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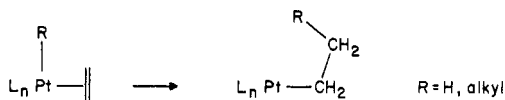
## The Olefin Insertion Reaction

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**Abstract:** A molecular orbital study of the insertion of ethylene into a Pt-H bond begins with an analysis of the interaction of a hydride with an ethylene in the absence of the metal. Identification of the crucial orbitals along a simplified reaction coordinate allows one to focus on how the metal atom with one to three other ligands attached to it facilitates the insertion. Associative and dissociative processes from a four-coordinate reactant lead to five- and three-coordinate intermediates whose complex polytopal rearrangements are explored in detail. We do not find an easy insertion pathway from a five-coordinate intermediate, nor a facile reaction by a direct route from a four-coordinate complex with ethylene and hydride trans to each other. The necessary final waypoint of ethylene and hydride cis seems in the calculations to be best achieved by a sequence of associative and, preferably, dissociative steps.

Insertion of unsaturated ligands into platinum-hydrogen and platinum-alkyl bonds has been known for many years.<sup>1</sup> The prototype case is the insertion of an olefin into Pt-H<sup>2</sup> or Pt-alkyl<sup>3,4</sup> bonds, illustrated schematically in **1**, but other



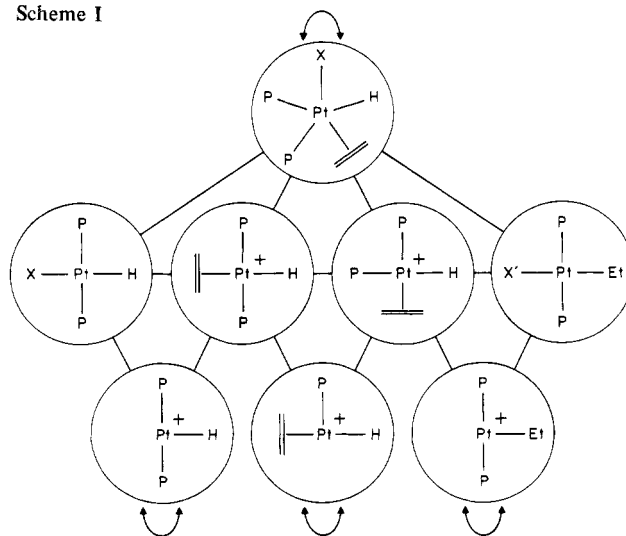
unsaturated reagents, such as acetylenes,<sup>5-7</sup> carbon monoxide,<sup>4,8</sup> isocyanide,<sup>9,10</sup> CO<sub>2</sub>,<sup>11</sup> and CS<sub>2</sub>,<sup>12</sup> can follow this course.

Similar processes occur in many analogous systems<sup>13</sup> and many aspects of pure and applied inorganic chemistry may depend on them: homogeneous hydrogenation of olefins and acetylenes;<sup>14</sup> the Wacker process;<sup>15</sup> hydroformylation reactions;<sup>16</sup> olefin isomerizations;<sup>17</sup> to name only a few. The platinum insertion reaction is only one member of the whole family of insertion-type reactions but has received considerable attention because of its relative experimental tractability.

Several detailed experimental studies of the kinetics and mechanism of platinum insertion reactions have been published,<sup>2e-h,3a,8</sup> and also some theoretical analyses.<sup>18-20</sup> We present here a molecular-orbital treatment of the parent reaction, **1**, with R = H. Our goal is to gain an understanding of the general reaction, and to provide some discrimination among mechanistic alternatives.

It is worthwhile to review briefly some of the experimental studies of this reaction and the mechanistic interpretations attached; more intricate details will be presented later. A typical mechanism is illustrated in Scheme I. Starting from

Scheme I



a four-coordinate hydrido Pt complex two courses have generally been assumed to be followed. There is a pathway in which "X" of the starting four-coordinate Pt complex is displaced by the ethylene to give a four-coordinate hydrido-olefin

complex, which presumably inserts readily with recoordination of a fourth ligand. Intermediate four-coordinate hydrido-olefin complexes have been isolated and demonstrated to have the trans geometry.<sup>2b,d</sup> This mechanism is assumed to be preferred when "X" is a weakly bound ligand (e.g., NO<sub>3</sub><sup>-</sup> or solvent). When "X" is more strongly bound (e.g., Cl<sup>-</sup>, CN<sup>-</sup>, CO), ethylene presumably adds to the complex to give a penta-coordinate ethylene adduct which subsequently undergoes insertion. Again, such pentacoordinate adducts have been characterized (although not with *ethylene*).<sup>2j</sup>

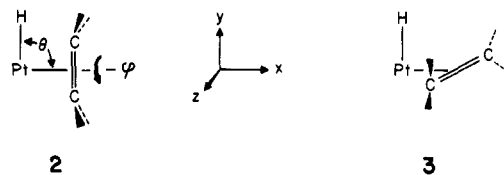
The available evidence suggests that the insertion is facile when the four-coordinate mechanism can operate, i.e., when "X" is labile. When "X" is more tightly bound, the insertion requires more forcing conditions or is not observed.<sup>2h</sup> Kinetic measurements<sup>2e-g</sup> have shown that the reaction is first order in Pt species, and is retarded by added NO<sub>3</sub><sup>-2g</sup> and Cl<sup>-2f</sup> in some cases, but not by added Cl<sup>-</sup> in another case.<sup>2e</sup> The evidence in hand suggests that the insertion reaction occurs between a hydride and an olefin bound to a single metal center<sup>2i</sup> and without intervention of free radicals.<sup>22</sup>

When we began our work on this problem we thought that it would be sufficient to explore the two most popular pathways discussed above. But the more detailed mechanistic Scheme I shows that life is not that simple. At least in principle one must consider a whole range of three-, four-, and five-coordinate intermediates and their interconversion. The problems may be classified as follows: (1) Associative and dissociative processes of three-, four-, and five-coordinate complexes; (2) substitutional preferences and rotational barriers in the same; (3) isomerizations or topological transformations of the various complexes retaining the coordination number; (4) reactions, such as the actual insertion, occurring in the ligand sphere, which change the coordination number; (5) intermolecular reactions. All of these have to be studied not for an ML<sub>n</sub> molecule but for a much more unsymmetrical ligand set, typically ML<sub>2</sub>L'L'' for a four-coordinate complex. The reader will not blame us for feeling that if we understood all these details we would understand a good part of inorganic chemistry. While we have indeed gained from past work a reasonable degree of comprehension of some of these matters, e.g., points 2 and 3 above, we do not make any pretense of having achieved the same for the other points, 1, 4, and 5. In fact the approximate molecular orbital procedure that we use, the extended Hückel method,<sup>23</sup> is unsuitable for problems involving significant bond length changes and so simply cannot resolve the questions raised by points 1 and 5 above. We are obliged to qualify our eventual conclusions about the ease or lack thereof of a given reaction by statements such as "if the reaction proceeds through a five-coordinate intermediate then such and such a transition state is of high (or low) energy". If we fail to make such a statement explicitly the reader must supply it implicitly. Nevertheless we feel that this procedure, with details given in the Appendix, does in the end provide us with a degree of understanding. The trends we obtain, and the reasons behind them, are fundamental enough to survive in calculations of superior quality on a higher dimensional energy surface.

We begin with an examination of a greatly simplified insertion coordinate with and without the metal center present. Identification of one or more levels responsible for the barrier or its lowering will set the stage for the subsequent detailed discussion of mechanistic alternatives differing in coordination number.

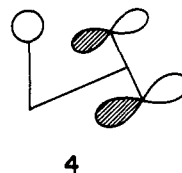
### General Electronic Features of the Insertion Reaction

The primitive reaction coordinate we consider is formed by fixing a hydrogen and ethylene to a platinum atom, and diminishing the angle  $\theta$ , **2**, between the Pt-H bond and the line from Pt to the center of the ethylene.<sup>24</sup> Another angle,  $\varphi$ , defines the torsion of the ethylene about the Pt-center line.  $\varphi =$



0 has H, Pt, and both carbons in one plane, and will be referred to as the "coplanar" approach, to contrast with  $\varphi = 90^\circ$ , **3**, an "upright" ethylene. Other ligands, here Cl and PH<sub>3</sub>, can be placed around the Pt to model the insertion in alternative coordination geometries. (The precise structures are given in the Appendix.) The simple motion which we consider, diminishing  $\theta$ , cannot do justice to the later stages of the reaction but should provide a reasonable picture of the earlier stages, up to the transition state. Note that in this simplified model it is a moot point whether the process is hydride migration or ethylene insertion. In reality, the difference may be discernible.

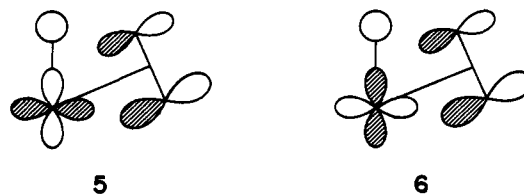
We begin the analysis of the insertion by considering the orbitals of the interacting hydride and ethylene alone. When the hydride approaches the ethylene in plane in the specified manner but without the platinum atom present, the molecular orbitals evolve as seen in Figure 1. The HOMO of the system, sketched in **4**, consists mainly of an antibonding combination



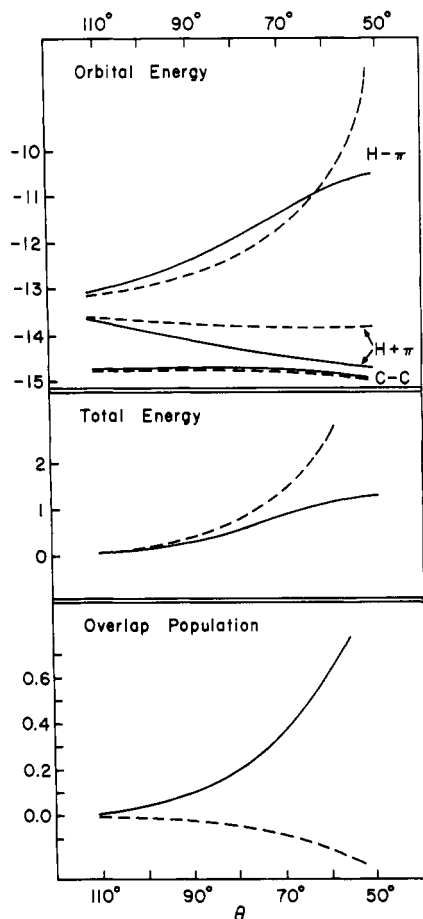
of ethylene  $\pi$  and hydride, and rises as  $\theta$  is diminished. Simultaneously, the  $\pi^*$  of the ethylene is mixing into this orbital, diminishing the antibonding repulsion between H and C <sub>$\beta$</sub> . This repulsion dominates and the energy, both total and in the highest occupied molecular orbital (HOMO), opposes bringing the hydride onto the ethylene. Mixing in the  $\pi^*$  is vital to forming the H-C <sub>$\beta$</sub>  bond, however, and the H-C <sub>$\beta$</sub>  overlap population (also in Figure 1) rises nicely as the hydride and ethylene approach.<sup>24</sup>

The importance of the  $\pi^*$  mixing can be seen by causing the hydride to approach the center of the ethylene in the upright geometry, **3**. Now, by symmetry, the ethylene  $\pi^*$  cannot mix and the repulsive H- $\pi$  combination rises much more steeply. Also, the overlap population becomes more and more negative, from filled-orbital-filled-orbital repulsion of the hydride with the ethylene C-C  $\pi$  and  $\sigma$  orbitals. Therefore, only the "end-on" coplanar approach will be considered as permitting insertion. This requirement has been noted in many of the references cited, as has been the specific significance of mixing in  $\pi^*$ .

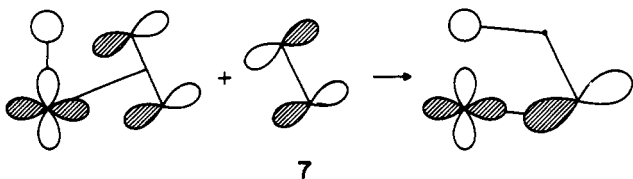
Repeating the coplanar process with a platinum atom present gives Figure 2. Now, it is one of the d-block orbitals which rises most steeply. The HOMO of the hydride-olefin complex, **4**, forms bonding and antibonding combinations with one of the d orbitals, **5** and **6** below. In this coordinate system



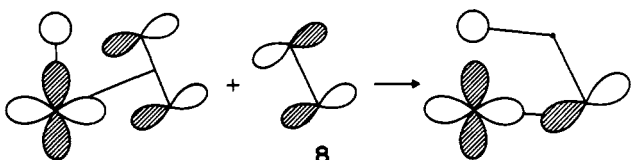
the d orbital in question is mostly  $x^2 - y^2$ .<sup>25</sup> Orbital **5**, so marked in Figure 2, no longer rises rapidly; although there is still H-C <sub>$\beta$</sub>  repulsion, the  $\pi^*$  mixing helps both to relieve the repulsion and to form the Pt-C <sub>$\alpha$</sub>  bond. Thus this orbital smoothly develops into a Pt-C bonding orbital, **7**, and rises no further. The other orbital, **6**, is in a less happy situation. At the



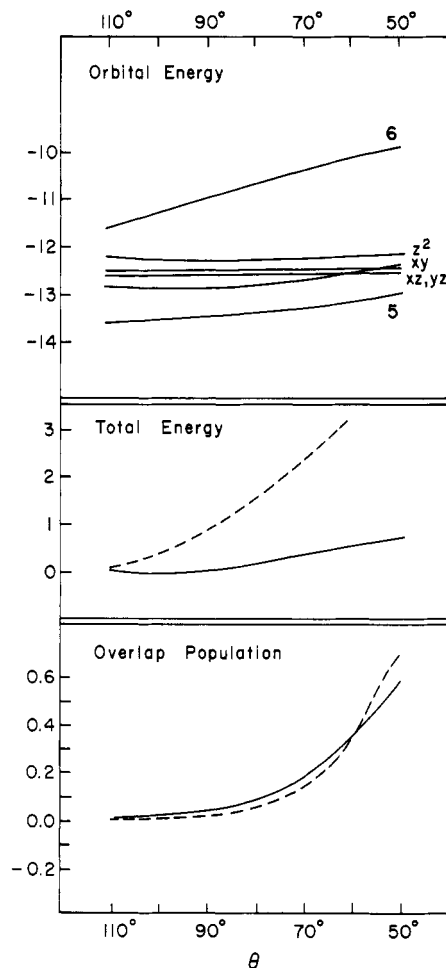
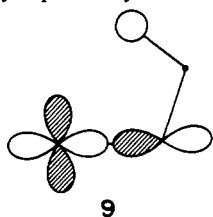
**Figure 1.** Molecular orbitals, total energy, and H-C $\beta$  overlap population for ethylene plus hydride. Solid line = coplanar ethylene, 2; dashed line = upright ethylene, 3. The energy scales are in eV, that for the total energy measured from an arbitrary energy zero.



beginning of the reaction the d orbital is repelled by the hydride and ethylene. Moving the hydride and ethylene toward each other causes increased H-C $\beta$  repulsion and the  $\pi^*$  mixes to relieve it, again. This time, however, the mixing in of the  $\pi^*$  serves to aggravate an already unfavorable Pt-C $\alpha$  interaction, 8. The orbital climbs to appreciably high energy in the transition state region.



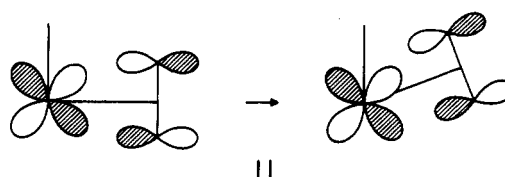
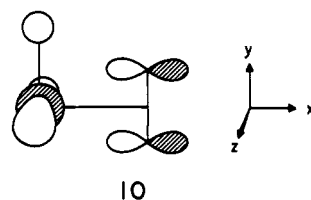
Eventually, once the hydrogen has detached itself from the metal, the antibonding combination 6 will become a d-block orbital that is slightly repelled by the ethyl donor, 9. There is



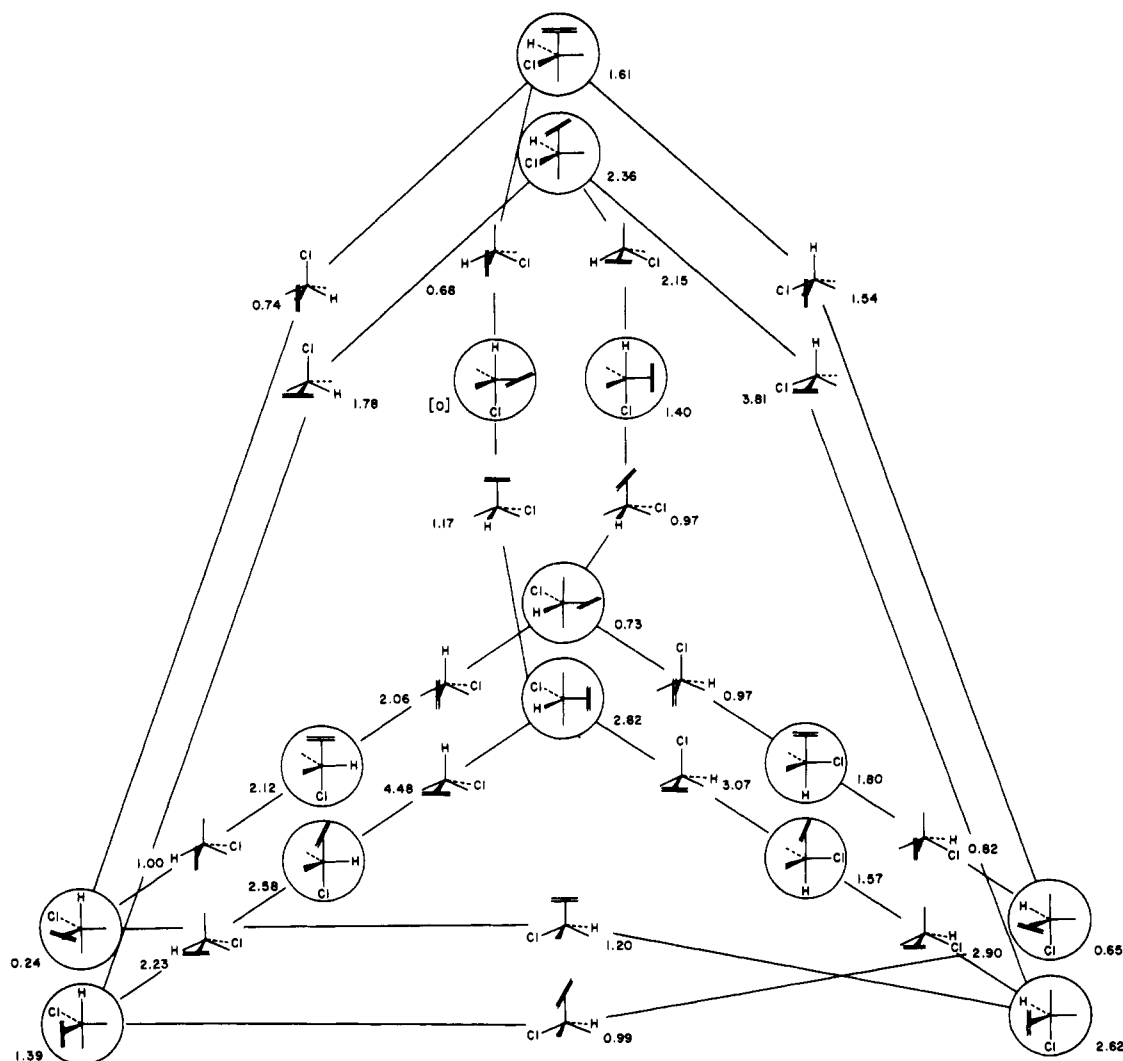
**Figure 2.** Molecular orbitals, total energy, and H-C $\beta$  overlap population for PtH(ethylene) as a function of  $\theta$  (see 2). Solid line = orbital 6 empty; dashed line = orbital 6 filled. The energy scales are in eV, that for the total energy measured from an arbitrary energy zero. The orbital labels 5 and 6 refer to text structures.

no convincing reason why it should then be any higher than its origin, 6.<sup>26</sup> But the correlation is not smooth, and indeed if there were any symmetry present one would see a level crossing typical of symmetry-forbidden reactions.

The other d-block orbitals show little change as the insertion progresses.  $xz,yz$  cannot sense the hydride or the H-C interaction and do not change at all.  $z^2$  sees a slight stabilization as the process occurs, since the H and C $\beta$  components of the "z<sup>2</sup>" orbital (10) are mutually attractive although each individually repels the  $z^2$ . Destabilization is seen for  $xy$ , 11, as some



back-bonding into the ethylene  $\pi^*$  is lost. Figure 2 is complicated by an avoided crossing between  $z^2$  and  $xy$ .



**Figure 3.** Trigonal bipyramidal (circled) and square pyramidal isomers of  $\text{PtHCl}(\text{PH}_3)_2(\text{ethylene})$ . For each isomer two ethylene conformations are shown. Each line represents a Berry pseudorotation pathway. The numbers are energies in eV relative to the most stable conformation. The graph excludes enantiomers. The unmarked sites contain phosphines.

The overlap population,  $\text{H}-\text{C}_\beta$ , is plotted in Figure 2 for the  $d^8$  case,  $\text{Pt}(\text{II})$ . It rises smoothly along the reaction coordinate. The total energy also stays low for this  $d$  electron configuration, but would not do so for the  $d^{10}$  complex.

With the Pt present, we see one  $d$ -block orbital rising sharply as the reaction approaches the transition state. Much of the subsequent analysis focuses on this orbital and how it affects the energy surface for the insertion reaction. It possesses lobes of opposite phase pointing at the hydride and ethylene, and in the coordinate system of Figure 2 is the  $x^2 - y^2$  orbital but in another coordinate system it will have another name. In  $\text{Pt}(\text{II})$   $d^8$  complexes, where one  $d$ -block orbital is empty, insertion will prove to be difficult unless this orbital, **6**, is the empty  $d$  orbital, whatever the system.

We now investigate the insertion reaction in several model  $\text{Pt}(\text{II})$  molecules. The calculations and analyses will consider and compare various possible mechanisms for the reaction, by noting energy changes and overlap population trends along the modeled reaction coordinate. Crude estimates for an activation energy will also be obtained. We cannot make reliable predictions about the thermodynamics of the process, and this must constantly be borne in mind when experimental results are discussed.

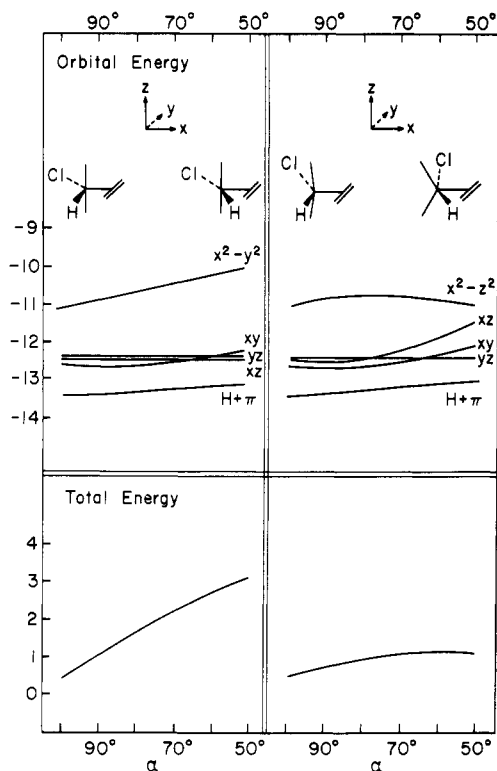
### Insertion via a Five-Coordinate Mechanism

One of the possible mechanisms for the insertion reaction is initiated by an associative formation of a five-coordinate

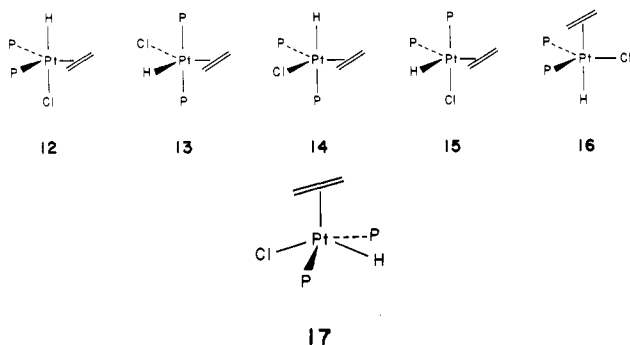
hydrido-ethylene complex, which returns to four coordination as the insertion proceeds. To model this possible mechanism we have studied  $\text{PtHCl}(\text{PH}_3)_2(\text{ethylene})$ .

Any time that one encounters a five-coordinate molecule one had better worry about the potentially soft surface for polytopal rearrangements of such a species.<sup>27</sup> The substitution pattern of the complex in question allows a distressing number of possible isomers. Imposing the admittedly arbitrary requirement of either a trigonal-bipyramidal (TBP) or square-pyramidal (SP) framework, there are 25 isomers (10 TBP, 15 SP). The collection is mapped out in Figure 3. Here the circled structures are TBP, and the connecting lines are Berry "pseudorotation" processes which interconvert them, via SP structures. We do not consider but cannot rule out "turnstile" mechanisms<sup>28</sup> which would interconvert different TBP isomers. An additional degree of freedom, the rotational orientation of the ethylene, must also be studied. Allowing only two orientations of the ethylene, one parallel to the  $\text{Pt}-\text{H}$  bond and the other perpendicular, "doubles" each gross structure as in Figure 3. Beside each structure is the calculated energy (eV), relative to the most stable one. The structures are not optimized, since most are unstable (not local minima) and relax into TBP isomers **12-16**. Standardized structures (see Appendix) were assumed.

When ethylene attacks the four-coordinate complex  $\text{PtHCl}(\text{PH}_3)_2$ , the preferred approach is along (or very close to) the  $z$  axis to give, initially, **17**, the entry point into the

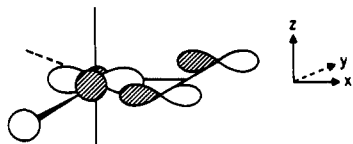


**Figure 4.** (a, Left) Insertion from a trigonal bipyramid, phosphines held in axial positions. (b, Right) Same as (a), but phosphine locations optimized throughout. The energy scales are in eV.



five-coordinate manifold. This structure relaxes directly into either **12** (the most stable calculated isomer) or **13**, and we first consider insertion from these two complexes.

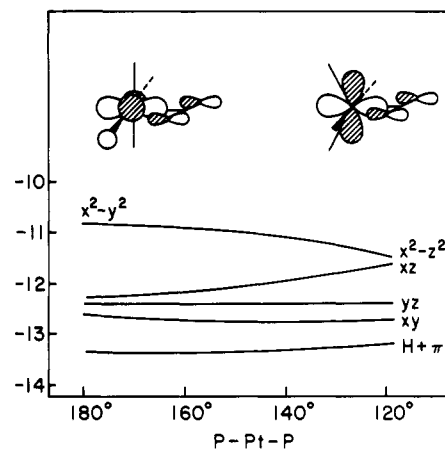
Structure **13** is a very attractive candidate for insertion, with the hydride and olefin already cis and coplanar; a smooth, least motion reaction leading to a square planar ethyl complex can be envisioned. However, calculating this process reveals a surprising energy barrier (Figure 4a). The orbital responsible is the HOMO, **18**. It is largely an " $x^2 - y^2$ " orbital and



**18**

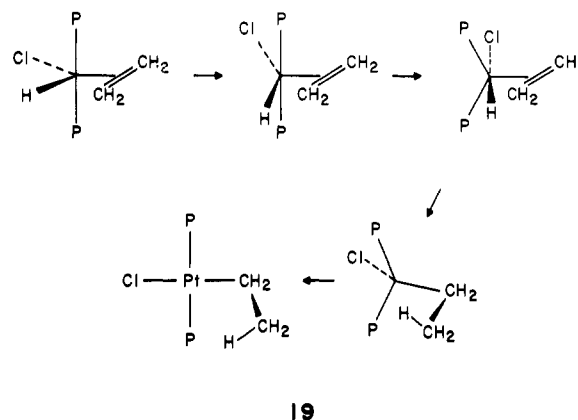
strongly resembles the d orbital considered before, with a node between H and  $C_\beta$ . Because of this orbital, the reaction is difficult and the H- $C_\beta$  overlap population is consistently small.

Recalculating this process, while optimizing the P-Pt-P angle, previously held fixed at  $180^\circ$ , gives a much lower energy barrier and more favorable overlap population trends (Figure



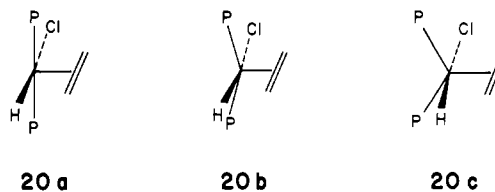
**Figure 5.** Walsh diagram for bending back the phosphines in an idealized  $\text{PtHCl}(\text{PH}_3)_2(\text{ethylene})$ .

4b). The optimum P-Pt-P angle goes from  $180^\circ$  at the beginning to ca.  $120^\circ$  in the transition state. The geometry of the process is shown in **19**.



**19**

Despite the awkward-looking, near-tetrahedral transition state produced, bending back the phosphines remarkably aids the insertion reaction. To see why, consider the Walsh diagram for the process **20a-c** (Figure 5). In **20a**, the HOMO, sketched



**20 a**

**20 b**

**20 c**

in Figure 5, has a repulsive interaction between H and  $C_\beta$ —it is the d orbital considered before—and rises sharply as the insertion is continued. With the phosphines bent ( $\text{P-Pt-P} = 120^\circ$ ) in **20c**, the HOMO loses most of the H- $C_\beta$  repulsion; now it is the LUMO which resembles the essential d orbital, and its H- $C_\beta$  antibonding nature does not inhibit insertion.

This motion, bending the phosphines, is essentially a progression along a Berry pseudorotation pathway. The exchange of HOMO and LUMO in this process is fundamental; Figure 6 shows the generalized Walsh diagram for the Berry mechanism.<sup>29</sup> The important feature here is that the repulsive interaction between the two starred ligands (to be thought of as ethylene and hydride) disappears from the HOMO and reappears in the LUMO as the orbitals evolve along the pseudorotation coordinate.

Insertion from **13** along a least motion pathway is energetically very unfavorable; insertion via the least energy pathway involves first a Berry pseudorotation. There are actually two Berry processes which bend back the phosphines and aid the

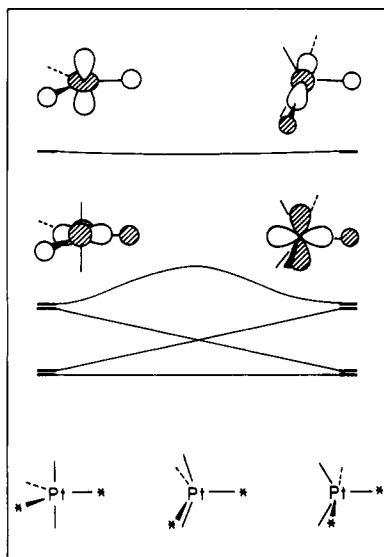
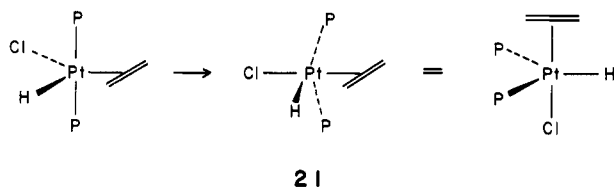


Figure 6. Idealized Walsh diagram for the d-block levels of a five-coordinate complex undergoing a Berry pseudorotation.

insertion from **13**, namely, the one considered (**19**) and also **21** below. Either motion has the effect of relieving the H-C $\beta$



repulsion, by causing the essential d orbital to become the LUMO, and insertion by either path gives virtually the same barrier. This is probably an accident of our model geometries and a complete surface (i.e., Pt-H, Pt-C, C-C bonds all optimized) would undoubtedly prefer one over the other. Overlap populations suggest that **21** might insert more readily; it also less strongly resembles a tetrahedron in its transition state.

The conjunction of insertion and Berry pseudorotation makes for a complicated picture. We wish that it were not so, but find that it is necessary for a complete description of the system. Perhaps Figure 7 may help. It shows a slightly non-continuous energy pathway for the two insertion modes considered above. Note from this figure that while pseudorotation from **13** is essential for the reaction, it itself costs energy. Structures **20c** and **21**, the two other trigonal bipyramids in the figure, are not local minima but relax spontaneously back to **13**. **20c** and **21** are well set up for insertion, but the activation energy must be measured from **13**, or even more properly from the global minimum **12**.

How can one achieve insertion from **12**, the lowest energy geometry with the hydrogen axial and the ethylene in the equatorial plane? With the ethylene in the preferred orientation as shown, insertion is very unlikely; the ethylene must rotate at least partly out of the equatorial plane. The structure so attained is exactly the same as **20c**, just discussed. The rotation requires at least 1.4 eV in our calculations, if the rest of the complex is kept rigid. Insertion from this structure **20c** appears energetically and orbitally reasonable, but for the >1 eV required to attain it.

Thus the only TBP structures from which insertion will occur easily are those with an axial hydride and an equatorial, upright ethylene, or axial ethylene and equatorial hydride. Any other TBP structure, if forced to undergo the insertion, will necessarily rearrange to resemble one of these. Likewise, a SP complex with a basal ethylene and axial hydride, or vice versa, evolves into such a TBP complex as insertion progresses. The

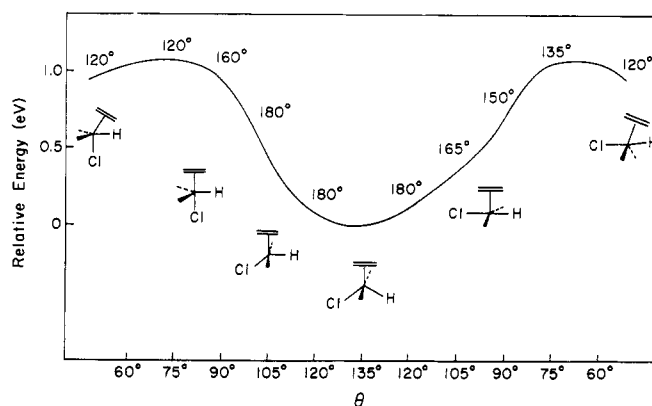


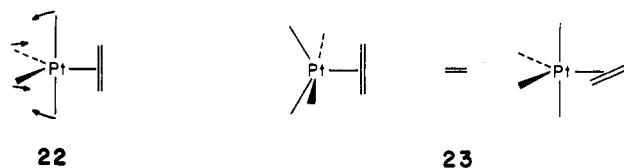
Figure 7. Total energy for the two insertion modes considered in the text. The optimized P-Pt-P angle is given above some waypoints.

remaining possibility for insertion is a SP complex with cis basal hydride and ethylene. Such a complex is calculated to have a low barrier to insertion; insertion from this structure is from the point of view of orbitals or energy virtually identical with insertion from a cis square planar complex, to be discussed later.

Returning to Figure 3, it can be seen that the TBP structures from which insertion is likely are, without exception, relatively high-energy structures with a marked tendency (0.6 eV or more) to relax into nearby TBP structures from which insertion will not occur. The "global minimum" **12** provides a deep potential hole from which at least 0.8 eV is required to reach an insertion-favorable structure. Similarly, SP complexes with cis basal hydride and planar ethylene are very high-energy species. This will be contrasted with the insertion from a four-coordinate complex, where such high-energy structures can be avoided.

Let us consider why the insertion-favorable structures are conformationally unfavorable.<sup>30</sup>

1. In a TBP, an equatorial ethylene strongly prefers a planar orientation over an upright orientation (by ca. 1.0–1.4 eV calculated). Back-bonding is significantly better in the planar orientation, and some destabilizing filled-orbital-filled-orbital repulsions ("steric repulsions") are minimized. If the ethylene is placed upright, the complex either twists it back or is driven to pseudorotate, **22** to **23**.

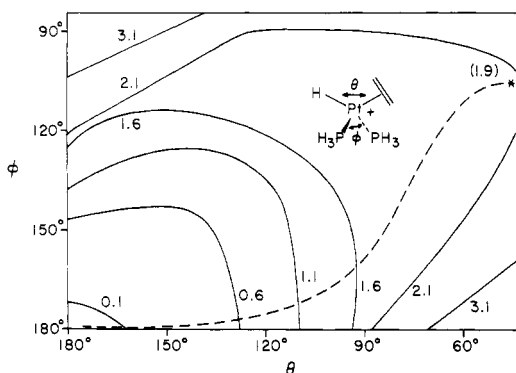


2. The ethylene is unhappy in the axial site of a TBP. There appear to be marked steric repulsions with the equatorial ligands, coupled with better back-bonding when the ethylene returns to an equatorial site.

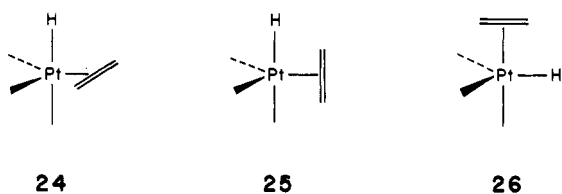
3. The strong  $\sigma$ -donating hydride shows a preference for axial sites in TBP structures, basal sites in SP. In TBP it avoids equatorial sites.

4. A basal ethylene in a SP structure has a powerful drive (1–2 eV) to stand upright. Both better back-bonding and diminished steric repulsions contribute to this.

What might be done to make insertion more facile in the five-coordinate manifold? The major task is to force the system out of its global minimum, **24**, toward structures more conducive to insertion, **25** and **26**. The structures **25** and **26** would be stabilized by  $\pi$  acceptors in the equatorial plane; regrettably, so would **24**. Making the axial ligand a good  $\pi$  acceptor stabilizes all the structures slightly, but favors a pseudorotation to a geometry which puts both the ethylene and the hydride



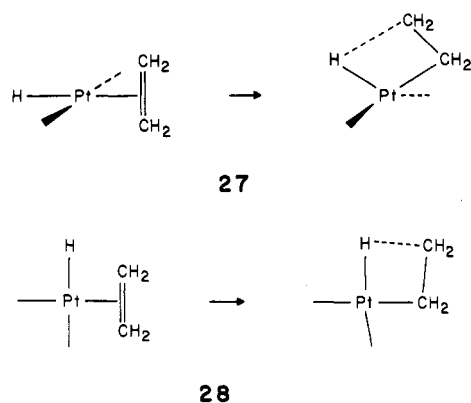
**Figure 8.** Potential energy surface for an insertion that begins in a trans-H ethylene complex. The contours are marked in eV. The reaction path corresponds roughly to the dashed line.



back in the equatorial plane and does not especially favor insertion. However, a general substitution of poorer donors and/or better acceptors should lower the back-bonding into the ethylene, thus lessening the barrier to forming **25** or **26** and aiding insertion. Also substituting a potent  $\sigma$  donor trans to the hydride (axial in **24**) should weaken the Pt-H bond and facilitate insertion. A more drastic approach is to expel or abstract a ligand to go to a four-coordinate complex, from which we calculate the insertion to proceed more readily.

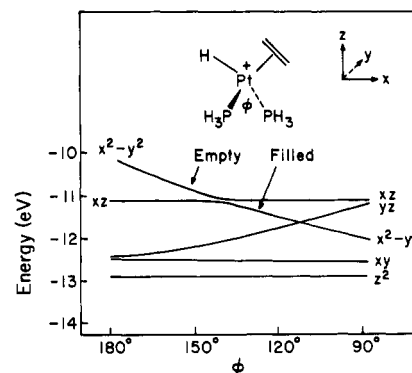
#### Insertion via a Four-Coordinate Complex

Two possible ways for the reaction to go via a four-coordinate complex were implied in Scheme I and are illustrated below: **27**, where a trans hydrido-ethylene complex inserts



directly through a quasi-tetrahedral transition state; and **28**, where the insertion is accomplished from a cis hydrido-ethylene complex.

Modeling the trans mechanism suggests that it is extremely unlikely. A two-dimensional energy surface for the reaction is given in Figure 8 where the two variables are  $\theta$  (H-Pt-ethylene angle) and  $\phi$  (P-Pt-P angle). The insertion requires 1.9 eV; this number cannot be taken literally but must be compared to activation energies we calculate for the other mechanisms. There are two reasons for the relatively large barrier: first, with the given parameters *any* Pt(II) four-coordinate complex avoids tetrahedral geometries, and second, the insertion-unfavorable d orbital is (usually) filled. These two factors are quite closely related.



**Figure 9.** Walsh diagram for the effect of bending phosphines in the trans insertion mechanism.  $\theta$ , as defined in Figure 8, is  $90^\circ$ .

When any planar four-coordinate Pt(II) complex is forced to distort, along a  $D_{2d}$  or  $C_{2v}$  type of motion, the energy rises as the ligands begin to repel filled  $xz$ ,  $yz$  orbitals.<sup>31</sup> For small angular distortions the energy cost is small. Indeed there are a number of crystal structures of sterically encumbered Pt(II) complexes which show distortions from an ideal square-planar geometry.<sup>32</sup> However, the energy increases rapidly as the distortion continues; to bend two nominally trans ligands from  $180^\circ$  to  $90^\circ$  costs ca. 1.5–2.0 eV in a typical calculation. In the case at hand, bending the hydride and ethylene to an angle of  $90^\circ$  requires 1.6 eV. Once one attains this angle, continuing on to the inserted product can be either difficult or facile, depending on the P-Pt-P angle. Figure 9 shows the orbitals for H-Pt-ethylene =  $90^\circ$  as the phosphines are bent. If the P-Pt-P angle is  $180^\circ$ , the HOMO of the complex ( $xz$ ) opposes the insertion, as discussed. But, as the phosphines are bent together, the LUMO ( $x^2 - y^2$ ) drops, eventually becoming the HOMO. At this point the  $xz$  orbital is emptied and the insertion can proceed.

The situation is very like that of the five-coordinate complex **13**. Again, bending back the phosphines is necessary to avoid impossibly large energy requirements for insertion, but is itself a motion costly in energy; Figure 9 shows the  $yz$  orbital rising as the phosphines bend. The combination of these trends causes the sinuous reaction path in Figure 8. From the planar trans complex the least energy motion towards insertion leaves the phosphines at  $180^\circ$ , to avoid the destabilization of the  $yz$ . Eventually the hydride and ethylene start repelling each other, coupled by the  $xz$  orbital, and the phosphines then bend so as to bring in the LUMO ( $x^2 - y^2$ ) and relieve this repulsion.

Small HOMO-LUMO gaps and near crossings (expected for nearly tetrahedral structures) are characteristic of the trans mechanism. If the reaction goes in this manner, the complex probably prefers a high-spin transition state, for which our orbital analysis is not strictly applicable. In first-row transition elements (e.g., Ni(II)) high-spin tetrahedral four-coordinate complexes are energetically competitive with low-spin planar structures, and perhaps in such systems the reaction may go by this mechanism. The heavier transition elements (e.g., Pt(II)) are experimentally known to strongly prefer low-spin states<sup>33</sup> and in all probability do not utilize this mechanism.

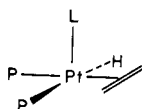
The alternative four-coordinate mechanism, direct cis insertion, is the most favorable of all. The essential d orbital, now  $x^2 - y^2$ , is empty and stays empty. The energy surface is featureless, showing little activation energy for the reaction if the ethylene is in the coordination plane. The computed favored path indicates that the ligand cis to the ethylene tends to follow it along, **29**. This opens up a coordination site between the two ligands where an entering ligand or solvent molecule could eventually bind to form the final trans ethyl complex. The modeled reaction coordinate is not sufficiently detailed for us to say whether the entering group actually does attack between



29

the phosphines, or whether it initially takes the site vacated by the hydride (see ref 5a,c). In the calculations the phosphines spread from an optimum angle of  $95^\circ$  in the starting cis complex to  $110^\circ$  in the "transition state",  $\theta = 50^\circ$ . A chelating ligand which enforces a small angle (ca.  $90^\circ$  or less) throughout the insertion probably slows it down, regardless of the preferred site of attack by the entering ligand.

Implicitly assumed in this cis insertion is that the ethylene is oriented in the square coordination plane, instead of upright, or perpendicular to it. In all known structures there is a preference for the upright orientation,<sup>34</sup> but in this and related systems it can be traced to filled-orbital-filled-orbital repulsions in the planar structure.<sup>35</sup> In other words, we think that the preferred ethylene orientation in Zeise's salt type  $d^8$  complexes is set by steric effects. In the model compound,  $\text{HPt}(\text{PH}_3)_2(\text{ethylene})^+$ , the calculated preference is only 0.3 eV in favor of the upright structure. Again we can compare with the pentacoordinate complex: Insertion from **20c** orbitally and energetically resembles insertion from the in-plane complex **28**, except that **20c** required 1.4 eV to twist the olefin from the most stable orientation while **28** required 0.3 eV. The fifth ligand of **20c** creates a strong electronic preference for aligning the olefin away from the hydride *in addition to* the "steric" preference seen also for the in-plane four-coordinate complex. Likewise, putting on a fifth ligand to form **30** has little effect



30

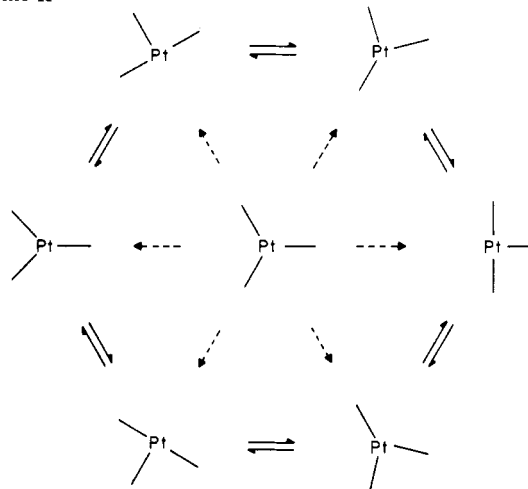
on the energy or orbitals of the reaction but does create a powerful tendency to twist the olefin and relax into a TBP.

A remaining difficulty with the cis complex is the necessary rearrangement which forms it from the characterized trans compound. Mechanisms proposed for this include multiple displacements; addition of a fifth ligand, followed by polytopal rearrangement of the pentacoordinate intermediate and return by a dissociative step to the four-coordinate isomer; and loss of a ligand to form a three-coordinate, 14-electron complex which can rearrange prior to or simultaneously with readdition of the ligand.<sup>1a</sup> We do not trust our calculations to evaluate these possibilities, since bond formation or breaking is involved, and extended Hückel calculations do not treat properly these elementary steps. Three-coordinate complexes deserve some attention as possible routes to insertion, and we now turn to these.

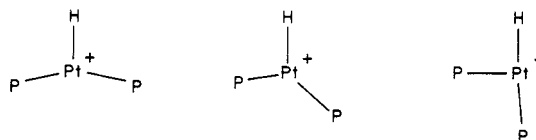
### Three-Coordinate Complexes

A possible means for forming *cis*- $\text{HPt}(\text{PH}_3)_2(\text{ethylene})^+$  from the trans isomer is by loss of ethylene to form  $\text{HPt}(\text{PH}_3)_2^+$ , which could rearrange and then read ethylene to form the cis complex. Three-coordinate  $\text{ML}_3 d^8$  structures are highly interesting in that they are Jahn-Teller systems which avoid the most symmetrical  $D_{3h}$  trigonal geometry in favor of less symmetrical T- and Y-shaped  $C_{2v}$  structures. This is shown in Scheme II, and was discussed by us elsewhere in the context of the deformations of trimethylgold.<sup>36</sup> The Pt system at hand is less symmetrical and so avoids the degeneracy directly responsible for the distortion from the  $D_{3h}$  form. Though the calculated barriers are lower, several important

Scheme II



features of the parent Jahn-Teller system are remembered. A potential surface for the rearrangement of  $\text{HPt}(\text{PH}_3)_2^+$  reveals minima for structures **31a** and **31c** with a very small



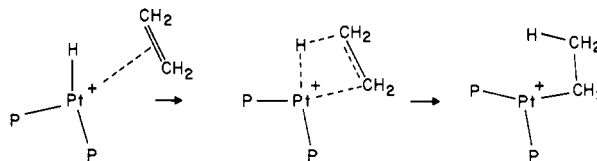
31a

31b

31c

barrier (ca. 0.1 eV) for their interconversion via the "Y" structure **31b**. If the ethylene is indeed labile in this system, this appears a very feasible mechanism for rearrangement.

Insertion could proceed once the ethylene has reattached itself to form the cis complex  $\text{HPt}(\text{PH}_3)_2(\text{ethylene})^+$ . Alternatively, insertion and reattachment may proceed simultaneously, as drawn in **32**. The calculations indicate this to be a reasonable process, competitive with the cis mechanism.



32

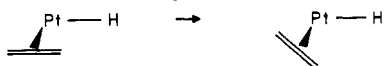
Two other three-coordinate complexes can be considered. If a phosphine were to dissociate from *trans*- $\text{HPt}(\text{PH}_3)_2(\text{ethylene})^+$  leaving a T-shaped intermediate with H and ethylene trans, then there is again a very easy rearrangement to another T-shaped structure in which the olefin and H ligands are cis to each other. This complex could undergo insertion directly or await reattachment of the fourth ligand. Dissociation of a hydride seems very unlikely; loss of H as a proton would leave behind the well-known complex  $\text{Pt}(\text{phosphine})_2(\text{ethylene})$ .<sup>37</sup> The proton could attack this complex at Pt to regenerate the trans hydrido complex or form the cis isomer, or it could attack at the olefin directly. These latter possibilities warrant more study, experimentally and theoretically.<sup>5d</sup>

### Extensions

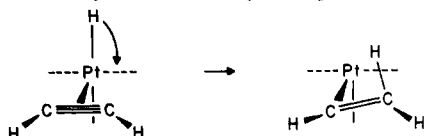
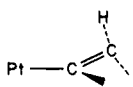
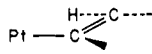
Considerable experimental work has been done on insertion of acetylenes into  $\text{Pt-H}^5$  and  $\text{Pt-CH}_3^6$  bonds. Replacing H by  $\text{CH}_3$  in our analysis will change the numbers but probably not the trends, and the conclusions would be the same. Acetylenes should behave similarly to olefins, except for the additional  $\pi-\pi^*$  pair. If the additional acetylenic  $\pi^*$  orbital can be utilized, the initial assumption of required coplanar end-on ap-



proach may break down. This has been probed by taking the "transition state" ( $\theta = 50^\circ$ ) and twisting the ethylene (or acetylene) about the Pt-ethylene axis, **33**. For ethylene, any

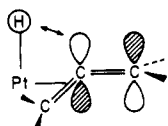
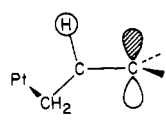
**33**

deviation from coplanarity is quite unfavorable (as assumed) but acetylene shows a very slight tendency to twist to ca.  $20^\circ$  from coplanarity. The main difference is that  $H_{Pt}-H_{C\beta}$  repulsion diminishes upon twisting the acetylene but increases when ethylene is twisted. Some loss of  $C-H_{Pt}$  bonding is observed when twisting ethylene (contributing to the instability) but some stabilizing participation of the extra  $\pi^*$  orbital can be seen when twisting the acetylene. This could open an alternative pathway in pentacoordinate acetylene complexes, illustrated in **34**. The geometrical end result of this is a badly twisted, presumably unstable, vinyl complex, **35**, in contrast

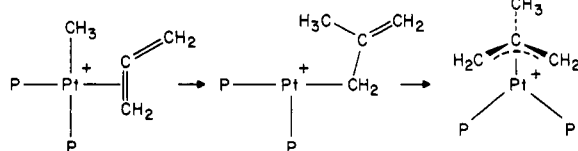
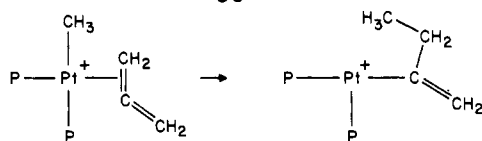
**34****35****36**

to the planar cis vinyl group formed by coplanar end-on approach, **36**. We do not believe this pathway to be important in the usual cases. Trans vinylic complexes can be formed, possibly by free-radical processes.<sup>38</sup> The twisted vinyl complex also may be accessible as a transition state for cis-trans vinyl isomerizations in a rhodium system.<sup>39</sup>

Allene also has an "extra"  $\pi^*$  orbital, but again it is not likely to be important in insertion reactions. Attack into this "extra"  $\pi^*$  orbital (**37**) would build up electron density on the dangling  $CH_2$  without any stabilization by the metal (**38**).

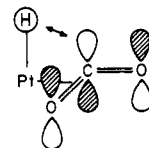
**37****38**

Allene insertions probably proceed by the same coplanar end-on approach as ethylene. An interesting question is why the observed insertions of allene<sup>3</sup> into  $Pt-CH_3$  put the methyl group on the central carbon to eventually form a  $\pi$ -allyl complex, **39**, instead of on an end carbon to form a  $\sigma$ -vinyl complex, **40**. One possible explanation is that in the early stages of in-

**39****40**

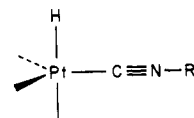
sertion, the allene orientation of **39** has less steric repulsion with the phosphine substituents than in **40**.

$CO_2$  and  $CS_2$  both possess two  $\pi^*$  orbitals. Again a coplanar end-on approach is a likely mechanism. However, now the other  $\pi^*$  orbital **41** may be utilized—it is delocalized to both

**41**

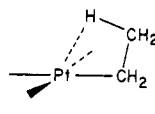
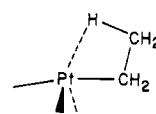
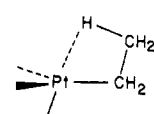
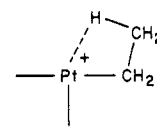
ends of the molecule, so the metal can stabilize the built-up electron density. Furthermore, the "twisted" transition state is more likely to be accessible than the analogous geometry in acetylene insertions. A much more elaborate potential surface will be required to evaluate this possibility.

An orbital analysis similar to ethylene insertion applies to CNR and CO insertions into  $Pt-H$  and  $Pt-alkyl$  bonds. Again there is repulsion between the hydride and a filled donor orbital (in this case, a carbon lone pair), relieved by mixing in of an empty  $\pi^*$  orbital. The geometric conclusions of the ethylene insertion apply here, with the exception that there is no longer a preferred rotational orientation of the inserting group. Consequently, insertion from pentacoordinate isocyanide complexes like **42** does not face the ca. 1.4 eV rotational barrier

**42**

of the analogous ethylene complex, and is a likely mechanism for CNR insertions.<sup>9</sup> The preferred mechanism of CO and CNR insertions is under study in our group.

The reverse reaction,  $\beta$ -elimination from coordinated alkyl groups, should proceed via the same transition state as insertion and the same considerations apply. In particular,  $\beta$ -elimination from a four-coordinate complex is predicted *not* to occur from the most intuitively likely structure **43**, but requires first (or simultaneously) an appreciable distortion to **44** or **45**. If a li-

**43****44****45****46**

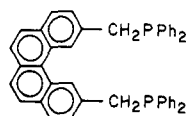
gand can be lost to form a three-coordinate, 14-electron complex **46**,  $\beta$ -elimination should be very fast. A five-coordinate alkyl complex might not undergo  $\beta$ -elimination at all.

Replacing  $Pt(II)$  by other  $d^8$  metal centers should not essentially change our analysis or conclusions. However, another metal may have different high-spin-low-spin characteristics, or may have different pentacoordinate preferences. Replacing  $Pt$  by a  $d^6$  (or less) metal center changes drastically the nature of the problem and lies outside the scope of this work.

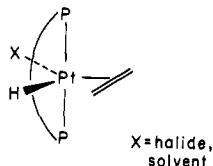
Finally, let us consider some specific experimental studies and see how they relate to the conclusions above.

In the specific case of ethylene and H-Pt, the bulk of the evidence favors the four-coordinate mechanism.<sup>2h</sup> The complex (CO)PtH(PR<sub>3</sub>)<sub>2</sub><sup>+</sup> has been shown to insert ethylene without loss of CO, so apparently the five-coordinate mechanism operates here. The reaction is relatively slow.<sup>2h</sup> Insertion of ethylene into Pt-H of PtHCl(PR<sub>3</sub>)<sub>2</sub> requires forcing conditions;<sup>2a</sup> abstracting Cl<sup>-</sup> by silver cation permits much more facile insertion.<sup>2d</sup> However, SnCl<sub>2</sub> also catalyzes the insertion, forming (SnCl<sub>3</sub>)HPT(PR<sub>3</sub>)<sub>2</sub> which presumably inserts five-coordinate.<sup>2e</sup> A possible reason for the relative inertness of ethylene toward PtHCl(PR<sub>3</sub>)<sub>2</sub> might be that the complex simply does not bind ethylene unless Cl<sup>-</sup> is abstracted. We do not know if this has been proven experimentally; our argument is that even if ethylene does bind to PtHCl(PR<sub>3</sub>)<sub>2</sub>, it will not insert easily until another ligand is removed. We do not understand fully the catalytic power of SnCl<sub>2</sub>. It has been proposed<sup>2e</sup> that two ethylenes are bound to the Pt in the transition state, with subsequent insertion of one of them. We have not yet considered this possibility explicitly, though we think that our conclusions about the unlikelihood of a five-coordinate transition state are not likely to be changed in such a case.

Insertion also occurs for ethylene + *trans*-(PP)PtH(acetone)<sup>+</sup>,<sup>2i</sup> where PP is the ligand **47**. If the PP ligand constantly spans *trans* positions (P-Pt-P angle 180°) the insertion is virtually forced to go from **48** for which we have calculated an

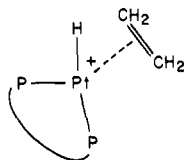


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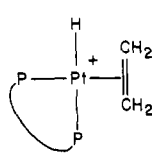


48

impossibly high barrier. However, we note a crystal structure in which the P-M-P angle of this ligand is diminished to 132°.<sup>40</sup> Geometries favorable to insertion are therefore attainable. Alternatively, insertion via a three-coordinate complex **49** is feasible. Insertion from a *cis* four-coordinate planar complex **50** looks somewhat strained but not impossible.

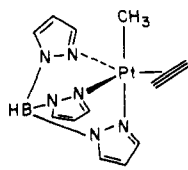


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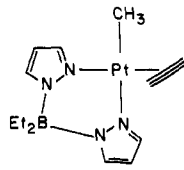


50

The methylplatinum-acetylene systems offer considerable support for several features of our analysis. The complex ClPt(As(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>) forms stable pentacoordinate complexes with acetylenes which insert slowly if at all.<sup>44</sup> Likewise, "(CH<sub>3</sub>)Pt(HB(Pz)<sub>3</sub>)" forms very stable pentacoordinate complexes with acetylenes and olefins, *none* of which undergoes insertion.<sup>42</sup> Structure determinations show that the acetylene lies in the equatorial plane of a trigonal bipyramid, **51**.<sup>43,44</sup> NMR gives no evidence of acetylene rotation. In



51



52

contrast to these systems, Et<sub>2</sub>B(Pz)<sub>2</sub>Pt(CH<sub>3</sub>)(acetylene) complexes,<sup>6c,d</sup> which are four-coordinate with *cis* methyl and

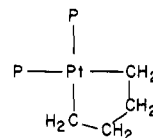
acetylene,<sup>45</sup> **52**, insert very readily if the acetylene is F<sub>3</sub>CC≡CCF<sub>3</sub>. This same acetylene does not insert from the five-coordinate complex **51**. Even so, other acetylenes, for instance, PhC≡CPh, do not insert. Apparently insertion into Pt-methyl bonds is more difficult than into Pt-H, and electron-withdrawing groups on the acetylene are required even in favorable geometries.<sup>6c,d</sup> However, this point needs further theoretical study.

Studies of the reverse reaction, β-elimination from BrPt(PR<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5-n</sub>D<sub>n</sub>), reveal hydrogen-deuterium scrambling as the elimination proceeds.<sup>46</sup> The proposed mechanism involves a five-coordinate hydrido-olefin intermediate from which reinsertion and scrambling are more facile than olefin departure. Our calculations make us prefer a mechanism whereby a ligand (phosphine or halide) is initially lost to form a three-coordinate alkyl complex, where elimination and reinsertion could be very rapid, with the olefin being finally expelled by reattaching the ligand.

The observation of a single NMR peak for the five ethyl hydrogens of Ni(acac)(PPh<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>) led to the postulate of H scrambling by a rapid elimination-olefin rotation-reinsertion sequence.<sup>47</sup> Later <sup>13</sup>C NMR studies showed that this was not occurring,<sup>48</sup> in accordance with our analysis. The single <sup>1</sup>H resonance in these systems is still mysterious. However, the Ni reaction need not proceed according to the mechanism suggested by us for Pt, since, as was pointed out earlier, alternative geometries and spin states are available in the first transition series.

The complex Pt(Et)<sub>2</sub>(bpy) eliminates ethylene when treated with methyl acrylate.<sup>49</sup> Evidence is provided that the chelating ligand bpy is entirely displaced by methyl acrylate to permit β-elimination from a three-coordinate complex.

Studies of the decomposition of Pt(*n*-Bu)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> showed that dissociation of a phosphine is prerequisite to β-elimination, and added phosphine can suppress it entirely.<sup>50</sup> Interestingly, the related metallocyclic compounds **53** are much more stable



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and decompose by different mechanisms, because the coplanar Pt-CH<sub>2</sub>-CHR-H orientation (the "reverse" of coplanar end-on insertion) cannot be achieved.<sup>51</sup> Metallocyclic nickel systems similar to **53** can undergo β-elimination after loss of phosphine.<sup>52</sup> This may happen by direct hydride migration, despite the apparent geometrical constraints, but free-radical or bimolecular processes have not been ruled out.

Despite the dangerously simplified model used for the insertion reaction, our analysis of its electronic requirements has led us to some interesting conclusions about the geometrical and coordination preferences involved. In particular insertion from a five-coordinate complex requires some rearrangement and unexpected distortion from preferred equilibrium geometries which add up to a modestly large energy barrier. If a ligand is lost to form a four-coordinate complex, then there remains a requirement of a *trans* to *cis* (ethylene and hydride) rearrangement, but the insertion barrier becomes appreciably smaller. The *trans* four-coordinate complex should not insert directly. Experimental and theoretical studies are both complicated by polytopal rearrangements and problems involving ligand dissociation, for which our calculations may not give reliable results. We think, however, that some recent experimental work supports our conclusions and that further studies can be designed to probe the suggested pathways.

Table I

Orbital	$H_{ii}$	Exponent	Ref
Pt	6s	-9.077	54
	6p	-5.475	
	5d	-12.59	
		2.696 (0.5513)	
H	1s	-13.6	1.30
C	2s	-21.4	1.625
	2p	-11.4	1.625
P	3s	-18.6	1.60
	3p	-14.0	1.60
Cl	3s	-30.0	2.033
	3p	-15.0	2.033

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### Appendix

The parameters of the extended Hückel calculations are listed in Table I. A "weighted  $H_{ij}$ " formula was used for most of the calculations.<sup>53</sup> The  $H_{ii}$  values for Pt were obtained by quadratic charge iteration on  $\text{Pt}(\text{PH}_3)_4^{2+}$  (without the weighted  $H_{ij}$ ), with virtually identical values obtained for charge iteration on  $\text{PtHCl}(\text{PH}_3)_2$  (with the weighted  $H_{ij}$ ).

For all calculations the ethylene was given the following structure: C-C, 1.34 Å; C-H, 1.07 Å; C-C-H, 120°; H-C-H, 113.548° (this corresponds to "bending back" the hydrogens by 15°). For the phosphine, H-P, 1.415 Å; H-P-H, 93.3°. Other distances: H-Pt, 1.6 Å; P-Pt, 2.28 Å; Cl-Pt, 2.36 Å; C-Pt, 2.1092 Å; Pt-(ethylene midpoint), 2.0 Å.

For standardized TBP calculations the above distances were used, and idealized  $D_{3h}$  angles. Standardized SP calculations used  $C_{4v}$  angles, with apical-Pt-basal angle 105°. For the reaction paths, angles around Pt were optimized (within the constraint of  $C_s$  symmetry, for those structures possessing it).

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## Metal Clusters in Catalysis. 14.<sup>1</sup> The Chemistry of Dinuclear Metal–Acetylene Complexes

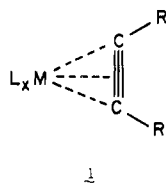
E. L. Muetterties,<sup>\*2a</sup> W. R. Pretzer,<sup>2a</sup> M. G. Thomas,<sup>2a</sup> B. F. Beier,<sup>2a</sup>  
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**Abstract:** Acetylene and diaryl- and dialkylacetylenes are uniformly bound in a  $\mu_2$ - $\eta^2$  fashion in dinuclear metal complexes so as to generate an  $\text{M}_2\text{C}_2$  tetrahedral core structure with a substantially increased acetylenic C–C bond distance. One class of these dinuclear complexes,  $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$ , was shown to react at 20 °C with hydrogen and with hydrogen plus  $\text{RC}\equiv\text{CR}$ , respectively, to form stoichiometrically and catalytically the cis alkene (>95% selectivity). In contrast,  $\text{Fe}_2(\text{CO})_6$ - $[(\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3]$  reacted only stoichiometrically with hydrogen at 20 °C in the presence of free di-*tert*-butylacetylene with conversion of only the initially bound acetylene to a mixture of hydrocarbons comprised of trans and cis alkenes and traces of the alkane. The trans alkene predominated in this iron system. The coordinately saturated complexes,  $\text{Co}_2(\text{CO})_6$ - $(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$  and  $\text{Ni}_2(\text{C}_5\text{H}_5)_2(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ , showed neither reactivity toward hydrogen at 20–80 °C nor acetylene ligand exchange in solutions with  $\text{C}_7\text{H}_7\text{C}\equiv\text{CC}_7\text{H}_7$  at 50 °C. These chemically distinguished features are discussed and some relationships of this acetylene chemistry to acetylene–metal surface chemistry are examined. Acetylene ligand lability, established for the  $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR})$  species, arises from a monomer–dimer equilibrium:  $\text{Ni}_2(\text{COD})_2(\text{RC}\equiv\text{CR}) + \text{RC}\equiv\text{CR} \rightleftharpoons 2 \text{Ni}(\text{COD})(\text{RC}\equiv\text{CR})$ . The monomer is probably the active catalyst in the observed acetylene trimerization reaction whereas the dimer appears to be the primary solution species that interacts with hydrogen.

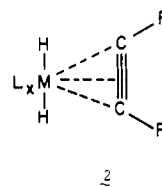
### Introduction

Complexation of acetylenes by a single transition metal in a molecular complex is adequately described in terms of  $\sigma$  and  $\pi$  bonding interactions that involve the  $\pi$  and  $\pi^*$  orbitals of the acetylene.<sup>3</sup> These complexes schematically represented in **1** are designated as  $\eta^2$  acetylene complexes following the



hapto notation proposed by Cotton.<sup>4</sup> Structural data for these complexes have been critically reviewed by Ittel and Ibers.<sup>5</sup> In all instances, the acetylenic C–C bond distances increase from the  $\sim 1.20$  Å reference for free acetylenes to  $1.30 \pm 0.70$  Å.<sup>6</sup> All structural data are limited to acetylene and dialkyl- or diarylacetylenes; no data are available for  $\text{RC}\equiv\text{CH}$ .<sup>6</sup> This bond order reduction on complexation should be and is sufficient to activate the acetylene for reduction or specifically for hydrogenation.<sup>7,8</sup> For example, Osborne and Schrock<sup>9</sup> have shown that complexes of the form  $\text{Rh}(\text{norbornadiene})\text{L}_2^+$

effectively and selectively catalyze the hydrogenation of acetylenes to cis alkenes ostensibly through intermediates formally analogous to **1** and **2**.



In the binding of acetylenes to transition metals in dinuclear or polynuclear (cluster) complexes, the prevailing mode is not of form **1** but rather a cluster form where there is a rehybridization of the carbon orbitals so that relatively strong metal–carbon  $\sigma$  bonds are formed between the acetylenic carbon atoms and two or more metal atoms as illustrated in **3** for the

