

since the forward rate constants are the same for all the substitution reactions, eq 6, 7, and 1, is comparable to that of the monosubstituted complex rather than the bisubstituted complex.

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Geometries of Ethylene and Acetylene in Platinum–Ethylene and –Acetylene Complexes

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The literature is replete with examples of the prediction of geometry within the framework of MO theory for both *ab initio* and semiempirical calculations. Varying degrees of success have been achieved in computing a predicted geometry by means of extended Hückel semiempirical calculations. Predicting geometry implies a quantitative bias and consequently noniterative modes of computation have generally been used for the development of computational methods (or qualitative results).¹

Blizzard and Santry, by using CNDO calculations, have investigated changes in the bond angles of acetylene as a function of the population of various orbitals in order to compute the geometry of transition metal–acetylene complexes.²

The observed³ cis-bent configurations of the acetylenes in these complexes was hypothesized to be the result of extensive population of an acetylene π -antibonding orbital, analogous to an excited state of acetylene.² Unfortunately, however, the calculations suffered from the rather severe approximation that they were unable to include the metal.

Both zerovalent and divalent platinum–acetylene and –olefin complexes have recently been calculated by noniterative rather than self-consistent techniques.^{4,5}

Although no angles were scanned within the organic group, extensive population of the π -antibonding orbitals normally associated with the olefin or acetylene was found, implying partial support for Blizzard and Santry. In fact, population of the olefin or acetylene π antibonding orbitals is part of a synergic stabilizing mechanism in complexes of this type implied by Blizzard and Santry and computationally verified in these laboratories.⁶

Justification for noniterative computations is becoming increasingly available. Moffat has demonstrated that among a homologous series of molecules represented by various basis sets, differences in energy converged to a constant value more rapidly for smaller basis sets than did the energies.⁷ This result, coupled with others which indicate that certain molecular properties such as conformational barriers are as accurately calculated by either iterative or noniterative techniques,⁸ leads us to believe that noniterative calculations are more valuable than has generally been recognized. As long as the convergence properties of the system of equations representing a molecular situation remain parallel, the trends and relative energies predicted *via* noniterative computations for a series of compounds should be as valid as self-consistent or iterative modes.

This is an elementary result of the variation theorem. A first-order error in the wave function leads to a second-order error in energy. Since the convergence of the iteration process will be approximately parallel for different similar molecules, the error in the noniterative calculations will be second order. Hence chemical trends may be discussed in a meaningful fashion and possibly utilized for prediction.

Use of a noniterative mode of semiempirical MO calculation for the purpose of predicting geometries seemed especially appealing. Fixing the basis set comparisons among various geometries is computationally economical and consistently⁹ more reliable than in iterative schemes. The results of such geometrical studies for the platinum–olefin and –acetylene complexes $(\text{PH}_3)_2\text{Pt}(\text{C}_2\text{H}_2)$, $(\text{PH}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$, and *trans*- $(\text{NH}_3)\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2$ are reported here. The method of calculation and functions employed have been previously reported.^{4,5}

The variation in the total overlap populations (summed over all pairs of atoms), overlap energies, and one-electron orbital energy sums was studied as a function of the CCH and HCH angles to determine the most stable configuration. The angle δ (Figure 1) was varied from 0 to 90° and ω from 100 to 120° (these angles are the dihedral angles of interest within the organic moiety). Comparison with X-ray data has facilitated evaluation of the method.³ This is in contrast to the previous studies on the barrier to rotation of the organic

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(2) (a) A. C. Blizzard and D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 5749 (1968); (b) H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, **47**, 792 (1967); (c) H. W. Kroto and D. P. Santry, *ibid.*, **47**, 2736 (1967).

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(5) K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen *ibid.*, **92**, 5110 (1970).

(6) Although Blizzard and Santry discussed transition metal–acetylene complexes in terms of σ and π bonding, this was used to rationalize the cis-bent configuration rather than proposing a synergic mechanism.

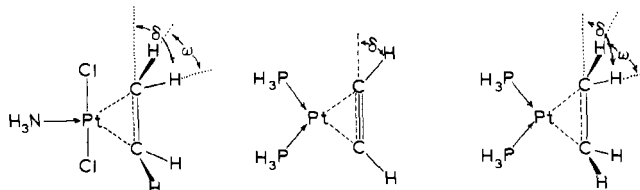
(7) J. B. Moffat, *Can. J. Chem.*, **48**, 1820 (1970). Moffat employed the SCF method but the dependence on the iteration process is parallel to that used here.

(8) K. S. Wheelock, H. B. Jonassen, and L. C. Cusachs, *Int. J. Quantum Chem.*, in press.

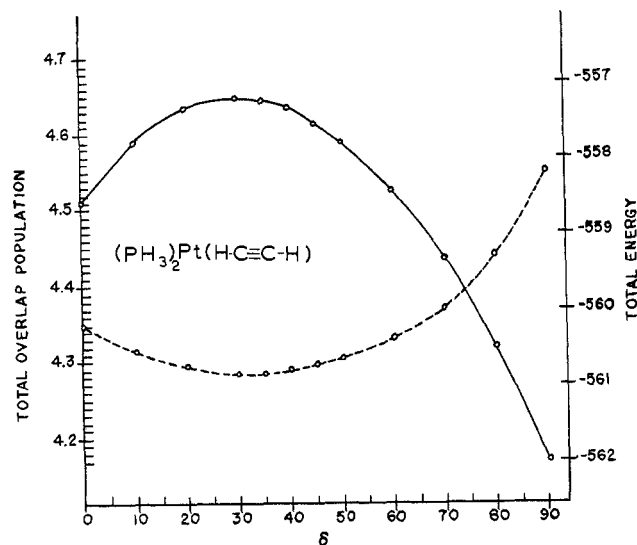
(9) L. C. Cusachs and D. J. Miller, *Advan. Sulfur Chem.*, in press; J. H. Corrington, H. S. Aldrich, C. W. McCurdy, and L. C. Cusachs, *Int. J. Quantum Chem.*, in press; L. C. Cusachs, J. B. Flory, C. W. McCurdy, and H. S. Aldrich, *J. Amer. Chem. Soc.*, in press.

TABLE I
 ANGLES AS DETERMINED BY LEAST-SQUARES ANALYSES

Complex	Angles	Overlap population	Orbital energy sum	Overlap energy
$(\text{PH}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$	$\epsilon(\text{HCH})$	$100.41 \pm 5 \times 10^{-4}$	$111.83 \pm 9 \times 10^{-4}$	$111.00 \pm 6 \times 10^{-3}$
	$\delta(\text{CCH})$	$31.42 \pm 5 \times 10^{-4}$	$15.09 \pm 9 \times 10^{-4}$	$20.14 \pm 6 \times 10^{-3}$
<i>trans</i> - $\text{NH}_3\text{Cl}_2\text{Pt}(\text{C}_2\text{H}_4)$	$\epsilon(\text{HCH})$	$101.77 \pm 6 \times 10^{-4}$	$111.13 \pm 2 \times 10^{-3}$	$108.32 \pm 7 \times 10^{-3}$
	$\delta(\text{CCH})$	$27.46 \pm 6 \times 10^{-4}$	$8.69 \pm 2 \times 10^{-3}$	$23.64 \pm 7 \times 10^{-3}$
$(\text{PH}_3)_2\text{Pt}(\text{C}_2\text{H}_2)$	$\delta(\text{CCH})$	$30.76 \pm 2 \times 10^{-3}$	$31.99 \pm 8 \times 10^{-2}$	Not calculated

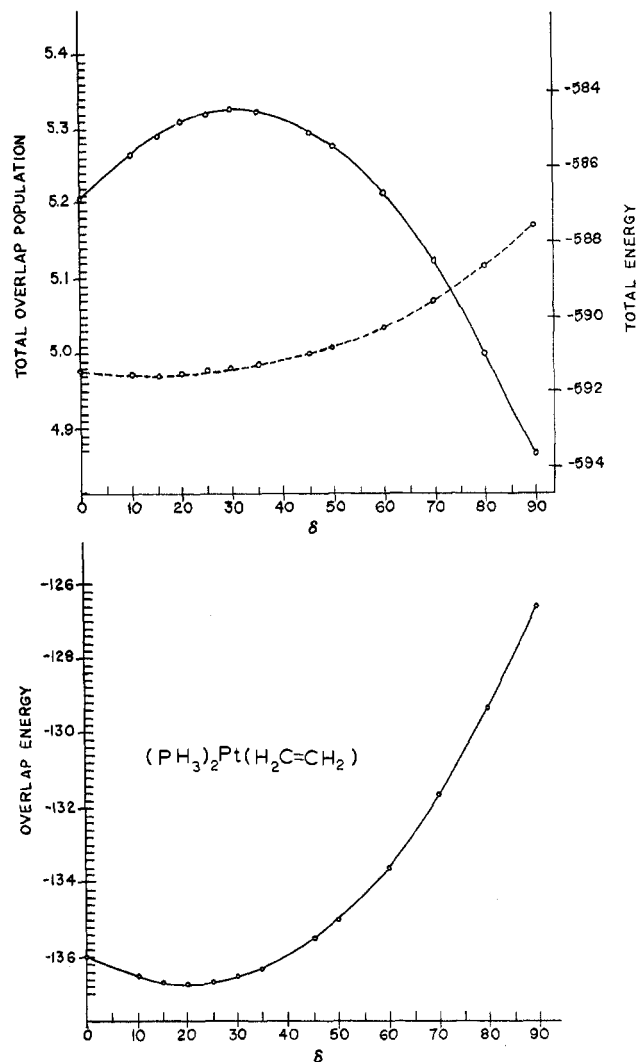
Figure 1.—Geometric definition of angles δ and ω .

moiety in these complexes, where such rotation has not yet been observed.^{5,10}


 Figure 2.—Variation in total energy (---) (one-electron orbital energy sum) and total overlap population (—) for $(\text{PH}_3)_2\text{Pt}(\text{C}_2\text{H}_2)$ as a function of δ .

Figures 2–4 display the variation in these computed quantities as the angles δ and ω are varied. The results for all three computed quantities are smooth parabolic curves which do not possess sharp maxima or minima. Consequently, these quantities were subjected to a least-squares parabolic fit treating each computed variable as a function of the angle varied. The results are presented in Table I along with the uncertainty (2σ). The most stable configuration was determined by minimizing the overlap energy or orbital energy sum or by maximizing the overlap population. The rms values indicate that the orbital energy sum is the least precise of the three criteria employed.

Depending on the formal oxidation state of the metal, δ varies from 8.69 to 31.99° and ω from 100.41 to 111.83°. It is noteworthy that the angles predicted by the overlap population follow chemical trends al-


 Figure 3.—Variation in total energy (---), total overlap population (—), and overlap energy for $(\text{PH}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ as a function of δ .

ready observed.¹¹ The coupling constants $J^{13}\text{C-H}$ determined from ^{13}C nmr studies predict δ to be 41° for $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_2)$ and $\delta = 26^\circ$ and $\omega = 115^\circ$ for $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$.¹² Angles of 40° for δ have been determined by X-ray crystallographic studies of $(\text{PPh}_3)_2\text{Pt}(\text{PhC}\equiv\text{CPh})$ and $\delta = 26\text{--}30^\circ$ for $\text{K}[\text{PtCl}_3(\text{CC}_2\text{H}_4)] \cdot \text{H}_2\text{O}$.³ The geometric calculations based on the ^{13}C nmr data assumed that the hybridization of the carbon determined the coupling constants $J^{13}\text{C-H}$. Since the most stable configuration was found by varying the angles δ and ω and since these angles are putatively a function of the carbon "hybridization," support for this view may be inferred from these calculations.

(10) This statement refers specifically to the failure to observe rotation of the acetylene in the acetylene complexes whereas rotation has been observed in the olefin complexes. For a more complete discussion, see ref 3 and 9.

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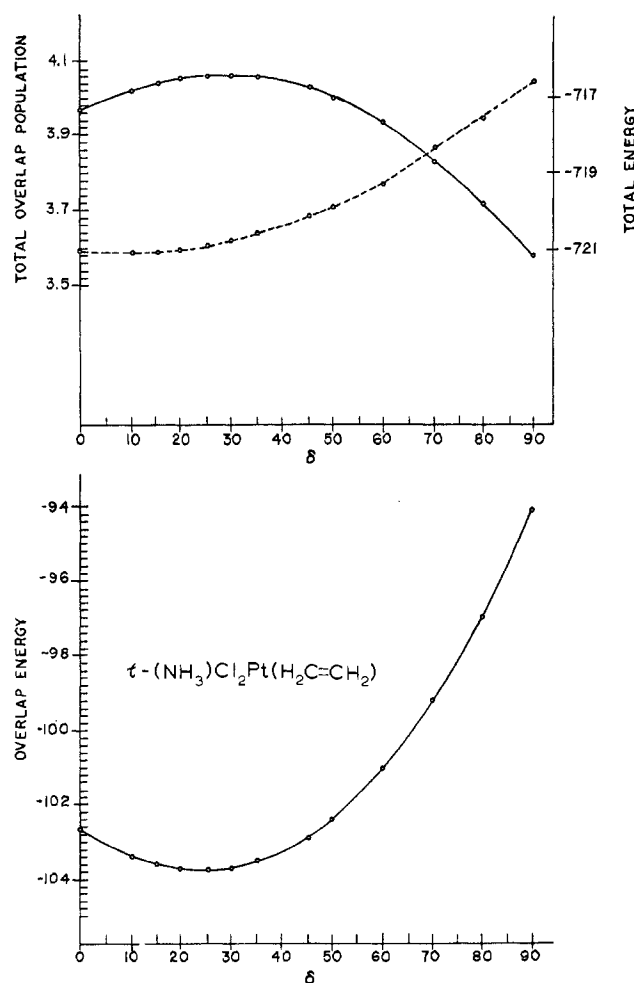


Figure 4.—Variation in total energy (---), total overlap population (—), and overlap energy for *trans*-(NH_3) $\text{PtCl}_2(\text{C}_2\text{H}_4)$ as a function of δ .

Recent photoelectron spectroscopic studies of similar complexes lend partial support to our results.¹³ The charge on the carbon atoms is estimated to be -0.4 ± 0.1 for the olefinic carbon and -0.35 ± 0.1 for the acetylenic carbon in $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ and $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{Ph}_2)$, respectively. In comparison, population analyses determine a computed charge for the olefinic carbon of -0.20 to -0.45 (Löwdin) or -0.74 to -0.84 (Mulliken) and for the acetylenic carbon of -0.50 to -0.66 (Löwdin) or -1.05 to -1.23 (Mulliken) as the angles δ and ω are varied. Greater negative charge on the acetylenic carbon than on the ethylenic carbon seems more reasonable since acetylene is a better π acceptor than ethylene, and acetylenes also have a greater versatility for participating in the proposed synergic mechanism.^{4,5,11}

Since the structure of the molecule was kept rigid while the angle δ or ω was varied, the variation of overlap population with δ or ω may be attributed to population variations analogous to that of Blizzard and Santry.² Hence the population of certain orbitals definitely affects the equilibrium geometry for free or complexed acetylenes and olefins. From previous results^{4,5} and calculations by other methods² we are inclined to ascribe this phenomenon to population of

an orbital which in a higher symmetry environment could be characterized as a π -antibonding orbital of the organic moiety.

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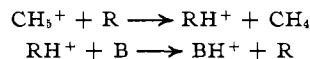
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The Proton Affinity of Borazine

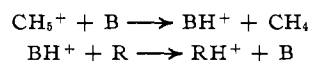
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Chemical ionization mass spectrometry is a relatively new technique that has been used to provide information on the proton affinities of molecules. To date this technique has been used almost exclusively for studies of organic molecules, but it should also be adaptable to inorganic systems. Borazine, an inorganic analog of benzene, has been the subject of many theoretical and experimental investigations. We recently reported results of a chemical ionization study of borazine that indicates that the proton affinity of this molecule was in excess of 7.7 eV.¹ More quantitative measurements of the proton affinity of borazine may be relevant to both its electronic structure and its chemical properties. To establish upper and lower boundaries on the proton affinity of borazine it is necessary to observe reactions in which protonated borazine is a proton donor and other reactions in which borazine is a proton acceptor. In order to study borazine by chemical ionization methods, it is essential that the carrier gases are chemically inert with respect to borazine. Since the choice of such gaseous reagents appears to be limited, we have devised a procedure involving the study of a three component gas mixture involving a small quantity of borazine (B), a small quantity of a second proton acceptor (R), and an excess of inert carrier gas. Since a large number of ions are produced in chemical ionization reactions when two hydrocarbons are present in a gas mixture, it is advantageous for purposes of establishing reaction sequences to use partially or totally deuterated compounds for one or two of the components. Two classes of reactions investigated were (1) reactions of a proton donor with borazine through the sequence



and (2) reactions of protonated borazine with a proton acceptor through the sequence



These reactions involve simple transfer of a proton between stable molecules and therefore no competing process is usually possible. Haney and Franklin² postulated that the nonoccurrence of reactions of this type is sufficient evidence of their endothermicity.

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