

10 min. Gas evolution occurred and the orange iron complex dissolved. Upon completion of the addition, the mixture was allowed to warm to room temperature and stirred for 30 min. TLC indicated a single purple band eluting with pentane. The mixture was filtered through a Celite pad with difficulty and the filtrate evaporated to dryness on a rotary evaporator. The resulting residue was extracted with a 20% dichloromethane/80% hexane mixture and filtered, and the solvent was removed on a rotary evaporator. This gave a black solid, which upon recrystallization from pentane at $-30\text{ }^{\circ}\text{C}$, yielded 0.962 g (2.0 mmol, 30%) of $\text{S}_2\text{Fe}_3(\text{CO})_9$ as black needles, mp $112\text{--}115\text{ }^{\circ}\text{C}$ (lit.¹⁸ $^{\circ}\text{C}$), identified by comparison of its IR spectrum with that of an authentic sample.

Conversion of Bis(μ_3 -thio)tris(tricarbonyliron) to (μ -Di-thio)bis(tricarbonyliron) by Treatment with Sulfur in Refluxing THF. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir-bar, a reflux condenser topped with a gas inlet tube leading to a Schlenk manifold, and no-air stoppers was charged with 0.344 g (0.7 mmol) of $\text{S}_2\text{Fe}_3(\text{CO})_9$ and 0.069 g (1.4 mmol) of sulfur, then evacuated, and refilled with nitrogen. THF (30 mL) was added by syringe, and carbon monoxide was bubbled through the purple solution for 10 min by using a syringe needle. The reaction mixture was heated at reflux for 24 h with

CO slowly bubbling through it. TLC indicated an orange band preceding a purple band eluting with pentane. More sulfur (0.035 g, 0.7 mmol) was added against a counterflow of CO and the mixture heated for another hour. No change in the amounts of the two bands was observed by TLC. The cooled reaction mixture was filtered and the solvent removed on a rotary evaporator. Filtration chromatography eluting with pentane was used to isolate the 2 fractions. The orange fraction was identified as $\text{S}_2\text{Fe}_2(\text{CO})_8$ (0.152 g, 0.4 mmol, 44% based on unrecovered $\text{S}_2\text{Fe}_3(\text{CO})_9$) by comparison of its melting point and IR spectrum with those of an authentic sample. The purple fraction was identified as unconverted $\text{S}_2\text{Fe}_3(\text{CO})_9$ (0.044 g, 0.09 mmol, 13% recovery) on the basis of its melting point and IR spectrum.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. (μ_3 -PhP)(μ_3 -S) $\text{Fe}_3(\text{CO})_9$, 82614-06-0; (μ_3 -*p*- $\text{CH}_3\text{C}_6\text{H}_4\text{P}$)(μ_3 -S) $\text{Fe}_3(\text{CO})_9$, 82614-07-1; (μ_3 -*t*-BuP)(μ_3 -S) $\text{Fe}_3(\text{CO})_9$, 82614-08-2; $\text{Fe}_3(\text{CO})_{12}$, 17685-52-8; PhP(S)Cl₂, 3497-00-5; *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{P}$ (S)Cl₂, 6588-16-5; *t*-BuP(S)Cl₂, 21187-18-8; (PhPS)₄, 1447-25-2; Fe, 7439-89-6.

Dimetalated Olefins

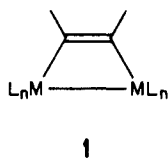
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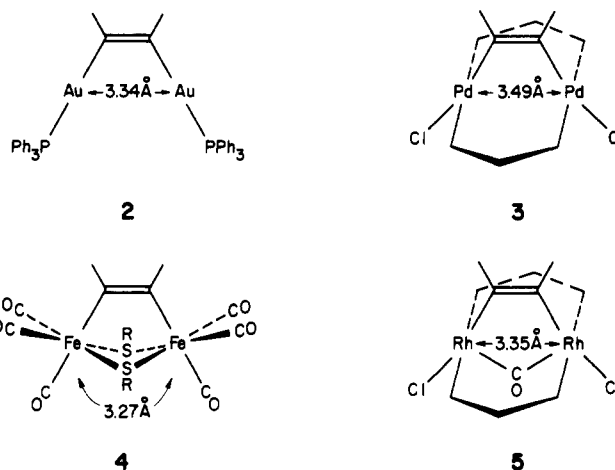
Received April 12, 1982

Extended Hückel calculations are performed on the subclass of transition-metal binuclear bridging acetylene complexes, $\text{L}_n\text{M}(\mu\text{-acetylene})\text{ML}_n$, that can be viewed as dimetalated olefins. The ethylene analogy is established and a clear bonding picture for the dimetalated olefins emerges once it is recognized that an isolobal analogy exists between the ML_n pieces of the known organometallic complexes and organic R or H. The simple arguments developed provide a basis for speculation on as yet unknown complexes in this class of molecules.

Passages of the mind between organic and inorganic chemistry serve not only to make us feel comfortable about unusual structural types but may in fact suggest new chemistry. In the course of a study of binuclear transition-metal acetylene complexes¹ we had occasion to look at the electronic structure of a number of "parallel" complexes of type 1. In some of these molecules no metal-



metal bond is forced by molecular orbital reasoning or 18-electron rule considerations nor is much bonding to be inferred from the observed long metal-metal separations. Examples are the complexes $\text{Au}_2(\text{PPh}_3)_2(\mu\text{-C}_2(\text{CF}_3)_2)$, $\text{Pd}_2\text{Cl}_2(\mu\text{-dpm})_2(\mu\text{-C}_2(\text{CF}_3)_2)$ (dpm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$), $\text{Fe}_2(\text{CO})_6(\mu\text{-SCF}_3)_2(\mu\text{-C}_2(\text{CF}_3)_2)$, and $\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-dpm})_2(\mu\text{-C}_2(\text{CO}_2\text{Me})_2)$, 2-5, respectively.² As is evident here, the substituent on the acetylene carbon is most often CF_3 , sometimes CO_2R . We have left it unspecified in the



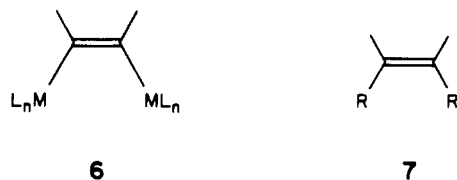
drawings, indicated only by a line. A possible reason for the common acceptor substitution in the known complexes has been discussed in ref 1.³

The basic acetylene-containing structural unit in these may be summarized as 6, which can be viewed as a dimetalated olefin. This paper traces in detail the analogy

(1) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* 1982, 104, 3858.

(2) (a) 2: Gilmore, C. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1971, 1233-1234. Mitchell, C. M.; Stone, F. G. A. *Ibid.* 1970, 1263-1264. (b) 3: Balch, A. L.; Lee, C. L.; Linsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* 1979, 177, C22-C26. (c) 4: Davidson, J. L.; Harrison, W.; Sharp, D. W. A.; Sim, G. A. *Ibid.* 1972, 46, C47-C49. (d) 5: Cowie, M.; Southern, T. G. *Ibid.* 1980, 193, C46-C50; *Inorg. Chem.* 1982, 21, 246-253. A similar molecule with $\mu\text{-CO}$ replaced by $\mu\text{-CH}_2$ has been prepared: McKeer, I. R.; Cowie, M., private communication.

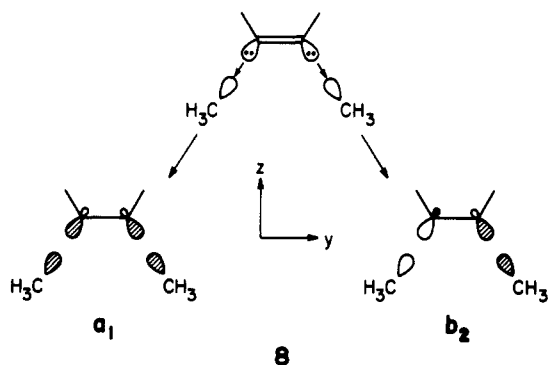
(3) There are parallel bonded acetylene complexes in which the acetylene does not have CF_3 or CO_2R substituents. See the following: (a) Rossell, O.; Sales, J. *Inorg. Chim. Acta* 1981, 64, L43-L44. (b) Staal, L. H.; von Koten, G.; Vrieze, K.; Ploeger, F.; Stam, C. H. *Inorg. Chem.* 1981, 20, 1830-1835. (c) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* 1977, 99, 7870-7876. (d) Bennett, M. J.; Graham, W. A. G.; Stewart, Jr., R. P.; Tuggle, R. M. *Inorg. Chem.* 1973, 12, 2944-2947.



to a cis olefin, 7, and explores some of the consequences. We use extended Hückel calculations to support our symmetry-based arguments, with details provided in the Appendix.

The Organic Analogy

In the context of an electron-counting formalism most chemists, we believe, would prefer to consider the parallel bonded acetylene ligand in $ML_n(\mu\text{-acetylene})ML_n$ as the dianion (ac^{2-}). Taking an organic olefin, says *cis*-2-butene, and formally rearranging the electrons to be consistent with the inorganic counting mode gives ac^{2-} and $(CH_3\cdots CH_3)^{2+}$. Viewed this way, the bonding in the butene is simply the interaction of two lone pairs on ac^{2-} with the empty sp^3 hybrids of the two pyramidal CH_3^+ units. Two "dative" σ bonds are formed, 8. Converting to molecular



orbital language, we have two filled CC bonding orbitals, a_1 and b_2 in 8. These are the bonding combinations of the filled π and π^* remnants of the *cis* bent ac^{2-} ($120s$) with the in-phase and out-of-phase combinations of CH_3^+ sp^3 hybrids. By analogy, one expects that any dimetalated olefin, 6, should be substituted by ML_n^+ fragments with an empty orbital (remember, count ac^{2-}) of similar shape and direction to the CH_3^+ hybrids. In other words we should have ML_n^+ isolobal⁴ to CH_3^+ .

Examine the known structures 2–4, breaking each into ac^{2-} and two ML_n^+ fragments. Once the role of the bridging units is dissected, it is easy to see that we have two $d^{10} ML$ in 2, $d^8 ML_3$ in 3 and $d^6 ML_5$ in 4. The molecular orbitals (MO's) of the three ML_n fragments⁵ and the CH_3 hybrid are compared in Figure 1. Each fragment contains a low-lying MO of a_1 symmetry that is empty for the appropriate electron count.⁶

The MO schemes for 2–4 ought to resemble the MO picture for an organic *cis* olefin. So they do. We have constructed interaction diagrams for each type, and while other metal orbitals complicate matters, the essentials of

(4) Elian, M. Chen, M. M.-L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* 1976, 15, 1148–1155; Elian, M.; Hoffmann, R. *Ibid.* 1975, 14, 1058–1076 and references therein.

(5) A more detailed analysis of these fragments can be found in the following references: (a) Albright, T. A.; Hoffmann, R.; Thibault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* 1979, 101, 3801–3812. (b) Burdett, J. K. "Molecular Shapes"; Wiley: New York, 1980; Chapter 13. (c) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* 1981, 103, 4308–4320.

(6) The isolobal relationships of the ML fragment have been analyzed in detail: Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* 1982, 232, 171–191. See also: Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* 1981, 103, 7648–7650.

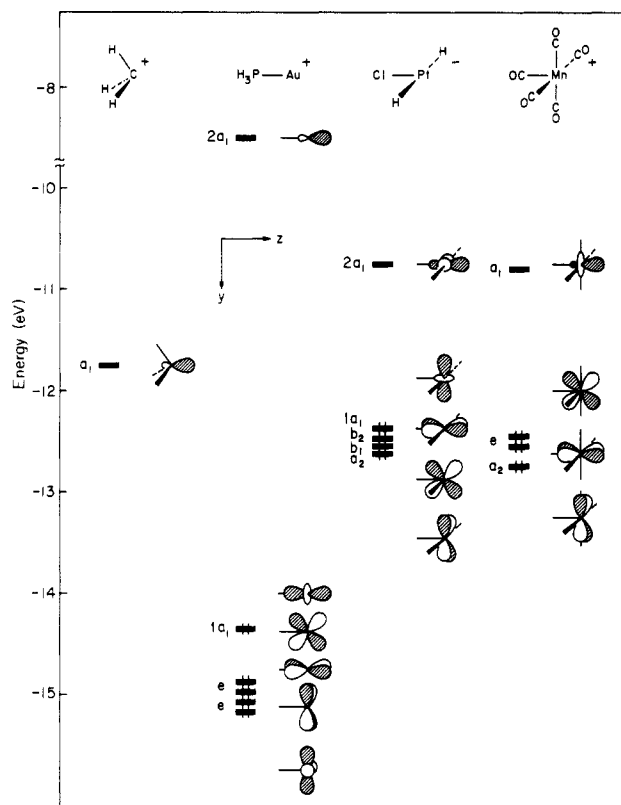
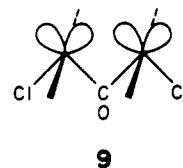


Figure 1. A comparison of the frontier orbitals of the fragments CH_3^+ , $d^{10} ML$, $d^8 ML_3$, and $d^6 ML_5$.

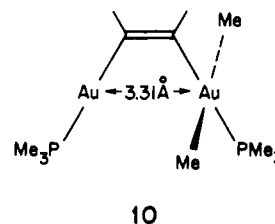
the bonding analogy are preserved. In particular we can identify in each case M–C σ -bonding orbitals analogous to a_1 and b_2 in 8.

The *cis*-butene analogy for the carbonyl-bridged complex 5 is more difficult to see. If we count the bridging carbonyl as CO^{2-} ,^{1,7} the underlying d^6 - d^6 dimetal fragment for 5 has four empty hybrids as schematically illustrated in 9.



The hybrids in 9 point at the sites that, if occupied, would define distorted octahedral local metal environments. (Counting the μ -CO as occupying two coordination sites, one to each metal.) In 9, the two hybrids that point inward are the ones that bond to the ac^{2-} ligand. They are the analogues of the sp^3 hybrids of $(CH_3\cdots CH_3)^{2+}$ in 8. The hybrids that point outward in 9, trans to the μ -CO, are not tied up in ligand bonding. They are the sites of ligand unsaturation in the composite complex.

Before pursuing the olefin analogy further, we point out some other known dimetalated olefins. For instance 10



is an example which highlights the intimate relationship

(7) Robinson, S. D. *Inorg. Chim. Acta* 1978, 27, L108.

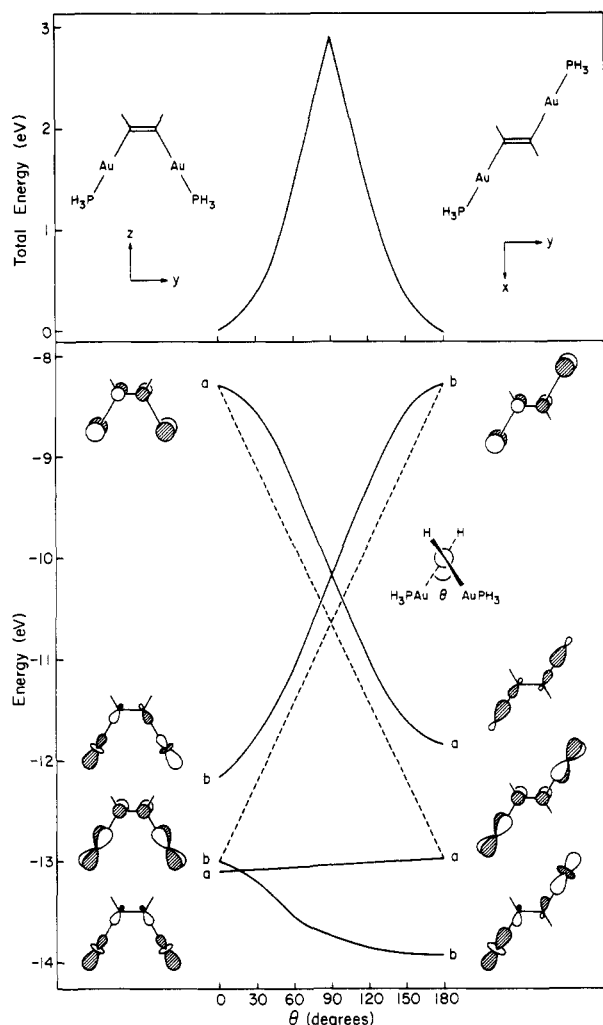
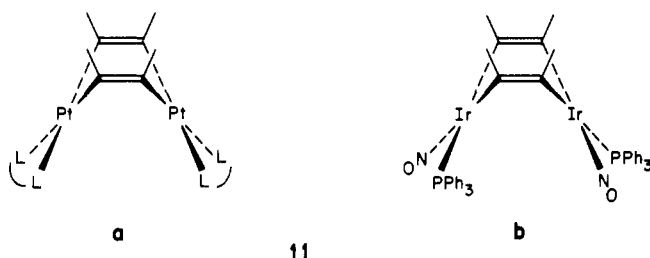


Figure 2. At bottom, the molecular orbitals of $(\text{PH}_3)\text{Au}(\mu\text{-C}_2\text{H}_2)\text{Au}(\text{PH}_3)$ for the cis \rightarrow trans isomerization. The total energy for the transit is at top. The pathway chosen preserves C_2 symmetry with $\theta = 0^\circ$ and $\theta = 180^\circ$ representing the cis and trans geometries, respectively.

among the ML_n fragments in Figure 1. Here we have d^{10} ML and d^8 ML_3 bonded to the same acetylene.⁸

The two diacetylenes, $\text{Pt}_2(\text{COD})_2(\mu\text{-C}_2(\text{CF}_3)_2)_2$ (COD = 1,5-cyclooctadiene), 11a, and the related $\text{Ir}_2(\text{NO})_2$ -



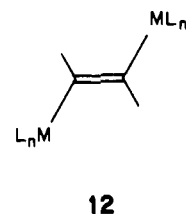
$(\text{PPh}_3)_2(\mu\text{-C}_2(\text{CF}_3)_2)_2$, 11b, can be looked at as dimetalated olefins.⁹ Both complexes have near square-planar M centers. If we formally remove one ac^2- ligand from 11a or 11b, we are left with two d^8 T-shaped ML_3 fragments tied by the remaining acetylene bridge. Viewed this way,

the relationship between 3 and 11 is obvious.

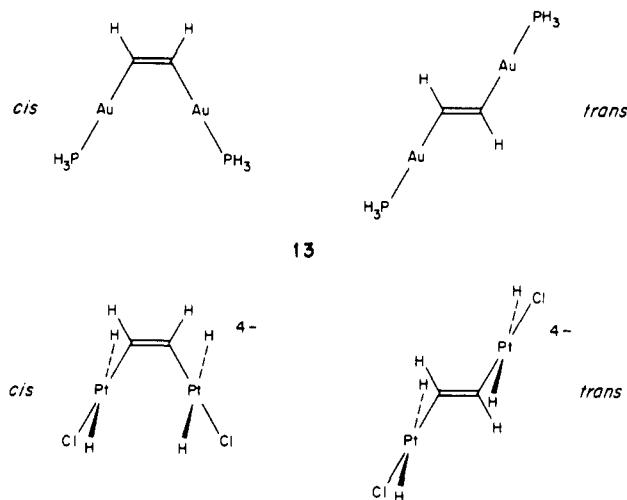
There is another alternative bonding scheme available to molecules of type 6. This is multiple bonding between the "acetylene" carbons and the ML_n fragments, i.e., a dimetallabutadiene. This form does not play an important role; according to our calculations the π and π^* orbitals of acetylene orthogonal to the $\text{M}_2(\text{acetylene})$ plane do not overlap well enough with the metal orbitals in the parallel bonding mode.¹

Trans Dimetalated Olefins

Following up the olefin analogy, one might wonder about the possible stability of the trans isomers of the dimetalated olefins 12. There is little novel in our suggestion



of this possibility, for the trans alternative was specifically considered in the case of the gold dimer 2^{2a} and a trans complex for d^8 ML_5 , $(\text{CN})_5\text{Co}(\mu\text{-MeO}_2\text{CC}_2\text{CO}_2\text{Me})\text{Co}(\text{CN})_5^{6-}$, has recently been prepared.¹⁰ Extended Hückel calculations on the model cis and trans pairs 13 show (a) a normal electronic structure, with a sizable gap between filled and unfilled levels for the trans as well as the cis isomer, and (b) very little energy difference between the isomers.



There is a reason for our referring to the cis and trans forms of 13 as "isomers". If one twists the two CH_2 groups of an olefin against each other, a likely mechanism for cis-trans isomerization, one encounters a level crossing at the orthogonal geometry.¹¹ This is a prototype forbidden reaction. No wonder that one encounters a large activation energy for cis-trans isomerization, reduced from ~ 60 kcal/mol only by "push-pull" electronic asymmetry induced by substitution.

Since the transition-metal acetylene complexes of type 13 are analogues of olefins in their electronic structure, we would expect also for these molecules a large barrier to torsion around the central CC bond. An actual computed

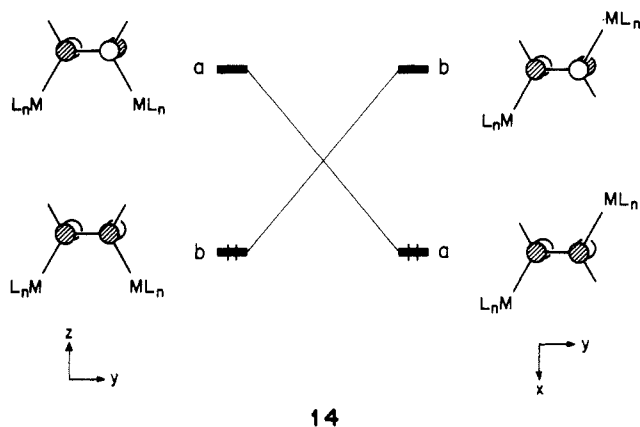
(8) (a) Jarvis, J. A.; Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* 1973, 373-374. (b) Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* 1978, 980-985. (c) Another example of a complex of this type can be found in ref 3a.

(9) (a) Smart, L. E.; Browning, J.; Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 1777-1785. (b) Clemens, J.; Green, M.; Kuo, M.-C.; Fritchie, C. J.; Mague, J. T.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1972, 53-54.

(10) Grande, K. D.; Kunin, A.; Stuhl, L. S.; Foxman, B. M., to be submitted for publication.

(11) Heilbronner, E.; Bock, H. "The HMO Model"; Wiley: New York, 1976, Problem 6.18.

correlation diagram for the gold case, Figure 2, confirms this. The levels that should cross, by analogy to ethylene, are shown in 14. The actual correlations are different from

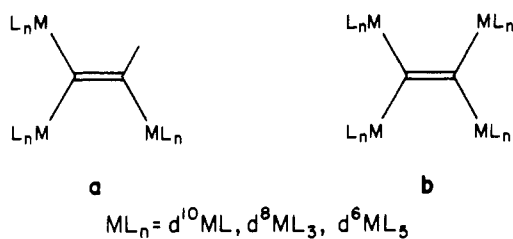


the intended one, as may be seen in Figure 2. This is a consequence of the peculiarities of the $ML_n(\mu\text{-}RC_2R)ML_n$ level scheme, for instance that one M-C σ -bonding combination comes above the ethylene-like π level. The dashed lines in the figure show the correlations by shape, i.e., the intended correlations of 14.

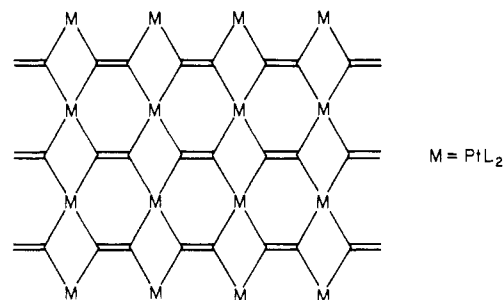
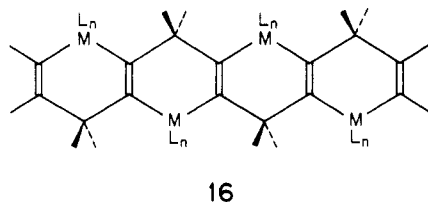
Our computed barriers to isomerization are large, >60 kcal/mol. These are the ascents to the level crossing, without configuration interaction which would reduce the height of the barrier. They are also extended Hückel estimates, not quantitatively reliable. Nevertheless, the conclusion that the barriers are high is a firm one. The orbital patterns of the trans isomers in 13, are, from our experience, typical of kinetically stable organometallic complexes. We would encourage synthetic approaches to the trans isomers, including the photochemical cis-trans isomerization which is so common in organic chemistry.

Some Hypothetical Molecules

The metallo olefin analogy can be extended in a trivial way to three and four metal arrays of type 15. Steric restrictions for the ML_5 and ML_3 choices might necessitate tying the metal fragments together in such systems.



Perhaps more interesting are some hypothetical one- and two-dimensional structures of type 16 and 17. In 16 we have a one-dimensional zig-zag conjugated chain, $ML_n\text{-}C=C\text{-}ML_n$, held together by saturated methylene spacers.¹²



Appendix

All calculations were performed by using the extended Hückel method,¹³ with weighted H_{ij} 's.¹⁴ Bond distances used include $C_{ac}\text{-}C_{ac} = 1.32 \text{ \AA}$, $Au\text{-}C_{ac} = 2.05 \text{ \AA}$, $Au\text{-}P = 2.28 \text{ \AA}$, $P\text{-}H = 1.44 \text{ \AA}$, $Pt\text{-}C_{ac} = 2.10 \text{ \AA}$, $Pt\text{-}H = 1.7 \text{ \AA}$, and $Pt\text{-}Cl = 2.4 \text{ \AA}$.

The parameters for C, O, and H are the standard ones.¹³ The Fe, Pt, Au, and Mn parameters are from previous publications.¹⁵⁻¹⁷

(12) (a) Discrete clusters containing the C_2 unit are known. Brice, M. D.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1381-1384. Albano, V. G.; Chini, P.; Martinengo, S.; Sansoni, M.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1978**, 459-463. Simon, A.; Warkentin, E.; Masse, R. *Angew. Chem.* **1981**, *93*, 1071; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1013-1014. The C_2 unit is, of course, common in many extended structures of the CaC_2 type. (b) For some related linear chains with a $MC\equiv CM$ framework see: Hanack, M.; Seelig, F. F.; Strähle, J. *Z. Naturforsch., A* **1979**, *34A*, 983-985. Seelig, F. F. *Ibid.* **1979**, *34A*, 986-992; Hanack, M.; Mitulla, K.; Pawlowski, G.; Subramanian, L. R. *Angew. Chem.* **1979**, *91*, 343. Also: Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 150-179.

(13) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397-1412. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179-2195; **1962**, *37*, 2872-2883.

(14) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann R. *J. Am. Chem. Soc.* **1978**, *100*, 3686-3692.

(15) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240-7254.

(16) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255-7265.

(17) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578-1590.