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Synthesis and Theoretical Studies of a Diorganohydridoplatinum(IV) Complex, $PtHMe_2\{(pz)_3BH\text{-}N,N',N''\}$ ($[(pz)_3BH]^- =$ Tris(pyrazol-1-yl)borate)

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Summary: The platinum(II) tris(pyrazol-1-yl)borate complex $[PtMe_2\{(pz)_3BH\text{-}N,N'\}]^-$ reacts with phenol or aqueous HBF_4 in acetone to form the dimethylhydridoplatinum(IV) complex $PtHMe_2\{(pz)_3BH\text{-}N,N',N''\}$. The complex decomposes above ~140 °C in toluene-d_8 to give methane. Theoretical calculations at the SCF and MP2 levels for the species $PtXMe_2\{(H_2C{=}N{-}NH)_3BH\text{-}N,N',N''\}$ (where X = H, OH, Me and the fragment $[(H_2C{=}N{-}NH)_3BH]^-$ is a model for $[(pz)_3BH]^-$) yield geometries that compare well with structural reports for $Pt(OH)Me_2\{(pz)_3BH\}$ and $PdMe_3\{(pz)_3BH\}$.

Studies of the chemistry of complexes containing both σ-bonded organo and hydrido groups have been fundamental to the development of organometallic chemistry and catalysis.[1] For platinum, one of the most important metals in catalysis, organohydridoplatinum(II) chemistry is well established[2] but the first reports of alkylhydridoplatinum(IV) complexes occurred only in 1995.[3] The latter complexes, which include $PtCl(H)Me_2(N{\sim}N)$[3b] (N~N = 2,2′-bipyridyl) and $PtCl_2(H)(CH_2Ph)(N{\sim}N)$[3c] (N~N = *N,N,N′,N″*-tetramethylethylenediamine), are formed by reaction of HCl with platinum(II) substrates and readily decompose at or below ambient temperature. We report here the synthesis of a dimethylhydridoplatinum(IV) complex which decomposes above ~140 °C in the solid state and in solution, $PtHMe_2\{(pz)_3BH\text{-}N,N',N''\}$ ($[(pz)_3BH]^-$ = tris(pyrazol-1-yl)borate), together with theoretical calculations of the structure of the complex and closely related species. The calculations appear to be the first reports of theoretical modeling for the now classical[4] tris(pyrazol-1-yl)borate ligand.

The platinum(IV) complex may be isolated in the reaction of phenol with an acetone solution containing $[PtMe_2\{(pz)_3BH\}]^-$, generated from $[PtMe_2(SEt_2)]_2$ and $K[(pz)_3BH]$.[5] The complex has spectroscopic properties consistent with the formulation $PtHMe_2\{(pz)_3BH\}$;[6] in particular, the ^1H NMR spectrum exhibits appropriate integration, pyrazole ring environments in 2:1 ratio, a single PtMe resonance with $^2J_{PtH} = 68.4$ Hz as expected for Pt(IV),[2,3b,7] δ(H) −20.2 ppm with $^1J_{PtH} = 1358$ Hz as expected for a hydridoplatinum(IV) species,[3] and $^4J_{PtH} \approx 9$ Hz for the pyrazole groups and the IR spectrum shows ν_{B-H} (2475 cm^{-1}) and ν_{Pt-H} (2250 cm^{-1}) absorptions. The complex decomposes above ~140 °C in toluene-d_8 to form platinum metal and methane, but neither ethane nor ethene could be detected by NMR or GC−MS.[8] The hydridoplatinum(IV) complex is assumed to be formed by protonation of platinum(II) by phenol, and consistent with this interpretation a solution of the hydrido complex is rapidly formed on addition of aqueous HBF_4 (54%, Aldrich) to $[PtMe_2\{(pz)_3BH\}]^-$ in acetone-d_6.

Protonation of the platinum atom of $[PtMe_2\{(pz)_3BH\}]^-$ could occur by direct means or perhaps via protonation of the uncoordinated pyrazole group, since these groups in other complexes of this ligand appear to be easily protonated.[9] Moreover, it is known that "platinum(II)···protonated amine" interactions occur in some complexes.[10,11] Calculations on protonated metal cen-

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(5) Synthesis of $PtHMe_2\{(pz)_3BH\}$, where all work was performed with dry solvents under nitrogen: A solution of $[PtMe_2(SEt_2)]_2$ (0.050 g, 0.080 mmol) and $K[(pz)_3BH]$ (0.044 g, 0.175 mmol) in acetone (7 mL) was stirred at ambient temperature for 30 min. Phenol (0.015 g, 0.160 mmol) in acetone (1 mL) was added dropwise, and after the mixture was stirred for 4 h, the solvent was removed under vacuum to give a white oily solid. The solid was dissolved in the minimum quantity of acetone and the mixture extracted with diethyl ether (3 × 5 mL) to remove insoluble inorganic products. The solvent was removed under vacuum to give a white powder, which was washed with hexane (3 × 2 mL) and dried under vacuum (0.050 g, 72% yield).

(6) Spectroscopic and analytical data are as follows. ^1H NMR (acetone-d_6): δ 7.68 (d, 3H, H5), 7.63 (d with poorly resolved sidebands, 2H, H3 trans to Me, $^4J_{PtH} \approx 9$ Hz), 7.56 (d with poorly resolved sidebands, 1H, H3, $^4J_{PtH} \approx 9$ Hz), 6.21 (m, 3H, H4), 1.08 ("t", $^2J_{PtH} = 68.4$ Hz, 6H, PtMe), −20.2 ("t", $^1J_{PtH} = 1358$ Hz, 1H, PtH). IR (KBr disk): 2475 (ν_{B-H}), 2250 cm^{-1} (ν_{Pt-H}). Anal. Calcd for $C_{11}H_{17}BN_6Pt$: C, 30.1; H, 3.9; N, 19.1. Found: C, 31.0; H, 4.1; N, 18.5.

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(8) A solution of the complex (0.01 g) in toluene-d_8 (0.4 mL) was sealed under argon in a 5 mm NMR tube and the temperature raised in 10 °C intervals from ambient temperature over a period of 3 h. Decomposition was detected above 140 °C, and at 150 °C the decomposition was complete within 10 min.

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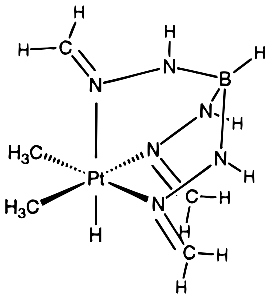
ters, and on protonation of donor atoms adjacent to metal centers, have been undertaken recently in our laboratory, in particular for palladium as the metal center in calculations.[11,12] We have developed this work further to include a model for the tris(pyrazol-1-yl)borate ligand system in order to explore the mechanism of protonation and to calculate a structure for the platinum(IV) complex. Thus, theoretical calculations were carried out using the Gaussian 94 program[13] on the model systems **1** and **4**, together with **2** and **3**, in view of X-ray structural reports for closely related $\mathrm{PdMe_3\{(pz)_3BH\}}$[14] and $\mathrm{Pt(OH)Me_2\{(pz)_3BH\}}$,[15] where the simple ligand skeleton $\mathrm{[(H_2C{=}N{-}NH)_3BH]^-}$ in place of $\mathrm{[(pz)_3BH]^-}$ serves to reduce the computations to a workable range.



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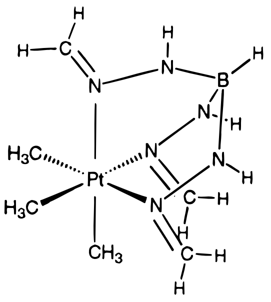

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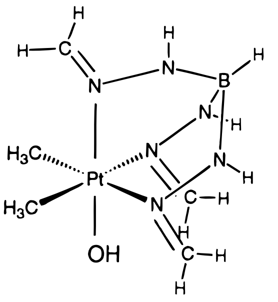

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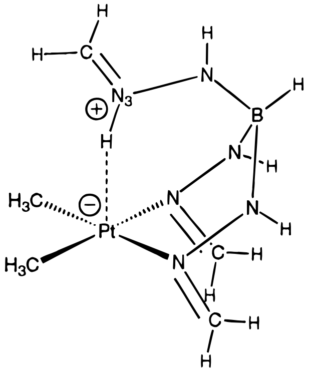

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The results reported here were obtained from a geometry optimization of **1**−**4** carried out with a gradient technique at the SCF level, followed, for the assessment of the relative stabilities of **1** and **4**, by an MP2 geometry and energy determination (MP2//MP2 level)[16] of these two systems. This showed (*vide infra*) that optimizing the geometry at the MP2 level does not change the main conclusions from the MP2//HF level calculations.[10b,21]

The SCF-computed bond lengths are in good agreement with X-ray structural data for **3** and the palladium analogue of **2** (Table 1), except for the equatorial Pt−N bonds, which are systematically too long. This may be due to the neglect of electron correlation in the geometry optimization process and/or to the model used for the ligand, which lacks conjugation for the pyrazole rings. Consistent with the first hypothesis, an MP2 geometry optimization carried out on **1** yielded a shortening of the two equatorial Pt−N bonds from 2.23 to 2.18 Å on going from SCF to MP2 and of the axial Pt−N bond from 2.27 to 2.21 Å (Table 1). However, the variations in the Pt−N bond length are well reproduced at the SCF level, and thus for X = OH the computed Pt−N bond length trans to the hydroxo group is shorter than the equatorial length by 0.11 Å, as found in the X-ray structure for $\mathrm{Pt(OH)Me_2\{(pz)_3BH\}}$, where the shortening is 0.13 Å. The Pt−N bond trans to X is lengthened by 0.12 Å on going from X = OH to X = Me, reflecting the stronger trans influence of the methyl group. Although the structure of $\mathrm{PtMe_3\{(pz)_3BH\}}$ has not been determined, a similar lengthening of 0.16 Å occurs for $\mathrm{PdMe_3\{(pz)_3BH\}}$ compared to $\mathrm{Pt(OH)Me_2\{(pz)_3BH\}}$. The SCF-optimized geometry of the $\mathrm{PdMe_3\{(H_2C{=}N{-}NH)_3BH\}}$

Table 1. Computed Bond Lengths (Å) at the SCF Level for Species 1−3 That Model $\mathrm{PtXMe_2\{(pz)_3BH\}}$ (X = H, OH, Me)

	Pt−X	$\mathrm{Pt{-}N_{ax}}$	$\mathrm{Pt{-}N_{eq}}$	$\mathrm{Pt{-}C_{Me}}$
1: X = H	1.51 (1.53)[a]	2.27 (2.21)[a]	2.23 (2.18)[a]	2.07 (2.10)[a]
2: X = Me	2.06 (2.03)[b]	2.24 (2.18)[b]	2.24 (2.18)[b]	2.06 (2.03)[b]
3: X = OH	1.96 (1.98)[b]	2.12 (2.02)[b]	2.23 (2.15)[b]	2.06 (2.05)[b]

[a] MP2 values. [b] Values determined by X-ray structural studies for $\mathrm{PdMe_3\{(pz)_3BH\}}$ (Pd−C = 2.024(5), 2.032(7), 2.034(4) Å; Pd−N = 2.174(3), 2.177(3), 2.178(4) Å)[14] and $\mathrm{Pt(OH)Me_2\{(pz)_3BH\}}$ (Pt−O = 1.984(5) Å; Pt−N = 2.022(5), 2.151(3) Å; Pt−C = 2.048(5) Å).[15]

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(16) (a) The basis set was a split-valence-type basis set without polarization functions, except for the active hydrogen atom. The 60 innermost core electrons (up to 4d) of the platinum atom were described by the relativistic pseudopotential of Hay and Wadt[17] and the remaining outer core and valence electrons by an (8,6,4) ⟨3,3,2⟩ basis set.[17] The carbon, nitrogen, and oxygen atoms were described by a (9,5) basis set contracted into ⟨3,2⟩[18] and the hydrogen atoms of the $\mathrm{CH_3}$, $\mathrm{NH_3}$, and $\mathrm{[(H_2C{=}N{-}NH)_3BH]}$ ligands by a (4) contracted to ⟨2⟩ basis set.[19] The hydrido ligand of **1** was described by a somewhat more flexible (6,1) contracted to ⟨3,1⟩ basis set,[18] where the exponent of the p polarization function was set at 0.8. The basis set for the oxygen atom in **3** was also supplemented by a d polarization function of exponent 1.0. (b) C_s symmetry was maintained throughout the calculations. For X = OH the orientation of the OH group, with H below the methyl groups, was considered. Related calculations on the palladium analogue[20] with two different orientations for OH, one with H below the methyl groups and another below the $\mathrm{[(H_2C{=}N{-}NH)_3BH]^-}$ group, showed both to be essentially the same, the energy difference between the two isomers being less than 1 kcal mol^{-1}. (c) The MP2 calculations were carried out with a frozen core. (d) Total energies (in au) of the local minima are as follows: for **1**, SCF −668.1864, MP2//HF −669.5696, MP2//MP2 −669.5897; for **2**, SCF −707.1638; for **3**, SCF −743.0013; for **4**, SCF −668.1851, MP2//HF −669.5337, MP2//MP2 −669.5558.

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

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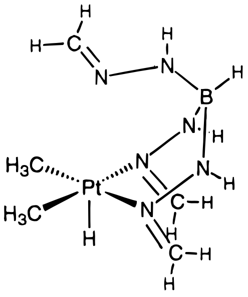
(21) The same conclusion was also reached from calculations on simpler palladium model systems. For example, when the hydridopalladium(IV) system $\mathrm{PdCl(H)_3(NH_3)_2}$ is compared with its zwitterionic palladium(II) tautomer $\mathrm{[PdCl(H)_2(NH_3)^-{\cdots}H{-}NH_3^+]}$, energy differences in favor of the Pd(IV) system are found: 11.1 kcal mol^{-1} at the MP2//HF level and 10.3 kcal mol^{-1} at the MP2//MP2 level. Thus, the level of the optimization (either HF or MP2) has no strong influence on the energy difference. Improving either the level of electron correlation (by performing MP4 calculations) or the quality of the basis set (by adding diffuse and polarization functions) also does not cause substantial changes. In the first case the energy difference is reduced by 3.4 kcal mol^{-1}, and in the second case it is increased by 3.3 kcal mol^{-1}; thus, the two improvements essentially cancel each other.

model system is also in good agreement with the experimental structure of $PdMe_3\{(pz)_3BH\}$.[20,22] Thus, all these results give credence to the values optimized for **1** and suggest that $[(H_2C{=}N{-}NH)_3BH]^-$ is a suitable model for $[(pz)_3BH]^-$.

The computed Pt−H bond length for **1**, 1.51 and 1.53 Å at the SCF and MP2 levels, respectively, appears reasonable when compared with the (apparently) single organohydridoplatinum(II) structure, for which Pt−H has been determined by X-ray crystallography (1.56(5) Å for $PtH(CH_2CMe_3)(Cy_2PCH_2CH_2PCy_2)$[23]).

Calculations for species **4**, involving protonation of the uncoordinated pyrazole group, result in a local minimum on the potential hypersurface, although it is much less stable than the hydridoplatinum(IV) species **1** by 22.5 and 21.3 kcal mol^{-1} at the MP2//HF and MP2//MP2 levels, respectively.[24] The calculated structure for the Pt···H−N unit (Pt···H = 1.89 Å, N−H = 1.11 Å, Pt···H−N = 164.5°) is quite similar to that observed in the X-ray structure for square-pyramidal $PtBr(1\text{-}C_{10}H_6\text{-}NMe_2\text{-}8\text{-}C,N)(1\text{-}C_{10}H_6NHMe_2\text{-}8\text{-}C,NH)$,[10b] which has Pt···H in the axial position (Pt···H = 2.11(5) Å, N−H = 0.88(5) Å, Pt···H−N = 168(4)°).

Another interesting feature revealed by the theoretical study is that no local minimum corresponding to a *five-coordinate* platinum(IV) complex, with the imino nitrogen atom either on top of the platinum atom (**5**) or on top of the hydrido ligand (**6**), could be obtained. Instead, geometry optimizations (either at the SCF or MP2 levels) starting from such structures converged invariably to **1** and **4**, respectively.



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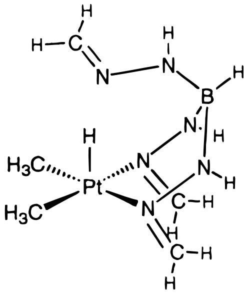

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Thus, the theoretical results for model species **2** and **3** show good agreement with X-ray structural studies of related complexes, enhancing the validity of the calculated structure for the title complex $PtHMe_2\{(pz)_3BH\}$ and indicating that $[(H_2C{=}N{-}NH)_3BH]^-$ is a satisfactory model for the tris(pyrazol-1-yl)borate ligand. In addition they indicate that, at least in the gas phase, protonation of $[PtMe_2\{(pz)_3BH\}]^-$ occurs on the face opposite to the uncoordinated nitrogen atom and leads to the six-coordinate platinum(IV) complex **1**, the model species corresponding to $PtHMe_2\{(pz)_3BH\}$.

Acknowledgment. We thank the Australian Research Council for financial support and Johnson Matthey Ltd. for generous loans for platinum salts. The theoretical calculations were carried out on the IBM RS 6000 workstations of our laboratory and of the Institut du Développement et de Ressources en Informatique Scientifique (IDRIS, Orsay, France). We thank the staff of IDRIS for their cooperation and Dr. L. Padel and Mrs. S. Fersing for their help and technical assistance.

Supporting Information Available: Tables of Cartesian coordinates for the optimized structures **1**−**4** (6 pages). Ordering information is given on any current masthead page.

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(22) The SCF-optimized bond lengths are Pd−C = 2.05 Å and Pd−N = 2.29 Å. This yields a value of 0.17 Å for the lengthening of the metal−nitrogen bond trans to X for $PdMe_3\{(H_2C{=}N{-}NH)_3BH\}$ compared to $Pt(OH)Me_2\{(H_2C{=}N{-}NH)_3BH\}$, in excellent agreement with the experimental value (0.16 Å).

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(24) It is interesting to note that this conclusion is obtained only when electron correlation is taken into account. At the SCF level **4** is less stable than **1** by only 0.8 kcal mol^{-1}. This is traced to the underestimation, by the HF calculations, of the energy of protonation at the metal.[12] A similar feature is found for the palladium(IV) system and its zwitterionic tautomer. For this, the analogue of **4** is more stable than the analogue of **1** by 22 kcal mol^{-1} at the HF//HF level and less stable by 11.3 kcal mol^{-1} at the MP2//HF level.[20] The decrease in the differential effect on going from Pd to Pt is traced to the fact that in the Pd zwitterionic complex the metal···hydrogen interaction is mainly electrostatic, whereas it has more covalent character in the Pt system.[11] An indication of the increase in the covalent character for the Pt system is the change in the geometrical parameters for the Pt···H−N unit on going from SCF to MP2: the SCF level gives Pt−H = 2.17 Å and N−H = 1.03 Å; the MP2 level gives 1.89 and 1.11 Å, respectively.