Journal of Organometallic Chemistry, 247 (1983) C32—C36
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE FLUXIONAL BEHAVIOUR OF BIS-μ-{BIS(DIPHENYLPHOSPHINO)-METHANE} CHLORODIHYDRIDODIPLATINUM(II) HEXAFLUOROPHOSPHATE: A VT ^{195}Pt NMR STUDY

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(Received February 7th, 1983)

Summary

^{1}H, ^{31}P and ^{195}Pt NMR studies upon the title compound, $[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$ (dppm = $Ph_2PCH_2PPh_2$), reveal that (in solution at low temperature) it possesses a novel unsymmetrical structure involving a donor—acceptor metal—metal bond; the previously accepted "A"-frame structure represents the time-averaged structure at ambient temperature, the fluxional process corresponding to an intramolecular chloride ion transfer.

The complexes $[Pt_2H_3(\mu\text{-dppm})_2][PF_6]$, $[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$, $[Pt_2Cl_2H(\mu\text{-dppm})_2][PF_6]$ and $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$) have been known for some time [1,2]; the structures of the first three complexes **1a**—**1c** were deduced from ambient temperature ^{1}H and ^{31}P NMR and IR spectroscopic measurements [1], whilst that of the last complex (**2**) was also confirmed by a later crystallographic study [3,4]. Interest in the complexes **1** has increased recently, with the publication of a theoretical study [5] of "A"-frame complexes (as exemplified by **1**), and the important observation that **1a** and **1b** both undergo a photoinduced elimination of dihydrogen [6]. Indeed, if structure **1b** is correct, the photoelimination of H_2 from this complex is somewhat surprising, and Geoffroy [6] proposed that the reaction occurred via an intramolecular hydride migration to give an

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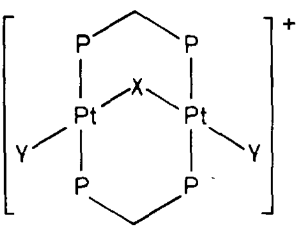
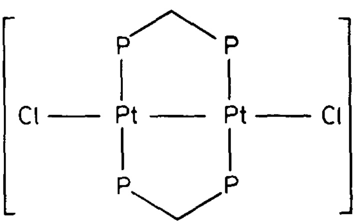


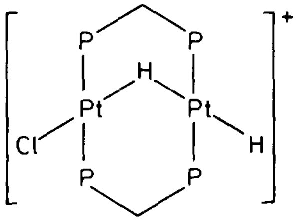
(1a, X = Y = H;
1b, X = Cl, Y = H;
1c, X = H, Y = Cl)



(2)

(P⌒P = dppm)

activated intermediate with both hydrides bound to the same platinum atom, such as **3** or **4**. We will show, in this communication, that structure **1b** for the complex $[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$ represents only the time-averaged structure of a fluxional molecule, and that its true static structure in solution involves a novel example of a donor—acceptor metal—metal bond.



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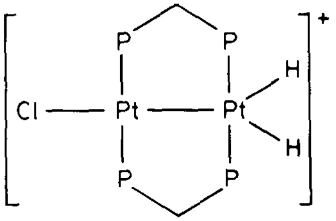
(P⌒P = dppm)



(4)

As part of a reinvestigation of all the complexes **1** and **2** by ^{195}Pt, ^{31}P and ^{1}H NMR spectroscopy over a wide range of temperatures [7], it was apparent that **1b** was anomalous. Apart from the expected "A"-frame inversion [8], complexes **1a**, **1c** and **2** show no evidence for fluxional behaviour between 183 and 298 K. However, although the gross features of the ambient temperature ^{1}H (90 MHz) and ^{31}P (36.43 MHz) NMR spectra of $[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$ in CD_2Cl_2 support the originally proposed structure **1b** [1], a detailed examination of its ^{31}P NMR spectrum reveals the absence of the expected $\chi_i(1)$ lines [9,10] due to the AA'A''A'''XX' isotopomer [1]. Moreover, its ambient temperature ^{195}Pt (19.16 MHz) NMR spectrum yielded a value of ^{1}J(PtPt) 1260 Hz, a value which is almost an order of magnitude higher than expected for a complex of structure **1b** if Hoffmann's treatment [5] of "A"-frame molecules is accepted (viz. for **1a**, ^{1}J(PtPt) 630 Hz; Hoffmann's treatment would predict that the value of ^{1}J(PtPt) for **1b** would be significantly lower than this). Upon cooling to 203 K the ^{195}Pt spectrum changed to reveal two discrete platinum resonances (see Fig. 1) of equal intensity, which showed a direct ^{1}J(PtPt) coupling constant of 1320 Hz. Observation of this spectrum over a range of intermediate temperatures (Fig. 1) yielded a value of the coalescence temperature, T_c, of 248 K, corresponding to an approximate value of $\Delta G^{\ddagger}$ of 40.7 kJ mol^{-1} [11]. Observation of the ^{31}P NMR (36.27 MHz) spectrum from 183—298 K showed a similar phenomenon (T_c 205 K; $\Delta G^{\ddagger}$ 39.2 kJ mol^{-1} [11]), the low temperature limiting spectrum showing two discrete phosphorus resonances. Thus, the structure of the complex in solu-

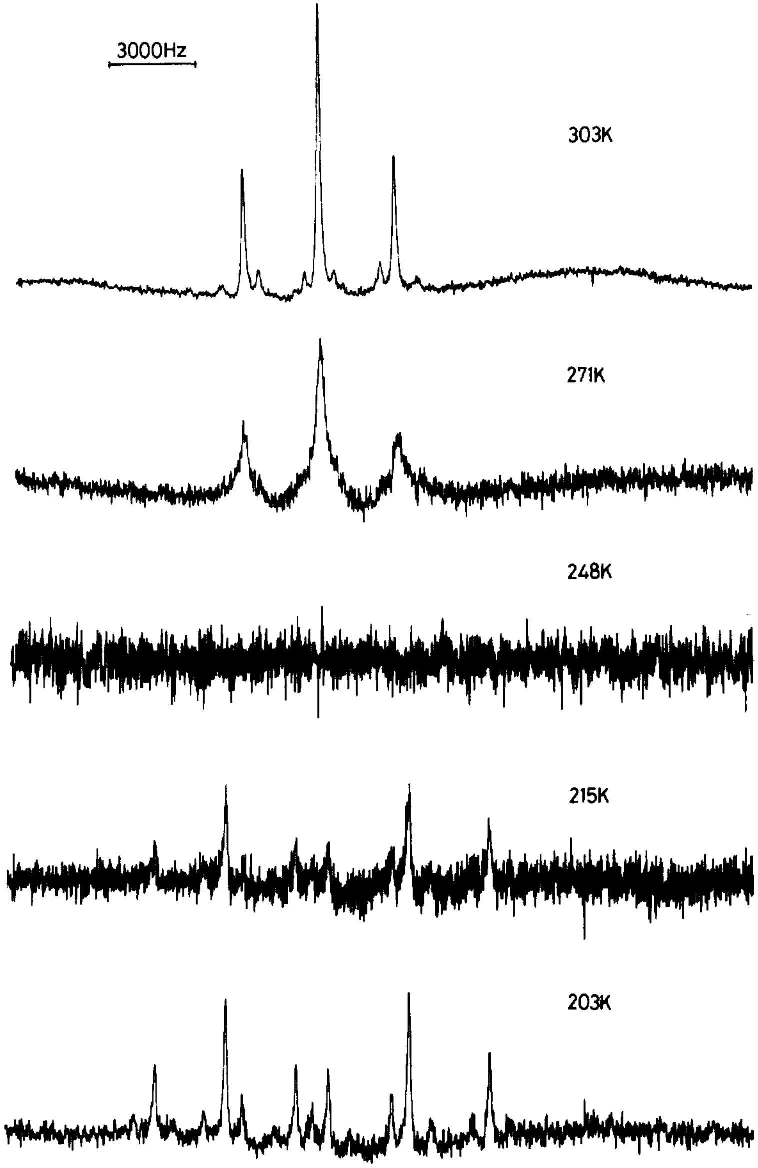
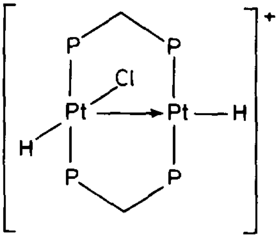


Fig. 1. Variable temperature $^{195}Pt\{^1H\}$ NMR spectra (19.16 MHz) of $[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$ in CD_2Cl_2. Some of the chemical shifts and coupling constants of the time-averaged high temperature spectrum and the low temperature spectrum were (a) T 303 K: δ −348 ppm, $^1J(PtPt)$ 1260 Hz, $^1J(PtP)$ 2612 Hz, $^2J(PtP)$ 3 Hz; (b) T 203 K: δ_X −526 ppm, δ_Y −200 ppm, $^1J(Pt_XPt_Y)$ 1320 Hz, $^1J(Pt_XP_A)$ 2756 Hz, $^1J(Pt_YP_B)$ 2404 Hz, $^2J(Pt_XP_B)$ −35 Hz, $^2J(Pt_YP_A)$ −35 Hz. Subscripts A and X refer to the Pt atom bearing both a terminal Cl and a terminal H; subscripts B and Y refer to the Pt atom bearing only a terminal H. Chemical shift is measured relative to a frequency of 21.4 MHz, for an NMR machine with a ^1H TMS frequency of exactly 100 MHz.

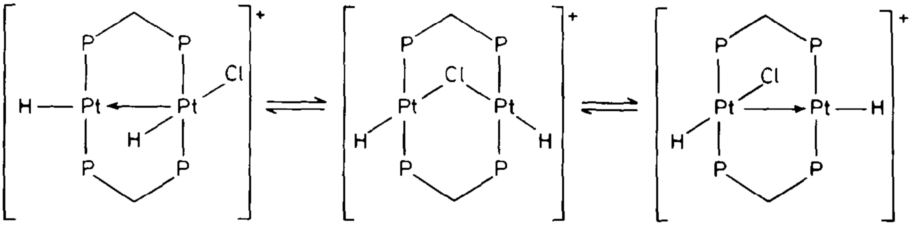
tion must be unsymmetrical, and could be (on the basis of the data discussed so far), structure **3**, **4** or the novel structure **5**.

A variable temperature ^1H (400 MHz) NMR study of $[Pt_2H_2Cl(\mu\text{-dppm})_2]$-$[PF_6]$ also exhibited a similar dynamic process (T_c 235 K; $\Delta G^{\ddagger}$ 40.9 kJ



(5)

mol^{-1} [11]); the low temperature limiting spectrum revealed two discrete hydridic proton resonances, immediately eliminating structure **4**. Moreover, the satellite structure of both these resonances was characteristic of terminal (as opposed to bridging) hydride ligands, thus eliminating structure **3**. Structure **5**, however, is completely consistent with all the spectroscopic data, and a complex of similar stoicheiometry but with a *cis*-configuration, $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$, also containing a donor—acceptor bond, has previously been characterised [13]. Thus the fluxional process may be envisaged as occurring according to equation 1, corresponding to an intramolecular chloride ion transfer. A simple extension of this mechanism would easily account for the formation of photoactivated intermediates of type **3**, and indeed such an intermediate has also been invoked in the thermally promoted "A"-frame inversion mechanism [8].



(1)

In summary, this report demonstrates the value of VT ^{195}Pt NMR studies, and provides a *caveat* concerning the assignment of "A"-frame structures based upon ambient temperature NMR data. It represents the first observation of a fluxional process of the type illustrated in equation 1, and has important implications for many mechanistic studies (viz. "A"-frame inversion [8]).

Acknowledgements. We thank Dr. G. Hawkes and Mr. M. Buckingham (ULIRS WH-400 NMR Service, Queen Mary College, University of London), Mr. D. Parkinson (JEOL FX-90Q, Bedford College, University of London) for their assistance with recording multinuclear magnetic resonance spectra, and the S.E.R.C. for the provision of a studentship (R.P.M.).

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