Inorganica Chimica Acta, *128* (1987) 215–217

Synthesis, Reactivity, and X-ray Crystal Structure of a Remarkably Stable Bis(alkoxo)platinum Complex

NATHANIEL W. ALCOCK, ANDREW W. G. PLATT and PAUL G. PRINGLE*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

(Received September 18, 1986)

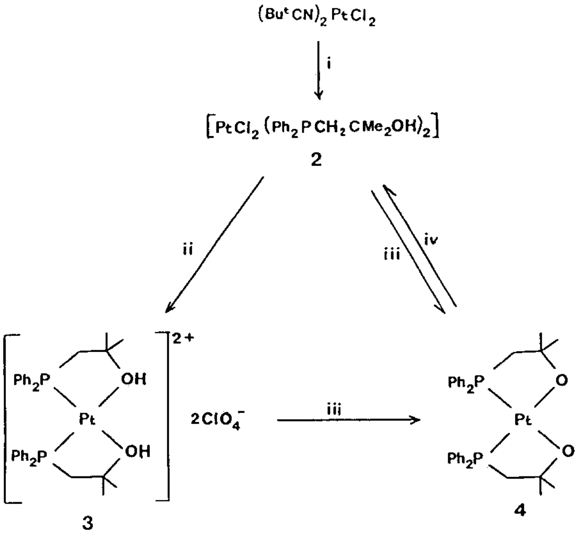
Abstract

Platinum complexes of the ligand $Ph_2PCH_2CMe_2OH$ are described including $[Pt(PPh_2CH_2CMe_2O)_2]$ which contains Pt–O bonds of unprecedented stability that readily undergo insertion of SO_2 and CO.

Few alkoxo–platinum complexes have been fully characterised because they are often strongly basic, extremely moisture and base sensitive, and very labile, undergoing β-hydrogen elimination rapidly [1–4]. Despite this high instability, considerable effort [1, 5–7] has recently been expended in attempts to synthesise complexes containing alkoxo–platinum bonds so that their reactivity can be systematically investigated. In this communication we report the synthesis of chelate-stabilised alkoxo complexes of platinum which are very stable both thermally and hydrolytically and are suitable model compounds for the study of the reactivity of Pt–O bonds.

We reasoned that $Ph_2PCH_2CMe_2OH$ (**1**) would form chelate stabilised alkoxo–platinum complexes.

The synthesis of platinum complexes of **1** are summarised in Scheme 1.** The white complex **2** isolated on treatment of $[PtCl_2(NCBu^t)_2]$ with **1** in acetone, was assigned the *cis*-structure **2a** on the basis of the IR spectrum: ν(Pt–Cl) 310, 285 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of a $CDCl_3$ solution of **2** at 25 °C was a broad singlet with ^{195}Pt satellites. At −60 °C the spectrum showed a sharp AX pattern with chemical shifts and coupling constants (Table I) fully consistent [8] with the salt structure **2b**, in which the alcohol donor group has displaced a chloro ligand. Complex **2** dissolves in methanol to give a conducting solution ($\Lambda = 78$ Ω^{-1} cm^2 mol^{-1}). This indicates that the OH donor in ligand **1** is a stronger donor for platinum than



Scheme 1. (i) Ligand **1** in acetone, +25 °C; (ii) $AgClO_4$ in acetone, +25 °C; (iii) Et_3N, $CHCl_3$, +25 °C; (iv) $Et_3N/CHCl_3$ or KOH/MeOH or $LiN(SiMe_3)_2$/THF at 25 °C; (v) Dilute HCl, $CHCl_3$, +25 °C.

TABLE I. ^{31}P NMR Data[a]

Complex	δ (P) (ppm)	$^1J(PtP)$ (Hz)	$^2J(P_AP_B)$ (Hz)
2^b	$+30.7^c$	3749	18
	-1.2^d	3937	
3	+16.0	3952	
4^e	+23.1	3303	
5	4.6	2723	
6^f	5.4, 0.6		325
7	35.9	3121	388
	13.4	3142	

[a] In $CDCl_3$ unless stated otherwise; 36.4 MHz, chemical shifts (±0.1 ppm) are to high frequency of 85% H_3PO_4. [b] At −60 °C. [c] P_A in structure **2b**. [d] P_B in structure **2b**. [e] In $(CD_3)_2CO$. [f] ^{195}Pt satellites not observed due to low intensity.

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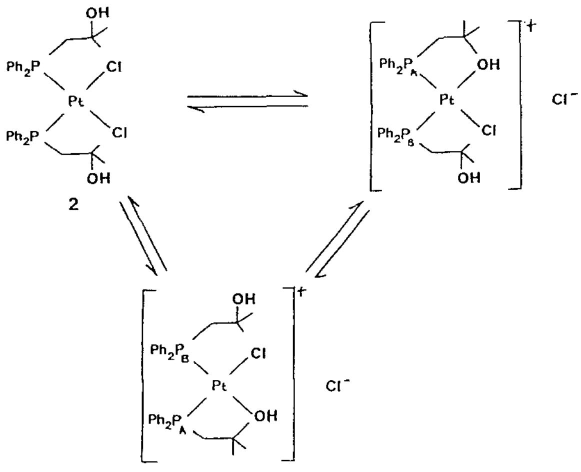
*Author to whom correspondence should be addressed.

**All new complexes have been characterised by elemental analysis (C, H, Cl), IR, ^1H and ^{31}P NMR spectroscopy.

0020-1693/87/$3.50

the OMe in $Ph_2PCH_2CH_2OMe$ [9] or the SPh in $Ph_2PCH_2CH_2SPh$ [10], both of which give neutral complexes of the type $[PtCl_2(P)_2]$. The fluxionality observed in solutions of **2** at ambient temperatures may be due to rapid reversible Cl^- coordination or intramolecular interchange of OH donors (Scheme 2).



Scheme 2.

The bis-chelate dicationic species **3** is prepared quantitatively by the addition of $AgClO_4$ to solutions of **2**. The neutral bis(alkoxo)platinum species **4** is readily formed by treatment of **2** with a variety of bases under mild conditions or by deprotonation of **3** with triethylamine (see Scheme 1). Complex **4** is remarkably stable thermally and hydrolytically, e.g. it was recovered unchanged after treatment with boiling ethanolic KOH for 16 h and can be recrystallised from aqueous methanol solutions. Thus it contrasts with the recently reported [1] [Pt(dppe)-$(OMe)_2$], the first bis(alkoxo)platinum complex, which decomposes in CH_2Cl_2 solution at +25 °C and could not be isolated in pure form.

It may be predicted [11] from the mismatch of hard donor (alkoxo) and soft acid [platinum(II)] that alkoxo–platinum bonds would be weak, and if correct, this would help explain the instability of such complexes. The X-ray crystal structure of **4** was determined to confirm the structural identification, and obtain the Pt–O bond distance. It reveals (Fig. 1) that the Pt–O bond is of absolutely normal length. The average Pt–O distance in **5** of 2.024(3) Å can best be compared with the Pt–C distance of 2.120(4) Å in $[(Ph_2MeP)_2PtMe_2]$, as this contains closely similar phosphine ligands coordinated to Pt(II) [12]; it also has a Pt–P distance (2.284(1) Å) reasonably similar to that in **4**. The 0.11 Å difference in covalent radius of C and O (obtained by comparing C–C and C–O bonds) corresponds very closely to the difference between the Pt–C and Pt–O bonds.

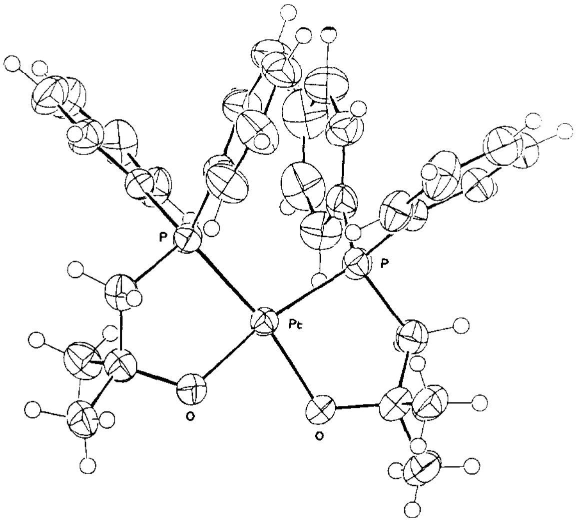
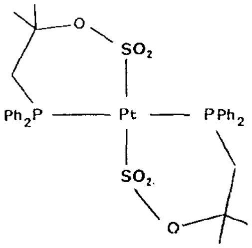


Fig. 1. Molecular structure of $[Ph_2PCH_2C(CH_3)_2O]_2Pt$. The crystals are rhombohedral, space group $R\bar{3}$, a = 17.026(2) Å, α = 92.76(1)°, with $Z = 6$. $R = 0.029$ for 3914 unique observed reflections ($I/\sigma(I)$ 3.0). Principal dimensions are Pt–P 2.222(1), Pt–O 2.024(3) Å (averages) P(1)–Pt–P(2) 105.7(1)°, O(1)–Pt–O(2) 85.7(1)°. The crystals contain 3.5 molecules of H_2O per molecule of complex and show a network of hydrogen bonds involving the solvent and the oxygen atoms of the ligand molecules.

The value of $^1J(PtP)$ for **3** is very large, indicating that the OH group is a weak donor ligand but the value of $^1J(PtP)$ for the alkoxo complex **4** is in the range expected for P *trans* to Cl [13]. This reinforces the X-ray crystallographic evidence that the Pt–O bonding is not inherently weak and the observed instability of alkoxo–platinum complexes is almost certainly kinetic, *i.e.* facile β-hydride elimination.

The methyl substituents on ligand **1** are not essential for the stability of the alkoxo–platinum species since we have recently found that the ligands $Ph_2PCH_2CHMeOH$ and $Ph_2PCH_2CH_2OH$ give analogous chelate complexes to **3** and **4** which are less soluble but have similar stability. The β-hydrogens in the chelates formed by these ligands are oriented away from the metal centre and are thus not available for elimination; the stability of metallacarbacycles relative to dialkyls is explained similarly [14].

Preliminary results show that **4** is a suitable model compound for studying the reactivity of Pt–OR bonds. Hence a solution of **4** in $CDCl_3$ reacts rapidly with an excess of SO_2 to give the bis sulphinate complex **5**, the product of SO_2 insertion into both of the Pt–O bonds of **4** with concomitant *cis–trans* isomerisation. Structure **5** is assigned on the basis of elemental analysis, IR [17] (ν(SO) 1370(m), 1360(m), 1150(s) cm^{-1}), ^{31}P (Table I) and ^1H NMR (virtual triplet at δ 2.91 for the CH_2 resonance). An intermediate species, characterised only in solu-



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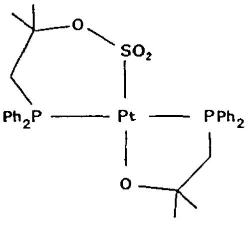

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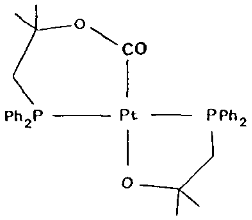

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tion by its ^{31}P NMR spectrum (Table I), is assigned structure **6**, the product of mono insertion. Similarly $CDCl_3$ solutions of **4** react with CO (30 atm) to give a single product assigned structure **7** on the basis of ^{31}P NMR (Table I) and IR (ν(CO) 1625 cm^{-1} evidence).

Acknowledgements

We thank the SERC for financial support and Johnson Matthey PLC for the generous loan of platinum salts.

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