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A Computational Study of Reductive Elimination Reactions to Form C−H Bonds from Pt(II) and Pt(IV) Centers. Why Does Ligand Loss Precede Reductive Elimination from Six-Coordinate but Not Four-Coordinate Platinum?

Kevin L. Bartlett, Karen I. Goldberg,* and Weston Thatcher Borden*

*Contribution from the Department of Chemistry, Box 351700, University of Washington,
Seattle, Washington 98195-1700*

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Abstract: In agreement with the experimental results of Halpern on $(PPh_3)_2Pt(CH_3)H$, B3LYP and CCSD(T) calculations on the model species $(PH_3)_2Pt(CH_3)H$ (**1**) find that reductive elimination of methane from this four-coordinate, Pt(II) complex proceeds without prior PH_3 ligand loss. The free energy of activation calculated for reductive elimination of methane from **1** is in good agreement with the value measured for $(PPh_3)_2Pt(CH_3)H$. In contrast to the case for **1**, we were unable to find a genuine pathway for direct reductive elimination of methane, without concomitant ligand loss, from $(PH_3)_2Cl_2Pt(CH_3)H$ (**13**). This computational finding is in accord with the observation that reductive eliminations from six-coordinate, Pt(IV) complexes almost invariably take place via a pathway involving loss of a ligand, prior to the reductive elimination step. PH_3 ligand loss is found to lower the barrier to reductive elimination by slightly more in the Pt(IV) complexes than in the Pt(II) complexes. However, our calculations indicate that the difference between the preferred pathways for reductive elimination from **1** and **13** can be primarily attributed to a reduction in the enthalpic cost of PH_3 ligand loss from the six-coordinate, Pt(IV) complex (**13**), compared to the four-coordinate, Pt(II) complex (**1**).

Reductive elimination is often the product-forming step in homogeneous, metal-mediated, organic transformations.[1] As a fundamental organometallic reaction of considerable importance, reductive elimination has been the subject of a great deal of research. Numerous theoretical[2−6] and experimental[7−17] investigations of this reaction have been reported.

In studies of C−C and C−H reductive eliminations, key differences in the coordination environment of the metal at the time of bond formation have been identified. For example, when these reactions occur from square planar d^8 metal complexes, loss of an ancillary ligand to form a three-coordinate intermediate, prior to the actual reductive elimination step, is sometimes observed.[3,7−9] In other cases, ligand association has been found to promote the reductive elimination, so that bond formation occurs from a five-coordinate species.[10] Nevertheless, examples of direct reductive elimination from d^8 square-planar complexes, without ligand addition or loss, have been documented as well.[11,12]

For reductive elimination reactions that form C−C and C−H bonds from d^6 octahedral complexes, direct elimination without ligand loss has also been reported.[13] However, a significantly larger fraction of the reactions that have been studied proceed via initial ligand dissociation and formation of a five-coordinate

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[1] Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley-Interscience: New York, 1992.

[2] (a) Su, M.-D. Chu, S.-Y. *Inorg. Chem.* **1998**, *37*, 3400. (b) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115. (c) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482. (d) Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. *Inorg. Chem.* **1982**, *21*, 2162.

[3] (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (b) Hoffmann, R. In *Frontiers of Chemistry*, Laidler, K. J., Ed.; Pergamon Press: Oxford, 1982; p 247.

[4] Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478.

[5] Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4442.

[6] (a) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006. (b) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 8321. (c) Eisenstein, O.; Jean, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1177. (d) Rabaâ, H.; Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327. (e) Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609. (f) Daniel, C.; Koga, N.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773. (g) Koga, N.; Morokuma, K. *J. Phys. Chem.* **1990**, *94*, 5454. (h) Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10557. (i) Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636. (j) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 6883. (k) Siegbahn, P. E. M.; Svensson, M. *J. Am. Chem. Soc.* **1994**, *116*, 10124. (l) Cundari, T. R. *J. Am. Chem. Soc.* **1994**, *116*, 340. (m) Siegbahn, P. E. M.; Blomberg, M. R. A. *Organometallics* **1994**, *13*, 354. (n) Siegbahn, P. E. M. *Organometallics* **1994**, *13*, 2833. (o) Siegbahn, P. E. M.; Blomberg, M. R. A. In *Theoretical Aspects of Homogeneous Catalysis*; van Leeuwen, P. W. N. M.; Morokuma, K.; van Lenthe, J. H., Eds. Kluwer Academic Publishers: Netherlands, 1995; pp 15−63. (p) Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 799. (q) Margl, P.; Ziegler, T.; Blöchl, P. E. *J. Am. Chem. Soc.* **1995**, *117*, 12625. (r) Musaev, D. G.; Matsubara, T.; Mebel, A. M.; Koga, N.; Morokuma, K. *Pure Appl. Chem.* **1995**, *67*, 257. (s) Espinosa-García, J.; Corchado, J. C.; Truhlar, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 9891. (t) Avdeev, V. I.; Zhidomirov, G. M. *Kinet. Catal.* **1998**, *39*, 476. (u) Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1998**, *120*, 6169. (v) Sakaki, S.; Biswas, B.; Sugimoto, M. *Organometallics* **1998**, *17*, 1278.

[7] 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.

[8] (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868.

[9] DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601.

[10] (a) Yamamoto, T.; Abla, M. *J. Organomet. Chem.* **1997**, *535*, 209. (b) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466. (c) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181.

[11] (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (b) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831.

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intermediate, prior to the reductive elimination step.[14–17] In general, it seems that, although reductive elimination is possible from four-coordinate, d^8 square-planar and six-coordinate, d^6 octahedral complexes, this reaction is much faster from three- and five-coordinate species.[7]

It has been suggested that in reductive eliminations which intrinsically have low activation barriers, for example, those involving C–H rather than C–C bond-forming reactions, the preference for a lower degree of metal coordination is not as critical.[7] Indeed, C–H reductive elimination reactions to form alkanes from the Pt(II) complexes, $(PPh_3)_2PtRH$, R = CH_3[11a] and CH_2CF_3,[11b] have been shown to proceed without ligand dissociation or ligand association. However, related C–C reductive eliminations to form ethane from the Pd(II) complex, $L_2Pd(CH_3)_2$, or dimethylcyclopropane from the Pt(II) complex, $L_2Pt[(CH_2)_2C(CH_3)_2]$, have both been observed to require prior ligand loss.[8,9]

In contrast to this difference between the mechanisms for C–H and C–C reductive elimination reactions from square planar Pt(II) complexes, both alkyl C–H and alkyl C–C reductive eliminations from octahedral Pt(IV) have been shown to proceed via prior ligand dissociation, so that alkane formation actually occurs from a five-coordinate intermediate.[14,15] It is noteworthy that all of the stable Pt(IV) alkyl hydride complexes which have been isolated all contain chelating ligands,[18] and the stability of these complexes is almost certainly due to inhibition of ligand dissociation. This finding provides additional support for prior ligand dissociation as a requirement for both alkyl C–C and alkyl C–H reductive eliminations from Pt(IV).

To try to understand the reasons for the differences between the mechanisms of C–H reductive elimination reactions from Pt(II) and Pt(IV) complexes, we have performed calculations using both density functional theory (DFT) and ab initio coupled-cluster methodology. We have investigated pathways involving both ligand predissociation and direct elimination for square-planar Pt(II) and for octahedral Pt(IV) model complexes. In this paper we report the results of our calculations and compare them with the results of experimental investigations of reductive elimination reactions from related Pt(II) and Pt(IV) alkyl hydrides. Based on our computational results, a rationale for the experimentally observed differences between the reaction pathways for Pt(II) and Pt(IV) complexes is offered.

Computational Methodology

Stationary points were located[19] and vibrational analyses were performed using the B3LYP version of DFT, which is comprised of Becke's hybrid three-parameter exchange functional[20] and the correlation functional of Lee, Yang, and Parr.[21] Single-point coupled-cluster calculations, which included single and double excitations[22] and a noniterative estimate of the effects of triple excitations,[23] [CCSD(T)], were performed at the B3LYP optimized geometries. The relatavistic, compact effective potential and basis set of Stevens, Basch, Krauss, and Jasien[24] was used for platinum. The polarized, Dunning/Huzinaga, double-ζ, D95** basis set[25] was used for all of the other atoms, except for the phosphine hydrogens, for which the 2p polarization functions were omitted. The zero-point and thermal corrections from the B3LYP vibrational analyses were used, without scaling to convert the B3LYP and CCSD(T) electronic energies to enthalpies at 298 K. The relative enthalpies and energies for phosphine loss from **1** and **13** were corrected for basis set superposition errors[26] in the reactants, using the full counterpoise method. 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.[27]

Results and Discussion

Comparison of B3LYP and CCSD(T) Results. Before correction for basis set superposition errors, the energy increases

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(12) (a) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892. (b) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356. (c) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.

(13) (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6492. (b) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. (c) Harper, T. G. P.; Desrosiers, P. J.; Flood, T. C. *Organometallics* **1990**, *9*, 2523. (d) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.

(14) Examples of alkyl C–C reductive elimination from octahedral Pt(IV), Pd(IV): (a) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (b) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889. (c) Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408. (d) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121. (e) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (f) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83 and references therein. (g) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363. (h) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (i) van Asselt, R.; Rijnberg, E.; Elsevier: C. J. *Organometallics* **1994**, *13*, 706. (j) Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2000**, *122*, 962.

(15) Examples of C–H reductive elimination from octahedral Pt(IV): (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (c) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (d) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156.

(16) Examples of C–H and C–C reductive elimination from octahedral Ir(III), Rh(III): (a) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221 and references therein. (b) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649. (c) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972. (d) Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1999**, 435.

(17) Saunders, D. R.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2133.

(18) (a) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (b) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845. (c) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (d) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745. (e) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209.

(19) Geometries with low-energy XH_3-rotation vibrational modes were difficult to optimize. Optimizations of some structures (**3** and **4b**) were considered to be converged, based on extremely low forces and RMS forces, even though the displacements and RMS displacements were not below the default convergence criteria in Gaussian 98. The geometries of two structures (**6** and **4a** + **2Cl**) were fully converged but were found to have one small, imaginary vibrational frequency, despite the fact that the optimiztions were done in C_1 symmetry and that analytical second derivatives were calculated at each step in the geometry optimizations.

(20) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(21) (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.

(22) (a) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35. (b) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (c) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1988**, *89*, 7382. (d) Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3700.

(23) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(24) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.

(25) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*, H. F. Schaefer, III, Ed. Plenum: New York, 1976, 1–28.

(26) For a very recent review and leading references, see: 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.

(27) 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.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

for phosphine dissociation from both four- and six-coordinate complexes were computed to be 5−6 kcal/mol larger by CCSD(T) than by B3LYP. Similar results have been reported by Frenking and co-workers.[28] However, we found that the basis set superposition errors were also larger in the CCSD(T) than in the B3LYP calculations by ~6 kcal/mol.[29] Therefore, as shown in Tables 1−3, after correction for basis set superposition, nearly the same energy increases for phosphine dissociation were computed by both B3LYP and CCSD(T).

It seems likely that basis-set superposition errors also tend to overestimate the stability of the reactant complexes with respect to the products of reductive elimination and, to a lesser extent, to the transition structures leading to these products. These basis-set superposition errors are again expected to be larger in the CCSD(T) than in the B3LYP calculations. In fact, the results in Tables 1−3 show that CCSD(T) does give larger energy differences than B3LYP between the reactants and the transition structures, and smaller energy differences between the reactants and the products of reductive elimination.

Since counterpoise corrections cannot sensibly be made to the energies computed for the reductive elimination reactions, the larger basis set superposition errors that are likely to be present in the CCSD(T) calculations lead us to base the discussion of our results on the B3LYP energies. Therefore, in the Tables we have converted only the B3LYP electronic energy differences to enthalpy differences. Nevertheless, a discussion of our results that was based on the CCSD(T) energies in Tables 1−3 would be qualitatively the same as the following discussion, which is based on the B3LYP energies.

Reductive Elimination of Methane from Three- and Four-Coordinate Pt(II) Complexes. Calculations on the elimination of methane from the four-coordinate model compound, *cis*-$(PH_3)_2Pt(CH_3)H$ (**1**), have been reported,[2] but not at either the CCSD(T) or B3LYP levels of theory. The B3LYP geometries of the reactant (**1**), the $(PH_3)_2Pt{\cdot}CH_4$ product (**3**), and the transition structure connecting them (**2**) are shown in Figure 1. The B3LYP and CCSD(T) energies and the B3LYP enthalpies of **2** and **3**, relative to **1**, are given in Table 1.

Reactant **1** exhibits a slightly distorted square planar geometry with a P−Pt−P bond angle of 101.4° and a C−Pt−H bond angle of 83.2°. In transition structure **2**, the biggest change in geometry from **1** is the decrease in the C−Pt−H bond angle by 41.7°, which shortens the C−H distance by 0.986 Å. Nevertheless, the C−H bond length of 1.494 Å in **2** is still significantly longer than the 1.095 Å in the product (**3**). In going from **1** to **2**, much smaller changes are seen in the bond lengths to platinum. The Pt−C distance increases by 0.151 Å, but the Pt−H distance increases by only 0.037 Å. The length of the Pt−P bond *cis* to the hydride decreases by 0.043 Å, whereas the Pt−P bond *trans* to the hydride barely changes. The angle between the phosphines opens, but only by 7.8°.

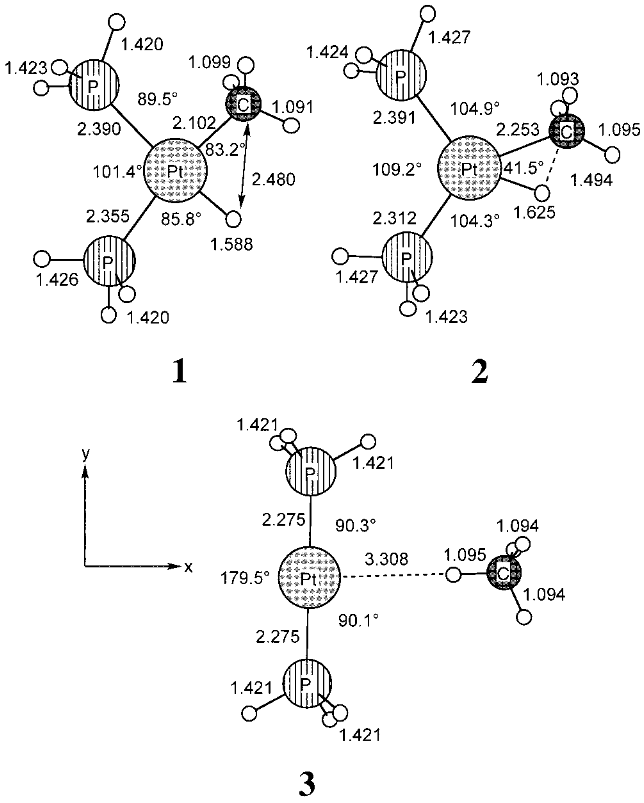

Figure 1. Optimized geometries of $(PH_3)_2Pt(CH_3)H$ (**1**), $(PH_3)_2Pt{\cdot}CH_4$ (**3**), and the transition structure (**2**) which connects them. Bond lengths are in Å, and bond angles are in degrees.

Table 1. Relative CCSD(T) Energies, and B3LYP Energies and Enthalpies (kcal/mol) for Pt(II) Species at 298 K, after Correction of Phosphine Dissociation Energies for Basis Set Superposition Errors[a]

complex	*E* [CCSD(T)]	*E* (B3LYP)	ΔH_{298} (B3LYP)
1	0	0	0
2	21.4	18.0	16.5
3	−6.1	−13.9	−11.8
4a + PH_3	20.1 (0)[b]	20.5 (0)[b]	18.0 (0)[b]
4b + PH_3	25.5 (5.4)	25.7 (5.2)	23.8 (5.8)
5 + PH_3	30.1 (10.0)	27.4 (6.9)	24.2 (6.2)
6 + PH_3	15.8 (−4.3)	12.6 (−7.9)	11.8 (−6.2)

[a] See Supporting Information for BSSE corrections. [b] Values in parentheses are relative to **4a** + PH_3.

Performing a geometry optimization on the product side of transition structure **2** leads to **3**, a very weak complex of methane with $(PH_3)_2Pt$. The length of the methane C−H bond that is directed toward the platinum is nearly the same as the other three C−H bonds. The distance between the metal center and this unique hydrogen is over 3 Å, and the $(PH_3)_2Pt$ fragment is essentially linear. As suggested by the geometry of **3**, its energy is essentially the same as that of fully dissociated $(PH_3)_2Pt$ plus CH_4.

As shown in Table 1, the reductive elimination of methane from **1** to form **3** is computed to be exothermic, with $\Delta H = -11.8$ kcal/mol; and the enthalpy of activation at 298 K is calculated to be $\Delta H^{\ddagger} = 16.5$ kcal/mol. Using absolute rate theory, Halpern's experimental rate constant of $k = 4.5 \times 10^{-4}$ sec^{-1} at −25 °C[11a] gives a value of $\Delta G^{\ddagger}_{248} = 18.5$ kcal/mol for the reductive elimination of methane from $(PPh_3)_2Pt(CH_3)H$. Halpern showed that this reaction proceeds without prior ligand loss; thus, like **2**, the actual transition structure involves four-coordinate platinum. Our value of $\Delta G^{\ddagger}_{248} = 16.5$ kcal/mol for passage from **1** to **2**[30] is in good agreement with Halpern's experimental value for the corresponding complex with PPh_3 ligands.

The generalization[7] that reductive elimination from a three-coordinate d^8 complex has a lower barrier than reductive

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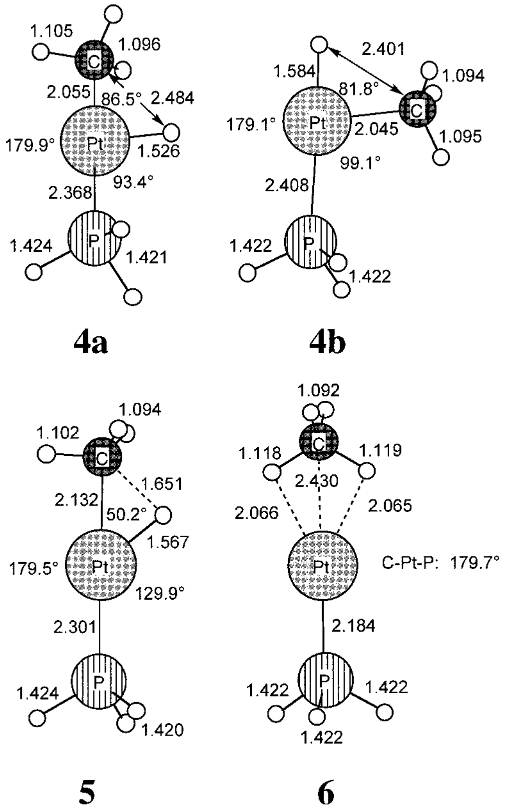
[28] Schmid, R.; Herrmann, W. A.; Frenking, G. *Organometallics* **1997**, *16*, 701.

[29] Table S-1 of the Supporting Information gives uncorrected CCSD(T) and B3LYP energies and the basis set superposition errors for each. Unlike B3LYP, CCSD(T) uses virtual orbitals for electron correlation, so basis set superposition causes larger errors in CCSD(T) calculations than in B3LYP calculations.

[30] The values of $\Delta H^{\ddagger}$ at 248 and 298 K are essentially the same, and $\Delta S^{\ddagger} \approx 0$.



4a **4b**

5 **6**

Figure 2. Optimized geometries of two stereoisomers of $(PH_3)Pt(CH_3)H$ (**4a** and **4b**), $(PH_3)Pt{\cdot}CH_4$ (**6**), and the transition structure (**5**) which connects **4** with **6**. Bond lengths are in Å, and bond angles are in degrees.

elimination from a similar four-coordinate species was tested by performing calculations on formation of methane from the Pt(II) complex (**4**) that results from loss of one phosphine from **1**. Our calculations found that, starting from **4a**, reductive elimination of methane has $\Delta H^{\ddagger} = 6.2$ kcal/mol. This barrier is, in fact, 10.3 kcal/mol lower than the barrier to reductive elimination from the four-coordinate complex (**1**), without prior loss of PH_3.

As shown in Figure 2, the transition structure (**5**) for methane elimination from **4a** maintains the distorted T-shape of the reactant, in which the more electronegative methyl, rather than the hydride, is *trans* to the phosphine group. To show that the stereochemistry of reactant **4a** did not determine the geometry of transition structure **5**, we also attempted to find a transition structure from the T-shaped, three-coordinate reactant complex (**4b**), in which hydride rather than methyl is *trans* to the phosphine.

The enthalpy of the optimized structure for **4b** was calculated to be 5.8 kcal/mol higher than that of **4a**, and the barrier to rearrangement of **4b** to **4a** was computed to be 3.2 kcal/mol. As the H−Pt−C bond angle in **4b** was closed, the PH_3 reoriented itself to be *trans* to the methyl, rather than to the hydride. Thus, the barrier to isomerization is apparently lower than the barrier to reductive elimination from **4b**, and both isomers undergo reductive elimination to product **6** through transition structure **5**.

The enthalpy difference between **4a** and **6** was calculated to be $\Delta H = -6.2$ kcal/mol. In contrast to the case in the product (**3**), formed from the four-coordinate reactant (**1**), two of the methane C−H bonds in **6** interact with platinum. The Pt−H distances of 2.065 and 2.066 Å in **6** are each more than 1 Å shorter than the Pt−H distance in **3**. The shorter Pt−H bonds and the lengthened C−H bonds in **6** suggest that the Pt-methane interaction is much stronger in **6** than in **3**. Indeed, after correction for basis set superposition errors, the B3LYP platinum−methane binding enthalpy in **6** was computed to be 10.8 kcal/mol. In contrast, as already noted, the $Pt-CH_4$ binding enthalpy in **3** is negligible.

Comparison of the barriers to reductive elimination of methane from **4a** and from **1** in Table 1 shows that the barrier to this reaction is 10.3 kcal/mol lower in the three-coordinate than in the four-coordinate complex. This difference cannot be due to the difference between the thermodynamics of these two reactions, since the reductive elimination from **1** is the more exothermic. However, comparison of the geometries of the transition structures and products in Figures 1 and 2 provides an explanation for the very large difference between barrier heights.

The geometries of transition structure **5** and product **6** in Figure 2 are rather similar, with the phosphine ligand occupying a site *trans* to the carbon of the methane. In contrast, in transition structure **2** the P−Pt−P bond angle is only 109.2°, but in product **3** this angle opens to 179.5°. We attribute the high energy of transition structure **2**, relative to both the reactant (**1**) and product (**3**), to the small P−Pt−P bond angle in **2**. The reason the transition structure is destabilized by this small angle has been previously discussed by Hoffmann,[3] but we present the following explanation as a succinct reformulation of Hoffmann's analysis.

In the Pt(II) reactant (**1**), the out-of-phase combination of phosphine lone-pair orbitals, as well as the methyl group and hydride, donate electron density into the platinum $5d_{xy}$ orbital. However, following reductive elimination of methane, $5d_{xy}$ becomes doubly occupied in the Pt(0) product (**3**). Consequently, the lowest-energy, unfilled platinum orbital in **3** that is available to interact with the out-of-phase combination of phosphine lone-pair orbitals is $6p_y$. The phosphine lone pair interaction is, of course, strongest when the P−Pt−P bond angle is 180°, which is the reason the bis-phosphine Pt(0) product (**3**) has a linear geometry.

However, in transition structure **2** the presence of the methyl group and the hydride, still bonded to platinum, prevents the P−Pt−P bond angle from opening substantially. Therefore, the phosphines cannot interact maximally with $6p_y$ in **2**. This makes the Pt−P bonding in **2** weaker than that in **3**, as evidenced by longer Pt−P bonds (especially the Pt−P bond *trans* to the hydride) in **2** than in **3**. We calculate that the energy lowering on allowing the P−Pt−P bond angle in $(PH_3)_2Pt$ to open from the 108.3° in **2** to the equilibrium angle of 180° in **3** amounts to 20.0 kcal/mol.

As already noted, transition structure **5** for reductive elimination of methane from tri-coordinate complex **4a** does not suffer from the problem, which besets transition structure **2**, of having a very different geometry from that of the product. We believe this is the reason **4a** is calculated to have a 10.3 kcal/mol lower enthalpy of activation than **1** for reductive elimination of methane.

However, the enthalpic cost of PH_3 loss from **1** to form **4a** is calculated to be 18.0 kcal/mol. Thus, as shown graphically in Figure 3, this makes the enthalpy of transition structure **5** + PH_3 higher than that of transition structure **2** by 7.7 kcal/mol.[31] Therefore, in agreement with the results of the experimental study of $(PPh_3)_2Pt(CH_3)H$ by Halpern,[11a] our calculations find that direct reductive elimination of methane from the analogous PH_3 complex (**1**) is enthalpically a more favorable pathway than phosphine ligand loss to form **4a**, followed by reductive elimination.

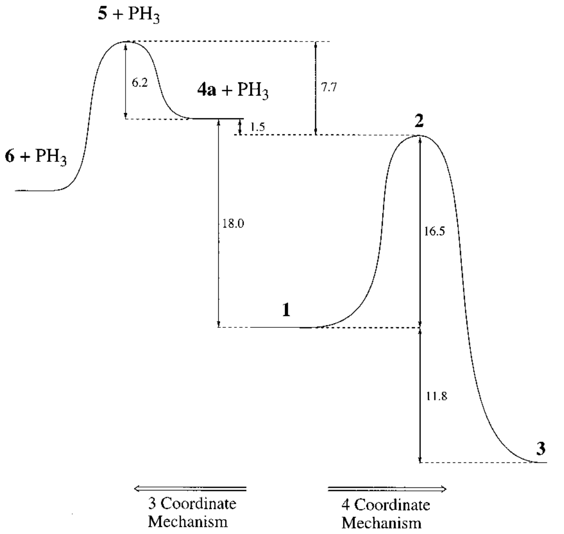
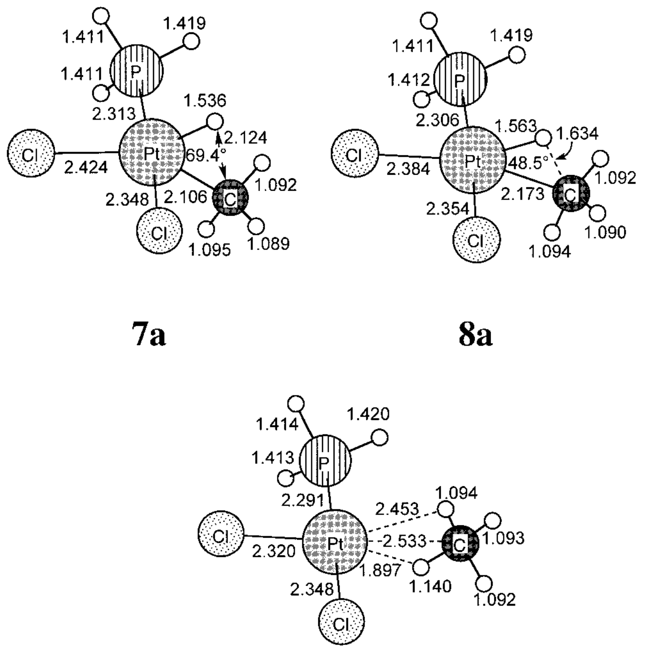


Figure 3. Schematic depiction of the calculated enthalpies (kcal/mol for reductive elimination from **1**, without prior phosphine ligand loss to form **3**, and with phosphine ligand loss to form **6**, via the intermediacy of **4a**.

Frenking and co-workers have argued that $(CH_3)_3P$ ligands have metal binding energies that are closer to those of PPh_3 ligands than to those of PH_3 models.[28] Therefore, although performing all the calculations for this study with the much more computationally demanding $(CH_3)_3P$ ligands was beyond our resources, we did optimize and compute the relative B3LYP energies of $[(CH_3)_3P]_2Pt(CH_3)H$ and $[(CH_3)_3P]Pt(CH_3)H$ + $(CH_3)_3P$. After corrections for basis set superposition errors, we found $\Delta H = 22.6$ kcal/mol for trimethylphosphine loss from $[(CH_3)_3P]_2Pt(CH_3)H$, an enthalpy increase that is 4.6 kcal/mol larger than that for loss of a PH_3 ligand from **1** to form **4a**.

This finding indicates that PPh_3 binding enthalpies are probably underestimated by our calculations, which use PH_3 model ligands.[32] This is presumably the case not only in the four-coordinate, Pt(II) complex (**1**) but also in the six-coordinate, Pt(IV) complexes (**13**) which are discussed in the next section.

Reductive Elimination of Methane from Five- and Six-Coordinate Pt(IV) Complexes. Intuitively, it might seem that adding two axial ligands to the planar, three- and four-coordinate Pt(II) complexes, discussed in the previous section, should have only a small effect on their reductive elimination reactions. The bond making and bond breaking that occur during these reactions take place in a plane which is orthogonal to the bonds to the two additional ligands. However, all of the experimental studies to date have found that six-coordinate, hydridomethyl-platinum(IV) complexes undergo loss of a ligand prior to methane elimination,[15] whereas both our calculations and experimental investigations[11] show that at least some four-coordinate Pt(II) complexes (e.g., **1** and its $(PPh_3)_2Pt$ analog) reductively eliminate methane without ligand loss.



7a **8a**

9a

Figure 4. Optimized geometries of $(PH_3)Cl_2Pt(CH_3)H$ (**7a**), the $(PH_3)Cl_2Pt{\cdot}CH_4$ product complex (**9a**), and the transition structure (**8a**) which connects **7a** with **9a**. Bond lengths are in Å, and bond angles are in degrees.

How do the two additional ligands in Pt(IV) complexes change the preferred pathway for reductive elimination of methane? In an effort to answer this question, we performed calculations on methane elimination from the five-coordinate Pt(IV) complexes, $(PH_3)Cl_2Pt(CH_3)H$ (**7**) and $(PH_3)_2ClPt(CH_3)H^+$ (**10**), and the six-coordinate Pt(IV) complex, $(PH_3)_2Cl_2Pt(CH_3)H$ (**13**).

Since reductive eliminations of alkanes from Pt(IV) have been found experimentally to take place only from five-coordinate intermediates, we began by performing calculations on methane elimination from three stereoisomers of the neutral five-coordinate complex, $(PH_3)Cl_2Pt(CH_3)H$ (**7**). The geometry of isomer **7a**, which is shown in Figure 4, can be described as a pinched trigonal−bipyramidal structure, with one of the electronegative chlorines occupying the axial position that is *trans* to the phosphine.

The H−Pt−C bond angle in **7a** is 69.4°, which is substantially smaller than the corresponding angles of 83.2° and 86.5° in **1** and **4a**, respectively. This difference suggests that **7a** is farther along the pathway toward methane elimination than **1** or **4a**. In fact, as shown in Table 2, reductive elimination of methane from **7a** proceeds through a very early transition structure (**8a**) with an enthalpy of activation of only 1.2 kcal/mol. This activation enthalpy is not only 15.3 kcal/mol lower than that calculated for the four-coordinate Pt(II) complex **1**, but also 5.0 kcal/mol lower than that computed for the three-coordinate Pt(II) complex, **4a**. As shown in Table 2, the enthalpy change for methane elimination from **7a** to form **9a** is $\Delta H = -7.9$ kcal/mol.

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(31) The entropy increase associated with loss of a phosphine ligand would, of course, make the difference in free energies between **5** + PH_3 and **2** smaller than the difference between their enthalpies. Our calculations provide a value of $\Delta S_{298} = 25.1$ eV (for a standard state of 1 mol/L), which would make the free energy barriers for the two pathways nearly identical. However, this value for ΔS_{298} is based on the assumptions that (a) the hindered PH_3 rotors in **1** and **4** can be satisfactorily treated using the partition functions for harmonic oscillators, and (b) solvent has no effect on the entropies. These assumptions make the calculated entropy difference between **2** and **5** + PH_3 no more than semiquantitively correct. Nevertheless, it seems very likely that inclusion of entropy would overcome the 1.5 kcal/mol enthalpy difference between **2** and **4** + PH_3, thus predicting that exchange of PH_3 ligands with added phosphine should be competitive with direct reductive elimination from **1**.

(32) We have found that increasing the energetic cost of phosphine loss is not the only effect that is associated with the change from PH_3 to PMe_3 ligands. Preliminary calculations on the reductive elimination of methane from $[(CH_3)_3P]_2Pt(CH_3)H$ indicate that replacing PH_3 by $P(CH_3)_3$ ligands also raises the barrier for direct elimination by ~3 kcal/mol. Thus, these two effects of methyl substituents on the competition between ligand loss and direct elimination appear to cancel partially.

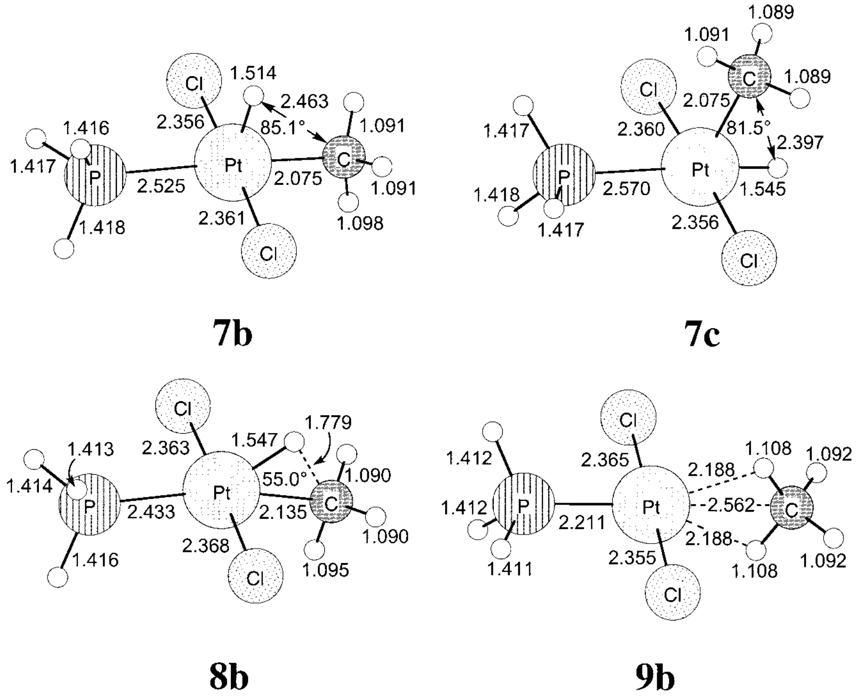

Figure 5. Optimized geometries of two isomers of $(PH_3)Cl_2Pt(CH_3)H$ (**7b** and **7c**), the $(PH_3)Cl_2Pt{\cdot}CH_4$ product complex (**9b**), and the transition structure (**8b**) which connects both **7b** and **7c** with **9b**. Bond lengths are in Å, and bond angles are in degrees.

Table 2. Relative CCSD(T) Energies and B3LYP Energies and Enthalpies (kcal/mol) for Neutral Pt(IV) Species at 298 K, after Correction of Phosphine Dissociation Energies for Basis Set Superposition Errors[a]

complex	*E* [CCSD(T)]	*E* (B3LYP)	ΔH_{298} (B3LYP)
13a	−1.5	−1.7	−1.3
13b	1.1	1.1	1.5
13c	0	0	0
14	23.2	17.8	17.0
15	13.1	3.2	5.1
7a + PH_3	12.2 (0)[b]	12.5 (0)[b]	10.9 (0)[b]
8a + PH_3	15.9 (3.7)	14.8 (2.2)	12.1 (1.2)
9a + PH_3	6.3 (−6.0)	3.7 (−8.8)	3.0 (−7.9)
7b + PH_3	13.7 [0][c]	12.8 [0][c]	10.2 [0][c]
7c + PH_3	16.0 [2.3]	15.2 [2.4]	13.3 [3.1]
8b + PH_3	18.6 [4.9]	16.4 [3.6]	13.2 [3.0]
9b + PH_3	−4.0 [−17.8]	−6.9 [−19.7]	−7.4 [−17.6]
1 + **2Cl**	3.2	3.8	
2 + **2Cl**	22.7	20.4	
4a + **2Cl** + PH_3	16.0 [2.3][c]	15.3 [2.5][c]	
5 + **2Cl** + PH_3	21.5 [7.8]	18.4 [5.6]	

[a] See Supporting Information for BSSE corrections. [b] Values in parentheses are relative to **7a** + PH_3. [c] Values in brackets are relative to **7b** + PH_3.

In the product (**9a**) of reductive elimination from **7a**, one C−H bond of the methane interacts strongly with Pt.[33] Upon release of methane from **9a**, the *cis*-$Cl_2(PH_3)Pt$ fragment rearranges to the *trans* isomer. The large exothermicity of this rearrangement actually makes the Pt−CH_4 binding enthalpy of **9a** negative by 6.2 kcal/mol.

Isomers **7b** and **7c**, which are shown in Figure 5, differ from **7a** by having the chlorines mutually *trans* in the trigonal bipyramid. In **7b** the phosphine is *trans* to the methyl group, and as in the case of **4**, this geometry is preferred to that of isomer **7c**, in which the phosphine is *trans* to the hydride. The enthalpy difference of 3.1 kcal/mol between **7b** and **7c** is 2.7 kcal/mol less than that between **4a** and **4b**. As shown in Table 2, **7b** is calculated to be 0.7 kcal/mol lower in enthalpy than **7a**.

Decreasing the H−Pt−C bond angle in **7c** causes it to rearrange to a geometry in which the phosphine is *trans* to the methyl group. The barrier for this rearrangement was computed to be only 1.3 kcal/mol. Thus, as is the case with **4a** and **4b**, **7b** and **7c** are both predicted to undergo reductive elimination by passage through the same transition structure (**8b**). The enthalpic barrier to reductive elimination of methane from **7b** is $\Delta H^{\ddagger} = 3.0$ kcal/mol, and the enthalpy change on forming product **9b** is $\Delta H = -17.6$ kcal/mol.

Even though reductive elimination of methane from **7b** is calculated to have a slightly higher barrier than from **7a**, the product (**9b**) formed from **7b** is 9.7 kcal/mol lower in enthalpy than the product (**9a**) formed from **7a**. The much lower enthalpy of **9b** is probably due to situation of the more strongly electron-donating phosphine ligand, rather than a chlorine, *trans* to the very weakly bound methane molecule. The methane binding enthalpy of **9b** is calculated to be 3.6 kcal/mol after correction for basis set superposition errors.

We also performed calculations on methane elimination from a cationic five-coordinate Pt(IV) complex, $(PH_3)_2ClPt(CH_3)H^+$ (**10**). Hill and Puddephatt[4] have carried out a DFT study of C−C and C−H reductive eliminations from several cationic, five-coordinate, Pt (IV) complexes, and their calculations found that reductive elimination of methane from $(PH_3)_2Pt(CH_3)_2H^+$ proceeds with an energy barrier of only 4 kcal/mol. DFT calculations on **10** might also be expected to find a low barrier to reductive elimination of methane, and in fact, they do.

We optimized the structures of two stereoisomers with distorted square-pyramidal geometries. As shown in Figure 6, in **10a** the apical group is hydrogen, and in **10b** the apical group is methyl. We found **10a** to be lower in enthalpy than **10b**, but only by 1.1 kcal/mol. Methane elimination from cations **10a** and **10b** is predicted to proceed through the same pinched, trigonal−bipyramidal, transition structure (**11**).

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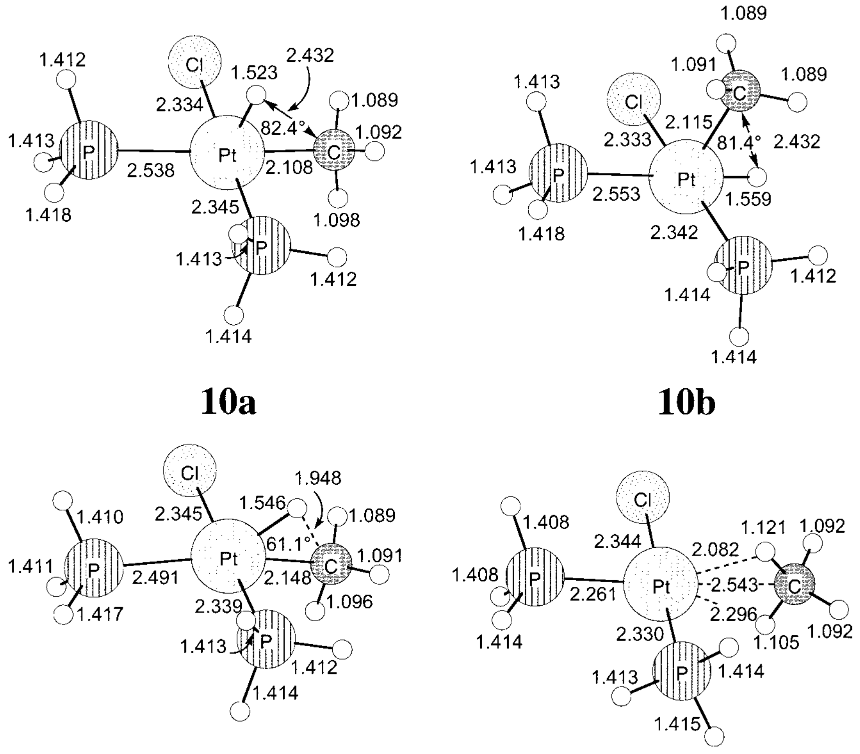
(33) Similar adducts of methane to transition metal complexes have previously been found computationally.[4,5,6g−l,p,q,s−u] Calculations have found that adduct geometries, in which one or two C−H bonds are coordinated, are very close in energy.[6g,l]



10a **10b**

11 **12**

Figure 6. Optimized geometries of two isomers of $(PH_3)_2ClPt(CH_3)H^+$ (**10a** and **10b**), the $(PH_3)_2ClPt{\cdot}CH_4^+$ product complex (**12**), and the transition structure (**11**) which connects **10** with **12**. Bond lengths are in Å, and bond angles are in degrees.

Table 3. Relative CCSD(T)//B3LYP Energies, and B3LYP Energies and Enthalpies for Cationic Pt(IV) Species at 298 K, All in kcal/mol

complex	*E* [CCSD(T)]	*E* (B3LYP)	ΔH_{298} (B3LYP)
10a	0	0	0
10b	0.7	0.6	1.1
11	1.9	0.9	0.4
12	−21.0	−23.4	−21.5

As shown in Table 3, the enthalpic barrier to reductive elimination of methane from **10a** via transition structure **11** is only $\Delta H^{\ddagger} = 0.4$ kcal/mol, and the reaction which forms **12** is exothermic by $\Delta H = -21.5$ kcal/mol. Figure 6 shows that in the elimination product (**12**) two C−H bonds of the methane interact with the platinum to different extents.[33] The platinum-methane binding enthalpy in **12** is computed to be $\Delta H = 9.5$ kcal/mol, a value significantly larger than that calculated for **9b** ($\Delta H = 3.6$ kcal/mol). The larger methane binding enthalpy in **12** is presumably due to the fact that the $(PH_3)_2ClPt^+$ fragment in it is cationic, whereas the $(PH_3)Cl_2Pt$ fragment in **9** is neutral.

Experiments[15] indicate that reductive elimination of methane from the six-coordinate complex, $(PH_3)_2Cl_2Pt(CH_3)H$ (**13**), should be calculated to have a higher activation enthalpy than the same process in **7** and **10**, the five-coordinate complexes that are derived from **13** by loss of, respectively, a PH_3 or a Cl^- ligand. Indeed, despite the fact that reductive elimination of methane from **13** is allowed by orbital symmetry,[34] we were unable to identify a pathway for this process that did not involve concomitant ligand loss.

We began by performing calculations on **13a**, the six-coordinate species that would result from addition of HCl to the square-planar Pt(II) complex, *cis*-$(PH_3)_2PtCl(CH_3)$. As shown in Figure 7, the structure of **13a** is a slightly distorted octahedron. When the H−Pt−C bond angle was reduced incrementally from its equilibrium value of 85.6° and the geometry of **13a** was reoptimized at each step, the Pt−Cl bond *trans* to the hydride was found to lengthen. Although we were able to find a transition structure (**14**) for reductive elimination of methane from **13a**, in this structure the length of the Pt−Cl bond *trans* to hydrogen is 2.793 Å, 0.258 Å longer than in **13a**. Moreover, a geometry optimization begun on the product side of transition structure **14** found that this Pt−Cl bond continues to lengthen until it reaches 3.392 Å in the product (**15**) of reductive elimination from **13a**.

The vibrational mode with the imaginary frequency in **14** has large contributions from motions of C and H, but it does not involve significant motion of the chlorine. However, the mode in **14** that corresponds to chlorine loss does have a fairly low frequency (212 cm^{-1}). Thus, although reductive elimination of methane from **13a** does not require prior loss of Cl^-, ejection of the Cl^- ligand that is *trans* to the hydrogen apparently accompanies attempts to force methane elimination directly from **13a**. Comparison of Tables 2 and 3 shows that the barrier to reductive elimination of methane from **13a** (18.3 kcal/mol) is considerably higher than that (0.4 kcal/mol) in **10a**, the five-coordinate complex formed from **13a** by complete loss of the chloride ligand that is *trans* to the hydrogen.

In the product (**15**) formed from **13a**, the ligands that interact strongly with the platinum are arranged in a manner very similar to that in the product (**12**) formed by reductive elimination from **10a**. It is not surprising that the presence of the chlorine in **15**, 3.4 Å away from the platinum, has little effect on the rest of the geometry.

Product complex **15** is 6.4 kcal/mol higher in enthalpy than reactant **13a**, but replacement of the methane in **15** by the dissociated chloride is computed to make the reaction that forms $Pt(PH_3)_2Cl_2$ and CH_4 from **13a** exothermic by $\Delta H = -28.3$

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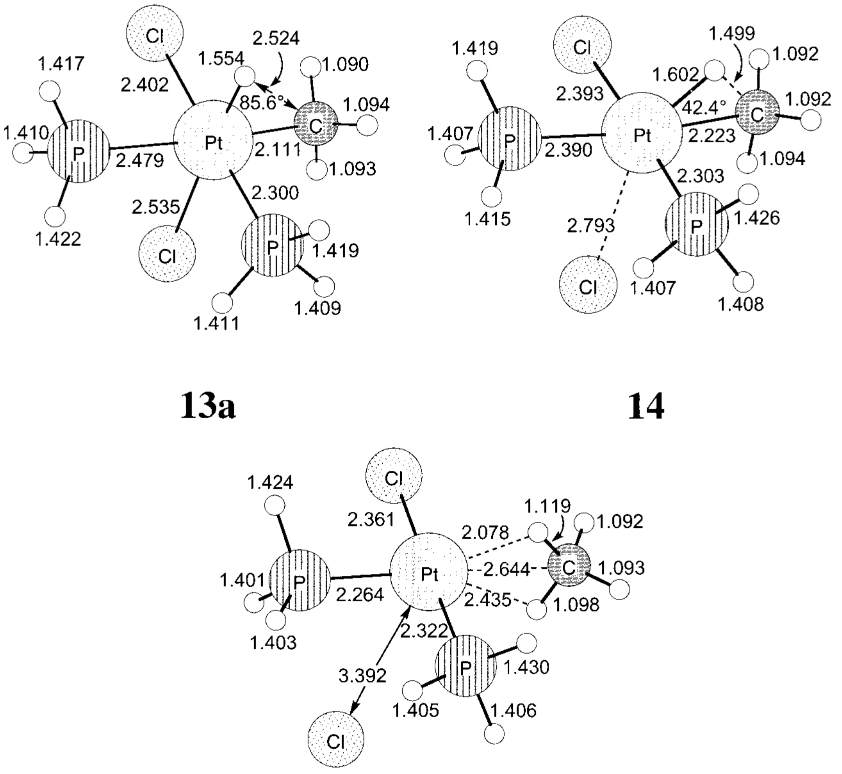
(34) Åkermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1979**, *182*, 59.



13a **14**

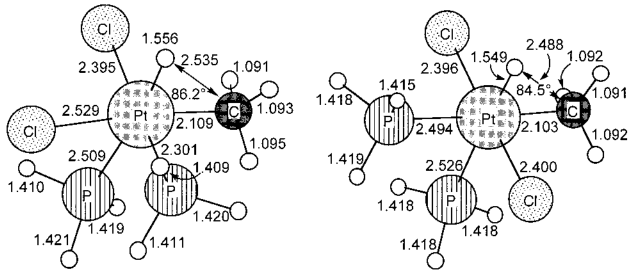
15

Figure 7. Optimized geometries of one isomer of $(PH_3)_2Cl_2Pt(CH_3)H$ (**13a**), the product complex (**15**) formed from it on attempting to force reductive elimination of methane, and the transition structure (**14**) which connects **13a** with **15**. Bond lengths are in Å, and bond angles are in degrees.

kcal/mol. The Mulliken charge on the dissociated chloride in **15** is −0.72, compared to −0.44 for the chlorine than remains bonded to the platinum. Therefore, the large exothermicity that is calculated for replacement of neutral methane by the negatively charged chloride in **15** is easily understandable. It is rather surprising that the chloride leaves at all. The fact that it does testifies to the difficulty of keeping both of the ligands that lie in the $H-Pt-CH_3$ plane bonded to Pt(IV) during reductive elimination.

In our simulation of the gas-phase reductive elimination of methane from **13a**, why is the ligand that dissociates from the metal center a negatively charged chloride, rather than a neutral phosphine? We suspected that chloride is lost because it is *trans* to the hydride in **13a**, and hydride is a more strongly electron donating ligand than the methyl. To test this conjecture, we also performed calculations on the elimination of methane from **13b**, in which, as shown in Figure 8, phosphine, rather than chlorine, occupies the site that is *trans* to the hydride.

As the H−Pt−C bond angle in **13b** was reduced, the phosphine *trans* to hydride did, in fact, dissociate from the complex. We were unable to locate a true transition structure for six-coordinate reductive elimination from **13b**, since the energy rose monotonically until the phosphine was ejected. A geometry optimization in which the H−Pt−C bond angle was fixed at 46.2°, close to the 48.5° bond angle in the transition structure (**8a**) for methane loss from **7a**, resulted in a structure which had a Pt−P distance of 2.67 Å and an energy 18.0 kcal/mol above that of **13b**. Decreasing the H−Pt−C bond angle by an additional 5.0° lowered the energy by 5.5 kcal/mol and gave an optimized geometry with a P−Pt distance of 4.24 Å. As the phosphine dissociates from **13b**, the reaction path resembles that for reductive elimination from the corresponding five-coordinate complex (**7a**). Thus, the lowest energy pathway for reductive elimination of methane from both **13a** and **13b** appears to involve concomitant loss of the ligand *trans* to hydride.



13b **13c**

Figure 8. Optimized geometries of two additional isomers of $(PH_3)_2Cl_2Pt(CH_3)H$ (**13b** and **13c**). Bond lengths are in Å, and bond angles are in degrees.

A third stereoisomer of **13** can be constructed in which the chlorine ligands are *trans* to each other. This six-coordinate complex (**13c**) is thus the Pt(IV) analogue of four-coordinate, Pt(II) complex **1**, with chlorines occupying the two octahedral coordination sites that are vacant in **1**. From the results of the calculations on reductive elimination of methane from **13a** and **13b**, one would expect that reductive elimination of methane from **13c** should proceed by expulsion of the phosphine ligand *trans* to the hydride; and this was, in fact, found to occur.

As in the case of **13b**, when the H−Pt−C bond angle in **13c** was reduced from its equilibrium value of 84.5°, the energy increased monotonically until the phosphine *trans* to the hydride had essentially dissociated. At an H−Pt−C bond angle of 44.4°, the optimized Pt−P distance was found to be 2.68 Å, an increase in bond length of 0.15 Å over the equilibrium bond length in **13c**; and the energy was found to be 16.2 kcal/mol higher than **13c**. When the H−Pt−C bond angle was reduced by another 5°, the Pt−P distance increased to 4.37 Å, and the energy dropped by 7.4 kcal/mol.

Thus, our B3LYP calculations on three isomers of the six-coordinate Pt(IV) complex **13** found that ligand loss accompanies attempts to force the reductive elimination of methane.[35] This computational finding is consistent with the low energy barriers computed for methane elimination from the five-coordinate complexes, formed by prior ligand loss. Our computational results are also consistent with not only the results of mechanistic studies of C−H reductive elimination from Pt(IV) alkyl hydrides,[15] but also with the recent discovery that Pt(IV) alkyl hydrides can be stabilized toward reductive elimination by employing ligands that are not easily dissociated.[18]

Since our calculations did not find a pathway for reductive elimination of methane via a true, least-motion, six-coordinate transition structure, we were unable to compute the barrier for such a reaction. However, we did attempt to estimate the barrier height by constructing a model for the direct elimination of methane from **13c**. A pair of axial chlorine ligands was added to the optimized structures for the four-coordinate reactant complex (**1**) and transition structure (**2**) for reductive elimination of methane from it. In the resulting structures, **1** + **2Cl** and **2** + **2Cl**, only the coordinates of the chlorines were optimized.[36] As shown in Table 2, the B3LYP energy of **1** + **2Cl** is 3.8 kcal/mol higher than the fully optimized geometry of **13c**. The energy difference between the partially optimized geometries of **1** + **2Cl** and **2** + **2Cl** is $\Delta E = 16.6$ kcal/mol, which is slightly less than the energy difference between **1** and **2** of $\Delta E = 18.0$ kcal/mol in Table 1.

The accuracy in modeling the energy required for direct reductive elimination from **13c** by the energy difference between **1** + **2Cl** and **2** + **2Cl** was assessed. We compared the energy difference between similar models for **7b** and **8b** with the actual energy difference between this five-coordinate reactant and the transition structure for reductive elimination of methane from it. Axial chlorines were added to the optimized geometries of the three-coordinate, Pt(II) reactant (**4a**) and transition structure (**5**) for methane elimination from it. Only the coordinates of the chlorines were optimized in the geometries of **4a** + **2Cl** and **5** + **2Cl**, the models for, respectively, **7b** and **8b**. As shown in Table 2, the B3LYP energy difference between **4a** + **2Cl** and **5** + **2Cl** is $\Delta E = 3.1$ kcal/mol, compared to $\Delta E = 3.6$ kcal/mol between **7b** and **8b**. Thus, the model based on adding axial chlorines to **4a** and **5** underestimates the actual effect of the chlorines in the optimized reactant (**7b**) and transition structure (**8b**) by a very small amount, only 0.5 kcal/mol.

It seems likely that the value of $\Delta E = 16.6$ kcal/mol between **1** + **2Cl** and **2** + **2Cl** also includes a small error of about this size. Therefore, a reasonable estimate of the actual energy difference between **13c** and the six-coordinate transition structure for direct reductive elimination of methane from it is $\Delta E \approx 17$ kcal/mol.

An energy barrier of this size would place the transition structure for direct reductive elimination of methane from **13c** less than 1 kcal/mol higher in energy than **8b**, the five-coordinate transition structure for reductive elimination. However, the six-coordinate transition structure should be further disfavored by having a higher zero-point energy than **8b**. Of course, we could not perform a vibrational analysis on our **2** + **2Cl** model for the six-coordinate transition structure, because its geometry is not fully optimized. However, based on the zero-point and thermal corrections to the energy difference between **13c** and **7b**, we estimate that the enthalpy of the six-coordinate transition structure should be about 3 kcal/mol higher than that of **8b**.

Reductive elimination via transition structure **8b** would additionally be favored by the increase in entropy associated with phosphine loss. Therefore, the free energy of activation for reductive elimination of methane from **13c** should be substantially smaller for a two-step mechanism, involving loss of phosphine and formation of a five-coordinate intermediate (**7b**), than for a one-step mechanism, involving reductive elimination directly from **13c**.

Comparison of Reductive Eliminations from Pt(II) and Pt(IV). The calculations on reductive elimination of methane, reported in the previous two sections, reproduce the experimental findings that alkyl C−H reductive eliminations from platinum can take place without prior ligand loss from four-coordinate complexes, but apparently not from six-coordinate complexes. The results of our calculations also provide at least a partial answer to the question of why this is the case.

Removal of an equatorial phosphine ligand from Pt(IV) complex **13c** to form **7b** is calculated to have an enthalpic cost of $\Delta H = 10.2$ kcal/mol. This is substantially less than the enthalpic price of $\Delta H = 18.0$ kcal/mol for removing a phosphine from Pt(II) complex **1** to form **4a**. Adding two axial chlorine ligands to **1**, to form **13c**, thus makes loss of an equatorial ligand 7.8 kcal/mol less unfavorable.

The two axial chlorines also make the barrier to reductive elimination of methane from the resulting five-coordinate Pt(IV) complex (**7b**) lower than that for the analogous three-coordinate Pt(II) complex (**4a**). The barrier to this reaction in **7b** via transition structure **8b** is $\Delta H^{\ddagger} = 3.0$ kcal/mol. This is 3.2 kcal/mol lower than the barrier of $\Delta H^{\ddagger} = 6.2$ kcal/mol to reductive elimination of methane from **4a** via transition structure **5.**

Thus, the presence of two axial chlorine ligands in **13c** lowers the enthalpy of transition structure (**8b**) for reductive elimination of methane via a pathway involving prior ligand loss by a total of 7.8 + 3.2 = 11.0 kcal/mol, relative to the three-coordinate transition structure (**5**) in the analogous reaction of **1**.

Our model calculations indicate that the two axial chlorines in **13c** also lower the barrier to direct reductive elimination, from the value of $\Delta E = 18.0$ kcal/mol in the four-coordinate complex (**1**), but only by ca. 1 kcal/mol. Thus, the effect of the axial chlorines on the barrier to direct reductive elimination is estimated to be ca. 2 kcal/mol smaller in the six-coordinate complex **13c** than in the five-coordinate complex (**7b**).

Although the chlorine ligands are calculated to have a ca. 2 kcal/mol smaller effect on lowering the barrier to reductive elimination in **13c** than in **7b**, this is not the principal reason these axial ligands favor reductive elimination via a mechanism that involves prior ligand loss. Instead, the difference between the mechanisms for reductive elimination in four-coordinate Pt(II) complex **1** and six-coordinate Pt(IV) complex **13c** is principally due to the effect that the two axial chlorines in **13c** have on lowering the enthaply for loss of an equatorial phosphine ligand by 7.8 kcal/mol. An enthalpy advantage of 7.8 kcal/mol corresponds to a rate difference at room temperature of greater than 10^5. A selective acceleration of this

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[35] Siegbahn and Crabtree[5] also found that ligand dissociation accompanies C−H bond formation in their investigation of methane elimination from $(H_2O)_2Cl_2Pt(CH_3)H$.

[36] When a partial optimization of **2** + **2Cl** was conducted with only the H−Pt−C angle fixed, using the angle in transition structure **2**, the phosphine ligand trans to the hydride moved away from the metal center to a distance greater than 4 Å. This finding is consistent with the result obtained when the direct elimination of methane from **13c** was investigated.

magnitude of the rate of reductive elimination by a pathway that requires prior ligand loss can easily account for the general observation that such a pathway is almost invariably followed by six-coordinate Pt(IV) complexes, even in cases where their four-coordinate Pt(II) analogues undergo direct reductive elimination.

It seems likely that the effect of axial ligands on reducing the size of the enthalpy increase for phosphine ligand loss has at least some steric component. Then, for phosphine ligands with substituents bulkier than hydrogen, ligand loss should be even more enthalpically advantaged in six-coordinate Pt(IV) than in four-coordinate Pt(II). On the other hand, the enthalpy increases for loss of phosphine ligands that have higher binding energies to Pt than PH_3 does, might be less affected by the presence of a pair of axial ligands. Which of these two effects dominates is an interesting subject for future computational studies.

Summary and Conclusions

In agreement with the experimental results of Halpern on $(PPh_3)_2Pt(CH_3)H$,[11a] our B3LYP calculations on a $(PH_3)_2Pt(CH_3)H$ model (**1**) find that reductive elimination of methane from this four-coordinate, Pt(II) complex proceeds without prior ligand loss. A pathway involving PH_3 ligand loss from **1** and reductive elimination from the resulting three coordinate complex (**4a**) is computed to be 7.7 kcal/mol higher in enthalpy. The 18.0 kcal/mol increase in enthalpy on PH_3 loss from **1**, to yield **4a**, more than offsets the 10.3 kcal/mol lower enthalpy of activation for reductive elimination of methane from **4a** than from **1**. The free energy of activation calculated for reductive elimination of methane from **1** at 248 K is in good agreement with the value measured for $(PPh_3)_2Pt(CH_3)H$.[11a]

In contrast to the case for **1**, we were unable to find a genuine pathway for direct reductive elimination of methane, without ligand loss, from $(PH_3)_2Cl_2Pt(CH_3)H$ (**13**). This computational finding is in accord with the experimentally based generalization[14,15] that reductive elimination from six-coordinate, Pt(IV) complexes almost invariably takes place by a pathway involving loss of a ligand, prior to the actual reductive elimination step.

Our calculations indicate that addition of a pair of axial chlorine ligands to the three- and four-coordinate Pt(II) complexes, respectively **4a** and **1**, makes the barrier to reductive elimination of methane smaller by ca. 3 kcal/mol in the five-coordinate complex (**7b**), and by ~1 kcal/mol in the six-coordinate complex (**13c**). The differential effect of the axial chlorines on the barriers to reductive elimination from these two complexes is, thus, a minor contributor to the contrasting preferences of **13c** for undergoing reductive elimination from the five-coordinate complex (**7b**), following ligand loss, and of **1** for undergoing direct reductive elimination, without prior ligand loss.

The major difference between the preferred pathways for reductive elimination in **1** and **13c** can be attributed to a decrease in the enthalpic cost of equatorial ligand loss in the six-coordinate, Pt(IV) complex (**13c**), compared to the four-coordinate, Pt(II) complex (**1**). This reduction, due to the axial chlorines in **13c**, is computed to be 7.8 kcal/mol. Presumably, the steric bulk of the chlorines serves to destabilize **13c**, relative to **1**, and electron donation from the chlorines into the 6s orbital of platinum may also help to stabilize **7b**, relative to **4a**.

Therefore, the almost universal preference in six-coordinate, Pt(IV) complexes for ligand dissociation, prior to reductive elimination,[14,15] is largely attributable the effect of the two axial ligands on facilitating loss of an equatorial ligand. Ligand loss lowers the activation enthalpy for reductive elimination from both Pt(II) and Pt(IV) complexes by making it geometrically possible for the transition structures to profit maximally from the same orbital interactions that stabilize the products. Our calculations provide no evidence to support the proposal[14d,f,g,15a] that ligand loss accelerates alkane reductive eliminations by allowing an agostic interaction between a C−H bond of the alkyl fragment and the empty coordination site.

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Supporting Information Available: Calculated geometrical parameters, energies, and vibrational frequencies of all the complexes whose energies are given in Tables 1−3, and comparison of B3LYP and coupled-cluster basis set superposition errors (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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