transition state calculated in eq 5. It is apparent that the magnitude of parameter f is similar for reactions 1-4. On the other

$$f = (\psi_{ii}^{\ddagger} - \psi_{ii}^{\mathrm{react}})/(\psi_{ii}^{\mathrm{prod}} - \psi_{ii}^{\mathrm{react}}) \qquad (5)$$

hand, the values are quite different for reaction 6; in particular the parameter for the N-C bond stretch is very small, which is consistent with the structure of the transition state (see Figure 1). It can be concluded from these results that the force constants are strongly related to the structure of the transition state. It seems reasonable therefore to assume that the magnitudes of kinetic isotope effects are a direct measure of the structure of the transition state.

Comparison with S_N2. Similar investigations have been reported for S_N2 reactions by Wolfe et al.[34] They calculated the structures and the energy of a series of methyl transfer reactions and found that the transition-state structure varies with the change in the reaction energy in a manner expected by the Bell-Evans-Polanyi-Leffler-Hammond rule: the more exothermic the reaction, the more closely the transition-state structure resembles the higher energy reactant. It was also demonstrated by Wolfe[34] and Murdoch[13a] that the Marcus relationship holds for the methyl transfer step between the two ion-molecule complexes of the double-well coordinate. In sharp contrast to the case of S_N2, the present reaction showed that the transition-state structure is essentially unchanged with the change in the reaction energy for reaction 1-5. It emphasizes the importance of the intrinsic barrier in governing substituent effects on the energetics and the geometries of the chemical reactions; the intrinsic barriers of the carbonyl addition reactions are, as described earlier in the Transition State Structure section, substantially larger than the changes in the endothermicity while the intrinsic barriers of S_N2 obtained by Wolfe and Murdoch are in many cases not large compared to the changes in endothermicity.[13a,34] The present study shows that an ab initio MO calculation is useful for increasing our knowledge on the principle of chemical reactions.

Summary

The results of the present study can be summarized as follows. (1) Except for the NHF_2-CH_2O case, the Bell-Evans-Polanyi-Leffler-Hammond rule holds energetically but the structure of the transition state is essentially unchanged. This indicates that the barrier height and the structure of the transition state correlate in different manners with the reaction energy. These results can be rationalized in terms of the magnitude of the intrinsic barrier of the reactions. (2) The differences in the structures of the transition state between the NHF_2-CH_2O case and others is consistent with the prediction based on the More O'Ferrall-Jencks diagram. (3) Both isotope effects and force constants are nicely related to the geometries of the compounds studied. Thus it can be concluded that the kinetic isotope effects are a good measure of the structure of the transition state.

Acknowledgment. Numerical calculations were carried out at the Computer Center of the Institute for Molecular Science.

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[34] Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7692-7694, 7694-7696.

Inductive Effects on the Electron Distribution of the Vinyl Group: A Correlation between Substituent Electronegativity and Bond Point Shift

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Abstract: The complementary merits of two theories are discussed in this paper. One is the perturbational molecular orbital (PMO) theory as applied to σ orbital systems, and the other is a theory of atoms in molecules, and their properties, based on the charge distribution. A case study of a series of substituted ethylenes is reported. It shows how the theory of atoms in molecules provides a useful tool for testing the extent to which PMO predictions concerning substituent effects are realized in good quality wave functions. Conversely it is shown that the PMO model provides a way of estimating—and thus partially understanding—the changes in atomic charges (as uniquely defined by the theory of atoms in molecules) that occur on substitution. Along the way a method of estimating group electronegativities is shown to arise naturally from the PMO treatment of inductive effects.

This paper reports ab initio wave functions at optimized geometries for a series of vinyl compounds and analyzes the electron distributions so obtained. The purpose of these calculations is to test a simple model of substituent inductive effects, namely Dewar's version of perturbational molecular orbital (PMO) theory[1] as applied to σ bonds.

Ab initio calculations provide more direct means for testing models of molecular behavior than experimental data such as equilibrium and rate constants. Thus, they can provide added insight into the accuracy and physical basis of models. The electron distribution is a particularly appropriate tool for the purpose as it enables the predictions of models to be measured against quantities which are well-defined, obtainable directly from experiment in principle, and physically meaningful. One way of obtaining such quantities is to employ a theory of atoms in molecules developed recently,[2] which provides definitions of atoms in molecules based on the topology (the general form) of the electron distribution. The atoms defined by this approach are

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[1] Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975.

[2] Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9-15. Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389-1395. Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 894-947.

0002-7863/86/1508-0606$01.50/0

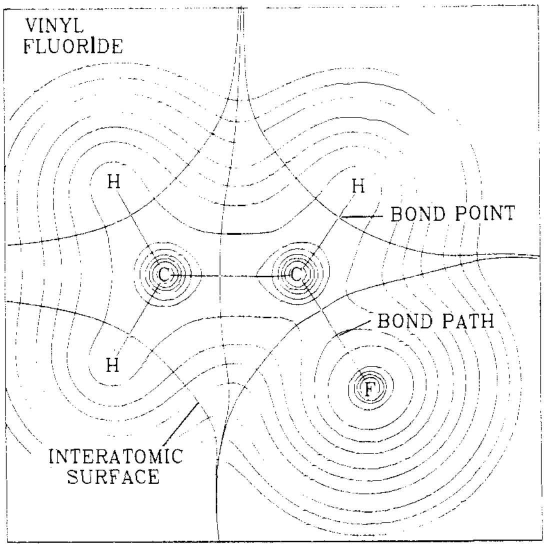

Figure 1. A contour plot of the electron distribution in the molecular plane of vinyl fluoride, from a 6-31G* wave function. The only maxima in the distribution occur at the nuclei. The "ridges" between bonded nuclei are called bond paths, and the lowest point on the ridge is called the bond point. The interatomic surface dividing neighboring atomic basins consists of the lines of steepest descent from the bond point.

"quantum subsystems"[3] and so have uniquely defined properties. In particular, if we wish to assign a unique energy to a bounded region of space then the atoms as defined by the theory of atoms in molecules emerge as the only such regions that can be defined and that contain a single atomic nucleus.[3]

The correlation of PMO-based expectations of changes in molecular electron distributions with the results of ab initio computations, as analyzed and described by the theory of atoms in molecules, provides two benefits: one being a method for judging the applicability of the PMO model to a particular case so that the need for additions and refinements to the theory can be better judged, and the other being a better understanding of the various factors that influence the properties of atoms in molecules.

The elements of the theory of atoms in molecules necessary for reading this paper are presented in the following section. The predictions of the PMO model as applied to vinyl systems are then outlined, and following a brief description of the computational methods employed the results are reported and discussed.

The Theory of Atoms in Molecules

Figure 1 illustrates the partitioning of a molecular charge distribution into atoms, so showing most of the elements of the theory used in this paper. A primary observation is that the only local maxima in the distribution occur at the positions of the nuclei. For molecules in the neighborhood of their equilibrium geometry the theory then defines when two atoms are bonded and when they are not: two bonded atoms are connected by a line (called the bond path) along which charge is a maximum to any transverse displacement (the three-dimesional equivalent of a ridge between two mountain peaks). For the more general case of an arbitrary geometry, the line of maximum charge density connecting two nuclei is called an interaction line, but this paper will be restricted to the study of equilibrium geometry molecules and so the term "bond path" is sufficient. Associated with each bond is a saddle point or "bond point", which is the lowest point on the "ridge". The network of bonds employed by the PMO model should thus correspond to the network of bonds as revealed by the electron distribution, if a reasonable localized orbital model has been chosen as the starting point for the PMO analysis.

The bond point is only symmetrically placed between two nuclei when the molecule is symmetric about that point, as in a homonuclear diatomic, or in the CC bond of ethylene. Shifts of the bond point toward one nucleus or another reflect a transfer of charge between the two atoms, with the bond point shifting toward the positive end of the bond dipole. Molecular dipoles are *not* always reflected in the atomic charges, however, as the atoms defined by the theory are in general not spherical and so have dipoles as well as net charges. The overall dipole of a molecule is given by the contribution from the atomic charges (centered at the nuclear positions) plus the contribution of the atomic dipoles. The necessity of including the atomic dipoles when estimating the electrostatic field due to the electron distribution, even when qualitatively assigning sites of attack on the basis of charges, must not be overlooked.

PMO Theory for σ Systems

It was recenly shown by Dewar[4] that if a localized bond model is adopted as an initial approximation to the electronic structure of hydrocarbons, and if the resonance integrals taken into consideration are not only those between hybrid orbitals on different nuclei but also those between hybrids on a given center, then PMO theory could be applied to σ orbital systems with only a few modifications from the familiar π orbital case. This model predicts the additive energies that are associated with "localized" bonds despite the energetically important interactions between geminal hybrid orbitals and also accounts for many anomalies in hydrocarbon chemistry, including deviations from additivity schemes in the case of methane and branched alkanes and also some ill-understood conformational problems.

One difference between PMO theory as applied to π systems and as applied to σ systems is that in the former case there is only one resonance integral in the problem as opposed to two in the latter, corresponding to geminal interactions (on the same center) and to bonding interactions (on neighboring centers). Herndon has shown[5] that the geminal resonance integral can be taken as 0.355 of the bonding resonance integral in alkanes and that this accounts for the more rapid damping of inductive effects than of π orbital effects. As reviewed below, an alternating pattern of formal charges on the hybrid orbitals is predicted by PMO theory when a heteratom substituent is introduced, and in the case of σ systems this leads to formal charges on the *atoms* that fall off monotonically from the site of perturbation or (equivalently within this model) to a monotonically decaying set of bond dipoles all pointing in the same direction. Thus the simple fact that in a σ system each center possesses two directional hybrid orbitals within the localized bond model (rather than the one orbital per center in the case of p_π systems) together with the difference in magnitude between geminal and "bond" resonance integrals leads to the familiar short range, monotonically decaying inductive effect rather than to the long range, alternating mesomeric effects produced in p_π systems. The similarity in formalism between the σ and π cases has led to the coining of the name "σ conjugation"[6] to describe the interaction between adjacent bonds.

In this case study of the σ PMO treatment of inductive effects on vinyl compounds the discussion is almost exactly analogous to the treatment of electromeric substituents in conjugated systems by π PMO theory. One immediate byproduct of the analysis is a new method for estimating group electronegativities for substituents with more than one heteratom from the electronegativities of the individual heteroatoms involved.

PMO Theory of Inductive Substituent Effects

In this section the PMO predictions of substituent effects on the hybrid orbital populations in a carbon–carbon bond are presented. There are two cases to consider: one where only one heteroatom is present, directly bonded to the substituted carbon, and a second where a substituent with more than one heteroatom is attached. Although the single heteroatom case is simple in itself, it is necessary to sketch the calculation in order to define the group electronegativity of substituents with more heteroatoms.

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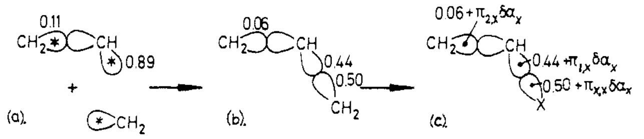
(3) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1982**, *14*, 62–124.

(4) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669–682.

(5) Herndon, W. C. *Tetrahedron Lett.* **1979**, 3801–3804; *J. Chem. Educ.* **1979**, 448–451.

Scheme I[a]



[a] Part (a) displays the populations of the atomic orbitals in the nonbonding molecular orbital (NBMO) of the vinyl radical, together with the methylene radical. The starred orbitals indicate the alternant nature of the systems and are the only orbitals with non-zero coefficients in the NBMO. In (b) these two are combined to give a semilocalized σ-bonding orbital of the allyl radical, and in (c) the CH_2 group is replaced by an isoelectronic substituent X, with an electronegatively differing from CH_2 by $\delta\alpha_X$. The populations of the atomic orbitals depend linearly on the electronegativity of the substituent. Refer to the text for a more detailed discussion of the populations and their changes.

In the PMO model of the combination of two odd alternant systems (in this case vinyl radical and substituent), the only two orbitals that are significant are the nonbonding molecular orbitals (NBMO's) of the two systems. An estimate of the relative effects of substituents on the CC bond can be obtained by first combining the vinyl NBMO (ϕ_{Vi}) with a single hybrid orbital (ϕ_{CH2}) of the same energy to obtain one of the orbitals of the "alternant hydrocarbon" system isoconjugate with the substituted vinyl compounds in which we are interested and then altering the electronegativity of the substituent orbital to that of the heteratom as a second perturbation. Both perturbations yield first-order changes to the system and so can be summed to give the total effect. The process is depicted in Scheme I.

The distribution of electronic charge in the vinyl radical NBMO (ϕ_{Vi}) is easy to obtain within the "C-approximation",[1] i.e., neglecting the CH bonds which are peripheral to the problem of the substituent's effect on the CC bond. With Herndon's value[5] of $m = 0.355$, the unbonded hybrid orbital on the CH carbon (C1) has a population of 0.887 and the CC bonding hybrid orbital on the CH_2 carbon (C2) has a population of 0.111. The other hybrid orbital in the system, the bonded hybrid on C1, has zero population as a consequence of the alternant nature of the system. The orbital of the combined (vinyl + CH_2) system is given by

$$\phi_{ViCH2} = 2^{-1/2}(\phi_{Vi} + \phi_{CH2}) \qquad (1)$$

and so has a distribution of 0.056 in the C2 carbon hybrid, 0.444 in the previously unbonded C1 hybrid, and 0.500 in the substituent hybrid orbital ϕ_{CH2}. The change in the population of a hybrid orbital i (δq_i) on substituting ϕ_{CH2} with an orbital ϕ_X of different electronegativity is given to first order by

$$\delta q_i = \pi_{i,X}\delta\alpha_X \qquad (2)$$

where, within the frontier orbital approximation we are using, the atom–atom polarizability[8] is given by

$$\begin{aligned}\pi_{i,X} &= -4a_ib_ia_Xb_X/2ab\beta \\ &= -2.123a_ib_ia_Xb_X/\beta \\ &= -1.06a_ib_i/\beta \end{aligned} \qquad (3)$$

where a_i and b_i are coefficients of basis function i in the antibonding and bonding MOs, a and b are the coefficients in the radical MOs of the interacting hybrid orbitals, and where $\delta\alpha_X = \alpha_X - \alpha_C$, with α_C being the Coulomb integral for an sp^2 hybrid on a neutral carbon atom.

The resulting changes in hybrid orbital populations are $-0.059\delta\alpha_X/\beta$ for the hybrid orbital on the unsubstituted C2 and $-0.470\delta\alpha_X/\beta$ for the CX bonding hybrid on the substituted C1. As we shall see, the proportionality constant is needed in order to extend the correlation of polarization of the CC bond with substituent electronegativity to substituents with more than one heteroatom.

The cyano and formyl substituents require the combination of two vinyl radical NBMO's, followed by the alteration of the coulomb integral of the terminal atom for CH═O and of both atoms for CN to obtain the final distribution in the substituted vinyl compound. The results are, for the formyl group,

$$\delta q = -0.007\delta\alpha_O/\beta \qquad (4)$$

which can be rewritten so as to take the same form as the expression for the single orbital substituents, eq 2

$$\delta q = -0.059(0.119\delta\alpha_O)/\beta \qquad (5)$$

so that the effective electronegativity of the formyl group is given by

$$\alpha_{CHO} = 0.119\alpha_O + 0.881\alpha_C \qquad (6)$$

For the cyano group there are two heteroatoms, as the sp hybridized carbon is more electronegative than the sp^2 hybrids which form the unperturbed system, and the result is

$$\begin{aligned}\delta q &= -0.007\delta\alpha_N/\beta - 0.052\delta\alpha_C/\beta \\ &= -0.059(0.119\delta\alpha_N + 1.135\delta\alpha_C)/\beta\end{aligned} \qquad (7)$$

so that

$$\alpha_{CN} = 0.119\alpha_N + 1.135\alpha_{C(sp)} - 0.254\alpha_C \qquad (8)$$

Using the group electronegativities defined here, we can see that PMO theory predicts a linear correlation between change in the population of the orbitals in the substrate and the electronegativity of the substituent. Of course, as we have used a first-order treatment this result was clear for the single orbital substituents without going through the whole calculation, but the calculation was needed in order to find out how the larger substituent groups behaved.

CH bonds can be included in this problem with few alterations from the C approximation.[5,7] If the approximation is made that the resonance integrals are the same for either type of bond, then the combination of the two NBMO's will lead again to the linear dependence on group electronegativity that was seen for the C approximation.

σ Conjugation and the Electron Distribution

The changes in populations of the hybrid orbitals predicted by PMO theory should correlate with a shift in the position of the bond point toward the formally positive end of the bond dipole, if the PMO model does indeed reflect actual changes in the electronic structure of these molecules. What is more, this shift in bond point should give a first approximation to the changes in the charges of the atoms, for two reasons. First, as bond points in unstrained bonds are positioned on the internuclear axis the density at such a bond point is, within the Hückel model, entirely "σ density" and hence atomic populations should respond to inductive effects more than to mesomeric effects. Second, π substituent effects on the double bond (an "even alternant hydrocarbon") are only second order, being principally from the "π inductive effect"[1] within the PMO scheme. Thus we may expect a correlation between atomic charges as well as bond point position with the changes in hybrid orbital populations.

More can be said about the nature of the correlation between bond point shift and the change in population of the interacting vinyl orbital by using another first-order approximation model. Consider the unperturbed charge density, $\rho^0(x)$, and choose a coordinate system such that the x axis is along the CC bond, with the substituent at positive x. We know that the position of the bond point, x^0, is given by the condition

$$\partial\rho^0(x^0)/\partial x = 0 \qquad (9)$$

The bond point in the substituted system, x^1, will be given by the analogous condition for the perturbed charge distribution $\rho^1(x)$. The two charge densities are related by

$$\rho^1(x) = \rho^0(x) + \delta q_i\rho_i(x) \qquad (10)$$

where $\rho_i(x)$ is the density of the hybrid orbital ϕ_i at x. If we now model the profile of the unperturbed charge density along the bond

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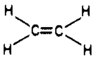
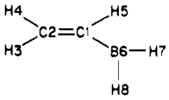
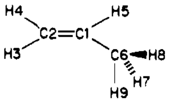
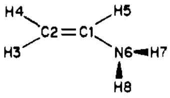
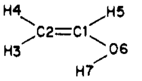
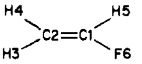
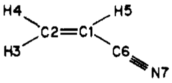
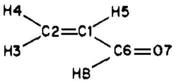
(6) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 95–967.

(7) Sandorfy, C. *Can. J. Chem.* **1955**, *33*, 1337–1351.

(8) Dewar, W. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw Hill: New York, 1969; p 197.

Table I. Geometries and Energies of Substituted Vinyl Compounds, All Computed at the 6-31G*/6-31G* Level

molecule	geometrical parameters (Å, deg)	energy (hartrees)
	CC = 1.317, CH = 1.076, CCH = 121.82	−78.031718
	C1C2 = 1.3310, C2H3 = 1.0777, C2H4 = 1.0765, C1H5 = 1.0796, CB = 1.5506, BH7 = 1.1917, BH8 = 1.1926, CCH3 = 122.783, CCH4 = 121.336, CCH5 = 117.790, CCB = 121.080, CBH7 = 121.690, CBH8 = 119.502	−103.289707
	C1C2 = 1.3185, C2H3 = 1.0773, C2H4 = 1.0756, C1H5 = 1.0790, C1C6 = 1.5026, C6H7 = 1.0869, C6H9 = 1.0843, CCH3 = 121.866, CCH4 = 121.644, CCH5 = 121.911, CCC = 125.253, C1C6H7 = 110.922, C1C6H9 = 111.425, C1C2C3H7 = 120.609	−117.071472
	C1C2 = 1.3218, C2H3 = 1.0733, C2H4 = 1.0768, C1H5 = 1.0766, CN = 1.3931, NH7 = 0.9974, NH8 = 0.9983, CCH3 = 120.522, CCH4 = 122.125, CCH5 = 119.961, CCN = 126.752, CNH7 = 114.082, CNH8 = 114.244, CCNH7 = 144.975, CCNH8 = 15.937	−133.061699
	C1C2 = 1.3176, C2H3 = 1.0726, C2H4 = 1.0770, C1H5 = 1.0735, CO = 1.3473, OH7 = 0.9483, CCH3 = 120.145, CCH4 = 122.308, CCH5 = 122.437, CCO = 126.920, COH7 = 110.394	−152.888887
	C1C2 = 1.3084, C2H3 = 1.0728, C2H4 = 1.0735, C1H5 = 1.0720, CF = 1.3289, CCH3 = 119.716, CCH4 = 121.513, CCH5 = 125.701, CCF = 122.362	−176.881952
	C1C2 = 1.3201, C2H3 = 1.0739, C2H4 = 1.0741, C1H5 = 1.0739, C1C6 = 1.4432, C6N7 = 1.1363, CCH3 = 120.707, CCH4 = 121.918, CCH5 = 122.088, CCC = 122.144, C2C1N7 = 122.445	−169.768016
	C1C2 = 1.3211, C2H3 = 1.0769, C2H4 = 1.0745, C1H5 = 1.0755, C1C6 = 1.4784, C6O7 = 1.1897, C6H8 = 1.0948, CCH3 = 121.532, CCH4 = 122.099, CCH5 = 122.360, CCC = 121.254, CCO = 123.838, O7C6H8 = 120.879	−190.762426

(x) axis by a Taylor expansion up to quadratic terms in the region of the bond point, i.e.

$$\rho^0(x) = \rho^0(x^0) + \lambda(x-x^0)^2/2 \qquad (11)$$

then the position of the bond point in the perturbed density is given by

$$\partial\rho^1(x^1)/\partial x = \partial\rho^0(x^1)/\partial x + \delta q_i \partial\rho_i(x^1)/\partial x = 0 \qquad (12)$$

so that

$$\begin{aligned} x^1 - x^0 &= -\delta q_i(\partial\rho_i(x^1)/\partial x)/\lambda \\ &= 0.059\delta\alpha_X\ (\partial\rho_i(x^1)/\partial x)/\lambda\beta \\ &= c\delta\alpha_X/\lambda, \text{ with } c = 0.059(\partial\rho_i(x^1)/\partial x)/\beta \end{aligned} \qquad (13)$$

No explicit form is given to the hybrid orbitals within the Hückel model and so the $(\partial\rho_i(x^1)/\partial x)$ factor is undefined. If its value is approximated as a negative constant over the region of interest then the shift in bond point should be proportional to the change in electronegativity of the substituent with an increase in substituent electronegativity leading to a shift in bond point position toward the unsubstituted carbon. Also, the shift is inversely proportional to the curvature of the electron density at the unperturbed bond point position. This result explains the greater population changes observed in unsaturated organic systems as compared to saturated systems in previous work,[9] as the curvature of the charge density along the bond is much less in double bonds than in single bonds. In the present paper the implication is that shifts in CH bond points ($\lambda = 0.47$ in ethylene) should be considerably less than those in the CC bond ($\lambda = 0.19$ in ethylene). It also reemphasizes the fact that such changes in populations do not *necessarily* imply large dipole moments or large charge separations within the molecule.

Computational Details

In this paper I wish to show the extent to which the predictions of the PMO model when applied to the inductive effects of substituents are realized in good quality ab initio wave functions. To this end, a series of calculations was carried out on the vinyl group with a variety of substituents attached, namely the isoelectronic series F, OH, NH_2, CH_3, and BH_2, as well as CH═O and CN. The calculations were carried out by using the GAUSSIAN 80[10] program with a set of standard options. All calculations employed the 6-31G* basis set with extensive gradient geometry optimization also at the 6-31G* level: only C_s symmetry was assumed, all other parameters were allowed to relax, and in vinylamine the NH_2 group was allowed to pyramidalize. The convergence criterion for maximum displacement of a nucleus was 0.018 Å and the largest allowed force constant was 0.000 45 atomic units.

The analysis of the electron distributions was carried out by using the PROAIMS series of programs developed in this laboratory,[11] again with use of only standard options. The positions of the critical points are evaluated with an accuracy of 10^{-12} au, and the numerical integrations over the atomic basins that are needed to obtain the atomic charges and other properties were carried out such that the integral of $\nabla^2\rho$ over the atom (which would be zero if the integration was exact) was less than $5 \times 10^{-3} a_0^{-5}$. This criterion is not directly related to the atomic charges themselves: the only direct test on these being how closely they summed to the total number of electrons in the system. They all satisfied this requirement to within 0.005 e, so that an uncertainty in the population of any one atom should be in the order of 10^{-3} e.

Results and Discussion

The geometries of the molecules studied are presented in Table I. Two features are of note: first, the changes in CC bond length are extremely small, covering a range of less than 0.05 au, and the changes in carbon hydrogen bond lengths are likewise small, a range of less than 0.02 au. These facts have been noted before in studies at a lower quality basis set.[11] Some trends are apparent, however, as shown in Figure 2 which correlates the CC bond length with the electronegativity of the substituent. Despite the scatter, an underlying trend of shorter bond length with increasing electronegativity of substituent is apparent and can be explained by noting that the substituted carbon becomes more electronegative

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[9] Bader, R. F. W., Tang., T.-H., Tal, Y., Biegler-König, F. W., *J. Am. Chem. Soc.*, **1982**, *104*, 946–952.

[10] Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topio, S.; Kahn, L. R.; Pople, J. A., Indiana University, Quantum Chemistry Program Exchange, Program No. 421.

[11] Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H., *J. Comput. Chem.* **1982**, *13*, 317–328.

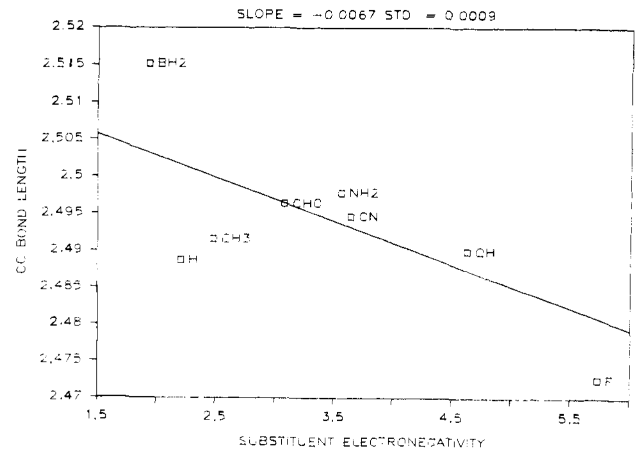

Figure 2. CC bond length (in atomic units) plotted against the electronegativity of the substituent (using the Pauling scale). In this and all subsequent graphs the slope indicated is the least-squares fit, and "STD" is the standard deviation of the slope, calculated with y as the dependent variable.

as the CX bond polarity increases. This should lead to an increase in the CC bond resonance integral, which is often taken to be related to the mean of the coulomb integrals of the two orbitals involved in the bond and so to an increasing bond strength. This effect is countered by the overall removal of charge from the bond region by the substituent, leading to the very small changes in length observed. The lack of any correlation with the predictions of π orbital models has been noted before.[12]

As discussed above, the PMO model predicts that the population of the hybrid on the unsubstituted carbon (C2) would be reduced by an amount proportional to the electronegativity of the substituent as a result of the bond dipole created in the CX bond, and this should be reflected in a shift of the bond saddle point toward C2 for electron-withdrawing substituents. The actual results are shown in the graph in Figure 3A. The variation in the shift is over a range of 0.7 au, so that the variations of CC bond length will not noticeably affect the correlation observed, being a factor of almost 20 smaller. As always, there is some ambiguity in the values of electronegativities chosen: I have chosen Mulliken's definition, assuming sp hybridization for N in CN, sp^2 for O in CHO, 23% s for N in NH_3 (the standard value for ammonia), 20% s for O in OH (the standard value for water), s^2p^5 for F, and sp^2 for B in BH_2.[13] The correlation between the shift in bond point position and electronegativity that is predicted by the PMO model is reasonably good, especially considering the drastic approximations made in the model. There is some noticeable scatter, which appears to give π withdrawing substituents (CN, CHO, and BH_2) lower shifts than expected.

A correlation between the charge on the CH_2 group and the substituent electronegativity value would also be expected if the shift in bond point caused by the inductive effect of the substituent is indeed the principal change in the electron distribution affecting the population. Figure 4A shows this correlation, which is as good as that of the bond point shift itself. What is more, as the CC shift is larger than the CH shifts a correlation exists between the charge on C2 itself and the electronegativity: see Figure 4B.

These results provide us with two conclusions of interest. One is that the PMO model of inductive effects gives a remarkably good picture of actual changes in molecular electron distributions considering the simplicity of the model. Second, we now have a semiempirical way of estimating the charge on the unsubstituted carbon atom in these systems. This provides us with a possible route to a relationship between the well-defined atomic charges of the theory of atoms in molecules and qualitative orbital models of electronic structure, thus enhancing our understanding of these charges.

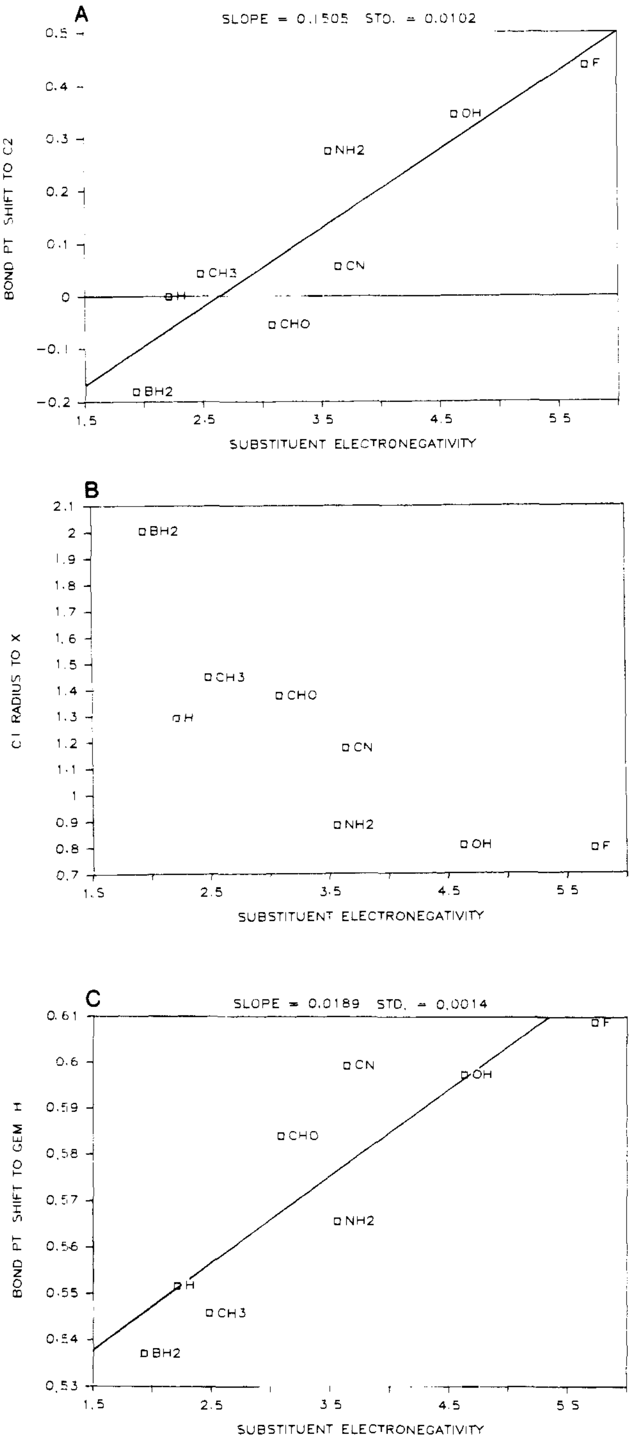

Figure 3. In all three graphs the electronegativity is that of the substituent, on the Pauling scale. (A) The "bond point shift" is the difference between the distance from the bond point to the C1 nucleus and the distance from the bond point to the C2 nucleus. It is plotted in atomic units. (B) "C1 radius to X" is the distance from the carbon nucleus to the CX bond point. (C) The bond point shift to the geminal hydrogen is the difference between the distance from the bond point to the C1 nucleus and the distance from the bond point to the H nucleus.

Let us now look briefly at the effects of substitution on the other atoms and bonds in the system. Figure 3B shows the correlation between substituent electronegativity and the distance from the carbon nucleus to the CX bond point. The more electronegative the substituent, the more the carbon bonded radius is decreased, but a limiting value is reached where the bond point is essentially shifted right to the core of the carbon atom, and all the valence charge in the bond is assigned to the heteroatom. This does not

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[12] Marriott, S.; Topsom, R. D. THEOCHEM **1984**, *109*, 305–310.

[13] The values are tabulated in the following: Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978. Purcell, K. F.; Kotz, J. C. "An Introduction to Inorganic Chemistry"; Saunders College; Philadelphia, 1980.

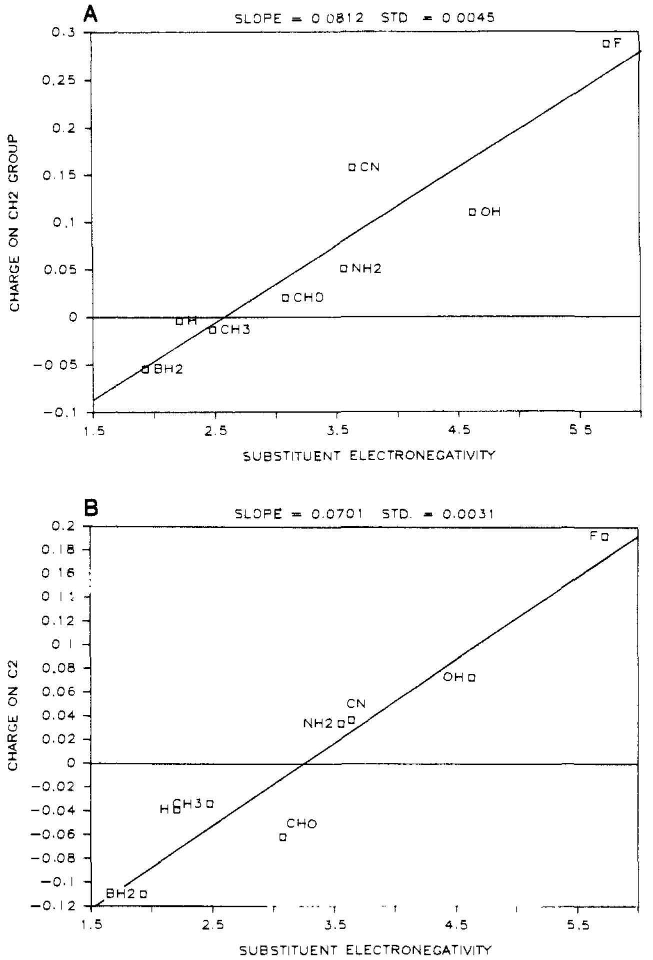

Figure 4. The charge in these graphs is in units of electrons. The electronegativity is plotted as in preceding figures.

imply ionic bonding; the following should be noted: there is a substantial electron density at the bond point in contrast to ionic bonds. Thus, these bonds are very polar but are still "shared" interactions.[14]

The geminal CH bond should show similar behavior to the CC bond except that the shift in bond point position will be smaller due to the substantially larger curvature of the density along the bond at the saddle point in this case. As in the case of the CC bond, the shift in bond point position is an order of magnitude larger than the variation in bond length and so can be discussed in an essentially unambiguous manner. The graph in Figure 3C shows the results of the calculations. Again, the correlation is reasonable and the trend unmistakeable.

The discussion of the shifts in bond point positions, of the atomic charges, and how these quantities respond to substitution has been the main concern of this paper, but two other quantities that arise in the study of bond points should also be mentioned. The *ellipticity* of a bond point is defined[15] by the ratio of the two principal curvatures perpendicular to the bond path. If these are denoted λ_1 and λ_2 in decreasing magnitude (both are negative) then the ellipticity is given by

$$\epsilon = \lambda_1/\lambda_2 - 1 \tag{14}$$

and is zero for a single CC bond, increasing with the "π character" of the bond to a value of 0.45 for ethylene (at the 6-31G* basis set). In the paper that introduced this quantity[15] ϵ was related to the "π character" of a bond, as it reflects the deviation of the charge at the bond point from the cylindrical symmetry found in single bonds.

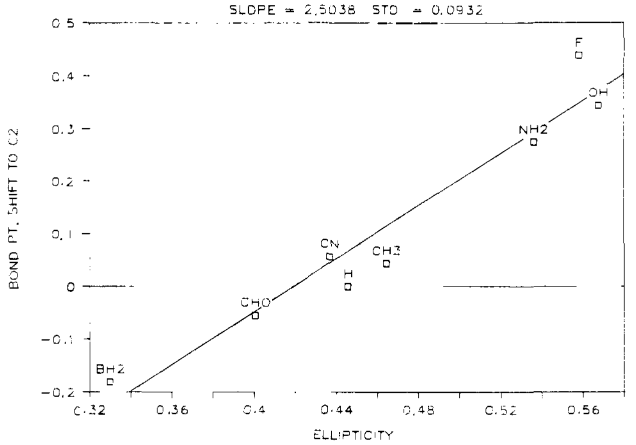

Figure 5. A correlation is shown between the bond point shift as defined in Figure 3A and the ellipticity of the carbon bond, defined in the text. Both quantities are plotted in atomic units.

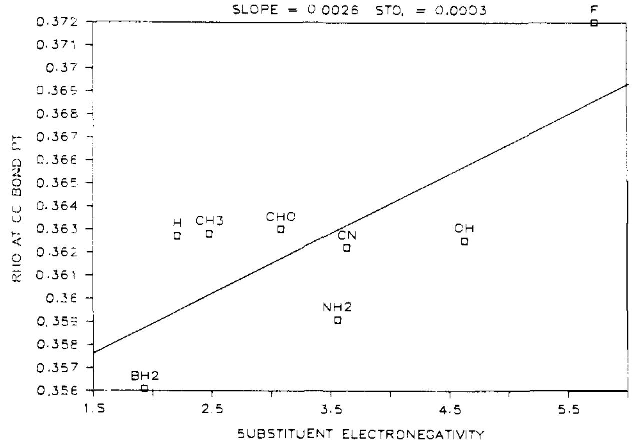

Figure 6. The charge density at the CC bond point in atomic units is plotted along the *y* axis. There is little correlation with the electronegativity of the substituent, a result that is expected: see the text for explanation.

Table II. Bond Length and Charge Density at the CC Bond Point for the Substituted Ethylenes (There Is Essentially No Correlation between the Two)

substituent	CC bond length (a_0)	ρ at bond point (a_0^{-3})
H	2.49	0.3627
F	2.47	0.3720
OH	2.49	0.3635
NN2	2.50	0.3591
CH3	2.49	0.3628
BH2	2.52	0.3561
CN	2.49	0.3622
CHO	2.50	0.3630

Figure 5 shows that the ellipticity of a CC double bond is related to the shift in bond point position: the more the bond point shifts to the unsubstituted carbon atom the larger ϵ becomes. Although the PMO model does not quantitatively lead us to expect such a relationship, it can be rationalized within that model. We have seen that the shift of bond point to the unsubstituted carbon is associated with the removal of charge from the sp^2 hybrid on that carbon and also with a polarization of the π cloud toward the unsubstituted end of the bond. Both these effects would be expected to increase the ratio of π density to σ density in the region of the bond point and so increase the "π character" of the bond point, increasing ϵ.

In previous works correlation between charge density at the bond point and bond length[9] or bond order[15] have been noted over a wide range of CC bonds. Within the very small length range of the current series of CC double bonds the correlation with bond length is not good (these results are tabulated in Table II). It

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(14) Bader, R. F. W.; Essén, H. F. B. *J. Chem. Phys.* **1984**, *80*, 1943–1960.

(15) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061–5068.

is interesting to note also that the PMO model predicts the charge density at the new bond point to be given by, using the approximations mentioned above,

$$\begin{aligned} \rho^1(x^1) &= \rho^0(x^1) + \delta q \rho_i(x^1) \\ &= \rho^0(x^0) + \lambda(x^1 - x^0)^2/2 - c\delta\alpha_X \rho_i(x^1)/\lambda \\ \Rightarrow \quad \delta\rho &= c^2\delta\alpha_X{}^2/2\lambda - c\delta\alpha_X \rho_i(x^1)/\lambda \end{aligned} \qquad (15)$$

so that no simple linear correlation between $\rho(x)$ and electronegativity of the substituent is expected. The computations show (see Figure 6) that none is found.

In summary, it has been shown that the theory of atoms in molecules based on the electron distribution provides a useful tool for investigating in a quantitative manner the extent to which the predictions of qualitative orbital models concerning the changes in the electronic structure of selected systems are realized. Conversely, it has been shown that with a little thought and the use of "back of the envelope" calculations, trends in the well-defined properties of the electron distribution arising from the theory of atoms in molecules can be accounted for in a manner consistent with current models of molecular electronic structure. Further studies will extend this approach to the analysis of trends in energies of reaction of ethylenes and to other groups.

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Migratory Aptitude of Hydride and Methyl toward Carbon Monoxide, Thiocarbonyl, and Carbene in $RMn(CO)_4XY$ (XY = CO, CS, CH_2; R = H, CH_3). A Theoretical Study by the Hartree–Fock–Slater Transition-State Method

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Abstract: A theoretical study based on the Hartree–Fock–Slater method has been carried out on the intramolecular migration of hydride and methyl toward CO, CS, and CH_2 in $RMn(CO)_4XY$ (R = H, CH_3; XY = CO, CS, CH_2). The elusive hydride migration reaction to CO with a calculated enthalpy of $\Delta H_4 = 159$ kJ mol^{-1} was found to be considerably more endothermic than the corresponding methyl migration ($\Delta H_5 = 75$ kJ mol^{-1}) as well as the migrations of H and CH_3 to CS with calculated enthalpies of $\Delta H_{6b} = 71$ kJ mol^{-1} and $\Delta H_{6a} = 20$ kJ mol^{-1}, respectively. Exploratory calculations along the paths of the four migratory reactions revealed only minor activation barriers. It is concluded that the coordinatively unsaturated 16-electron formyl and acyl complexes $RC(O)Mn(CO)_4$ (R = H, CH_3) can interconvert readily from the square pyramidal monohapto conformation initially formed in the migration process to a dihapto structure and that the dihapto geometries are 79 and 68 kJ mol^{-1} more stable for formyl and acyl, respectively. The corresponding dihapto stabilizations for the thioformyl and thioacyl complexes are 130 and 136 kJ mol^{-1}, respectively. The hydride and methyl migrations to CH_2 with $\Delta H_{7b} = -113$ kJ mol^{-1} and $\Delta H_{7a} = -71$ kJ mol^{-1} were both found to be exothermic processes.

The intramolecular migration (1) of an alkyl or aryl group R from a metal center to a cis carbon monoxide ligand

$$L_nRM{-}CO \rightarrow L_nM{-}C(O)R \qquad (1)$$

comprises among the class of organometallic shift reactions 2

$$L_nXM{-}Y \rightarrow L_nM{-}Y{-}X \qquad (2)$$

where a group X bound to the metal center migrates to an unsaturated ligand Y (Y = C_2, CO_2, C_2H_4, etc.), one of the more synthetically useful and well-studied[1,2] examples.

The corresponding shift reaction (3)

$$L_nHM{-}CO \rightarrow L_nM{-}C(O)H \qquad (3)$$

with hydride instead of alkyl has, although inferred[3] in substituted reactions on $HMn(CO)_5$ and $HCo(CO)_4$, proven to be rather elusive, and it has in spite of considerable efforts[4] only been possible to detect a 1,2-shift rearrangement (3) in a hydrido metal carbonyl to the corresponding formyl complex conclusively in a few cases.[5]

The apparent poor migratory aptitude of hydride toward CO (3) in comparison to methyl seems surprising in view of the fact that hydride appears[6] to be on a par with methyl as a migratory group toward other ligands such as CO_2, CS_2, CS, and CH_2. Recent experimental investigations[4a,7] have indicated that (3)

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[1] (a) Coffield, T. H.; Kozikowski, J.; Closson, R. D. *J. Org. Chem.* **1957**, *22*, 598. (b) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (c) McHugh, T. M.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2323. (d) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J Am. Chem. Soc.* **1981**, *103*, 4411. (e) Butler, I. S.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074. (f) Demuynck, J.; Kochanski, E.; Veillard, A. *J. Am. Chem. Soc.* **1979**, *101*, 3467.

[2] (a) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (b) Feder, H. M.; Ratheke, J. M.; Chen, M. J.; Curttiss, L. A. *ACS Symp. Ser.* **1981**, *No. 152*, 19. (c) Bellagamba, V.; Ercoli, R.; Bamba, A.; Suffritti, G. B. *J. Organomet. Chem.* **1980**, *190*, 381. (d) Saddei, D.; Freund, H. J.; Hohlneicher, G. *J. Organomet. Chem.* **1980**, *186*, 63. (e) Howell, J. M.; Olsen, J. F., unpublished results quoted in ref 2a. (f) Fonnesbech, N.; Hjorikaer, J.; Johansen, J. *Int. J. Quantum Chem.* **1977**, *12*, 95. (g) Anikin, N. A.; Bagatur Uants, A. A.; Shidomirov, G. M.; Kazanskii, V. B. *Russ. J. Phys. Chem. (Engl. Transl.)* **1983**, *57*, 393. (h) Nakamura, S.; Dedieu, A. *Chem. Phys. Lett.* **1984**, *111*, 243.

[3] Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.

[4] (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (b) Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. (c) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. (d) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

[5] (a) Wayland, B. B.; Duttahmed, A.; Woods, B. A.; Pierce, R. *J. Chem. Soc., Chem. Commun.* **1983**, 143-144. (b) Fagan, P. J.; Manriquers, J. M.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 2206. (c) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051.

[6] Collman, H. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980, pp 259-315.

[7] (a) Lane, K. L.; Sallans, L.; Squires, R. R. *Organometallics* **1984**, *4*, 408. (b) Connor, J. A.; Zafarani-Moattar; Bickerton, J.; El-Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

0002-7863/86/1508-0612$01.50/0