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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The following molecular-orbital criteria for bond reforming and reductive elimination from organotransition-metal complexes have been found: 1. The existence of an occupied molecular orbital that is antibonding between the metal (M) site and reactants (H, CH ₃) and bonding between the reactants (H, CH ₃). 2. This orbital should be the highest or nearly highest occupied molecular orbital of the metal-reactant complex for the reaction to occur at low		

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temperature. The difference between the energy of this orbital and that of the highest occupied orbital, if nonzero, is a qualitative indication of the relative facility of the bond reforming activation energy

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MOLECULAR ORBITAL CRITERIA FOR REDUCTIVE
ELIMINATION FROM ORGANOTRANSITION-METAL COMPLEXES

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Bond formation by intramolecular reductive elimination has frequently been postulated as a crucial step in a variety of catalytic reactions involving organotransition-metal complexes. Examples of such reactions include the reforming of hydrocarbons¹ and the hydrogenation of alkenes.² However, little is known about the role of the metal catalyst in this process for either the homogeneous or heterogeneous case. For example, it is not understood why some reductive elimination reactions are fast and why certain metals are more effective than others in initiating these reactions. However, evidence is accumulating that indicates reductive elimination involving transition-metal complexes usually proceeds through a concerted mechanism. Moreover, the evidence suggests that these complexes display a general mechanistic preference for concerted reductive elimination as a primary mode of decomposition.³ In this article, we present molecular-orbital criteria for facile concerted reductive elimination from coordinatively unsaturated platinum complexes as a first step toward understanding catalytic bond formation. This molecular orbital theory will also attempt to qualitatively explain the fast reaction rates and low activation energies displayed in these catalytic reactions.

Calculations and Results

We have examined the square planar $\text{cis}-(\text{PPh}_3)_2\text{PtH}_2$ and $\text{cis}-(\text{PPh}_3)_2\text{PtH}(\text{CH}_3)$ complexes, since both have been reported to undergo facile intramolecular reductive elimination to yield $(\text{PPh}_3)\text{Pt}$ and H_2 ⁴ for the former complex and $(\text{PPh}_3)_2\text{Pt}$ and CH_4 ,² for the latter. Moreover, the coordinatively unsaturated complex $(\text{PPh}_3)_2\text{Pt}$ exhibits a chemical reactivity which can be compared with the catalytic activity of a chemisorption site on a platinum surface.^{5,6} Hence, such studies may be relevant not only to homogeneous but

also to heterogeneous catalysis.

The electronic structures of the L_2Pt , L_2PtH_2 , and $L_2PtH(CH_3)$ complexes, in which the triphenylphosphine ligands ($L = PPh_3$) have been modeled by electronically similar but simpler phosphine ligands ($L = PH_3$), have been calculated by the self-consistent-field X-alpha scattered wave (SCF-X α -SW) molecular orbital method.⁷ Similar SCF-X α -SW studies of $(PH_3)_2PtO_2$ and $(PH_3)_2PtC_2H_4$ have previously been reported by Norman⁸ and the results successfully used to explain the photoelectron spectra and homogeneous catalytic activity of these complexes. The resulting molecular orbital energy levels for the L_2Pt , L_2PtH_2 , and $L_2PtH(CH_3)$ complexes are displayed in Fig. 1(a), labeled according to the irreducible representations of the appropriate symmetry groups. Also shown, for comparison, are the SCF-X α -SW energy levels for the hydrogen molecule H_2 [at its equilibrium internuclear distance (1.2 Å)], the Pt atom and the $L = PH_3$ ligand. In a previous paper,⁶ we have described how the phosphine ligands interact with the metal atom to promote oxidative addition of H_2 and how these results can be used as a basis for understanding H_2 dissociation on platinum surfaces and supported catalysts. In the present communication, we apply a similar approach to the reductive elimination of H_2 from the L_2Pt complex.

In Fig. 1(a), the primary Pt-H σ -bonding and antibonding molecular orbitals, $1a_1$ and $4a_1$, respectively, bracket the nonbonding d and π -bonding ($2b_2$) levels, as would be predicted by molecular orbital theory.⁹ The proximity of the reactive L_2Pt levels to the hydrogen orbitals leads to considerable metal and hydrogen character in both the $1a_1$ and $4a_1$. Thus, for orbitals of a_1 symmetry, there is a net cancellation of bonding and antibonding interactions between the metal and hydrogen. This effective nonbonding interaction weakens the platinum-hydrogen bond and so provides a favorable condition for reductive

elimination. Other necessary conditions may be found by examining the "frontier molecular orbitals."

The importance of the frontier molecular orbitals, or HOMO and LUMO, for predicting chemical reactivity has been widely discussed.¹⁰ Though several models cite electron promotion as the mechanism for decomposition,¹¹ it now appears that excitation from a nonbonding level to the antibonding LUMO is not an important thermal process.³ Moreover, promotion from the HOMO to the LUMO (for both L_2PtH_2 and $L_2PtH(CH_3)$, $\Delta E_{LUMO-HOMO} = 0.2$ Rydbergs) requires far more energy than is needed to initiate the facile reductive elimination of H_2 or CH_4 . Almost all the square planar transition metal complexes are diamagnetic,³ therefore precluding the existence of the high-spin ground state¹² (one electron in the HOMO and one in the LUMO). Clearly, since the LUMO does not play a significant role in these facile reactions, the HOMO governs the mechanism for facile concerted reductive elimination.

The wave vector directions perpendicular to the surface play a privileged role in catalysis; incoming substituents are more likely to interact with d-orbitals pointing normal to the surface. Especially well suited is the high lying $s + d_{z^2}$ hybrid with its dumbbell lobe strongly pointed along the z direction.¹³ This substituent-metal d_{z^2} interaction is encountered in the HOMO of this complex.

The HOMO displays not only attraction and overlap between the σ_g and dumbbell moiety but also antibonding repulsion between the σ_g and the d_{z^2} torus. There results an exaggerated node between this dumbbell moiety and the rest of the metal orbital (see Fig. 2a). By attracting charge to the region between their centers, the hydrogens have amplified their mutual bonding interaction while simultaneously intensifying their repulsion with the torus. Unmistakably then, this molecular orbital reveals net bonding between the hydrogens

and antibonding between H_2 and the Pt. We see the key role of platinum as a catalyst is to act as a "bridging" agent. The substituents, attached to the metal as ligands, can bond together by using the metal d orbitals to route electrons into the required region of space.

It will be recalled that in concerted reductive elimination "bond-making accompanies bond-breaking" with no free radical intermediates.³ It is clear how our picture describes just such a situation, thus satisfying the above rule.

The electronic energy levels for $(PH_3)_2PtH(CH_3)$ are shown in Fig. 2(a). The only symmetry operations which leave this molecule invariant are the yz mirror plane and the identity. The resultant point group has two, one-dimensional irreducible representations: the symmetric one, which we shall call "a," and the antisymmetric one which we shall call "b." The d_{yz} and d_{z^2} orbitals form basis functions for "a," while d_{xz} , d_{xy} , and $d_{x^2-y^2}$ transform according to "b." Levels 1a and 2a reveal Pt-H bonding character which is offset by the strong Pt-H antibonding character displayed in the 5a and 8a (HOMO) orbitals. This counterbalancing interaction is also present between carbon and platinum: the 3a reveals bonding, while 8a displays C-Pt antibonding. The important cancellation effects evidenced here result in a nonbonding interaction with each of H and C with the Pt d_{z^2} , allowing the Pt-substituent bond to be labile. The 4a orbital, which displays Pt-H and Pt-C bonding character, is undiminished by a corresponding Pt d_{yz} antibonding orbital. This obviously lends a necessary stability to the $L_2PtH(CH_3)$ complex.

Again, examination of the HOMO should provide a clue to the reactivity of this complex. Belonging to the symmetric representation, the HOMO, 8a, displays the crucial geometry: bonding between CH_3 and H and antibonding

between CH_4 and Pt (note the node between the metal and CH_4 moiety). Once more, the CH_3 and H can bond by using the metal d orbitals to route electrons into the required region of space. This routing is accomplished by a net attraction for the "in-phase" portion of the d_{z^2} dumbbell which, due to the "out-of-phase" torus, also creates a nodal cone and strong repulsion between the newly formed bond and the rest of the metal d moiety. In this way charge is localized in the region between the two substituents and the bond with the metal can be broken.

The 8a level has greater CH_3 than H character, reflecting the greater proximity of the CH_3 radical level to the metal level so that the Pt- CH_3 interaction is stronger here than the Pt-H interaction. Hence we see that the d_{z^2} is tipped away from the z-axis and oriented toward the carbon (see Fig. 2).

Discussion

Our m.o. calculations have pointed out a unique and highly synergistic relationship in these transition-metal complexes. The electron density which contributes to the embryonic ligand-ligand σ bond is derived by overlap and bonding with a lobe of the metal d orbital. Yet, it is precisely this charge buildup in the ligand moiety that intensifies the repulsion between the ligands and the metal, until the HOMO is best described by saying that it is ligand-metal antibonding.

This interaction is central to catalytic bond formation and reductive elimination. We conclude that the necessary molecular orbital criteria for facile concerted reductive elimination are:

1. The presence of a HOMO which displays (a) significant substituent as well as metal character and (b) net bonding between the "leaving" substituents and antibonding between this moiety and the metal.

2. This HOMO will be of the totally symmetric representation since the symmetry of this orbital must be consistent with the existence of a σ -bond between the "leaving" substituents.
3. The sum of the metal- σ bonding and $M-\sigma^*$ antibonding orbitals is such as to yield a nonbonding interaction between the metal and the substituents. (The HOMO contributes to offset the $M-\sigma$ bonding interaction.)
4. The metal and reactive substituent levels should lie close in energy.

As the compatibility between the metal d and ligand levels increases, so also the ligand participation in the antibonding orbitals increases.¹⁴ Hence, Rule 4 insures that part (a) of Rule 1 is satisfied, the latter being a necessary condition since there should be sufficient metal charge to bind the ligands and sufficient ligand charge to make this catalytic behavior meaningful.

The low activation energy and fast reaction rates displayed in catalytic reductive elimination reactions can be understood in terms of the above criteria. The "transition state" and motion along the reaction coordinate can be viewed as the ligands moving closer together, pulled by the attractive potential between their centers, and moving away from the metal, repelled by the strong metal-ligand antibonding interaction. Due to the occupation of the HOMO described above, there is virtually no activation-energy barrier to this migration.

In addition, we can see that the high reactivity of transition metals is partly due to the geometry of the d orbitals. Not only can a migrating group find a suitable d-lobe (or combination of d-lobes) with which to bond, but also, since the adjacent d-lobe is of opposite phase to this bonding region, the antibonding repulsion of the lobe (or lobes) stimulates the

catalytic elimination process. This again accounts for the low activation energy for bond breakage. This model has the advantage of not having to invoke the thermal population of excited states to account for the high reactivity of these complexes.

Clearly, d^{10} systems will provide the best catalysts for reductive elimination since the probability of the occupancy of the orbital described in Rule 1 increases with the number of electrons in the d shell. But even among d^{10} systems there will be variance in the rate and facility of the reaction. Rule 4 also leads us to believe that an incompatibility in energies between the metal and substituent is a contributing factor to sluggish reactions. It is in this manner that transition-metals whose d levels lie closer in energy to the reactant levels are more effective than others in facilitating reductive elimination. For this reason, nickel is more reactive than platinum in initiating carbon-carbon bond formation by reductive elimination.¹⁵

Recent evidence shows that concerted elimination of certain R_2 substituents from $cis-L_2PtR_2$ exhibit a pronounced negative entropy of activation, suggestive of a conformationally restricted transition state.¹ A transition state displaying the molecular orbital characteristics described above would support these findings. The ligands are initially constrained to lie in the plane of the complex, localized by the orbital overlap in the yz plane (for our coordinate system). Here, we can see a driving force for the completion of the reaction: ligand-metal bond scission would obviously give the cleaved molecule, R_2 , more degrees of freedom (rotational, translational, etc.) resulting in an entropy increase for the entire system.

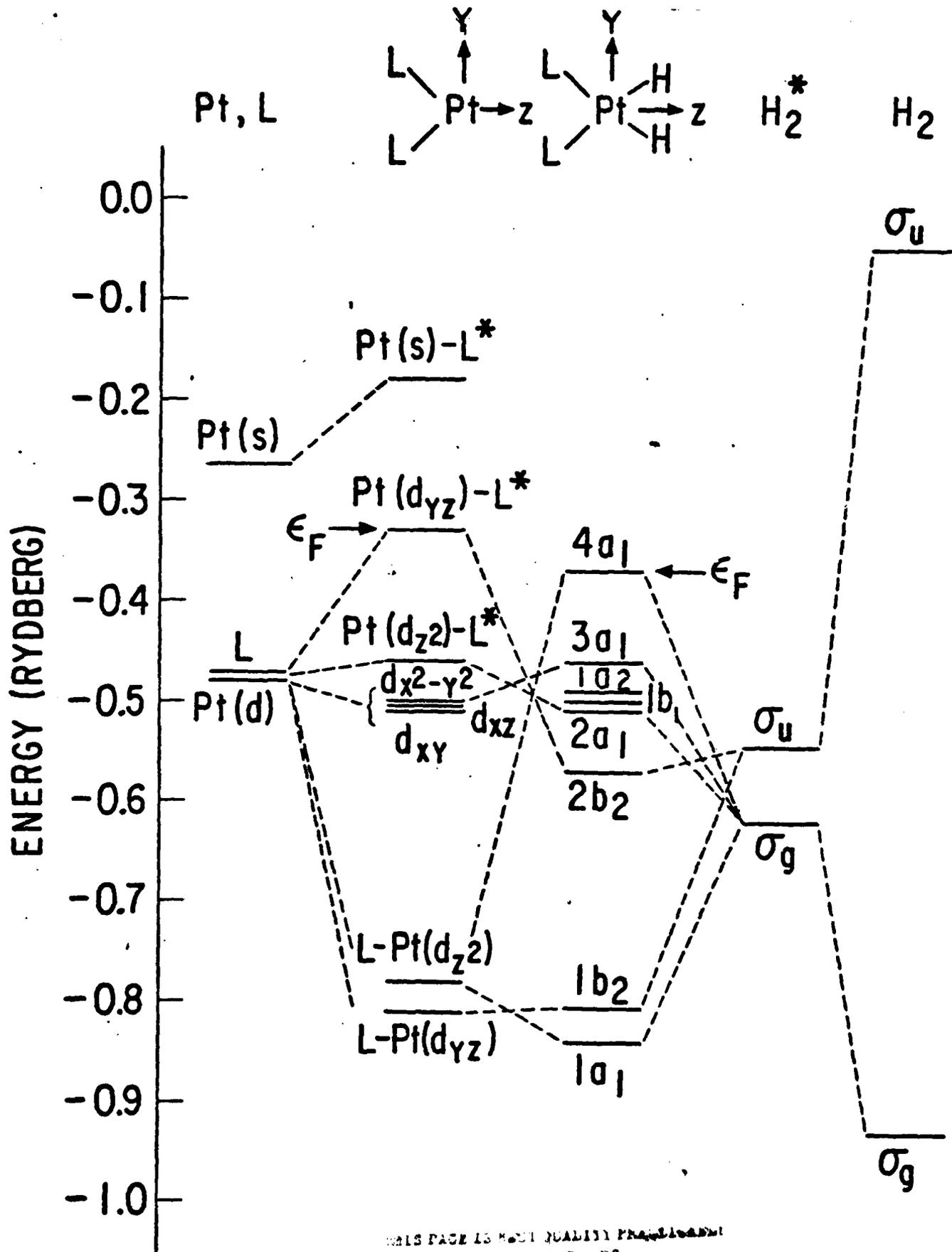
Additional energy for the bond scission may come from the vibrational modes of molecules or for surface reactions, phonons may provide this extra

energy. Specifically for heterogeneous catalysts, recent studies indicate that chemical energy released during the course of an exothermic reaction can be channeled into vibrationally and translationally excited product molecules, making them capable of escaping the reaction site.¹⁶

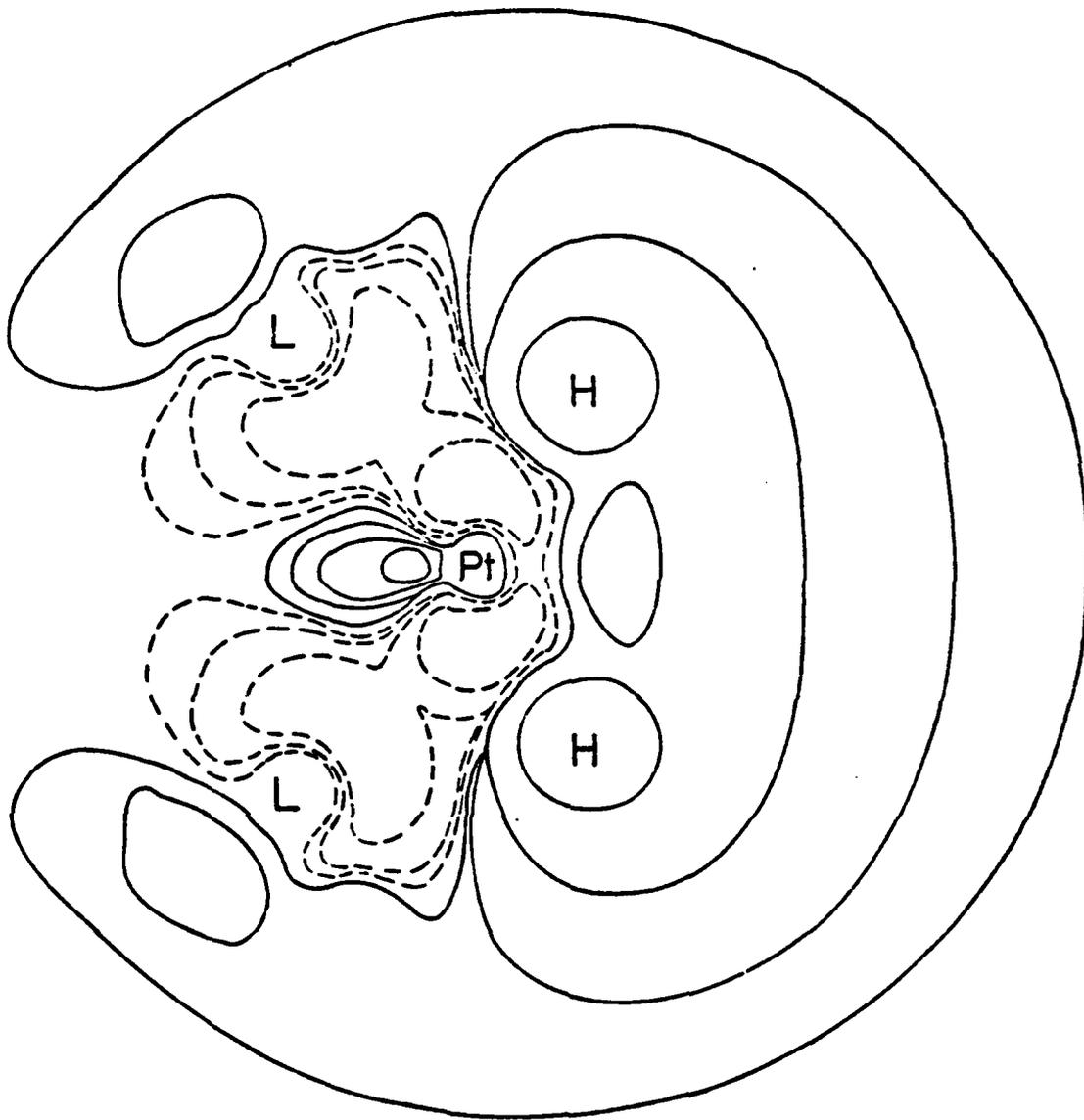
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