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Preliminary Communication

Synthesis, NMR spectra and X-ray crystal structure of the trinuclear complex $[CH_3C\{CH_2SPtH(PPh_3)\}_3] \cdot CH_2Cl_2$

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Abstract

The trinuclear hydride platinum complex $[CH_3C\{CH_2SPtH(PPh_3)\}_3]$ has been synthesized by oxidative addition of $CH_3C(CH_2SH)_3$ to $[(PPh_3)_2Pt(C_2H_4)]$ and it has been characterized by X-ray diffraction studies and multinuclear NMR spectroscopy.

Oxidative addition reactions of thiols with low-oxidation state metal complexes can yield thiolato-derivatives. These reactions proceed via hydrido-intermediates, which can sometimes be isolated [1]. Our interest in metal-sulphur clusters prompted us to consider the tripod-like thiol $CH_3C(CH_2SH)_3$. Indeed the related thiolate $\{CH_3C(CH_2S)_3\}^{3-}$ forms a monometal complex only, with the highly charged cation Re^{5+} [2], but otherwise it links three metal centres [3,4]. The oxidative addition of trithiol to low oxidation state transition metal substrates would appear to be a convenient route to metal ion aggregates. We report here the preparation, spectra and the X-ray crystal structure of the triplatinum complex $[CH_3C\{CH_2SPtH(PPh_3)\}_3]$. It was prepared in high yield, as air-stable, yellow crystals, by treatment of $[(PPh_3)_2Pt(C_2H_4)]$ with $CH_3C(CH_2SH)_3$, at room temperature [5*].

$$3[(PPh_3)_2Pt(C_2H_4)] + CH_3C(CH_2SH)_3 \longrightarrow$$
$$[CH_3C\{CH_2SPtH(PPh_3)\}_3] + 3PPh_3 + 3C_2H_4$$

The IR spectrum of the solid (Nujol mull) shows bands at 2095 and 2145 cm^{-1} attributable to ν(Pt–H).

The single-crystal X-ray structure determination [7*] shows that the structure consists of $[CH_3C\{CH_2SPtH(PPh_3)\}_3]$ and CH_2Cl_2 solvent. A perspective view of the complex unit is given in Fig. 1, together with important bond distances and angles.

The three platinum atoms at the vertices of a triangle whose edges range from 3.485(1) to 3.587(1) Å are held together by sulphur thiolate bridges. Alternating metal and sulphur atoms form a six membered ring with a chair configuration and approximate C_{3v} symmetry. The ring angles at the metals, 96.0(1)–96.9(1)° are similar to those at the sulphur atoms, 95.5(2)–98.8(1)°. There is no evidence for a direct metal–metal interaction and the compound may be considered as constituted of three square planar platinum(II) moieties. Each platinum metal completes its square planar geometry with a triphenylphosphine and a hydride. The presence of the hydrides, directly detected in the IR and NMR spectra (*vide infra*), is also implied by the angler in the co-ordination sphere of the metals. Each

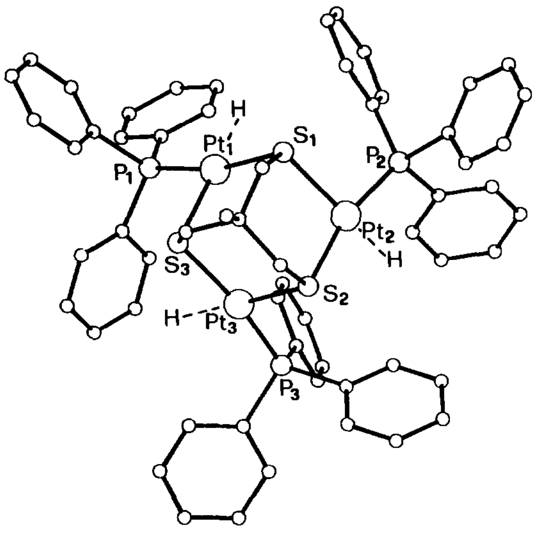

Fig. 1. Perspective view of $[CH_3C\{CH_2SPtH(PPh_3)\}_3]$ PLUTO drawing. Selected bond distances (Å) and angles (deg): Pt(1) ··· Pt(2) 3.587(1), Pt(1) ··· Pt(3) 3.485(1), Pt(2) ··· Pt(3) 3.541(1), Pt(1)–S(1) 2.344(4) Pt(1)–S(3) 2.387(5), Pt(1)–P(1) 2.240(4), Pt(2)–S(1) 2.381(4), Pt(2)–S(2) 2.328(2), Pt(2)–P(2) 2.230(5), Pt(3)–S(2) 2.388(4), Pt(3)–S(3) 2.323(4), Pt(3)–P(3) 2.221(4), S(1)–Pt(1)–S(3) 96.5(1), S(1)–Pt(1)–P(1) 167.7(2), S(3)–Pt(1)–P(1) 93.8(2), S(1)–Pt(2)–S(2) 96.0(1), S(1)–Pt(2)–P(2) 97.6(2), S(2)–Pt(2)–P(2) 165.9(2), S(2)–Pt(3)–S(3) 96.9(1), S(2)–Pt(3)–P(3) 96.8(1), S(3)–Pt(3)–P(3) 166.2(2), Pt(1)-S(1)–Pt(2) 98.8(1), Pt(2)–S(2)–Pt(3) 97.3(2), Pt(1)–S(3)–Pt(3) 95.5(2).

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* Reference number with asterisk indicates a note in the list of references.

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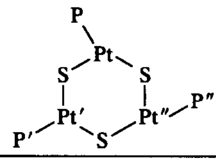
platinum displays two different Pt–S values owing to the *trans*-influence of the hydride atom the Pt–S bonds *trans* to hydride being significantly larger than those *trans* to the phosphine (av. 2.385(2) *vs.* av. 2.331(7) Å).

The ligating capability of the thiolate has scarcely been investigated. The unique rhenium mononuclear complex [2], and two trinuclear derivatives with a complete X-ray analysis [3,4] have been reported (Ir and Hg).

The iridium compound $[Ir_3(CH_3C(CH_2S)_3)(CO)_6]$ shows the same geometry as the platinum complex, it forms a two-dimensional network and displays shorter metal–metal distances (3.315(1)–3.366(1) Å *vs.* 3.485(1)–3.587(1) Å), with smaller M–S–M angles (88.8(1)–90.7(1)° *vs.* 95.5(2)–98.8(1)° [3]. The mercury derivative $[CH_3C(CH_2SHgCH_3)_3]$ has a completely different structure: the trithiolate acting as a 6-electron donor, linearly coordinates three CH_3Hg groups, with metal–metal distances all larger than 3.7 Å [4].

The multinuclear NMR spectrum [8*] (CD_2Cl_2 solution, room temperature) is consistent with the symmetrical molecular structure determined by the X-ray analysis. The ^1H NMR spectrum exhibits signals at δ 7.8–7.0 (m, 45H, C_6H_5), 2.39 (m, 6H, CH_2S), 0.56 (s,

TABLE 1. Observed chemical shifts (δ/ppm) and coupling constants (J/Hz)



(a) Chemical shifts

Pt	P
−4672	22.2

(b) Coupling constants

	Pt'	Pt''	P	P'	P''
Pt	10.9	10.9	3628	−23.3	−3.2
Pt'		10.9	−3.2	3628	−23.3
Pt''			−23.3	−3.2	3628
P				−0.3	−0.3
P'					−0.3

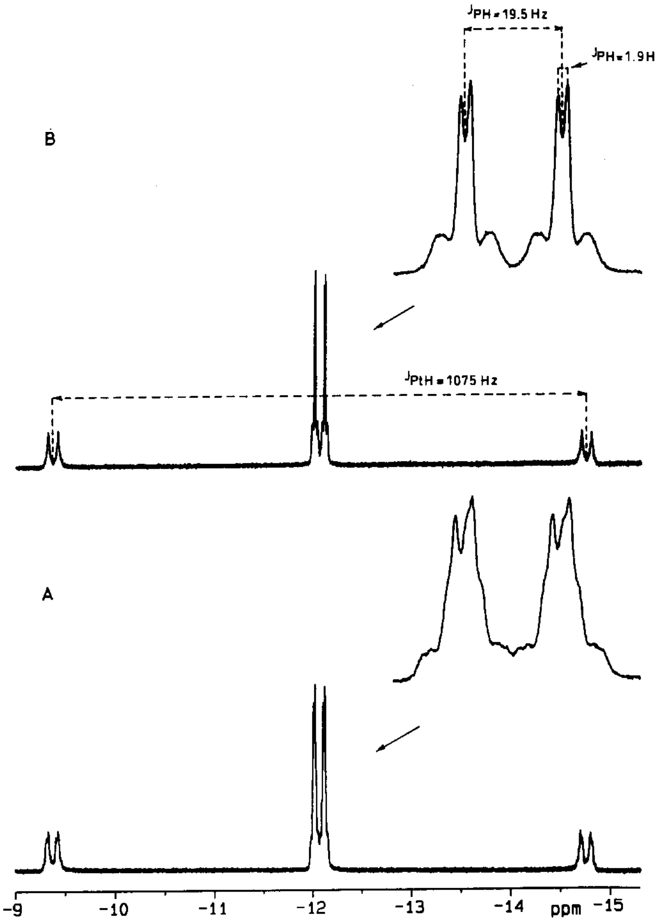


Fig. 2. High field undecoupled (A) and CH_2S-protons homo-decoupled (B) ^1H NMR spectra of $[CH_3C\{CH_2SPtH(PPH_3)\}_3]$.

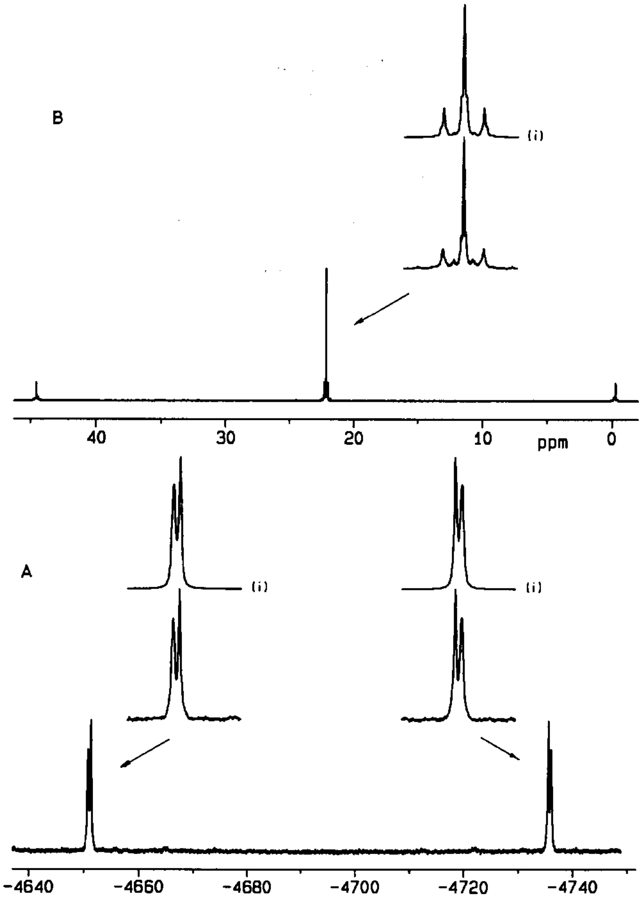


Fig. 3. $^{195}Pt\{^1H\}$ (A) and $^{31}P\{^1H\}$ (B) NMR spectra of $[CH_3C\{CH_2SPtH(PPH_3)\}_3]$. Simulated signals (i) are in the upper trace of insets.

3H, CH_3C) and −12.06 (m, 3H, PtH). The high field resonance, which is assigned to the three chemically equivalent hydride hydrogens (Fig. 2, A) is complicated, by four subspectra, due to the spin systems AA′A″MM′M″, AA′A″MM′M″X, AA′A″MM′M″XX′ and AA′A″MM′M″XX′X″ ($A = {}^1H$, $M = {}^{31}P$, $X = {}^{195}Pt$). Yet further complication stems from the coupling of the hydride hydrogens with the CH_2 protons of the trithiolate. The hydride resonance, homo-decoupled from the CH_2S protons is reported in Fig. 2, B. The couplings of 1075, 19.6 and 1.9 Hz, which appear in Fig. 2, B are $^1J_{PtH}$, $^2J_{PH}$, and $^4J_{PH}$, respectively. The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ spectra might be less complicated because of the smaller spin systems, even if different isotopomers are present. The analysis of these spectra has been attempted using a new computer program to best fit the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ experimental multiplets simultaneously. Preliminary results are listed in Table 1 and the experimental and calculated multiplets are shown in Fig. 3.

A complete analysis of the spectra is in progress, and the detailed results will be published elsewhere.

Acknowledgment

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5 The compound $[(PPh_3)_2Pt(C_2H_4)]$ (2.23 g, 3 mmol) in THF (20 cm^3) was added, at room temperature to a solution of $CH_3C(CH_2SH)_3$ [6] (0.145 cm^3, 1 mmol) in the same solvent (20 cm^3). n-Butanol (30 cm^3) was added to the resultant yellow solution, and the solvent was evaporated until yellow crystals precipitated. These were filtered off, washed with n-butanol, then with hexane and dried in a current of nitrogen (1.15 g, 75%). (Found: C, 46.15; H, 3.85; S, 6.10. $C_{59}H_{57}P_3Pt_3S_3$ requires C, 46.00; H, 3.73; S. 6.24%). Crystal of composition $[CH_3C\{CH_2SPtH(PPh_3)\}_3] \cdot CH_2Cl_2$, suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/n-butanol.

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7 Crystallographic data for $[CH_3C\{CH_2SPtH(PPh_3)\}_3]$: $C_{60}H_{59}Cl_2P_3Pt_3S_3$, M = 1625.43, triclinic, space group $P\bar{1}$, $a = 3.093(3)$, $b = 14.080(6)$, $c = 16.289(9)$ Å, $\alpha = 86.93(6)$, $\beta = 74.09(4)$, $\gamma = 81.45(3)°$, $Z = 2$, $U = 2855.5$ Å^3, $d_{calc} = 1.890$ g cm^{-3}, $\lambda = 0.7107$ Å, μ(Mo-Kα) = 77.3 cm^{-1}, $F(000) = 1560$, room temperature, Enraf Nonius CAD4 automatic diffractometer, $\omega - 2\theta$ mode with a scan speed of 8.24° min^{-1} and a scan width $= 0.70 + 0.35 \tan\theta$, $2.5 < \theta < 25°$, graphite monochromated Mo-Kα radiation; structural solution by heavy atom method. 5996 observed, absorption corrected reflections with $I \geqslant 3\sigma(I)$ used in the full-matrix least-squares refinement; final values of the R and R_w factors, 0.054 and 0.053 respectively. Atomic parameters have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

8 ^1H, $^{31}P\{1H\}$, $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker ACP-200 spectrometer at 200.13, 81.01 and 42.95 MHz respectively. Chemical shifts are relative to internal TMS, external 85% H_3PO_4 and external $Na_2[PtCl_6]$ respectively, with down-field values reported as positive.