Non-empirical Valence-electron Calculations on Ethylene Complexes of Silver(I) and Palladium(0)

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Non-empirical valence-electron calculations have been made on the complexes $[Ag(C_2H_4)]^+$ and $[Pd(C_2H_4)_n]$ (n = 1, 3, or 4). The conclusion of earlier *ab-initio* calculations on $[Ag(C_2H_4)]^+$ that donation of electrons from ethylene π to Ag 5*s* and 5*p* orbitals is the dominant bonding feature is confirmed. For the palladium(0) complexes, electron transfer occurs mainly from Pd to ethylene with both σ^* and π^* orbitals accepting electrons. A Mulliken-population analysis shows that the net charge residing on the ligands has a greater component in σ than in π orbitals. The important role of σ^* orbitals in the bonding provides an explanation of why C_2F_4 complexes are more stable than C_2H_4.

THE qualitative theory of the transition metal–olefin bond proposed by Dewar [1] and by Chatt and Duncanson [2] has had an important influence on organometallic chemistry over the past 20 years. The concept of a synergic donation of electrons from olefin π orbitals to a vacant metal σ orbital and acceptance into π^* orbitals from metal *d* orbitals or *dp* hybrids has allowed a rationalization of structure and other properties of such molecules to be made. In addition to their position as a cornerstone in the theory of organometallic chemistry, the transition metal–olefin complexes are important models for the heterogeneous catalysis of hydrocarbons by transition metals. The adsorption of ethylene on to Pt(100) surfaces has been attributed to the initial formation of a π complex.[3,4]

A few non-iterative and iterative Hückel-type calculations [5-11] and semiempirical CNDO calculations [12-14] have been made on transition metal–olefin complexes. Some of these have given useful insight into the structure and stability of such complexes, but the difficulty in deciding optimum parameters for such calculations means that they have limited value for the prediction of electron distributions and of orbital energies, and for the confirmation or refutation of established models of bonding. The only *ab-initio* SCF–MO calculation that has been

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reported is that of Basch[15] on $[Ag(C_2H_4)]^+$, and the only other non-empirical calculations are of the X-α type on platinum(II)–ethylene complexes.[16]

In this paper we present non-empirical SCF–MO calculations in a valence-electron basis on some palladium(0)–ethylene complexes using a method that has already been tested on main-group and transition elements.[17,18] We have also studied the Ag^+–C_2H_4 system in order to compare the results of our model with those of Basch.[15] Calculations on the complexes of Pd^0 with one, three, and four ethylenes will be described, the first of these to allow a comparison to be made with the silver(I) complex. Green *et al.*[19] prepared recently a compound which they believe is either the tris- or tetrakis-(ethylene)palladium(0) complex. We are as yet unable to extend our calculations to Pt because a program to handle f-electrons in the core is not available to us.

RESULTS AND DISCUSSION

The method used for the calculations has been described fully in an earlier paper[17] and is implemented on the ATMOL program.[20] It is a valence-electron method which aims to reproduce the results of an equivalent all-electron calculation. Up to two orbitals of a given symmetry type can be included in the basis. It has been shown in calculations on compounds of the first transition series that $3s$, $3p$, $3d$, $4s$, and $4p$ orbitals need to be included in the valence basis in order to get good agreement with the all-electron results: treating $3s$ and $3p$ orbitals as part of the core gives markedly poorer results and sometimes fails to give convergence to the correct electron configuration.

The nuclear potentials used in the calculation are Coulombic, but a correction is made to the one-centre one-electron integrals to allow for the non-Coulomb nature of the core potential. This correction is determined by separate calculations on the component atoms of the molecule.[17] In earlier calculations on first-row elements,[21] the $1s$ electrons were taken as the core, but the saving in integral time by removing the $1s$ orbital from the basis is trivial. In these calculations we therefore included the carbon $1s$ orbitals in the basis, and no separate atomic calculation is needed on this atom. The carbon basis is therefore the best-atom single-zeta orbitals of Clementi and Raimondi,[22] and the hydrogen $1s$ orbital is a single Slater function with exponent 1.2.

Atomic Calculations on Ag *and* Pd.—Although it is recognized that a minimal basis of Slater-type orbitals will give a far from accurate representation of Hartree–Fock orbitals for atoms or molecules, it is generally found to be adequate to reproduce the correct ordering of the orbital energies. However, for the transition metals, with nearly closed d shells, a minimal STO basis for the d orbitals is extremely bad. Although it will give the correct order of orbital energies for the atoms, the relative energies are so far from the Hartree–Fock limits that when such orbitals are combined in a molecular calculation with orbitals of main-group elements they may give an incorrect order for the molecular orbitals and unrealistic electron distributions in the molecule.

There is, however, relatively little to be gained in computing time by ignoring core orbitals in a calculation which uses a double-zeta basis for d orbitals. The reason for this is that most of the time for integral evaluation is taken up by integrals involving the d orbitals and one would therefore only make a saving from what is a relatively small part of the total integral time. Our valence method must therefore be used in a minimal basis for d orbitals in order to justify the errors introduced through our approximations by the saving in computer time. The compromise we made was to work in a single STO basis but with the exponents for the valence d orbitals chosen to reproduce (approximately) the d-orbital eigenvalue of a double-zeta d-orbital basis.

Table 1 shows the valence-orbital energies obtained in three all-electron calculations on Ag^+ ($4d^{10}5s^0$). The first calculation used the single STO basis reported by Clementi *et al.*[23] for Ag ($4d^95s^2$; ^2D). The $4d$ exponent for this is 3.8064. This basis was augmented by $5p$ orbitals with the same exponent as that of the $5s$. The second calculation employed the same basis except that double-zeta $4d$ orbitals were used with exponents deduced by Roetti and Clementi[24] for their complete double-zeta basis (2.583 74 and 4.988 96). Lastly we return to the minimal basis but with the $4d$ exponent of 3.10 which reproduced to a good approximation the $4d$ eigenvalue of column 2.

TABLE 1

Valence-orbital energies (a.u.) of Ag^+ using the same minimal bases but with different choices of $4d$ orbitals

Orbital	Minimal ζ_{4d} 3.806 4	Minimal except for double $4d$	Minimal ζ_{4d} 3.10
$4s$	−3.651 1	−4.167 9	−4.587 2
$4p$	−2.438 6	−2.916 4	−3.290 2
$4d$	−0.289 2	−0.775 5	−0.781 1
$5s$	−0.142 1	−0.179 1	−0.181 6
$5p$	−0.007 8	−0.049 4	−0.054 7
Total energy	−5 154.307 1	−5 156.658 1	−5.153 014 6

We note from these calculations that the $4d$ eigenvalue obtained by the use of ζ_{4d} 3.1 is close to that predicted from experiment[25] on the basis of Koopmans' theorem: $Ag^+(4d^{10}) \longrightarrow Ag^{2+}(4d^9)$; $I_{exp} = 0.789$ a.u.* Although

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* Throughout this paper: 1 a.u. = 27.211 652 eV; 1 eV ≈ 1.60×10^{-19} J.

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[25] C. E. Moore, 'Atomic Energy Levels,' vol. III, Nat. Bur. Stand., Circular no. 467, 1958.

the 4*s* and 4*p* energies differ quite appreciably in our three calculations, this is not likely to be important as these orbitals are effectively part of the core. The virtual-orbital 5*s* and 5*p* energies are quite similar in the double-zeta and ζ_{4d} 3.10 calculations. The total energy calculated for Ag^+ with ζ_{4d} 3.1 is greater by 1.3 a.u. than for the energy-optimized exponent, but this is of little relevance for our molecular calculations as we are only interested in relative energies. However, we still must show that the molecular results obtained with our basis are sensible, and this we have done by comparing our calculations on $[Ag(C_2H_4)]^+$ with those of Basch.

Calculations were made on Pd^0 similar to those described above for Ag^+. Preliminary calculations on Pd^0–C_2H_4 indicated that the valence state of Pd^0 was approximately $4d^{10}$, and the optimum 4*d* exponent was chosen by atomic calculations on this state. The results are shown in Table 2. We note again that the energies of the 4*d*, 5*s*, and 5*p* orbitals are very similar in the two calculations.

Table 2

Valence-orbital energies (a.u.) of $Pd(4d^{10})$ calculated from the minimal basis of ref. 24 except for the 4*d* functions which are single or double as defined in the text

Orbital	$\zeta_{4d}\begin{cases}4.771\ 73\\2.471\ 21\end{cases}$	ζ_{4d} 2.87
4*s*	−3.358 1	−3.747 3
4*p*	−2.169 0	−2.514 6
4*d*	−0.194 9	−0.193 6
5*s*	0.120 6	0.116 2
5*p*	0.246 4	0.238 0

$[Ag(C_2H_4)]^+$.—To test our method against the results of Basch[15] we used his geometrical parameters. The ethylene molecule was taken to be planar, although the evidence of related compounds[26] is that the hydrogen atoms are likely to be pushed back from the side of the Ag^+. Table 3 shows the valence-orbital energies and binding energy of the complex obtained from our calculations, and its comparison with all-electron calculations using the same basis and the results of Basch. The valence-electron calculations were some four times faster than the all-electron calculations.

The valence-electron method is seen to be very successful as measured against the orbital energies of the corresponding all-electron calculation. The only differences greater than 0.01 a.u. are in the virtual orbitals. The binding energy is, however, less accurate, and suggests that the accumulation of small errors in the orbital energies is effective in this case. The comparison with the results of Basch is also quite satisfactory for orbitals above $4b_2$. The lowest four orbitals ($9a_1$, $10a_1$, $5b_1$, and $4b_2$) are predominantly the Ag 4*s* and 4*p* orbitals and these are effectively part of the core. Table 1 shows that the error in these is transferred almost exactly from the atomic calculations.

The orbital wavefunctions obtained from our valence basis are also in qualitative agreement with those obtained by Basch. Table 4 shows the Mulliken populations of the four top-occupied molecular orbitals in terms of the component valence orbitals of Ag^+ and C_2H_4. The occupancies of all the σ orbitals of C_2H_4 were accumulated. There are no differences between the two calculations other than what one would expect from the different bases. The net charge deduced on the Ag from these calculations is +0.85 from the valence calculations and +0.95 from that of Basch.

Table 3

Comparison of valence- and all-electron calculations on $[Ag(C_2H_4)]^+$ using the basis defined in the text, with the contracted Gaussian basis of Basch[15] (Ag: 5*s*, 4*p*, 3*d*; C: 2*s*, 2*p*; H: 1*s*). Energies in a.u. Valence-electron calculations on $[Pd(C_2H_4)]$ are also included for comparison and those levels shown with an asterisk have an order different from that in the silver(I) complex

Symmetry in C_{2v}	Valence-electron	All-electron	Basch[15]	Valence-electron $[Pd(C_2H_4)]$
$9a_1$	−4.572	−4.558	−4.192	−3.894
$10a_1$	−3.280	−3.261	−2.873	−2.669
$5b_1$	−3.272	−3.260	−2.872	−2.649
$4b_2$	−3.271	−3.259	−2.872	−2.644
$11a_1$	−1.253	−1.254	−1.247	−1.023
$6b_1$	−1.003	−1.005	−1.006	−0.784
$5b_2$	−0.855 1	−0.856 6	−0.858 3	−0.629 6
$12a_1$	−0.791 4	−0.790 9	−0.800 8	−0.562 0
$13a_1$	−0.762 1	−0.754 7	−0.749 4	−0.415 1 *
$2a_2$	−0.759 9	−0.751 1	−0.745 9	−0.493 9 *
$14a_1$	−0.755 6	−0.748 0	−0.743 2	−0.289 6 *
$6b_2$	−0.755 2	−0.746 6	−0.741 0	−0.293 4 *
$7b_1$	−0.757 4	−0.748 3	−0.740 7	−0.295 0 *
$3a_2$	−0.710 4	−0.711 9	−0.715 0	−0.286 5 *
$15a_1$	−0.594 9	−0.579 0	−0.592 3	−0.248 8
Virtual				
$16a_1$	−0.122 1	−0.133 3		0.138 5
$8b_1$	−0.070 1	−0.078 3		0.175 2
$7b_2$	−0.020 5	−0.030 7		0.238 3
$9b_1$	0.072 4	0.068 8		0.347 2
$17a_1$	0.110 3	0.101 9		0.412 4
Binding energy	0.060 7	0.045 8	0.044 2	0.103 2

Table 4

Mulliken populations of the four highest-occupied molecular orbitals from the valence calculation (*i*) and from the results of Basch (*ii*)

		Ag^+			C_2H_4		
		5*s*	5*p*	4*d*	π	π*	σ + σ*
$6b_2$	(*i*)			0.959			0.040
	(*ii*)			0.98			0.02
$7b_1$	(*i*)			0.980		0.008	0.011
	(*ii*)			0.98		0.02	
$3a_2$	(*i*)			0.032			0.968
	(*ii*)			0.08			0.92
$15a_1$	(*i*)	0.072	0.047	0.070	0.805		0.005
	(*ii*)	0.065	0.035	0.08	0.82		

We conclude from these calculations on $[Ag(C_2H_4)]^+$ that the valence-electron method is a good approximation to the corresponding all-electron calculation and the basis used gives results very similar to those obtained by Basch from a larger Gaussian basis. We would not therefore expect to reach any conclusions about the nature of the Ag^+–C_2H_4 bond that were not reached by

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[26] W. C. Hamilton, K. A. Klandermann, and R. Sprately, *Acta Cryst.*, **1969**, **A25**, S172.

Basch. The most important conclusion is that donation of electrons from the ethylene π orbital to the Ag 5*s* and 5*p* orbitals, which shows up mainly in the Mulliken population of the highest-occupied orbital ($15a_1$), is much more important than the donation (backbonding) from 4*d* orbitals into the ethylene π* (showing in $7b_1$). However, the backbonding will be inhibited by the charge already residing on the silver atom, and we can expect a different conclusion for the palladium–ethylene complexes. Basch also showed that approximately half of the total binding energy of the complex can be accounted for by the polarization energy of the ethylene in the field of the positive charge of Ag^+. This polarization is accompanied by a mixing of π and σ orbitals of ethylene, and this is shown in our calculation mainly in the populations of the lower a_1 orbitals ($11a_1$—$14a_1$). This mixing is accompanied by a net transfer of 0.05 from the π to the σ orbitals.

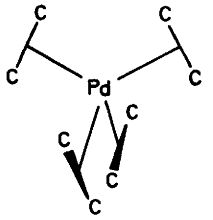

FIGURE 1 Structure of $[Pd(C_2H_4)]$ adopted from ref. 11. Each ethylene is face-centred to the metal

Palladium(0)—*Ethylene Complexes*.—As no structural parameters are known for these complexes, we inferred data from platinum(0) complexes with a reduction of the metal–carbon bond lengths to allow for the fact that the atomic radius of Pd is slightly less than that of Pt.[27] Green *et al.*[19] found Pt–C bond lengths of 225 pm in $[Pt(C_2F_4)(C_2H_4)]$ and 222 pm in $[Pt(C_7H_{10})_3]$. We adopted the value of 220 pm for $[Pd(C_2H_4)]$ and $[Pd(C_2H_4)_3]$, and 230 pm in $[Pd(C_2H_4)_4]$ to allow for the effect of steric crowding as predicted by Rösch and Hoffman.[11] In all cases the ethylene unit was assumed to be planar with the same geometry as used for the $[Ag(C_2H_4)]^+$ calculations: C–C 137, C–H 108.6 pm, HCH 117.6°. In all the complexes the ethylene units were taken as face-centred to the metal. A D_{3h} configuration was adopted for $[Pd(C_2H_4)_3]$, in conformity with the structure of the known platinum complexes,[19] and a quasidodecahedral D_{2d} geometry (as in Figure 1) was adopted for $[Pd(C_2H_4)_4]$: this was the predicted favoured structure of $[Ni(C_2H_4)_4]$ from the extended-Hückel calculations of Rösch and Hoffmann.[11] We did not attempt any optimization of geometry as, even with our valence-electron calculations, the computing time for a single structure is considerable.

Table 3 lists the orbital energies from the valence-electron calculation on $[Pd(C_2H_4)]$ for comparison with the $[Ag(C_2H_4)]^+$ calculations. The order of orbitals is the same except for those indicated with an asterisk. There is a good correlation between the two sets of orbital energies, with those of the neutral complex being raised by an amount varying from 0.7 to 0.25 a.u. from their position in the positively charged complex. We have information to show that the valence-electron energies are as close to the all-electron calculations as for the silver(I) calculations, and that the levels above $4b_2$ have energies close to those of a double-zeta 4*d* calculation. This information may be obtained from the authors on request.

The binding energy for $[Pd(C_2H_4)]$ is predicted to be 70% greater than that of the silver complex, and although we expect our method to overestimate the value appropriate to an all-electron calculation this ratio should be approximately correct. As there will be only a small polarization contribution to the binding energy of the neutral complex, this increase suggests a much larger increase in the covalent (overlap-dependent) contribution to the binding energy.

Examination of the orbital populations (some of which are shown in Table 5) confirms the increased covalent bonding in the palladium complex; and we calculate a net loss of 0.19 e from the metal which is made up primarily of two parts. There is a gain of 0.05 e in the a_1 orbitals (much less than the 0.17 e in the case of Ag^+) and a loss of 0.24 e in the b_1 orbitals (much greater than the 0.02 e in the case of Ag^+). The relative importance of the two charge-transfer processes is therefore the reverse of that found for the silver(I) complex; donation from the metal (mainly 4*d*) into vacant C_2H_4 orbitals is the dominant contribution. These conclusions can obviously be rationalized by the relative positions of the metal and olefin orbitals (Figure 2).

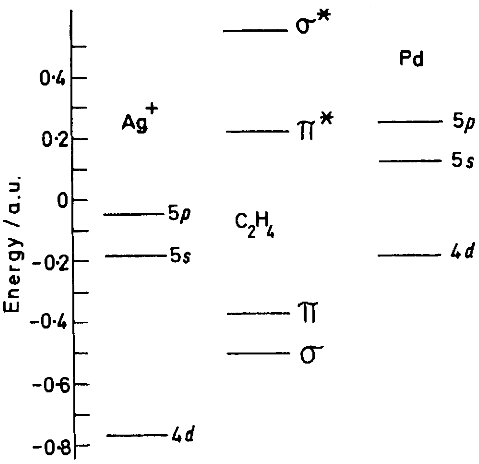

FIGURE 2 Energies of the highest-occupied and lowest-vacant orbitals of the components which are most important for bonding

Although there are no strong polarization forces on the ethylene in the palladium complex, we still find that there is appreciable mixing of π and σ orbitals as shown by the coefficients of the a_1 and b_1 orbitals. Of the net 0.19 e gained by the ethylene, 0.06 e go into the π system and

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[27] G. H. Aylward and T. J. V. Findlay, 'SI Chemical Data,' Wiley, Sydney, 1971.

0.13 e into the σ. We therefore conclude that direct donation from Pd(4*d*) orbitals into ethylene antibonding σ* as well as π* is occurring. The relative position of the orbitals in Figure 2 shows that donation to σ* is likely to be energetically quite favourable. Mulliken-population analyses show that of the 0.13 e gained by the σ system, 0.02 e are accommodated in σ (b_1) orbitals and 0.11 e in σ* (a_1) orbitals. Similarly, of the net 0.06 e gained by the π system, 0.22 e are gained by the π* orbital through b_1 orbitals and 0.16 e are lost by the π orbitals to Pd through a_1 orbitals.

TABLE 5

Energies (a.u.) and Mulliken populations of the highest-occupied orbitals of palladium(0)–ethylene complexes

Designation	Energy	4*s* + 5*s*	4*p* + 5*p*	4*d*	π + π*	σ + σ*
Mono						
$1a_2$	−0.493 9			0.010		0.990
$6a_1$	−0.415 1	0.008	−0.001	0.200	0.769	0.023
$4b_1$	−0.295 0			0.873	0.108	0.019
$3b_2$	−0.293 4		0.004	0.981		0.015
$7a_1$	−0.289 6		0.001	0.992	0.002	0.005
$2a_2$	−0.286 5			0.990		0.010
$8a_1$	−0.248 8	0.114	0.040	0.695	0.143	0.010
Tris						
$5a_1'$	−0.499	−0.006		0.251	0.725	0.030
$1a_1''$	−0.490					1.000
$7e'$	−0.439		−0.006	0.447	0.454	0.104
$3e''$	−0.381			0.934		0.064
$6a_1'$	−0.329	0.109		0.669	0.216	0.007
$8e'$	−0.300		0.066	0.302	0.605	0.027
Tetrakis						
$2a_2$	−0.49					1.000
$7b_2$	−0.46		−0.008	0.415	0.184	0.408
$7a_1$	−0.45	0.022		0.017	0.336	0.625
$9e$	−0.44		−0.006	0.456	0.193	0.357
$8a_1$	−0.38	0.004		0.828	0.044	0.124
$3b_1$	−0.38			0.951		0.049
$10e$	−0.28		0.058	0.414	0.142	0.383
$8b_2$	−0.27		0.082	0.417	0.228	0.272

Although Table 3 shows the similarity of the orbital patterns in the two complexes, the differences in relative energies of the component metal and olefin orbitals shows up in the orbital wavefunctions. Thus the four highest-occupied orbitals of the neutral complex are predominantly Pd(4*d*), whereas for the positively charged complex, orbitals $15a_1$ and $2a_2$ are (as can be seen from Table 4) predominantly ethylene orbitals.

Our conclusion that electron transfer from the Pd to ethylene is the dominant contribution to bonding is supported by several pieces of evidence for the platinum complexes. First, it has been noted [28-30] that electronegative substituents on the olefin increase the stability; secondly, from *X*-ray photoelectron studies on [Pt(C_2H_4)-($PPh_3)_2$] it has been deduced that the Pt loses 0.8 e to the olefin, although this is thought to be an overestimate.[31]

Schematic orbital-interaction diagrams for the tris- and tetrakis-(ethylene) complexes have been given by Rösch and Hoffman [11] for the geometries we are considering. Table 5 shows the occupied valence energies of the tris-and tetrakis-(ethylene) complexes above −0.5 a.u. These orbitals contain the majority of the 4*d*, π, and π* orbitals. Convergence of the SCF cycle to the usual accuracy was not reached with these molecules, for reasons of time, and the energies are only quoted to three and two places of decimal respectively. The binding energies of the tris and tetrakis complexes are calculated to be 0.256 and 0.29 a.u. respectively. These are 2.5 and 2.8 times the binding energies calculated for the mono complex, so that the binding energy per ligand falls slightly as more are added.

The Mulliken populations of the occupied orbitals whose energies are above −0.5 a.u. are shown in Table 5 for all three palladium–ethylene complexes. The mixing of 4*d* orbitals with ligand orbitals increases from mono to tris and again to tetrakis. For the mono complex only six of the molecular orbitals have significant 4*d* character (populations greater than 0.1) whereas for tris and tetrakis this rises to eight (accounting for degeneracies). Likewise the mixing of π and σ orbitals of the ethylene increases with more ligands.

The net charges on the metal are +0.78 for the tris and +0.80 for the tetrakis complex and these are, per ligand, both greater than for the mono complex (+0.19). Of the electrons gained by the ligands, more goes into the σ system than the π (tris: π 0.09, σ 0.17; tetrakis: π 0.05, σ 0.15 e) supporting the conclusion from the mono complex that donation from 4*d* into σ orbitals of the ligands makes an important contribution to the bonding.

Conclusions.—It has been shown that a non-empirical valence-electron method, previously developed, can give a good approximation to exact *ab-initio* calculations on transition-metal–ethylene complexes. The most important qualitative conclusion from our calculations is that the net electrons gained by the ethylene in the palladium(0) complexes are found mainly in the σ orbitals, although we recognize that a Mulliken-population analysis may not always give a reliable guide to electron distributions.[32]

A recognition of the importance of σ* orbitals leads to a better understanding of the reasons why electronegative substituents, such as fluorine, on the ethylene give rise to stronger complexes. It is known from the evidence of photoelectron spectroscopy [33,34] that fluorine substituents stabilise σ more than π orbitals. Calculations by Snyder and Basch [35] on C_2H_4 and C_2F_4 show that the lowest π* orbital is actually raised by 0.002 a.u. by the fluorines, whereas the lowest σ* orbital in C_2H_4 is 0.042 a.u. lower than that in C_2H_4. This increase of *ca.* 1 eV in the σ-

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electron affinity should lead to a considerably enhanced bonding for the tetrafluoroethylene.

Our calculations have all been based on model geometries with planar ethylene molecules. The out-of-plane distortion of the ethylene, which has been determined for some complexes, would lead to an initial mixing of σ with π and σ^* with π^* orbitals. Inverting this line of argument, we could say that it is this mixing of orbitals by bonding with the metal which is the driving force for the distortion of the ethylene molecule.

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