

## Cyclometalated Platinum(II) Hydrides with Nitrogen Ligands

Antonio Zucca,\* Sergio Stoccoro, Maria Agostina Cinellu, Giacomo Luigi Petretto, and Giovanni Minghetti

Università degli Studi di Sassari, Dipartimento di Chimica, via Vienna 2, 07100 Sassari, Italy

Received May 31, 2007

Platinum(II) (N–N–C) cyclometalated hydrides, [Pt(N–N–C)H], (N–N–CH = 6-R-2,2'-bipyridine, R = benzyl, phenyl, alkyl) have been obtained by reaction of the corresponding chlorides with NaBH<sub>4</sub>. Alternatively, some of them can also be synthesized from formato derivatives [Pt(N–N–C)(OC(O)H)] by loss of CO<sub>2</sub> or from cationic carbonyl species, [Pt(N–N–C)(CO)]<sup>+</sup>, by reaction with NaBH<sub>4</sub>. <sup>1</sup>H NMR characterization reveals <sup>1</sup>J(Pt–H) values among the largest ever reported, ca. 1600 Hz. Dinuclear derivatives with a bridging hydride, [(N–N–C)Pt(μ-H)Pt(N–N–C)]<sup>+</sup>, both symmetric and unsymmetric, can be built up through a classical approach, i.e., by reaction of a mononuclear terminal hydride and a solvento cationic complex [Pt(N–N–C)(S)]<sup>+</sup>.

### Introduction

Since the first report in the late 1950s,<sup>1</sup> the chemistry of platinum(II) hydrido complexes mostly entails phosphorus donors as ancillary ligands.<sup>2</sup> In the almost 50 years elapsed since the beginning of their history, due to the growing general interest in the reactivity of transition metal–hydrogen bonds, an array of platinum(II) hydrides have been synthesized and their properties have been deeply investigated.<sup>3</sup> Nowadays, species with terminal, Pt–H, or bridging, Pt(μ-H)Pt, bonds are known: they comprise mono-, di-, and trinuclear derivatives as well as polynuclear species.<sup>4</sup> The most common ligands are tertiary phosphines, mono- or bidentate, the latter ones<sup>5</sup> tailored to act either as bridging or chelating ligands.

Complexes that contain, in addition to a Pt–P bond, a platinum–nitrogen bond are rare.<sup>6</sup> Other examples include species obtained by insertion of a zerovalent Pt(PR<sub>3</sub>)<sub>n</sub> moiety

into an N–H bond, e.g. *trans*-[Pt(H)(tetrazolato)(PPh<sub>3</sub>)<sub>2</sub>],<sup>7</sup> *trans*-[Pt(H)(imide)(PR<sub>3</sub>)<sub>2</sub>],<sup>8</sup> *trans*-[Pt(H)(C<sub>12</sub>H<sub>8</sub>N)(PR<sub>3</sub>)<sub>2</sub>](C<sub>12</sub>H<sub>9</sub>N = carbazolo),<sup>9</sup> and *trans*-[Pt(H)(1-azoly)(PEt<sub>3</sub>)<sub>2</sub>].<sup>10</sup> A mononuclear hydride with a hemilabile P–C–N pincer ligand, [Pt(H)(P–C–N)], H *trans* to C, has been described by Milstein.<sup>11</sup> The synthesis and X-ray structure of a hydride formed by N–H activation of an imidazolylphosphine ligand has been quite recently reported, H *trans* to N.<sup>12</sup> A dinuclear species, [(H)Pt-(PPh<sub>3</sub>)<sub>2</sub>(C<sub>10</sub>N<sub>8</sub>)(PPh<sub>3</sub>)<sub>2</sub>Pt(H)], where C<sub>10</sub>N<sub>8</sub>H<sub>2</sub> is 4,4',5,5'-tetra-cyano-2,2'-biimidazolo, was reported by Rasmussen et al.<sup>13</sup>

Prior literature reports of species with only nitrogen ligands are few in number: (i) a dinuclear complex stabilized by a N–C–N pincer ligand, [(N–C–N)Pt(μ-H)Pt(N–C–N)]<sup>+</sup>, H *trans* to C, was described several years ago by Grove and van Koten as an unusual species in which the metals are only bridged by a single atom.<sup>14</sup> The related terminal hydride, [Pt(N–C–N)(H)], was not isolated although the formation of the dinuclear complex implies a Lewis acid–base pairing reaction between a terminal hydrido and a solvento cationic species; (ii) the first mononuclear cyclometalated hydride, [Pt(N–N–C)H], H *trans* to N, was isolated and spectroscopically characterized by us with a chiral substituted 2,2'-bipyridine, (N–N–CH = 6-(1-methylbenzyl)-2,2'-bipyridine).<sup>15</sup> A Lewis acid–base approach

\* Corresponding author. E-mail: zucca@uniss.it.

(1) (a) Chatt, J.; Duncanson, L. A.; Shaw, B. L. *Proc. Chem. Soc.* **1957**, 343. (b) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.

(2) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, sixth edition; John Wiley & Sons Inc.: New York, 1999; p 1077.

(3) e.g. (a) Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic Press: London, 1974. (b) *Comprehensive Coordination Chemistry* 2nd ed.; Elsevier: New York, 2003; Vol. 6, pp 717–720. (c) Butts, M. D.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831.

(4) Anderson, G. K. In *Chemistry of the Platinum Group Metals, Recent Development*; Hartley, F. R., Ed.; Elsevier: New York, 1991; pp 376–383.

(5) Bridging phosphines: (a) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L27. (b) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc. Dalton Trans.* **1978**, 516. (c) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Gossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642. (d) Xu, C.; Anderson, G. K. *Organometallics* **1994**, *13*, 3981. (e) Xu, C.; Anderson, G. K. *Organometallics* **1996**, *15*, 1760. Chelating phosphines: (a) Minghetti, G.; Banditelli, G.; Bandini, A. L. *J. Organomet. Chem.* **1977**, *139*, C80. (b) Tulip, T. H.; Yamagata, T.; Yoshida, T.; Wilsom, R. D.; Ibers, J. A.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 2239. (c) Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1983**, *22*, 2324. (d) Chiang, M. Y.; Bau, R.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Koetzle, T. F. *Inorg. Chem.* **1984**, *23*, 122. (e) Bandini, A. L.; Banditelli, G.; Cinellu, M. A.; Sanna, G.; Minghetti, G.; Demartin, F.; Manassero, M. *Inorg. Chem.* **1989**, *28*, 404. (f) Craswell, L. E.; Spencer, J. L. *J. Chem. Soc. Dalton Trans.* **1995**, 2391. (g) Mole, L.; Spencer, J. L.; Litsler, S. A.; Redhouse, A. D. Carr, N.; Orpen, A. G. *J. Chem. Soc.* **1966**, 2315.

(6) e.g. (a) Gavrilova, I. V.; Gel'fman, M. I.; Razumosvskii, V. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1974**, *19*, 1360. *trans*-[Pt(H)(NH<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. (b) Cowan, R. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 2451. *trans*-[Pt(H)(NHPh)(PEt<sub>3</sub>)<sub>2</sub>]. (c) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3974. *trans*-[Pt(H)(NH<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>]. [Pt(H)(μ-NH<sub>2</sub>)-(PR<sub>3</sub>)<sub>2</sub>]. (d) Chang, X.; Lee, K.-E.; Kim, Y.-I.; Lee, S. W. *Inorg. Chim. Acta* **2006**, *359*, 4436. *trans*-[Pt(H)(N<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>].

(7) Nelson, J. H.; Schmitt, D. L.; Henry, R. A.; Moore, D. W.; Jonassen, H. B. *Inorg. Chem.* **1970**, *9*, 2678.

(8) Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254.

(9) Garcia, J. J.; Casado, A. L.; Iretskii, A.; Adams, M.; Maitlis, P. M. *J. Organomet. Chem.*, **1998**, *558*, 189–192.

(10) Chantson, J. T.; Lotz, S. J. *Organomet. Chem.* **2004**, *689*, 1315–1324.

(11) Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Chem. Eur. J.* **2004**, *10*, 4673.

(12) Grotjahn, D. B.; Gong, Y.; Di Pasquale, A. G.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2006**, *25*, 5693–5695.

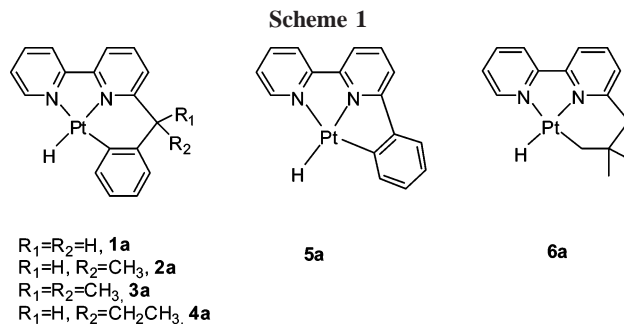
(13) Bayon, J. C.; Kolowich, J. B.; Rasmussen, P. G. *Polyhedron* **1987**, *6*, 341–343.

(14) Grove, D. M.; Van Koten, G.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4285–86.

(15) Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Chelucci, G.; Zucca, A. *Inorg. Chem.* **1990**, 5137–5138.

allowed us to obtain also in this case a cationic dinuclear complex,  $[(N-N-C)Pt(\mu-H)Pt(N-N-C)]^+$ ; (iii) recently, two other dinuclear cyclometalated platinum(II) hydrido species,  $[Pt_2(\text{terpy-2H})(H)_2(L)_2]$  ( $\text{terpy-2H} = 2\text{-fold deprotonated } 2,2':6',2''\text{-terpyridine}$ ;  $L = \text{DMSO, PPh}_3$ ),  $H$  trans to  $N$ , have been described by us<sup>16</sup> and spectroscopic evidence for the formation of a hydride in the reaction of a  $[Pt(N-N-C)Cl]$  complex ( $N-N-CH = 2\text{-phenyl-6-(2-aminoisopropyl)pyridine}$ ) with  $K[BH_3(\text{t-Bu})_3]$  has been provided by Song and Morris;<sup>17</sup> (iv) recent examples include a cationic species with a neutral diamino ligand,  $[Pt(=C(\text{CH}_3)\text{OCH}_2\text{CH}_3)(\text{tmeda})H]^+$ ,<sup>18</sup> trispyrazolylborato mono- and dinuclear species<sup>19</sup> and a few Pt(II) olefin hydride complexes.<sup>20</sup>

On the whole, the platinum(II) hydrides stabilized only by nitrogen donors are still rare and their properties and reactivity are mostly unexplored. In contrast, in recent years, especially in organometallic chemistry, much attention has been paid to the analogous platinum(IV) hydrides.<sup>21</sup> Indeed diimine and diamine complexes of platinum(II) are currently investigated as models for the C–H bond-activation step in selective oxidation of hydrocarbons<sup>22</sup> and as being effective homogeneous catalysts for methane oxidation by sulfuric acid.<sup>23</sup> This implies that hydrido platinum(IV) species with nitrogen ligands can be involved in the path of a reaction of paramount importance such as the intermolecular activation of hydrocarbon C–H bonds. It is time, therefore, to extend our knowledge on analogous platinum(II) hydrides, to investigate their stability, properties, and reactivity, and eventually to gain information on their relationship with the corresponding platinum(IV) derivatives. A very recent work by Templeton and co-workers,<sup>24</sup> dealing with stoichiometric alkane dehydrogenation, reports for instance the conversion by protonation of a Pt(IV) hydride,  $[Pt(\kappa^3\text{-Tp}')(\eta^2\text{-cyclo-alkene})(H)]$  ( $\text{Tp}' = \text{hydridotris(3,5-dimethylpyrazolyl)-borate}$ ), into a cationic Pt(II) hydride,  $[Pt(\kappa^2\text{HTp}')(\eta^2\text{-cyclo-alkene})(H)]^+$ , characterized, inter alia, by a X-ray structural analysis. Following our previous communication,<sup>15</sup> herein we report the synthesis and spectroscopic characterization of some new cyclometalated platinum(II) hydrides, both mono- and dinuclear,  $[Pt(N-N-C)H]$  and  $[\{Pt(N-N-C)\}_2(\mu-H)]^+$ , respectively, where  $N-N-CH$  is a 6-benzyl-, 6-phenyl-, and 6-alkyl-substituted 2,2'-bipyridine. As previously mentioned, the

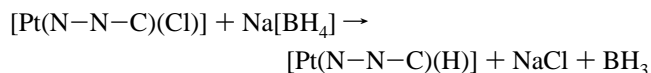


reactivity of these species is unknown: according to a recent review on C–H activation by platinum complexes,<sup>22g</sup> cyclometalated systems have hitherto been underutilized and may offer great opportunities for future investigations in the field of hydrocarbon functionalization.<sup>25</sup> In addition, platinum(II) hydrides are intrinsically worthy of interest, owing to their reactivity, in particular toward alkenes and alkyne.<sup>2,26</sup>

## Results and Discussion

**Mononuclear Hydrides,  $[Pt(N-N-C)(H)]$ , **1a–6a**.** The starting materials for their synthesis were in all cases the corresponding chlorides,  $[Pt(N-N-C)(Cl)]$  that were obtained by literature methods.<sup>27</sup> The ligands, 6-R-2,2'-bipyridine,  $N-N-CH$ , **1–7** ( $R = \text{benzyl, 1; 1-methylbenzyl, 2; 1,1'-dimethylbenzyl, 3; 1-ethylbenzyl, 4; phenyl, 5; neopentyl, 6; isopropyl, 7}$ ) were prepared as previously described from 6-nitrile-substituted pyridines and acetylene in the presence of a cobalt(I) catalyst.<sup>28</sup> Compounds **1a–4a** (Scheme 1) entail [5,6] fused cyclometalated rings, whereas **5a** contains [5,5] membered rings.

From the chlorides, compounds **1a–5a** can be obtained through an exchange reaction with  $Na[BH_4]$ :



In the case of compound **2a**, the synthesis was at first carried out in methanol solution, as reported in our preliminary communication:<sup>15</sup> the yields of these reactions have been later improved working in THF and adding solid  $Na[BH_4]$  little by little: some decomposition to metal however occurs and yields are moderate (ca. 70%). Compounds **1a–4a** have been fully characterized whereas complex **5a** has been identified spectroscopically in a mixture of mono- and dinuclear hydrides (see Experimental Section). Spectroscopic data account for the terdentate behavior of the  $N-N-C$  ligands: in particular in

(25) Reference 22g, page 2522.

(26) (a) Meyer, W. R.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 529. (b) Arnold, D. P.; Bennet, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (c) Minghetti, G.; Albinati, A.; Bandini, A. L.; Banditelli, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 120.

(27) (a) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107. (b) Sanna, G.; Minghetti, G.; Zucca, A.; Pilo, M. I.; Seeber, R.; Laschi, F. *Inorg. Chim. Acta* **2000**, *305/2*, 189–205. (c) Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, T. A. *J. Chem. Soc., Chem. Commun.* **1990**, 513. (d) Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, T. *J. Chem. Soc., Dalton Trans.* **1990**, 443. (e) Romeo, R.; Plutino, M. R.; Monsù Scolaro, L.; Stoccoro, S.; Minghetti, G. *Inorg. Chem.* **2000**, *39*, 4749–4755.

(28) (a) Bönnemann, H.; Brijoux, W. *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1984; Vol. 5, pp 75–196. (b) Azzena, U.; Chelucci, G.; Delogu, G.; Gladiali, S.; Marchetti, M.; Soccolini, F.; Botteghi, C. *Gazz. Chim. Ital.* **1986**, *116*, 307. (c) Botteghi, C.; Chelucci, G.; Chessa, G.; Delogu, G.; Gladiali, S.; Soccolini, F. *J. Organomet. Chem.* **1986**, *304*, 217.

(16) Stoccoro, S.; Zucca, A.; Petretto, G. L.; Cinellu, M. A.; Minghetti, G.; Manassero, M. *J. Organomet. Chem.* **2006**, *691*, 4135–4146.

(17) Song, D.; Morris, R. H. *Organometallics* **2004**, *23*, 4405–4413.

(18) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848–849.

(19) Reinartz, S.; Baik, M.-H.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **2001**, *40*, 4726–4732.

(20) (a) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804–6805. (b) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286–15287. (c) Kloek, S. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2007**, *129*, 3460–3461.

(21) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219–221*, 157–185.

(22) (a) Shilov, A. E.; Shul'pin G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic: Dordrecht, 2000; p 560. (b) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371. (d) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (e) Heyduk, A. F.; Zhong, H. A.; Labinger, J. E. In *Activation and Functionalization of C-H Bonds*; Goldberg, K. I., Goldman, A. S., Eds.; ACS Symposium Series No. 885; American Chemical Society: Washington, D.C. 2004; pp 250–263. (f) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (g) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471–2526.

(23) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560. (b) Young, K. J. H.; Meier, S. K.; Gonzales, J.; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2006**, *25*, 4734–4737 and references therein.

(24) Kostelansky, C. N.; MacDonald, M. G.; White, P. S.; Templeton, J. L. *Organometallics* **2006**, *25*, 2993–2998.

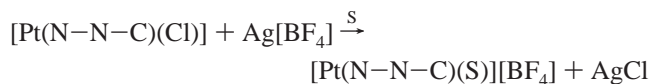
the IR spectra the absence of the band around  $700\text{ cm}^{-1}$  typical for monosubstituted phenyl groups, is indicative of the persistency of the ortho metalation; in the  $^1\text{H}$  NMR spectra the strong deshielding of the H(6') resonance and its coupling to  $^{195}\text{Pt}$  warrants the bonding of the external nitrogen atom. The IR and  $^1\text{H}$  NMR spectra also provide unambiguous evidence for a terminal Pt–H bond. In the IR spectra (both in Nujol and in solution), a medium band, typically in the range of  $2157\text{--}2126\text{ cm}^{-1}$ , can be assigned to a Pt–H stretch. In the case of complex **2a**, the assignment was confirmed by comparison with the corresponding deuteride. In the  $^1\text{H}$  NMR spectra of compounds **1a–4a**, a signal at high field, around  $\delta -13.5$  ppm, is diagnostic for a hydrido ligand. The resonance is a singlet, flanked by satellites due to coupling with  $^{195}\text{Pt}$  (natural abundance 33.8%) in the ratio 1:4:1 expected for a mononuclear complex. The coupling constants  $^1\text{J}(\text{Pt–H})$ , ca. 1600 Hz, anticipated to be large as a consequence of the hydride being trans to a donor with a low trans influence, are among the largest ever reported.<sup>29</sup> Somewhat different values of chemical shift,  $\delta -9.72$  ppm, and  $^1\text{J}(\text{Pt–H})$ , 1460 Hz, are observed for complex **5a**, which is unique, having a [5,5] in place of a [5,6] fused cyclometalated ring.

Compounds **1a–4a** are expected to have a boat-like conformation, as observed in the structures of related compounds, e.g., the corresponding chlorides.<sup>27a</sup> In solution, **1a** and **3a** are fluxional on the NMR time scale in a wide range of temperatures (from room temperature down to  $-80\text{ }^\circ\text{C}$ ), as shown by the single resonance of the benzylic protons and of the methyl groups in **1a** and **3a**, respectively. In the NMR spectra of compounds **2a** and **4a**, only one set of signals is observed for the hydrogen and the alkyl substituent on the stereogenic carbon atom. The experimental data can fit either a rigid or a dynamic behavior: in the former hypothesis, the spectra are consistent with only one conformer in solution. In complex **2a**, if a boat conformation is assumed, the methyl substituent on the benzylic carbon can be directed toward the platinum atom: indeed in the  $^1\text{H}$  NMR spectrum, registered at low field (80 MHz), a small long-range Pt–CH<sub>3</sub> coupling (4 Hz) is observed, indicative of some kind of interaction of the methyl group with the metal. The resonance of the methyl group is shifted downfield with respect to the ligand, suggesting a “preagostic” interaction.<sup>30</sup> At variance, a dynamic behavior cannot be completely ruled out: the flipping of the boat can be rapid on the NMR time scale and the coupling of the methyl protons with the platinum atom can actually be an average value. Although in the case of the new hydrides no crystals of X-ray quality were obtained, the conformer with the substituent toward the platinum atom is likely to be favored, even in the solid state, as pointed out, e.g., by the structure of [Pd(N–N–C)Cl], (N–N–CH = **2**): the methyl group is shown to be on top of the metal at ca.  $2.9\text{ \AA}$  distance.<sup>27a</sup>

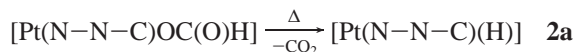
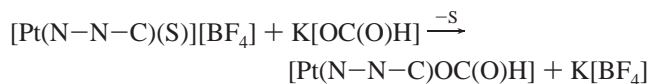
The presence of substituents on the benzylic carbon strongly affects the stability of the hydrido compounds **1a–4a**: compound **1a**, having no substituents, is the least stable in the series and decomposes also in the solid state in a few hours. In contrast, complex **3a** is extremely stable both in solution and in the solid state, in chlorinated solvents and in the presence of air. In the solid state, in air, it can be indefinitely stored. Compounds **2a**

and **4a**, with only one substituent on the benzylic carbon atom, are intermediate, showing a fair stability both in solution and in the presence of air. It is reasonable to assume that the peculiar stability supplied by the alkyl substituents is related to their interaction with the metal. Also, the  $^1\text{H}$  NMR data show a dependence on the presence of substituents: the  $^1\text{J}(\text{Pt–H})$  values in the series are 1600 Hz **1a**, 1606 Hz **2a** and **4a**, and 1628 Hz **3a**, indicative of a stronger Pt–H bond on going from **1a** to **3a**. The same trend has been previously observed as for the  $^1\text{J}(\text{Pt–P})$  values in analogous cationic phosphine derivatives [Pt–(N–N–C)(PPh<sub>3</sub>)]<sup>+</sup>.<sup>27b</sup> The weak (C–H)–Pt interaction may not be the only cause of stability; kinetic factors also can play a role: a relatively bulky substituent above the metal can contribute to provide inertness to the more substituted systems.<sup>31</sup>

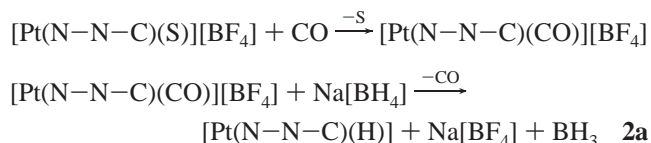
The hydrido derivatives can also be obtained by means of two alternative syntheses, as exemplified for complex **2a**, namely from a formate species



where S = acetone, methanol, or water



and from a cationic carbonyl complex:



Under strictly controlled conditions (see Experimental Section), mononuclear formate complexes<sup>32</sup> were obtained in good yields and were fully characterized analytically and spectroscopically (IR,  $^1\text{H}$  NMR, and FAB-MS). CO<sub>2</sub> elimination to give the hydride, e.g., **2a**, can be attained by heating a solid sample of the formate under vacuum for several hours. The carbonyl derivatives have been previously described:<sup>33</sup> the attack of the H<sup>−</sup> anion to the metal rather than to the coordinated carbonyl is likely favored by the cationic nature of the complex. An analogous conversion of a cationic carbonyl complex to a neutral hydride has been reported quite recently.<sup>34</sup>

All of the hydrido complexes **1a–5a** entail a platinum–carbon(sp<sup>2</sup>) bond: a terminal hydride, **6a**, with a cyclometalated 6-alkyl-2,2'-bipyridine, namely 6-neopentyl-2-2'-bipy, can be

(29) A comparable value has been reported only for [(tmeda)Pt(=C(Me)(OEt)H)]<sup>+</sup>: Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467–478.

(30) e.g. (a) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812–1817. (b) Albinati, A.; Anklin, C. G.; Ganazzoli, F.; Rüegg, H.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 508–513. (c) Lewis, J. C.; Wu, J.; Bergman, R. G.; Ellman, J. A. *Organometallics* **2005**, *24*, 5737–5736.

(31) One of the Referees argued that the stability of **3a** vs **1a** could be due to the lack of benzylic hydrogens rather than to the presence of the alkyl group. We note, however, even in **2a** as well as in **4a**, where a benzylic hydrogen is present, a certain increase in stability, so that complex **4a** is almost as stable as **3a**. Furthermore, as pointed out in the text, for **2a**, experimental evidence ( $^1\text{H}$  NMR) shows some kind of interaction, albeit small, of the alkyl group with the metal. In contrast, at least in platinum chemistry, in the course of our studies on the reactivity of species with these ligands, we never observed any involvement of the benzylic hydrogen atoms.

(32) Grove, M. D.; van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. *J. Organometal. Chem.* **1984**, *263*, C10.

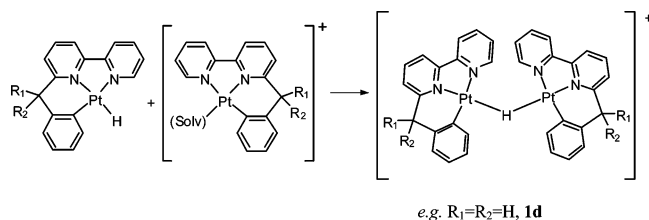
(33) Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2002**, 3336–3346.

(34) Schwartsburd, L.; Poverenov, E.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2007**, *26*, 2931–2936.



obtained from the corresponding cationic carbonyl derivative,  $[\text{Pt}(\text{N}-\text{N}-\text{C})(\text{CO})][\text{BF}_4]$ , provided a large excess of  $\text{Na}[\text{BH}_4]$  is employed. Complex **6a** has been characterized spectroscopically: the  $^1\text{H}$  NMR parameters, e.g.,  $^1\text{J}(\text{Pt}-\text{H}) = 1572$  Hz, give evidence for a terminal Pt-H bond. With a smaller  $\text{Na}[\text{BH}_4]/\text{Pt}$  molar ratio (ca. 3:1), a mixture of **6a** and a bridging hydride (see later) are formed. With respect to benzyl derivatives **1a-4a**, it seems that mononuclear hydrido complexes originated from ligands **6** and **7** (**6a**, **7a**) convert easier to dimeric species **6d** and **7d**, so that their isolation in pure form is hampered or requires a more troublesome work up and yields are somewhat erratic. On the whole, hydrides derived from the alkyl substituted bipyridines appear less stable in solution and in the solid state than **2a-4a**.

**Dinuclear Hydrides,  $[\text{Pt}_2(\text{N}-\text{N}-\text{C})_2(\mu-\text{H})][\text{BF}_4]$ , **1d-7d**.** Dinuclear hydrido-bridged cations,  $[\text{Pt}_2(\text{N}-\text{N}-\text{C})_2(\mu-\text{H})][\text{BF}_4]$ , **1d-4d**, have been obtained taking advantage of a general approach originally employed to synthesize mixed-metal clusters and called "metal hydride coupling".<sup>35</sup> In our case, it consists of the reaction between a mononuclear hydride, acting as a Lewis base, and a cationic solvento species able to act as a Lewis acid, to form a complex with a bridging hydride:<sup>36</sup>



In platinum(II) chemistry, this approach has been previously used, either directly, e.g., to synthesize dihydrido bridged cations,  $[(\text{PR}_3)_2\text{Pt}(\mu-\text{H})_2\text{Pt}(\text{PR}_3)_2]^+$ , by reaction of  $\text{Pt}(\text{H})_2(\text{PR}_3)_2$  and  $[\text{PtH}(\text{S})(\text{PR}_3)_2]^+$ ,<sup>37</sup> or indirectly, to rationalize the synthesis of other dinuclear species without isolation of a mononuclear hydride.<sup>14,5c</sup>

As a starting point, the reactions of the mononuclear hydrides **1a-4a** were carried out with the relevant solvento species (**1s-4s**), e.g. **1a+1s**, **2a+2s**, etc. The cationic species **1s-4s** were obtained from the corresponding chlorides by abstraction of the halide with  $\text{Ag}^+$  salts in poorly coordinating solvents (methanol or acetone). The resulting dinuclear hydrido-bridged cations **1d-4d** contain the same N-N-C ligand on each platinum atom.

All of the species have been isolated as the tetrafluoroborate salts: they are crystalline solids, air-stable, soluble in acetone and dichloromethane, which were characterized by elemental analyses, conductivity measurements, IR, and NMR spectroscopy. In the IR spectra, no absorption assignable to a bridging hydride is observed. In the hydride region, the  $^1\text{H}$  NMR spectra of compounds **1d** and **3d** show a quintet due to the existence in the dinuclear system of three isotopomers, namely Pt-Pt (43.8%), Pt-<sup>195</sup>Pt (44.8%), and <sup>195</sup>Pt-<sup>195</sup>Pt (11.4%) (where <sup>195</sup>Pt is the isotope with  $I = 1/2$  in 33.8% abundance and Pt represents all the other isotopes with  $I = 0$ ). The three isotopomers, present in the approximate ratio of 4:4:1, give rise respectively to a singlet, a doublet, and a triplet in the  $^1\text{H}$  resonances. The superposition of the three subspectra appears as a quintet of relative intensity 1:8:18:8:1, where the signals

are separated by  $1/2$   $^1\text{J}(\text{Pt}-\text{H})$ . The  $^1\text{J}(\text{Pt}-\text{H})$  values, 880 and 940 Hz for **1d** and **3d**, respectively, are large when compared with those previously observed for dinuclear species with phosphorus ligands as well as with those reported by van Koten,<sup>14</sup> (H trans to C), but reasonable taking account of the values in the corresponding H trans to N mononuclear species **1a** and **3a**. The  $^1\text{H}$  NMR spectra of complexes **2d** and **4d**, which contain two stereogenic carbon atoms, show two sets of signals assignable to two diastereoisomers in a roughly 1:1 ratio: in particular, in the hydride region, two resonances with the expected pattern (although not fully resolved) appear at  $\delta -14.90$  and  $-15.95$ , **2d**,  $\delta -14.80$  and  $-15.85$ , **4d** with  $^1\text{J}(\text{Pt}-\text{H})$  values comparable with those of compounds **1d** and **3d**.

Finally, as previously mentioned, also in the case of ligands **5-7** dinuclear hydrides, **5d-7d**, were observed in solution. Under strictly controlled conditions, complexes **6d** and **7d** can be separated from the mixture (see Experimental Section).

A reaction between a terminal hydride and a solvento cationic species with different metallacycles, e.g., reaction of **3a** with **2s**, allows us to achieve unsymmetric dinuclear hydrides, mostly rather unstable in the solid state. In solution, as revealed by the  $^1\text{H}$  NMR spectra, a mixture of hydrides is observed: the major product is always the dinuclear species with different metallacycles accompanied by the two hydrides with the same N-N-C ligand. Formation of the latter ones, identified by comparison with the isolated complexes **1d-4d**, suggests that both of the platinum-hydrogen bonds are rather labile.

## Experimental Section

Ligands **1-7** were prepared as previously described.<sup>28</sup> The chlorides  $[\text{Pt}(\text{N}-\text{N}-\text{C})(\text{Cl})]$  (NNCH = **1-5**) were synthesized according to ref 27; the carbonyl compounds  $[\text{Pt}(\text{N}-\text{N}-\text{C})(\text{CO})][\text{BF}_4]$  (N-N-CH = **6-7**) were synthesized as indicated in ref 33.

All of the solvents were purified and dried according to standard procedures.<sup>38</sup> Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240B by Mr. Antonello Canu (Dipartimento di Chimica, Università degli studi di Sassari, Italy). Infrared spectra were recorded with a FT-IR Jasco 480P using nujol mulls.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0 and 75.4 MHz, respectively. NOE difference and 2D-COSY experiments were performed by means of standard pulse sequences. Chemical shifts are given in ppm relative to internal TMS. The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11 250J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix. Conductivities were measured with a Philips PW 9505 conductimeter.

**Solvato Species:  $[\text{Pt}(\text{N}-\text{N}-\text{C})(\text{S})][\text{BF}_4]$  (S = Acetone or MeOH).** The solvato species **1s-4s** ( $[\text{Pt}(\text{N}-\text{N}-\text{C})(\text{S})][\text{BF}_4]$  (N-N-CH = **1-4**, S = acetone, methanol, or water) were obtained by reaction of the corresponding chlorides  $[\text{Pt}(\text{N}-\text{N}-\text{C})\text{Cl}]$  with  $\text{AgBF}_4$  (1:1 molar ratio) in acetone or methanol as previously described.<sup>15</sup>

**1s:** Yellow, yield 75%, mp > 270 °C. **2s:** yellow, yield 60%, mp 205 °C (dec).  $\Lambda_M$  70.4  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  ( $5 \cdot 10^{-2} \text{M}$ , acetone). **3s:** Yield 60%. **4s:** Yield 65%.

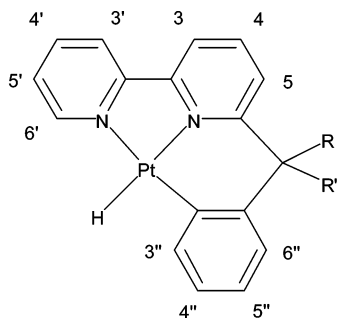
**1a-5a,  $[\text{Pt}(\text{N}-\text{N}-\text{C})\text{H}]$ , General Procedure.** To a refluxing suspension of the corresponding chloride  $[\text{Pt}(\text{N}-\text{N}-\text{C})(\text{Cl})]$  (0.4 mmol) in freshly distilled THF were added, under argon atmosphere, 3 equiv of  $\text{NaBH}_4$  in three parts every 20 min. After the additions,

(35) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8065.

(36) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

(37) (a) Bachechi, F.; Bracher, G.; Grove, D. M.; Kellenberger, B.; Pregosin, P. S.; Venanzi, L. M.; Zambonelli, M. *Inorg. Chem.* **1983**, *22*, 1031. (b) Paonessa, R. S.; Troglor, W. C. *Inorg. Chem.* **1983**, *22*, 1038.

(38) *Vogel's Textbook of Practical Organic Chemistry*, fifth edition; Longman Scientific and Technical Ed.: Harlow, 1989.



NMR Numbering scheme for species 1a-4a

the mixture was heated to reflux for 2 h to give a red suspension, which was cooled on an ice bath and filtered over celite. The solution was concentrated to small volume and treated with pentane. The precipitate formed was filtered and vacuum pumped to give the analytical sample as an orange-red compound. (Workup procedures under inert atmosphere using standard Schlenk-type techniques).

The hydrides **1a** and **2a** can also be obtained by keeping a solid sample of the corresponding formate (see later) under vacuum in a dry oven at 150 °C for several hours.

**1a:** Yield 72%, mp 170–175 °C (dec). Anal. calcd for  $C_{17}H_{14}N_2Pt$ : C, 46.26; H, 3.20; N, 6.35%. Found: C, 45.96; H, 3.19; N, 5.98.  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$ : 9.35 (d, 1H,  $H_{6'}$ ,  $J_{H-H} = 5.4$  Hz,  $J_{Pt-H} = 25$  Hz); 8.12–7.94 (m, 4H, overlapping signals,  $H_{4'}$ ,  $H_4$ ,  $H_{3'}$ ,  $H_{3''}$ ), 7.82 (d, 1H,  $H_3$ ,  $J_{H-H} = 7.8$  Hz); 7.61 (d, 1H,  $H_5$ ,  $J_{H-H} = 7.8$  Hz); 7.44 (m, 1H,  $H_{5'}$ ); 7.10 (d, 1H,  $H_{6''}$ ,  $J_{H-H} = 7.5$  Hz,  $J_{Pt-H} = 14$  Hz); 6.91 (t, 1H,  $H_{4''}$ ,  $J_{H-H} = 1.4$ , 7.5 Hz), 6.83 (t, 1H,  $H_{5''}$ ,  $J_{H-H} = 1.8$ , 7.5 Hz); 4.57 (s, 2H,  $CH_2$ ); –13.64 (1H, s with satellites, Pt–H,  $J_{Pt-H} = 1600$  Hz).  $^{13}C$  NMR ( $CD_2Cl_2$ )  $\delta$ : 50.7 ( $CH_2$ ), 120.1, 122.8, 122.9, 128.8, 126.1, 126.3, 127.7, 137.3, 137.9, 149.4, 155.4, 155.8 (quaternary carbon atom), 160.4 (quaternary carbon atom). MS FAB ( $m/z$ ): 441 [ $M^+$ ], 881 [ $M_2 - H^+$ ]. IR (Nujol,  $cm^{-1}$ ) 2139 s, 1600 s.

**2a:** Yield 75%, mp 210–212 °C. Anal. calcd for  $C_{18}H_{16}N_2Pt$ : C, 47.46; H, 3.51; N, 6.15%. Found: C, 47.35; H, 3.69; N, 6.15%.  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$ : 9.35 (d, 1H,  $H_{6'}$ ,  $J_{Pt-H} = 24$  Hz,  $J_{H-H} = 5.2$  Hz); 8.06 (td, 1H,  $H_{4'}$ ,  $J_{H-H} = 7.9$  Hz); 7.99 (t, 1H,  $H_4$ ,  $J_{H-H} = 7.9$  Hz); 7.96 (d, 1H,  $H_{3'}$ ,  $J_{H-H} = 7.9$  Hz); 7.92 (d, 1H,  $H_{3''}$ ,  $J_{H-H} = 7.5$  Hz), 7.88 (d, 1H,  $H_3$ ,  $J_{H-H} = 7.9$  Hz), 7.61 (d, 1H,  $H_5$ ,  $J_{H-H} = 7.9$  Hz); 7.44 (m, 1H,  $H_{5'}$ ); 7.10 (d, 1H,  $H_{6''}$ ,  $J_{H-H} = 7.5$  Hz); 6.92 (td, 1H,  $H_{4''}$ ,  $J_{H-H} = 1.4$ , 7.5 Hz); 6.87 (td, 1H,  $H_{5''}$ ,  $J_{H-H} = 1.8$ , 7.5 Hz); 4.42 (q, 1H;  $CHCH_3$ ,  $J_{H-H} = 7.0$  Hz); 1.77 (d, 3H,  $CH_3$ ,  $J_{H-H} = 7.0$  Hz). –13.52 (1H, s with satellites, Pt–H,  $J_{Pt-H} = 1606$  Hz). The assignment of NMR signals is based on 2D-COSY experiments. MS (FAB)  $m/z$ : 455 [ $M^+$ ]. IR (Nujol,  $cm^{-1}$ ) 2157 s.

The deuteride complex [Pt(N–N–C)(D)] (N–N–CH = 2) was obtained following the procedure described for the hydrides using  $NaBD_4$  instead of  $NaBH_4$ . Yield 50%.

**3a:** In this case, the reaction time was enhanced to 15 h, with five additions of  $NaBH_4$  of 1.5 equiv each: Yield 75%, mp 218 °C (dec). Anal. calcd for  $C_{19}H_{18}N_2Pt$ : C, 48.61; H, 3.86; N, 5.97%. Found: C, 47.98; H, 3.27; N, 5.76%.  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$ : 9.37 (dd, 1H,  $H_{6'}$ ,  $J_{H-H} = 5.5$  Hz,  $J_{Pt-H} = 22$  Hz); 8.10 (td, 1H,  $H_{4'}$ ,  $J_{H-H} = 1.4$ , 7.8 Hz); 8.01 (t partially overlapping, 1H,  $H_4$ ,  $J_{H-H} = 7.8$  Hz); 7.99 (d partially overlapping,  $H_{3'}$ ,  $J_{H-H} = 7.8$  Hz), 7.89 (d,  $H_3$ ,  $J_{H-H} = 7.8$  Hz), 7.79 (2d overlapping, 2H,  $H_{3''} + H_5$ ), 7.44 (m, 1H,  $H_{5'}$ ,  $J_{H-H} = 1.4$ , 5.5, 7.8 Hz), 7.26 (dd,  $H_{6''}$ ,  $J_{H-H} = 1.4$ , 7.5 Hz,  $J_{Pt-H} = 17$  Hz), 6.87 (td, 1H,  $H_{5''}$ ,  $J_{H-H} = 1.8$ , 7.5 Hz), 6.75 (td, 1H,  $H_{4''}$ ,  $J_{H-H} = 1.4$ , 7.5 Hz), 2.09 (s, 6H,  $CH_3$ ); –13.47 (s with satellites, 1H, Pt–H,  $J_{Pt-H} = 1628$  Hz). The assignment of NMR signals is based on NOE difference and 2D-COSY experiments. MS (FAB)  $m/z$ : 469 [ $M^+$ ]. IR (Nujol,  $cm^{-1}$ ) 2126 s, 1589, 1566.

**4a:** Yield 60%, mp 208 °C (dec). Anal. calcd for  $C_{19}H_{18}N_2Pt$ : C, 48.61; H, 3.86; N, 5.97%. Found: C, 48.15; H, 3.98; N, 5.69%.  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 9.36 (d, 1H,  $H_{6'}$ ,  $J_{H-H} = 5.3$  Hz,  $J_{Pt-H} = 24$  Hz); 8.08 (td, 1H,  $H_{4'}$ ,  $J_{H-H} = 1.6$  Hz, 7.6 Hz); 8.00–7.93 (m, 3H overlapping,  $H_4$ ,  $H_{3'}$ ,  $H_{3''}$ ); 7.88 (d, 1H,  $H_3$ ,  $J_{H-H} = 7.5$  Hz); 7.56 (d, 1H,  $H_5$ ,  $J_{H-H} = 7.5$  Hz); 7.40 (ddd, 1H,  $H_{5'}$ ,  $J_{H-H} = 1.1$ , 5.3, 7.6 Hz); 7.04 (dd, 1H,  $H_{6''}$ ,  $J_{H-H} = 1.8$ , 7.5 Hz); 6.92 (td, 1H,  $H_{4''}$ ,  $J_{H-H} = 1.8$ , 7.5 Hz); 6.88 (td, 1H,  $H_{5''}$ ,  $J_{H-H} = 1.8$ , 7.5 Hz); 4.00 (t, 1H, C–H,  $J_{H-H} = 7.5$  Hz); 2.28 (m, 1H,  $CH_2$ ); 2.20 (m, 1H,  $CH_2$ ); 0.76 (t, 3H,  $CH_3$ ,  $J_{H-H} = 7.5$  Hz); –13.56 (s with satellites, 1H, Pt–H,  $J_{Pt-H} = 1606$  Hz). IR (Nujol,  $cm^{-1}$ ): 2156 s, 1592 m, 1568.

**5a:** In this case, a mixture of terminal (**5a**) and bridging (**5d**) hydrides is formed, as indicated by  $^1H$  NMR spectra (terminal: bridging molar ratio 5:2). In spite of making several attempts, we were not able to separate the compounds. Selected  $^1H$  NMR signals ( $CDCl_3$ )  $\delta$ : 9.45 (d,  $J_{H-H} = 5.2$  Hz,  $J_{Pt-H}$  not resolved,  $H_{6'}$ , bridging hydride); 9.18 (d,  $J_{H-H} = 5.4$  Hz,  $J_{Pt-H} = 20$  Hz,  $H_{6'}$ , terminal hydride), 8.53–7.02 (m, aromatics); –9.72 (s, Pt–H,  $J_{Pt-H} = 1460$  Hz, terminal hydride); –12.98 (s, Pt– $\mu$ H,  $J_{Pt-H} = 920$  Hz, bridging hydride).

**6a:** Isolation of the mononuclear species with N–N–CH = 6-neopentyl-2,2'-bipyridine, **6a**, is described later with the synthesis of the corresponding dinuclear hydride, **6d**.

**Dinuclear Hydrides [Pt<sub>2</sub>(N–N–C)<sub>2</sub>( $\mu$ -H)][BF<sub>4</sub>], 1d–7d: General Procedure.** To an acetone (or methanol) solution (20 mL) of a solvato species [Pt(N–N–C)(S)][BF<sub>4</sub>] (0.06 mmol) was added 1 equiv of the corresponding hydrido complex [Pt(N–N–C)(H)], **1a–4a**, under stirring. The solution was stirred for 1.5 h, filtered over celite, evaporated to small volume, and treated with diethyl ether. The precipitate formed was filtered and washed with Et<sub>2</sub>O to give the analytical sample.

**1d:** Yield 30%. Anal. calcd for  $C_{34}H_{27}BF_4N_4Pt_2$ : C, 42.16; H, 2.81; N, 5.78%. Found: C, 41.53; H, 3.02; N, 5.47%.  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$ : 10.40 (d, 2H,  $H_{6'}$ ,  $J_{H-H} = 5.3$  Hz); 8.28–6.81 (m, 20 H, aromatics), 4.64 (s, 4H,  $CH_2$ ); –16.00 (s with satellites, 1H, Pt–H,  $J_{Pt-H} = 880$  Hz). IR (nujol): 1060 s, br.

**2d:** Yield 70%, mp 225–30 (dec). Anal. Calcd for  $C_{36}H_{31}BF_4N_4Pt_2$ : C, 43.37; H, 3.11; N, 5.62. Found: C, 42.77; H, 3.36; N, 5.64.  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  10.8–6.7 (m, aromatics); 4.73 (q, CH,  $J_{H-H} = 7.5$  Hz); 4.67 (q, CH,  $J_{H-H} = 7.2$  Hz); 1.99 (d,  $CH_3$ ,  $J_{H-H} = 7.2$  Hz); 1.96 (d,  $CH_3$ ,  $J_{H-H} = 7.5$  Hz), 1.77 (d,  $CH_3$ ,  $J_{H-H} = 7.2$  Hz); –14.90 ( $J_{Pt-H} = 936$  Hz, singlet with satellites ca. 1:2:1); –15.95 ( $J_{Pt-H} = 880$  Hz, singlet with satellites ca. 1:2:1).  $L_M$  42  $ohm^{-1} cm^2 mol^{-1}$  ( $5 \times 10^{-4}$  M, acetone).

**3d:** Yield 75%, mp 199–200 °C. Anal. calcd for  $C_{38}H_{35}BF_4N_4Pt_2$ : C, 44.54; H, 3.44; N, 5.47%. Found: C, 44.84; H, 3.70; N, 5.31%.  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$ : 10.31 (d, 2H,  $H_{6'}$ ,  $J_{H-H} = 5.4$  Hz); 8.46 (d, 2H,  $J_{H-H} = 7.5$ , 1.1 Hz); 8.33–8.21 (m, 6H, aromatics); 8.02 (t, 2H); 7.90 (d, 2H); 7.39 (d, 2H); 7.18 (t, 2H); 7.03 (t, 2H); 6.80 (t, 2H); 2.15 (s,  $CH_3$ , 12H); –14.75 (1H, Pt–H,  $J_{Pt-H} = 940$  Hz). IR (nujol): 1060 s, br.  $L_M$  ( $5 \cdot 10^{-4}$  M, acetone) 40  $ohm^{-1} cm^2 mol^{-1}$ .

**4d:** In this case, dinuclear species **4d** is also formed by dropwise addition of  $NaBH_4$  to a solution of the solvato species **4s** (1:1 molar ratio). The mixture was stirred for 1.5 h, evaporated to dryness, and recrystallized from  $CH_2Cl_2/Et_2O$ . Yield 60%, mp 195 °C. Anal. calcd for  $C_{38}H_{35}BF_4N_4Pt_2$ : C, 44.54; H, 3.44; N, 5.47%. Found: C 44.68, H 3.79, N 5.28%.  $^1H$  NMR ( $CDCl_3$ ): the spectrum shows two sets of partially overlapping signals due to the presence of diastereoisomers;  $\delta$ : 10.81 (d, 1H,  $H_{6'}$ ); 10.38 (d, 2H,  $H_{6'}$ ), 10.24 (d, 1H,  $H_{6'}$ ); 6.76–8.54 (m, overlapping signals, 20H+20H, aromatics); 4.19 (m, 2H, CH); 3.98 (m 2H CH); 2.57 (m, 4H,  $CH_2$ ); 2.39 (m, 4H,  $CH_2$ ); 0.92 (t, 6H,  $CH_3$ ); 0.78 (t, 6H,  $CH_3$ ); –14.80 (s with satellites, 1H, Pt–H,  $J_{Pt-H} = 934$  Hz); –15.85 (s with satellites, 1H, Pt–H,  $J_{Pt-H} = 890$  Hz).  $L_M$  ( $5 \cdot 10^{-4}$  M,  $CH_2Cl_2$ ) 40.4  $ohm^{-1} cm^2 mol^{-1}$ .

**5d**: See **5a**.

**[Pt(N-N-C)(H)]**, **6a**, and **[Pt<sub>2</sub>(N-N-C)<sub>2</sub>(μ-H)][BF<sub>4</sub>]**, **6d**, (N-N-CH = **6**). To a suspension of [Pt(N-N-C)(CO)][BF<sub>4</sub>] in THF (N-N-CH = **6**) (31.5 mg, 0.059 mmol in 10 mL) was added under stirring a solution of NaBH<sub>4</sub> in THF (22.5 mg, 10:1, in 10 mL). A red solution immediately formed. After 5', the solution was filtered and concentrated to small volume to give **6a**. <sup>1</sup>H NMR (acetone d<sub>6</sub>): δ 9.30 (dd, 1H, H<sub>6'</sub>, J<sub>H-H</sub> = 5.2 Hz); 8.36–8.24 (m, 3H); 8.16 (t, 1H, H<sub>4</sub>, J<sub>H-H</sub> = 7.7 Hz); 7.47–7.52 (m, 2H); 2.75 (s, 2H, CH<sub>2</sub>); 2.56 (s, 2H, Pt-CH<sub>2</sub>, J<sub>Pt-H</sub> = 74 Hz); 1.03 (s, 6H, CH<sub>3</sub>); -14.54 (s, 1H, Pt-H, J<sub>Pt-H</sub> = 1572 Hz).

If the reaction is carried out with a smaller NaBH<sub>4</sub>:Pt molar ratio (e.g., 3:1) with slightly prolonged reaction times (e.g., 30'), a mixture of terminal and bridging hydrides is formed. The reaction mixture was filtered and concentrated: addition of hexane gave the bridging hydride, **6d**. Yield 35%. <sup>1</sup>H NMR (acetone d<sub>6</sub>): δ 10.04 (d, 2H, H<sub>6'</sub>, J<sub>H-H</sub> = 5.2 Hz); 8.58 (d, 2H, J<sub>H-H</sub> = 8.2 Hz); 8.51 (dd, 2H, J<sub>H-H</sub> = 7.8 Hz); 8.40 (t, 2H, H<sub>4</sub>, J<sub>H-H</sub> = 7.8 Hz); 8.31 (dt, 2H, H<sub>4'</sub>, J<sub>H-H</sub> = 7.8, 1.4 Hz); 7.75 (d, 2H, H<sub>5</sub>, J<sub>H-H</sub> = 8.0 Hz); 7.63 (m, 2H, H<sub>5'</sub>); 3.00 (s, 4H, CH<sub>2</sub>); 2.82 (s, Pt-CH<sub>2</sub>, 4H, J<sub>Pt-H</sub> not resolved); 1.06 (s, 12H, CH<sub>3</sub>); -17.96 (s, Pt-H, J<sub>Pt-H</sub> = 868 Hz).

**[Pt<sub>2</sub>(N-N-C)<sub>2</sub>(μ-H)][BF<sub>4</sub>]**, **7d** (N-N-CH = **7**). **7d** was obtained as **6d** from the corresponding carbonyl complex. In this case, no mononuclear hydride was isolated.

**NMR (CDCl<sub>3</sub>)**: Two species A and B are present in solution, in an approximate 1:1 molar ratio: δ 9.37 (m, H<sub>6'</sub> overlapping, 2H+2H), 8.23–8.08 (m, 8H+8H); 7.56–7.48 (m, 4H+4H); 3.52 (m, CH 2H+2H); 3.04 (dd, 1H+1H, CH<sub>2</sub>, J<sub>H-H</sub> = 7.5, 11.9 Hz); 2.60 (dd, 1H+1H, CH<sub>2</sub>, J<sub>H-H</sub> = 5.7, 11.9 Hz); 1.46 (d, 3H+3H, CH<sub>3</sub>, J<sub>H-H</sub> = 7.1 Hz); -15.50 (s with satellites, Pt-H, J<sub>Pt-H</sub> = 860 Hz); -15.55 (s with satellites, Pt-H, J<sub>Pt-H</sub> = 860 Hz).

**Mixed Dinuclear Hydrides: 3s+2a**. Anal. calcd for: C<sub>37</sub>H<sub>33</sub>-BF<sub>4</sub>N<sub>4</sub>Pt<sub>2</sub>: C 43.97, H 3.29, N 5.54%. Found C 44.51, H 3.53, N 5.36%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): the spectrum shows a mixture of three species: 3-H-2, 2-H-2 (**2d**), 3-H-3 (**3d**) in a 2/1/trace molar ratio.

**1s+2a**. Anal. calcd for C<sub>35</sub>H<sub>29</sub>BF<sub>4</sub>N<sub>4</sub>Pt<sub>2</sub>: C 42.78, H 2.97, N 5.70%, Found C 42.88, H 3.45, N 5.29%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): the spectrum shows a mixture of three species: 1-H-2, 2-H-2 (**2d**), 1-H-1 (**1d**) in a 2/1/0.5 molar ratio.

**2s+1a**. <sup>1</sup>H NMR (CDCl<sub>3</sub>): the spectrum shows a mixture of three species: 1-H-2, 2-H-2 (**2d**), 1-H-1 (**1d**) in a 2/1/trace molar ratio.

**1s+3a**. Anal. calcd for C<sub>36</sub>H<sub>31</sub>N<sub>4</sub>BF<sub>4</sub>Pt<sub>2</sub>: C 43.39, H 3.14, N 5.62%, Found C 43.03, H 3.49, N 5.27%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): the spectrum shows a mixture of three species: 1-H-3, 3-H-3 (**3d**), 1-H-1 (**1d**) in a 2/1/trace molar ratio

**<sup>1</sup>H NMR Data for Pt-H Signals in the Mixed Dinuclear Hydrides (CDCl<sub>3</sub>)**. **1-H-2**: δ -15.29, s with satellites, J<sub>Pt-H</sub> = 903 Hz. **1-H-3**: δ -15.32, s with satellites, J<sub>Pt-H</sub> = 905 Hz. **2-H-3**: δ -14.67, s with satellites, J<sub>Pt-H</sub> = 938 Hz.

**[Pt(N-N-C)(OCOH)] (N-N-CH = 1)**. To a large excess of HCOOK (86.2 mg, 41.0 mmol) in a water/acetone solution a solution of the solvato species **1s** (150 mg, 0.256 mmol) in acetone was added. After filtration the solution was concentrated to small volume and extracted with CH<sub>2</sub>Cl<sub>2</sub>. From the solution, a crude solid was obtained by addition of Et<sub>2</sub>O and filtered off. From the solid (a mixture of terminal and bridging formate, IR criterion) the mononuclear derivative was extracted with hot benzene and the solution was concentrated to small volume. After addition of Et<sub>2</sub>O, a precipitate was filtered and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as a yellow solid (70 mg, yield 56%). Mp 168 °C. Anal. calcd for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 44.54; H, 2.91; N, 5.77%. Found: C, 43.97; H, 2.71; N, 5.47%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.70 (dd, 1H, H<sub>6'</sub>, J<sub>H-H</sub> = 0.9, 5.4 Hz); 8.63 (s, 1H, HCOO, J<sub>Pt-H</sub> = ca. 93 Hz); 7.99 (dd, 1H, H<sub>3</sub> or H<sub>3'</sub>, J<sub>H-H</sub> = 0.9, 8.1 Hz); 7.90–7.82 (m, 2H); 7.53 (dd, 1H, J<sub>H-H</sub> = 0.9, 7.6 Hz); 7.47–7.41 (m, 2H); 7.11–7.07 (m, 4H). IR (Nujol, cm<sup>-1</sup>): 1630 vs, br, 1300 s, 1270 s.

The corresponding formate obtained for N-N-CH = **2** was obtained as previously described (ref 15).

**Acknowledgment.** Financial support from Ministero dell'Università e della Ricerca Scientifica (MIUR, PRIN 2005) and Università di Sassari (FAR) is gratefully acknowledged. We thank Johnson Matthey for a generous loan of platinum salt.

OM7005276