

increase in total oxidation yield was accompanied by a marked increase in the ratio of alcohol to ketone, this ratio reaching 10, a remarkable value for an oxidation catalysed by a Mn-porphyrin, in the case of heptane.

We have already reported that the SiO₂-supported Mn(tmpyp)Cl catalyst led to higher yields of hydroxylation of poorly reactive linear alkanes with markedly higher ratios of alcohol to ketone than the corresponding homogeneous Mn-porphyrin catalysts.² This tendency is even more pronounced with ClaypMn (*ca.* 50% yield for heptane). In order to know whether the different environments of the Mn catalyst in ClaypMn and in SiO₂pMn could change the substrate specificity in favour of linear alkanes, competition experiments were performed on alkane mixtures (in fact pentane-alkane 2 : 1 mixtures). As shown in Table 2, the ratio between the oxidation products derived from pentane and those derived from either adamantane, cyclo-octane, or heptane were always higher with ClaypMn than with SiO₂pMn. The largest difference was observed for competitions between pentane and adamantane as the ratio obtained with ClaypMn was seven times more in favour of pentane than with SiO₂pMn. Actually, pentane was found to be much less reactive than adamantane in oxidations catalysed by SiO₂pMn or soluble Mn(tmpyp)Cl (relative reactivity ratio of 0.05 : 1 with both catalysts under the conditions used), but only three times less reactive in oxidations catalysed by ClaypMn (ratio of 0.35 : 1). This difference between ClaypMn and SiO₂pMn was much lower for competitions between pentane and heptane, suggesting that it was related to a particular ability of ClaypMn to oxidize small and not bulky alkanes. Further experiments are required to characterize the mode of binding of Mn(tmpyp) to montmorillonite and to understand its substrate specificity.

The ClaypMn catalyst, which is very easily prepared in one step from commercially available compounds and easily recovered by simple filtration at the end of the reactions, presents two main advantages when compared with homogeneous or silica-supported Mn-porphyrin catalysts. It can be used in a wide variety of solvents including CH₃OH and H₂O, and it exhibits a particular ability to oxidize poorly reactive short linear alkanes.

Received, 30th April 1990; Com. 0101907K

References

- 1 For recent reviews: (a) T. J. McMurry and J. T. Groves, in 'Cytochrome P-450, Structure, Mechanism and Biochemistry,' ed. P. R. Ortiz de Montellano, Plenum Press, New York and London, 1986, pp. 1-28; (b) B. Meunier, *Bull. Soc. Chim. Fr.*, 1986, **4**, 578; (c) D. Mansuy, *Pure Appl. Chem.*, 1987, **59**, 579; (d) D. Mansuy, P. Battioni, and J. P. Battioni, *Eur. J. Biochem.*, 1989, **184**, 267.
- 2 P. Battioni, J. P. Lallier, L. Barloy, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1989, 1149.
- 3 N. Herron, *J. Coord. Chem.*, 1988, **19**, 25.
- 4 T. J. Pinnavaia, *Science*, 1983, **220**, 365.
- 5 S. S. Cady, T. J. Pinnavaia, *Inorg. Chem.*, 1978, **17**(6), 1501.
- 6 H. Van Damme, M. Crespin, F. Obrecht, M. I. Cruz, and J. J. Fripiat, *J. Colloid Interface Sci.*, 1978, **66**(1), 43.
- 7 H. Kameyama, H. Suzuki, and A. Amano, *Chem. Lett.*, 1988, 1117.
- 8 A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 1532.
- 9 V. Joshi and P. K. Ghosh, *J. Am. Chem. Soc.*, 1989, **111**, 5604.
- 10 J. R. Lindsay Smith and D. N. Mortimer, *J. Chem. Soc., Chem. Commun.*, 1985, 410.

A Hydrogen Atom in an Organoplatinum-amine System: Tautomers having either a Bridging Hydrogen with Platinum(II) or a Hydride on Platinum(IV). The X-Ray Crystal Structure at 100 K of [Pt{C₁₀H₆(NMe₂)-8-C,N}{C₁₀H₆(NHMe₂)-8-C}(Br)]

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The unique zwitterionic complexes [Pt{C₁₀H₆(NMe₂)-8-C,N}{C₁₀H₆(NHMe₂)-8-C}(X)] (X = Br, Cl) with a hydrogen atom bridging between the platinum(II) centre and the formerly co-ordinating nitrogen ($\delta_{\text{H}} \text{NH} + 15.8$ ppm [$^1J_{\text{PtH}} 180$ Hz]; X-ray structure, X = Br), can be obtained from the reaction of *cis*-[Pt{C₁₀H₆(NMe₂)-8-C,N}₂] with R₂SnX₂ (R = Me, Ph; X = Br, Cl) in CH₂Cl₂-MeOH; in non-protic solvents this reaction gives the isolable Pt^{IV} hydride complex [Pt{C₁₀H₆(NMe₂)-8-C,N}₂(H)(X)] ($\delta_{\text{H}} \text{PtH} - 20.35$ ppm [$^1J_{\text{PtH}} 1540$ Hz], X = Br).

Much interest exists in hydrogen-transfer routes with platinum-group metal complexes.¹ Although most of this work has concentrated on phosphine complexes,² recently an increasing number of investigations have been reported on organoplatinum complexes with amine ligands.³ The latter are not always passive spectator ligands, but can sometimes actively participate in metal-centred reactions; for example, in the thermal rearrangement of diarylbis(pyridine)platinum(II) complexes pyridine is proposed to be a reservoir site for transferred hydrogen.⁴ We now wish to report new hydrogen complexes

of the cyclometallated platinum complex *cis*-[Pt{C₁₀H₆(NMe₂)-8-C,N}₂] (**1**): namely a unique zwitterionic Pt^{II} complex, in which a proton is caught between the Pt^{II} centre and a non-co-ordinating stereochemically fixed amine group, and its remarkably stable Pt^{IV} hydride tautomer.

The reaction of (**1**)⁵ with Me₂SnBr₂ in dichloromethane or benzene unexpectedly gave the platinum hydride [Pt{C₁₀H₆(NMe₂)-8-C,N}₂(H)(Br)] (**2**) which was isolated as an off-white powder in 58% yield (Scheme 1). The solid complex is air-stable and it is slightly soluble in dichloro-

methane or chloroform, though these solutions decompose on leaving to stand within a few hours. The ^1H NMR spectrum of (2)[†] shows a characteristic aromatic pattern and four different-NMe signals which are indicative for the perpendicular positioning of the naphthyl \ddagger ligands to a metal centre.^{5,6} The most distinctive aspect of this spectrum is the singlet resonance at -20.35 ppm (one H) with a ^{195}Pt coupling constant of 1540 Hz. Together with a sharp IR (KBr) absorption at 2275 cm^{-1} , these data are consistent with this complex being a platinum(IV) hydride complex having the structure shown in Scheme 1.

When the reaction of (1) with Me_2SnBr_2 was carried out in the presence of methanol, instead of (2), the complex $[\text{Pt}\{\text{C}_{10}\text{H}_6(\text{NMe}_2)\text{-8-C,N}\}\{\text{C}_{10}\text{H}_6(\text{NHMe}_2)\text{-8-C}\}(\text{Br})]$ (3a), was isolated as an off-white powder in 80% yield (Scheme 1). The chlorine analogue (3b), was prepared by a similar reaction of (1) with R_2SnCl_2 ($\text{R} = \text{Me}, \text{Ph}$) or by the addition of gaseous HCl to (1) in CDCl_3 . Both complexes have limited solubility in common organic solvents and are air-stable. The ^1H NMR spectra of these compounds, \S like those of (2), show a characteristic aromatic pattern and four different -NMe signals, of which two are unexpectedly doublet resonances. Furthermore, instead of a hydride signal at high field as for (2), there is now a broad low-field resonance at *ca.* 16 ppm with a ^{195}Pt coupling constant of *ca.* 180 Hz. These data point to an unusual $\text{Pt}\cdots\text{H-NMe}_2$ bridged structure in which the central hydrogen atom is coupled to both the metal centre and to the NMe₂ protons. The geometry of the naphthyl ligands and this bridging unit were ascertained by an X-ray crystal structure determination of one of the compounds. Figure 1 \P shows the molecular structure of (3a). The naphthyl ligands are *cis* positioned and perpendicular to each other. One of these naphthyl ligands is chelate [C(1), N(1)] bonded [Pt-N(1) 2.193(4) Å], whereas the second naphthyl ligand is monodentate bonded *via* C(13) only, with no Pt-N bond [Pt \cdots N(2) 2.982(4) Å]. The Pt^{II} centre has overall a square-planar co-ordination geometry in which a bromide atom positioned

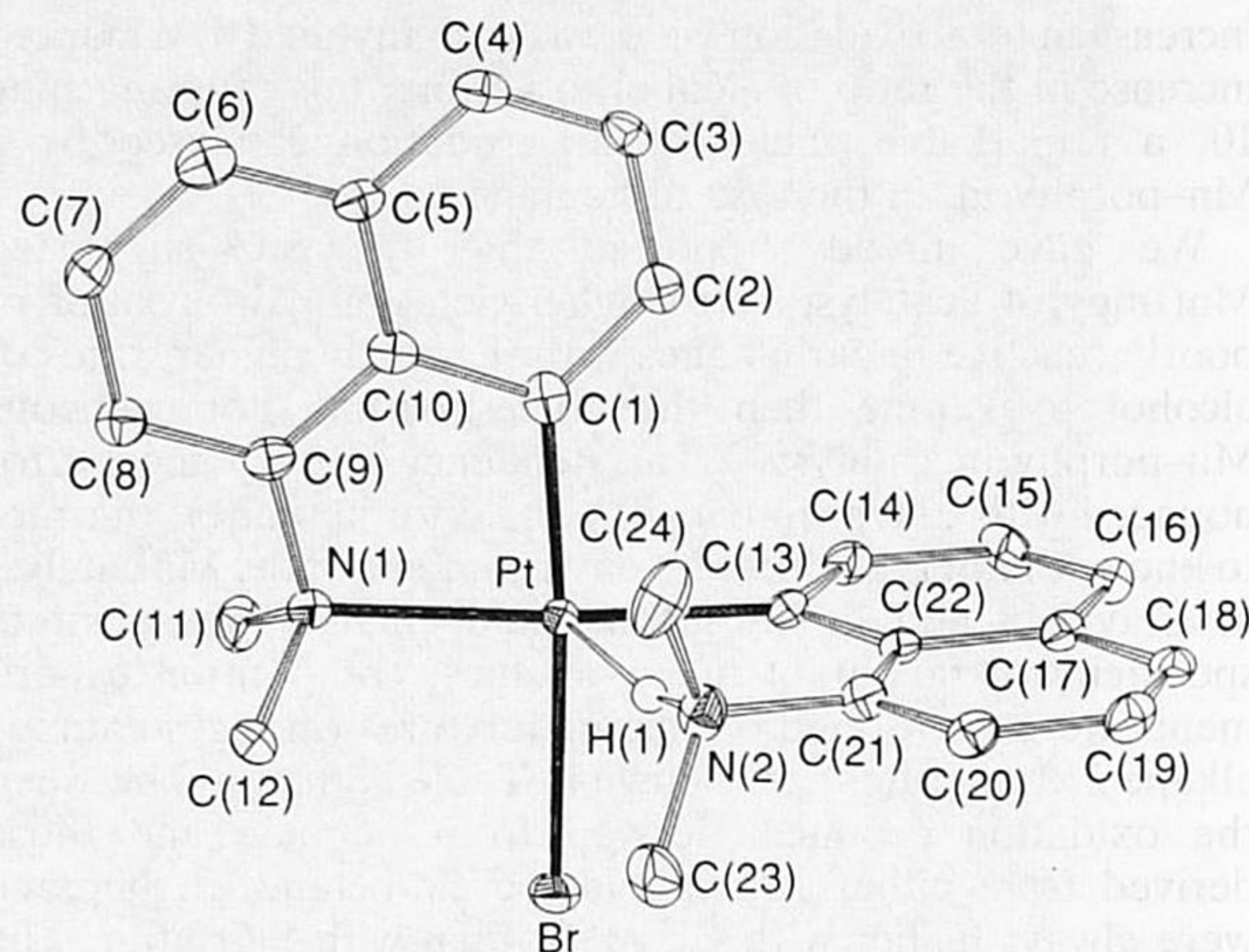


Figure 1. Thermal motion ellipsoid plot (50% probability level) for $[\text{Pt}\{\text{C}_{10}\text{H}_6(\text{NMe}_2)\text{-8-C,N}\}\{\text{C}_{10}\text{H}_6(\text{NHMe}_2)\text{-8-C}\}(\text{Br})]$ (3a). Selected bond lengths (Å) and angles ($^\circ$): Pt-Br 2.5316(6), Pt-N(1) 2.193(4), Pt-C(1) 1.995(5), Pt-C(13) 1.993(5), Pt \cdots N(2) 2.982(4), Pt \cdots H(1) 2.11(5), N(2)-H(1) 0.88(5); C(1)-Pt-N(1) 82.77(16), C(1)-Pt-C(13) 93.56(19), N(1)-Pt-Br 93.05(9), C(13)-Pt-Br 90.56(13), C(13)-Pt \cdots H(1) 73.7(12).

trans to C(1) is the fourth ligand. On one side of the plane, the unco-ordinated N(2) centre is a quaternary ammonium site; the amine H atom, thus, occupies a pseudo octahedral position [Pt \cdots H(1) 2.11(5) Å]. These structural features indicate that (3a) is a mononuclear zwitterionic platinum complex with, to our knowledge, the first example of a Pt \cdots H-N bridge-like unit.

It is of interest to note that in the recently reported zwitterionic species $[\text{Pt}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{NHMe}_2)_2\text{-2,6-C}\}_2\text{I}_4][\text{CF}_3\text{SO}_3]_2$ the Pt-N distances are 3.2 and 3.3 Å and in the solid state there is no interaction between the central anionic $[\text{Pt}_2\text{I}_4]^{2-}$ moiety and the $-\text{CH}_2\text{NHMe}_2^+$ groups.⁷

The Pt \cdots H-N bridge unit of (3) can be envisaged either in terms of a quaternary ammonium salt of (1) with the sterically undemanding N-H bond in the observed position because of the rigidity of the 8-dimethylamino-1-naphthyl ligand, or as an agostic hydrogen bridging between platinum and nitrogen. Investigations into the nature of this unit using Proton Sponge[®] [1,8-bis(dimethylamino)naphthalene]⁸ show the bridging hydrogen atom to be tightly bonded. In fact, it is possible to describe the rigid *cis*- $[\text{Pt}\{\text{C}_{10}\text{H}_6(\text{NMe}_2)\text{-8-C,N}\}_2]$ (1), the precursor of (3), as an organometallic analogue of this organic Proton Sponge[®].

The formation of (2) or (3) from R_2SnX_2 and (1) could involve as a first step either the generation of HX from R_2SnX_2 and MeOH, or an oxidative addition of a Sn-X bond to the Pt centre; this latter occurs in the reaction of (1) with MeSnCl_3 to give the Pt^{IV} complex $[\text{Pt}\{\text{C}_{10}\text{H}_6(\text{NMe}_2)\text{-8-C,N}\}_2(\text{MeSnCl}_2)(\text{Cl})]$ (4).^{6b} Indeed, the reaction of (1) with Me_2SnBr_2 in dichloromethane or benzene (*i.e.*, in the absence of methanol) affords an as yet not fully characterized Pt-Sn species, which may be either an octahedral Pt^{IV} complex like (4) or a Pt^{II} complex with a Sn-Br moiety side-on co-ordinated [(A) in Scheme 1] as in $[\text{Ir}\{\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)\text{-2-C,N}\}(\text{Me}_2\text{SnBr})(\text{Br})(\text{cyclo-octa-1,5-diene})]$.⁹

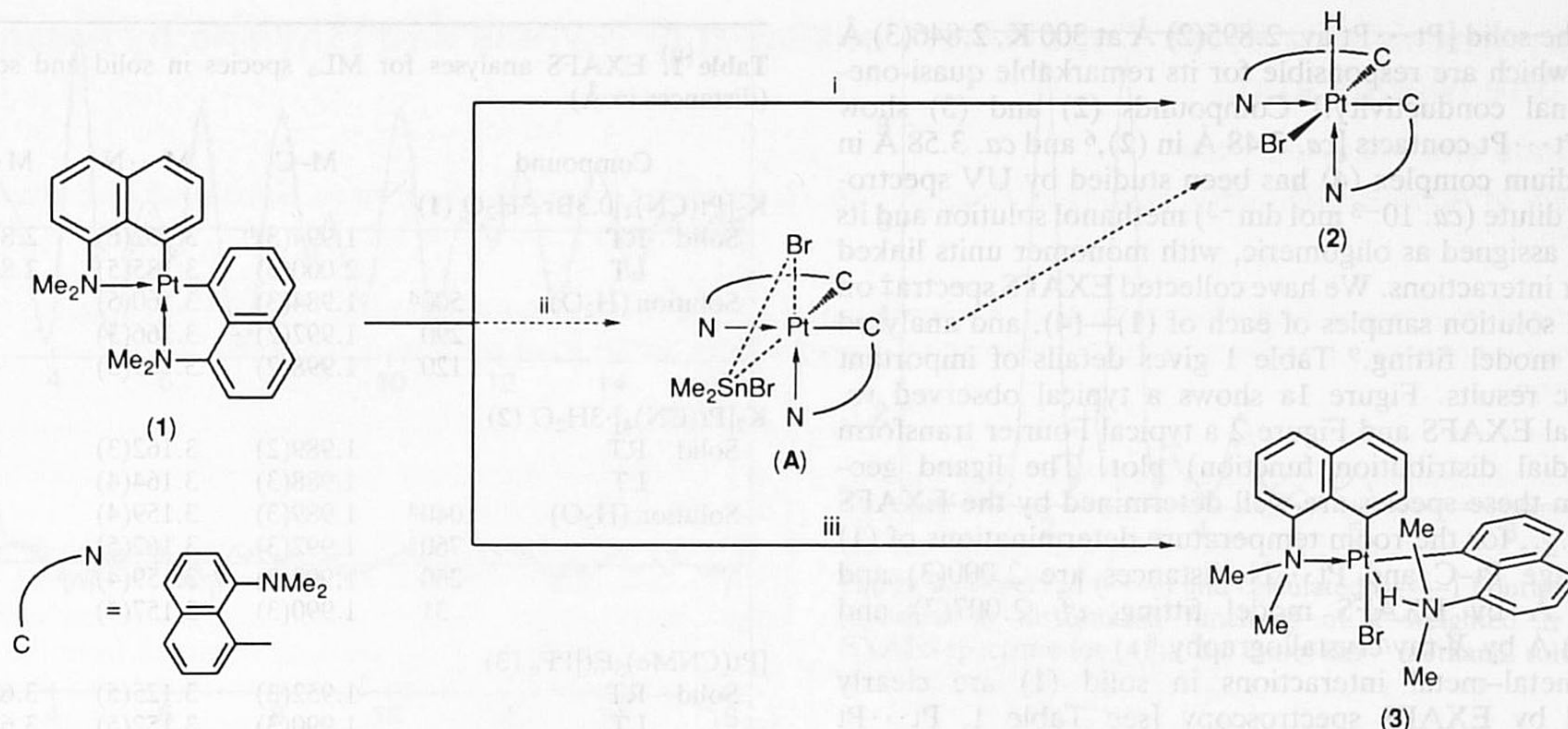
The X-ray data were collected by A. J. M. Duisenberg. We gratefully thank Shell Netherlands B.V. (I.C.M.W.-O.) for financial support. The investigations were supported in part (A. L. S.) by the Netherlands Foundation for Chemical

[†] ^1H NMR data: (2), (200.13 MHz, CDCl_3 , 298 K) δ -20.35 (1 H, s, $^1J_{\text{PtH}}$ 1540 Hz, PtH), 2.15 (3 H, s, $^3J_{\text{PtH}}$ 12 Hz, NCH₃), 3.44 (3 H, br s, NCH₃), 3.57 (3 H, s, $^3J_{\text{PtH}}$ 24 Hz, NCH₃), 3.70 (3 H, br s, NCH₃), 6.11 (1 H, d, $^3J_{\text{PtH}}$ 60 Hz, ArH), 6.92 (1 H, t, $^3J_{\text{PtH}}$ 14.5 Hz, ArH), 7.15–7.92 (10 H, m, ArH).

\ddagger In this manuscript we use the more commonly encountered radical name naphthyl instead of naphthalenyl.

\S ^1H NMR data: (3a), (200.13 MHz, CDCl_3 , 298 K) δ 2.64 (3 H, d, $^3J_{\text{HH}}$ 6 Hz, NCH₃), 3.33 (3 H, d, $^3J_{\text{HH}}$ 6 Hz, NCH₃), 3.59 (6 H, br s, NCH₃), 6.27 (1 H, d, $^3J_{\text{PtH}}$ 78 Hz, ArH), 6.89–7.92 (10 H, m, ArH), 8.39 (1 H, d, $^3J_{\text{PtH}}$ 72 Hz, ArH), 15.78 (1 H, br s, $^1J_{\text{PtH}}$ 176 Hz, Pt \cdots H-N). (3b) δ 2.66 (3 H, d, $^3J_{\text{HH}}$ 6 Hz, NCH₃), 3.32 (3 H, d, $^3J_{\text{HH}}$ 6 Hz, NCH₃), 3.56 (6 H, br s, NCH₃), 6.34 (1 H, d, $^3J_{\text{PtH}}$ 78 Hz, ArH), 6.90–7.95 (10 H, m, ArH), 8.41 (1 H, d, $^3J_{\text{PtH}}$ 72 Hz, ArH), 15.88 (1 H, br s, $^1J_{\text{PtH}}$ 180 Hz, Pt \cdots H-N).

\P Crystal data for (2a): $\text{C}_{24}\text{H}_{25}\text{BrN}_2\text{Pt}$, $M = 616.46$, rod-shaped (0.13 \times 0.13 \times 0.26 mm), yellow, monoclinic; space group Cc , $a = 9.469(1)$, $b = 30.481(1)$, $c = 7.298(1)$, Å, $\beta = 91.81(1)^\circ$, $U = 2105.3(4)$ Å³, $D_c = 1.945\text{ g cm}^{-3}$, $Z = 4$, $F(000) = 1184$, Zr-filtered Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 86.2\text{ cm}^{-1}$. Intensities for 5353 reflections were collected at 100 K (CAD-4F; $\theta_{\text{max.}} = 29.4^\circ$; $\omega/2\theta$ -scan) and averaged ($R_{\text{int}} = 1.6\%$) into 2781 absorption corrected (gaussian integration) reflections with $I > 2.5\sigma(I)$. The structure was solved by use of Patterson techniques (SHELXS-86) and refined by full-matrix least-squares techniques to $R = 0.016$ [$wR = 0.016$, $w = 1/\sigma^2(F)$, $S = 1.83$]. Hydrogen atoms were introduced at calculated positions except for H(1), which was located from a difference Fourier map and refined. Co-ordinates, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.



Scheme 1. Reagents and conditions: i, 1 equiv. Me_2SnBr_2 , benzene or dichloromethane, 4 days or 6 h, room temp., (58%); ii, 1 equiv. Me_2SnBr_2 , benzene, 2 days, room temperature; iii, 1 equiv. R_2SnX_2 ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{Br, Cl}$), dichloromethane-methanol 12:1, 0.5 h, room temp., (80%).

Research (S.O.N.) with financial aid from the Netherlands Organization for Scientific Research (N.W.O.).

Received, 4th April 1990; Com. 0/01528H

References

- R. Romeo, D. Minniti, and S. Lanca, *J. Organomet. Chem.*, 1979, **165**, C36; R. E. Stevens, R. D. Guettler, and W. L. Gladfelter, *Inorg. Chem.*, 1990, **29**, 451; D. Sellmann, I. Barth, and M. Moll, *ibid.*, 176.
- N. W. Alcock, J. M. Brown, and T. D. MacLean, *J. Chem. Soc., Chem. Commun.*, 1984, 169; T. M. Miller and G. M. Whitesides, *Organometallics*, 1986, **5**, 1473; M. M. T. Khan, B. T. Khan, and S. Begum, *J. Mol. Catal.*, 1988, **45**, 305.
- D. C. Griffiths and G. B. Young, *Polyhedron*, 1983, **2**, 1095; A. C. Skapski, V. F. Sutcliffe, and G. B. Young, *J. Chem. Soc., Chem. Commun.*, 1985, 609.
- S. E. Himmel and G. B. Young, *Organometallics*, 1988, **7**, 2440.
- E. Wehman, G. van Koten, C. T. Knaap, H. Ossor, M. Pfeffer, and A. L. Spek, *Inorg. Chem.*, 1988, **27**, 4409.
- (a) J. A. M. van Beek, G. van Koten, I. C. M. Ooyevaar, W. J. J. Smeets, and A. L. Spek, unpublished work; (b) J. A. M. van Beek, G. van Koten, K. Vrieze, W. J. J. Smeets, and A. L. Spek, unpublished work.
- M. F. Davidson, D. M. Grove, G. van Koten, and A. L. Spek, *J. Chem. Soc., Chem. Commun.*, 1989, 1562.
- R. L. de Groot and D. J. Sikkema, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 10.
- A. A. H. van der Zeijden, G. van Koten, J. M. A. Wouters, W. F. A. Wijsmuller, D. M. Grove, W. J. J. Smeets, and A. L. Spek, *J. Am. Chem. Soc.*, 1988, **110**, 5354.

Linear Molecular Aggregation in Solution: EXAFS studies of ML_4 Complexes

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Analysis of Pt or Ir L_{III} -edge EXAFS spectra for $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 0.3\text{Br} \cdot 3\text{H}_2\text{O}$ (1), $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (2), $[\text{Pt}(\text{CNMe})_3\text{Et}]\text{PF}_6$ (3), and $[\text{Ir}(\text{CNMe})_4]\text{Cl}$ (4) in solid and solution phases shows evidence for metal...metal interactions in solid (1), (3), and (4) and in solutions of (4).

The aggregation of molecules is fundamental to the growth of solid molecular materials from solution. In certain well known cases unusual, highly anisotropic, solid-state properties arise when molecular metal complexes of general formula ML_4 ($\text{M} = \text{Pt}^{\text{II}}, \text{Ir}^{\text{I}}$ etc., $\text{L} = \text{CN, CO, CNR}$ etc.) interact strongly with one another through linear-chain metal...metal ($\text{M} \cdots \text{M}$) contacts.¹ It is clearly of interest to characterize the processes by which the monomeric complexes form into chain polymer species. Spectroscopic studies on solutions of these complexes have shown evidence for chain formation, especially at high concentrations.¹⁻⁴ We report EXAFS studies on representative examples of such metal complexes which provide, for the first time, geometric information on intermolecular association of this sort in both solution and solid states.

The complexes studied were $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 0.3\text{Br} \cdot 3\text{H}_2\text{O}$ (1), $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (2), $[\text{Pt}(\text{CNMe})_3\text{Et}]\text{PF}_6$ (3), and $[\text{Ir}(\text{CNMe})_4]\text{Cl}$ (4) in solid and solution phases.[†] The solid state structures of (1),⁸ (2),⁶ and (3)³ are known from crystallographic studies. Compound (1) shows strong Pt...Pt interac-

[†] Compound (1) was prepared as the crystalline hydrate $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 0.3\text{Br} \cdot 3\text{H}_2\text{O}$ by literature methods.⁵ Compound (2) was purchased from Aldrich and recrystallised from water immediately prior to measurement of EXAFS spectra; solid samples were prepared under air saturated with water vapour to minimise water loss from crystals which are very prone to dehydration.⁶ Compounds (3) and (4) were prepared by literature methods^{2,7} and characterised by uv/visible spectroscopy.