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$\{C_{10}H_6(NMe_2)$-8-*C,N*$\}\{C_{10}H_6(NHMe_2)$-8-*C*$\}$(Br)]

Ingrid C. M. Wehman-Ooyevaar,[a] David M. Grove,[a] Paul van der Sluis,[b] Anthony L. Spek,[b] and Gerard van Koten*[a]

[a] *Debye Research Institute, Department of Metal-Mediated Synthesis, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands*

[b] *Bijvoet Research Institute, Laboratorium voor Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands*

The unique zwitterionic complexes [Pt$\{C_{10}H_6(NMe_2)$-8-*C,N*$\}\{C_{10}H_6(NHMe_2)$-8-*C*$\}$(X)] (X = Br, Cl) with a hydrogen atom bridging between the platinum(II) centre and the formerly co-ordinating nitrogen (δ_H N*H* +15.8 ppm [$^1J_{PtH}$ 180 Hz]; *X*-ray structure, X = Br), can be obtained from the reaction of *cis*-[Pt$\{C_{10}H_6(NMe_2)$-8-*C,N*$\}_2$] with R_2SnX_2 (R = Me, Ph; X = Br, Cl) in CH_2Cl_2–MeOH; in non-protic solvents this reaction gives the isolable Pt^{IV} hydride complex [Pt$\{C_{10}H_6(NMe_2)$-8-*C,N*$\}_2$(H)(X)] (δ_H Pt*H* −20.35 ppm [$^1J_{PtH}$ 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$\{C_{10}H_6(NMe_2)$-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 Me_2SnBr_2 in dichloromethane or benzene unexpectedly gave the platinum hydride [Pt$\{C_{10}H_6(NMe_2)$-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 dichloromethane or chloroform, though these solutions decompose on leaving to stand within a few hours. The ^{1}H NMR spectrum of (**2**)† shows a characteristic aromatic pattern and four different–NMe signals which are indicative for the perpendicular positioning of the naphthyl‡ 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 [Pt{$C_{10}H_6(NMe_2)$-8-*C,N*}{$C_{10}H_6(NHMe_2)$-8-*C*}(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 (R = Me, 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 ^{1}H NMR spectra of these compounds,§ 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 Pt ·· H–NMe_2 bridged structure in which the central hydrogen atom is coupled to both the metal centre and to the NMe_2 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¶ 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 ··· N(2) 2.982(4)Å]. The Pt^{II} centre has overall a square-planar co-ordination geometry in which a bromide atom positioned 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 ·· 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 ·· H–N bridge-like unit.

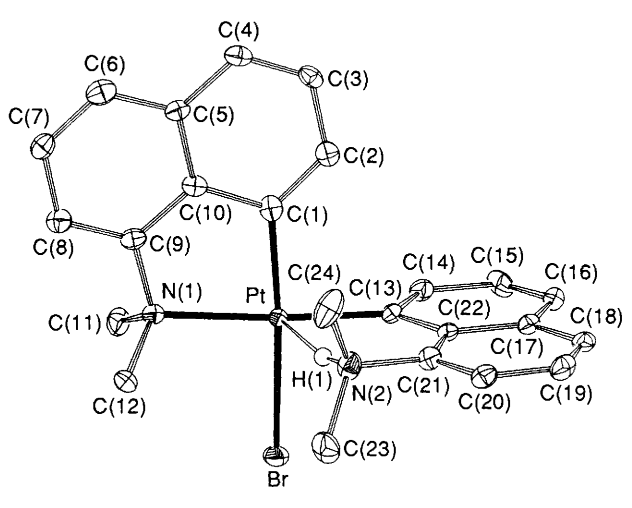


Figure 1. Thermal motion ellipsoid plot (50% probability level) for [Pt{$C_{10}H_6(NMe_2)$-8-*C,N*}{$C_{10}H_6(NHMe_2)$-8-*C*}(Br)] (**3a**). Selected bond lengths (Å) and angles (°): Pt–Br 2.5316(6), Pt–N(1) 2.193(4), Pt–C(1) 1.995(5), Pt–C(13) 1.993(5), Pt ··· N(2) 2.982(4), Pt ·· H(1) 2.11(5), N(2)–H(1) 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 ·· H(1) 73.7(12).

It is of interest to note that in the recently reported zwitterionic species [Pt_2{$C_6H_3(CH_2NHMe_2)_2$-2,6-*C*}$_2I_4$]-[CF_3SO_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 [Pt_2I_4]$^{2-}$ moiety and the –$CH_2NHMe_2{}^+$ groups.[7]

The Pt ·· 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*-[Pt{$C_{10}H_6(NMe_2)$-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 [Pt{$C_{10}H_6(NMe_2)$-8-*C,N*}$_2$-($MeSnCl_2$)(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 [Ir{$C_6H_4(CH_2NMe_2)$-2-*C,N*}-(Me_2SnBr)(Br)(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

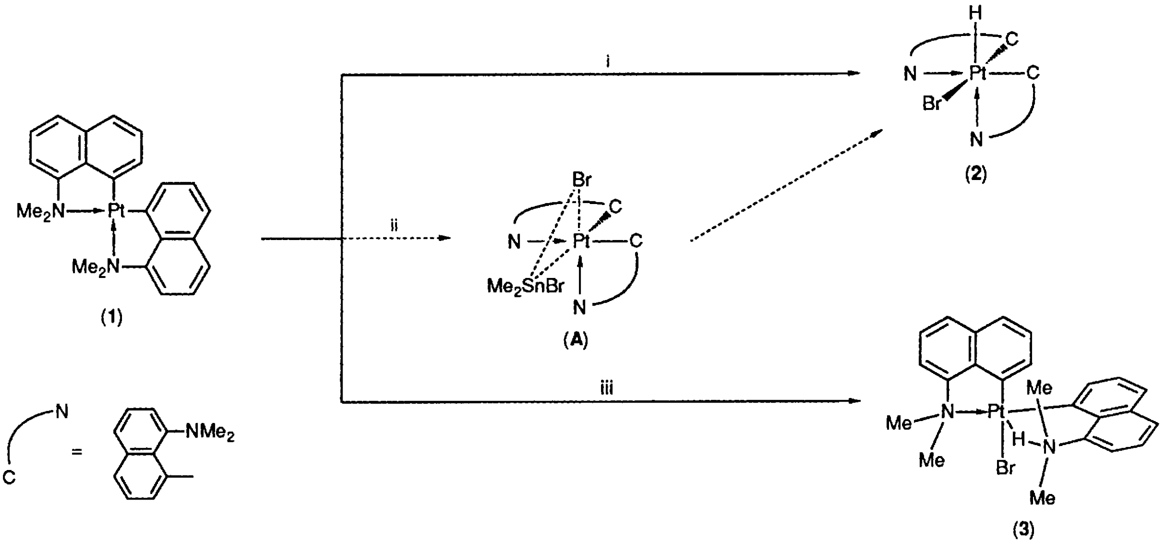
---

† ^{1}H NMR data: (**2**), (200.13 MHz, $CDCl_3$, 298 K) δ −20.35 (1 H, s, $^1J_{PtH}$ 1540 Hz, PtH), 2.15 (3 H, s, $^3J_{PtH}$ 12 Hz, NCH_3), 3.44 (3 H, br s, NCH_3), 3.57 (3 H, s, $^3J_{PtH}$ 24 Hz, NCH_3), 3.70 (3 H, br s, NCH_3), 6.11 (1 H, d, $^3J_{PtH}$ 60 Hz, ArH), 6.92 (1 H, t, $^3J_{PtH}$ 14.5 Hz, ArH), 7.15—7.92 (10 H, m, ArH).

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

§ ^{1}H NMR data: (**3a**), (200.13 MHz, $CDCl_3$, 298 K) δ 2.64 (3 H, d, $^3J_{HH}$ 6 Hz, NCH_3), 3.33 (3 H, d, $^3J_{HH}$ 6 Hz, NCH_3), 3.59 (6 H, br s, NCH_3), 6.27 (1 H, d, $^3J_{PtH}$ 78 Hz, ArH), 6.89—7.92 (10 H, m, ArH), 8.39 (1 H, d, $^3J_{PtH}$ 72 Hz, ArH), 15.78 (1 H, br s, $^1J_{PtH}$ 176 Hz, Pt ·· H–N). (**3b**) δ 2.66 (3 H, d, $^3J_{HH}$ 6 Hz, NCH_3), 3.32 (3 H, d, $^3J_{HH}$ 6 Hz, NCH_3), 3.56 (6 H, br s, NCH_3), 6.34 (1 H, d, $^3J_{PtH}$ 78 Hz, ArH), 6.90—7.95 (10 H, m, ArH), 8.41 (1 H, d, $^3J_{PtH}$ 72 Hz, ArH), 15.88 (1 H, br s, $^1J_{PtH}$ 180 Hz, Pt ·· H–N).

¶ Crystal data for (**2a**): $C_{24}H_{25}BrN_2Pt$, *M* = 616.46, rod-shaped (0.13 × 0.13 × 0.26 mm), yellow, monoclinic; space group *Cc*, *a* = 9.469(1), *b* = 30.481(1), *c* = 7.298(1), Å, β = 91.81(1)°, *U* = 2105.3(4) Å^3, D_c = 1.945 g cm^{-3}, *Z* = 4, *F*(000) = 1184, Zr-filtered Mo-K_α radiation (λ = 0.71073 Å), μ(Mo-K_α) = 86.2 cm^{-1}. Intensities for 5353 reflections were collected at 100 K (CAD-4F; $\theta_{max.}$ = 29.4°; ω/2θ-scan) and averaged (R_{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 [*w R* = 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 (R = Me, Ph; X = 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

1 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.

2 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.

3 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.

4 S. E. Himmel and G. B. Young, *Organometallics*, 1988, **7**, 2440.

5 E. Wehman, G. van Koten, C. T. Knaap, H. Ossor, M. Pfeffer, and A. L. Spek, *Inorg. Chem.*, 1988, **27**, 4409.

6 (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.

7 M. F. Davidson, D. M. Grove, G. van Koten, and A. L. Spek, *J. Chem. Soc., Chem. Commun.*, 1989, 1562.

8 R. L. de Groot and D. J. Sikkema, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 10.

9 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.