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A Hydrogen Atom in an Organoplatinum–Amine System. 2.[1] The First Isolated Arylplatinum(IV) Hydrides: Synthetic and Theoretical Study (SCF and CAS–SCF Calculations) on Model Complexes with a N–M(IV)–H/M(II)$^-$···H–N$^+$ Unit (M = Pd, Pt)

Ingrid C. M. Wehman-Ooyevaar,[†] David M. Grove,[†] Peter de Vaal,[‡] Alain Dedieu,[‡] and Gerard van Koten[*],[†]

Department of Metal-Mediated Synthesis, Debye Research Institute, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands, and Laboratoire de Chimie Quantique, UPR 139 du CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, F 67000 Strasbourg, France

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The reaction of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ with Me_2SnX_2 (X = Cl, Br) in C_6H_6 or a mixture of CH_2Cl_2 and *t*-BuOH affords the novel Pt(IV) hydride complexes PtX(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (X = Cl, Br) by a process involving intramolecular H abstraction from an SnMe grouping. Starting from *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$ and Me_2SnBr_2, one also initially obtains a Pt(IV) hydride complex, but this then isomerizes to the zwitterionic hydrogen-bridged complex PtBr($C_6H_4CH_2NMe_2$-2-*C,N*)($C_6H_4CH_2NHMe_2$-2-*C,H*).[1] The Pt(IV) hydride complex Pt($OOCCF_3$)(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ is obtained from the reaction of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ with the organic acid CF_3COOH. However, with HCl, the zwitterionic hydrogen-bridged complex PtCl(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) (δ(N*H*) = +15.9 ppm, $^1J(^{195}Pt,^1H)$ = 180 Hz, $^1J(^{15}N,^1H)$ = 59 Hz) is formed. The Pt(IV) hydride complexes, which are unstable in solution, are characterized by a ^1H NMR hydride resonance of ca. −20 ppm with $^1J(^{195}Pt,^1H) \cong 1600$ Hz and a ν(Pt–H) IR band at ca. 2280 cm^{-1}. A mechanistic study of the formation of the hydride versus the zwitterionic hydrogen-bridge complexes shows the Lewis basicity of the anion to be an important factor. Molecular orbital (SCF and CAS–SCF) calculations on a model system (with Pd instead of Pt) show that the zwitterionic hydrogen Pd(II) complex [PdCl(Me)$_2$(NH_3)···H–NH_3] is more stable than its Pd(IV) hydride tautomer [PdCl(H)(Me)$_2$(NH_3)···NH_3]. The stability of the former complex is mainly caused by favorable electrostatic interactions between the anionic palladium and cationic ammonium NH units, orbital interactions playing only a minor role. The reactivity of the Pt(IV) hydrides and the zwitterionic hydrogen-bridge complexes toward alkynes is described. Highly activated dimethyl acetylenedicarboxylate reacts with Pt($OOCCF_3$)(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ as well as Pt($OOCCF_3$)(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*), both containing the weakly coordinating anion $OOCCF_3$, to afford the same "insertion" product Pt($OOCCF_3$){η^1-C(COOMe)=CH(COOMe)}(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$.

Introduction

Many reactions that are catalyzed by transition metal complexes involve interactions between hydrogen and the metal centers.[2] Besides side-on H_2 bonding,[3] both terminal and bridging hydride bonds are known,[4] and many examples of the so-called agostic M···H–C (three-center two-electron) interaction have been reported.[5,6] However, there are only a few known examples of an intramolecular M···H–N (three-center four-electron) interaction.[1,7–9] In this interaction, in contrast to the three-center two-electron interaction, an electron pair of a filled metal orbital (e.g. d_{z^2}) is also involved. The only theoretical investigations of these M···H–N interactions are the molecular orbital calculations carried out on a model system of the d^{10} nickel complex [(Hnp$_3$)NiCO][BPh$_4$] (Hnp$_3$ = NH($CH_2CH_2PPh_2$)$_3$).[10] These calculations, carried out at the extended Hückel level, could not evaluate the magnitude of the electrostatic component of the interactions.

The relationship between M^n···H–N interactions and tautomeric H–M^{n+2}–N (metal hydride) systems is in this context extremely relevant. Most transition metal hydride complexes are synthesized directly from appropriate acids. Such reactions with d^8 organometallic complexes can proceed in several ways: (i) by an oxidative addition reaction to the metal center (eq 1a),[11] (ii) by electrophilic attack on a metal–carbon bond (eq 1b),[12] or (iii) by reaction at the ligand (eq 1c).[13]

In a previous communication we reported that Pt(IV) hydride complexes PtX(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (X = Cl, Br) can be synthesized from the reaction of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$

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[*] To whom correspondence should be addressed.

[†] University of Utrecht.

[‡] Université Louis Pasteur.

(1) Part 1: Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916.

(2) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1.

(3) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299 and references cited therein. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

(4) (a) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176. (b) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167.

(5) Anklin, C. G.; Pregosin, P. S. *Magn. Reson. Chem.* **1985**, *23*, 671.

(6) (a) Carr, N.; Dunne, B. J.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 926. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(7) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1986**, *5*, 336.

(8) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Orpen, A. G.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1789.

(9) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1367.

(10) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922.

(11) (a) Blake, D. M.; Kubota, M. *Inorg. Chem.* **1970**, *9*, 989. (b) Crabtree, R. H.; Quirk, J. M.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *181*, 203. (c) Imhoff, P.; Nefkens, S. C. A.; Elsevier, C. J.; Goubitz, K.; Stam, C. H. *Organometallics* **1991**, *10*, 1421.

(12) (a) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813. (b) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565.

(13) Crociani, B.; Di Bianca, F.; Giovenco, A.; Scrivanti, A. *J. Organomet. Chem.* **1983**, *251*, 393.

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$$LM^{n} + HX \longrightarrow LM^{n+2}(X)(H) \quad (1a)$$

$$LM^{n}\text{-}CR_3 + HX \longrightarrow LM^{n}(X) + HCR_3 \quad (1b)$$

$$LM^{n} + HX \longrightarrow [(LH)^{+}M^{n}]X^{-} \quad (1c)$$

with Me_2SnX_2 (X = Cl, Br) in an aprotic solvent.[9] We now show that this type of Pt(IV) hydride complex can *also* be obtained in a conventional reaction type, i.e. by oxidative addition of HX. However, this method is only successful with CF_3COOH. With HCl, the zwitterionic hydrogen $Pt(II)^{-}\cdots H\text{–}N^{+}$ complex PtCl(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) is obtained; this complex is a tautomer of the corresponding Pt(IV) hydride species. The mechanisms that lead to either a Pt(IV) hydride or the tautomeric Pt(II)···H–N system and the interrelationship between these tautomers are the subject of the present paper. Their electronic structure and their relative stability have been analyzed through ab-initio SCF and CAS–SCF calculations carried out on the $[PdCl(H)(Me)_2(NH_3)\cdots NH_3]$ and $[PdCl(Me)_2(NH_3)\cdots H\text{-}NH_3]$ model systems and on the Pt analogs. It is shown that favorable electrostatic interactions play a major role in the stabilization of the zwitterionic hydrogen complex.

The reactivity of both types of complexes toward unsaturated reagents has also been studied, and with dimethyl acetylenedicarboxylate both complex types give the same Pt(IV) product; a mechanism involving electron transfer is proposed to explain this result.

Experimental Section

General Procedures. Syntheses were carried out using standard Schlenk techniques in an atmosphere of purified nitrogen. All solvents were dried and distilled under nitrogen prior to use. The compounds *cis*-Pt(1-$C_{10}H_6$-NMe_2-8-*C,N*)$_2$,[14] *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$,[15] *cis,cis*-$PtBr_2$(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$,[16] and PtX(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) (X = Cl, Br, $OOCCF_3$)[1] were prepared by literature methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer. Elemental analyses were obtained from the Section Elemental Analyses of the Institute For Applied Chemistry TNO, Zeist, The Netherlands.

Synthesis of PtCl(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (1a). To a yellow suspension of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (0.5 g; 0.93 mmol) in toluene (40 mL) was added a solution of Me_2SnCl_2 (0.21 g; 0.94 mmol) in toluene (5 mL). The suspension slowly became clearer, and after 1 h of stirring, a clear solution was obtained. This solution was stirred for 5 days, after which time a white solid had precipitated. The solid was collected by filtration, washed with hexane (20 mL), and dried in air, affording **1a** as an off-white powder (0.35 g; 66% yield). Infrared spectrum in KBr: ν(N–H) at 2280 cm^{-1}.

Evaporation in vacuo of the toluene filtrate to dryness afforded a yellow powder. According to ^1H NMR data, this was a mixture of unreacted *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ and Me_2SnCl_2.

Synthesis of PtBr(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (1b). a. To a stirred yellow suspension of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (0.4 g; 0.75 mmol) in C_6H_6 (40 mL) was added a solution of Me_2SnBr_2 (0.24 g; 0.78 mmol) in C_6H_6 (5 mL). The suspension slowly became clearer, and after 1 h, a clear solution was obtained. After another hour of stirring, a solid began to precipitate and the mixture was stirred for a further 60 h. The solid was collected by filtration and dried in air to afford pure **1b** as an off-white powder (0.2 g; 43% yield). Anal. Calcd for $C_{24}H_{25}BrN_2Pt$: C, 46.76; H, 4.09; N, 4.54; Br, 12.96. Found: C, 46.29; H, 4.09; N, 4.44; Br, 14.45. Infrared spectrum in KBr: ν(Pt–H) at 2275 cm^{-1}.

Evaporation in vacuo of the C_6H_6 filtrate to dryness yielded a yellow powder. According to ^1H NMR data, this was a mixture of four compounds, i.e. **1b**, *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$, Me_2SnBr_2, and PtBr($SnBrMe_2$)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$.

b. With C_6D_6 as solvent. The procedure is the same as described in method a, starting with 0.27 g of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ in 20 mL of C_6D_6. The suspension was filtered after 18 h of stirring, and the solid was identified as a 5:1 mixture of **1b** and PtBr(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) (total yield: 0.1 g; 33%).

c. To a stirred yellow solution of *cis,cis*-$PtBr_2$(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (0.22 g; 0.32 mmol) and a catalytic amount of azobis(isobutyronitrile) in CH_2Cl_2 (25 mL) was added *n*-Bu_3SnH (87 μL; 0.32 mmol). After 2 min, the solution was evaporated in vacuo to an oily residue. Upon addition of Et_2O (20 mL) and 0.5 h of stirring, a solid precipitated. This was isolated by filtration and dried in vacuo to afford **1b** as an off-white powder (0.11 g; 55% yield).

d. A solution of Me_2SnBr_2 (0.31 g; 1 mmol) in CH_2Cl_2 (7 mL) was added to a stirred yellow solution of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (0.54 g; 1 mmol) in a 6:1 (v/v) mixture of CH_2Cl_2 and *t*-BuOH (35 mL). After 3 h, the dark solution was evaporated in vacuo to a brownish powder. This solid was suspended in C_6H_6 (15 mL), and the suspension was stirred for 30 min. The solid was collected by filtration, washed with C_6H_6 (5 mL), and dried in air to afford a 5:1 mixture of **1b** and PtBr(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,N*) (total yield: 0.25 g; 41%).

Reactions of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ with Me_2SnBr_2 in CH_2Cl_2/ROH. The same procedure as described for the synthesis of **1b**, method d, was followed using ROH(D) (MeOH(D), EtOH, CF_3CH_2OH, and *t*-BuOD) instead of *t*-BuOH. The products were washed with C_6H_6 (*t*-BuOD), Et_2O (EtOH, CF_3CH_2OH), or hexane (MeOH(D)). The types of products and yields are shown in Table II.

Reaction of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ with Ph_2SnCl_2 in Toluene. A solution of Ph_2SnCl_2 (0.27 g; 0.8 mmol) in toluene (6 mL) was added to a stirred yellow suspension of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (0.42 g; 0.8 mmol) in toluene (35 mL). After 4 h, a slightly turbid solution was obtained, which was stirred for another 5 days. The solvent was then removed in vacuo to afford a sticky residue. After addition of hexane (25 mL), a yellow solid was obtained. This was collected by filtration and washed once with hexane (10 mL). Drying in air afforded a yellow powder, which was according to ^1H NMR data a mixture of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ and PtCl($SnClPh_2$)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ with other unidentified products.

Reaction of *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$ with Me_2SnBr_2 in Benzene. To a stirred white suspension of *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$ (0.7 g; 1.5 mmol) in benzene (40 mL) was added a solution of Me_2SnBr_2 (0.47 g; 1.5 mmol) in benzene (6 mL). The suspension became clearer, and after 0.5 h a 3-mL sample was taken and evaporated in vacuo to afford an off-white powder. According to ^1H NMR data, this was a mixture of *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$, Me_2SnBr_2, PtBr($BrSnMe_2$)($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$, and PtBr($C_6H_4CH_2NMe_2$-2-*C,N*)($C_6H_4CH_2NHMe_2$-2-*C,H*).[1] The slightly turbid benzene solution was stirred for another 48 h. After this time, the mixture was filtered. The resulting white solid (0.19 g) was identified by its ^1H NMR data as unreacted *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$. The yellow benzene filtrate was evaporated in vacuo to an off-white powder, which was identified by its ^1H NMR data as a mixture of PtBr($C_6H_4CH_2NMe_2$-2-*C,N*)($C_6H_4CH_2NHMe_2$-2-*C,H*), Me_2SnBr_2, and a tin-containing product. The powder was resuspended in CH_2Cl_2 (5 mL), and Et_2O was added (20 mL). After stirring of this mixture for 0.5 h, the solid was isolated by filtration and dried in air to afford PtBr($C_6H_4CH_2NMe_2$-2-*C,N*)($C_6H_4CH_2NHMe_2$-2-*C,H*) as an off-white powder (0.48 g; 60% yield).

Reaction of *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$ with Me_2SnBr_2 in CH_2Cl_2/*t*-BuOH. To a solution of *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$ (0.45 g; 1 mmol) in a 10:1 (v/v) mixture of CH_2Cl_2/*t*-BuOH (33 mL) was added a solution of Me_2SnBr_2 (0.31 g; 1 mmol) in CH_2Cl_2 (5 mL). The suspension was stirred for 5 h and then evaporated in vacuo to afford an off-white powder, which was identified by its ^1H NMR data as a mixture of PtBr($C_6H_4CH_2NMe_2$-2-*C,N*)($C_6H_4CH_2NHMe_2$-2-*C,H*), *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$, Me_2SnBr_2, PtBr($BrSnMe_2$)($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$, and a tin-containing product. The powder was redissolved in a 10:1 (v/v) mixture of CH_2Cl_2/*t*-BuOH (33 mL), and the solution was stirred for 18 h, after which the resulting suspension was filtered. The yellow filtrate was concentrated in vacuo to 2 mL, and Et_2O (15 mL) was added. After stirring of this suspension for 0.5 h, the solid was collected by filtration and dried in air, affording PtBr($C_6H_4CH_2NMe_2$-2-*C,N*)($C_6H_4CH_2NHMe_2$-2-*C,H*) as an off-white powder (0.41 g; 75% yield).

Reaction of Me_2SnBr_2 with *t*-BuOH. To a solution of Me_2SnBr_2 (0.03 g; 0.1 mmol) in $CDCl_3$ (0.5 mL) was added a 4-fold excess of C_6H_5-CH(Me)NMe_2 and then an excess of *t*-BuOH. The solution was

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(14) Wehman, E.; van Koten, G.; Knaap, I. C.; Ossor, H.; Pfeffer, M.; Spek, A. L. *Inorg. Chem.* **1988**, *27*, 4409.

(15) Longoni, G.; Fantucci, P.; Chini, P.; Canzioni, F. *J. Organomet. Chem.* **1972**, *39*, 413.

(16) van Beek, J. A. M.; van Koten, G.; Wehman-Ooyevaar, I. C. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1991**, 883.

subsequently monitored with ^{1}H NMR spectroscopy and followed in time. No reaction was observed.

Reaction of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ and CF_3COOH. For a typical NMR experiment, a yellow solution of ca. 25 mg of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ in 1 mL of dry $CDCl_3$ was prepared. To this solution was added CF_3COOH in the following amounts: 0.5, 1, 1.5, and 2 equiv and an excess (0.1 mL). The ^{1}H NMR spectra of the resulting pale brownish solutions were subsequently recorded and followed in time. In all experiments, **1c** was the main product and only traces (1–5%) of Pt($OOCCF_3$)(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) were seen.[1]

Reactions of 1 and PtX(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) (X = Br, $OOCCF_3$) with Alkenes and Alkynes. For a typical NMR experiment, an excess of the unsaturated reagent (ethene, styrene, neohexene, methyl methacrylate, vinyl acetate, dimethyl maleate, phenylacetylene, diphenylacetylene, or dimethyl acetylenedicarboxylate) was added to a solution of ca. 5 mg of one of the Pt complexes **1b** or PtX(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) (X = Br, $OOCCF_3$) in 0.7 mL of dry $CDCl_3$. The solution of **1c** was prepared by addition of an excess of CF_3COOH to a solution of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ in $CDCl_3$. ^{1}H NMR spectra were subsequently recorded and then followed in time. Only in the case of **1c** and Pt($OOCCF_3$)(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*) with dimethyl acetylenedicarboxylate was a new product formed. In both cases this was Pt($OOCCF_3$){η^1-C(COOMe)=CH(COOMe)}(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (**3**).

^{1}H NMR ($CDCl_3$, 24 °C): δ 2.09 (s, –NC*H*$_3$, $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ = 16.2 Hz), 2.75 (s, –COOC*H*$_3$), 3.12 (s, –NC*H*$_3$, $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ = 7.8 Hz), 3.45 (s, –NC*H*$_3$, $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ = 14.4 Hz), 3.62 (s, –COOC*H*$_3$), 3.68 (s, –NC*H*$_3$), 5.71 (d, 2-*H* of Ar, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 6.5 Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ = 48 Hz), 6.5 (s, C=C*H*, $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ = 77 Hz), 6.76 (t, 3-*H* of Ar, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 6.5 Hz), 7.13 (d, *H* of Ar, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 6.5 Hz), 7.2–7.8 (m, *H* of Ar), 8.08 (d, 2-*H* of Ar′, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 6.5 Hz, $^3J(^{195}\mathrm{Pt},^1\mathrm{H})$ = 51 Hz).

^{119}Sn NMR Measurements. ^{119}Sn NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 74.63 MHz. Chemical shifts in ppm are relative to external $SnMe_4$. The complex Ir(μ-BrSnBrMe$_2$)($C_6H_4CH_2NMe_2$-2-*C,N*)(cycloocta-1,5-diene) was prepared by literature methods.[17] The complex PtBr(SnBrMe$_2$)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (**2**) was prepared by mixing *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (0.22 g; 0.4 mmol) and Me_2SnBr_2 (0.12 g; 0.4 mmol) in CD_2Cl_2 (3 mL) and placed in a 10 mm o.d. tube. For the separate study of the tin-containing byproduct, a nonpurified material obtained from the filtrate from the reaction of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ with Me_2SnBr_2 (synthesis of **1b**, method a) was used.

^{119}Sn NMR data (CD_2Cl_2, 24 °C) for the three complexes are as follows. Ir(μ-BrSnBrMe$_2$)($C_6H_4CH_2NMe_2$-2-*C,N*)(cycloocta-1,5-diene): δ –161.6 (br s). Mixture of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ and Me_2SnBr_2: δ 56.8 (s, Me_2SnBr_2), –49.2 (s, $^1J(^{195}\mathrm{Pt},^{119}\mathrm{Sn})$ = 13 070 Hz, **2**), –72.4 and –119 (2 × s, tin-containing byproduct). Tin-containing byproduct: δ –72.4 (s, $J(^{195}\mathrm{Pt},^{119}\mathrm{Sn})$ = 67 Hz), –119 (s, $J(^{195}\mathrm{Pt},^{119}\mathrm{Sn})$ = 67 Hz).

Technical Details of the MO Calculations. SCF[18] and CAS-SCF[19] calculations were carried out on the *trans*-[PdCl(H)(Me)$_2$(NH$_3$)···NH$_3$] and *trans*-[PdCl(Me)$_2$(NH$_3$)···H-NH$_3$] systems, which serve as models for **1a** and PtCl(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*), respectively. The simplifications made leading to the model complex, i.e. Pd instead of Pt, Me and NH$_3$ ligands instead of the large $C_{10}H_6NMe_2$-8 groups, and the symmetric trans geometry instead of the asymmetric cis geometry, all serve to reduce computation time into a workable range. In order to verify whether the calculations on complexes with the trans geometry yield results comparable to those on the cis models, we carried out a few representative calculations on the latter. We also checked whether the calculations on the Pd complex are comparable with those on the same model with Pt as the metal. In order to do this, we performed some calculations at the SCF level using for the Pt atom a relativistic effective core potential (RECP). Use was made of the following Gaussian basis sets: Pd (16,11,9) [contracted to 7,5,5], Cl (11,7) [4,3], C and N (9,5) [3,2], H(4) [2], hydride or bridging H (6,1) [3,1].[20,23] For calculations on the Pt complex, use was made of the RECP of Hay and Wadt[24] with a (3,3,3) [2,2,3] basis set[25] for Pt and the ECP of Barthelat et al.[26] with a (4,4) [3,3] basis set for Cl. Details of the geometries were mostly derived from the X-ray crystal structure of PtBr(1-$C_{10}H_6NMe_2$-8-*C,N*)(1-$C_{10}H_6NHMe_2$-8-*C,H*)[9] and from reported average palladium–ligand bond lengths.[27] This yielded the following bond lengths and bond angles: Pd–C = 2.03 Å, Pd–N = 2.04 Å, Pd–Cl = 2.33 Å, Pd–H = 1.61 Å, C–H = 1.07 Å, H–C–H = 109.5°, N–H = 1.023 Å, H–N–H = 114.2°. For the free NH$_3$, N–H was set to 1.01 Å and the angle H–N–H to 107°. A tetrahedral geometry was assumed for NH_4^+ with N–H = 1.02 Å. In the Pd(IV) hydride system, the NH$_3$ molecule was put at 10 Å from the hydride ligand; see **F** in Chart I. In the Pd(II)···H–N system the Pd···N and Pd···H distances of the Pd···H–NH$_3$ linkage were optimized to 3.03 and 2.01 Å, respectively, in good agreement with the X-ray crystal structure of the Pt system[9] (see **A** in Chart I). The other geometrical parameters were kept constant. Although a geometry optimization might change somewhat the relative energies of the various isomers, it should not alter our conclusions on their relative positioning and on the nature of the metal···H–N linkage. Moreover it has been experimentally found that the bond lengths in the Pd(II)···H–N system were comparable to the ones in the system without this interaction.[1] In addition to these two geometries, a few others shown in Chart I and characterized by various Pd–H and N–H bond lengths were also investigated. The use of a MC-SCF type wave function (here CAS-SCF) was found to be necessary to obtain a reliable description of the electronic structure of the Pd(IV) hydride complexes and of the associated energetics. On the other hand, the SCF wave functions turned out to be a reasonable description of the Pd(II) complexes and of the zwitterionic hydrogen Pd(II) systems. For this reason the platinum calculations (which were of SCF type) were also limited to the Pt(II) and the zwitterionic hydrogen Pt(II) systems. The geometries were not reoptimized at the CAS-SCF level. Such an optimization would probably not change the relative energies of the various isomers to a greater extent. It has been shown by Siegbahn and coworkers that the potential energy surfaces for the Pd–H and the Pd–L bonding are quite flat around the equilibrium bond lengths and that geometry optimization is not expected to change the calculated interaction energies very much.[28]

Results

A. Formation and Characterization of the Pt(IV) Hydride Complexes PtX(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (1a, X = Cl; 1b, X = Br). When the Pt(II) complex *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ is treated with Me_2SnX_2 (X = Cl, Br) in dry CH_2Cl_2 or C_6H_6 (C_6D_6), the new Pt(IV) hydrides PtX(H)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (**1a**, X = Cl; **1b**, X = Br) are formed after 4 days in reasonable yields; see eq 2 in Scheme I. Complex **1b** can also be formed by an alternative route in which *cis,cis*-PtBr$_2$(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ is reacted with *n*-Bu$_3$SnH (eq 3). Treatment of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ with Ph_2SnCl_2 does not afford a Pt(IV) hydride but, instead, affords a complex that contains, on the basis of ^{1}H NMR data, a Pt–Sn moiety. Such a complex with a Pt–Sn moiety, PtBr(BrSnMe$_2$)(1-$C_{10}H_6NMe_2$-8-*C,N*)$_2$ (**2**), was also observed by ^{1}H NMR spectroscopy as an intermediate in reaction 2.

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(17) van der Zeijden, A. A. H.; van Koten, G.; Wouters, J. M. A.; Wijsmuller, W. F. A.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 5354.

(18) (a) Ernenwein, R.; Rohmer, M. M.; Bénard, M. *Comp. Phys. Commun.* **1990**, *58*, 305. (b) Rohmer, M.-M.; Demuynck, J.; Bénard, M.; Wiest, R. *Comp. Phys. Commun.* **1990**, *60*, 127. (c) Wiest, R.; Demuynck, J.; Bénard, M.; Rohmer, M.-M.; Ernenwein, R. *Comp. Phys. Commun.* **1991**, *62*, 107.

(19) (a) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157. (b) Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. *J. Chem. Phys.* **1981**, *74*, 2384. (c) Roos, B. O. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980**, *14*, 175.

(20) Veillard, A.; Dedieu, A. *Theor. Chim. Acta* **1984**, *65*, 215. The original (15,9,8) basis set was modified by the addition of an s primitive of exponent 0.305 60 to suppress the gap between the functions needed to describe the widely separated 4s and 5s shells, two p functions of exponents 0.235 60 and 0.083 86 to describe the 5p shell, and one d function of exponent 0.078 90. These exponents were chosen according to the even-tempered criterion.

(21) Hyla-Kryspin, I.; Demuynck, J.; Strich, A.; Bénard, M. *J. Chem. Phys.* **1981**, *75*, 3954.

(22) Huzinaga, S. Technical Report, University of Alberta, Edmonton, 1971.

(23) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(24) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

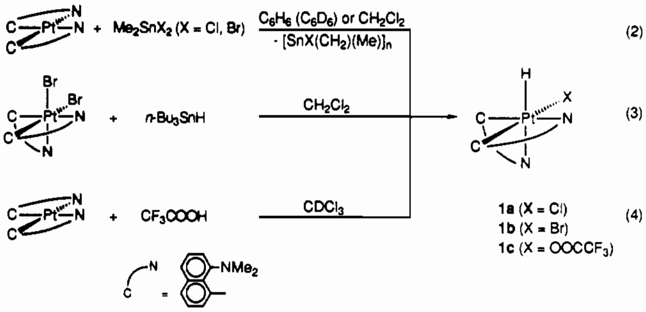
(25) Jeung, G. H.; Liddell, M. Private communication.

(26) Bouteiller, Y.; Mijoule, C.; Nizam, M.; Barthelat, J. C.; Daudey, J. P.; Pelissier, M.; Silvi, B. *Mol. Phys.* **1986**, *65*, 295.

(27) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(28) (a) Blomberg, M. R. A.; Schüle, J.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1989**, *111*, 6156 and references cited therein. (b) Blomberg, M. R. A.; Siegbahn, P. E. M.; Nagashima, U.; Wennerberg, J. *J. Am. Chem. Soc.* **1991**, *113*, 424.

Scheme I. Synthetic Routes for $PtX(H)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$



The ^1H NMR spectrum of the tin-containing byproduct of reaction 2 contains two broad multiplets at ca. 3.5 and 1.3 ppm, while the ^{119}Sn NMR spectrum shows two singlets at −72 and −119 ppm, both with platinum satellites ($J(^{195}Pt,^{119}Sn) = 67$ Hz) (see Experimental Section). According to the stoichiometry of reaction 2, this byproduct should be based on a tin–carbene complex, $[SnX(CH_2)(Me)]$, but platinum is also present; unfortunately, full characterization of this material was not successful.[29]

Complexes **1** are stable in the solid state, but in solution decomposition begins within 15 min to generate the free ligand $C_{10}H_7NMe_2\text{-}8$ and unidentified Pt-containing products. The Pt(IV) hydride $Pt(OOCCF_3)(H)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ (**1c**) can be prepared and characterized in situ in an NMR tube reaction of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with an excess of CF_3COOH; see eq 4 in Scheme I. However, attempts to isolate this chemically unstable product from a large-scale reaction failed. Another attempted synthesis of **1c** from an anion-exchange reaction of **1b** with $AgOOCCF_3$ was similarly unsuccessful. Complexes **1a** and **1b** have been characterized by ^1H NMR, IR, and elemental analysis. These are the first isolable aryl–Pt(IV) hydrides. The complexes are off-white neutral species with reasonable solubility in chloroform and dichloromethane.

^1H NMR and IR Spectroscopy of the Pt(IV) Hydrides 1. The ^1H NMR spectra of **1** (see Table I) show all the characteristics of an asymmetric octahedral structure. For the –NMe groups, there are four singlets; two of them are somewhat broadened and the other two have distinct Pt satellites. One can deduce that the naphthyl ligands are positioned mutually perpendicular, since in the aromatic region there is an upfield shift for one of the ortho protons; i.e., it is held near the aromatic ring of the second naphthyl ligand. The ortho proton of the latter shows no extreme up- or downfield shifts. Besides these signals for the two C,N bonded naphthyl ligands, there is a distinctive upfield resonance at −20.4 ppm (1H) with a large $^1J(^{195}Pt,^1H)$ value of ca. 1550 Hz (1610 Hz for **1c**). These data are characteristic for a hydride ligand that is trans to a nitrogen ligand on a Pt(IV) center.[30] This trans-N position of the hydride in **1** is to be expected, since the N-donor ligands have a lower trans influence than C-donor ligands. Literature data for Pt(IV) hydrides, prepared in situ, show that Pt coupling constants are normally in the range 650–1250 Hz,[30a,b] but these compounds have halides, phosphines, or cyanides as trans ligands. Separate evidence for complexes **1** being Pt(IV) species comes from two different sources. First, XPS measurements show the Pt center to have the oxidation state 4+.[31] Second, complex **1b** can be independently synthesized from the Pt(IV) complex *cis,cis*-$PtBr_2(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ and *n*-Bu_3SnH (reaction 3). The presence of a terminal hydride ligand in **1a** and **1b** is confirmed by their IR spectra (see Experimental Section) that show sharp absorption bands at 2280 and 2275 cm^{-1}, respectively. These values are consistent with literature data for terminal hydrides (2300–1900 cm^{-1}) and exclude the possibility that **1** is a dinuclear species with a bridging hydride (ν(M–H–M) = 1600–1500 cm^{-1}).[32] In complexes **1**, the two C,N bonded naphthyl ligands and the hydride occupy five coordination sites; the sixth is occupied by an anion (Cl, **1a**; Br, **1b**; CF_3COO, **1c**). Detailed analysis of the ^1H NMR spectra of **1** allows us to propose the specific geometric structure for these complexes shown in Scheme I. The possible position of the halide, for example, can be deduced from the fact that there is no downfield shift of the second naphthyl ortho proton; i.e, this proton is not in the neighborhood of the halide. If this halide had been positioned near an ortho proton, the latter would be expected to show a downfield shift as in, for example, *cis,cis*-$PtBr_2(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$.[16] Therefore, the second ortho proton is held near the hydride. The proposed structure is closely related to that of the tautomer of **1**, i.e. $PtX(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$.[1] However, the ^1H NMR spectrum of the latter is remarkably different and shows, instead of the upfield hydridic resonance, a very low field protonic resonance at 15.8 ppm.

^1H and ^{119}Sn NMR Spectroscopy of $PtBr(BrSnMe_2)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ (2). The complex $PtBr(BrSnMe_2)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ (**2**) can be formed in situ by mixing equimolar amounts of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ and Me_2SnBr_2 in CD_2Cl_2. It is also present in samples taken at the beginning of reaction 2 (Me_2SnBr_2 with *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$). In both cases, the ^1H and ^{119}Sn NMR spectra also show the resonances of the starting compounds. The presence of a Pt–Sn interaction in **2** is clearly shown by the ^{119}Sn NMR spectrum (see Experimental Section) in which the resonance at −49.2 ppm has a $^1J(^{195}Pt,^{119}Sn)$ value of 13 070 Hz, which lies in the large range of 2–35 kHz known for Pt–Sn coupling constants.[33] This Pt–Sn interaction is also clear in the ^1H NMR spectrum, in which several Me resonances exhibit both Sn and Pt satellites. For Sn–Me groups, two singlets are found at 0.47 ppm ($^2J(Sn,^1H) = 55$ Hz) and 1.21 ppm ($^2J(Sn,^1H) = 51$ Hz; $^3J(^{195}Pt,^1H) = 6$ Hz), and for the –NMe groups, there are four singlets at 2.02, 2.97, 3.68, and 3.99 ppm. The former two singlets of the –NMe groups have both Pt and Sn satellites ($^3J(^{195}Pt,^1H) = 10$ Hz, $^4J(Sn,^1H) = 17$ Hz; $^3J(^{195}Pt,^1H) = 6$ Hz, $^4J(Sn,^1H) = 13$ Hz), whereas the other two have only Pt satellites ($^3J(^{195}Pt,^1H) = 6$ Hz, $^3J(^{195}Pt,^1H) = 20$ Hz). The aromatic region shows a multiplet at ca. 7.4 ppm, a triplet at 6.88 ppm ($^4J(^{195}Pt,^1H) = 14$ Hz), and a doublet at 6.07 ppm ($^3J(^{195}Pt,^1H) = 43$ Hz), pointing to a perpendicular orientation of the naphthyl ligands. For **2**, two structural proposals (see Figure 1) can be made. Structure **a** is a Pt(IV) complex in which the Sn–Br bond is oxidatively added to the Pt center, as found for $PtCl(Cl_2SnMe)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$,[34] and structure **b** is a Pt(II) complex in which the Sn–Br bond is side-on coordinated to the Pt center and consequently lengthened, as in $Ir(\mu\text{-}BrSnBrMe_2)(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(COD)$ (μ-Br–Sn = 2.934 (1) Å vs Sn–Br = 2.608 (1) Å).[17] We have been unable

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[29] A tin–carbene moiety is expected to form a polymeric material, as was proposed for the byproduct of the decomposition reaction of the Ir–Sn complex $Ir(\mu\text{-}BrSnBrMe_2)(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)$(cycloocta-1,5-diene).[17]

[30] (a) Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton* **1073**, 854. (b) Blacklaws, I. M.; Brown, L. C.; Ebsworth, E. A. V.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877. (c) van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Grove, D. M. *Organometallics* **1988**, *7*, 1556.

[31] Monochromatic X-ray photoelectron spectroscopy was used for determination of the Pt 4f binding energy of the Pt center in **1b**. Apparatus and methods are described in the publication about the XPS measurements of the Pt complexes $PtX[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$: Muijsers, J. C.; Niemantsverdriet, J. W.; Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 2655.

[32] Green, M.; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Chem. Commun.* **1976**, 671.

[33] (a) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11. (b) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G.; Dakternieks, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1686. (c) Ammann, C.; Pregosin, P. S.; Rüegger, H.; Grassi, M.; Musco, A. *Magn. Reson. Chem.* **1989**, *27*, 355.

[34] Smeets, W. J. J.; Spek, A. L.; van Beek, J. A. M.; van Koten, G. *Acta Crystallogr.* **1992**, *C48*, 745.

Table I. ^{1}H NMR Data for the Hydride Complexes $PtX(H)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ (**1**)[a]

X	aryl H	NMe_2	Pt–H; $^1J(^{195}Pt,^1H)$, Hz
Cl (**1a**)	6.14 d (58), 6.92 t (13), 7.26–7.94 m	2.18 s (12), 3.31,[b] 3.55 s (23), 3.60[b]	–20.39 s; 1569
Br (**1b**)	6.11 d (60), 6.92 t (14.5), 7.15–7.92 m	2.15 s (12), 3.44,[b] 3.57 s (24), 3.70[b]	–20.35 s; 1540
$OOCCF_3$ (**1c**)	6.01 d (60), 6.87 t (14.5), 7.25–8.0 m	2.19 s (11), 3.18,[b] 3.43,[b] 3.50[b]	–19.37 s; 1610

[a] Recorded in $CDCl_3$ at room temperature; δ in ppm relative to external TMS; $^nJ(^{195}Pt,^1H)$ in Hz in parentheses. [b] Broad resonance; $^3J(^{195}Pt,^1H)$ not observed.

a (Pt^{IV}) **b** (Pt^{II})

Figure 1. The Pt(IV)–Sn complex (**a**) versus the Pt(II)–Sn complex (**b**) as possible structures for **2**.

Table II. Products and Yields from the Reactions of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ or *cis*-$Pt(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2$ with Me_2SnBr_2 in 6–10:1 Mixtures of CH_2Cl_2/ROH(D)[a]

		cis-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$		*cis*-$Pt(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2$
ROH(D)	pK_a	**1b**:H^+ [b]	tot. yield, %	yield of $H^{+\prime}$ [c]
C_6H_6[d,e]		1	43[f]	60[f]
C_6D_6[d,g]		5:1	33[f]	
MeOH	15.5	1	95	90
MeOD		1[h]	67	
EtOH	15.9	1:1	88	
CF_3CH_2OH	12.4	1	76	
t-BuOH	18	5:1[f]	41	75[f]
t-BuOD[e]		3:1[f,i]		

[a] No Pt–Sn intermediates were observed during the reaction unless stated otherwise. [b] H^+ = $PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$. [c] $H^{+\prime}$ = $PtBr(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(C_6H_4CH_2NHMe_2\text{-}2\text{-}C,H)$. [d] Used as solvent. Neither CH_2Cl_2 nor ROH is present. [e] After 60 h of stirring. [f] Pt–Sn intermediate $(PtBr\{SnBr(Me)_2\}(L\text{-}C,N)_2)$ observed during the reaction. [g] After 24 h of stirring. [h] $PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NDMe_2\text{-}8\text{-}C,D)(=D^+)$ instead of H^+. [i] **1b-D** instead of H^+; traces of D^+ present.

to isolate **2** in a pure form but believe, on spectroscopic grounds, that it has structure **a**. First, $J(^{195}Pt,^1H)$ values in the ^{1}H NMR spectrum of **2**, especially those in the aromatic region, are indicative for a Pt(IV) rather than a Pt(II) complex. Second, the Sn chemical shift of –49.2 ppm for **2** points to a tetrahedral geometry of the Sn center; cf. δ(Sn) = –50 ppm for the Pt–Sn complex $[\{N(CH_2CH_2PPh_2)_3\}Pt(SnMe_3)][BPh_4]$.[33b] Last, the NMR data do not compare favorably with those of the iridium complex $Ir(\mu\text{-}BrSnBrMe_2)(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(COD)$, which has trigonal bipyramidal tin geometry (type **b**); δ(Sn) = –161.6 ppm (see Experimental Section) with $^2J(Sn,^1H)$ values for the Sn–Me groups of 60 and 49 Hz.[17,35]

B. Reactions of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ or *cis*-$Pt(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2$ with Me_2SnBr_2 in CH_2Cl_2/ROH (R = Me, Et, CF_3CH_2, *t*-Bu). Without MeOH, the reaction of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with Me_2SnX_2 affords the hydride **1** whereas, with MeOH, the same reaction provides the tautomeric zwitterionic hydrogen complex $PtX(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$.[1] To extend our study into the mechanism of these contrasting reactions, alcohols other than MeOH with varying steric and electronic properties have been used in the specific reaction of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ and *cis*-$Pt(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2$ with Me_2SnBr_2. The results (products and yields) are shown in Table II.

With *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$, the acidic alcohol CF_3CH_2OH gives the same reaction as MeOH; i.e., $PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ is formed in good yield. When less acidic EtOH is used, this zwitterionic hydrogen complex is formed, but now in a 1:1 mixture with the Pt(IV) hydride **1b**. From *t*-BuOH, with a low pK_a value, the main product is the Pt(IV) hydride **1b** and only 16% of the zwitterionic hydrogen species is formed. From these results one can clearly see that product formation is directly related to the alcohol pK_a. To determine the hydride source in the *t*-BuOH reaction, the deuterated alcohol *t*-BuOD was used and this gives a 3:1 mixture of **1b** and **1b-D**, with only traces of $PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NDMe_2\text{-}8\text{-}C,D)$; no $PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ was formed. This result shows that Pt(IV) hydride formation occurs without direct interference of the added alcohol, in this case *tert*-butyl alcohol.

When the starting Pt complex is the less rigid complex *cis*-$Pt(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2$, the reaction with Me_2SnBr_2 and *t*-BuOH affords only the zwitterionic hydrogen complex, i.e. $PtBr(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(C_6H_4CH_2NHMe_2\text{-}2\text{-}C,H)$. However, the same product, not the expected Pt(IV) hydride, is also obtained when the reaction is carried out in dry benzene. This result and its consequences for the mechanistic proposals are dealt with in the Discussion.

C. Reactions of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with HX (X = Cl, $OOCCF_3$). The product resulting from treatment of a $CDCl_3$ solution of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with an excess of HX depends strongly on the anion X. When X = Cl, the zwitterionic hydrogen complex $PtCl(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ is formed, together with a previously identified product, which results from a subsequent reaction with excess HCl.[1] In contrast, the reaction of CF_3COOH with *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ gives the hydride complex **1c** as the main product (see eq 4 in Scheme I) and only traces of the zwitterionic hydrogen complex $Pt(OOCCF_3)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$.

D. MO Calculations. Using the systems *trans*-$[PdCl(H)(Me)_2(NH_3)\cdots NH_3]$ and *trans*-$[PdCl(Me)_2(NH_3)\cdots H\text{–}NH_3]$ as models for **1a** and $PtCl(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$, respectively, SCF and CAS–SCF calculations indicate that **A**, the five-coordinate zwitterionic palladium(II) system, is the lowest point on the energy hypersurface (or close to it), since other geometrical deformations from **A** resulted in a net destabilization of the system; see Chart I.[36] In particular, the five-coordinate palladium(IV) hydride system **F**, which does not experience any interaction with NH_3, is destabilized by 25.6 kcal/mol. When NH_3 remains in the vicinity of the Pd–H bond, the destabilization is lower, however (see for instance **D**).[37]

The analysis of the wave function of **A** reveals the nature of the Pd$\cdots$H–N linkage. The two bonding orbitals **c** and **d** are shown in Figure 2.[38] Orbital **c** is the bonding combination of the

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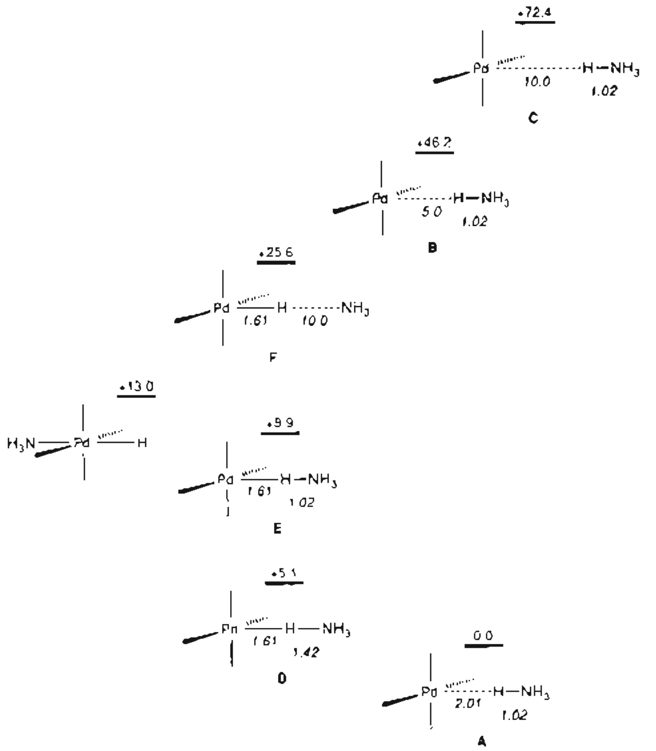
(35) Jastrzebski, J. T. B. H.; Grove, D. M.; Boersma, J.; Ernsting, J.-M.; van Koten, G. *Magn. Reson. Chem.* **1991**, *29*, 25.

(36) Computed CAS–SCF total energies (in au; 1 au = 627.5 kcal/mol): **A**, –5578.3535; **B**, –5578.2799; **C**, –5578.2382; **D**, –5578.3453; **E**, –5578.3393; **F**, –5578.3127. In these calculations, six electrons in six active orbitals were correlated. These active orbitals were chosen so as to describe the Pd–H and N–H bonds, the other 4d orbital of a_1 symmetry (in the C_s symmetry point group), and the 5s orbital of Pd.

(37) An optimum distance of 1.32 Å is found for the approach of NH_3 toward the platinum hydride. This geometry is destabilized by 4.8 kcal/mol with respect to **A**.

(38) These orbitals are doubly occupied in the SCF wave function and strongly occupied in the CAS–SCF wave function.

Chart I. Energy Levels (Underlined) and Bond Distances (Italic) of the [PdCl(Me)$_2$(NH$_3$)···H–NH$_3$] System[a]



[a] Relative energies in kcal/mol; bond distances in Å.

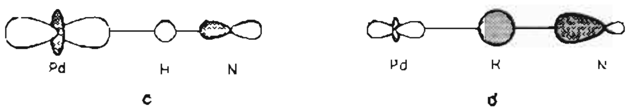


Figure 2. The two bonding orbitals c and d.

4d$_{z^2}$ with the σ^*_{N-H} orbital and is almost entirely localized on the palladium atom. A Mulliken population analysis indicates that it has 88% of the electronic density on Pd, 3% on H, and 6% on N. Moreover there is no hybridization of 4d$_{z^2}$ with 5s and 5p$_z$: the contributions of 5s and 5p$_z$ to c are only 1% and 0.7%, respectively. Orbital d, bonding σ_{N-H}, remains largely localized on N–H (95%). The interaction between the Pd orbitals and the NH$_3$ orbitals is therefore quite minimal and probably best described as a 4e–3c interaction due to the absence of the empty 5s and 5p$_z$ orbitals in the bonding scheme. Conversely the electrostatic (or ionic) type interaction in the zwitterion is maximized. A clear-cut indication of this feature is given by an electrostatic potential map computed for the deprotonated [PdCl(Me)$_2$(NH$_3$)···NH$_3$]$^-$ system (with the previously optimized Pd···N distance of 3.03 Å) (see Figure 3); a negative area is found between the Pd and the N atoms. Moreover, its minimum corresponds precisely to the position of the proton in A. When NH$_3$ is displaced toward the Cl atom, this minimum is also displaced but stays on the Pd···N axis (in this case the energy of the corresponding protonated system is slightly lowered, by 6.8 kcal/mol for a 30° bending). A similar map has been determined for the *cis*-[PdCl(Me)$_2$(NH$_3$)···NH$_3$]$^-$ isomer and does not reveal any significant difference with the map obtained for the trans isomer. In contrast, the Pd(IV) hydride system has a Pd–H bond which is, as expected, quite covalent in character. This is best seen from the two orbitals which describe this bond in the CAS-SCF wave function. The 4d$_{z^2}$ + s$_H$ bonding combination which is strongly occupied (occupation number of 1.88 e) has 60% of the electronic density on Pd and 38% on H. The correlating weakly 4d$_{z^2}$–s$_H$ antibonding combination (with an occupation number of 0.12 e) has 40% of the electronic density on Pd and 52% on H.

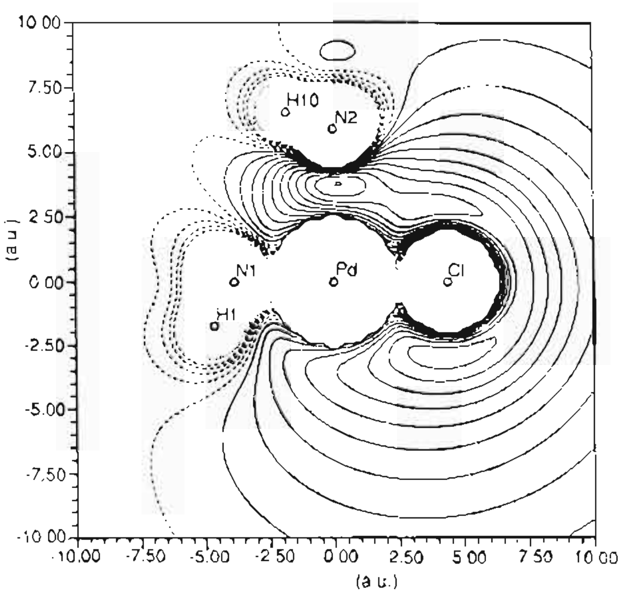


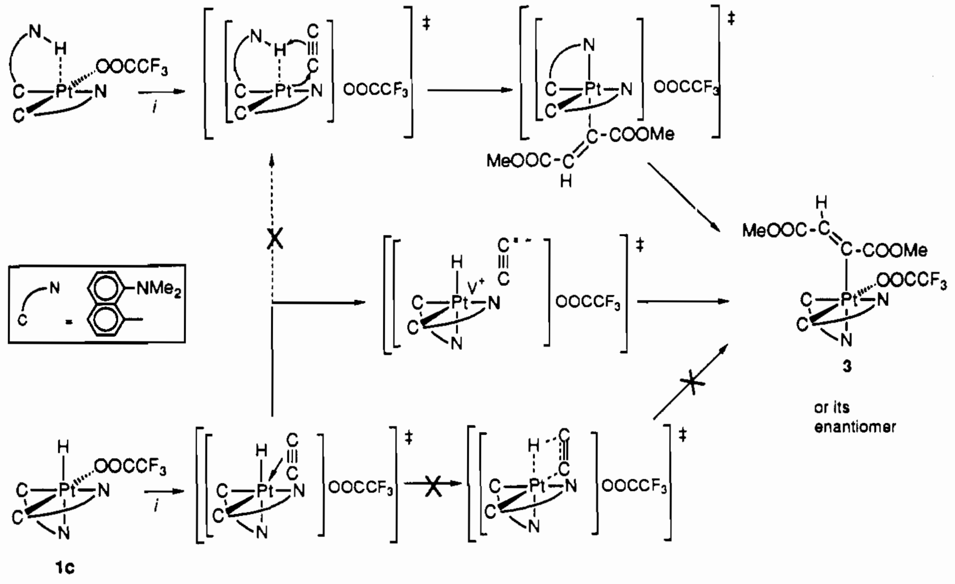
Figure 3. Molecular electrostatic potential map of the deprotonated [PdCl(Me)$_2$(NH$_3$)···NH$_3$]$^-$ system. The most negative contour line (around the minimum) is at −0.290 au, and the contour values increase from this value to 0.090 au (the value of the most internal dotted line) by steps of 0.020 au. For the sake of clarity, the two methyl ligands pointing out of the plane of the map have been omitted.

All these features are therefore consistent with the fact that, in the Pd(II)···H–NH$_3$ system, the electrostatic (or ionic) component is the main contributor to the M···H–N interaction energy, at least in the palladium systems. Calculations for the Pt analogs show that the orbital interactions play a somewhat greater role in the stabilization: now, in c, 76% of the electronic density is localized on Pt, 3% on H, and 8% on N. In d, 89% of the electronic density is localized on N–H. The corresponding Pt–H overlap population, which can be taken as a measure of the orbital interactions, has increased to 0.34 e from 0.15 e in the Pd system. In the Pt case, one also observes a greater participation of the s and p$_z$ empty orbitals in the bonding. More specifically, in c the d$_{z^2}$ orbital is hybridized with the empty s orbital, the respective participations being 62% for d$_{z^2}$ and 12% for s. In this sense, the Pt···H–N linkage has more bonding character than the Pd···H–N interaction. All these features are reflected in the energetics of the interaction: in the platinum case, the stabilization gained on going from a metal–hydrogen distance of 10 Å to a metal–hydrogen distance of 2.01 Å is greater; it amounts to 88.5 kcal/mol at the RECP–SCF level of theory, whereas the value for the Pd system at the same level of theory is 65.5 kcal/mol.

E. Reactions of the Hydride Complexes 1 and PtX(1-C$_{10}$H$_6$-NMe$_2$-8-*C,N*)(1-C$_{10}$H$_6$NHMe$_2$-8-*C,H*) with Alkynes. The hydride complexes 1 and the zwitterionic hydrogen complexes PtX(1-C$_{10}$H$_6$NMe$_2$-8-*C,N*)(1-C$_{10}$H$_6$NHMe$_2$)-8-*C,H*) have been investigated as potential starting compounds for the synthesis of alkyl or alkenyl complexes. To this end, reactions of these complexes were carried out using a variety of alkenes or acetylenes, with differing electronic and steric properties, i.e. ethene, styrene, neohexene, methyl methacrylate, vinyl acetate, dimethyl maleate, phenylacetylene, diphenylacetylene, and dimethyl acetylenedicarboxylate. Of these, only the last showed any reactivity and then only with the CF$_3$COO$^-$ complexes 1c and Pt(OOCCF$_3$)(1-C$_{10}$H$_6$NMe$_2$-8-*C,N*)(1-C$_{10}$H$_6$NHMe$_2$-8-*C,H*). Both reactions afford the same Pt(IV) alkenyl product, i.e. Pt(OOCCF$_3$){η^1-C(COOMe)=CH(COOMe)}(1-C$_{10}$H$_6$NMe$_2$-8-*C,N*)$_2$ (3); see Scheme II.

The ^{1}H NMR spectrum (see Experimental Section) of this product shows that the *Z* isomer is stereoselectively formed; the

Scheme II. Mechanism of the Reactions of **1** and $Pt(OOCCF_3)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ with Dimethyl Acetylenedicarboxylate[a]



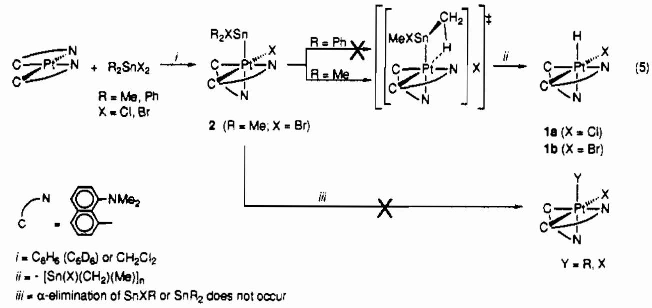
[a] i = +MeOOCC≡CCOOMe.

chemical shift value of the olefinic proton is 6.5 ppm.[39] Although the $^3J(^{195}Pt,^1H)$ value of 77 Hz for the alkenyl proton seems to be relatively small for the *Z* geometry, this is not a Pt(II) species and the value is consistent with a Pt(IV) complex. Furthermore, the ^1H NMR spectrum shows four singlets with Pt satellites for the –NMe groups, two singlets for the –OMe groups, and an aromatic pattern similar to that of **1**. On the basis of this evidence, **3** is proposed to have the structure shown in Scheme II with a general Pt geometry related to that of **1**.

Discussion

Formation of the Hydride Complexes 1a and 1b. Mechanism of the Me_2SnX_2 Reaction. The complexes **1** are the first isolable aryl–Pt(IV) hydride species to be characterized. In the literature Pt(IV) hydrides have often been proposed as intermediates in catalytic cycles and they have sometimes been detected in solution by spectroscopic measurements.[30a,b,40]

The formation of hydrides **1** in reaction 2 (*cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with Me_2SnX_2) was unexpected. Usually, reactions of square planar d^8 organometallic complexes with Sn(IV) reagents lead to oxidative addition products or to side-on coordination of the Sn–Y (Y = halide, alkyl, aryl, or hydride) bond to the d^8 metal center.[17,33a,41] In the first stage of the reaction affording **1**, we have good spectroscopic evidence for a complex containing a Pt–Sn moiety and we believe the first step toward **1** is indeed an oxidative addition of Me_2SnX_2 to the Pt center to form **2**; see eq 5. As to be expected for Me_2SnX_2, an electron-poor Sn(IV) reagent, the stereochemistry of this oxidative addition reaction results in a cis geometry. Literature examples show that oxidative addition of a Sn–X bond can result in either trans or cis geometries, depending on the electron density on the Sn atom. For example, the reaction of $SnBr_4$ with *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ results in a trans oxidative addition whereas reaction with the less strong Lewis acid $MeSnCl_3$ results in a cis oxidative addition.[34,42a] Complexes like **2** with a M–Sn bond are often labile and, for example, the complex $[\{N(CH_2CH_2PPh_2)_3\}Pt(SnMe_3)][BPh_4]$ in solution is only stable for a few hours.[33b] Complex **2** in solution reacts further to form the Pt(IV) hydride **1** with elimination of a tin-containing byproduct. In the literature there are precedents for such reactions involving both α-elimination (for example, $PtBr(SnBr_3)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ forms the complex *trans,cis*-$PtBr_2(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ by eliminating $SnBr_2$)[34,42a] and β-elimination[42b] (for example, $Ir(\mu\text{-}BrSnBrMe_2)(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)(COD)$ forms $C_6H_5CH_2NMe_2$ and $[IrCl(COD)]_2$ via an Ir(III) hydride intermediate).[17] Since the product of the decomposition of **2** is a hydride, we believe the β-elimination route, in which the hydride atom is derived from an Sn–Me group, is operative. Experiments in C_6D_6 confirmed that the solvent was not the hydride source. In this β-elimination from one of the $Pt\text{–}Sn\text{–}CH_3$ units of **2** (see eq 5), a carbene complex $[BrSn(CH_2)Me]$ should be formed.[29] In our study, the tin-containing complex was found (by ^{119}Sn NMR spectroscopy) to also contain platinum, and this helps explain the low yield of the hydride obtained by method a. Further evidence that the Pt(IV) hydrides result from a β-elimination reaction is given by the reaction of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with Ph_2SnCl_2, which stops at the stage of a Pt–Sn complex like **2**: a β-elimination, in this case from a phenyl group which would give a benzyne, is not likely.



The bromo hydride complex **1b** could also be synthesized via another route, i.e. from the reduction of *cis,cis*-$PtBr_2(1\text{-}C_{10}H_6\text{-}$

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(39) (a) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G. Rüegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961. (b) Reger, D. L.; Baxter, J. C.; Garza, D. G. *Organometallics* **1990**, *9*, 16.

(40) (a) Ebsworth, E. A. V.; Henderson, S. G. D.; Rankin, D. W. H. *Inorg. Chim. Acta* **1981**, *48*, 159. (b) Jones, R. F.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1245.

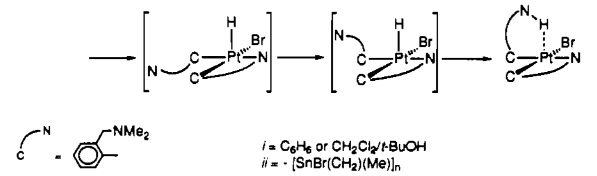
(41) (a) Kuiper, J. *Inorg. Chem.* **1977**, *16*, 2171; **1978**, *17*, 77. (b) Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1979**, *181*, 47. (c) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159. (d) Schubert, U.; Kunz, E.; Harkers, B.; Willnecker, J.; Meyer, J. *J. Am. Chem. Soc.* **1989**, *111*, 2572.

(42) (a) van Beek, J. A. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. To be published. (b) This process in the proposed route (eq 5) involves a free coordination site created by either Pt–X or Pt–N dissociation. This detail of the β-elimination process is being studied further.

NMe_2-8-*C*,*N*$)_2$ by *n*-Bu_3SnH in the presence of azobis(isobutyronitrile) (abbreviated as AIBN) (eq 3). This organometallic reaction resembles the well-documented reductions of organic halides by organotin hydrides that are very useful in organic synthesis.[43] The use of AIBN is simply to accelerate the reduction that (in organic systems) is known to usually involve free-radical intermediates. A further analogy of *cis*,*cis*-$PtBr_2$(1-$C_{10}H_6NMe_2$-8-*C*,*N*$)_2$ to organic halides is that only monoreduction takes place with this reagent; cf. reduction of CCl_4 to $CHCl_3$ and not CH_2Cl_2.[44]

Formation of the Hydride Complexes 1 versus the Zwitterionic Hydrogen Complexes PtX(1-$C_{10}H_6NMe_2$-8-*C*,*N*)(1-$C_{10}H_6NHMe_2$-8-*C*,*H*). For selective formation of the zwitterionic hydrogen complexes, a proton source is necessary, and we have shown that the reaction of R_2SnX_2 with ROH, assisted by the presence of Pt(II) amine species, generates HX.[1] For the formation of Pt(IV) hydrides the first step in the reaction of R_2SnX_2 with the Pt(II) species is formation of a Pt–Sn complex (**2**). In all reactions where ROH is present, there are thus two competitive reactions with markedly different reaction rates and the dominant path is seen to be dependent on the pK_a value of ROH (see Table II). More acidic alcohols (CF_3CH_2OH, MeOH) promote formation of the zwitterionic hydrogen species whereas a weaker one (*t*-BuOH, EtOH) also allows Pt(IV) hydride formation and gives rise to a product mixture. The fact that CF_3CH_2OH and EtOH give such different results also shows that steric factors are not playing an important role. In the mechanism to form the hydrides, the second step, β-elimination, does not seem to be adversely affected by the presence of a protic solvent and complex **2**, for example, was identified spectroscopically in the presence of *t*-BuOH. The experiments with *t*-BuOD give further insight into the role of protic solvents. The formation of small amounts of the deuterated zwitterionic complex is consistent with the *t*-BuOH reaction and the formation of a small amount of acid. However, although the presence of significant amounts of the Pt(IV) deuteride alongside the Pt(IV) hydride seems to suggest that the solvent is also playing a role in the step from the Pt–Sn complex **2** to the final product; this is not the case. The deuteride results from proton/deuterium exchange of the originally formed Pt(IV) hydride with *t*-BuOD; such exchange reactions are well-known for terminal metal hydrides in the presence of protic solvents.[45]

The results of the reactions of *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C*,*N*$)_2$ with Me_2SnBr_2 (see Table II) contrast markedly with those of *cis*-Pt(1-$C_{10}H_6NMe_2$-8-*C*,*N*$)_2$; the zwitterionic hydrogen complex PtBr($C_6H_4CH_2NMe_2$-2-*C*,*N*)($C_6H_4CH_2NHMe_2$-2-*C*,*H*) is always formed, never the corresponding tautomeric Pt(IV) hydride. The mechanism to explain this begins, as for *cis*-Pt(1-$C_{10}H_6$-NMe_2-8-*C*,*N*$)_2$, with the formation of a Pt–Sn complex (see eq 6), which is indeed observed by ^1H NMR spectroscopy during the reactions. Then, in the next step the β-elimination takes place to form the corresponding Pt(IV) hydride.[42b] What we propose (see eq 6) is that this hydride PtBr(H)($C_6H_4CH_2NMe_2$-2-*C*,*N*$)_2$ is an intermediate which can now isomerize, because of the presence of the flexible $-CH_2NMe_2$ moiety, to the more stable tautomer PtBr($C_6H_4CH_2NMe_2$-2-*C*,*N*)($C_6H_4CH_2NHMe_2$-2-*C*,*H*). With the $[C_6H_4CH_2NMe_2\text{-}2]^-$ ligand, the N-donor atom can move away from the platinum center and rotation of 180° around the C_{ipso}–C_{para} axis can take place. This is not possible in **1**, where the rigid naphthyl skeleton always keeps the nitrogen atoms within the Pt coordination sphere; isomerization of **1** to the zwitterionic hydrogen complex PtX(1-$C_{10}H_6NMe_2$-8-*C*,*N*)(1-$C_{10}H_6NHMe_2$-8-*C*,*H*) has never been observed or induced. Interestingly, the CAS–SCF energy difference between **F** and the Pd(IV) hydride system $[PdCl(H)(Me)_2(NH_3)_2]$[46] (in which the remote NH_3 of **F** now occupies the sixth coordination site trans to the hydride) is computed to be 12.6 kcal/mol, (see Chart I), thus indicating that (as expected from the strong trans influence of the hydride) the dissociation of an axial amine type ligand is relatively easy, at least in the Pd(IV) model complexes.



(6)

The Nature of the M···H-NH_3 Linkage and the Relative Stability of the Zwitterionic Hydrogen System and Its Hydride Tautomer. How do the present theoretical results for the M···H–NH_3 (M = Pd, Pt) system compare with the experimental results and other theoretical studies? In their review article, Green and Brookhardt characterize the agostic interaction as a two-electron donation of the σ C–H bond to an empty metal orbital.[6b] This results in a bent M–H–C geometry. In the zwitterionic species we have studied, i.e. PtBr(1-$C_{10}H_6NMe_2$-8-*C*,*N*)(1-$C_{10}H_6$-$NHMe_2$-8-*C*,*H*), the Pt···H–N linkage is almost linear, as it is in the $[(PtCl_4)\text{-}cis\text{-}PtCl_2(NH_2Me)_2]^{2-}$ dianion, where Orpen et al. also favor a 3c–4e description (with an electrostatic component).[8] Note that, in our complexes and that of Orpen et al., an anionic entity is involved. Another characteristic of agostic bonds is that they are easily displaced by a nucleophile.[6b] However, there is no indication of such behavior in our zwitterionic hydrogen complexes. Finally, there is an important gain in stabilization energy on going from **C** to **A** of 72.4 kcal/mol (the stabilization is even greater for the platinum system; see above), i.e. much higher than the 5–15 kcal/mol usually expected (experimentally[47] and theoretically[48]) for an agostic type of interaction.

One can now consider the role of an extra two-electron-donor ligand on the energy difference between the Pt(IV) hydride system and the zwitterionic hydrogen Pt(II) complex. To this end calculations were performed on the model system with an extra NH_3 group; the results are shown in Chart II (for the sake of comparison, the systems of this chart and those of Chart I are positioned in a similar way).[49] One sees that the addition of an extra ligand brings extra destabilization, except for the six-coordinate Pd(IV) hydride system. This is now comparatively less destabilized than the five-coordinate Pd(IV) hydride with respect to the zwitterionic hydrogen Pd(II) isomer (compare for instance the destabilization of **F** with respect to **A**, which amounts to 25.6 kcal/mol, and the destabilization of **E′** with respect to **A′**, which amounts to 12.8 kcal/mol). This 12.8 kcal/mol energy difference between the six-coordinate Pd(IV) hydride complex and the five-coordinate zwitterionic hydrogen Pd(II) complex makes formation of the former via the use of an electron-donating group most unlikely, unless differential solvation effects—not

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(43) For example: (a) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047. (b) Grady, G. L.; Kuivila, H. G. *J. Org. Chem.* **1969**, *34*, 2014.

(44) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 2.

(45) (a) Baker, M. V.; Field, L. D. *Organometallics* **1986**, *5*, 821. (b) Park, S.; Johnson, M. P.; Roundhill, D. M. *Organometallics* **1989**, *8*, 1700.

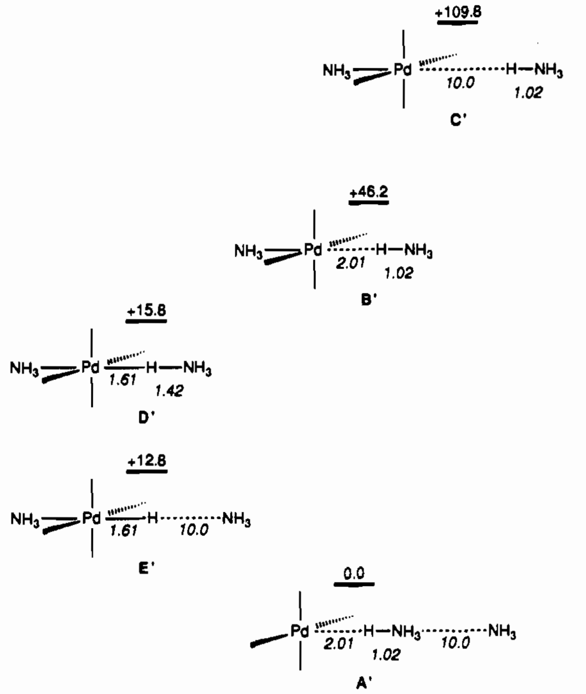
(46) The CAS–SCF energy of $[PdCl(H)(Me)_2(NH_3)_2]$ is −5578.3328 au.

(47) (a) Lichtenberger, D. L.; Kellog, G. L. *J. Am. Chem. Soc.* **1986**, *108*, 2560. (b) Gonzalez, A. A.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Khalsa, G. R. K.; Kubas, G. J. *ACS Symp. Ser.* **1990**, *428*, 133.

(48) (a) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108.

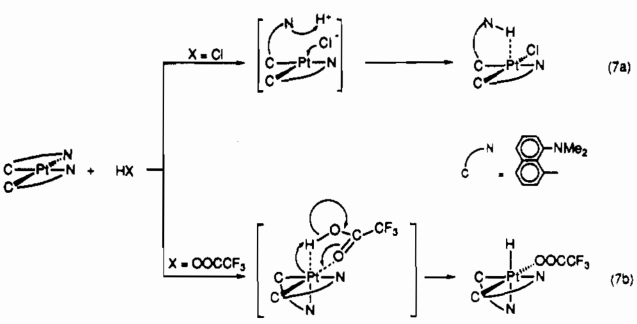
(49) CAS–SCF energies (in au): **A′**, −5634.4909; **B′**, −5634.4506; **C′**, −5634.3160; **D′**, −5634.4657; **E′**, −5634.4705. In these calculations eight electrons in eight active orbitals were correlated. This active space was obtained by adding to the active space described in ref 36 the lone pair of the second NH_3 ligand and its antibonding combination with $4d_{z^2}$.

Chart II. Energy Levels (Underlined) and Bond Distances (Italic) of the $[PdCl(H)(Me)_2(NH_3)_2\cdots NH_3]$ System[a]



[a] Relative energies in kcal/mol; bond distances in Å.

Scheme III. Mechanism of the Reaction of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with HX



taken into account here—turn out to be important. Finally, in the context of the interconversion process, it can be seen that the amine ligand, which is protonated in the zwitterionic system, does not need to depart too much from the coordination sphere to obtain an isomer with a typical palladium–hydride bond length: note, for instance, the relatively low destabilization of **D** and **E** with respect to **A** in Scheme I.

Reactions with HX. Reactions of HX with d^8 organometallic complexes have been widely reported, and a variety of mechanisms are known.[11-13] The reaction of *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ with an excess of HCl leads to protonation of the ligand and formation of the zwitterionic hydrogen complex $PtCl(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$,[1] whereas with CF_3COOH the hydride complex **1c** is obtained in an oxidative addition reaction. The Lewis basicity of the anion might be determining the reactivity pattern, but it is certainly not the factor that determines the possible type (zwitterionic versus hydridic) of the resulting complex. This is shown by the fact that the zwitterionic hydrogen complex $Pt(OOCCF_3)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ (formed in the reaction of $PtBr(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ with $AgOOCCF_3$) does not isomerize to the trifluoroacetate Pt(IV) hydride complex **1c**.

For these reactions of HX with *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ to form either a zwitterionic or hydridic product, we might propose two common mechanistic pathways. One is the oxidative addition reaction that begins with nucleophilic attack of the filled d_{z^2} orbital of the Pt center on the H^+ cation to form the five-coordinate square pyramidal Pt(IV) complex $[PtH(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2]^+$. The other involves a nucleophilic attack of the anion on an empty Pt orbital, and this is attended by nitrogen ligand dissociation and protonation. The second pathway (see eq 7a in Scheme III) was proposed as the operating mechanism for the formation of the zwitterionic complex $PtX(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$.[1] Formation of the hydride complex **1c**, containing a Pt(IV) center, is more in line with an oxidative addition reaction. However, in this case also, we propose nucleophilic attack of CF_3COOH on the metal complex attended by nitrogen dissociation. The fact that N protonation does not take place can be probably explained by the bridging character of the acetate group that "protects" the hydride during its formation; see the proposed intermediate in eq 7b in Scheme III. A precedent for such an intermediate comes from the reaction of *cis*-$Pt(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2$ with $Hg(OOCMe)_2$;[50] an X-ray structure shows that the product, i.e. $Pt(\mu\text{-}MeCO_2)(HgO_2CMe)(C_6H_4CH_2NMe_2\text{-}2\text{-}C,N)_2$, possesses an acetate group bridging over and stabilizing the Pt–Hg interaction.

Reactivity of the Hydride Complexes 1 and the Zwitterionic Hydrogen Complexes $PtX(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$. In the reactions of **1** and $PtX(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ with unsaturated reagents, the only reaction observed takes place when the poorly coordinating anion CF_3COO^- is present, i.e. when a free coordination site is available. The fact that **1c** and $Pt(OOCCF_3)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$ only reacted with dimethyl acetylenedicarboxylate shows that a highly activated unsaturated reagent with electron-withdrawing substituents is needed, to compete with the coordinating ability of the anion. Although we have not carried out mechanistic studies on this reaction, the trans stereochemistry of the final product **3** rules out the involvement of a four-center cyclic transition state (see Scheme II), which could be formed in a concerted addition of the alkyne to **1c**. This stereochemistry of **3** can be explained by an electron-transfer process as proposed earlier for insertion of acetylenes into Pt–H bonds.[39a] First, after dissociation of the CF_3COO^- anion and the coordination of the alkyne, electron transfer from the Pt center takes place. This is then followed by transfer of H^+ and of the Pt-containing moiety to the acetylene functionality, resulting in formation of **3**. This proposal gains support from the fact that the same product (**3**) is also obtained from the reaction of this alkyne with the zwitterionic hydrogen complex $Pt(OOCCF_3)(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,H)$, which has a bridging hydrogen with a protonic character. However, the Pt(IV) hydride reaction does not go through the zwitterionic transition state (as indicated in Scheme II); if this were so, rotation of the naphthyl ligand would have to take place, and this is not to be expected (vide supra). Therefore, in view of the fact that **3** is chiral, we think that the product of the zwitterionic reaction is the enantiomeric form of that of the hydride reaction. This is consistent with the fact that both products give the same ^1H NMR resonance pattern.

Conclusions

From the Pt(II) species *cis*-$Pt(1\text{-}C_{10}H_6NMe_2\text{-}8\text{-}C,N)_2$ and tin(IV) complexes some remarkably stable Pt(IV) hydride complexes containing a rigid C,N-chelating naphthylamine ligand have been synthesized and isolated. These Pt(IV) hydrides result from a β-H elimination from a Pt(II) intermediate containing a side-on-bonded Sn–X bond. An oxidative addition approach to such hydrides using HX is only successful when X = CF_3COO, because this group can provide anchimeric assistance; with HCl, a tautomeric zwitterionic hydrogen-bridged Pt(II) species results. Theoretical calculations show that a Pt(IV) hydride complex is not as stable as its corresponding Pt(II)$\cdots$H–N tautomer. Despite

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(50) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.

this stability difference, isomerization from the Pt(IV) hydride to the more stable tautomeric form has not been observed for the naphthylamine ligand system. However, a more flexible benzylamine ligand system allows such an isomerization and only the zwitterionic hydrogen Pt(II) tautomer has been found from the reaction of *cis*-Pt($C_6H_4CH_2NMe_2$-2-*C,N*)$_2$ with Me_2SnBr_2 in benzene or a mixture of *t*-BuOH and CH_2Cl_2. Although both theoretical and experimental results show no direct relationship between the hydride and zwitterionic tautomers, the fact that both complexes gave the same (enantiomeric) product in a reaction with dimethyl acetylenedicarboxylate is good evidence that they are chemically related.

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