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Articles

Computational Study of Reductive Elimination Reactions to Form C−H Bonds from Platinum(II) and Platinum(IV) Centers with Strongly Coordinating Trimethylphosphine Ligands

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B3LYP calculations have been performed on the effects of replacing PH_3 with PMe_3 ligands in the reductive elimination of methane from *cis*-hydridomethyl−bisphosphine platinum(II) and platinum(IV) model complexes. In both the Pt(II) and Pt(IV) complexes, the replacement of PH_3 ligands by the more strongly basic PMe_3 ligands is predicted to favor a direct mechanism for reductive elimination over one in which the initial step is phosphine ligand loss. However, the effect of the increased platinum−phosphine binding enthalpy on the ligand-predissociation mechanism was found to be partially canceled by an increase in the barrier height computed for the direct mechanism. It was possible to locate the transition structures for direct reductive elimination of methane from several isomers of $Cl_2(PMe_3)_2Pt(CH_3)H$. In contrast, the lower binding enthalpy of PH_3, compared to PMe_3, made it impossible to locate the transition structures for direct elimination from the corresponding isomers of $Cl_2(PH_3)_2Pt(CH_3)H$. Our computational results suggest that destabilizing cis interactions between the atoms of the axial and equatorial ligands that are coordinated to platinum are responsible for the lower phosphine binding enthalpy in six-coordinate Pt(IV), compared to four-coordinate Pt(II) complexes. The much greater propensity of Pt(IV) than of Pt(II) complexes to undergo reductive elimination via a ligand-predissociation mechanism can be attributed to these interactions. Our calculations suggest that Pt(IV) complexes with chelating trialkylphosphine ligands should be good candidates for undergoing C−H reductive eliminations by a direct mechanism, rather than by a ligand predissociation pathway.

Introduction

The mechanism of reductive elimination of alkanes from platinum complexes has been the subject of considerable research.[1−6] It has been shown experimentally that the mechanism of alkyl C−H reductive elimination is dependent on the oxidation state and coordination number of the metal. Eliminations of alkanes from octahedral Pt(IV) complexes have been found to require loss of an ancillary ligand, prior to the reductive elimination step,[4,5] while all hydridoalkyl Pt(II) complexes that have been studied were found to

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] Alkyl C−C elimination from Pt(II): DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601.

[3] Alkyl C−H elimination from Pt(II): (a) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831. (b) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

[4] Alkyl C−C elimination from Pt(IV): (a) Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2000**, *122*, 962. (b) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (c) Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408. (d) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889. (e) van Asselt, R.; Rijnberg, E.; Elsevier: C. J. *Organometallics* **1994**, *13*, 706. (f) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121. (g) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (h) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576.

[5] Alkyl C−H elimination from Pt(IV): (a) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831. (b) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854. (d) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156. (e) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (f) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209. (g) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (h) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (i) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.

[6] Theoretical investigations of reductive elimination from Pt(II) and Pt(IV): (a) Dedieu, A. *Chem. Rev.* **2000**, *100*, 543. (b) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456. (c) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 2041. (d) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1999**, *121*, 4633. (e) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478. (f) Su, M.-D. Chu, S.-Y. *Inorg. Chem.* **1998**, *37*, 3400. (g) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4442. (h) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115. (i) Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609. (j) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482. (k) Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. *Inorg. Chem.* **1982**, *21*, 2162. (l) Hoffmann, R. In *Frontiers of Chemistry*; Laidler, K. J., Ed.; Pergamon Press: Oxford, 1982; p 247. (m) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

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reductively eliminate alkane directly from the square-planar complex.[3] The origin of this difference between the mechanistic preferences of Pt(IV) and Pt(II) is not immediately obvious, since the two reactions appear to be, at least superficially, analogous.

We have previously carried out calculations on the mechanism of methane reductive elimination from the model platinum complexes $(PH_3)_2Pt(CH_3)H$ and $Cl_2(PH_3)_2Pt(CH_3)H$.[6b] In both complexes the activation enthalpy for the reductive elimination step was computed to be substantially lowered by ligand loss. However, the activation enthalpies for the reductive elimination steps, with ligand loss and without ligand loss, were computed to be relatively invariant to the oxidation state of the platinum. The difference in mechanistic preferences between these Pt(II) and Pt(IV) complexes was found to arise predominantly from the difference between the enthalpies required for phosphine ligand loss. The enthalpy required to remove an ancillary phosphine ligand was computed to be substantially less for the octahedral Pt(IV) complex than for the square-planar Pt(II) complex.[6b]

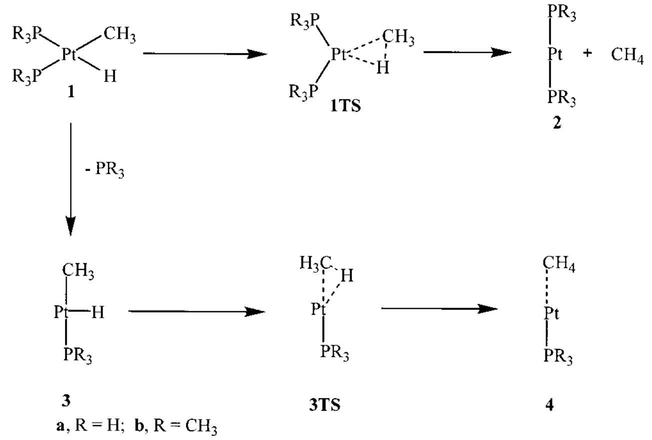
If the ligand loss step were sufficiently disfavored, the mechanistic preference for reductive elimination from Pt(IV) complexes should switch from the ligand-predissociation pathway to the direct mechanism. We have investigated this possibility by carrying out calculations on reductive elimination of methane from Pt(II) and Pt(IV) complexes that have PMe_3 rather than PH_3 ligands. PMe_3 ligands are more basic[7] and should bind more strongly than PH_3 ligands to both Pt(II) and Pt(IV). Herein we report the results of these calculations.

Computational Methodology

The density function theory (DFT) methodology we used was identical to that described in our previous paper.[6b] Stationary points were located[8] and vibrational analyses were performed with the B3LYP version of DFT, which is comprised of Becke's hybrid three-parameter functional[9] and the correlation functional of Lee, Yang, and Parr.[10]

In our previous study, B3LYP was found to give results that were nearly the same as those obtained from CCSD(T) calculations. In fact, the largest apparent disagreement between these two types of calculations—the enthalpies of the phosphine dissociation reactions—essentially disappeared after application of the full counterpoise method to correct for errors due to basis-set superposition.[11,12] In the calculations whose results are reported here, the phosphine dissociation enthalpies were also corrected for basis-set superposition errors in the reactant complexes, using the full counterpoise method.

Scheme 1



The relativistic effective core potential and basis set of Stevens, Basch, Krauss, and Jaisen were used for platinum.[13] The polarized Dunning/Huzinaga double-ζ D95** basis set[14] was employed for all other atoms, except for the hydrogens of the phosphine methyl groups, for which the 2p polarization functions were omitted.

Using the unscaled frequencies from the vibrational analyses, zero-point energy and thermal corrections were applied to the electronic energies, to obtain relative enthalpies[15] at 298 K. Full descriptions of the geometries and energies of all species are available as Supporting Information. All of the calculations were carried out with the Gaussian 98 package of electronic structure programs.[16]

Results and Discussion

Methane Reductive Elimination from Pt(II). We began by investigating reductive elimination of methane from the square-planar bistrimethylphosphine hydri-

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[7] (a) The gas-phase proton affinity of PMe_3 is 40.1 kcal/mol larger than that of PH_3.[7b] Our calculations agree well with this value, yielding a $\Delta PA = 42.4$ kcal/mol (enthalpy at 298 K). In aqueous solution, the pK_a of $HPMe_3^+$ is ca. 22 pK_a units higher than PH_4^+.[7c,d] (b) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 6252. (c) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791. (d) Weston, R. E.; Bigeleisen, J. *J. Am. Chem. Soc.* **1954**, *76*, 3074.

[8] Stationary points were characterized as having zero (minima) or one (transition structure) mode(s) with imaginary frequencies. Structures with low energy XH_3 internal rotational modes were difficult to optimize. Many optimizations were considered converged, based on low maximum and RMS forces, even though the maximum and RMS displacements were not fully converged. A few optimizations (**3b** and **6b**) resulted in fully converged structures, which should have been minima, but which had one very small imaginary frequency. This frequency could not be made real, despite the fact that the optimizations were performed in C_1 symmetry and analytical second derivatives were calculated at each step in the geometry optimizations.

[9] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[10] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

[11] The enthalpies required for six phosphine dissociation reactions were higher by 6.1 ± 0.7 kcal/mol at CCSD(T) than at B3LYP, prior to correction for basis-set superposition error (BSSE). After correction, the average of the differences between the B3LYP and CCSD(T) dissociation enthalpies was only 0.1 kcal/mol, and the root-mean-square difference was ±0.7 kcal/mol. (See the Supporting Information for ref 6b.)

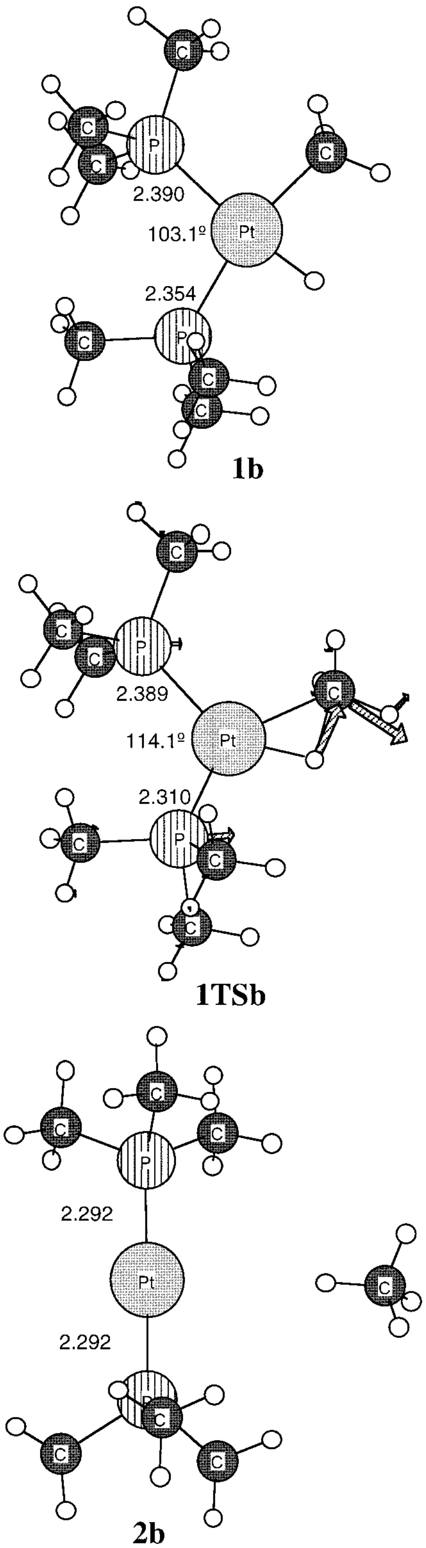
[12] Kestner, N. R.; Combariza, J. E. In Lipkowitz, K. B.; Boyd, D. B. *Reviews in Computational Chemistry*; Wiley-VCH: New York, 1999; Vol. 13, pp 99−132.

[13] Stevens, W. J.; Krauss, M.; Bausch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.

[14] Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; pp 1−28.

[15] Computed entropic contributions to the gas-phase free energies are available in the Supporting Information. Unfortunately, the gas-phase entropies are not the same as the solution-phase entropies, which are chemically relevant. In addition, the use of harmonic oscillator partition functions by Gaussian 98 for the low-frequency, hindered rotations in the complexes in this article makes the accuracy of even the gas-phase entropies suspect. Consequently, the computed entropic contributions to free energies are not discussed in the text.

[16] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98 (Revision A.7)*; Gaussian, Inc.: Pittsburgh, PA, 1998.

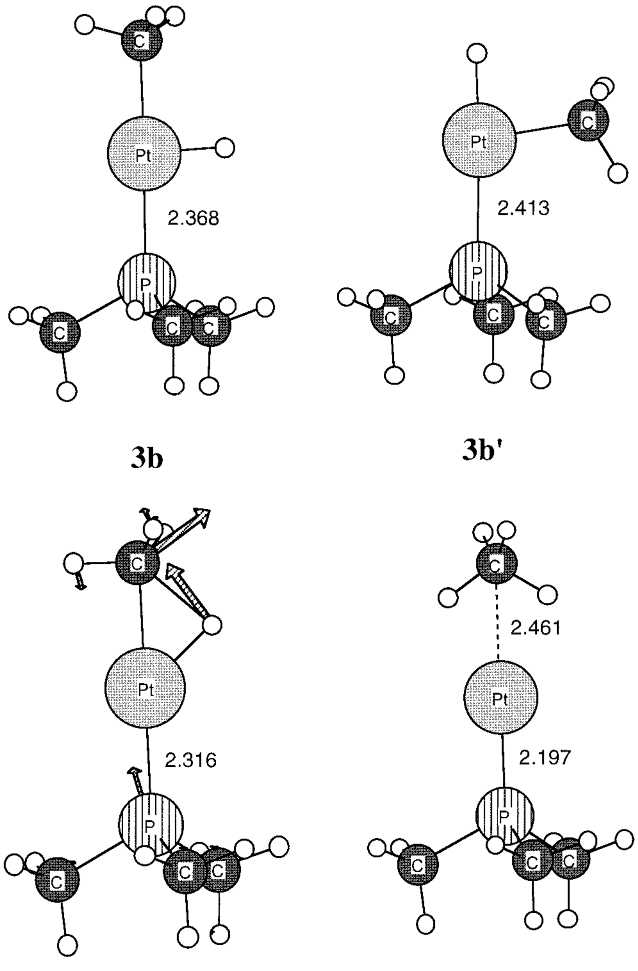


1b

1TSb

2b

Figure 1. Optimized geometries of $(PMe_3)_2Pt(CH_3)H$ (**1b**), $(PMe_3)_2Pt$ (**2b**) + CH_4, and the transition structure (**1TSb**) that connects **1b** with **2b** + CH_4. Bond lengths are in angstroms, and bond angles are in degrees. The products (**2b** + CH_4) optimized to a Pt−C distance of 4.39 Å. The arrows in **1TSb** show the motion along the reaction coordinate in this transition structure.



3b

3b'

3TSb

4b

Figure 2. Optimized geometries of two stereoisomers of $(PMe_3)Pt(CH_3)H$ (**3b** and **3b′**), $(PMe_3)Pt{\cdot}CH_4$ (**4b**), and the transition structure (**3TSb**) that connects both **3b** and **3b′** with **4b**. Bond lengths are in angstroms, and bond angles are in degrees. The arrows in **3TSb** show the motion along the reaction coordinate in this transition structure.

domethyl Pt(II) complex **1b**, in Scheme 1. A transition structure (**1TSb**) for reductive elimination of methane directly from **1b** was located and is shown in Figure 1.[17] A transition structure (**3TSb**) for reductive elimination of methane from the T-shaped three-coordinate complex (**3b**), formed by trimethylphosphine loss from **1b**, was also found. It is shown in Figure 2.[18]

The overall potential surface for reductive elimination of methane from **1b** is qualitatively similar to that for the PH_3 ligated species (**1a**).[6b] However, differences due to the increased ligand basicity in **1b** are evident in Table 1. The enthalpy required for phosphine ligand loss, which occurs preferentially trans to the hydride,[18] is 4.6 kcal/mol larger for PMe_3 loss from **1b** than for PH_3 loss from **1a**. Following ligand loss, the barrier to reductive elimination from the three-coordinate intermediates is only 0.2 kcal/mol higher for **3b** than for **3a**. Therefore, as anticipated, the ligand-predissociation mechanism is disfavored by the more basic PMe_3 ligands, and the difference between the relative enthal-

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(17) The graphics used in all the figures were created with the program MacMolPlot, v. 5.2.1, written by Brett Bode. Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Mod.* **1999**, *16*, 133.

(18) Similar to the case in the PH_3 ligated system, **1a**,[6b] removal of the trimethylphosphine trans to the methyl to form **3b′** required significantly more energy (see Table 1). Attempted reductive elimination of methane from **3b′** caused the phosphine to reorient, yielding **3b** prior to methane elimination. The barrier for the isomerization of **3b′** to **3b** is 2.8 kcal/mol.

Table 1. Relative Energetics of Methane Reductive Elimination from $L_2Pt(CH_3)H$, (1), via Both Direct and Ligand-Predissociation Mechanisms[a]

complex	**a** (L = PH_3[b])	**b** (L = PMe_3)
1	0	0
1TS	16.5	19.5
2 + CH_4	−11.8	−12.9
3 + L	18.0 (0)[c]	22.6 (0)[c]
3′ + L	23.8 (5.8)	29.6 (7.0)
3TS + L	24.2 (6.2)	29.0 (6.4)
4 + L	11.8 (−6.2)	16.7 (−5.9)

[a] Reported as enthaplies at 298 K relative to **1**, after correction of phosphine dissociation enthalpies for basis set superposition error. [b] See ref 6b. [c] Values in parentheses are relative to **3** + L.

Scheme 2

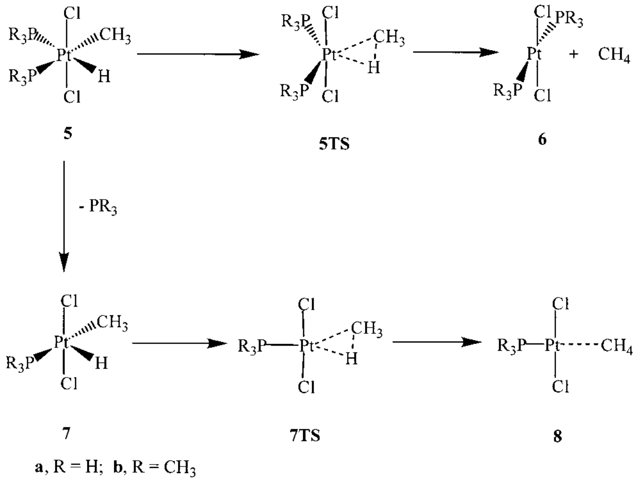

Table 2. Relative Energetics of Methane Reductive Elimination from $L_2Cl_2Pt(CH_3)H$, Isomer 5, via Both Direct and Ligand-Predissociation Mechanisms[a]

complex	**a** (L = PH_3[b])	**b** (L = PMe_3)
5	0	0
5TS	~15−16[c]	16.8
6 + CH_4	−31.9	−39.1
7 + L	10.2 (0)[d]	18.1 (0)[d]
7′ + L	13.3 (3.1)	21.6 (3.5)
7TS + L	13.2 (3.0)	18.8 (0.7)
8 + L	−7.4 (−17.6)	−6.1 (−24.2)

[a] Reported as enthaplies at 298 K relative to **5**, after correction of phosphine dissociation enthalpies for basis set superposition error. [b] See ref 6b. [c] Estimated relative enthalpy. A true transition structure could not be located.[6b] [d] Values in parentheses are relative to **7** + L.

pies of **3TSa** and **3TSb** is almost entirely due to the difference between the enthalpies required for PH_3 loss from **1a** and PMe_3 loss from **1b**.

However, the activation enthalpy for direct reductive elimination of methane from the square-planar complex **1** also increases upon replacing PH_3 with PMe_3. The barrier of 19.5 kcal/mol for direct reductive elimination from **1b** via **1TSb** is 3.0 kcal/mol higher than that for **1a** via **1TSa**. Thus, the enthalpy difference between the transition structures for the direct mechanism (**1TS**) and the ligand-predissociation mechanism (**3TS**) is only 1.8 kcal/mol larger for PMe_3 ligated species than for PH_3 ligated species, despite the 4.6 kcal/mol greater phosphine ligand binding enthalpy in **1b**.

Methane Reductive Elimination from Pt(IV). Complex **5** in Scheme 2 is a Pt(IV) analogue of the Pt(II) complex **1**. Complex **5** differs from **1** by the addition of two chlorine atoms to the vacant axial sites in **1**. Replacing the PH_3 ligands in **5a** with PMe_3 in **5b** was found to cause significant changes in the potential surface for methane reductive elimination. Our previous computational study found that a phosphine ligand was ejected from **5a**, concomitant with methane elimination. In contrast, it was possible to locate a transition structure (**5TSb**) for direct methane elimination from **5b**, without accompanying phosphine loss.

Starting with a geometry on the product side of **5TSb**, a full geometry optimization led to the square-planar Pt(II) complex, *trans*-$(Me_3P)_2PtCl_2$ (**6b**), plus a molecule of methane. The formation of **6b** from **5b** was computed to have a barrier of $\Delta H^{\ddagger} = 16.8$ kcal/mol and to be exothermic by $\Delta H = -39.1$ kcal/mol (Table 2).[19]

As shown in Figure 3, the transition vector in **5TSb** consists predominantly of motion of the hydride and the methyl. However, unlike the case in **1TSb**, in which both PMe_3 ligands move toward the positions that they occupy in the product (**2b**),[19] in **5TSb** the PMe_3 ligand trans to the hydride moves away from the metal. In fact, in **5TSb** the bond to this PMe_3 ligand is 0.078 Å longer than in the reactant (**5b**), whereas the bond to the other PMe_3 ligand is shorter by 0.071 Å in **5TSb** than in **5b**. Nevertheless, in contrast to the case in **5a**, where the PH_3 ligand trans to hydride is actually lost before the transition state for methane elimination is reached, PMe_3 loss was not found to accompany reductive elimination of methane from **5b**.

In addition to locating transition structure **5TSb** for direct reductive elimination of methane from **5b**, without ligand loss, we also found the transition structure for reductive elimination of methane from **5b** via a ligand-predissociation mechanism (**7TSb**). Removing the PMe_3 ligand trans to hydride from **5b**, to give the five-coordinate intermediate **7b**, requires 18.1 kcal/mol (Table 2).[20] The geometries of **7b** and **7TSb** are shown in Figure 4.

Even though reductive elimination of methane from **7b**, through **7TSb**, requires only 0.7 kcal/mol, the overall activation enthalpy for reductive elimination of methane from **5b** via this ligand-predissociation mechanism is 18.8 kcal/mol. This activation enthalpy is 2.0 kcal/mol larger than that for direct reductive elimination via **5TSb**. Therefore, our calculations predict that, on replacing the PH_3 ligands in **5a** with more basic PMe_3 ligands in **5b**, the direct mechanism for reductive

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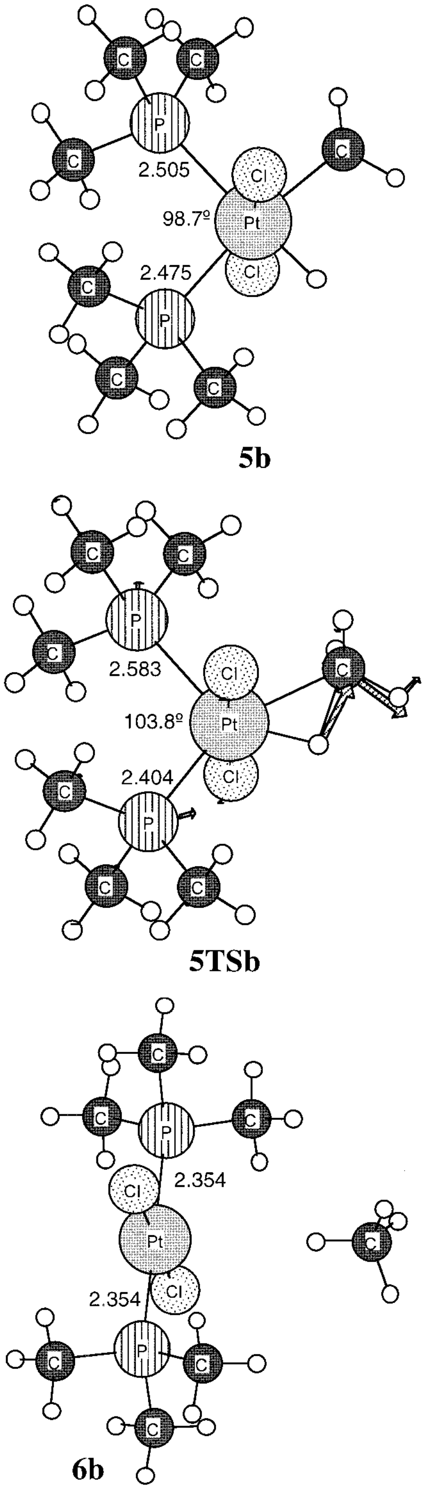
(19) The methane binding enthalpies of all reductive elimination complexes have been calculated and corrected for BSSE. As expected, the methane binding enthalpies of the four- and six-coordinate reductive elimination products (**2b**, **6b**, and **10b**) are negligible. In fact, after adjustment of the electronic energies to enthalpies at 298 K and correction for BSSE, the methane binding enthalpies of these structures are −1.0, −0.9, and −2.5 kcal/mol, respectively, despite the fact that the structures as reported represent electronic energy minima. The methane binding enthalpies of products **4b** and **8b** are 8.2 and 1.1 kcal/mol, respectively. A comparable methane binding enthalpy could not be calculated for product **13b**, since the complex reoriented to place the chloride ligands mutually trans upon removal of the methane, with a significant energetic benefit. As a result, the adiabatic methane binding enthalpy for **13b** was computed to be −13.4 kcal/mol.

(20) Removal of the PMe_3 ligand cis to the hydride in **5b** forms **7b′**. As shown in Table 1, the enthalpy of **7b′** is computed to be 3.5 kcal/mol higher than that of **7b**. The barrier for the isomerization of **7b′** to **7b** is 0.2 kcal/mol. Methane reductive elimination from **7b′** was found to proceed via initial isomerization to **7b** and subsequent elimination.



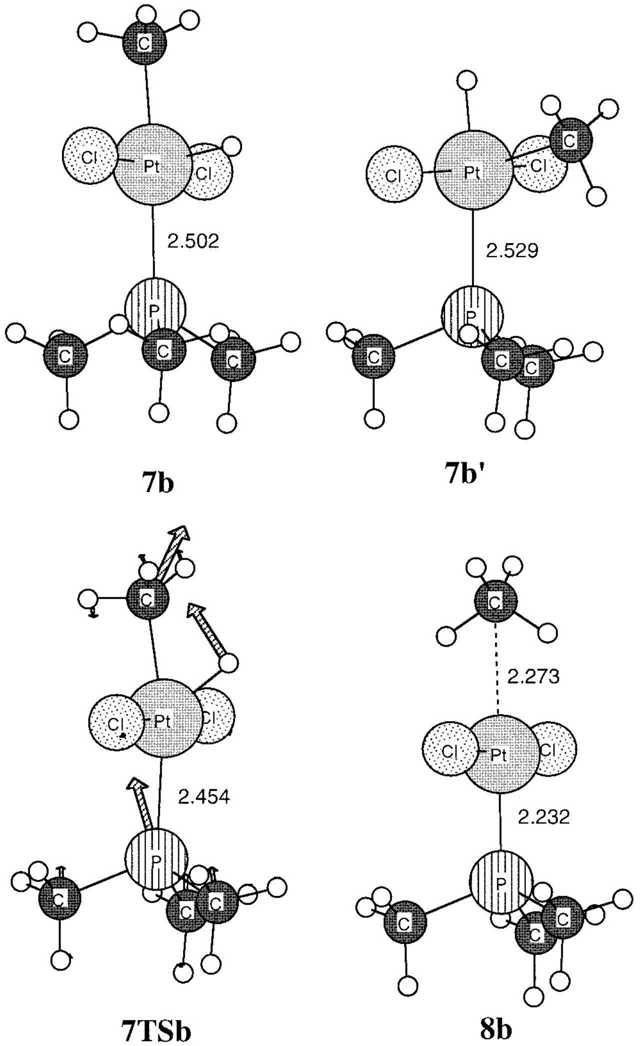
5b

5TSb

6b

Figure 3. Optimized geometries of $(PMe_3)_2Cl_2Pt(CH_3)H$ (**5b**), $(PMe_3)_2Cl_2Pt$ (**6b**) + CH_4, and the transition structure (**5TSb**) that connects **5b** with **6b** + CH_4. Bond lengths are in angstroms, and bond angles are in degrees. The products (**6b** + CH_4) optimized to a Pt−C distance of 4.21 Å. The arrows in **5TSb** show the motion along the reaction coordinate in this transition structure.

elimination of methane from six-coordinate Pt(IV) becomes favored enthalpically.



7b

7b'

7TSb

8b

Figure 4. Optimized geometries of two isomers of $(PMe_3)Cl_2Pt(CH_3)H$ (**7b** and **7b′**), $(PMe_3)Cl_2Pt{\cdot}CH_4$ (**8b**), and the transition structure (**7TSb**) that connects both **7b** and **7b′** with **8b**. Bond lengths are in angstroms, and bond angles are in degrees. The arrows in **7TSb** show the motion along the reaction coordinate in this transition structure.

Table 2 shows that the difference between **5a** and **5b** in the preferred mechanism for reductive elimination is caused primarily by the 7.9 kcal/mol larger binding enthalpy of PMe_3 in **5b** than PH_3 in **5a**. The activation enthalpy for direct reductive elimination is estimated to be 1−2 kcal/mol higher in **5b** than in **5a**, and the activation enthalpy for reductive elimination from the five-coordinate species is actually computed to be 2.3 kcal/mol lower for **7b** than for **7a**.

As in our previous study of **5a**, we also investigated reductive elimination of methane from several other stereoisomers of **5b**. Interchanging one of the equatorial PMe_3 ligands and an axial chloride in **5b** can yield two stereoisomers, depending on which PMe_3 ligand is replaced by chloride (Scheme 3). In **9b**, the equatorial chloride is trans to the hydride, and in **11b**, these two ligands are cis.

Unlike the case in the PH_3-ligated complexes **9a** and **11a**, a transition structure for direct reductive elimination of methane, without ligand loss, was found for both **9b** and **11b**. The reactants and transition structures are shown in Figure 5. The same product (**10b**)[19] was found to be formed from both **9b** and **11b**. The activation enthalpies for formation of **10b** from **9b** and from **11b** were computed to be 18.8 and 21.9 kcal/mol, respectively (Table 3).

Scheme 3

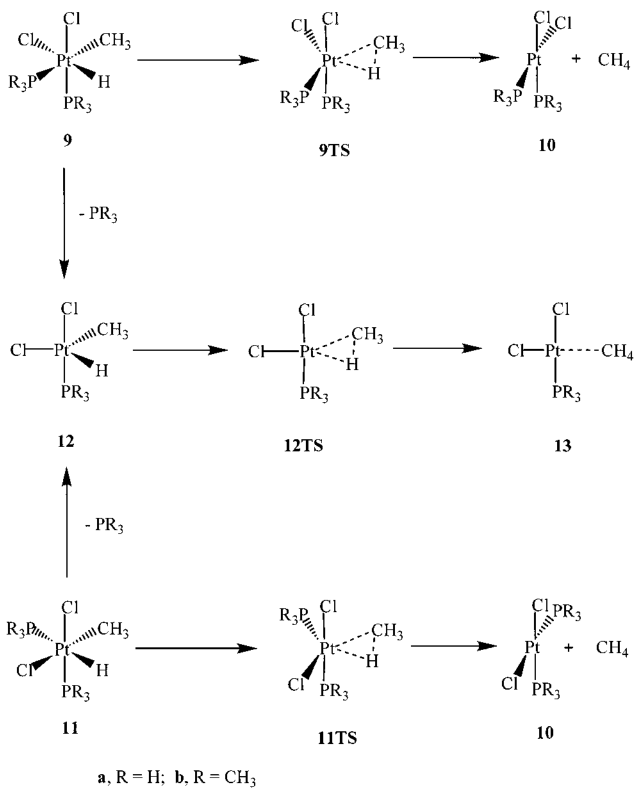


Table 3. Relative Energetics of Methane Reductive Elimination from $L_2Cl_2Pt(CH_3)H$, Isomers 9 and 11, via Both Direct and Ligand-Predissociation Mechanisms[a]

complex	**a** (L = PH$_3$[b])	**b** (L = PMe$_3$)
9	0[c]	0[d]
9TS	18.3[e]	18.8
10 + CH$_4$	−27.9	−25.9
11	2.8	2.1
11TS		24.0
12 + L	12.2 (0)[f]	19.2 (0)[f]
12TS + L	13.4 (1.2)	21.1 (1.9)
13 + L	4.3 (−7.9)	13.0 (−6.2)

[a] Reported as enthaplies at 298 K relative to **9**, after correction of phosphine dissociation enthalpies for basis set superposition error. [b] See ref 6b. [c] Enthalpy, relative to **5a**, is −1.3 kcal/mol. [d] Enthalpy, relative to **5b**, is −4.8 kcal/mol. [e] This barrier is for a reaction that actually involves both methane reductive elimination and ejection of a chloride ligand. [f] Values in parentheses are relative to **12** + L.

Comparison of the transition structures **9TSb** and **11TSb** in Figure 5 shows that the equatorial Pt−Cl bond is lengthened in both, despite the fact that in **11TSb** the chloride is trans to the methyl rather than the hydride. This finding is likely due to the fact that, in both transition structures, buildup of electron density in a σ^* orbital is more favorable in the Pt−Cl bond than in the Pt−PMe$_3$ bond. This explanation is consistent with the fact that **9b**, in which the hydride is trans to the chloride, is 2.1 kcal/mol lower in enthalpy than **11b**, in which these two ligands are cis. Hydride is a stronger trans donor than methyl,[21] so having chloride trans to hydride is more favorable than having chloride trans to methyl.

The preference for chloride being trans to hydride is even larger in the transition structures than in the reactants. This fact is evidenced not only by the 5.2 kcal/mol enthalpy difference between **9TSb** and **11TSb**, which is 3.1 kcal/mol larger than between **9b** and **11b**, but also in the differences between the Pt−Cl bond lengths in these pairs of structures. The equatorial Pt−Cl bond length is only marginally longer in **9b** than in **11b** (0.008 Å), but it is substantially longer in **9TSb** than in **11TSb** (0.105 Å).

Removing the equatorial PMe$_3$ ligand from either **9b** or **11b** yields the same five-coordinate structure (**12b**). As shown in Figure 6, the equatorial chloride ligand in **12b** reorients, so that the complex has a slightly "pinched" trigonal-bipyramidal structure. Phosphine loss to form **12b** is computed to require 19.2 kcal/mol from **9b** and 17.1 kcal/mol from **11b** (Table 3). Since reductive elimination of methane from **12b** via **12TSb** has a calculated barrier of $\Delta H^\ddagger = 1.9$ kcal/mol, the overall activation enthalpies for the ligand-predissociation mechanism for methane elimination from **9b** and **11b** are, respectively, 21.1 and 19.0 kcal/mol.

Comparison of the calculated activation enthalpies for reductive elimination from **9b** in Table 3 shows that the direct mechanism is favored over the ligand-predissociation mechanism by 2.3 kcal/mol. This result is similar to the finding that direct methane elimination from the isomeric **5b** is preferred to a ligand-predissociation pathway by 2.0 kcal/mol. In contrast, the ligand-predissociation mechanism for reductive elimination of methane from **11b**, involving formation of five-coordinate intermediate **12b**, is computed to be favored by 2.9 kcal/mol over direct methane elimination from **11b**.[22] This difference between the mechanisms favored by **9b** and **11b** obviously has its origin in the fact that **11TSb** is calculated to be 5.2 kcal/mol higher in enthalpy than **9TSb**. As already noted, this enthalpy difference is 3.1 kcal/mol larger than the enthalpy difference between **9b** and **11b**.

Ligand Binding Enthalpies in 1 and 5. The following facts emerge from the computational results, summarized in Tables 1 and 2: (1) A phosphine ligand has a lower ligand binding enthalpy when it is trans to hydride, rather than to methyl. (2) Pt(II) and Pt(IV) both bind PMe$_3$ more strongly than PH$_3$. (3) The difference between the PMe$_3$ and PH$_3$ binding enthalpies is greater for Pt(IV) (7.9 kcal/mol between **5b** and **5a**) than for Pt(II) (4.6 kcal/mol between **1b** and **1a**). (4) Six-coordinate Pt(IV) binds both PH$_3$ and PMe$_3$ ligands less strongly than four-coordinate Pt(II) does.

When taken together, the third and fourth observations seem paradoxical. Why should replacement of PH$_3$ by PMe$_3$ have a 3.3 kcal/mol larger effect on the phosphine binding enthalpies in the Pt(IV) complexes, when in these complexes PH$_3$ and PMe$_3$ ligands are each less strongly bound than in the Pt(II) complexes? As will be discussed in this section, the resolution of this apparent paradox—that the binding enthalpies in the

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(21) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin, Inc.: New York, 1965.

(22) Although the dissociative mechanism is favored by 2.9 kcal/mol after BSSE correction, without this correction, the PMe$_3$ binding energy of **11TSb** is 1.3 kcal/mol. Because BSSE corrections are not made during geometry optimizations or searches for transition structures, it was, therefore, possible to locate **11TSb**, in which the PMe$_3$ group remains bound. In contrast, with the more weakly bound PH$_3$ ligands in **5a** and **11a**, attempts to find **5TSa** and **11TSa** led to loss of the PH$_3$ ligand trans to hydride.[6b]

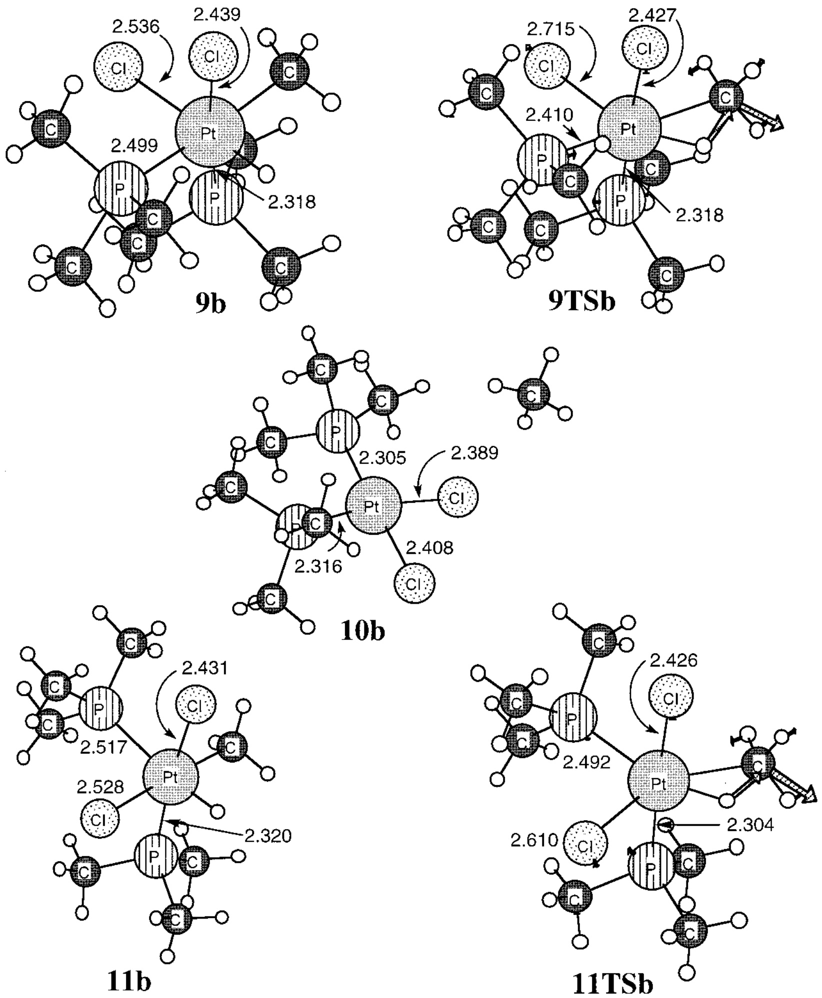
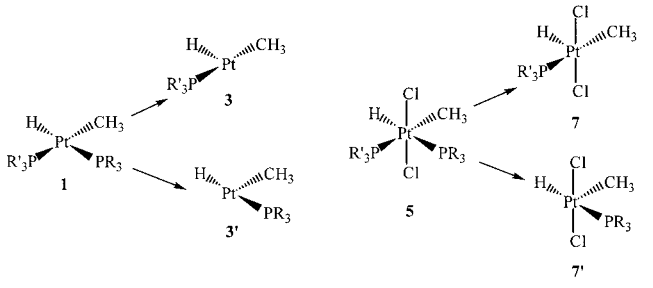


Figure 5. Optimized geometries of two isomers of $(PMe_3)_2Cl_2Pt(CH_3)H$ (**9b** and **11b**) in which the chloride ligands are cis, the $(PMe_3)_2Cl_2Pt$ (**10b**) + CH_4 products formed from both **9b** and **11b**, and the transition structures (**9TSb** and **11TSb**) that connect, respectively, **9b** and **11b** with **10b** + CH_4. Bond lengths are in angstroms, and bond angles are in degrees. The products (**10b** + CH_4) optimized to a Pt−C distance of 4.96 Å. The arrows in **9TSb** and **11TSb** show the motion along the reaction coordinate in each of these transition structures.

Scheme 4



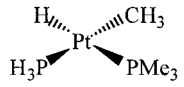
a, R = R' = H; **b**, R = R' = CH_3; **c**, R = CH_3, R' = H; **d**, R = H, R' = CH_3

less strongly bound complexes are more sensitive to ligand basicity than the binding enthalpies in the more strongly bound complexes—provides an important clue to the question of why six-coordinate Pt(IV) binds phosphine ligands less strongly than four-coordinate Pt(II) does.

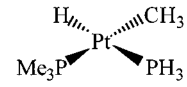
The reason for the first of the above observations has already been discussed. Hydride is a stronger trans donor than methyl.[21] Therefore, a phosphine ligand is more easily lost when it is trans to hydride, instead of to methyl.

An obvious explanation for the second of the above observations, that binding of PMe_3 is stronger than binding of PH_3 for both Pt(II) and Pt(IV), is that PMe_3 is a stronger Lewis base than PH_3.[7] However, the results in Tables 1−3 would also be explicable if binding of a phosphine, regardless of whether it were PMe_3 or PH_3, were made stronger by the "spectator" phosphine ligand being PMe_3 , rather than PH_3.

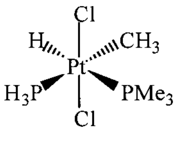
To rule out the latter possibility, we computed the enthalpies of PMe_3 and PH_3 loss from complexes **1c**, **1d**, **5c**, and **5d** in Scheme 4. Each of these complexes



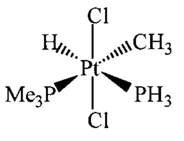
1c



1d



5c



5d

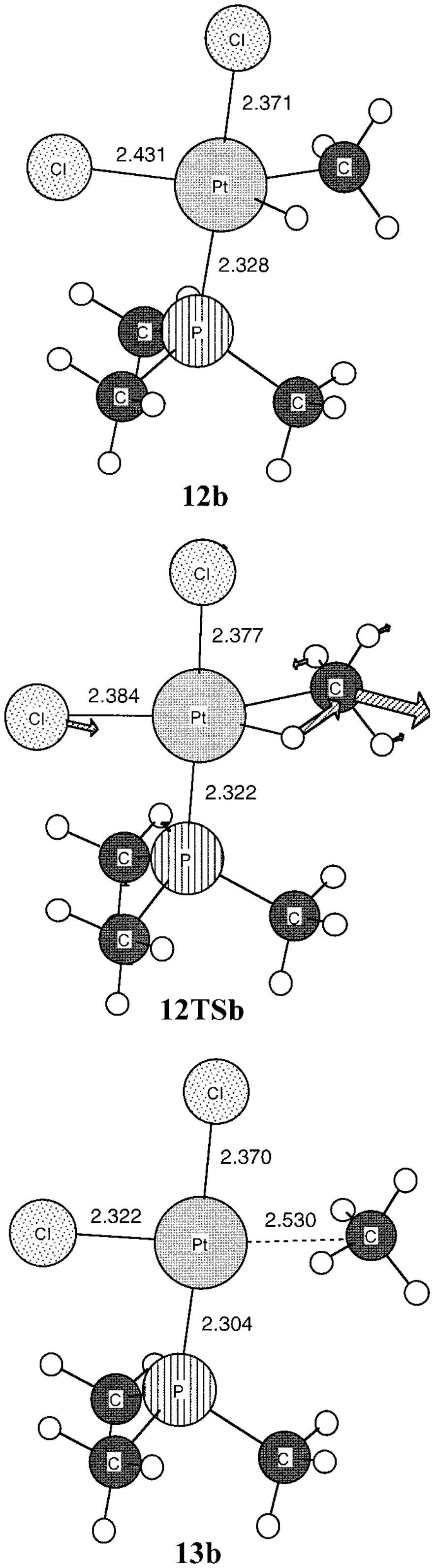


Figure 6. Optimized geometries of $(PMe_3)Cl_2Pt(CH_3)H$ (**12b**), in which the chloride ligands are cis, the $(PMe_3)Cl_2$-$Pt{\cdot}CH_4$ (**13b**) product formed from it, and the transition structure (**12TSb**) that connects **12b** with **13b**. Bond lengths are in angstroms, and bond angles are in degrees. The arrows in **12TSb** show the motion along the reaction coordinate in this transition structure.

contains both a PMe_3 and a PH_3 phosphine ligand. The results of our calculations are given in Table 4, where they are compared with the enthalpies for PH_3 loss from **1a** and **5a** and PMe_3 loss from **1b** and **5b**.

Table 4. Enthalpies[a] of Loss of Phosphine Ligand L from Several Pt(II) and Pt(IV) Complexes

complex	H-trans ligand lost	complex formed	ΔH_{rxn}	CH_3-trans ligand lost	complex formed	ΔH_{rxn}
1a	PH_3	**3a**	18.0[b]	PH_3	**3a′**	23.8[b]
1b	PMe_3	**3b**	22.6	PMe_3	**3b′**	29.6
1c	PMe_3	**3a**	25.2	PH_3	**3b′**	23.8
1d	PH_3	**3b**	17.8	PMe_3	**3a′**	32.1
5a	PH_3	**7a**	10.2[b]	PH_3	**7a′**	13.3[b]
5b	PMe_3	**7b**	18.1	PMe_3	**7b′**	21.6
5c	PMe_3	**7a**	20.2	PH_3	**7b′**	12.9
5d	PH_3	**7b**	9.8	PMe_3	**7a′**	23.7

[a] Enthalpies at 298 K in kcal/mol, after correction for BSSE. [b] Reference 6b.

The results in Table 4 show that in both **1** and **5** dissociation of PH_3 from the position either cis or trans to the hydride requires 0.0−0.4 kcal/mol less enthalpy when the spectator ligand is PMe_3, rather than PH_3. Clearly, the identity of the spectator has only a small effect on the PH_3 dissociation enthalpy. However, the identity of the spectator ligand has a much larger effect on the enthalpy of dissociation of PMe_3, since PMe_3 loss from these complexes requires 2.1−2.6 kcal/mol less enthalpy when the spectator ligand is PMe_3, rather than PH_3.

The spectator ligand effects in Table 4 are easily interpretable in terms of a small steric effect on the phosphine dissociation enthalpies. Since PMe_3 is larger than PH_3, a steric effect would explain why a PMe_3 spectator ligand gives lower phosphine dissociation enthalpies than a PH_3 spectator ligand. Since a PMe_3−PMe_3 steric interaction would be expected to be substantially more destabilizing than a PMe_3−PH_3 steric interaction, the finding that replacement of PH_3 by a PMe_3 spectator ligand lowers phosphine dissociation enthalpies more for loss of PMe_3 than of PH_3 is also consistent with the operation of a steric effect.

When the spectator ligand is PH_3, the difference between the PMe_3 and PH_3 binding enthalpies is 7.2−8.3 kcal/mol in **1**, but 10.0−10.4 kcal/mol in **5**. When the spectator ligand is the more sterically demanding PMe_3, PMe_3 is computed to be bound more strongly than PH_3 by 4.8−5.8 kcal/mol in **1** but by 8.3−8.7 kcal/mol in **5**. Thus, the difference between the PMe_3 and PH_3 binding enthalpies is 2−3 kcal/mol larger in **5** than in **1**.

The six-coordinate Pt(IV) complex (**5**) is obviously more sterically congested than the four-coordinate Pt(II) complex (**1**). Therefore, whatever causes the difference between the PMe_3 and PH_3 binding enthalpies to be larger in **5** than in **1** does not have a steric origin.

Instead, it seems likely that the higher formal oxidation state of Pt in **5** than in **1** allows **5** to take better advantage of the increase in Lewis basicity associated with the substitution of PMe_3 for PH_3. All other things being equal, one might expect the phosphine binding enthalpies in the complex with the higher metal oxidation state to be stronger and, hence, more sensitive to the basicity of the phosphines.

However, all other things are obviously not equal. This type of electronic argument, based on the difference between the Pt oxidation states of **1** and **5**, does not explain the fact that **1** actually binds phosphines more strongly than **5**. The average difference between the phosphine binding enthalpies of **1** and **5** in Table 4 is 7.9 kcal/mol. If the higher oxidation state of Pt in **5** than in **1** explains the greater *sensitivity* of the binding enthalpies in **5** to phosphine basicity, what explains the fact that **5** has an average phosphine binding enthalpy that is 7.9 kcal/mol lower that in **1**?

We have previously attributed the lower phosphine binding enthalpies in **5**, relative to **1**, to the fact that Pt is six-coordinate in **5** but four-coordinate in **1**.[6b] The destabilizing cis interactions between the phosphorus atoms of the phosphine ligands and the two axial chlorides that are present in **5** are absent in **1**. We believe that these cis interactions are the reason the enthalpy required for phosphine ligand dissociation is lower in **5** than in **1**, even though the oxidation state of Pt is higher in the six-coordinate Pt(IV) complex than in the four-coordinate Pt(II) complex.

Effects of PR_3 Basicity on the Barriers to Methane Reductive Elimination. Increasing the Lewis basicity of the phosphine ligands obviously acts to disfavor the ligand-predissociation mechanism for reductive elimination in both **1** and **5** by increasing the phosphine binding enthalpies. However, the results in Tables 1 and 2 show that replacement of PH_3 by PMe_3 also raises the barrier height for direct elimination from **1** and **5** by 1−3 kcal/mol.

In the latter reaction, a Pt 5d orbital accepts electron density from the methyl and hydride ligands.[6b] Since this AO also interacts with the phosphine lone pairs, replacement of PH_3 by the more strongly electron donating PMe_3 would be expected to raise the energy of the transition structure for direct elimination. This is the result found by our B3LYP calculations on this reaction of **1** and **5**.

Unlike the case in the direct mechanism, in the ligand-predissociation mechanism for reductive elimination, the remaining phosphine lies near the nodal plane of the Pt 5d orbital that accepts electron density from the methyl and hydride ligands.[6b] It is presumably for this reason that substitution of PMe_3 for PH_3 has little effect on $\Delta H^{\ddagger}$ for the reductive elimination of methane from **3** to form **4**. Table 1 shows that the substitution of PMe_3 for PH_3 also has little effect on the overall enthalpy of this reaction.

In contrast, as shown in Table 2, substitution of PMe_3 for PH_3 makes both ΔH and $\Delta H^{\ddagger}$ lower for **7b** → **8b** than for **7a** → **8a**. The 6.6 kcal/mol more negative ΔH for the former reaction presumably accounts for the 2.3 kcal/mol lower $\Delta H^{\ddagger}$.

The difference of 6.6 kcal/mol between the enthalpies of these two reactions means that the difference between the PMe_3 and PH_3 binding enthalpies is larger by this amount in the product (**8**) than in the reactant (**7**). This result is somewhat surprising, since **7** is a Pt(IV) complex and **8** is a Pt(II) complex. Based on the finding that the difference between PMe_3 and PH_3 binding enthalpies is 2−3 kcal/mol larger in Pt(IV) complex **5** than in Pt(II) complex **1**, one might have expected the difference between the PMe_3 and PH_3 binding enthalpies to be slightly larger in **7** than in **8**, rather than 6.6 kcal/mol smaller.

However, this comparison between very different Pt(II) and Pt(IV) complexes is not really valid. The previous comparisons in this paper have been made between Pt(II) and Pt(IV) complexes with very similar coordination spheres. In particular, the ligand trans to the phosphine of interest was always kept the same. In contrast, the phosphine in **7** is trans to a strongly donating methyl ligand, whereas in **8**, it is trans to a very weakly bound methane ligand. As a result, the phosphine binding enthalpy shows a greater sensitivity to phosphine basicity in **8** than in **7**, despite the fact that **7** is Pt(IV) and **8** is Pt(II).[23,24]

In contrast, Table 1 shows that the enthalpy for the reductive elimination of methane from **3** to form **4** is rather insensitive to the substitution of PMe_3 for PH_3. In fact, this substitution is computed to make the reaction 0.3 kcal/mol less exothermic, meaning that the difference between the PMe_3 and PH_3 binding enthalpies is actually slightly larger in the reactant than in the product. Presumably, the fact that **4** is a Pt(0) complex makes it slightly less sensitive to phosphine ligand basicity than Pt(II) complex **3**, despite the fact that **4** lacks the equatorial methyl and hydride ligands that are present in **3**.

Conclusions

Our calculations suggest that destabilizing cis interactions between axial and equatorial ligands reduce ligand binding enthalpies in six-coordinate Pt(IV) complexes, relative to their four-coordinate Pt(II) counterparts. The lower ligand binding enthalpies in six-coordinate Pt(IV) complexes are the reason that they exhibit a far greater propensity toward undergoing methane reductive elimination via a ligand-predissociation mechanism than comparable four-coordinate Pt(II) complexes.

Replacing PH_3 ligands with more strongly basic PMe_3 ligands selectively disfavors the ligand-predissociation mechanism for reductive elimination of methane. In two out of three of the Pt(IV) systems that we studied computationally, replacing PH_3 by PMe_3 resulted in the direct mechanism being favored enthalpically over the ligand-predissociation pathway, albeit by only 2 kcal/mol.

Of course, the entropy associated with ligand loss would almost certainly overcome the slight enthalpic preference predicted for direct elimination of methane in Pt(IV) complexes **5b** and **9b**.[15] However, with chelating ligands, most of the entropic advantage inherent in the ligand-predissociation mechanism would be lost. Therefore, our calculations predict that six-coordinate Pt(IV) complexes that have chelating trialkylphosphine ligands should be good candidates for undergoing methane reductive elimination by a direct mechanism, rather than a ligand-predissociation pathway.

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(23) The greater sensitivity to ligand basicity of **8**, compared to **7**, is almost certainly due to the fact that **8** binds phosphine more strongly than **7**. This is evident from comparing the Pt−P bond lengths in **7b** and **8b** in Figure 5. The Pt−P bond distance in **7b** is 0.270 Å longer than in **8b**.

(24) Because the difference between PMe_3 and PH_3 binding enthalpies is 2−3 kcal/mol larger in Pt(IV) complex **5** than in Pt(II) complex **1**, one might expect the difference between the PMe_3 and PH_3 binding enthalpies to be larger by about the same amount in Pt(IV) complex **7** than in Pt(II) complex **3**. Our calculations do, indeed, find that $\Delta H = -12.5$ kcal/mol for the ligand exchange reaction, **7a** + PMe_3 → **7b** + PH_3, which is 3.1 kcal/mol more exothermic than the analogous reaction involving **3a** and **3b**.

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Supporting Information Available: Calculated geometrical parameters, energies, and vibrational frequencies of all the complexes whose energies are given in Tables 1−4, as well as information regarding the basis set superposition error calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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