as a polarization of π electrons by the lithium cation that gives partial lone-pair character to each carbon with concomitant bending away of C–H bonding electrons. This interpretation implies that, in those organometallic ring compounds in which hydrogens bend towards a central metal, bonding is predominantly covalent rather than ionic; that is, the corresponding rehybridization at each carbon is such to improve the directional character of orbitals used for ring-metal covalency. If this interpretation is correct, it has the important corollary of providing an operational approach to the determination of ionic and covalent character of ring-metal bonding in organometallic ring compounds. By this criterion, for example, the bending of methyl groups[31] toward the central uranium atom in bis(η-1,3,5,7-tetramethylcyclooctatetraene)uranium(IV) is indicative of covalent bonding in the uranocene ring system.

Finally we note the predicted dissociation energy of CpLi. Using the double ζ basis, we find CpLi to lie 167.2 kcal[32] below infinitely separated $Cp^- + Li^+$. By subtracting the experimental ionization potential (124.3 kcal) of Li atom and adding the electron affinity of Cp (42.4 kcal)[33] we find a dissociation energy of 85.3 kcal for the process

$$Li(C_5H_5) \rightarrow Li + C_5H_5$$

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Model Organometallic Systems. The Interaction of ^2S Be^+, ^1S Be, and ^3P Be with Acetylene and Ethylene[1]

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Abstract: To model the interaction between metal atoms and unsaturated hydrocarbons, several electronic states of the Be–C_2H_2 and Be–C_2H_4 systems have been investigated using ab initio electronic structure theory. Double ζ basis sets have been used (after some experimentation with polarization functions) at the self-consistent-field level of theory. For ten different electronic arrangements, potential energy curves have been predicted for the perpendicular approach of the Be nucleus to the midpoint of the carbon–carbon bond. The interaction of Be^+ ion (ground ^2S state) with both acetylene and ethylene is attractive, yielding equilibrium Be midpoint separations of 2.03 and 2.09 Å and binding energies of 30 and 33 kcal/mol. In contrast the ^1S ground state of the neutral Be atom has an essentially repulsive interaction. The threefold degenerate excited ^3P state splits into $^3A_1$, $^3B_1$, and $^3B_2$ components as it approaches the ethylene molecule. The $^3B_2$ state is rather strongly bound, 19 kcal for Be–C_2H_2 and 25 kcal for Be–C_2H_4. The $^3A_1$ state is strongly repulsive, while the $^3B_1$ state assumes an intermediate role. These trends are readily explained by qualitative molecular orbital concepts.

During the past five years some of the most spectacular advances in chemical research have occurred in the areas of organometallic[2-5] and surface[6-10] chemistry. Much of the research in both these fields has as its goal a fundamental understanding of catalysis. Actually, neither type of research is precisely relevant to the understanding of the type of catalysts used most commonly in industrial processes. Such catalysts typically consist of finely divided metal particles[11-14] (containing perhaps 50 metal atoms) distributed on a support material, e.g., silica or alumina. Thus, it is apparent that catalytic organometallic cluster compounds[15,16] (with two, three, or four metal atoms) contain a smaller number of metal atoms, while the surface chemist's clean surface (of $\sim 10^{23}$ atoms) in fact has much less surface area per atom than the most effective industrial catalysts. In this sense it is not unreasonable to state that catalysis lies at the interface of organometallic chemistry with surface chemistry. The present research, although again probably not of immediate relevance to industrial catalysts, lies at this same interface between the organometallic and surface areas.

Hypothesis Concerning the Nature of the Surface Chemical Bond

The motivation for the present investigation came from several directions. Three years ago, in their theoretical study of the simple diatomic hydride manganese hydride (MnH), Bagus and Schaefer[17] made some interesting observations. The electronic ground state of MnH is known experimentally to be a $^7\Sigma^+$ state with electron configuration

$$\ldots\ldots 6\sigma^2\, 7\sigma\, 1\delta^2\, 3\pi^2\, 8\sigma \qquad {}^7\Sigma^+$$

The orbital energies obtained by Bagus and Schaefer in their near Hartree-Fock (i.e., using a very large basis set) study were -0.3979 (6σ), -0.6240 (7σ), -0.6560 (1δ), -0.6488 (3π), and -0.2689 (8σ). It was initially surprising that the doubly occupied 6σ orbital lies much higher than the singly occupied 7σ orbital. However, inspection of the wave function shows that the 7σ, 1δ, and 3π orbitals are essentially pure (although somewhat distorted) manganese 3d orbitals. That is the $3d^5\ {}^6S$ configuration of the atom is carried over directly to the diatomic hydride. The bonding may be thought to occur in the 6σ orbital, which is primarily a linear combination of Mn 4s, Mn 4p, and H 1s basis functions. The half-occupied σ orbital may be thought of as a 4s-4p hybrid nonbonding orbital. This simple picture has been supported by more recent ab initio calculations by Scott and Richards[18] and by Kunz and coworkers.[19]

Actually the above picture is not too surprising if one realizes that for transition metals V through Ni the atomic 3d orbitals lie considerably below the 4s orbital. For vanadium, the 3d and 4s orbital energies[20] are -0.510 and -0.231 hartrees, while for Ni the analogous results are -0.707 and -0.276 hartrees. It would be unwise, of course, to immediately assume that 3d orbitals play no role at all in the bonding of transition metal compounds. In many situations (e.g., in solution) the metal is able to shed its 4s electrons and the resulting M^{2+} ion has its 3d orbitals exposed for interactions of various kinds. For example, in the NiF_6 systems the Ni 4s basis functions are essentially unoccupied.[21] However, the point of the present argument is that this is less likely to be the case for transition metal surfaces and metal particles. Here the adsorbates are less likely to be sufficient in quantity and electron withdrawing ability to depopulate the 4s (and 4p) orbitals. The presence of 4s-4p bonds in bulk transition metals is certainly well established.[22] For these reasons, our research has for some time been motivated by the hypothesis that bonding in catalytic systems involves the 4s and 4p orbitals of the transition metals in question.

If the 3d orbitals of transition metals do not play the most important role, then one naturally raises the question, are there simpler metals which might show the same qualitative behavior? If, as model theoretical studies suggest, the key feature in the bonding is the presence (in the isolated metal atom) of a doubly occupied 4s orbital and a companion nearly degenerate (but unoccupied in the atom) 4p orbital, the answer is certainly yes. In this case the simplest example of a metal atom of this general type is the Be atom, with electron configuration $1s^22s^2$ and a $1s^22s2p\ {}^3P$ state lying at 2.72 eV = 62.7 kcal higher.[23] The Mg and Ca atoms also suggest themselves as models, but in the calcium case the proximity[23] of the 4s, 4p, and 3d orbitals could conceivably cause complications. Note, of course, that the 3d and 4s orbitals of V-Ni are much more widely separated than those of Ca. One must be very cautious not to push the analogy between Be and V-Ni surfaces too far, since there are many obvious differences. For example, the crystal structure of Be metal is hexagonal close packed, while that of V and Ni are body centered cubic and cubic close packed.

It is well to point out that several other groups have independently come to related qualitative conclusions concerning the role of 4s and 4p orbitals in transition metal clusters and surfaces. We have already noted the diatomic work of Richards[18] and Kunz[19] in this regard. Kunz and co-workers especially have gone into the implications of their results for catalysis. Considerably earlier and continuing work by Baetzold[24] has shown the d band of metal clusters of Pd, Ag, Cu, and Au to be rather narrow and considerably below the valence-like 4s-4p band. In their work on chemisorption of atomic hydrogen on nickel surfaces, Fassaert, Verbeek, and Van der Avoird[25] have emphasized the importance of 4s orbitals. Their conclusion for the Ni-H system has since been supported by the more sophisticated calculations of Blyholder[26] and by Melius and co-workers.[27]

In our theoretical research on metal clusters (as large as Be_{36}) we have studied[28] the chemisorption of atomic hydrogen at several possible sites on the (0001) surface. The most favorable of these allow chemisorptive bond energies of ~ 55 kcal/mol, a result in qualitative agreement with the values 60-70 kcal found experimentally for atomic hydrogen on transition metal surfaces. Thus the beryllium analogy is given further qualitative support. Although the most favorable site is *not* the directly overhead site (as previously assumed),[29] the predicted chemisorptive bond energy is nevertheless quite comparable to that for the diatomic BeH molecule, 48.8 ± 0.7 kcal.[30] The analogous correlation of diatomic hydride dissociation energies with transition metal-hydrogen chemisorptive bond energies is also qualitatively observed experimentally.[31,32] Thus, there may be some merit to the adoption of the diatomic molecule as a very rough model of the surface-adsorbed atom bond.

Theoretical Model

The latter model is obviously very attractive from a theoretical point of view, since the interaction between a single metal atom (even, e.g., an atom as heavy as platinum) and a single atom or molecule may be treated with a fair degree of theoretical rigor. In this spirit we have considered in the present research the interactions between several Be species (Be^+, ground state Be, and the $1s^2\ 2s\ 2p\ {}^3P$ excited state) and the simple organic molecules C_2H_2 and C_2H_4.

In principle the same insight into the surface chemical bond could be obtained by an experimental study of, e.g., the Ni-C_2H_4 molecule. Unfortunately, elementary organometallic molecules of this type appear extremely difficult if not impossible to prepare in the laboratory. An exception is the Ag-C_2H_4 species, whose ESR spectrum was recently reported by Kasai and McLeod.[33] In this light it should also be noted that molecules such as $Ni(C_2H_4)_3$ have recently been synthesized[34] and appear to have a fair degree of stability. In fact, our initial interest in the present class of molecules was spurred by the elegant qualitative molecular orbital treatment by Rösch and Hoffmann[35] of the molecules $Ni(C_2H_4)_n$, with $n = 2$, 3, and 4. However, it is probably true that the $Ni(C_2H_4)_3$ molecule, although fascinating in its own right, does not represent a good model for the nickel-ethylene chemisorptive bond, as the ratio of ethylene molecules to Ni atoms is too high. In addition, one naturally expects d orbital bonding involvement to be more important in such multiligand systems.

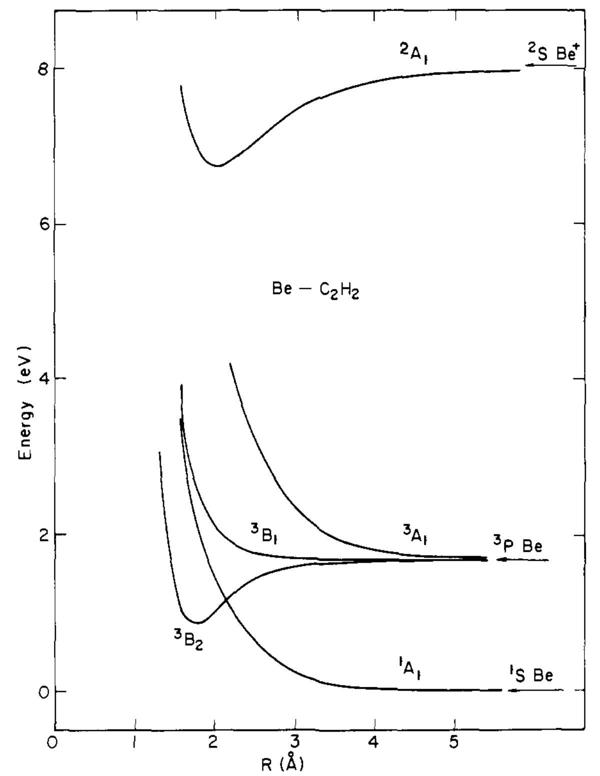

Figure 1. Theoretical potential energy curves for the approach of atomic beryllium to a rigid acetylene molecule. The Be atom approaches along the perpendicular bisector of the C≡C bond and R is the Be–bond midpoint separation.

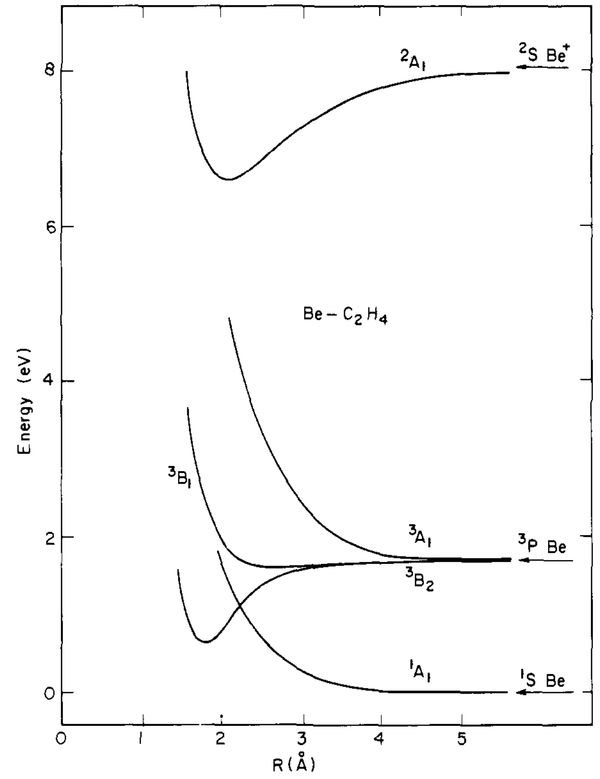

Figure 2. Theoretical potential energy curves for tlhe approach of atomic beryllium to a rigid ethylene molecule. R is the distance between the Be nucleus and the C=C bond midpoint. The chosen orientation of approach is on the line passing through the bond midpoint and perpendicular to the ethylene plane.

The goals of the present research then are first to begin to understand the nature of the transition metal surface-unsaturated hydrocarbon chemisorptive bond. In this vein it is possible that the bonding in systems such as Mn-C_2H_4 may be related to that of Be-C_2H_4. In time we plan to directly test this hypothesis. Second, we feel that compounds such as Be-C_2H_2 and Be-C_2H_4 are of fundamental importance in the development of a satisfactory theory[35] of bonding in organometallic systems.

Theoretical Details

Throughout this work the single configuration self-consistent-field (SCF) approximation has been consistently applied. All of the electronic states of Be-C_2H_2 and Be-C_2H_4 dissociate within this formalism to the appropriate SCF wave functions for the separated species. For this reason SCF predictions in these cases are expected to be qualitatively correct. Further, there is no ambiguity concerning the choice of electron configurations for these systems, since the 2s and 2p orbitals of Be lie considerably higher than any of the occupied molecular orbitals of C_2H_2 or C_2H_4. For the Be systems we have

$^2S\ Be^+$	$1s^2\,2s$	→	$1a_1^2\,2a_1$	$^2A_1$
^1S Be	$1s^2\,2s^2$	→	$1a_1^2 2a_1^2$	$^1A_1$
^3P Be	$1s^2\,2s\,2p$	→	$1a_1^2\,2a_1\,3a_1$	$^3A_1$
			$1a_1^2\,2a_1\,1b_1$	$^3B_1$
			$1a_1^2\,2a_1\,1b_2$	$^3B_2$

where the resolution[36] into the point group C_{2v} (of the Be-C_2H_2 and Be-C_2H_4 systems) is given explicitly. Similarly, for the acetylene molecule, the electron configuration

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^4 \qquad {}^1\Sigma_g^+$$

becomes in C_{2v} symmetry

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 2b_2^2\ 3a_1^2\ 4a_1^2\ 1b_1^2 \qquad {}^1A_1$$

For ethylene in full D_{2h} symmetry the ground-state electron configuration is

$$1a_g^2\ 1b_{1u}^2\ 2a_g^2\ 2b_{1u}^2\ 1b_{2u}^2\ 3a_g^2\ 1b_{3g}^2\ 1b_{3u}^2$$

which becomes, when resolved into C_{2v}

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 2b_2^2\ 1b_1^2\ 3a_1^2\ 1a_2^2\ 4a_1^2$$

The point group C_{2v} is appropriate, since we have assumed that the Be atom (ion) approaches along the line perpendicular to the ethylene plane and passing through the midpoint of the C=C bond. This is an obvious choice and is supported by the work of Rösch and Hoffmann[35] and by Basch's research[37] on the Ag^+-C_2H_4 complex.

Double ζ basis sets of contracted Gaussian functions were used in this work. For carbon the (9s5p/4s2p) Huzinaga-Dunning set[38,39] was adopted and the same procedure was used for the hydrogen (4s/2s) basis, which was scaled by a factor of 1.2 (i.e., each Gaussian exponent was multiplied by 1.44). For the Be atom Yarkony's (9s4p/4s2p) basis,[40] with s functions appropriate to $1s^22s^2$ and p functions optimized for $1s^22s2p\ ^3P$, was employed. For the Be^+-C_2H_4 case in particular we were concerned that the lack of polarization functions on ethylene might be a serious deficiency.[41] For this reason, several test calculations were carried out using s, p_x, p_y, and p_z primitive Gaussians ($\alpha = 1.0$) located at the ethylene bond midpoint. However, these proved to lower the energy by ~0.01 hartree both near the equilibrium geometry and for separated Be^+ plus C_2H_4.

In every case the geometries of the C_2H_2 and C_2H_4 molecules were frozen at their experimentally determined equilibrium values. For C_2H_2 this is[42] $r_e(CH) = 1.060$ and $r_e(CC) = 1.203$ Å, while for C_2H_4 we used[43] $r_e(CH) = 1.076$, $r_e(CC) = 1.330$ Å, and $\theta(HCH) = 116.6°$.

Most of the computations were carried out on the Harris Corporation Slash Four minicomputer, using the Cal Tech-

Table I. Predicted Structures of Several Bound Beryllium-Unsaturated Hydrocarbon Systems[a]

System	Be–bond midpoint separation, Å	Dissociation energy, kcal/mol
$^2A_1$ Be–$C_2H_2^+$	2.032	30.0
$^3B_2$ Be–C_2H_2	1.771	19.1
$^2A_1$ Be–$C_2H_4^+$	2.088	33.2
$^3B_2$ Be–C_2H_4	1.782	24.5

[a] Note that in each case the geometry of the acetylene or ethylene entity was constrained to be that known from experiment[42,43] for the isolated molecule.

Ohio State-Berkeley version of POLYATOM,[44] which employs the open-shell SCF methods of Goddard and co-workers.[45] In the latter stages the CDC 7600 of the Lawrence Berkeley Laboratory was used to bring this study to completion.

Results and Discussion

Our results for Be-C_2H_2 and Be-C_2H_4 are summarized in Figures 1 and 2. The similarity of these two sets of potential energy curves is certainly striking and one is forced to conclude that the double and triple bonds interact with a single metal atom in a very similar fashion.

Figures 1 and 2 show clearly that there is not a strong chemical bond between the ground states of the two neutral species, either for Be-C_2H_2 or Be-C_2H_4. The present theoretical results do not take into account electron correlation,[46] but in the present case (proper dissociation within the Hartree-Fock method) this should not be too important. That is, we would expect electron correlation to properly predict the weak (or van der Waals) attraction of Be to C_2H_2 and C_2H_4, but binding energies of more than ~5 kcal/mol would be surprising. The lack of a substantial chemical bond here seems quite clear in light of the diatomic MnH results of Bagus and Schaefer[17] (see also the discussions of Kunz, Guse, and Blint[19]). That is, the acetylene and ethylene molecules are relatively contented close-shell species and find little attractive in the doubly occupied 2s orbital of the beryllium atom. Chemical bonding will require the disruption of the $1s_2 2s_2$ Be electron configuration, or (less likely) the promotion of C_2H_2 or C_2H_4 to an excited electronic state. In the case of MnH, of course, it is the fact that the H atom 1s orbital is singly occupied which provides the mechanism for the disruption of the manganese $4s^2$ pair of electrons. In fact we would expect any monovalent radical (e.g., CH_3, NH_2, OH, or F) to be similarly bound to Mn.

Consistent with the above picture is the attractive well found for the Be^+-C_2H_2 and Be^+-C_2H_4 systems. The predicted equilibrium separations and dissociation energies for these species are given in Table I. As pointed out by Basch[37] in his paper on the Ag^+-C_2H_4 complex, there are at least two possible explanations for the origin of these potential minima. The first is some sort of chemical bonding and the second is a physical or classical electrostatic attraction due essentially to the Be^+ positive charge. Given our fascination in the chemistry of these systems, the latter type of attraction is much less interesting. Following Basch, in an attempt to sort out the contributions from the two effects, we have carried out analogous calculations with a bare positive charge P (or proton, with no basis functions centered on it) at the precise equilibrium positions of the Be^+ nuclei. Basch has already demonstrated that the shifts in orbital energies in the complex are essentially reproduced by such a bare positive charge at the analogous separation. Here we point out that the P-C_2H_2 and P-C_2H_4 systems are bound by 28.4 and 32.2 kcal at the appropriate proton-bond midpoint separations. Thus we see that using this criterion only 1.5 kcal of the binding in Be-$C_2H_2^+$ and 1.0 kcal of the dissociation energy of Be-$C_2H_4^+$ are due to "chemical" effects. Since these ion-molecule interactions are essentially of a classical electrostatic nature, they will not be discussed further here.

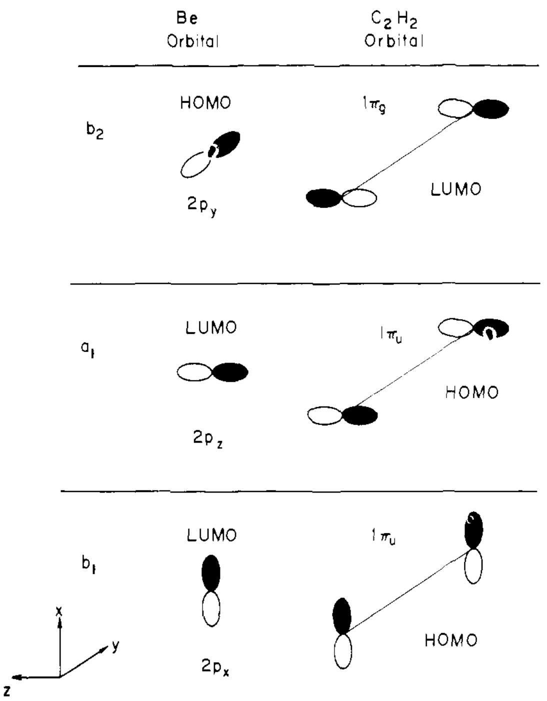

Figure 3. Symmetry matching of some of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of Be ^3P and the electronic ground state of acetylene, combining to form the $^3B_2$ state of Be-C_2H_2.

Certainly the most fascinating aspect of the present work is the interaction of the three components of the ^3P excited state of Be with the two organic molecules. In summary, one finds *very* different results for the three sets of potential energy curves. The $^3A_1$ curve is repulsive, the $^3B_1$ curve relatively flat, and the $^3B_2$ attractive. The latter case is especially interesting, since the attraction is clearly chemical in nature. The bonding must be similar in character for Be-C_2H_2 and Be-C_2H_4 since the equilibrium separations (1.77 and 1.78 Å) and dissociation energies (19.1 and 24.5 kcal) are quite comparable. In line with our earlier discussion, it seems clear that the disruption of the $2s^2$ pair (to 2s2p ^3P) is a key feature leading to the favorable attraction. However, it is equally obvious that this cannot be the only ingredient, since the other two states ($^3A_1$ and $^3B_1$) fall into the same category but do not display such a chemical well.

The key to understanding the differences between the $^3A_1$, $^3B_1$, and $^3B_2$ potential curves must then be the fact that the respective components of the Be 2p orbital are (in our coordinate system) $2p_z$, $2p_x$, and $2p_y$. That is, the $2p_z$ (or $7a_1$ orbital in $^3A_1$ Be-C_2H_2) orbital is directed from the Be nucleus to the midpoint of the carbon-carbon bond; the $2p_x$ ($2b_1$ in $^3B_1$ Be-C_2H_2) orbital is directed perpendicular to the plane of the Be-C_2H_2 complex; and the $2p_y$ ($3b_2$ in $^3B_2$ Be-C_2H_2) orbital is directed parallel to the C-C axis. This situation is shown perhaps more clearly in Figure 3. Also depicted in Figure 3 are the acetylene π orbitals of the analogous symmetries.

There are at least two plausible types of explanations[47,48] of the bonding between ^3P Be and acetylene (or ethylene). The first would involve the interaction between the highest occupied molecular orbital (HOMO) of beryllium, namely the 2p orbital, and the lowest unoccupied orbital (LUMO) of acetylene. From spectroscopic considerations it is well established[49] that the LUMO of acetylene is the $1\pi_g$ orbital, which has degenerate components (for C_{2v} point group) of a_2 and b_2 symmetry.

Table II. Orbital Energies (in hartrees) and Mulliken Populations for the $^3B_2$ Excited Bound State of Be–C_2H_2[a]

	Beryllium			Carbon			H		Beryllium			Carbon			H
Be–C_2H_2	s	p	Total	s	p	Total	s	Be + C_2H_2	s	p	Total	s	p	Total	s
1a$_1$ −11.2933	–	–	–	2.00	–	2.00	–	1σ_g −11.2627	–	–	–	2.00	–	2.00	–
1b$_2$ −11.2897	–	–	–	2.00	–	2.00	–	1σ_u −11.2590	–	–	–	2.00	–	2.00	–
2a$_1$ −4.6883	2.00	–	2.00	–	–	–	–	1s −4.7433	2.00	–	2.00	–	–	–	–
3a$_1$ −1.1143	0.02	0.02	0.04	1.67	0.26	1.93	0.03	2σ_g −1.0420	–	–	–	1.70	0.23	1.94	0.06
2b$_2$ −0.7973	–	0.01	0.01	0.74	0.58	1.32	0.67	2σ_u −0.7651	–	–	–	0.67	0.60	1.27	0.73
4a$_1$ −0.7119	–	–	0.01	0.13	1.22	1.35	0.64	3σ_g −0.6825	–	–	–	0.09	1.24	1.32	0.68
5a$_1$ −0.5295	0.15	0.13	0.28	0.02	1.69	1.71	0.01	1π_u −0.4147	–	–	–	–	2.00	2.00	–
1b$_1$ −0.4636	–	0.05	0.05	–	1.95	1.95	–	1π_u −0.4147	–	–	–	–	2.00	2.00	–
6a$_1$ −0.2997	0.75	0.25	1.00	–	–	–	–	2s −0.3939	1.00	–	1.00	–	–	–	–
3b$_2$ −0.2446	–	0.53	0.53	0.02	0.44	0.46	0.01	2p$_y$ −0.2411	–	1.00	1.00	–	–	–	–
Total Mulliken populations (per atom)	2.92	0.99	3.91	3.29	3.08	6.36	0.68		3.00	1.00	4.00	3.23	3.03	6.26	0.74

[a] Comparison is given with the appropriate orbitals of separated Be ^3P plus acetylene $^1\Sigma_g{}^+$. A dashed entry is indicative of a population less than 0.01.

Table III. Orbital Energies and Mulliken Populations for the $^3B_2$ Excited Bound State of Be–C_2H_4[a]

	Beryllium			Carbon			H		Beryllium			Carbon			H
Be–C_2H_4	s	p	Total	s	p	Total	s	Be + C_2H_4	s	p	Total	s	p	Total	s
1a$_1$ −11.2475	–	–	–	2.00	–	2.00	–	1a$_g$ −11.2407	–	–	–	2.00	–	2.00	–
1b$_2$ −11.2459	–	–	–	2.00	–	2.00	–	1b$_{1u}$ −11.2390	–	–	–	2.00	–	2.00	–
2a$_1$ −4.6978	2.00	–	2.00	–	–	–	–	1s −4.7433	2.00	–	2.00	–	–	–	–
3a$_1$ −1.0928	0.01	0.01	0.02	1.61	0.16	1.77	0.21	2a$_g$ −1.0421	–	–	–	1.64	0.12	1.76	0.24
2b$_2$ −0.8206	–	0.01	0.01	1.01	0.29	1.30	0.69	2b$_{1u}$ −0.7958	–	–	–	0.91	0.36	1.27	0.73
1b$_1$ −0.6766	–	0.02	0.02	–	1.28	1.28	0.70	1b$_{2u}$ −0.6492	–	–	–	1.24	–	1.24	0.76
4a$_1$ −0.6125	0.01	0.02	0.03	0.03	1.42	1.45	0.51	3a$_g$ −0.5908	–	–	–	1.47	0.02	1.49	0.51
1a$_2$ −0.5242	–	–	–	–	1.04	1.04	0.96	1b$_{3g}$ −0.5052	–	–	–	–	0.96	0.96	1.04
5a$_1$ −0.4856	0.20	0.13	0.33	0.02	1.64	1.66	–	1b$_{3u}$ −0.3776	–	–	–	–	2.00	2.00	–
6a$_1$ −0.2998	0.70	0.29	1.00	–	0.01	0.01	–	2s −0.3939	1.00	–	1.00	–	–	–	–
3b$_2$ −0.2535	–	0.42	0.42	0.01	0.56	0.57	0.01	2p$_y$ −0.2411	–	1.00	1.00	–	–	–	–
Total Mulliken populations	2.93	0.91	3.84	3.34	3.20	6.54	0.77		3.00	1.00	4.00	3.28	3.08	6.36	0.82

[a] Comparison is given with appropriate orbitals of separated Be ^3P plus ethylene $^1A_{1g}$.

Thus the only possible HOMO-LUMO pairing for ^3P Be-C_2H_4 would involve the 2p$_y$ orbital (b$_2$) with the b$_2$ component of the unoccupied acetylene 1π_g orbital. This interaction is sketched at the top of Figure 3. Since in fact the $^3B_2$ states of Be-C_2H_2 and Be-C_2H_4 are the only strongly bound states of these systems, the above consideration is given strong support. A bit later we will look at orbital energies and Mulliken populations with this simple picture in mind.

The second idea would involve some sort of electron donation from the acetylene HOMO to the LUMO of the excited Be atom. As shown clearly in Table II the degenerate 1π_u (with a$_1$ and b$_1$ components) is the highest occupied orbital of acetylene. Thus, as sketched in Figure 3, this type of "charge transfer" is possible from the 1π_u orbital to both the 2p$_x$ (b$_1$) and 2p$_z$ (a$_1$) orbitals of beryllium. However, it is well to note that this interaction is possible for all three ($^3B_2$, $^3B_1$, $^3A_1$) excited states of Be-C_2H_2, since the 2p$_x$ and 2p$_z$ orbitals never become doubly occupied. In fact, one would argue that the effect would be largest for the $^3B_2$ state, where asymptotically the 2p$_x$ and 2p$_z$ orbitals are not occupied at all.

The explanation of why the $^3B_1$ potential curve (Figure 1) is flat relative to the much more repulsive $^3A_1$ curve is less obvious. Furthermore, we would certainly not claim to have the insight of the Hoffmann group[35,50] in such matters. However, it would seem that the unfavorable potential curve of the $^3A_1$ state is related to the fact that the 2p$_z$ (a$_1$) orbital is directly pointing into the carbon-carbon triple or double bond of acetylene or ethylene. In this regard our use of acetylene rather than ethylene in the above discussion was adopted only because we feel more comfortable with its $D_{\infty h}$ molecular orbitals (and their labels) than those of the D_{2h} ethylene molecule.

Now let us turn to a discussion of the orbital energies and population analyses in Tables II and III. These data appear to demonstrate that the bonding for the $^3B_2$ states of both Be-C_2H_2 and Be-C_2H_4 is as described qualitatively above. In both complexes the largest change in Mulliken populations (relative to the separated species) occurs for the 3b$_2$ orbital. Rather than being a purely 2p$_y$ orbital as for ^3P Be atom, this orbital is only 53% 2p$_y$ for Be-C_2H_2 and even less, 42% 2p$_y$, for Be-C_2H_4. The latter difference in Be character correlates nicely with the fact that the ethylene complex is more strongly bound. Among the C_2H_2 symmetrized basis functions contributing to the 3b$_2$ orbital, the acetylene π^* orbital does make by far the largest contribution, as expected on qualitative grounds.[47,48] There are, of course, smaller contributions from the carbon 2s and 2pσ functions and the hydrogen 1s functions. Despite the rather drastic changes in the form of this orbital as one goes from Be + C_2H_2 or Be + C_2H_4 to the molecular complex, it is interesting to note that the 3b$_2$ orbital energy for both complexes is rather close to the 2p orbital energy of the Be atom ^3P state.

The total atomic populations show only a relatively small charge separation for both systems, with a formal 0.09 Be charge in the acetylene case and 0.16 in the ethylene case. This, of course, also correlates with the greater dissociation energy for Be-C_2H_4. More important, however, these total Be populations indicate that in some orbital besides the 3b$_2$ there must be a significant transfer of electron density from acetylene or ethylene to beryllium. Tables II and III show very clearly that this transfer occurs in the $5a_1$ orbital of both systems. The transfer is to both the s and p basis functions of Be and corresponds to a total shift of 0.28 "electrons" for $Be-C_2H_2$ and 0.33 for $Be-C_2H_4$. Although these observations are in general agreement with Dewar-Chatt-Duncanson[47,48] model, it is fascinating that their model was intended to describe not metal sp interactions, but rather those between transition metal d orbitals and organic ligands.

One effect of the change in the character of the $5a_1$ orbital is the large degree of "stabilization" (as measured by the lowering by more than 0.1 hartree for both $Be-C_2H_2$ and $Be-C_2H_4$) relative to the acetylene $1\pi_u$ and ethylene $1b_{3u}$ orbitals. This effect is the greatest change in the orbital energies of the two complexes relative to the separated species. The second most noticeable change in orbital energies occurs for the $6a_1$ orbital, which is, of course, a pure Be 2s orbital for the separated species. In both cases $\epsilon(6a_1)$ is raised by nearly 0.1 hartree as the complex is formed. One might be tempted to argue that the excess of stabilization of the $5a_1$ orbital over the destabilization of the $6a_1$ orbital accounts for the overall binding in the complexes. However we think it better to refrain from this temptation, since it is well known[46] that the total Hartree-Fock energy is not a sum of orbital energies. It is also interesting to note that in the organometallic systems, the $6a_1$ orbital is no longer purely 2s on Be, but takes on a sizable (25% for $Be-C_2H_2$, 29% for $Be-C_2H_4$) amount of Be 2p character.

Finally we note that these $^3B_2$ states of both $Be-C_2H_2$ and $Be-C_2H_4$ are quite polar. That is, the predicted dipole moments at the respective equilibrium geometries are 1.83 and 1.19 D. Since these dipole moments go to zero as the components are separated, the origin of the dipole moments lies in the complex itself.

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