Pt(0)–Pt(0) Dimers. Bonding Relationships in a d^{10}–d^{10} System

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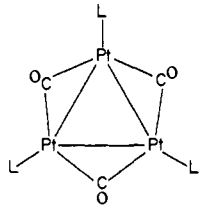
Abstract: The interaction of two d^{10} centers in a recently synthesized P_2PtPtP_2 dimer is analyzed in detail to discern the electronic factors which cause an attractive interaction between two formal closed shells. An admixture of metal s and p functions into molecular orbitals primarily composed of d functions converts, in part, bonding and antibonding interactions into more bonding and nonbonding ones, respectively. The bonding capabilities of the coordinatively unsaturated Pt_2L_4 system are explored with respect to the geometrical and electronic factors that operate in this system interacting with acetone, ethylene, $Fe(CO)_4$, and another PtL_2 fragment.

In a first, simplistic analysis one has difficulty in seeing why two or more d^{10} centers should come near each other. After all they are filled shells. Yet close contacts between d^{10} metals are not uncommon, and have caught our interest. In a separate paper[1] we present an analysis of Cu(I) clusters, while in this contribution we focus on some Pt(0) compounds.

Clusters of three or more Pt(0) centers have been synthesized[2-7] and the solid-state structures of several determined by x-ray crystallographic techniques.[2c,4,6,7] Perhaps typical of these is **1**,[6b] possessing a triangular structure which is also



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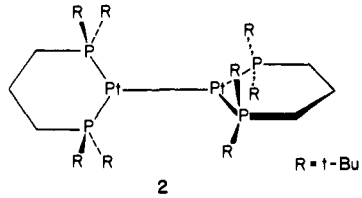

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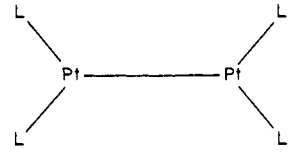
a building block of a fascinating series of stacked complexes $[Pt_3(CO)_6]_n^{2-}$.[8] In these clusters there are always several bridging groups, as there are in a handful of complexes containing two formal Pt(0) centers.[9-12] Our attention was captured by the recent synthesis and structure determination[13] of **2**, the first structurally characterized Pt(0) complex in which the two metal centers are not bridged.[14] The Pt–Pt bond length in this compound (2.765 Å) falls into the range of Pt(0)–Pt(0) separations in clusters[4,6,7] (2.65–2.79 Å), which are usually longer than Pt(I)–Pt(I) bond lengths (2.58–2.65 Å) in bridged and unsupported dimers.[15-19]

We present here a molecular orbital analysis of the metal–metal bonding in a Pt_2L_4 (L = PH_3, CO) system which serves as a model for **2**. We then proceed to study the further bonding capabilities of the coordinatively unsaturated Pt_2L_4. Our conclusions are derived from a fragment molecular orbital analysis, based on extended Hückel calculations. Computational details are specified in the Appendix.

Metal–Metal Bonding in the d^{10}–d^{10} Pt_2L_4 System

We shall construct the molecular orbitals of the Pt_2L_4 system by interacting two PtL_2 fragments. The orbitals of the ML_2 fragment are known[20] and are shown schematically in Figure 1. The occupied set is made of a group of three orbitals (yz, xy, and z^2)[21] which are almost degenerate, of an orbital "y^2" which is a hybrid of z^2 and $x^2 - y^2$, and of a high-lying xz orbital which has been destabilized through antibonding with the lone pairs of the donor L. xz has mixed in some x character, so that the two main lobes are pointing away from the L ligands. The unoccupied set is made of "hy", a hybrid of the x, z, and z^2 orbitals, and of the y orbital.

Let us now interact two such fragments to give the Pt_2L_4 system, considering first the planar form **3** (D_{2h} symmetry).



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Classifying levels according to linear pseudosymmetry, z^2 and hy are of σ symmetry, xy and yz of π symmetry, xy of δ symmetry, and "y^2" of mixed σ and δ symmetry. The biggest interactions are those of the σ and π fragment orbitals. We denote by σ_d and σ_d^*, π_d and π_d^*, and σ and σ^*, respectively, the resulting bonding and antibonding combinations of z^2, xz, and hy. The level pattern of Figure 2 shows that, according to our calculations, the interaction between the xz fragment orbitals is not large enough to bring their *antibonding* combination π_d^* above the *bonding* combination σ between the hy fragment orbitals (or that the interaction between the hy fragment orbitals is not large enough to bring their *bonding* combination σ below the *antibonding* combination π_d^* of the xz fragment orbitals). As a result, we do get an effective d^{10}–d^{10} situation where both bonding and antibonding combinations of the levels derived primarily from d-type functions are filled. We shall denote this configuration as $(\sigma_d)^2(\sigma_d^*)^2(\pi_d)^2(\pi_d^*)^2$.

As was mentioned in the introduction, the initial reaction if one has two filled shells interacting, be they s^2, p^6, or d^{10}, is that no bonding should occur, but only four-electron repulsive interactions.[22] This is an oversimplification. The reality of the matter is that whether bonding does or does not occur depends on the presence or absence of other unfilled orbitals sufficiently close in energy to and possessing sufficiently great overlap with the filled shell orbitals. The noble gases, characterized by s^2 or s^2p^6 configurations, do not form stable polymeric chains or metals. Beryllium, on the other hand, is not bound as a diatomic Be_2, but does form a respectable metal. The cohesive energy of the metal depends on the *relatively* low energy of the Be 2p levels. SCF calculations indicate that the smallest Be cluster that is bound is Be_4.[23a] Our parallel analysis of Cu(I) clusters indicates that closed shell d^{10}–d^{10} repulsive interactions are suppressed and may even be converted into weak attractive interactions by admixture of metal s and p combinations into the molecular orbitals primarily composed of d functions.[1,23b]

A similar stabilization mechanism provides the bonding between the Pt atoms in our dimer. σ_d and σ_d^* mix into themselves some hy (or σ and σ^*) character, as shown schematically by the dotted lines in Figure 2. The net effect is to convert bonding and antibonding MOs part way into still more

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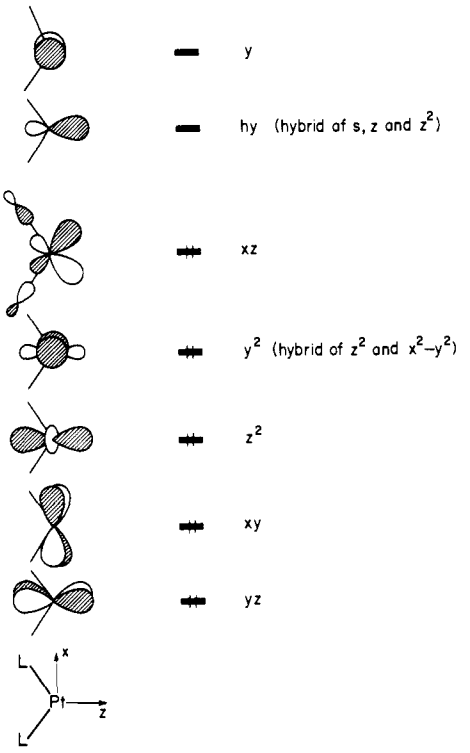
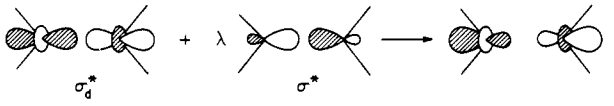


Figure 1. Orbitals of a PtL_2 fragment.

bonding and nonbonding ones, respectively. This is shown schematically in **4** and **5**. In the extended Hückel calculation



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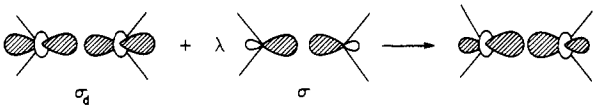

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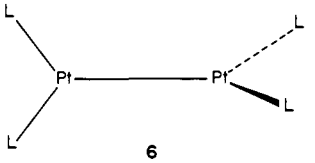
on $Pt_2(PH_3)_4$ the net Pt–Pt overlap population is 0.097 at a Pt–Pt distance of 2.75 Å.

Looking now at the torsion around the Pt–Pt bond, we found that there is almost no rotational barrier between the "planar" geometry **3** and the "perpendicular" geometry **6** (torsional



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angle of 90°, D_{2d} symmetry), the latter being favored according to our calculations by only 0.9 kcal/mol. A diagram (restricted to the biggest interactions between the two fragments) is shown in Figure 3. For the "perpendicular" geometry as well as during the whole torsional process, the Pt_2L_4 system keeps a d^{10}–d^{10} configuration. The primary factor responsible for Pt–Pt bonding, the admixture of σ and σ^* combinations into σ_d and σ_d^*, is invariant to the torsion, and this is behind the low barrier to rotation.

In principle there is an electronic factor that could have favored the perpendicular geometry. This is an overlap of a vacant p orbital on one Pt with a filled d orbital on the other Pt. This bonding pattern has been suggested by Otsuka,[13] and is illustrated in **7**. This is certainly a plausible idea, and there

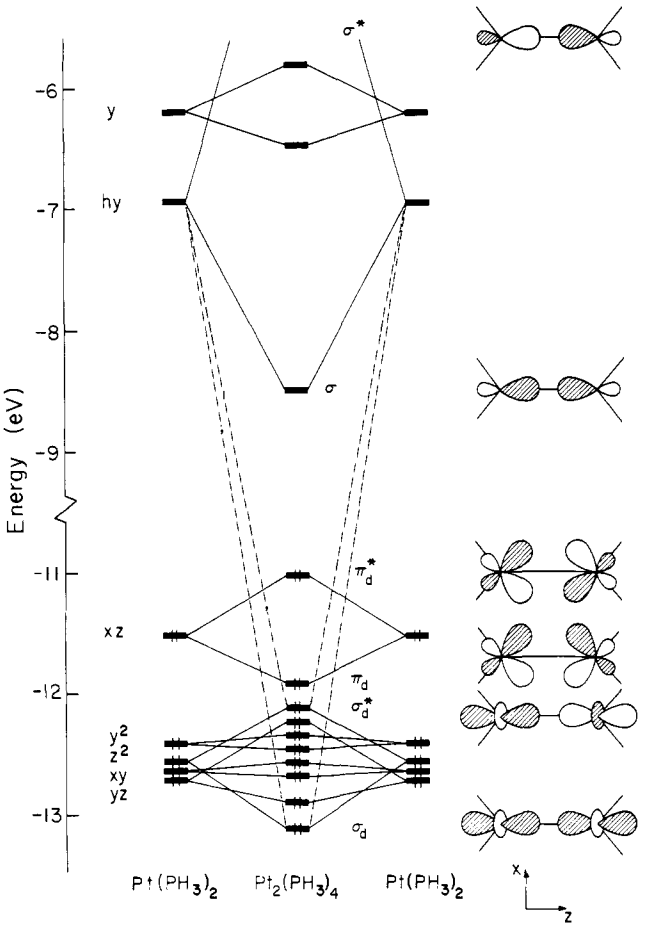
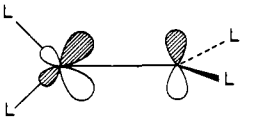


Figure 2. Interaction diagram for two $Pt(PH_3)_2$ fragments in a planar geometry. The important secondary mixings are shown by dashed lines.



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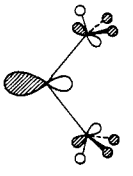
is no question that the mixing is allowed by symmetry. Unfortunately with our parametrization the interaction and the consequent contribution to stabilization of the perpendicular form is minute.

The crystal structure shows a near perpendicular orientation of the two P–Pt–P planes. Given the low barrier to internal rotation that we calculate for the model $Pt_2(PH_3)_4$ complex, we assume that the perpendicular geometry is set by the steric constraints of the bulky phosphine ligands. Indeed, Otsuka, Ibers, and co-workers[13] conclude that the only possible configuration which allows Pt–Pt contact is one where the rings are approximately perpendicular.

Is it possible to improve the Pt–Pt bonding in these molecules or to change their basic electronic configuration? One way to achieve better Pt–Pt bonding would be by stabilizing the *hy* orbital. If we look more carefully at this orbital for the $Pt(PH_3)_2$ fragment, **8**, we see that it is mixing in an in-phase



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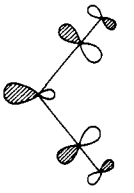

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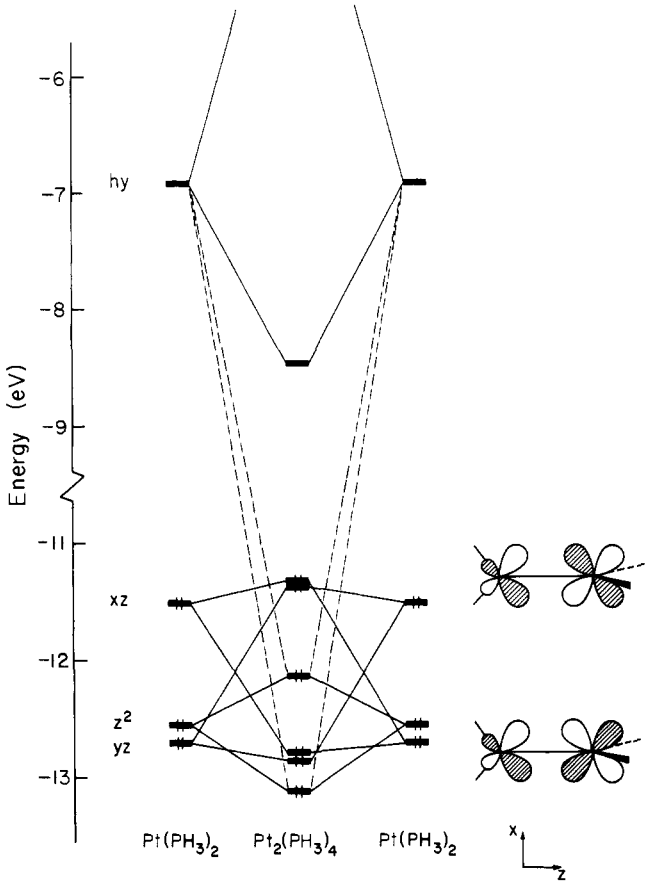


Figure 3. Interaction diagram for two $Pt(PH_3)_2$ fragments in a perpendicular geometry.

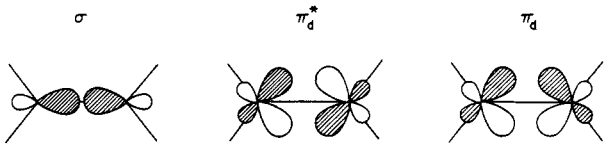
manner with one of the e antibonding orbitals of PH_3. A lowering in energy of *hy* may be achieved by substituting a good π acceptor, say CO, for PH_3. The resulting orbital is shown in **9**. Some further stabilization of the complex results. Incidentally, one should note that there are a number of well-characterized ML_2, M = Ni, Pd, Pt, molecules, all with bulky substituents.[24]

Were the *hy* and/or *xz* interaction greater, then one could attain the $(\sigma_d)^2(\sigma_d^*)^2(\pi_d)^2(\sigma)^2$ configuration, in which the σ level is below the π_d^* level. One would then expect a stronger metal-metal overlap, essentially a double bond, and a larger rotational barrier. This, as we have seen, does not happen in our calculations. We can simulate the possibility, however, by transferring two electrons from π_d^* to σ. A very large Pt-Pt overlap population of 0.826 results. The rotational barrier is 16 kcal/mol favoring the planar form. Were this the actual electronic configuration of the molecule, the steric effects would have to be substantial to overcome the electronic preference for a planar molecule.

The Bonding Capabilities of the Pt_2L_4 System

Pt_2L_4 is coordinatively unsaturated. Presumably the reactivity of the compound that exists[13] is suppressed by the bulky phosphine ligands and would be enhanced with smaller substituents. The Pt_2L_4 fragment is indeed a component of bigger molecules, and so we explore its bonding capabilities.

Interaction with a planar Pt_2L_4 will be controlled by three orbitals, in order of decreasing energy σ (**10**), π_d^* (**11**), and π_d (**12**). In the neutral fragments σ is the LUMO and π_d^* the HOMO, while in $Pt_2L_4^{2+}$ π_d^* is the LUMO and π_d the HOMO. The situation in $Pt_2L_4^{2+}$ is similar to the one in ethylene, with the difference that the π and π^* orbitals are not perpendicular to the plane of the molecule but lie in this plane.

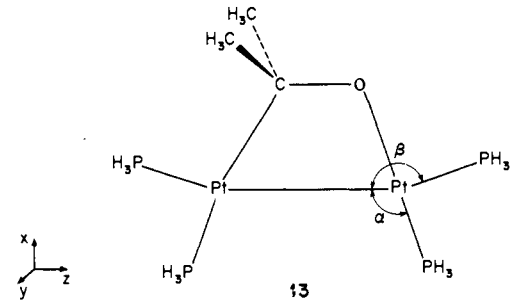


10 11 12

σ and π_d are of a_1 symmetry in the C_{2v} group (with the x axis as C_2); π_d^* is of b_1 symmetry. Therefore a good candidate for bonding to Pt_2L_4 would have a highest filled orbital of a_1 symmetry to interact with σ and/or a low-lying empty orbital of b_1 symmetry to interact with π_d^* or of a_1 symmetry to interact with π_d. This is, for instance, the case for $Fe(CO)_4$ and $(CF_3)_2CO$ in the molecules $Pt_2(1,5\text{-}C_8H_{12})_2(CF_3)_2CO$[11] and $Pt_2(CO)(P(OPh)_3)_3Fe(CO)_4$,[9] the electronic structure of which we shall discuss now in detail.

$Pt_2(1,5\text{-}C_8H_{12})_2(CF_3)_2CO$

As a model of this molecule, we took $Pt_2(PH_3)_4[(CH_3)_2CO]$ (**13**). We have already described the electronic structure of the



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$Pt_2(PH_3)_4$ fragment for local D_{2h} symmetry. Lowering the symmetry to C_{2v} by changing α and β, respectively, to 110 and 160° does not change drastically the pattern of the levels. The $(CH_3)_2CO$ fragment has π_y^* (**14**, a somewhat delocalized oxygen lone pair) and π_x^* (**15**), respectively, as HOMO and

14 15

LUMO. π_y^* is of a_2 pseudosymmetry and will interact with a δ^* orbital of $Pt_2(PH_3)_4$, but the interaction is of small magnitude because of a poor overlap. π_x^* is of b_1 pseudosymmetry, and has a good overlap and a good energy match with π_d^*. The interaction leads therefore to an important stabilization of the bonding combination as shown in Figure 4.

The $\pi_d^*(Pt_2L_4)$-π_x^* (acetone) interaction leads to a significant transfer of electrons from Pt_2L_4 to the acetone ligand. The lost metal fragment electrons come from an orbital that is Pt-Pt antibonding. The Pt-Pt bond should be significantly strengthened. This is reflected in the Pt-Pt overlap population, which increases from 0.142 in the $Pt_2(PH_3)_4$ fragment to 0.371 in the acetone complex. The observed Pt-Pt separation of 2.585 Å[11] is indeed short. The CO bond of the acetone also approaches a single bond value.

$Pt_2L_4Fe(CO)_4$ and Other Trinuclear Clusters

The known structure carries one CO and three $P(OPh)_3$ ligands.[9] We model it by **16**, $Pt_2(PH_3)_4Fe(CO)_4$. The orbitals of the $Fe(CO)_4$ fragment are well known.[20a,25] Let us focus our attention on the highest occupied one, **17**, which is of b_1 symmetry, and the lowest unoccupied one, **18**, of a_1 symmetry. **17** and **18** interact respectively with π_d^* and π_d as shown in Figure 5. The antibonding combination between a_1 (**18**) and π_d is stabilized by mixing with σ and consequently lies below π_d^*, which is destabilized through the interaction with b_1 (**17**).

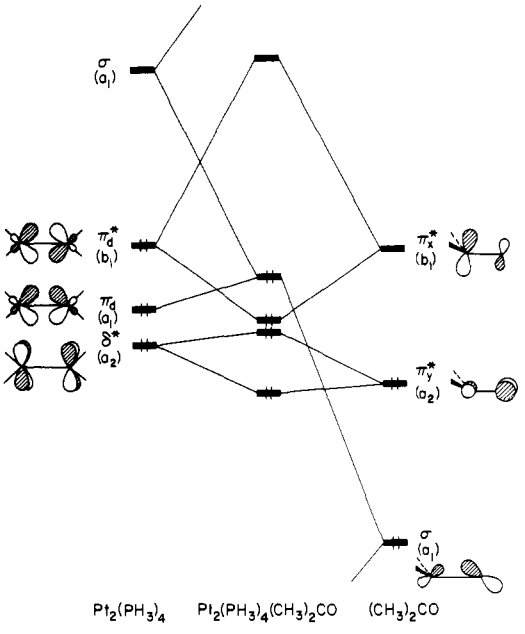
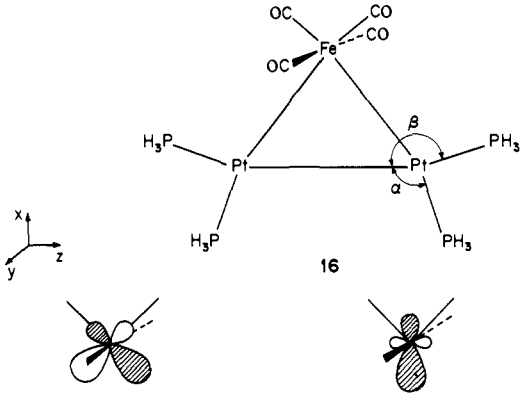


Figure 4. Interaction diagram for Pt_2P_4(acetone).



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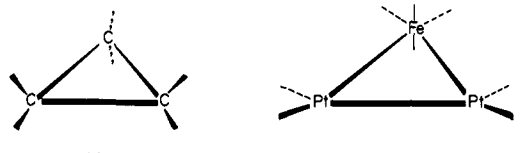
The strong $\pi_d^*(Pt_2L_4)$-$b_1(Fe(CO)_4)$ mixing once again depopulates the Pt-Pt antibonding π_d^* orbital and leads to an increase in the Pt-Pt overlap population, now 0.337. The observed Pt-Pt distance[9] of 2.63 Å is again shortened relative to Pt_2L_4.

One extreme view of the electron transfer out of the π_d^* orbital that we observe in the two complexes discussed is that two electrons have been shifted to the acetone or $Fe(CO)_4$ moiety, giving effectively a Pt(I)-Pt(I) bond. This is just a formalism, but is useful in the context of understanding the bond length changes and conformational preferences. For instance, if the system is no longer a d^{10}-d^{10} one, we would expect a substantial rotational barrier around the Pt-Pt bond. The calculations indeed give a 12.1 kcal/mol barrier. The π_d^*-b_1 interaction (Figure 5) is destroyed by this torsion.

To pursue the analogy with organic systems $Pt_2L_4Fe(CO)_4$ is similar to the cyclopropane dianion, $Fe(CO)_4$ playing the role of CH_2 and Pt_2L_4 the role of $C_2H_4^{2-}$. There is one structural difference, however, since the orbitals of b_1 symmetry are perpendicular to the C-H bonds in $C_2H_4^{2-}$ and CH_2, the H atoms are out of the plane of the carbons in $C_3H_6^{2-}$ (**19**),



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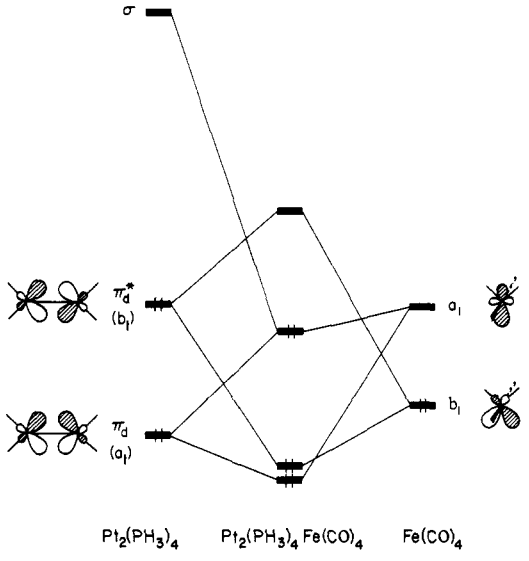
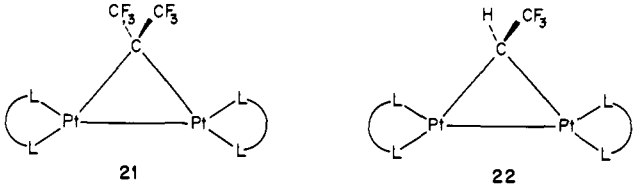


Figure 5. Interaction diagram (partial) for $Pt_2P_4Fe(CO)_4$.

whereas the phosphorus atoms and the two equatorial carbonyls of $Fe(CO)_4$ are in the plane of the molecule in $Pt_2L_4Fe(CO)_4$ (**20**). In this context it is interesting to note that the complexes $(Pt_2L_4)(C(CF_3)_2)$ and $(Pt_2L_4)(CHCF_3)$ have recently been obtained (L_2 = 1,5-C_8H_{12}).[26] The suggested structures, consistent with the ^{19}F NMR spectra, are shown in **21** and **22**. Here the bridging group is a carbene ligand with



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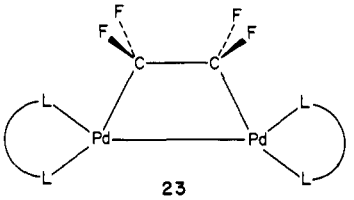
the carbene plane perpendicular to the Pt_2L_4 plane, consistent with our previous arguments.

Green, Stone, and co-workers[26] have also reported the formation of the complex $(Pd_2L_4)(C_2F_4)$ (L_2 = 1,5-C_8H_{12}). As in the case of $Pt_2L_4[(CF_3)_2CO]$, the interaction between π^* of the tetrafluoroethylene and π_d^* of Pd_2L_4 is setting the geometry of this complex as shown in **23**, with the C-F bonds out of the plane defined by the Pd and C atoms.



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Can one bridge the Pt-Pt bond of Pt_2L_4 by another PtL_2 group? There are two suggestions of such structures without bridging ligands,[3,27] but the structures were not well characterized.[28] This, of course, does not prevent a theoretical discussion of their potential geometries. Three possible structures are illustrated by **24, 25,** and **26.** The $Pt(PH_3)_2$ and $Pt_2(PH_3)_4$

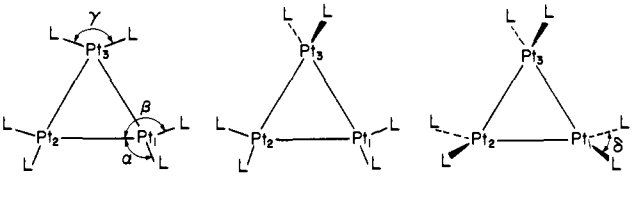

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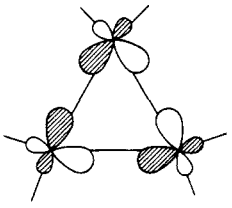
Table I. Energy of Formation Δ of $Pt_3(PH_3)_6$ (in eV) and Pt–Pt Bond Overlap Population

Geometry	Δ,[a] eV	Overlap population Pt_1–Pt_2	Overlap population Pt_1–Pt_3
24	+2.43	0.076	0.064
25	−0.11	0.124	0.136
26	−0.12	0.095	0.110

[a] $\Delta = E_{Pt_3(PH_3)_6} - [E_{Pt(PH_3)_2} + E_{Pt_2(PH_3)_4}]$. $\Delta < 0$ means stabilization.

fragments both lack low-lying orbitals which could match some of the highest occupied orbitals of the other fragment. For that reason we cannot expect a great stability of the $Pt_3(PH_3)_6$ system. Table I gives the energy of formation of the $Pt_3(PH_3)_6$ system from $Pt(PH_3)_2$ and $Pt_2(PH_3)_4$ and the Pt–Pt bond overlap population for the three structures.

From Table I it appears that *the only possible structures for a stable $Pt_3(PH_3)_6$ system are* **25** *and* **26.** That we do not have a stable structure for **24** is easy to understand. In **24** the two highest occupied orbitals of the two fragments [i.e., π_d* of $Pt_2(PH_3)_4$ and b_1 of $Pt(PH_3)_2$] overlap strongly as shown in **27.** This leads to a large four-electron destabilizing inter-



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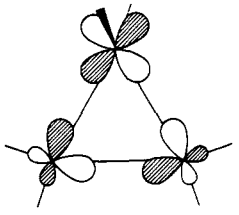

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action.[22] On the contrary, in **25** and **26** π_d* is not so strongly destabilized. In **25** π_d* interacts with the *yz* orbital of Figure 1 as shown in **28.** Since this *yz* orbital is low in energy, the destabilizing interaction is less important. Moreover, the antibonding combination of π_d* and *yz* is stabilized by the empty orbital *y* (**29**) of $Pt(PH_3)_2$. In **26** π_d* does not find any orbital

29

of $Pt(PH_3)_2$ of correct symmetry with which to interact, and consequently is not destabilized. As in **25,** the overall stabilization results from the interactions with the empty orbitals *y* of $Pt(PH_3)_2$ and σ (see Figure 2) of $Pt_2(PH_3)_4$.

From these calculations we cannot conclude that the Pt_3L_6 system exists in these triangular forms, since the stabilization energies obtained for **25** and **26** are rather small. But we can predict with some confidence that if such a system exists, then its geometry will probably be **25** or **26.**

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Appendix

The parameters used in the extended Hückel[29] calculations were taken from earlier work[30] and are listed in Table II. The modified Wolfsberg–Helmholz formula[31] was used throughout

Table II. Parameters Used in Extended Hückel Calculations

Orbital	H_{ii}, eV	ζ_1[a]	ζ_2[a]
Pt 6s	−9.077	2.554	
6p	−5.475	2.554	
5d	−12.59	6.013 (0.6334)	2.696 (0.5513)
Fe 4s	−9.10	1.9	
4p	−5.32	1.9	
3d	−12.6	5.35 (0.5505)	2.00 (0.6260)
P 3s	−18.6	1.75	
3p	−14.0	1.30	
C 2s	−21.4	1.625	
2p	−11.4	1.625	
O 2s	−32.3	2.275	
2p	−14.8	2.275	
H 1s	−13.6	1.3	

[a] ζ is the Slater exponent whose coefficient of the double ζ expansion is given in parentheses.

these calculations. All Pt–P and P–H distances were idealized at 2.30 and 1.42 Å, respectively. The Pt–Pt distance was set to 2.65 Å (unless otherwise specified) in $Pt_2(PH_3)_4$, $Pt_2(CO)_4$, and $Pt_3(PH_3)_6$, respectively, and to the experimental value of the related complex[9,11] in $Pt_2(PH_3)_4[(CH_3)_2CO]$ (2.585 Å) and in $Pt_2(PH_3)_4[Fe(CO)_4]$ (2.633 Å). In $Pt_2(PH_3)_4$-$[(CH_3)_2CO]$ the experimental geometry[11] was chosen for the Pt–C–O unit and the C–H bonds of the acetone fragment were set to 1.09 Å. α and β (defined in **13**) were chosen respectively as 110 and 160° for this system and for $Pt_2(PH_3)_4[Fe(CO)_4]$. In this latter complex the $Fe(CO)_4$ fragment had a C_{2v} symmetry with an equatorial angle C–F–C of 94°; Fe–C and C–O distances were set to 1.78 and 1.15 Å, respectively. The Fe–Pt distance was taken from the experimental work,[9] namely, 2.565 Å. In the $Pt_3(PH_3)_6$ systems α and β (see **24**) were set to 110 and 160°, respectively, for the geometries **24** and **25** (this results in a P–Pt–P angle of 90°). This P–Pt–P angle of 90° was kept for δ in the geometry **26.** The γ angle was set to 105° in all three systems.

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The Olefin Insertion Reaction

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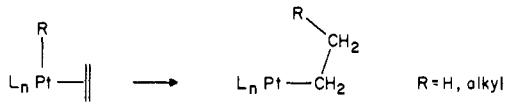
Abstract: A molecular orbital study of the insertion of ethylene into a Pt–H bond begins with an analysis of the interaction of a hydride with an ethylene in the absence of the metal. Identification of the crucial orbitals along a simplified reaction coordinate allows one to focus on how the metal atom 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.[1] The prototype case is the insertion of an olefin into Pt–H[2] or Pt–alkyl[3,4] bonds, illustrated schematically in **1**, but other



1

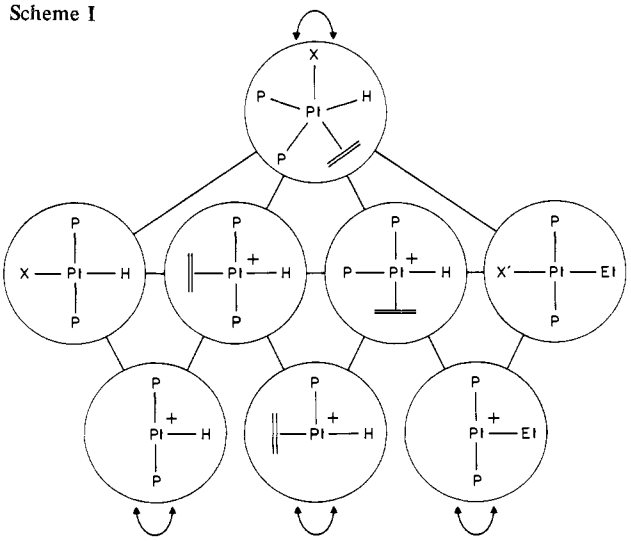
unsaturated reagents, such as acetylenes,[5-7] carbon monoxide,[4,8] isocyanide,[9,10] CO_2,[11] and CS_2,[12] can follow this course.

Similar processes occur in many analogous systems[13] and many aspects of pure and applied inorganic chemistry may depend on them: homogeneous hydrogenation of olefins and acetylenes;[14] the Wacker process;[15] hydroformylation reactions;[16] olefin isomerizations;[17] 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,[2e-h,3a,8] and also some theoretical analyses.[18-20] 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

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