of the interaction between H and Cl requires careful consideration. Once a subject of some debate, there is now strong evidence from solid-state structure determinations in support of the ability of hydrocarbonyl groups to act as donors in hydrogen bonding to electronegative groups or atoms (C-H...X) such as O,^{6a-c} N,^{6c} F⁷ and even to Se.⁸ Such interactions are of interest since they are important in determining crystal packing. A conclusion made on the basis of neutron diffraction data was that hydrocarbonyl groups may also hydrogen bond to otherwise discrete chloride ions in the crystal, the shortest (C)H...Cl distance (2.569 Å, C-H-Cl 157.9°) observed being in L-histidine hydrochloride monohydrate.^{6b} The shortest (C_{sp})H...Cl distance observed was previously 2.75 Å, found in (-)-(R)-deprenyl hydrochloride.⁹

Geometrical evidence for an attractive C≡CH...Cl interaction in **1** is provided by the short C...Cl [3.501(16) Å] and H...Cl distances, and the C-H...Cl angle of 157(14)° (C-H...O angles cluster between 150 and 160°).^{6a} Spectroscopic evidence for



Scheme 2 Preparation of organoplatinum complexes **1'** and **1**. Reagents: i, [PtCl₂(SEt₂)₂], Et₂O; ii, NBu₄F·3H₂O, CH₂Cl₂.



Scheme 1 NCN and two alkynyl functionalised derivatives

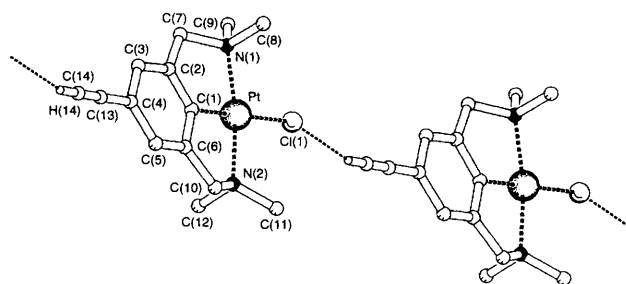
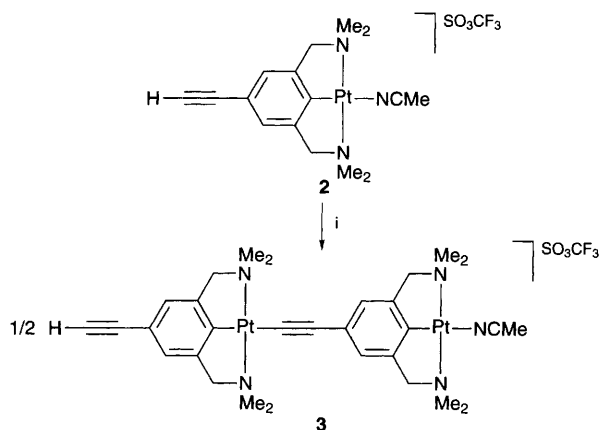


Fig. 1 Crystal and molecular structure of **1**. All H atoms except H(14) have been omitted for clarity. Relevant parameters: bond lengths (Å), Pt(1)-Cl(1) 2.414(4), Pt(1)-N(1) 2.083(9), Pt(1)-N(2) 2.090(10), Pt(1)-C(1) 1.911(12), C(13)-C(14) 1.19(2); bond angles (°), Cl(1)-Pt(1)-N(1) 98.5(3), Cl(1)-Pt(1)-N(2) 97.4(3), Cl(1)-Pt(1)-C(1) 179.7(4), C(4)-C(13)-C(14) 174.9(15), C(3)-C(13) 120.4(11), C(5)-C(4)-C(13) 119.1(11).



Scheme 3 Reaction of the solvento complex **2** with ethyldiisopropylamine. Reagents: i, NEtPr_2 , $-1/2 [\text{NHtPr}_2][\text{SO}_3\text{CF}_3]$.

this interaction is given by the $\text{C}_{\text{sp}}\text{-H}$ stretching frequency of **1**. In solution (CHCl_3) it appears as a single sharp band at 3306 cm^{-1} , whereas in the solid state it appears at 3202 cm^{-1} (Poflu mull, -185°C). The temperature dependence of the IR spectra in the solid state provides further qualitative proof of hydrogen bonding, the C-H band moving from 3210 cm^{-1} at 50°C to 3203 cm^{-1} at -185°C (KBr disc).

Interestingly, the related linear alkynyl functionalised isocyanoyl gold complex $[\text{AuCl}(\text{CNC}_6\text{H}_4\text{C}\equiv\text{CH})]$ does not exhibit a $\text{C}\equiv\text{CH}\cdots\text{Cl}$ interaction in the solid state $[(\text{C})\text{H}\cdots\text{Cl}\ 3.10\ \text{\AA}]$:¹⁰ another factor in determining the crystal packing in this case may be weak $\text{Au}\cdots\text{Au}$ interactions. We have recently observed an infinite linear hydrogen-bonded structure similar to that of **1** in the hydroxy substituted NCN platinum complex $[\text{PtCl}\{\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-}2,6\text{-(OH)-}4\}]$ with analogous $\text{OH}\cdots\text{Cl}$ interactions.¹¹

We are currently investigating the polymerisation of complexes such as **1** through the formation of platinum acetylide bonds. An initial observation is that a condensation reaction of the labile cationic acetonitrile complex $[\text{Pt}\{\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-}2,6\text{-(C}\equiv\text{CH)-}4\}(\text{NCMe})][\text{OSO}_2\text{CF}_3]$ **2** promoted by a tertiary amine (Scheme 3) leads to the highly insoluble dimer **3**. Efforts to increase solubility and chain length of this novel type of organometallic polymers are in progress.

The IR analysis by Mr Bert T. G. Lutz of the Department of Analytical Molecular Spectrometry, Faculty of Chemistry, University of Utrecht is greatly appreciated. This work is part of the COST-D4 chemistry action D4/04/92 'Towards Organometallic Polymers Containing Bis-cyclometallating Bridging Ligands'. This work was supported in part (A. L. S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Footnotes

† Additional characterising data for **1'** and **1**: For **1'**: $^1\text{H NMR}$ (CDCl_3 , 200 MHz) δ 6.93 (s, 2 H, aromatic), 3.97 (s, 4 H, $^3J_{\text{PH}}\ 47\ \text{Hz}$, CH_2), 3.05 (s, 12 H, $^3J_{\text{PH}}\ 37\ \text{Hz}$, NCH_3), 0.22 (s, 9 H, SiMe_3); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 147.4 (C_{ipso} , $^1J_{\text{PC}}\ 998\ \text{Hz}$), 143.2 (C_{ortho} , $^2J_{\text{PC}}\ 76\ \text{Hz}$), 122.9 (C_{meta} , $^3J_{\text{PC}}\ 35\ \text{Hz}$), 117.4 (C_{para}), 106.7 ($\text{ArC}\equiv$), 92.2 ($\equiv\text{CSiMe}_3$), 77.3 (CH_2 , $^2J_{\text{PC}}\ 64\ \text{Hz}$), 54.3 (NCH_3), 0.0 (SiCH_3). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})\ 2149\ \text{cm}^{-1}$. For **1**: $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 6.93 (s, 2 H, aromatic), 3.97 (s, 4 H, $^3J_{\text{PH}}\ 47\ \text{Hz}$, CH_2), 3.05 (s, 12 H, $^3J_{\text{PH}}\ 37\ \text{Hz}$, NCH_3), 3.01 (s, 1 H, $\text{C}\equiv\text{CH}$); $^{13}\text{C NMR}$

(CDCl_3 , 75 MHz) δ 147.6 (C_{ipso} , $^1J_{\text{PC}}\ 1001\ \text{Hz}$), 143.4 (C_{ortho} , $^2J_{\text{PC}}\ 77\ \text{Hz}$), 123.0 (C_{meta} , $^3J_{\text{PC}}\ 35\ \text{Hz}$), 116.4 (C_{para}), 85.2 ($\text{ArC}\equiv$), 77.3 (CH_2 , $^2J_{\text{PC}}\ 65\ \text{Hz}$), 75.4 ($\equiv\text{CH}$), 54.4 (NCH_3 , $^2J_{\text{PC}}\ 14\ \text{Hz}$). IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{C})\ 2101\ \text{cm}^{-1}$, $\nu(\text{C}_{\text{sp}}\text{-H})\ 3302\ \text{cm}^{-1}$. Elemental analysis. Found C 37.64, H 4.22, N 6.28. Calc. for $\text{C}_{14}\text{H}_{19}\text{ClN}_2\text{Pt}$: C 37.71, H 4.30, N 6.28%.

‡ Crystal data for **1**, $\text{C}_{14}\text{H}_{19}\text{ClN}_2\text{Pt}$, $M_r = 445.85$, yellowish cut to shape crystal ($0.03 \times 0.08 \times 0.38\ \text{mm}$), triclinic, space group $P\bar{1}$ (no. 2), $a = 6.0982(8)$, $b = 10.6813(10)$, $c = 11.8162(13)\ \text{\AA}$, $\alpha = 73.383(8)$, $\beta = 81.028(9)$, $\gamma = 81.030(9)^\circ$, $U = 723.45(15)\ \text{\AA}^3$, $Z = 2$, $D_c = 2.047\ \text{g cm}^{-3}$, $F(000) = 424$, $\mu(\text{Mo-K}\alpha) = 98.7\ \text{cm}^{-1}$, 2812 reflections measured, 2549 independent, $R_{\text{int}} = 0.085$, ($1.8 < \theta < 25^\circ$, ω scan, $T = 150\ \text{K}$, Mo-K α radiation, graphite monochromator, $\lambda = 0.71073\ \text{\AA}$) on an Enraf-Nonius CAD4-T diffractometer on rotating anode. Data were corrected for absorption (DIFABS, transmission range 0.564–1.000). The structure was solved by Patterson methods (DIRDIF92). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93). Refinement converged at $R_1 = 0.044$ [for 2547 reflections with $I > 2\sigma(I)$] [$wR_2 = 0.125$, $S = 1.06$; $w^{-1} = \sigma^2(F_o^2) = (0.074F^2)^2$, 170 parameters]. Hydrogen atoms were taken into account at calculated positions riding on their carrier atoms. A final difference map showed no features outside the range $-1.30 < \Delta\rho < 1.99\ \text{e}\text{\AA}^{-3}$ (near Pt). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/63.

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