Ab Initio Calculations on (H₃P)₂Pt(C₂H₄). The Effect of Alkene Pyramidalization on Internal Rotation and Alkene Binding Energies

Keiji Morokuma*,† and Weston Thatcher Borden*,‡

Contribution from the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and the Department of Chemistry, University of Washington, Seattle, Washington 98195. Received August 22, 1990

Abstract: Ab initio calculations have been performed on the title compound at both planar (**1**) and tetrahedral (**2**) coordination geometries. Calculations at these geometries have also been performed on a $(H_3P)_2Pt(C_2H_4)$ model for **3**, in which the ethylene fragment was constrained to have a pyramidalization angle of 60.6°. The model calculations predict that in $(Ph_3P)_2Pt$ complexes, where the alkene is constrained to be highly pyramidalized, the barrier to internal rotation from **1** to **2** will be found to be higher than in $(Ph_3P)_2Pt$ complexes of unconstrained alkenes. However, on alkene pyramidalization, the increase in the energy that is required for internal rotation is calculated not to be nearly as large as the increase in the alkene binding energy. It is shown that the computational results are consistent with the expected effect of pyramidalization on the ability of the alkene π^* LUMO to accept electron density from a filled metal d orbital.

Although Pt(0) complexes of alkenes are a well-studied class of compounds,[1] there are gaps in the experimental information about the $(Ph_3P)_2Pt$ complex of the simplest olefin, ethylene. The X-ray crystal structure of $(Ph_3P)_2Pt(C_2H_4)$ has been reported;[2] but, because the hydrogen atoms were not located, the amount of pyramidalization at the ethylenic carbons in the complex was not established. Also lacking are experimental values for the energy required to rotate from a planar (**1**) to a tetrahedral (**2**) Pt coordination geometry[3] and to dissociate ethylene from the complex. In order to provide computationally derived estimates of these important structural and energetic parameters, ab initio calculations on $(H_3P)_2Pt(C_2H_4)$ were undertaken, the results of which are reported here.

1   **2**   **3**
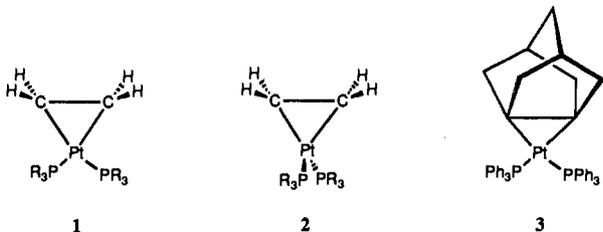
We also report the results of calculations on the effect of enforced alkene pyramidalization on the barrier to internal rotation from planar to tetrahedral Pt coordination and to alkene dissociation. Complexation to $(Ph_3P)_2Pt$ has been employed to stabilize various types of strained alkenes[4–9] and alkynes;[10] and, most recently, the $(Ph_3P)_2Pt$ complex (**3**) of a very highly pyramidalized alkene,[11] tricyclo[3.3.1.0³,⁷]non-3(7)-ene,[12] has been isolated and characterized by X-ray crystallography.[13] Calculations, designed to model this complex, were performed on $(H_3P)_2Pt(C_2H_4)$.

Computational Methodology

Calculations were performed with a relativistic, effective-core potential and an associated double-ζ valence basis set[14] for Pt and with double-ζ basis sets for all other atoms.[15,16] Geometries were optimized at the RHF level, using analytical energy gradients. The C–H bond distance was fixed at 1.084 Å, the optimized C–H bond length computed for the equilibrium geometry of $(H_3P)_2Pt(C_2H_4)$. Energies were recalculated with electron correlation included at the MP2 level.[17] All calculations were carried out with the IMS version of the Gaussian 86 series of ab initio programs.[18]

Results

The RHF optimized, equilibrium geometry of $(H_3P)_2Pt(C_2H_4)$ is given in Table I. The calculated Pt–C bond length (not shown

in the table but easily derived from the data in it) of 2.102 Å and the calculated C–C bond length of 1.444 Å are each in good agreement with the respective values of $R(Pt–C) = 2.11$ Å and $R(C–C) = 1.43$ Å, found in the X-ray structure of $(Ph_3P)_2Pt(C_2H_4)$.[2] The absence of polarization functions in the basis set for phosphorus is almost certainly responsible for the fact that the calculated Pt–P bond length of 2.436 Å is substantially longer than that of 2.27 Å found experimentally. However, the close agreement between the calculated and observed Pt–C and C–C bond lengths indicates that this deficiency in the basis set on phosphorus has little effect on the description of the bonding between the metal and the olefin.

The pyramidalization angle (ϕ)—the angle between the H–C–H plane and the extension of the C–C bond[11]—is calculated to be

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† Institute for Molecular Science.
‡ University of Washington.

27.1° in $(H_3P)_2Pt(C_2H_4)$. This predicted pyramidalization angle is smaller by about 10° than those found in $(Ph_3P)_2Pt$ complexes of halogenated alkenes[19] but comparable to that in the $(Ph_3P)_2Pt$ complex of TCNE.[20,21]

At the RHF level only 6.4 kcal/mol is computed to be required to dissociate $(H_3P)_2Pt(C_2H_4)$ to $(H_3P)_2Pt$ plus C_2H_4. When electron correlation is included at the MP2 level, the dissociation energy increases to 29.3 kcal/mol. Rigid internal rotation of the complex from a planar (1) to a tetrahedral coordination geometry (2) requires 32.3 kcal/mol at the RHF level and 30.3 kcal/mol at MP2.

The underestimation of the C_2H_4 dissociation energy at the RHF level causes the energy required for internal rotation to exceed the dissociation energy at this level of theory, even when relaxation of the bond lengths and angles in 2 is allowed. Consequently, attempted RHF optimization of the geometry of 2, subject only to the constraint of preservation of C_{2v} symmetry (with the C–C bond oriented orthogonal to the P–Pt–P plane), leads to dissociation of the complex to $(H_3P)_2Pt$ plus C_2H_4. Thus, it was necessary to perform geometry optimization of 2 with inclusion of electron correlation.

Practical considerations made impossible the full optimization of the geometry of 2 at the MP2 level of theory. Instead, single-point MP2 calculations were performed at a series of geometries that were optimized at the SCF level with different fixed values of the distance between Pt and the center of the C–C bond. The MP2 energies were fit to a quadratic potential, and a minimum was found at $R(Pt-C_2H_4) = 2.227$ Å. The interpolated, SCF optimized, geometry of 2 at this value of $R(Pt-C_2H_4)$ is given in Table I.[22]

As shown in Table I, the MP2 energy of 2 at this geometry is 23.5 kcal/mol above that of the equilibrium geometry (1) of the complex. A barrier to internal rotation of this magnitude is consistent with the observation that in the proton-decoupled ^{13}C NMR spectrum of $(Ph_3P)_2Pt(C_2H_4)$ at room temperature an AXY pattern is observed for the ethylene carbons, due to the different coupling constants between ^{13}C and the ^{31}P nuclei cis and trans to it.[13] Because the complex decomposes on heating in solution above 70 °C, the actual barrier height has not been determined experimentally. However, the temperature independence of the ^{13}C NMR spectrum up to 70 °C indicates that the free energy difference between 1 and 2 is probably greater than 20 kcal/mol.

Another calculation was performed on 2 at $R = 2.227$ Å, but with the bond angles in the rotated ethylene fragment fixed at the values in the equilibrium geometry of 1. The MP2 energy obtained was 2.8 kcal/mol higher than when these bond angles were unconstrained. Thus, relaxation of the bond angles in the ethylene fragment accounts for about 40% of the 6.8 kcal/mol MP2 energy lowering found on allowing all the bond lengths and angles in 2 to relax from those in 1.

In order to model the effects of having a highly pyramidalized geometry enforced on the alkene moiety, another series of calculations was performed with the bond angles in the ethylene fragment fixed at the values found by X-ray crystallography in the $(Ph_3P)_2Pt$ complex (3)[13] of tricyclo[3.3.1.0³,⁷]non-3(7)-ene. As shown in Table I, constraining the ethylene to have a pyramidalization angle of $\phi = 60.6°$ results in a more metallocyclopropane-like geometry for 1 with a shorter Pt–C₂H₄ distance and a longer C–C bond length than in the unconstrained ethylene

complex. The RHF optimized Pt–C bond length of 2.036 Å in the $(H_3P)_2Pt(C_2H_4)$ model for 3 is slightly shorter and the C–C bond length of 1.524 Å slightly longer than the respective values of $R(Pt-C) = 2.07$ (2) Å and $R(C-C) = 1.48$ (3) Å found in the actual complex.[13]

The calculated dissociation energy for loss of pyramidalized ($\phi = 60.6°$) ethylene from the $(H_3P)_2Pt(C_2H_4)$ model for 3 is 64.6 kcal/mol at the RHF level and 67.3 kcal/mol at MP2. However, not allowing the ethylene geometry to relax upon release from the complex overestimates the dissociation energy of complex 3.[23] A more realistic estimate of the dissociation energy of 3 can be obtained by modeling uncomplexed tricyclo[3.3.1.0³,⁷]non-3(7)-ene with ethylene that is constrained to have the geometry computed for the pyramidalized double bond ($\phi = 52.8°$) in this olefin.[24] As shown in Table I, recalculating the ethylene dissociation energy with this geometry for uncomplexed ethylene gives 36.7 kcal/mol at the RHF level and 50.6 kcal/mol at MP2.

Rigid internal rotation from a planar to a tetrahedral coordination geometry in the complex with $\phi = 60.6°$ is computed to require 42.6 kcal/mol at the RHF level and 37.1 kcal/mol at MP2. As shown in Table I, optimization of the tetrahedral coordination geometry in the manner described above, with ϕ fixed at 60.6°, gives an MP2 barrier to internal rotation of 31.6 kcal/mol.

Discussion

Our model calculations predict a very large increase in the binding energy of the pyramidalized alkene in 3, relative to the binding energy of ethylene in its $(Ph_3P)_2Pt$ complex. In our calculations designed to model 3 the $(H_3P)_2Pt$ binding energy of ethylene, constrained to have $\phi = 60.6°$ in the complex and $\phi = 52.8°$ when uncomplexed, exceeds that of unconstrained ethylene by 30.3 kcal/mol at the RHF level and 21.3 kcal/mol at the MP2 level.[25] The 9.0 kcal/mol greater increase in ethylene binding energy at the RHF level is attributable to the fact that the energy of 53.5 kcal/mol, required to pyramidalize an isolated ethylene to $\phi = 52.8°$ at the RHF level, is about 9 kcal/mol larger than the 44.3 kcal/mol that is required at the MP2 level.[26]

Pyramidalization increases the binding energy of an alkene in several ways. First, pyramidalization hybridizes the π and π^* orbitals of an alkene, thus increasing the overlap of the alkene's HOMO and LUMO with the atomic orbitals of any species to which the alkene coordinates. In addition, pyramidalization raises the energy of the π HOMO, but it has been shown to have even a larger effect on lowering the energy of the π^* LUMO.[24] The lowering of the LUMO of an alkene on pyramidalization should be particularly important in strengthening the bonding to a d^{10} transition metal such as Pt(0), since the alkene LUMO then becomes a better acceptor for transfer of electron density from one of the metal d orbitals.[27]

If backbonding in Pt(0) complexes increases with alkene pyramidalization, one would anticipate more transfer of electron density from $(H_3P)_2Pt$ to ethylene when the C_2H_4 moiety is constrained to be highly pyramidalized. In fact, this was found to be the case. A Mulliken population analysis showed 0.34

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(23) The dissociation energy of fully optimized $(H_3P)_2Pt(C_2H_4)$ is, of course, also overestimated if dissociated ethylene is constrained to have the same geometry that it does in the complex. The overestimation amounts to 20.6 kcal/mol at the SCF level and 12.7 kcal/mol at MP2.

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(26) Because the difference between the RHF and MP2 binding energies of pyramidalized ethylene is nearly the same as the difference between the RHF and MP2 ethylene pyramidalization energies, at both the RHF and MP2 levels of theory the energy of 1 with $\phi = 60.6°$ exceeds that of 1 with $\phi = 27.1°$ by almost exactly the same amount, 23 kcal/mol.

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Table I. Optimized Geometries[a] (Bond Lengths in Å, Bond Angles in deg, Fixed Geometrical Parameters in Italics) and Relative Energies (kcal/mol) Computed for Planar (**1**) and Tetrahedral (**2**) Complexes of $(H_3P)_2Pt$ with Ethylene

complex	$R(Pt-C_2H_4)$	$R(P-Pt)$	$R(C-C)$	P-Pt-P	H-C-C	ϕ^b	$E(RHF)$	$E(MP2)$
1	1.974	2.436	1.444	103.7	119.2	27.1	0[c]	0[d]
2[e]	*1.974*	*2.436*	*1.444*	*103.7*	*119.2*	*27.1*	32.3	30.3
2[f]	2.227	2.396	1.372	128.0	121.1	12.4	23.7	23.5
2[g]	*2.227*	2.399	1.380	129.7	*119.2*	*27.1*	27.8	26.3
$(H_3P)_2Pt + C_2H_4$	∞	2.325	1.333	180.0	121.8	0.0	6.4	29.3
1[h]	1.905	2.439	1.524	103.3	*107.0*	60.6	23.2 (0)	23.0 (0)
2[e,h]	*1.905*	*2.439*	*1.524*	*103.3*	*107.0*	60.6	65.8 (42.6)	60.1 (37.1)
2[f,h]	2.145	2.455	1.455	131.6	*107.0*	60.6	65.9 (42.7)	54.6 (31.6)
$(H_3P)_2Pt + C_2H_4{}^i$	∞	2.325	1.338	180.0	*109.5*	52.8	59.9 (36.7)	73.6 (50.6)

[a] Except for $R(Pt-C_2H_4)$ in **2**, all geometry parameters were optimized at the RHF level of theory. [b] Pyramidalization angle at carbon. [c] Relative to −880.5459 hartrees. [d] Relative to −881.0837 hartrees. [e] Rigid rotation of the geometry of **1**. [f] Interpolated MP2 energy minimum in $R(Pt-C_2H_4)$ with all other geometry parameters optimized at the RHF level. [g] $R(Pt-C_2H_4)$ fixed at the value at the MP2 minimum and H-C-C and ϕ fixed at the values in the equilibrium geometry of **1**. [h] H-C-C and ϕ fixed at the values shown, in order to model complex **3**. [i] H-C-C and ϕ fixed at the values shown, in order to model tricyclo[3.3.1.0^{3,7}]non-3(7)-ene.[24]

electron transferred from $(H_3P)_2Pt$ to ethylene in the complex with $\phi = 60.6°$, compared to 0.18 electron in the complex with $\phi = 27.1°$.

A decrease in metal–olefin backbonding has been shown to be largely responsible for the existence of a barrier to internal rotation from a planar (**1**) to a tetrahedral (**2**) coordination geometry in $(R_3P)_2Pt$ and other d^{10} transition-metal complexes of alkenes.[27] In $(R_3P)_2Pt$ a d orbital on Pt that lies in the P–Pt–P plane and, hence, interacts with the phosphine lone pairs is a better electron donor than is a d orbital that has a node in this plane. Thus, a planar coordination geometry is preferred in which the alkene LUMO can interact with the d orbital that is the better electron donor.

As the ability of an alkene to accept electron density from a metal is increased by increasing the pyramidalization of the alkene, the preference for a planar (**1**), rather than a tetrahedral (**2**), coordination geometry should also increase. Our calculations find this to be the case. For example, at the MP2 level comparison of the complexes with $\phi = 27.1°$ and 60.6° shows rigid internal rotation in the latter to require 6.8 kcal/mol more energy than in the former and 5.3 kcal/mol more energy when only the ethylene bond angles in both complexes are held fixed.[28]

Nevertheless, on constraining ethylene to have $\phi = 60.6°$, the size of the calculated increase in the energy required for internal rotation from **1** to **2** is not nearly as large as the size of the calculated increase (21.3 kcal/mol at the MP2 level) in the ethylene binding energy in **1**. Obviously, there must also be a substantial increase, amounting to about 15 kcal/mol at the MP2 level, in the ethylene binding energy in **2** upon constraining ethylene to have $\phi = 60.6°$. The reason for the increases in binding energy in both coordination geometries is that enforced pyramidalization causes the ethylene LUMO to become a better acceptor for electron donation, not only from a d orbital on Pt that lies in the P–Pt–P plane but also from a d orbital that has a node in this plane.

(28) Since, in our calculations to model **3**, we constrain ethylene in **1** to have $\phi = 60.6°$, we cannot allow in **2** for the change in the pyramidalization angle that presumably occurs on internal rotation of **3** from a planar to a tetrahedral coordination geometry. Therefore, we have no calculated barrier height for the $(H_3P)_2Pt$ complex of constrained ethylene which can be compared with the 23.5 kcal/mol MP2 barrier that is obtained when the ethylene geometries in both **1** and **2** are completely unconstrained. However, with some assumptions, it is possible to obtain an estimate of what this barrier height might be in **3**. Relaxation of the ethylene pyramidalization angle from $\phi = 27.1°$ in **1** to $\phi = 12.4°$ in **2** lowers the MP2 energy by only 2.8 kcal/mol, which is 22% of the lowering of 12.7 kcal/mol that is calculated at the MP2 level on allowing uncomplexed ethylene to relax totally from its geometry in **1** to its equilibrium geometry. Relaxation of uncomplexed ethylene from the geometry of the alkene moiety in **3** ($\phi = 60.6°$)[13] to the equilibrium geometry calculated for free tricyclo[3.3.1.0^{3,7}]undec-3(7)-ene ($\phi = 52.8°$)[23] lowers the MP2 energy by a slightly larger amount, 16.7 kcal/mol. If, on going from a planar to a tetrahedral coordination geometry for complex **3**, relaxation of the pyramidalization angle from $\phi = 60.6°$ also gives an energy lowering that is 22% of this estimate of the maximum relaxation energy possible for the highly pyramidalized alkene in **3**, the calculated MP2 barrier to internal rotation would be lowered by 3.7 kcal/mol to about 28 kcal/mol. An MP2 barrier height of this size would be about 4.5 kcal/mol greater than that in unconstrained ethylene.

The strengthening of $Pt-C_2H_4$ bonding with enforced ethylene pyramidalization in both planar and tetrahedral coordination geometries is also manifested in the calculated values of $R(Pt-C_2H_4)$. As shown in Table I, the RHF optimized value of $R(Pt-C_2H_4)$ in the planar coordination geometry decreases from 1.974 Å with $\phi = 27.1°$ to 1.905 Å with $\phi = 60.6°$. Similarly, in the tetrahedral coordination geometry the MP2 optimized value of $R(Pt-C_2H_4)$ decreases from 2.227 Å with $\phi = 12.4°$ to 2.145 Å with $\phi = 60.6°$.

Mulliken population analyses confirm that, not only at the planar coordination geometry (**1**) but also at the tetrahedral coordination geometry (**2**), electron transfer from $(H_3P)_2Pt$ to ethylene increases with pyramidalization of the alkene. Metal-alkene backbonding is so much weaker in **2** than in **1** that, when ethylene pyramidalization is unconstrained, 0.06 electron is computed to be transferred from ethylene to $(H_3P)_2Pt$ in **2**, compared to the 0.18 electron that is calculated to be transferred in the opposite direction in **1**. In contrast, when ethylene is constrained to have $\phi = 60.6°$, electrons are transferred from $(H_3P)_2Pt$ to ethylene in **2**, as well as in **1**.

As expected, the amount of electron density transferred from $(H_3P)_2Pt$ to an ethylene that is constrained to be highly pyramidalized is again less in coordination geometry **2** (0.09 electron) than in coordination geometry **1** (0.34 electron). Interestingly, the difference between geometries **1** and **2** in the amount of electron density transferred from $(H_3P)_2Pt$ to ethylene is nearly the same for both constrained and unconstrained ethylene, amounting to about 0.25 electron more transferred from $(H_3P)_2Pt$ to ethylene in **1** than in **2**.

Conclusions

Our calculations on $(H_3P)_2Pt(C_2H_4)$ predict a sizable increase in alkene binding energy upon enforced alkene pyramidalization. Increased back donation from a d orbital on Pt to the alkene LUMO, which is stabilized by pyramidalization, appears to play a key role in strengthening Pt–alkene bonding at both planar (**1**) and tetrahedral (**2**) coordination geometries.

Because metal–alkene backbonding is more important when both carbons lie in the P–Pt–P plane, than when they are orthogonal to it, alkene pyramidalization increases the energy difference between the former (**1**) and the latter (**2**) coordination geometries. Thus, our model calculations lead us to predict that in $(Ph_3P)_2Pt$ complexes such as **3**, where the alkene is constrained to be highly pyramidalized, the barrier to internal rotation will be found to be higher than in $(Ph_3P)_2Pt$ complexes of unconstrained alkenes. However, the increase in the energy that is required for internal rotation should not be nearly as large as the increase in the alkene binding energy.