

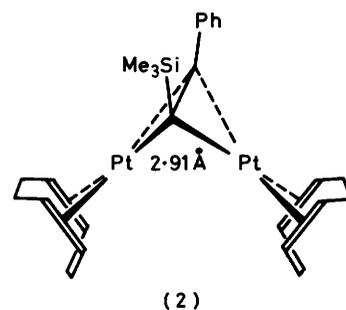
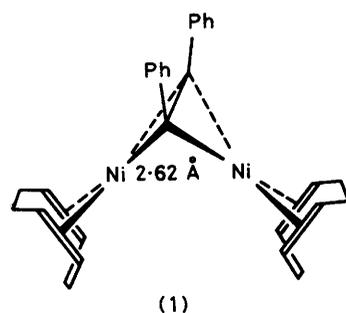
## The Transformations of Parallel and Perpendicular $L_2M(\mu\text{-acetylene})ML_2$ Complexes

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Acetylenes bond to two  $ML_2$  ( $M = \text{Pt}$  or  $\text{Ni}$ ) fragments in parallel and perpendicular geometries. The electronic structures of these complexes are analyzed using qualitative molecular-orbital theory. With each mode of acetylene co-ordination there is required a different co-ordination geometry at the metal. Various transformations between  $L_2M(\mu\text{-acetylene})ML_2$  isomers, known and unknown, are discussed and related by the isolobal analogy to common organic transits. Based upon the isolobal analogy and the calculated electronic structures, several as yet unknown complexes are proposed to be stable.

THE subject of this paper is the specific class of bridge-bonded acetylene (ac) complexes,  $L_2M(\text{ac})ML_2$ . This intricate system is a microcosm of polynuclear transition-metal cluster-acetylene bonding and dynamics, and illustrates nicely several general points made in our previous analysis of bridged acetylene complexes,  $L_nM(\text{ac})ML_n$ .<sup>1</sup>

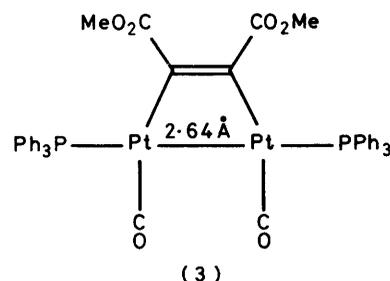
There are three complexes in the  $L_2M(\text{ac})ML_2$  class for which the crystal structures are known. Two which are related are shown in (1) and (2). Muetterties *et al.*<sup>2</sup> have characterized (1) as two  $d^{10}$   $L_2\text{Ni}$  groups each bonded to one of the two orthogonal  $\pi$  systems of ac. Stone



and co-workers<sup>3</sup> have given a similar description for the diplatinum species (2). In both cases the local metal environment is near planar and a 16-electron count seems appropriate. Both complexes are presumed to have little or no  $M-M$  bonding; an extended-Hückel calculation by Anderson<sup>4</sup> on a model for (1) showed a slight Ni-Ni antibonding interaction. In structures (1) and

(2) the C-C acetylene bond is perpendicular to the  $M-M$  vector, but this is not the only known orientation.

The structure of the  $L_2M(\text{ac})ML_2$  complex  $[\text{Pt}_2(\text{CO})_2(\text{PPh}_3)_2\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}]$  (3), established by Pierpont and



co-workers,<sup>5</sup> stands in stark contrast to (1) and (2). Complex (3) is nearly planar with the ac bonded parallel to the Pt-Pt vector. The local platinum environment could be termed square planar with the proposed Pt-Pt bond occupying one co-ordination site. This is consistent with the usual electron-count formalism of ac as  $\text{ac}^{2-}$  when parallel bonded.

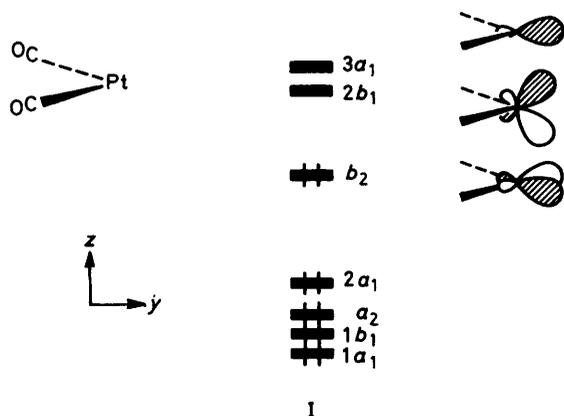
In this paper we examine theoretically the electronic requirements that enforce structures (1) [or (2)] and (3), the possible stability of alternative structures, and some of the pathways proposed for dynamic processes involving (2) and (3). Our theoretical method is the extended-Hückel approximation, coupled with symmetry arguments. Details of the calculations are provided in the Appendix.

### RESULTS AND DISCUSSION

*The Electronic Structure of  $L_2M(\text{ac})ML_2$  Complexes.*—The bonding relationships in structural types (1)–(3) are most easily derived using a fragment analysis. With this approach we artificially dissect the structures into  $ML_2$  and ac pieces and then assemble the electronic structure for the composite complex using the readily understandable molecular orbitals (m.o.s) of the constituent fragments.

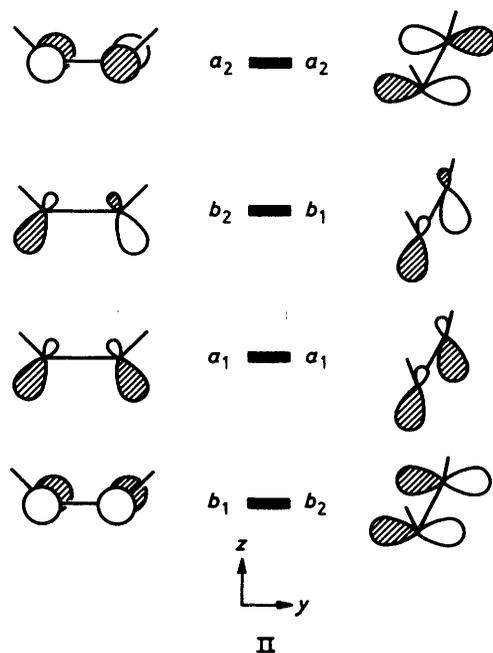
The complex  $[\text{Pt}_2(\text{CO})_4(\mu\text{-C}_2\text{H}_2)]$  is used as a model system for both (1) and (2). The appropriate  $ML_2$  fragment is  $\text{Pt}(\text{CO})_2$ , whose orbitals are presented sche-

matically in I. A detailed discussion of the  $ML_2$  m.o.s has been given before.<sup>6</sup> At low energy is a block of four  $d$  orbitals which are related to the similar block characteristic of a square-planar complex  $ML_4$ . Such an  $ML_4$  complex can be thought of as a parent to  $ML_2$ , and the two orbitals of primary concern to us,  $3a_1$  and  $b_2$ , can be viewed as in- and out-of-phase combinations of hybrids

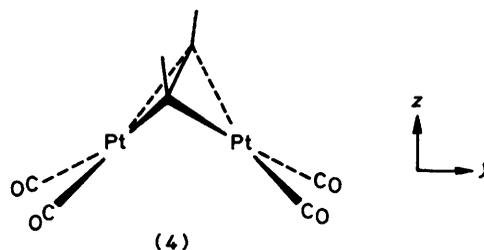


left behind by removing two ligands from  $ML_4$ . Orbital  $b_2$  is a  $pd$  hybrid ( $px + xy$ ) with lobes protruding toward the vacant '  $ML_4$  ' sites. Orbital  $3a_1$  is mainly a metal  $sp$  hybrid with some  $d$ -orbital character. The  $b_1$  orbital that lies in energy between  $b_2$  and  $3a_1$  is concentrated on the CO ligands and will not be of importance until later in our analysis.

Co-ordinated acetylenes, whether perpendicular or parallel, are invariably *cis* bent at the carbons. We prepare an acetylene for bonding in our complexes by taking an HCC angle of  $130^\circ$ . The resulting orbital pattern is shown in II. Bending breaks the ac  $\pi$  and



$\pi^*$  degeneracies, with some consequent rehybridization of one acetylene  $\pi$  system. When we examine parallel and perpendicular alternatives we will opt for the (arbitrary) choice of rotating the acetylene rather than the  $L_2MML_2$  framework. For this reason some of the acetylene orbitals change symmetry designation.



In Figure 1 is given an interaction diagram for a  $(CO)_2PtPt(CO)_2$  fragment with neutral *cis* bent ac to give (4). The orbital pattern on the left for  $(CO)_2PtPt(CO)_2$  consists of essentially the in-phase and out-of-phase combinations of the orbitals in I brought together in the geometry appropriate to (4). The lower eight-orbital

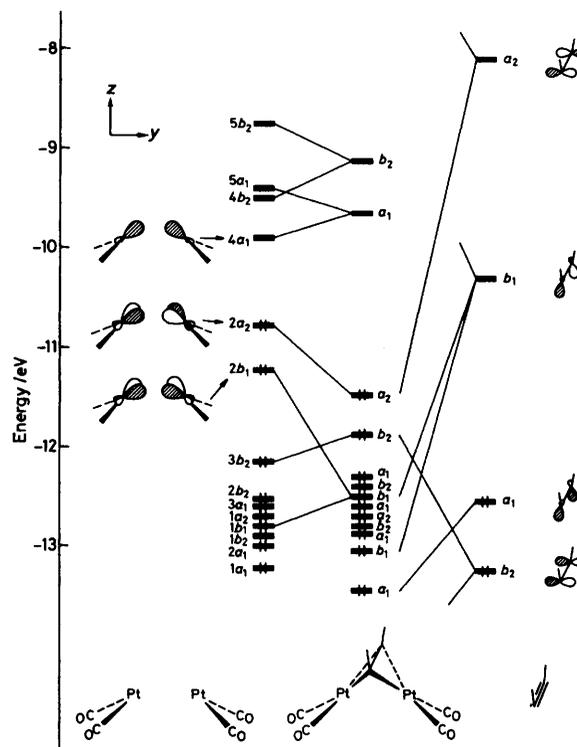
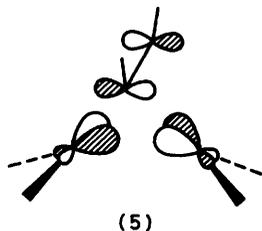


FIGURE 1 The interaction of  $(CO)_2PtPt(CO)_2$  with  $C_2H_2$  in the perpendicular geometry. The Pt-Pt distance is 2.82 Å

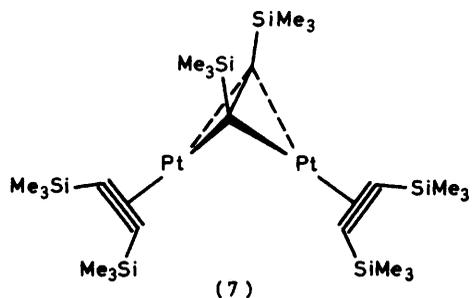
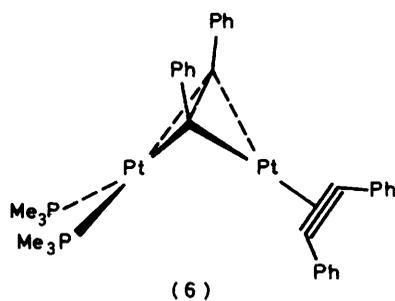
block is derived from  $1a_1$  through  $2a_1$  in I and the upper filled m.o.s,  $2b_1$  and  $2a_2$ , come from  $b_2$ . The empty orbitals above  $2a_2$  are combinations of  $2b_1$  and  $3a_1$  of  $Pt(CO)_2$ .

In the perpendicular orientation, the ac donor orbitals transform as  $a_1$  and  $b_2$ ,<sup>1</sup> see II. They interact with the

empty  $a_1$  and  $b_2$  acceptor orbitals of the  $Pt_2$  fragment lying above  $2a_2$ . The acceptor orbitals of ac,  $b_1$  and  $a_2$ , mix strongly with the filled  $2b_1$  and  $2a_2$ . This 'back-bonding' interaction is significant, and results in the partial occupation of both ac orbitals. The bonding mixing of  $2a_2$ - $a_2(ac)$  is the highest occupied molecular orbital (h.o.m.o.) for the model complex, (5).



Electron counting in the usual way leads one to write down either no bond, or perhaps two, for structures (1) and (2). As we mentioned earlier, Anderson<sup>4</sup> found no bonding between the Ni atoms in a model of (1). For our model system (4) we find a slight bonding interaction between the Pt atoms; the Pt-Pt overlap population is +0.0350. When we replace the CO terminal ligands with hydrides, a model for phosphines, the M-M bonding

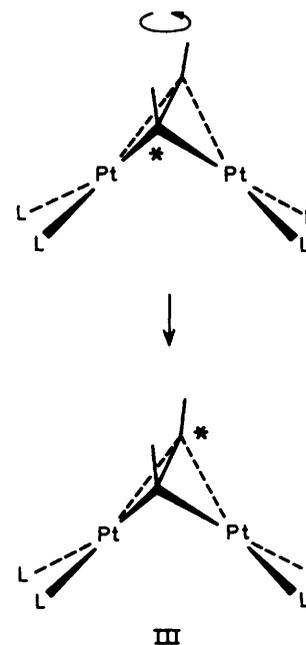


is lessened but the overlap population is still positive. The slight bonding between the two  $d^{10}$  M centres is not unusual.<sup>7</sup>

The interesting complexes made by Stone and co-workers,<sup>3,8</sup> (6) and (7), are of course related to (1) and (2). The molecular-orbital schemes for model complexes of (6) and (7),  $[Pt_2H_2(C_2H_2)(\mu-C_2H_2)]^{2-}$  and  $[Pt_2(C_2H_2)_2(\mu-C_2H_2)]$ , respectively, were similar to that for (4) in Figure 1. However, there are understandable differences in metal-acetylene bonding which lead to a greater

$C_{ac}-C_{ac}$  bond strength. The calculated  $C_{ac}-C_{ac}$  overlap populations reflect this: for (4) the calculated value is 1.2137 while for our models of (6) and (7) they are 1.2772 and 1.3257 respectively. These numbers are different enough to expect a shortening of the  $C_{ac}-C_{ac}$  distances in real complexes as the usual terminal ligands are substituted by acetylenes. The bond-length differences will be small, however, and changes in ac substitution could mask the effect.

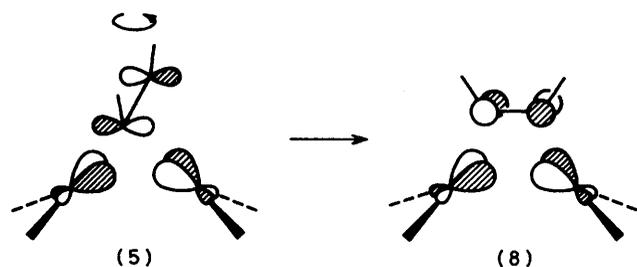
Before proceeding further we examine some of the dynamic processes proposed for (2) by Stone and co-workers.<sup>3</sup> These authors have observed in the n.m.r. for (2) a dynamic process formally equivalent to rotation of ac above the Pt-Pt vector, III. A rotation of the cyclo-octadiene groups is specifically excluded.



Using the  $[Pt_2(CO)_4(\mu-C_2H_2)]$  model system we tried a simple rotation of the ac group as in III. We kept the  $Pt_2(CO)_4$  fragment rigid and the Pt- $C_{ac}$  distance constant at 2.1 Å for the idealized motion. The barrier calculated is large, over 2 eV.\* Most of the barrier is traceable to the h.o.m.o. of the complex, drawn in (5). As the ac is rotated, the ac-Pt<sub>2</sub> bonding is lost and this orbital is destabilized. At the midpoint of the rotation one has a parallel acetylene geometry, a type of complex that we have analyzed elsewhere.<sup>1</sup> The corresponding  $a_2$  orbital in the parallel geometry, (8), is ac-Pt<sub>2</sub> antibonding; the destabilization of the h.o.m.o. could be thought of as an attempted correlation of (5) with (8).

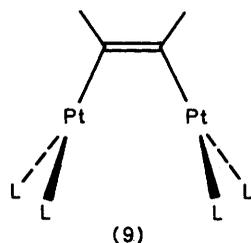
Although the large calculated barrier would seem to preclude a simple rotation of ac, we tend to be cautious. It turns out that geometric distortions of the half-way rotated structure, (9), those that would add more degrees of freedom to the simple rotation described here, are

\* Throughout this paper: 1 eV  $\approx$  1.60  $\times$  10<sup>-19</sup> J.

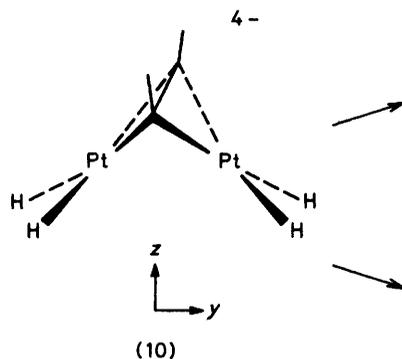


possibly available to lower the barrier. We discuss this in more detail later.

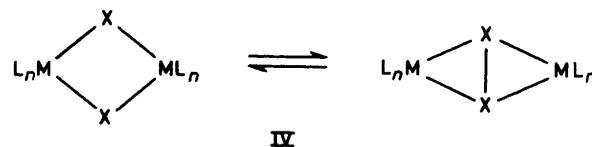
Another mechanism considered in the literature<sup>3</sup> suggests some sort of planar intermediate with or without breaking the acetylene C-C bond. Using the simple model system  $[\text{Pt}_2\text{H}_4(\text{C}_2\text{H}_2)]^{4-}$  we calculated two



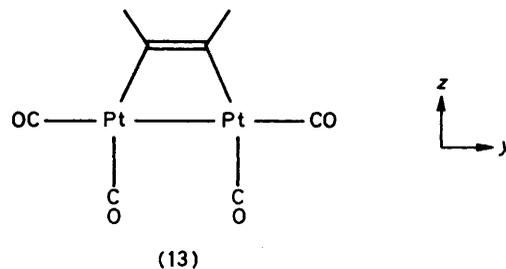
similar pathways involving a planar intermediate. One motion kept the  $\text{C}_{\text{ac}}-\text{C}_{\text{ac}}$  distance fixed at 1.32 Å,  $(10) \rightarrow (11)$ , and the other allowed the  $\text{C}_{\text{ac}}-\text{C}_{\text{ac}}$  distance to open,  $(10) \rightarrow (12)$ . The latter intermediate has  $\text{Pt}-\text{C}_{\text{ac}}-\text{Pt}$  and  $\text{C}_{\text{ac}}-\text{C}_{\text{ac}}-\text{Pt}$  angles of  $90^\circ$ .



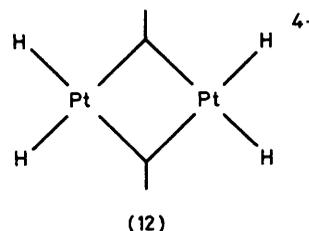
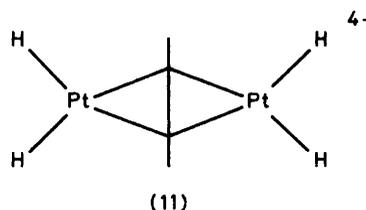
when the hydride model ligands are replaced by carbonyls. The origin of this substituent effect is not yet understood by us, and this makes us uncertain about championing the bis(carbyne) pathway,  $(10) \rightleftharpoons (12)$ ,



for effective acetylene rotation. However, this general problem, binuclear cleavage or coupling, IV, is obviously an interesting and important one. Just as we have recently analyzed the corresponding mononuclear problem,<sup>9</sup> we intend to solve this one.

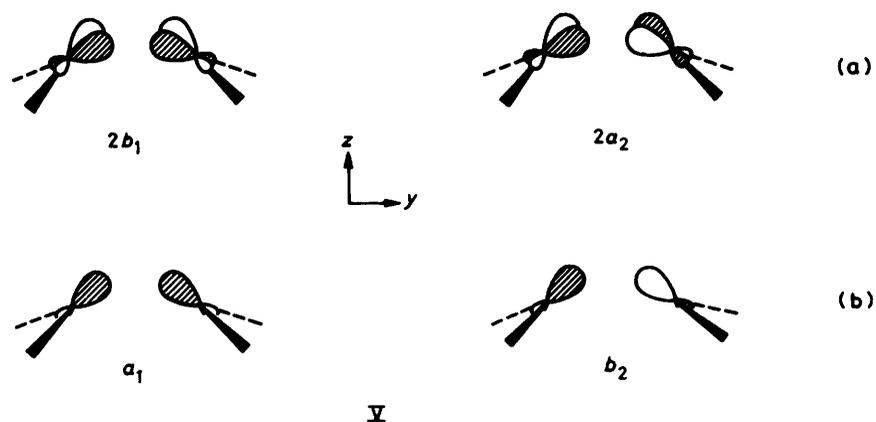


We take up now the other known  $\text{L}_2\text{M}(\text{ac})\text{ML}_2$  structure (3) using the  $[\text{Pt}_2(\text{CO})_4(\mu-\text{C}_2\text{H}_2)]$  model system, (13). As we discussed in relation to Figure 1, the important m.o.s of the  $\text{L}_2\text{MML}_2$  fragment for bonding to ac for



The calculated barrier for the process involving intermediate (11) was 1.67 eV and for (12) 0.52 eV. In each case (11) and (12) were at the top of the energy hill. The bis(carbyne) complex (12), however, is 1.2 eV above (10)

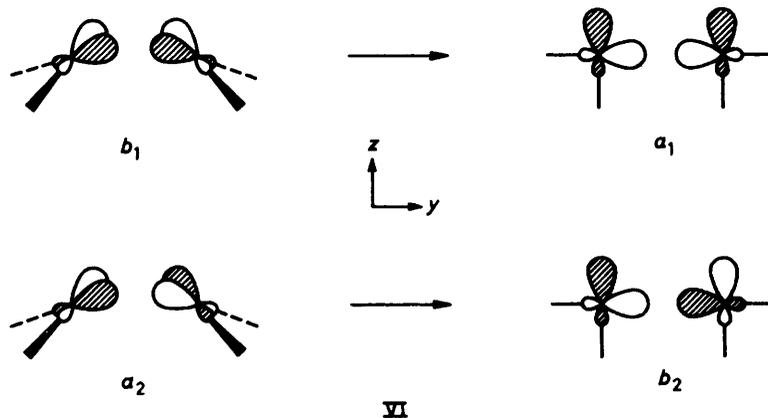
both structure types (1) and (2) are  $2b_1$  and  $2a_2$ ,  $V(a)$ , and acceptor orbitals lying above, which we represent as  $a_1$  and  $b_2$  in  $V(b)$ . These four orbitals will also be of primary importance to the bonding of ac for (13).



For the common co-ordinate system chosen in (4), (13), and V, it is evident that the  $(\text{CO})_2\text{PtPt}(\text{CO})_2$  fragments are related by a twist of the  $\text{Pt}(\text{CO})_2$  units. Turning the  $\text{Pt}(\text{CO})_2$  pieces to the correct orientation for (13) does not appreciably change the shape and direction of  $a_1$  and  $b_2$ , V(b). However,  $2b_1$  and  $2a_2$  are very much affected. In the arbitrary way we have chosen to turn the  $\text{ML}_2$  units in VI,  $2b_1$  becomes an orbital of  $a_1$  symmetry and

remnant  $b_2$  is with  $3b_2$ . Acetylene  $a_1$  mixes both with  $3a_1$  and to a lesser extent with  $a_1$  acceptor orbitals above. The antibonding combination between  $3a_1$  and ac  $a_1$ , stabilized by metal  $p$  mixing, is the h.o.m.o. for the complex. The h.o.m.o., shown schematically in (14), is strongly Pt-Pt bonding and contributes to an overall Pt-Pt overlap population of +0.3060.

Although we used a neutral ac plus neutral diplatinum



$2a_2$  becomes  $b_2$ . The orbitals are still shaped and directed nicely for interaction with the ac moiety, but it is obvious they must interact in a very different manner. This is brought out more clearly in the interaction diagram of  $(\text{CO})_2\text{PtPt}(\text{CO})_2$  with  $\text{C}_2\text{H}_2$  in Figure 2. At the left-hand side of Figure 2 are the diplatinum fragment m.o.s. Above the filled eight-orbital  $d$  block are the filled orbitals  $3a_1$  and  $3b_2$  (VI). Still further up in energy lie acceptor orbitals, the most important of which are those derived from  $a_1$  and  $b_2$  in V(b). The ac orbitals are on the right-hand side of the Figure. In the parallel geometry, the donor orbitals are labelled  $b_1$  and  $a_1$  and the acceptor orbitals are labelled  $b_2$  and  $a_2$ . The  $b$  symmetry orbitals of the acetylene switch labels, *i.e.*  $b_1$  and  $b_2$ , are interchanged, as the acetylene rotates from a perpendicular orientation. The reader is referred to diagram II in this context.

In the parallel geometry the primary bonding of an acetylene is through  $\sigma$  symmetry orbitals,  $a_1$  and  $b_2$ .<sup>1</sup> Indeed in Figure 2 the main interaction of the ac  $\pi^*$

fragment construction in Figure 2, the m.o. picture that emerges agrees with the natural description of (13) [structure (3)] as two 'square-planar'  $d^9$  Pt centres. Of the lower 11 orbitals shown in Figure 2 for the molecule, eight are mainly metal  $d$ . These eight orbitals can loosely be described as the symmetric and antisymmetric combinations of the lower four  $d$  orbitals of a square-planar complex. As (14) illustrates, the  $a_1$  h.o.m.o. can be identified, again approximately, as the in-phase combination derived from the orbital that at each centre points directly at the ligands in a square-planar complex, (15).

The description above for (13) brings to mind the  $d^9-d^9$   $\text{M}_2\text{L}_8$  complexes, such as  $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$  [dppm = bis-(diphenylphosphino)methane], (16).<sup>10</sup> The M-M bonds in (16) and some related complexes have been shown to have remarkable reactivity toward small ligands. The added ligand normally bridges the metal centres to form 'A-frame' complexes.<sup>11</sup> It is thus interesting that some complexes related to (3) undergo attack by a proton to form  $\text{Pt}(\mu\text{-H})\text{Pt}$  cationic species.<sup>12</sup> One wonders if the

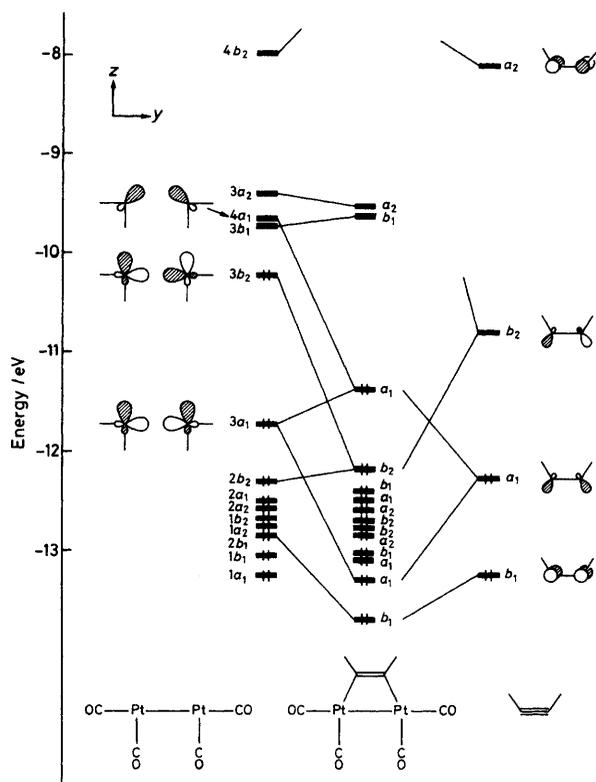
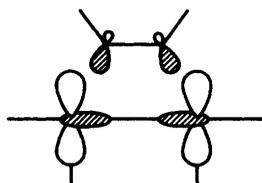


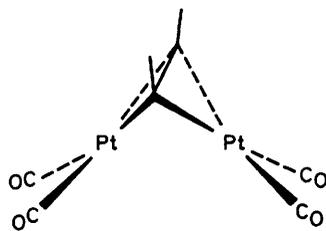
FIGURE 2 Neutral  $C_2H_2$  interacting with planar  $(CO)_2PtPt(CO)_2$ . Here, it was assumed that  $Pt-Pt = 2.64 \text{ \AA}$  and angles  $Pt-Pt-CO = 93^\circ$  and  $CO-Pt-CO = 90^\circ$

structures of these complexes are similar to that of the known molecule (17),<sup>11a</sup> and if other small molecules might similarly add to the  $\mu$ -ac complex.

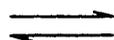


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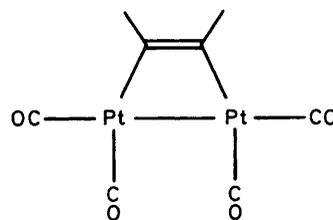
**Interconversion of  $L_2M(ac)ML_2$  Structural Types.**— Given there are available for the  $L_2M(ac)ML_2$  class of ac complexes two distinct structural types, one wonders about the possibility of some low-energy pathway for interconversion. A similar question arose in our pre-



(4)

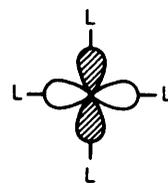


VII

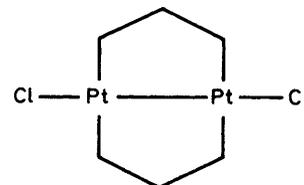


(13)

vious analysis of  $L_3M(ac)ML_3$  complexes.<sup>1</sup> There, when we took into account the desired change in metal coordination geometry that accompanied acetylene rotation, we found that the simple transit between the stable extremes was a symmetry-forbidden reaction. We proceed in a similar way, examining several ostensibly



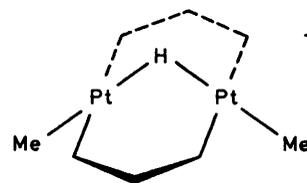
(15)



(16)

simple pathways for the model process shown in VII. It is when we consider such an isomerization as VII that the special relationship that exists between  $d^{10} ML_2$  and organic  $CH_2$  becomes valuable.

It has been pointed out before that there exists between the frontier orbitals of  $CH_2$  and  $d^{10} ML_2$  an 'islobal analogy': the frontier orbitals of  $CH_2$  and  $d^{10} ML_2$  are of similar shape, direction, and energy.<sup>13</sup> This is

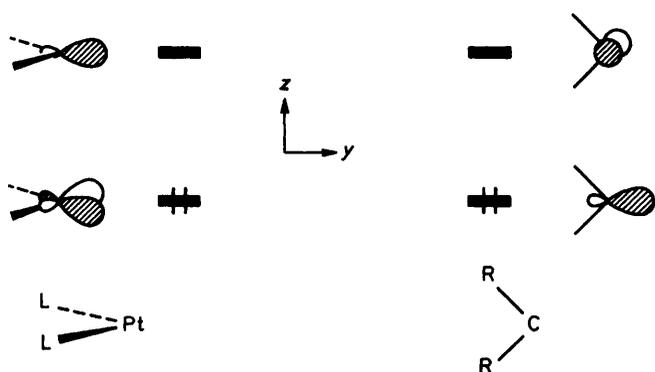


(17)

made clear in VIII where the two most important orbitals of the  $d^{10} Pt(CO)_2$  fragment and the  $\sigma$  and  $p_z$  orbital of  $CH_2$  are compared. Note the important orientational difference, however.

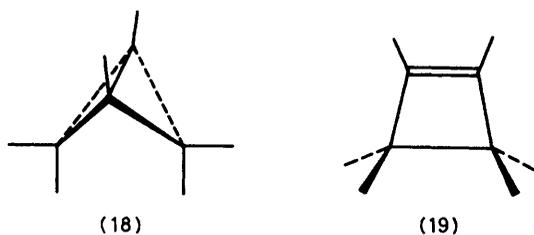
Using the islobal analogy, we can identify structures (1) and (2) as the inorganic structural analogues of organic bicyclobutane, (18). Similarly, structure (3) is the inorganic analogue of organic cyclobutene, (19). Thus, the process shown in VII is the inorganic counterpart of the bicyclobutane  $\rightleftharpoons$  cyclobutene isomerization, IX. Concerted, the organic isomerization as written in IX(a) is symmetry forbidden, in IX(b) allowed.<sup>14</sup>

The transits shown in X, where we simultaneously rotate the ac and twist the  $Pt(CO)_2$  units, represent

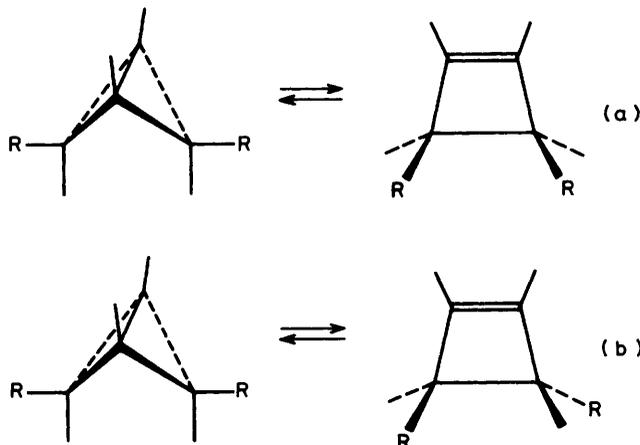


VIII

idealized pathways chosen for the isomerization VII. We have used the organic processes as a guide and so X(a) is identified with IX(a) and X(b) and X(c) with IX(b). The numbers given are the extended-Hückel (EH) calculated barriers.



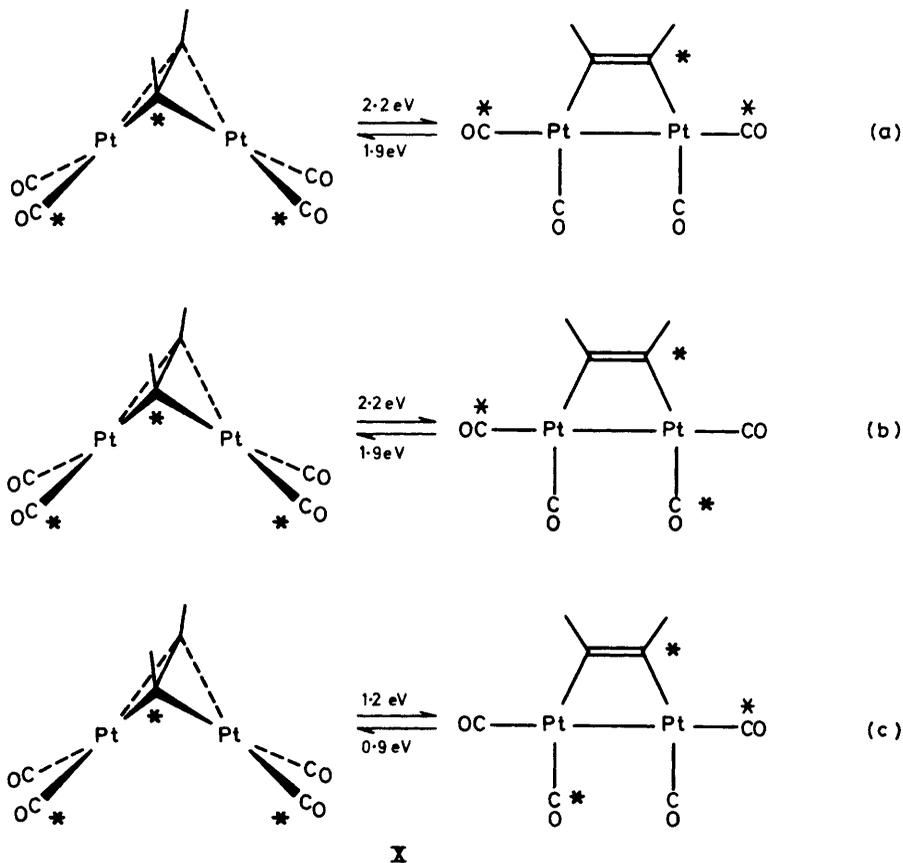
For transit X(a), there is an attempted correlation between the h.o.m.o. of (4) and the unoccupied  $\sigma^*$  orbital of (13), the antibonding counterpart to (14), that produces the large barrier. We schematically illustrate this



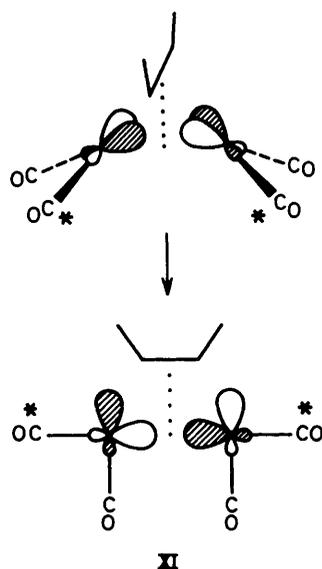
IX

in XI. This correlation is formally equivalent to the orbital correlation that makes IX(a) forbidden.

If one adheres to the isolobal analogy, X(b) and X(c) should be allowed and, perhaps, have low-energy barriers. Transit X(c) does have a substantially lower barrier

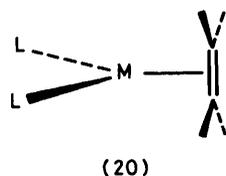


XI



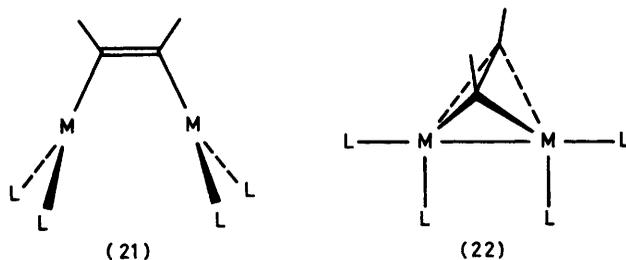
than X(a), but X(b) requires the same energy as X(a) (accidentally!).

The larger barrier calculated for X(b) is due to the local platinum environment. The twist of the  $\text{Pt}(\text{CO})_2$  unit and simultaneous rotation of ac results in a co-ordination



environment about Pt not unlike the 'wrong' orientation of an olefin in  $d^{10} \text{L}_2\text{M}(\text{olefin})$ , (20). This is contrasted with transit X(c) where the local environment about the Pt remains near 'planar'.

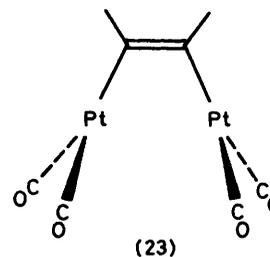
Although X(a)—X(c) all demand large energies, X(c) does require the least amongst the three idealized movements. It is difficult to say whether a more detailed



surface, allowing a few more degrees of freedom, would lower any or all of the calculated energies. However, we do expect any concerted isomerization equivalent to VII to occur with the stereochemical consequences equivalent to X(c).

$\text{L}_2\text{M}(\text{ac})\text{ML}_2$  Structural Alternatives.—We have shown that for the known  $\text{L}_2\text{M}(\text{ac})\text{ML}_2$  structures, (1) or (2) and (3), the orientation of ac is dependent upon the geometry

of the  $\text{L}_2\text{MML}_2$  fragment. A fundamental question we have not yet considered is why the obvious alternative structures, (21) and (22), are not known. The orbitals of the  $\text{L}_2\text{MML}_2$  fragment in hand, it is an easy matter to look at the electronic structures of (21) and (22) and decide what electronic problems, if any, there are with either or both.



In Figure 3 is shown the interaction diagram for neutral  $\text{C}_2\text{H}_2$  with  $(\text{CO})_2\text{PtPt}(\text{CO})_2$  to give (23). We choose for (23) a geometry where  $\text{CO-Pt-CO} = 90^\circ$  and the  $\text{C}_2\text{H}_2$  angles are  $120^\circ$  (Pt-Pt 3.42 Å). The diplatinum fragment m.o.s on the left in Figure 3 are just those in Figure 1 except for the longer Pt-Pt distance.

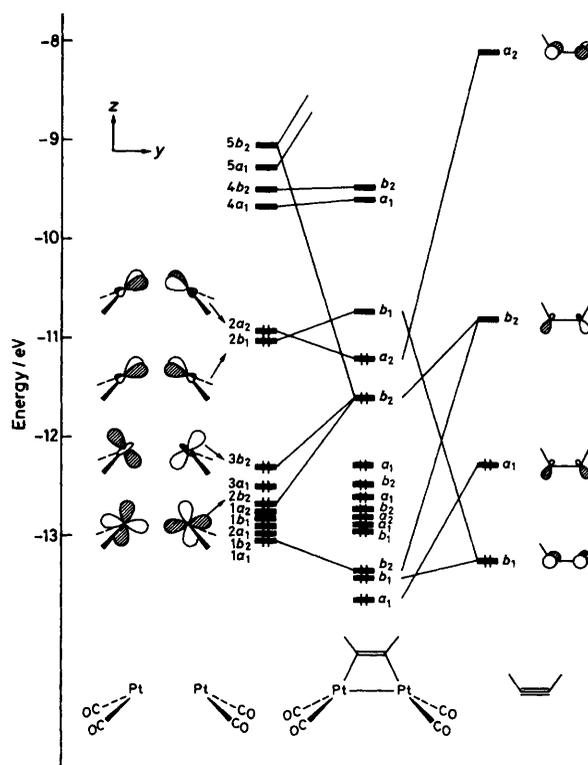
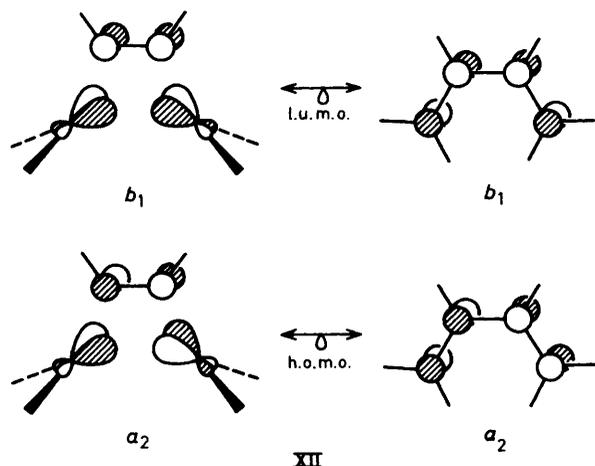


FIGURE 3 Interaction diagram of  $(\text{CO})_2\text{PtPt}(\text{CO})_2$  with neutral  $\text{C}_2\text{H}_2$  to form (23)

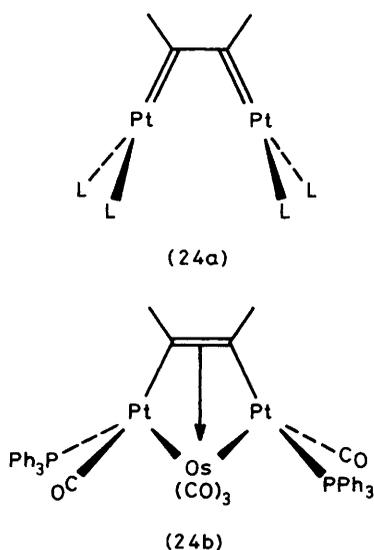
We discussed for Figure 1 the importance of the acceptor orbitals of neutral ac ( $\pi^*$  remnants) for stabilizing the filled  $2a_2$  and  $2b_1$  orbitals of  $(\text{CO})_2\text{PtPt}(\text{CO})_2$ . In Figure 3, the ac  $\pi^* a_2$  interacts very little with  $2a_2$  because of poor overlap.<sup>1</sup> The other  $\pi^*$  orbital,  $b_2$ , cannot

interact with  $2b_1$  because it is no longer of the same symmetry. Acetylene  $b_2$  mixes instead with two lower filled orbitals,  $2b_2$  and  $3b_2$ , and a higher-lying empty  $b_2$  orbital. The filled  $2b_1$  fragment m.o. of  $(\text{CO})_2\text{PtPt}(\text{CO})_2$  finds a symmetry match with the filled  $\pi b_1$  orbital of ac.

Structure (23) lies greater than 1.5 eV in energy above structure (4), our model for the known (1) and (2). This is due primarily to the poor overlap of  $a_2(\text{ac})$  with  $2a_2$  and, more importantly, to the loss of the stabilizing  $\pi^*(\text{ac})-2b_1$  interaction.

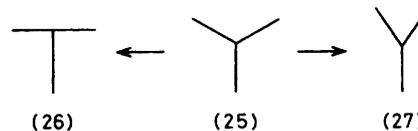


The m.o. scheme for (23) can be simply viewed using the isolobal analogy between  $\text{CH}_2$  and  $d^{10}\text{ML}_2$  discussed earlier (VIII). Replacing the  $\text{Pt}(\text{CO})_2$  by  $\text{CH}_2$  in (23), we can identify it as the inorganic analogue of organic *cis*-butadiene. The energy-level scheme given in Figure 3 is in agreement with this identification; the h.o.m.o. and l.u.m.o. (lowest unoccupied molecular orbital) of (23) are clearly related to the h.o.m.o. and l.u.m.o. of butadiene, XII. Also consistent with the butadiene analogy, the  $\text{C}_{\text{ac}}-\text{C}_{\text{ac}}$  overlap population for (23) is 1.2351 while for (13) it is 1.3575 for the same  $\text{C}_{\text{ac}}-\text{C}_{\text{ac}}$

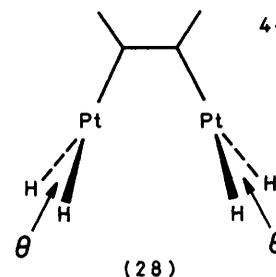


distance. Perhaps (21) is best written as (24a) to emphasize the butadiene connection. Interestingly, the stabilized complexed form of (24a) is known; (24b) is the isolobal analogue of  $[\text{Fe}(\text{CO})_3(\text{butadiene})]$ .<sup>15</sup>

A more conventional view of (21), using the usual electron-count formalism of ac as  $\text{ac}^{2-}$  in the parallel bonding mode, is that of two  $d^9$ , 15-electron three-coordinate platinum centres. Shortening the Pt-Pt distance did not result in a lower total energy as the 15-electron count might suggest (although the overlap population did become positive at shorter Pt-Pt distances).



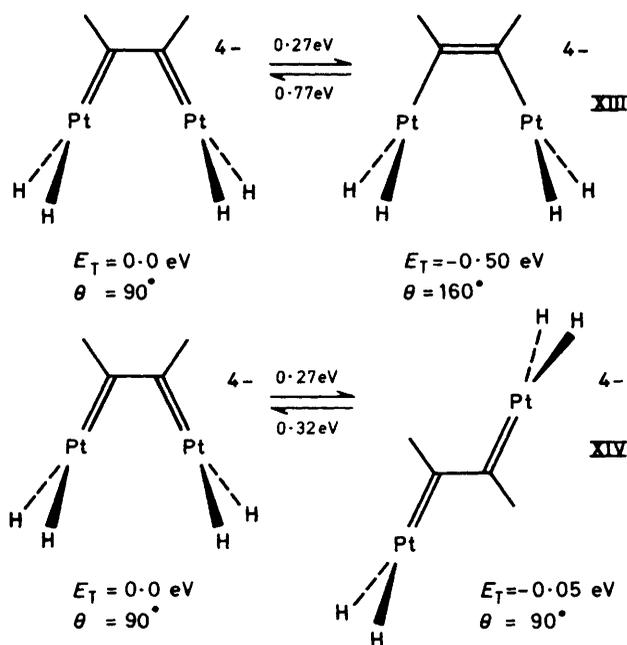
The two alternative descriptions above suggest geometric manoeuvres to stabilize (21). For instance, the butadiene identification suggests rotation about the  $\text{C}_{\text{ac}}-\text{C}_{\text{ac}}$  bond should be facile and, perhaps, stabilizing. The  $d^9$  three-coordinate description implies one might encounter behaviour such as seen in the related  $d^8\text{ML}_3$  complexes.<sup>16</sup> These are Jahn-Teller active systems: the attractive  $D_{3h}$  geometry, (25), has two electrons in a degenerate level. It deforms spontaneously to T- and Y-shaped conformers, (26) and (27). A typical Mexican-hat surface is generated, with easy motions interconverting T and Y shapes without passing through the trigonal  $D_{3h}$  geometry.<sup>16</sup>



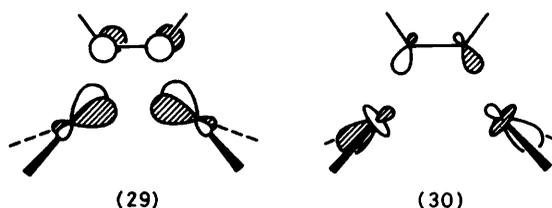
We did several calculations to test the ideas presented above, using the hydride model system  $[\text{Pt}_2\text{H}_4(\text{C}_2\text{H}_2)]^{4-}$ . A variation of the angle  $\theta = \text{H-Pt-H}$ , (28), is one way of achieving a local Y-shaped  $\rightleftharpoons$  T-shaped structure change. The results for the  $\theta$ -angle variation are summarized in XIII. As indicated, two minima were found,  $\theta = 90^\circ$  (Y shape) and  $160^\circ$  (T shape). The numbers above and below the arrows are the calculated barriers. The total energy,  $E_{\text{T}}$ , is relative to the  $\theta = 90^\circ$  species. In XIV we give the results for the rotation of the  $\text{PtH}_2$  groups about the  $\text{C}_{\text{ac}}-\text{C}_{\text{ac}}$  bond (*cis*  $\rightleftharpoons$  *trans*).

The reason for the  $\text{C}_{\text{ac}}\text{PtH}_2$  local Y and T minima is an extension of the arguments used to explain the similar behaviour exhibited by some  $d^8$  three-coordinate complexes<sup>16</sup> as discussed above. The facile *cis*  $\rightleftharpoons$  *trans* transit is a manifestation of the organic butadiene analogy.

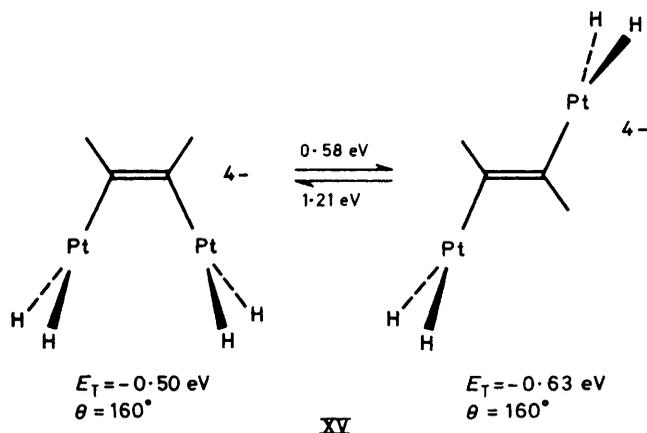
The butadiene analogy is not valid for all values of the



L-Pt-L angle  $\theta$ . At large  $\theta$  the orbital which was the l.u.m.o. at  $\theta = 90^\circ$ ,  $b_1$ , (29), is occupied, and a  $b_2$  orbital, (30), is vacated. The  $b_1$  and  $b_2$  orbitals shown here are  $C_{ac}-C_{ac}$  bonding and antibonding orbitals respectively. The crossing thus produces a much stronger  $C_{ac}-C_{ac}$  bond



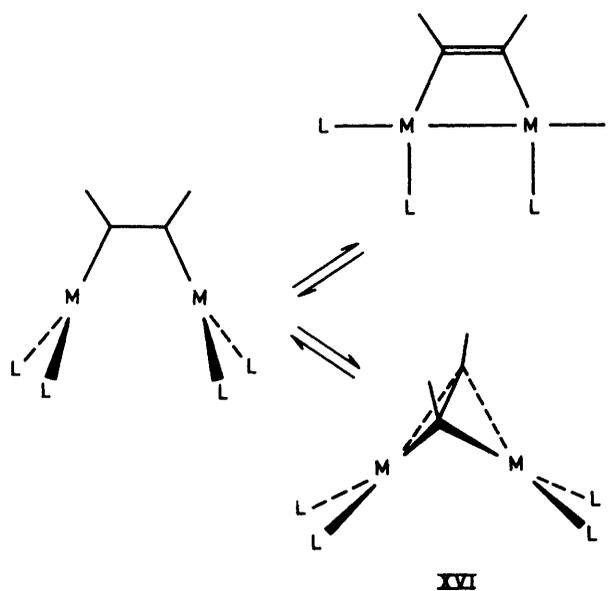
in the  $\theta = 160^\circ$  species; the  $C_{ac}-C_{ac}$  overlap population for  $\theta = 90^\circ$  is +1.2354 vs. +1.4121 for  $\theta = 160^\circ$ . We have emphasized in XIII the shift in  $C_{ac}-C_{ac}$  overlap population by writing a  $C_{ac}-C_{ac}$  double bond for the  $\theta = 160^\circ$  structure. As one might expect the strengthened  $C_{ac}-C_{ac}$  bond makes the rotation about the  $C_{ac}-C_{ac}$  bond



less facile, XV. Molecules such as  $L_2Pt(ac)PtL_2$ , (21), at large LPtL angles are really metalloethylenes, and are the subject of a separate study.<sup>17</sup>

One important point concerning Figure 3 we have not yet discussed is the relatively small h.o.m.o.-l.u.m.o. separation. This is a source of possible instability and it is worthy of note that none of the various deformations in XIII, XIV, or XV does much to increase the h.o.m.o.-l.u.m.o. gap; the largest h.o.m.o.-l.u.m.o. separation among the various species studied so far is 0.96 eV for the *trans*,  $\theta = 160^\circ$  complex. Because of the small h.o.m.o.-l.u.m.o. separations, we hesitate to make a firm prediction of the structure of (21). However, it seems likely that it will have a local T-shaped geometry.\*

If the alternative parallel acetylene structure (21) is a stable entity we must consider its interconversion with



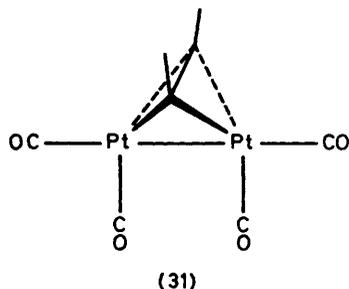
the known structural types, XVI. The available  $L_2-M(ac)ML_2$  structures all have terminal ligand-metal-terminal ligand angles near  $90^\circ$ , *i.e.* Y-shaped. If (21) does choose a T-shaped local metal environment, then any pathway for XVI would necessarily have to climb the energy hill associated with the T  $\rightarrow$  Y transformation. As shown in XIII, the barrier for such a geometry change is 0.77 eV for the hydride model. That value was calculated keeping all other geometric parameters fixed and so is only an indication of the energy involved.

It is interesting to note that if we restrict ourselves to geometries with an L-M-L angle of *ca.*  $90^\circ$ , all the structures in XVI have analogies on the organic side. All the concomitant stereoelectronic constraints<sup>14</sup> should carry over.

We take up now the alternative ac configuration for (3) shown for the  $[Pt_2(CO)_4(\mu-C_2H_2)]$  model system in (31).

\* A study of  $[Pt_2(CO)_4(\mu-C_2H_2)]$  gives similar results to those presented in the text for the model with hydride ligands, except that the local Y-shaped minima were unstable with respect to opening up to a T-shaped geometry.

Again we use a  $L_2MML_2$  plus ac construction to derive the m.o. scheme and thus in Figure 4  $(CO)_2PtPt(CO)_2$  interacts with neutral  $C_2H_2$ . The m.o. pattern for the diplatinum fragment is very similar to that shown in Figure 2.



Comparing Figures 2 and 4 once again shows the importance of the ac  $b$  orbital-symmetry label change associated with the ac orientation (see II and ref. I). In Figure 2, one  $\pi^*$  orbital of ac was of  $b_2$  symmetry and mixed nicely with the filled  $3b_2$  orbital of the  $Pt_2$  fragment. In Figure 4 this important stabilizing interaction is lost because  $\pi^*$  is now  $b_1$ . Filled  $3b_2$  finds a symmetry match here only with the filled ac  $\pi$  remnant,  $b_2$ . As a consequence, structure (31) lies almost 1.8 eV above the known geometry (13).

The small h.o.m.o.-l.u.m.o. gap for (31) and its high relative energy leaves us in doubt about the possible stability for this structural type. Good  $\pi$  donors on ac might help open the h.o.m.o.-l.u.m.o. gap by pushing the low-lying  $a_2$  and  $b_2$  empty orbitals up in energy and perhaps stabilize the structure.

The high energy of (31) relative to (13) indicates that a rotation of acetylene above the Pt-Pt vector as shown in XVII is not a facile process. This computational result

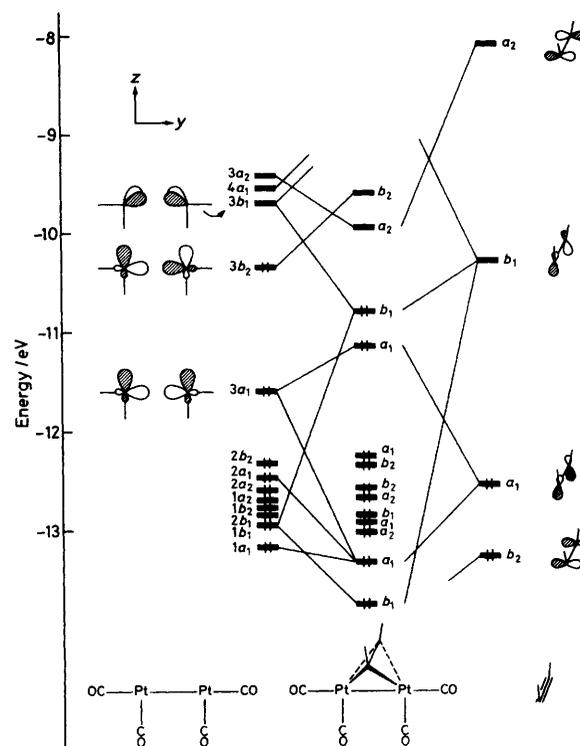
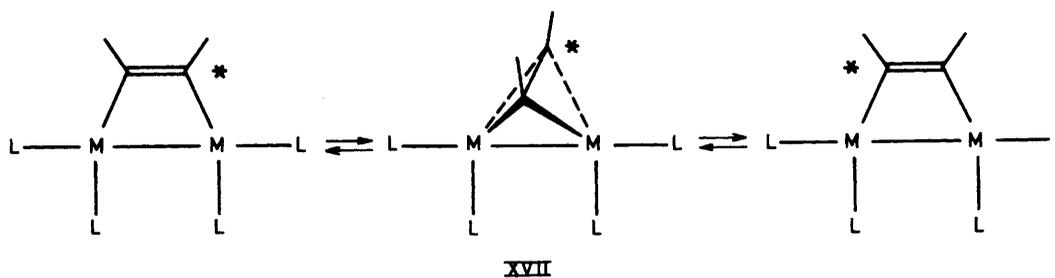


FIGURE 4 Interaction of  $C_2H_2$  with planar  $(CO)_2PtPt(CO)_2$  to form (31). A geometry was assumed where Pt-Pt = 2.82 Å and CO-Pt-CO =  $90^\circ$

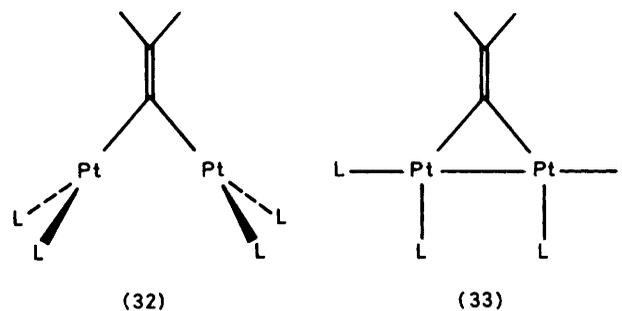
(34), and (33) is identified with methylenecyclopropane, (35). Calculations on a model for (32) reveal a near zero h.o.m.o.-l.u.m.o. gap and an electronic structure consistent with the trimethylenemethane identification. We do not expect (32) to be a stable entity, but it should exist stabilized by complexation with  $ML_3$  where M is a



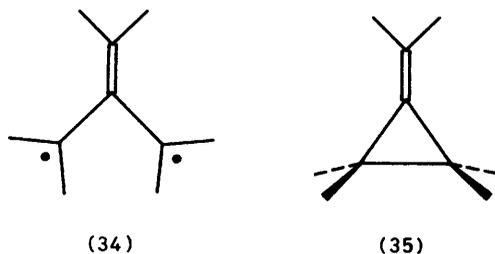
appears to be contrary to the experimental data reported by Stone and co-workers<sup>12</sup> for  $[Pt_2(cod)_2\{\mu-C_2(CF_3)_2\}]$  (cod = cyclo-octadiene).

Although we have restricted ourselves to  $L_2M(\mu-ac)ML_2$  geometries, one can imagine other structures of a general  $L_2M(C_2R_2)ML_2$  formula. Two intriguing ones are illustrated with  $L_2Pt(C_2R_2)PtL_2$  in (32) and (33).<sup>\*</sup> For L-Pt-L angles less than *ca.*  $120^\circ$ , (32) is the inorganic isolobal analogue of organic trimethylenemethane,

<sup>\*</sup> Structure (33) can be alternatively viewed as a bridged carbene. Complexes of type  $L_2Pt(\mu-CR_2)PtL_2$  are known.<sup>18</sup>



$d^8$  metal. Structure (33), on the other hand, has a sizeable h.o.m.o.–l.u.m.o. gap and no unusual electronic features. We believe it will soon be synthesized.



#### APPENDIX

All calculations were performed by the extended-Hückel method,<sup>19</sup> with weighted  $H_{ij}$  values.<sup>20</sup> Unless otherwise stated we assumed the following bond distances in our calculations: Pt–C<sub>ac</sub> 2.1, Pt–C(CO) 1.85, Pt–H 1.7, C–O 1.16, C<sub>ac</sub>–C<sub>ac</sub> 1.32, and C–H 1.09 Å. For perpendicular and parallel acetylene we assumed C–C–H angles of 130 and 120° respectively. The H, C, and O parameters for our calculations are standard ones.<sup>19</sup> The platinum parameters come from a previous publication.<sup>21</sup>

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