Reduction of Water to H$_2$ by Diorganopalladium(II) Complexes of Tris(pyrazol-1-yl)borate: Ab-Initio Theoretical Study of the Mechanism

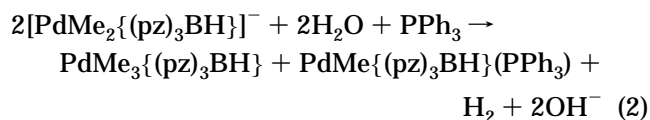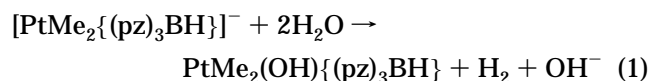Anne Milet,[†] Alain Dedieu,*,[†] and Allan J. Canty*,[‡]

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The reduction of water to H$_2$ by the tris(pyrazol-1-yl)borate complex [Pd(CH$_2$CH$_2$CH$_2$-CH$_2$){(pz)$_3$BH-*N*,*N*}]$^-$ with concomitant formation of the palladium(IV) complex Pd(CH$_2$-CH$_2$CH$_2$CH$_2$)(OH){(pz)$_3$BH-*N*,*N*′,*N*′} has been studied theoretically at the MP2//SCF level using [PdMe$_2${(H$_2$C=N−NH)$_3$BH}]$^-$ as a model for the pallada(II)cyclopentane reagent. The calculations suggest that the uncoordinated pyrazole group has a major role as an intramolecular nucleophile in delivering 2H$^+$ (per mole of H$_2$ formed) to the palladium center, with an eventual role as a coordinated group in the palladium(IV) product. Thus, initial protonation leads to formation of a N-protonated palladium(II) species Pd(CH$_2$CH$_2$CH$_2$CH$_2$)-{(pz)$_2$(pzH)BH-*N*,*N*} containing a "Pd···H−N" interaction, followed by hydroxide coordination and hydrido ligand formation to give a palladium(IV) species *trans*-[Pd(CH$_2$CH$_2$CH$_2$-CH$_2$)(H)(OH){(pz)$_3$BH−*N*,*N*}]$^-$, a second protonation to form *trans*-Pd(CH$_2$CH$_2$CH$_2$CH$_2$)-(H)(OH){(pz)$_2$(pzH)BH−*N*,*N*} prepared for a dihydrogen bond interaction "Pd−H···H−N", and finally by elimination of H$_2$ and coordination of the pyrazole group to form Pd(CH$_2$CH$_2$-CH$_2$CH$_2$)(OH){(pz)$_3$BH-*N*,*N*′,*N*′}.
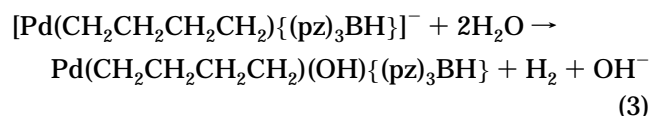
Introduction

For the late transition elements, there are few reports of the oxidation of M−C σ-bonded complexes by water with the concomitant reduction of water to H$_2$.[1−6] Examples appear to be limited to platinum(II)[1−3] and palladium(II),[2a,b,3,4] and for palladium(II) the presence of tripodal ligands such as tris(pyridin-2-yl)methanol[2a] or tris(pyrazol-1-yl)borate[2b,3,4] are required. Thus, PtMe$_2$-(bpy) (bpy = 2,2′-bipyridyl) is oxidized to form [PtMe$_2$-(OH)(bpy)(OH$_2$)]$^+$,[1a,b] but PdMe$_2$(bpy) does not react with water, [PtMe$_2${(pz)$_3$BH}]$^-$ forms PtMe$_2$(OH)(pz)$_3$-BH} (eq 1),[2b,d] and [PdMe$_2${(pz)$_3$BH}]$^-$ undergoes a more complex reaction which also involves oxidation of palladium(II) and release of H$_2$ (eq 2).[2a,4b] The reaction of

$$[PtMe_2\{(pz)_3BH\}]^- + 2H_2O \rightarrow$$
$$PtMe_2(OH)\{(pz)_3BH\} + H_2 + OH^- \quad (1)$$

$$2[PdMe_2\{(pz)_3BH\}]^- + 2H_2O + PPh_3 \rightarrow$$
$$PdMe_3\{(pz)_3BH\} + PdMe\{(pz)_3BH\}(PPh_3) +$$
$$H_2 + 2OH^- \quad (2)$$

eq 2 most likely proceeds via slow formation of an undetected palladium(IV) intermediate similar to PtMe$_2$-(OH){(pz)$_3$BH} followed by a rapid Me$^+$ transfer from this intermediate to nucleophilic [PdMe$_2${(pz)$_3$BH}]$^-$ to give the products.[4] Moreover, for the pallada(II)cyclo-

pentane reagent [Pd(CH$_2$CH$_2$CH$_2$CH$_2$){(pz)$_3$BH}]$^-$, a palladium(IV) analogue of PtMe$_2$(OH){(pz)$_3$BH} is isolated (eq 3), since the alkyl transfer reaction is inhibited by the palladacyclic structure.[2b,4]

$$[Pd(CH_2CH_2CH_2CH_2)\{(pz)_3BH\}]^- + 2H_2O \rightarrow$$
$$Pd(CH_2CH_2CH_2CH_2)(OH)\{(pz)_3BH\} + H_2 + OH^- \quad (3)$$

In view of the intriguing chemistry of eqs 2 and 3, the isolation of the product of eq 3 as the first stable dihydrocarbylpalladium(II) complex, and the fundamental importance of the reduction of water by inorganic species, we have examined the reaction of Scheme 1 using theoretical methods in an effort to deduce the mechanism of the reaction. This work[7] has followed our earlier calculations on the protonation of [PtMe$_2$-{pz)$_3$BH}]$^-$ to give the stable hydridoplatinum(IV) complex PtMe$_2$H{(pz)$_3$BH}[5] and involves a working hypothesis that the mechanism for the formation of H$_2$ in eqs

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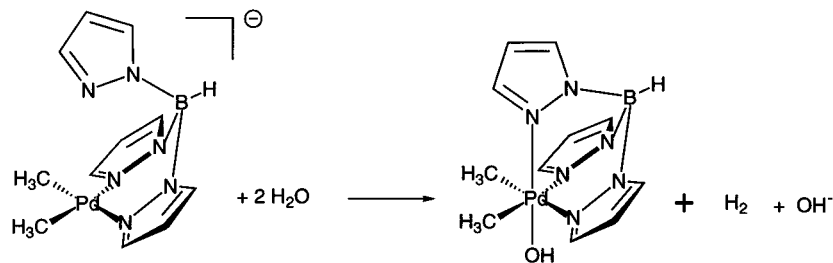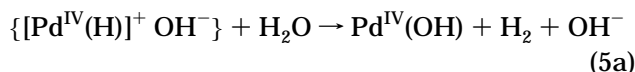
Scheme 1

2 and 3 involves the intermediacy of unstable hydri-dopalladium(IV) intermediate(s) (eqs 4 and 5).

$$Pd^{II} + H_2O \rightarrow \{[Pd^{IV}(H)]^+ OH^-\} \qquad (4a)$$

$$\{[Pd^{IV}(H)]^+ OH^-\} + H_2O \rightarrow Pd^{IV}(OH) + H_2 + OH^- \qquad (5a)$$

or

$$Pd^{II} + H_2O \rightarrow Pd^{IV}(H)(OH) \qquad (4b)$$

$$Pd^{IV}(H)(OH) + H_2O \rightarrow Pd^{IV}(OH) + H_2 + OH^- \qquad (5b)$$
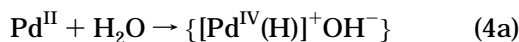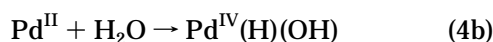
Computational Details

The SCF and MP2 calculations were carried out with the Gaussian 92 and Gaussian 94 programs.[8] The anionic ligand [(pz)$_3$BH]$^-$ was modeled by the tris(hydrazonyl)borate anion [(H$_2$C=N−NH)$_3$BH]$^-$. Previous calculations on Pt and Pd systems[5,9] have shown that this model is quite reliable for describing the geometrical and energy changes undergone by the actual complexes. A split-valence basis set was used. For the palladium atom, the innermost core electrons (up to 3d) were described by the relativistic pseudopotential of Hay and Wadt[10a] and the remaining outer core and valence electrons by a (5,6,4) ⟨3,3,2⟩ basis set.[10] The carbon, nitrogen, and oxygen atoms were described by a (9,5) contracted into ⟨3,2⟩ basis set,[11a] and the hydrogen atom was described by a (4) ⟨2⟩ basis set.[11b] The hydrogen atoms taking part actively in the various reactions and those bound to the oxygen atom of either water or hydroxide were described by a somewhat more flexible basis set, (6,1) contracted into ⟨3,1⟩,[11b] the exponent of the added p polarization function being 0.8. A d polarization function (of exponent $\alpha_d = 1.00$) was also added to the oxygen atom. The geometry optimization was performed at the SCF level with a gradient technique. Single-point energy calculations were then performed at the MP2 level, using the frozen-core approximation. Pilot calculations on model systems and previous results have shown that this MP2//SCF level of calculation is sufficient to obtain, for most of the elementary steps, a reliable qualitative description of the geometries and

energies of the various intermediates and transitions states.[5,9,12] This is true, in particular, for the oxidative addition of H$_2$O to model Pd(II) complexes[12b] and for σ-bond metathesis reactions involving the O−H bond,[35,12c] where the MP2//MP2 and MP2//SCF energies were found to differ by less than 5 kcal mol^{-1}. Our basis set is, however, more questionable for reactions involving the hydroxide anion, for which it is known that diffuse functions on the oxygen atom are necessary[13] and that the gas-phase model is somewhat inappropriate, owing to the large solvation energy of OH$^-$.[14] Thus, in order to get reasonable gas-phase energetics, diffuse functions (of exponent $\alpha_s = 0.0873$ and $\alpha_p = 0.0642$, according to the even-tempered criterion) were added on the oxygen atom for the energy determination in the reactions where OH$^-$ is a reactant (section D).[15] An accurate description of the solvent effects, including, in particular, the explicit handling of the three water molecules of the first solvation shell,[16] is presently out of the range of our computing capabilities. Nevertheless an assessment of the corresponding trends was made by carrying out calculations with one extra water molecule bound to OH$^-$ (section D). The optimized geometries of all important stationary points (intermediates and transition states) are given as Supporting Information, and the corresponding MP2//SCF energies are given in ref 17.

Results and Discussion

A. The [PdMe$_2${pz)$_3$BH}]$^-$ System. The optimized geometry of the corresponding model system [PdMe$_2${-(H$_2$C=N−NH)$_3$BH}]$^-$, **1**, is shown in Figure 1. It has great similarities to the X-ray crystal structures of [Pd-{(pz)$_3$BH}$_2$][18] and of the related Pt(II) complexes [PtMe-

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(15) Pilot calculations, carried out on the OH$^-$(H$_2$O) system with this augmented basis set, yielded a SCF-optimized geometry with the bridging hydrogen atom at 1.006 and 1.574 Å from the water oxygen atom and hydroxyl oxygen atom, respectively. The corresponding MP2 values are 1.087 and 1.403 Å, to be compared with 1.107 and 1.364 Å obtained by Xantheas with a very large basis set.[13] Thus, at both our SCF and MP2 levels, the expected asymmetric structure is found. The association energy is not sensitive to the geometry: the MP2//SCF and MP2//MP2 values are 27.4 and 28.1 kcal^{-1} mol^{-1} (to be compared to the value of 27.6 kcal mol^{-1} obtained with the very large basis and to the experimental value of 26.5 ± 1.0 kcal mol^{-1}).[13] The MP2 value obtained from a geometry that was optimized through SCF calculations carried out without diffuse functions (*i.e.*, a value corresponding to the level used in section D) is 27.8 kcal mol^{-1}, thus also in good agreement with the experimental value.
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(17) The MP2//SCF energies (in au, 1 au = 627.5 kcal mol^{-1}) computed with the basis sets described in the Computational Details are: **1**, −676.5645; **1a**, −676.5519; **1b**, −676.5606; **2**, −677.1298; **3**, −677.1118; **5**, −753.3213; **TS5**, −753.2182; **6**, −752.7376; **6a**, −828.9646; **7**, −752.7077; **8**, −752.7405, with diffuse functions on oxygen, −752.7534; **8a**, −828.9690; **9**, −752.7344; **10**, −752.7076; **11**, −752.7280; **13**, −753.2806; **14**, −753.2417; **15**, −753.2376; **16**, −752.1319; **17**, −753.2511; **18**, −753.2466; H$_2$, −1.1600; H$_2$O, −76.1932; (H$_2$O)$_2$, −152.3980; OH$^-$, −75.5693.

Figure 1. SCF-optimized geometries of the $[PdMe_2\{H_2C=N-NH)_3BH\}]^-$ model system **1**, of its C_s-constrained isomers (**1a** and **1b**), and of the two possible isomers (**2** and **3**) resulting from the protonation of **1**. Structures **2a** and **2b** are not local minima (section B). Bond lengths are in angstroms (Å), and angles are in degrees. The energies (in kcal mol^{-1}) are relative to **1** for **1a** and **1b** and to **2** for **3**.

$(CO)\{(pz)_3BH\}]^{19}$ and $[PtMe[CNC(CH_3)_3]\{(pz)_3BH\}]$,[20] all of which contain bidentate tris(pyrazol-1-yl)borate. The Pd−C bond lengths (2.08 Å) are in agreement with the experimental values, but the Pd−N bond lengths (2.27 Å) are probably too long. This may be traced to the SCF level of calculation. The optimized bond lengths and bond angles of the $[(H_2C=N-NH)_3BH]^-$ ligand are also in agreement with the experimental values of the tris(pyrazolyl)borate ligand. The noncoordinated $H_2C=N-NH$ group occupies the axial position on the boron atom, and its plane makes an angle of 56.6° with the PdN$_4$ plane. A similar angle (58.1°) has been

found in the crystal structure of $[Pd\{(pz)_3BH\}_2]$.[18] There is no tendency for the third imino nitrogen atom to interact with Pd, as found for $[PtMe(CO)\{(pz)_3BH\}]^{19}$ and $[PtMe[CNC(CH_3)_3]\{(pz)_3BH\}]$.[20] A constrained C_s geometry optimization with the $H_2C=N-NH$ group above the palladium atom yielded **1a**, where the Pd···N distance is 3.48 Å. This is clearly indicative of no interaction: typical Pd···N(sp^2) weak interactions are characterized by a distance of 2.7−2.8 Å.[21] **1a** is less stable than **1** by 7.9 kcal mol^{-1}. This may be considered a relatively high value in light of the known fluxionality of such compounds. For rhodium complexes, the equi-

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librium between various related structures has been shown to be dependent on the polarity of the solvent used.[22] Thus, our computed values are probably more reflective of the solid-state structures. Other rearrangements of the ligand are quite facile: the energy difference between **1** and **1b**, another C_s-constrained geometry corresponding to a 180° rotation around the B–N bond from **1a**, is only 5.5 kcal mol^{-1}.

That the third H$_2$C=N–NH group does not coordinate indicates that the palladium center is not electrophilic, but rather nucleophilic. This nucleophilic character is also suggested by reports of facile oxidative addition of iodomethane to [PdMe$_2${(pz)$_3$BH}]$^-$ and [Pd(CH$_2$CH$_2$-CH$_2$CH$_2$){(pz)$_3$BH}]$^-$.[6] It is, therefore, reasonable to expect that [PdMe$_2${(pz)$_3$BH}]$^-$ could react with H$_2$O to yield a Pd(IV) intermediate corresponding to either [Pd^{IV}(H)]$^+$ OH$^-$, eq 4a, or Pd^{IV}(H)(OH), eq 4b. The first case would simply involve a protonation of the Pd(II) system. In contrast, the other alternative would be the result of a more or less concerted oxidative addition of H$_2$O. These two mechanistic hypotheses are explored in the following sections.

B. Protonation of [PdMe$_2${pz}$_3$BH}]$^-$. Protonation of [PdMe$_2${pz}$_3$BH}]$^-$ could occur either on the metal center or on the noncoordinated nitrogen atom. As far as the protonation of related Pt(II) systems is concerned, both possibilities have been reported. Several platinum(IV) hydrides have been obtained by protonation of Pt(II) complexes,[2d,5,23–25] including those for tripod nitrogen donor ligands.[2d,5,25] In one case, which is of particular interest here since it involves [(pz2)$_3$BH]$^-$ (pz* = 3,5-Me$_2$pz) as a ligand, an X-ray crystal structure has been obtained.[25] N-protonated Pt-(II) complexes are also known.[3,22,26a,27–29] In the case of palladium, N-protonated Pd(II) complexes have been characterized[26,27] but to our knowledge organo(hydrido)-palladium(IV) species have not been fully characterized.[30] Calculations that we reported recently showed that for the protonation of the [PtMe$_2${(H$_2$C=N–NH)$_3$BH}]$^-$ model system, the Pt(IV) hydride was more stable than the N-protonated species by about 22 kcal mol^{-1}.[5]

For palladium, the optimized structures corresponding to the two possibilities are shown in **2** and **3**, see Figure 1. The optimized structure of **2** agrees reasonably well with the structure of the Pt(IV) analogue.[25] As in **1**, the Pd–N bond lengths obtained at the SCF level (2.27 and 2.30 Å for the equatorial and axial ligands, respectively) are somewhat too long. This is due in part to the neglect of electron correlation in the SCF level of the geometry optimization: a shortening of about 0.05 Å on going from SCF to MP2 was previously obtained for [PtMe$_2$(H){(H$_2$C=N–NH)$_3$BH}]. Moreover, for this platinum system, the computed MP2 values[5] (2.18 and 2.21 Å) agree rather well with the experimental values[25] (2.15 and 2.17 Å) published later.

In **3**, the proton lies above the palladium square plane. The calculated structure for the Pd···H–N unit (Pd···H = 2.19 Å, N–H = 1.02 Å, Pd···H–N = 160.5°) is quite similar to that of [PtBr(H)(1-C$_{10}$H$_6$NMe$_2$-8-C,N)(1-C$_{10}$H$_6$NMe$_2$-8-C,NH)] (Pt···H = 2.11(5) Å, N–H = 1.02(5) Å, Pt···H–N = 168(4)°),[29] although the metal hydrogen interaction is probably more electrostatic in the palladium system than in the platinum system.[5,23] Other systems with a protonated (pz)$_3$BH ligand are known,[31] including isoelectronic [Au^{III}Me$_2${(pz)$_2$(pzH)-BH-N,N'}]$^+$ (pK_a = 3.69(2))[31a] and [Rh^I(CO)$_2${(pz*)$_2$-(pz*H)BH-N,N'}]$^+$,[31b] but none of these exhibit a M···H–N interaction. Presumably, the metal centers are not sufficiently electron rich to support an electrostatic interaction with the proton.

The hydridopalladium(IV) structure **2** is more stable than the N-protonated structure **3** by 11.3 kcal mol^{-1} (MP2//SCF level).[32a] This is a much smaller difference than that in the Pt case (*vide supra*). Moreover, it is a gas-phase value and may be reduced further in solution, **3** being probably better solvated than **2**.[32b] The small energy difference between **3** and **2** does not necessarily mean that these two species are in equilibrium, and in fact for related [PtX(H)(1-C$_{10}$H$_6$NMe$_2$-8-C,N)$_2$] (X = Cl, Br) where both isomers were isolated, no equilibria between the species was found. But they could inconvert through equilibria involving a reagent anion, *e.g.*, OH$^-$. Interestingly, [PtMe$_2${(pz)$_3$BH}]$^-$ and [PtMe$_2$(H)-{(pz)$_3$BH}] are known to be interconvertible in aqueous solution by a change of pH (high pH, Pt(II); low pH, Pt-(IV)).[2d] It is also clear that a change in the coordination sphere of such a system may reverse the energy ordering: protonation of Rh(CO)$_2${(pz*)$_3$BH} occurs at one of the nitrogen atoms of the [(pz*)$_3$BH]$^-$ ligand,[31b] whereas it occurs at the metal for Rh(CNR)$_2${(pz*)$_3$BH} (R = neopentyl).[33]

The feasibility of the five-coordinate Pd(IV) complexes **2a** or **2b** as stable structures was also explored. Geometry optimizations starting from such structures

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(28) (a) Albinati, A.; Arz, C.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 508. (b) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Orpen, G.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1789. (c) Albinati, A.; Lianza, F.; Muller, B.; Pregosin, P. S. *Inorg. Chim. Acta* **1993**, *208*, 119. (d) Albinati, A.; Lianza, F.; Pregosin, P. S.; Muller, B. *Inorg. Chem.* **1994**, *33*, 2522.

(29) 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.

(30) NMR evidence for the presence of organo(hydrido)palladium-(IV) species as components of a mixture has been presented, see: Vedernikov, A. N.; Kuramshin, A. I.; Solomonov, B. N. *J. Chem. Soc., Chem. Commun.* **1994**, 121.

(31) (a) Byers, P. K.; Canty, A. J.; Minchin, N. J.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1183. (b) Ball, R. G.; Ghosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341. (c) Rheingold, A. L.; Haggerty, B. S.; Trofimenko, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1983.

(32) (a) Pilot calculations carried out up to the MP4//MP2 level on the [Pd(H)$_3$(Cl)(NH$_3$)$_2$] model system and its N-protonated [Pd(H)$_2$(Cl)-(NH$_3$)···H–NH$_3^+$] tautomer show that the MP2//SCF level of theory is quite reliable for assessing this energy difference, the increase in the quality of the basis set, and the increase in the order of the pertubational MPn treatment acting in opposite directions.[12] (b) SCRF calculations carried out at the MP2 level on the same systems show that the energy difference decreases on increasing the polarity of the solvent (Gaudé, S.; Dedieu, A. Unpublished results)

(33) Jones, W. D.; Hessel, E. T. *Inorg. Chem.* **1991**, *30*, 778.

converged invariably to the four-coordinate Pd(II) complex **2** and to the six-coordinate Pd(IV) complex **3**, respectively. We also checked whether protonation of the metal on the side facing the noncoordinated nitrogen atom could be helped by coordination of a water molecule on the opposite site, see the structure of **4**. The

4
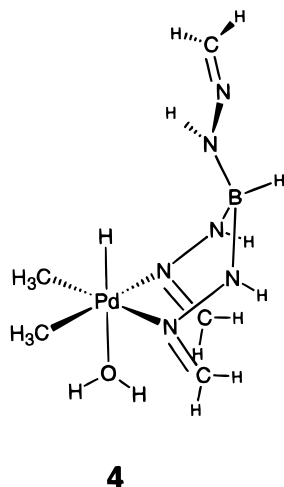
geometry optimization process starting from a reasonable guess for **4** showed a gradual dissociation of the water molecule and a transfer of H⁺ to the uncoordinated nitrogen atom, yielding, therefore, **3** + H_2O. It is, thus, clear that the $(pz)_3BH$ ligand, with its geometry suitable either for a Pd···H–N interaction or for easily achieving six coordination, plays an important role in stabilizing **2** and **3**.

C. Reaction of Water with [PdMe₂(H){pz)₃BH}]. The metathesis reaction to yield $[PdMe_2(OH)\{(pz)_3BH\}]$ shown in equation 5a, if it occurs, is expected to proceed via a dissociation of one pyrazole group, followed by coordination of water, and finally H_2 elimination from the $[PdMe_2(H)(H_2O)\{pz)_3BH\}]$ system via a σ-bond metathesis reaction.[34] The corresponding steps for the $[PdMe_2(H)\{(H_2C=N–NH)_3BH]$ model system (**2 → 5 → TS5 → 16**) are shown in Figure 2. Since in the metathesis reaction a proton is abstracted from water by the hydride ligand, the hydrogen atom bound to palladium would need to be quite negative. We have shown, in a separate study on the σ-bond metathesis reaction of water with model d^8 and d^6 palladium hydride complexes, that moderate energy barriers are associated with a negative charge on the reacting hydride.[35] In the $[PdMe_2(H)(H_2O)\{(H_2C=N–NH)_3BH]$ system **5**, where one hydrazone group of **2** has been replaced by H_2O, the Pd-H bond is quite covalent (as a result of a facial disposition of the two methyl groups and of the "hydride")[12b] and the hydrogen atom has a positive charge (+0.14 e). The energy barrier for the σ-bond metathesis process (**5 → TS5**) is accordingly quite high, 64.7 kcal mol⁻¹ (MP2//SCF value). Thus, H_2 elimination from the reaction of $[PdMe_2(H)\{pz)_3BH\}]$ with H_2O is not expected.[36] This is consistent with the
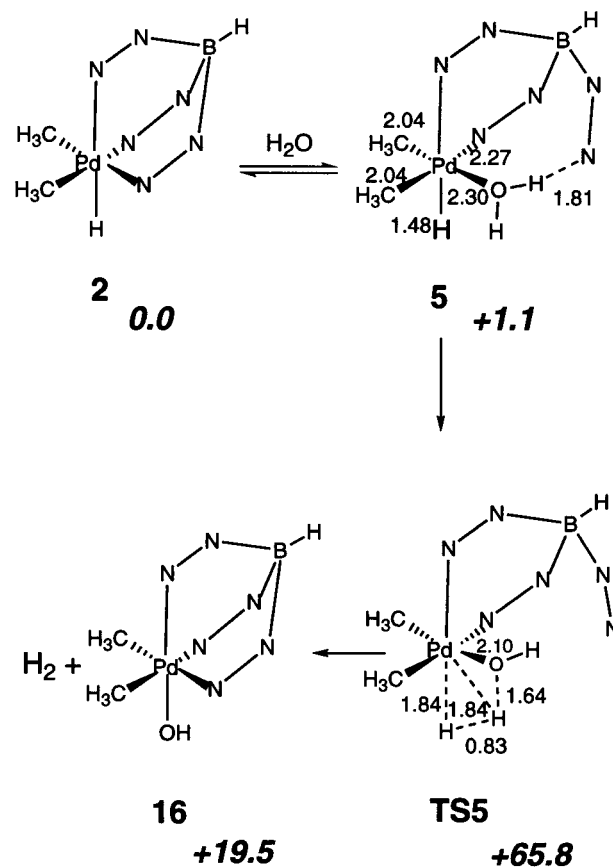

Figure 2. SCF-optimized geometries and MP2//SCF relative energies of the intermediate and transition state on the pathway of the σ-bond metathesis reaction between H_2O and $[PdMe_2(H)\{(H_2C=N–NH)_3BH\}]$. Bond lengths are in angstroms (Å). The relative energies are in kcal mol⁻¹.

experimental finding that in basic solutions the Pt(IV) analogue $[PtMe_2(H)\{(pz)_3BH\}]$ is in equilibrium with the Pt(II) anionic species $[PtMe_2(H)\{(pz)_3BH\}]^{-}$.[2d]

D. Oxidative Addition of Water to [PdMe₂-{pz)₃BH}]⁻. Since **2** does not appear to react easily with water, the second mechanistic hypothesis was examined in detail, *viz.* eqs 4b and 5b. It starts by oxidative addition to **1**, eq 4b. For this addition of H_2O to a d^8 square-planar system, two stereochemical courses need to be considered, either a *cis* or a *trans* addition. The oxidative addition of H_2O to $[Ir(PMe_3)_4]^{+}$ yields a *cis* product,[37] but addition of H_2O to $PtMe_2(bpy)$ is believed to yield a *trans* product.[1a,b] We are not aware of any unambiguous characterization (either by spectroscopy or an X-ray crystal structure) of a $Pd^{IV}(H)(OH)$ species, and thus, both of these products were considered. The resulting products are shown in Figure 3, where **6** and **7** correspond to the *cis* addition yielding the *cis,fac-* and *cis,mer-*isomers, respectively (under the *fac* and *mer* specification we refer to the three pure σ-donor ligands, namely the two methyls and the hydride), and **8** and **9** are the products of *trans* addition. They both correspond to a *fac* arrangement of the three pure σ donor ligands, but differ by the location of the

(34) There is no evidence from our previous theoretical study that an associative mechanism can operate in such metathesis reactions.[35] We searched in vain for a transition state corresponding to a one-step elimination of H_2 from **2** and H_2O. Attempts that used a cyclic transition state involving more than one molecule of water as a hypothesis, *i.e.* cyclic transition states involving two or three water molecules, were also unsuccessful.

(35) Milet, A.; Dedieu, A.; Kapteijn, G.; van Koten, G. *Inorg. Chem.* **1997**, *36*, 3223.

(36) (a) The reaction is also endothermic by 19.5 kcal mol⁻¹. (b) We may also note here that the reverse process, *i.e.*, H_2 + **16 → TS5 → 5** (which is a σ-bond metathesis process of H_2 with the Pd(IV)OH complex), is also unlikely, the energy difference between **16** and **TS5** being 46.3 kcal mol⁻¹.

(37) (a) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (b) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.
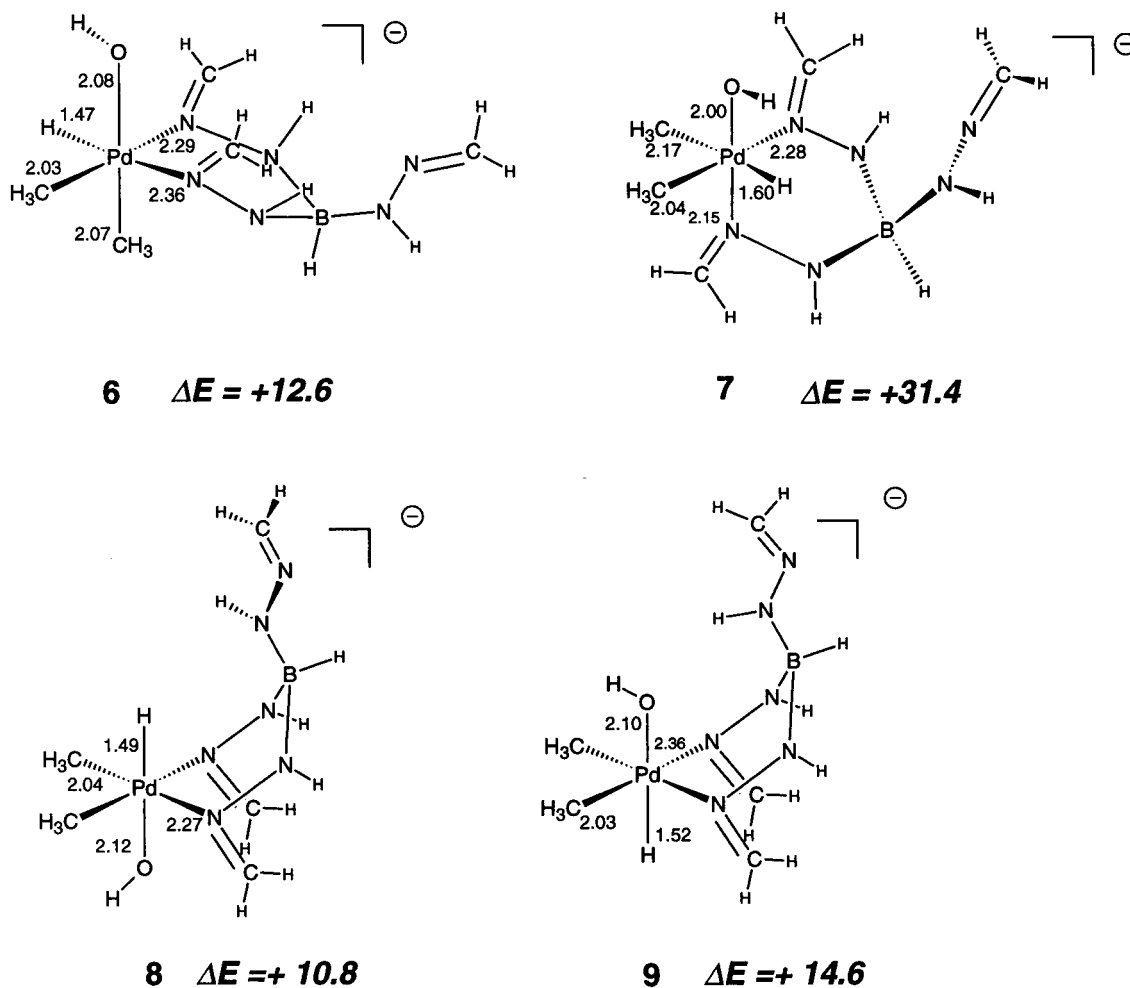
6 $\Delta E = +12.6$ **7** $\Delta E = +31.4$

8 $\Delta E =+ 10.8$ **9** $\Delta E =+ 14.6$

Figure 3. SCF-optimized geometries of the four possible isomer products of the oxidative addition reaction of H_2O to $[PdMe_2\{(H_2C=N-NH)_3BH\}]^-$. Bond lengths are in angstroms (Å). The relative MP2//SCF energies (in kcal mol^{-1}) refer to the $[PdMe_2\{(H_2C=N-NH)_3BH\}]^-$ and H_2O separated reactants.

hydride with respect to the uncoordinated hydrazone group, either facing it or opposite to it. The energies of these systems relative to the separated reactants, $[PdMe_2\{(H_2C=N-NH)_3BH\}]^-$ and H_2O, are also given in Figure 3 (MP2//SCF values). They all point to endothermic reactions, the endothermicity being much larger for the reactions leading to the *mer* isomer than for the reactions leading to the *fac* isomers, for which the endothermicity is moderate. This is not specific to this system since calculations carried out for the oxidative addition of H_2O to simpler Pd and Pt systems show the same feature. This is also consistent with the known structural data for Pd(IV) and Pt(IV) trialkyl complexes.[38]

The energy values in Figure 3 refer to the gas phase, and thus, they may be lowered by solvation effects arising from the solvent or from nonreacting water molecules. We have addressed this latter possibility for the two *fac* isomers **6** and **8**. For these two systems, a hydrogen bond is found between the hydroxo ligand and one water molecule (**6a** and **8a**), now leading to slight *exothermicities* of 1.3 and 4.1 kcal mol^{-1}, respectively.[39] Hydrogen bonding is characteristic of hydroxopalladium-(IV)[4b] and -platinum(IV) complexes,[2d] *e.g.,* [Pd(CH$_2$CH$_2$-

$CH_2CH_2)(OH)\{(pz)_3BH\}]$ is a white microcrystalline solid and forms a crystalline adduct with phenol containing a "Pd$-$O(H)$\cdots$H$-$O$-$Ph" interaction chacterized by X-ray diffraction. The computed structures of **6a** and **8a** compare well with these X-ray crystal structures, especially for the Pd$-$C and Pd$-$N bond distances. The optimized Pd$-$O bond length may seem to be too long compared to the experimental value 1.98 Å, but this may be ascribed to the greater *trans* effect of either the methyl or the hydride compared to that of pyrazole in the experimental structure. The O$\cdots$O distance is 2.69 Å, somewhat longer than that in the experimental structure (2.47 Å) of the phenol adduct but shorter than that in the X-ray structure of [PtMe$_2$(OH)$\{$(pz)$_4$B$\}\cdot$H$_2$O] (2.81 and 2.94 Å in a centrosymmetric dimer).[2d]

The explicit incorporation in our model of more hydrogen-bonded water molecules might further increase the exothermicity associated with the formation of **6a** and **8a**. On the other hand, it is not expected to greatly affect the high destabilization of **7** relative to **6**, **8**, and **9**. Also, separate studies of the *cis* oxidative addition of H_2O to the simpler systems [Pd(NH$_3$)-Cl(CH$_3$)$_2$]$^-$ [12b] and [Pd(H)$_2$(NH$_3$)$_2$][40] show that the energy barriers follow the energies of reaction, and thus, it is

(38) (a) Canty, A. J. *Acc. Chem. Res.* **1992**, *11*, 83. (b) Canty, A. J. in *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: London, 1995.
(39) These values correspond to the reaction of **1** with (H$_2$O)$_2$.

(40) The *cis* addition of H$_2$O to *cis*-[Pd(H)$_2$(NH$_3$)$_2$], which is endothermic by 5.5 kcal mol^{-1}, has a barrier of 28.9 kcal mol^{-1}, whereas the *cis* addition to *trans*-[Pd(H)$_2$(NH$_3$)$_2$], which is endothermic by 24.2 kcal mol^{-1}, has a barrier of 42.0 kcal mol^{-1}.[35]
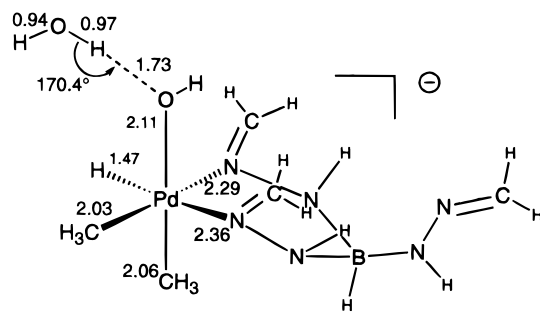
6a
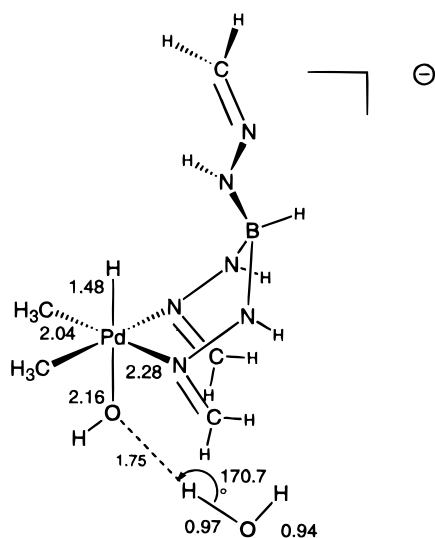
8a

expected that the barrier for the oxidative addition leading to **7** is greater than 40 kcal mol^{-1}. Thus, **7** will be, on both thermodynamic and kinetic grounds, an unproductive intermediate for the overall reaction of Scheme 1. The same is true of **9**, but for geometrical reasons: since the hydride is *trans* to both the hydroxo and the noncoordinated hydrazone group, it cannot couple in the following steps with the second proton that is added either on the oxygen atom or on the nitrogen atom (see section E). The only isomers to be considered further are, therefore, **6** and **8**.

The transition state for the oxidative-addition reaction leading to **6** has not been determined since it is shown in section E that it is much less reactive than **8** in the subsequent H$_2$-elimination reaction. We, therefore, only looked for the transition state of the *trans* addition leading to **8**, for which the subsequent H$_2$-elimination step turned out to be favorable (*vide infra*). We have also observed that there is no strong thermodynamic preference for either **2** or **3**, and it is known that protonation can be assisted by nucleophiles[3] (as discussed theoretically by Aullón and Alvarez).[41] Thus, a base-catalyzed mechanism should be considered in which after the initial protonation on the nitrogen atom to yield **3**, there would be a proton delivery to the palladium assisted by a more or less concomitant binding of the hydroxide ion. This hypothesis was checked by looking for possible intermediates and transition states for this process. The results are shown schematically in Figure 4.

(41) Aullón, G.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3137.

The computed exothermicity (with respect to **3** and OH$^-$) is probably strongly overestimated as a result of the neglect of differential solvation effects, since OH$^-$ is expected to be more solvated by the surrounding water molecules[13] than the hydroxo complex **7**. The experimental free energy of hydration of OH$^-$ is 104 kcal mol^{-1},[42] and the gas-phase experimental enthalpy of clusterification with six water molecules is 96.7 kcal mol^{-1}.[43] Smaller values are expected for the solvation of the less negatively charged hydroxo ligand. Indeed, adding one additional water molecule reduces the exothermicity by 6.7 kcal mol^{-1} at the SCF level and by 5.8 kcal mol^{-1} at the MP2 level. This differential effect should be enhanced with more water molecules. SCRF-MP2 calculations[44] were carried out in order to obtain an estimate of the dielectric effect of the bulk solvent. The result is again a decrease of the energy difference between **8** and **10**, from 28.8 kcal mol^{-1} in the gas phase, see Figure 3, to 12.8 kcal mol^{-1} for acetone and 11.3 kcal mol^{-1} for water. Other factors, such as the basis set superposition error or some overestimation of the Pd−(OH) bond energy, may be also at work.[46]

At the SCF level, both an intermediate **10** and a transition state **11**—characterized by one imaginary vibrational frequency (1230i cm^{-1})—are found. The decomposition of the imaginary mode into internal coordinate displacements shows that it indeed corresponds to the proton transfer. The energy barrier computed at the SCF level is moderate, 7.6 kcal mol^{-1}. It disappears at the MP2//SCF level, the transition state **11** being lower in energy than the intermediate **10**. Whether or not this is due to the lack of optimization at the MP2 level or to the neglect of differential solvation effects cannot be assessed precisely without carrying out calculations in which *both* the effects of the first solvation sphere and of the bulk are taken into account.[47] Such calculations could not be done owing to the size of the system.

The present results, however, point to the feasibility of a *trans* addition of water to **1** via a two-step process involving (i) protonation of the uncoordinated nitrogen atom and (ii) subsequent transfer of the proton to Pd, assisted or triggered by the binding of the hydroxide ion. It is important to note here that OH$^-$ is a strong base, much stronger than H$_2$O, thus accounting for the fact that on proton transfer OH$^-$ binds to Pd and yields the stable intermediate **8**, whereas **4** which has H$_2$O

(42) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109.

(43) Meot-Ner, M. *J. Am. Chem. Soc.* **1986**, *108*, 6189.

(44) The SCRF calculations were carried out at the MP2 level on the gas-phase-optimized SCF geometries, using the methodology and the program developed by Rinaldi and Rivail *et al.*[45] An ellipsoidal cavity based on the van der Waals surface was taken, and the multipole expansion used in the formulation of the electrostatic free energy was truncated after *l* = 6. Bulk dielectric constants of 20.7 and 78.5 were chosen for acetone and water, respectively.

(45) (a) See, for instance, ref 16 and references therein. (b) Rinaldi, D.; Pappalardo, R. R. *SCRFPAC*; QCPE, Indiana University: Bloomington, IN, 1992; program no. 622.

(46) We note here that the overall gas-phase exothermicity is reduced at the DFT//SCF level, down to 29.3 kcal mol^{-1}.

(47) This is probably not due to the MP2 level itself since DFT energy calculations carried out at the B3LYP level with the same basis set on the SCF-optimized geometries also yield **11** to be more stable than **10** by 7.5 kcal mol^{-1}. On the other hand, solvation of OH$^-$ will decrease its basicity and, thus, its affinity to bind palladium. In that sense, the SCF calculation may be a better model of the actual situation. In fact, SCRF-MP2 calculations carried out for the systems **10** and **11** with water as a solvent yielded **11** to be more stable than **10** by only 2.4 kcal mol^{-1}.
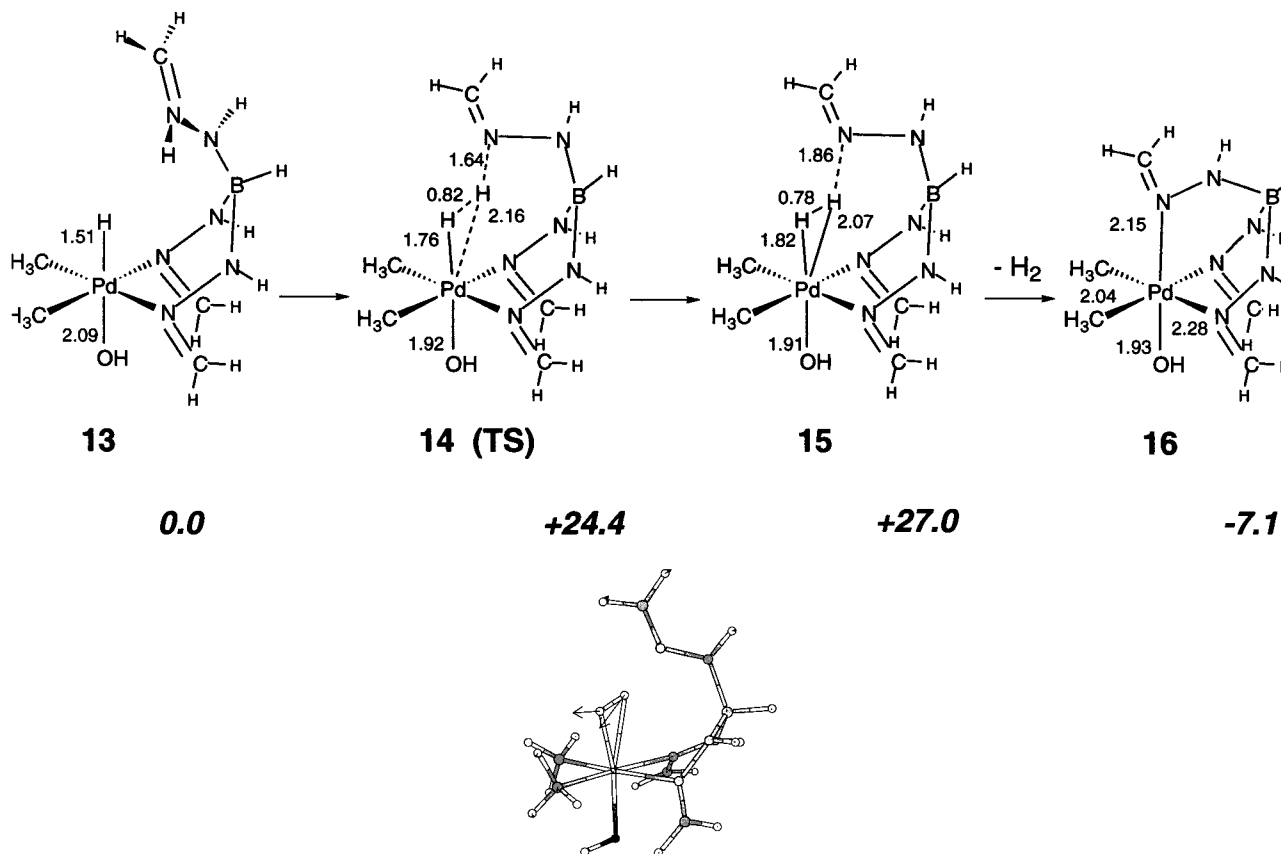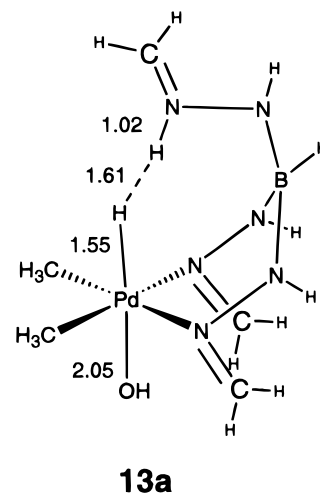
Figure 4. (*top*) SCF-optimized geometries and MP2//SCF relative energies (SCF values are in parentheses) of the structures relevant to the base-assisted proton transfer from the nitrogen atom to the palladium atom in **3**. The energies refer to separated OH⁻ and [PdMe₂{(H₂C=N−NH)₂(H₂C=NH−NH)BH}]. Bond lengths are in angstroms (Å), and energy values are in kcal mol⁻¹. (*bottom*) Plot of the imaginary mode of the SCF transition state **11**.

trans to the hydride is unstable and dissociates back to **3** and H₂O (v*ide supra*).

E. H₂ Elimination on Further Reaction of [PdMe₂(H)(OH){pz)₃BH}]⁻ with H₂O. Equation 5b describes a process in which the [PdMe₂(H)(OH)-{pz)₃BH}]⁻ system is protonated (by a water proton) and subsequent H₂ elimination takes place, releasing the six-coordinate [PdMe₂(OH){pz)₃BH}] product and OH⁻. As noted above, only **6** and **8** need to be considered as candidates for this sequence.

Two sites of protonation are *a priori* available in these two isomers, the oxygen atom of the hydroxo ligand or the nitrogen atom of the noncoordinated pyrazole ligand. However, the [PdMe₂(H)(H₂O){pz)₃BH}] systems **4** and **5** that result from the O-protonation of **8** and **6**, respectively,[48] cannot eliminate H₂. As noted above, **4** is not a stationary point, being unstable with respect to the dissociation of H₂O and H⁺ transfer to the noncoordinated nitrogen atom to form **3**. For **5**, the energy barrier for the σ-bond metathesis reaction that would yield H₂ has been computed to be very large (section C).

The two intermediates **12** and **13** that arise from protonation of the nitrogen atom in **6** and **8**, respec-

tively, differ greatly in their spatial arrangement. In **12**, the proton bound to the nitrogen atom is far from the hydride. Moreover, one cannot conceive any *easy* intramolecular rearrangement that would bring it to the vicinity of the hydride. Thus, **12** is discarded as a productive intermediate for the H₂-elimination process.

In contrast, **13** (Figure 5) has a structure where both hydrogen atoms are confined to the same region of space, thus positioned for H₂ elimination. In fact, **13** is strongly reminiscent of complexes displaying the so-called M−H···H−X "dihydrogen bond".[49−53] For some of these complexes there is evidence of either formation of H₂ adducts and/or loss of H₂ on heating. The

(49) (a) Lee, J. C., Jr.; Rheingold, A. L.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021. (b) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (c) Peris, E.; Lee, J. C., Jr.; Crabtree, R. H; *J. Chem. Soc., Chem. Commun.* **1994**, 2573. (d) Peris, E.; Lee, J. C., Jr.; Rambo, J.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485. (f) Patel, B. P.; Yao, W.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1996**, 991.
(50) (a) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201. (b) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (c) Xu, W.; Lough, A. J.; Morris, R. H.; *Inorg. Chem.* **1996**, *35*, 1549.
(51) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 10108.
(52) For intermolecular M−H···H−N hydrogen bonding, see: (a) Wessel, J.; Lee, J. C.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507. (b) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348.

(48) Note that in **5**, which results from the protonation of **6**, the arm of the hydrazone has folded back toward the water ligand in order to maximize the electrostatic interaction between the hydrogen atom of H₂O and the nitrogen atom of hydrazone.

13   **14 (TS)**   **15**   **16**

0.0   *+24.4*   *+27.0*   *-7.1*

Figure 5. (*top*) SCF-optimized geometries and MP2//SCF relative energies of the structures relevant to the H$_2$-elimination reaction from the N-protonated *trans*-Pd^{IV}(H)(OH) intermediate **13**. Bond lengths are in angstroms (Å), and energies are in kcal mol^{-1}. (*bottom*) Plot of the imaginary mode of the SCF transition state **15**.

dihydrogen-bond complexes are usually characterized by M−H and H−X bonds lying in the same plane, a negative charge of the hydride, and a H···H distance in the range 1.6−1.9 Å.[49−53] None of these features is found in **13**: the Pd−H and H−N bonds make an angle of 32.3° (corresponding to a dihedral angle of 88.5° between the HBN and NNH planes), the charge of the "hydride" is slightly positive (+0.01 e), and the H···H distance is too long for H-bonding, 2.95 Å. However, the positive charge of the hydride has decreased upon protonation, from 0.10 e in **8** to 0.01 e in **13**. Moreover, a rotation around the B−N bond that makes the Pd−H and H−N bonds coplanar, as in **13a**,[54] is not too energy demanding, 5.6 kcal mol^{-1}. It brings the nitrogen-bound proton much closer to the hydride—the H···H distance in **13a** is 1.61 Å. As a result the hydride is polarized, becoming negative with a charge of −0.08 e. This polarizability of the metal−hydrogen bond is also one of the characteristic features of the M−H···H−X dihydrogen bond.[49d]

It is, therefore, not surprising that an accessible transition state is found for the proton transfer to the hydride (**14** in Figure 5). The computed energy barrier

13a

is moderate, 24.4 kcal mol^{-1}, and **14** has been fully characterized by a frequency calculation which shows one imaginary vibrational frequency (275*i* cm^{-1}). The decomposition of this imaginary mode into internal coordinate displacements shows that it corresponds to the formation of the dihydrogen complex **15** as the primary product of the transfer. **14** and **15** are quite close to each other, structurally and energetically. In **14**, the H···H distance is 0.82 Å and the N−H distance is 1.64 Å, similar to the corresponding values in **15** of 0.78 and 1.86 Å. At our SCF-optimization level, **15** is more stable than **14** by only 0.2 kcal mol^{-1}, but it is less stable by 2.6 kcal mol^{-1} at the MP2//SCF level. This reversal is ascribed to the lack of MP2 geometry optimization. Optimizing these two structures at the
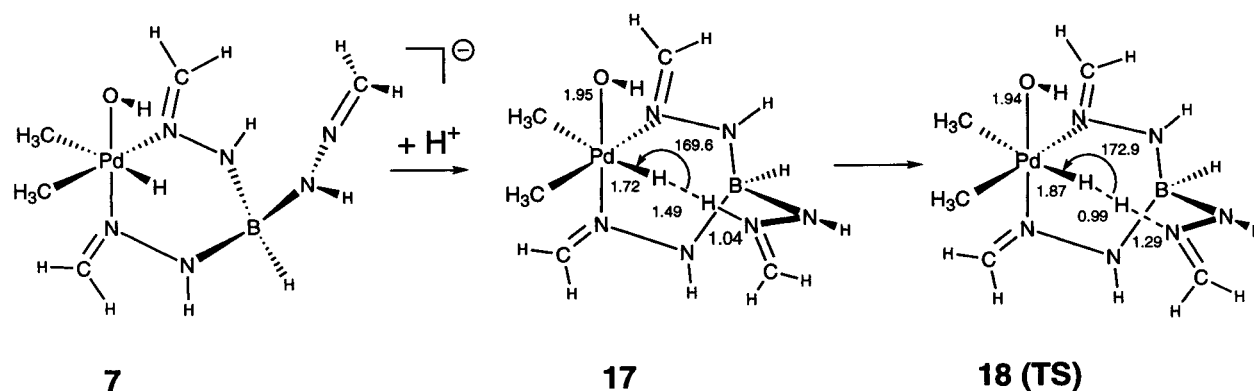
(53) For intermolecular M−H···H−O hydrogen bonding, see: (a) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105. (b) Belkova, N. V.; Shubina, E. S.; Ionidis, A. V.; Epstein, L. M.; Jacobsen, H.; Messmer, A.; Berke, H. *Inorg. Chem.* **1997**, *36*, 1522.

(54) The geometry optimization of **13a** was carried out by constraining the (H$_2$C=N(H)−NH)$^+$ group to lie coplanar with the Pd−H bond. Thus, **13a** is not a true intermediate but provides an estimate of the rotational barrier in **13** and of the polarization of the hydride when lying in the vicinity of the proton.[49d]

Figure 6. SCF-optimized geometries of the structures relevant to the H$_2$-elimination reaction from the N-protonated *trans*-Pd^{IV}(H)(OH) species **7**. Bond lengths are in angstroms (Å), and angles are in degrees.
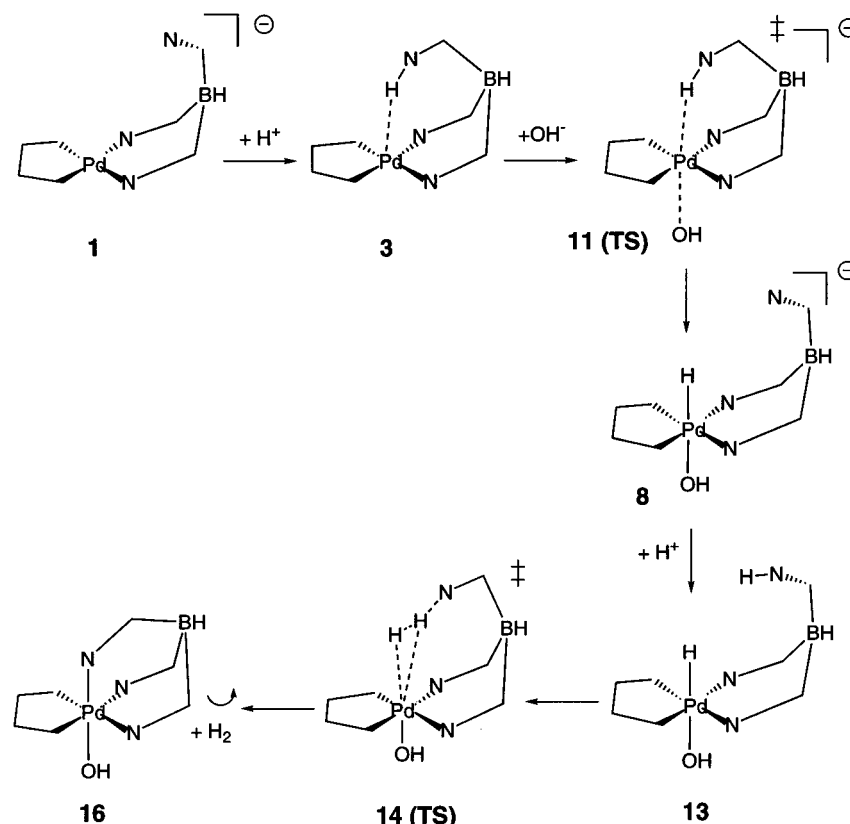

Figure 7. Proposed mechanism for the reaction of [Pd(CH$_2$CH$_2$CH$_2$CH$_2$){(pz)$_3$BH}]$^-$ with water to give Pd(CH$_2$CH$_2$CH$_2$-CH$_2$)(OH){(pz)$_3$BH} and H$_2$. The numbers refer to the structures derived theoretically for the reaction of the model species [PdMe$_2${(H$_2$C=N—NH)$_3$BH}]$^-$.

MP2 level would most likely also give **15** to be slightly more stable than **14**.

The ultimate product of the reaction is of course not **15** but the six-coordinate Pd(IV) complex [PdMe$_2$(OH)-{(H$_2$C=N—NH)$_3$BH}], **16** (Figure 5), which is more stable than **14** by 31.5 kcal mol^{-1} and more stable than **13** by 7.1 kcal mol^{-1}. Thus, the back-reaction of H$_2$ with the [PdMe$_2$(OH){pz)$_3$BH}] complex that would yield the *trans* Pd^{IV}(H)(OH) complex **13** is unlikely. We have already mentioned (see section C, ref 36b) that the same holds for the σ-bond metathesis reaction that would yield the Pd^{IV}(H)(H$_2$O) complex.

14 represents—to our knowledge—the first example of a fully characterized transition state for H$_2$ elimination from a dihydrogen bond. As anticipated from previous studies,[49d] the charge separation between the two hydrogen atoms is a crucial factor for the H$_2$

elimination. Part of the energy barrier between **13** and **14** is associated with the rotation around the B—N bound (**13 → 13a**). Once the charge separation is favorable, the elimination proceeds relatively easily. Should the charge distribution be favorable at the onset, then the energy barrier would be much lower. A representative example of this situation is provided by the H$_2$ elimination from **17** (see Figure 6), a species that would result from the protonation of the nitrogen atom in **7**. In contrast to **13**, the Pd-H and N-H bonds in **17** are coplanar, the optimized H···H distance is 1.49 Å, and as a result the hydride which was already negatively charged in **7**[55] now bears a strong negative charge, −0.28 e. The energy barrier to reach the transition state **18** for the H$_2$ elimination from **17** is, therefore,

(55) The negative charge of the hydride in **7** is the result of the *mer* disposition of the two methyl ligands and of the hydride ligand.[12b]

very small, 2.8 kcal mol^{-1}, thus clearly pointing to the importance of the charge separation for this process and to the electrostatic nature of the interaction in the dihydrogen bond.[56,57] However, **17**, similar to its parent complex **7**, is an inactive intermediate in the multistep process: **7** is highly destabilized with respect to **8**, 19.6 kcal mol^{-1} (section D), and the large energy difference is not affected by the protonation of the nitrogen atom to give **17**, as **17** is found to be 18.5 kcal mol^{-1} higher in energy than **13**. Both species have a meridional arrangement of three strong σ-donor ligands, a geometry not found in Pd(IV) chemistry and very rare in Pt(IV) chemistry.

Concluding Remarks

The results described above suggest key roles for **3**, **8**, and **13** in the reaction of the model species [PdMe$_2$-{(H$_2$C=N—NH)$_3$BH}]$^-$ with water. Thus, the overall mechanism for the reduction of water to hydrogen with the concomitant oxidation of the pallada(II)cyclopentane complex to an hydroxopalladium(IV) product (eq 3) is shown in Figure 7. The reaction involves the transfer of two protons to the palladium center via protonation of the uncoordinated pyrazole group and the occurrence of both "Pd···H—N" and "Pd—H···H—N" interactions. One should also stress here the role of the tris(pyrazol-1-yl)borate ligand: it acts as an intramolecular nucleophile for the two proton delivery steps (*i.e.*, **3** → **8** and **13** → **15**) and, thus, prevents an unfavorable entropy contribution in these steps.

Analogous reactions of Pt(II) complexes with water are much more facile than those for Pd(II) and do not require the presence of an uncoordinated intramolecular nucleophile.[1a,b] Platinum(II) undergoes more facile oxidative-addition reactions than Pd(II),[38,58] *e.g.*, the second-order rate constant for the reaction of iodomethane with PtMe$_2$(bpy) is about 12 times larger

than that for PdMe$_2$(bpy) and both of these reactions occur by the S$_N$2 mechanism where the electrophile Me$^+$ may be regarded as directly related to H$^+$. The mechanism in Figure 7 maintains the square-planar "MC$_2$N$_2$" moiety throughout, as expected in the reaction of PtMe$_2$-(bpy) with water, and hence this mechanism may closely relate to that which occurs for PtMe$_2$(bpy). Thus, the more nucleophilic Pt(II) center may permit successive direct attack by, for example, H$_2$O or H$_3$O$^+$ to form "Pt^{II}···H—OH$_x$" and "*trans*-Pt^{IV}(OH)H···HOH$_y$".[53,59] Stressing further the analogy with the mechanism of Figure 7, H$_2$O and H$_3$O$^+$ may be viewed as H$^+$ being delivered to platinum via the *intermolecular* nucleophiles OH$^-$ and H$_2$O, respectively, rather than by the *intramolecular* nucleophiles required for palladium in Figure 7. Thus, the mechanistic studies reported here appear to be of general relevance to the reduction of water to hydrogen by electron-rich transition metal complexes, as well as the delivery of H$^+$ to metal centers by intramolecular nucleophiles.[60]

Supporting Information Available: Tables of Cartesian coordinates for the theoretically optimized structures (**1**−**18**) (21 pages). Ordering information is given on any current masthead page.

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(56) Also noteworthy in addition to the 1.49 Å H···H distance is the quasi linearity of the bond, the N—H—H angle amounting to 169.6°, see Figure 6. Thus, the Pd—H···H—N interaction is a strong dihydrogen bond, much stronger than in **13** or **13a**. As for the charge increase, and related to it, this can be traced to the *trans* effect of the CH$_3$ ligand in **17**, which is greater than the *trans* effect of the OH ligand in **13** or **13a**.[49d]

(57) In this case, no dihydrogen complex is found, again as a result of the strong *trans* effect of the methyl ligand sitting *trans* to the leaving H$_2$ molecule: the optimization procedure led to the dissociation of H$_2$ and to the simultaneous association of the pyrazole group.

(58) Aye, K. T.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518.

(59) NMR evidence for an intermolecular dynamic proton-transfer equilibrium between (dppm)$_2$HRuH···HOR and [(dppm)$_2$HRu(H$_2$)]$^+$(OR)$^-$ has been reported after the initial submission of this paper, see: Ayllón, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000.

(60) Preliminary calculations carried out for the platinum model complex suggest that a pathway that would involve a *cis* oxidative addition of H$_2$O leading to the analog of **7**, followed by the sequence shown in Figure 6, might be a competitive pathway (the *cis* oxidative addition is much easier for Pt than for Pd and, thus, provides a feasible entry to the sequence of Figure 6).[12b]