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The Binding of Ethylene to Platinum and Palladium. An ab Initio Study of the $MCl_3(C_2H_4)^-$ Species

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Abstract: The structures and bonding of the metal-olefin π-complexes $PtCl_3(C_2H_4)^-$ and $PdCl_3(C_2H_4)^-$ are investigated with ab initio calculations in an extended basis. Relativistic effective core potentials are employed on Pd and Pt to replace the core electrons and to incorporate the relativistic effects on the valence electrons. The optimized geometries of the Pt-C_2H_4 and Pd-C_2H_4 complexes are discussed and compared with the structure determined by neutron diffraction for $KPtCl_3(C_2H_4)$. The calculated barrier to rotation in Zeise's salt (15 kcal/mol) is in good agreement with observed barriers (10-14 kcal) in platinum-olefin complexes. The barriers to rotation and binding energies both decrease in the order Pt > Pd. The results are compared to the Dewar-Chatt-Duncanson model of metal-olefin bonding.

Introduction

The binding of unsaturated hydrocarbons to transition metals has occupied a central position in organometallic chemistry[1-4] and the nature of the metal-olefin bond has been the subject of numerous theoretical studies.[5-14] In this work we report the first ab initio calculations on the classic π-complex Zeise's salt,[15] $PtCl_3(C_2H_4)^-$, and the related $PdCl_3(C_2H_4)^-$ complex. The focus of this study will be the role of ab initio calculations in providing structural and energetic information about transition-metal complexes. In particular the prediction of bond lengths and bond energies will be emphasized since these quantities are difficult or impossible to obtain reliably by other theoretical methods. Zeise's salt provides a sensitive test of structural predictions since it has been the subject of a recent neutron diffraction study.[16] Obtaining accurate structural and energetic information obviously is essential in transition-metal chemistry if one is to understand how effective catalysts achieve the delicate balance between unreactive species which are too strongly bound and unstable species which are too weakly bound.

Previously ab initio calculations on third-row transition-metal compounds have been virtually nonexistent because of the prohibitively large number basis functions on heavy metals that would be required to treat all the electrons explictly. In addition the relativistic mass-velocity, Darwin, and spin-orbit coupling effects on the valence electrons become sufficiently large that nonrelativistic treatments of electronic structure will lead to serious errors. Relativistic shifts of 2 eV in the 5d and 6s valence orbitals of Pt (Figure 1) are observed as well as significant changes in the radical extent of the orbitals. These effects are even quite significant for the second transition series as shown for the valence orbitals of Pd in Figure 2. We have developed ab initio relativistic effective core potentials[17-20] for the dual purposes (1) of replacing the chemically inert core selections, hence reducing the problem to a valence-electron problem, and (2) of incorporating the mass-velocity and Darwin relativistic terms into the potential. (For closed-shell ground-state complexes of the type treated here, spin-orbit coupling will not be a significant factor. The inclusion of the spin-orbit effects in excited states will be discussed in subsequent papers.)

Earlier theoretical studies of the d^8 Pt complex $PtCl_3(C_2H_4)^-$ have included extended Hückel[11] and other semiempirical treatments[13] and nonrelativistic Xα-SW[8] and Hartree-Fock-Slater[14] treatments. All-electron ab initio calculations of metal-olefin complexes include the d^{10} systems[10,12] $Ag(C_2H_4)^+$, $Ni(C_2H_4)_2$, and $Ni(C_2H_4)_3$, the sd^9 system[9] $Ni(C_2H_4)$, and the d^6 system[11] $MoL_4(C_2H_4)_2$. Practically all ab initio and approximate calculations on transition-metal compounds assume fixed bond lengths. Our calculations are thus among the first to attempt to predict geometrical parameters of ligands coordinated to transition metals.

Details of the Calculations

Hartree-Fock calculations were carried out with a flexible contracted Gaussian basis set consisting of a (3s 3p 4d) primitive set contracted to [3s 2p 2d] to represent the 5d, 6s, and 6p valence electrons of Pt and a (3s 4p) primitive set contracted to [2s 2p] to represent the 3s and 3p valence electrons of Cl. The [Xe]4f^{14} core of Pt was replaced with a relativistic effective core potential (ECP) and the [Ne] core of Cl was replaced with a nonrelativistic ECP. A similar contracted [3s 2p 2d] basis was used to represent the 4d, 5s, and 5p valence orbitals of Pd with the [Kr] core replaced with a relativistic ECP. Standard (9s 5p) and (4s) primitive basis or C and H were contracted to [3s 2p] and [2s], respectively.[21,22] The effect of polarization functions was examined by using a set of 3d Gaussians on each C with exponent 0.65.

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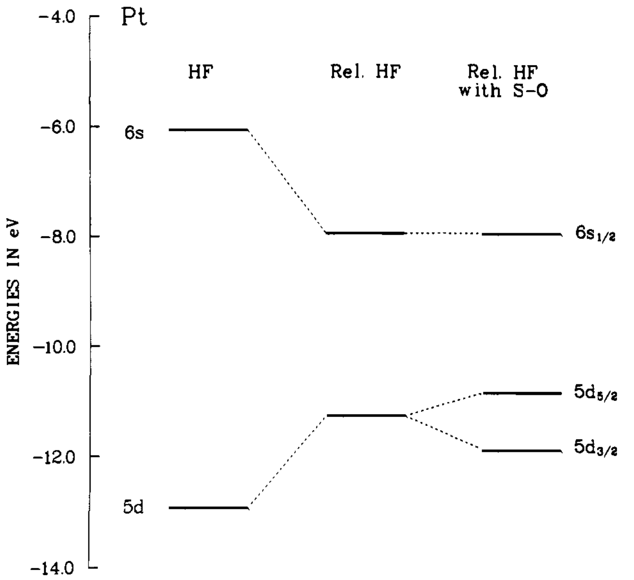

Figure 1. Orbital energies of the 5d and 6s valence orbitals of Pt from Hartree–Fock and relativistic Hartree–Fock calculations. Spin-orbit splittings for the 5d orbital are also shown.

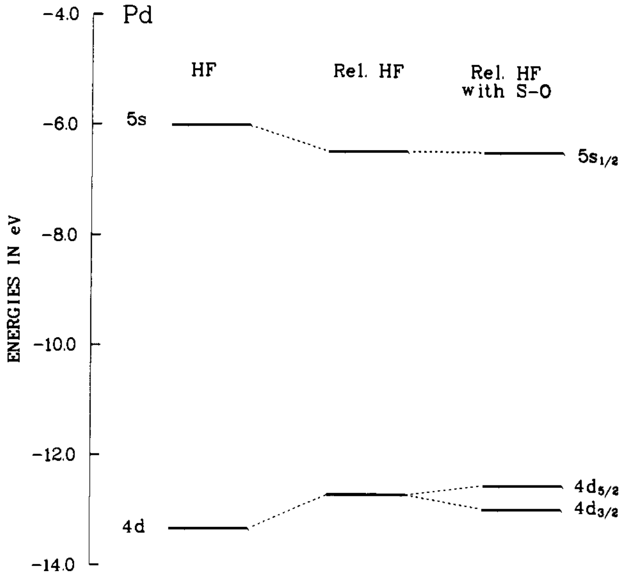

Figure 2. Orbital energies of the 4d and 5s valence orbitals of Pd from Hartree–Fock and relativistic Hartree–Fock calculations. Spin–orbit splittings for the 4d orbital are also shown.

The Cl, Pd, and Pt basis sets and ECP's are given in the supplementary material. The potentials were generated by using the standard procedure discussed in our earlier papers:[18] (1) starting with numerical Hartree–Fock atomic orbitals or Cowan–Griffin relativistic Hartree–Fock atomic orbitals,[23] one defines smooth nodeless valence pseudoorbitals, (2) a numerical ECP is generated from the numerical pseudoorbitals, (3) both the potential and orbitals are fit to Gaussians for use in molecular applications. In one significant departure from our earlier studies, the pseudoorbitals were defined by using a procedure suggested by Christiansen et al.[24] in making the pseudoorbitals as much like the Hartree–Fock orbitals as possible. The Pt s, p, and d potentials were obtained from the $5d^96s^1$ and $5d^96p^1$ states of Pt, and the analogous potentials for Pd were derived from the $4d^95s^1$ and $4d^95p^1$ states of Pd. The higher potentials were derived, as discussed previously, from states with a single electron (e.g., 5f or 5g in the case of Pt) in the field of the "bare" Pt^{10+} core.

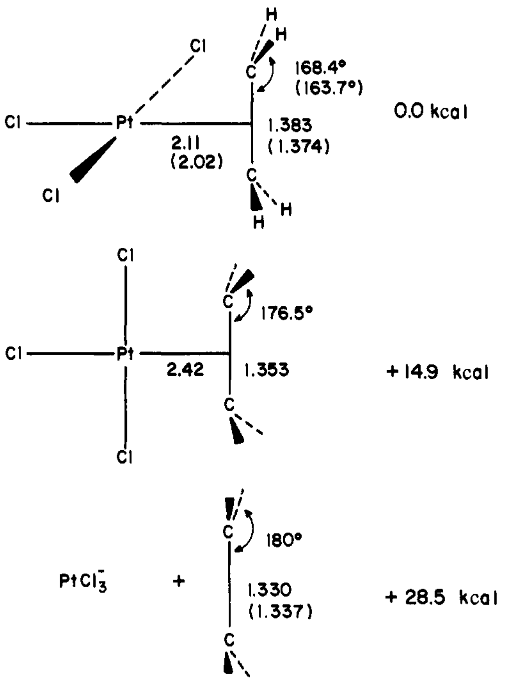

Figure 3. Calculated geometries for $PtCl_3(C_2H_4)^-$ for the upright and planar forms of coordinated ethylene along with uncoordinated ethylene. (Experimental values are shown in parentheses.)

In the geometry optimization the ML_3 fragment was held rigid (unless specified otherwise) with 90° bond angles and M–L distances of 2.34 Å (trans) and 2.30 Å (cis). CH distances (1.08 Å) and HCH angles (117°) on C_2H_4 were also held fixed. The remaining three degrees of freedom (metal–olefin distance, C–C distance, and the bending angle of the plane containing the CH_2 group) were then optimized for the perpendicular (upright) and planar modes of the ethylene bound to the metals.

Population analyses were carried out by using Mulliken's method[25] and a modified method due to Noell,[26] which we have found to give more chemically reasonable results for transition metals and species bound to them. In Mulliken population analyses the metal atom in a flexible basis usually has a nearly neutral or even negative overall charge. By contrast, the modified procedure assigns additional parts of the density in diffuse s, p, or d functions, which are centered on the metal but which have significant extent beyond the covalent radius of the metal, to the ligands. For example the Pt, with a formal +2 charge in this complex, has only a +0.02 charge with Mulliken analysis and a +1.40 charge with the modified analysis. (Obviously any scheme for analyzing wave functions in terms of atomic character will contain some inherent arbitrariness, and hence only qualitative significant should be attached to the results.) Briefly, in the modified procedure, instead of defining the population in atomic orbital χ_μ on the metal by the standard definition

$$P_\mu = \sum_{i,\nu} C_{\mu i} C_{\nu i} S_{\mu\nu}$$

it is weighted by the fraction of density F_μ assigned to the metal

$$P_\mu = \sum_{i,\nu} \sqrt{F_\mu F_\nu}\, C_{\mu i} C_{\nu i} S_{\mu\nu}$$

The quantity F_μ is defined as follows for metal-centered functions. (For ligand-centered functions F_μ is taken to be 1.) The total population of atomic orbital χ_μ is decomposed into three parts

$$\int \chi_\mu^2 \, dV = 1 = I_\mu + L_\mu + R_\mu$$

where I_μ is the portion within the covalent radius of the metal ($0 < r < R_c$), L_μ is the portion assigned to the ligands ($R_c < r < \infty$; θ, ϕ lie within cones of revolution defining the ligands), and R_μ

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Table I. Calculated Geometrical Parameters (with Experimental Values^a in Parentheses) and Relative Energies for Various Forms of $PtCl_3(C_2H_4)^-$ and $PdCl_3(C_2H_4)^-$

form	R(M-CC), Å	R(C-C), Å	ϕ(CH_2 bend), deg	rel energy, kcal/mol
		$PtCl_3(C_2H_4)^-$		
upright	2.11 (2.02) 2.06^d	1.383 (1.375)	168.4 (163.7)	0.0^b
planar	2.42	1.353	176.5	14.9
fragments	∞	1.330 (1.337)	180 (180)	28.5
		$PdCl_3(C_2H_4)^-$		
upright	2.25	1.354	172.4	0.0^c
planar	2.69	1.340	180	6.9
fragments	∞	1.330 (1.337)	180 (180)	12.3

^{a} Reference 16. ^{b} Total energy = −148.61276 au. ^{c} Total energy = −151.47847 au. ^{d} Calculated bond length with d functions added on the C atoms.

Table II. Population Analysis of the π-Donor and π-Acceptor Orbitals of Pt in $PtCl_3(C_2H_4)^-$ and the $PtCl_3^-$ + C_2H_4 Fragments^a

	complex	fragments	difference
	π Donation		
$5d_{yz}$	1.62 (1.77)	1.85 (2.00)	−0.22 (−0.23)
	σ Acceptance		
$5d_{x^2-y^2}$	0.72 (1.03)	0.62 (0.85)	0.10 (0.18)
$5d_{z^2}$	1.75 (1.95)	1.74 (1.94)	0.02 (0.01)
6s	0.41 (0.52)	0.38 (0.48)	0.04 (0.04)
$6p_y$	0.18 (0.29)	0.09 (0.15)	0.08 (0.14)
		σ(net)	
net chg on Pt	+1.40 (+0.02)	+1.42 (+0.18)	+0.24 (+0.37)

^{a} Modified Mulliken populations are given (with traditional Mulliken population in parentheses).

Table III. Population Analysis of the π-Donor and σ-Acceptor Orbitals of Pd in $PdCl_3(C_2H_4)^-$ and $PdCl_3^-$ + C_2H_4 Fragments^a

	complex	fragments	difference
	π Donation		
$4d_{yz}$	1.82 (1.93)	1.89 (2.00)	−0.07 (0.07)
	σ Acceptance		
$4d_{x^2-y^2}$	0.59 (0.92)	0.66 (0.86)	0.03 (0.06)
$4d_{z^2}$	1.83 (1.98)	1.80 (1.96)	0.03 (0.03)
5s	0.31 (0.39)	0.29 (0.36)	0.02 (0.03)
$5p_y$	0.13 (0.20)	0.08 (0.14)	0.04 (0.06)
		σ(net)	
net chg in Pd	+1.27 (+0.20)	+1.32 (+0.32)	+0.12 (+0.18)

^{a} Modified Mulliken populations are given (with traditional Mulliken population in parentheses).

is the remainder outside R_c not assigned to the ligands. F_μ is then defined as

$$F_\mu = I_\mu + R_\mu$$

In the analysis of square-planar complexes here, four equal 90° cones of revolution are made for the ligands and a covalent radius of 1.30 Å was used for both Pt and Pd.

Results and Discussion

The optimized structure for Zeise's salt is compared with the results of the neutron diffraction study of Love et al.[16] in Figure 3. (Also see ref 16 for an account of the earlier crystallographical studies on the complex.) The distortions of the ethylene ligand upon coordination are well represented by the calculated structure: the bending back of the CH_2 groups by 12.6° (compared to 16.3° experimentally) and the lengthening of the C–C band length by 0.053 Å (0.037 Å experimentally). The calculated metal–olefin bond distance of 2.11 Å is 0.09 Å longer than the observed bond length (2.02 Å). When 3d functions were added to the carbon atoms (see Table I), the predicted bond length is shortened to 2.06 Å. The influence of point charges on the predicted geometries of this negatively charged species was also explored, but little discernible effect was found.

The ethylene in the more stable upright form is calculated to be bound by 28 kcal/mol to $PtCl_3^-$ and the barrier to rotation about the platinum–olefin axis is calculated to be 15 kcal/mol. Hence rotation of the C_2H_4 can occur without dissociation. This barrier agrees well with experimentally observed barriers[27] in the range 10–14 kcal/mol. There are two significant features of the "in-plane" geometry: the longer platinum–olefin bond (by 0.3 Å) compared to the upright form and less distortion of C_2H_4 compared to free C_2H_4. A much higher rotational barrier (24 kcal/mol) is predicted if one does not let the Pt–CC bond length relax from the upright geometry. With a short metal–olefin bond length (2.1 Å), the Cl atoms will bend back ~7° away from the olefin in the planar form to reduce the barrier slightly (to 21 kcal/mol), but the increase in bond length has a much greater effect. At the optimum bond length (2.42 Å), bending of the Cl atoms has little stabilizing effect and the interior Cl–Pt–Cl bond angles remain essentially 90°. Extended Hückel calculations[11] correctly predict the orientation of the ethylene ligand but overestimate the rotational barrier. For fixed M–C_2H_4 separation, barriers of 35 kcal/mol (rigid ML_3) and 24 kcal/mol (relaxed ML_3) were obtained. The high barriers can probably be attributed to the assumption of fixed bond lengths, since computed bond lengths from Hückel calculations are usually erratic. This is in accord with out results which overestimate the barrier if M–C_2H_4 bond lengths are not optimized.

There appear to be no experimental structures with which to compare the calculated geometries of the Pd analogue $Pd(C_2H_4)Cl_3^-$ shown in Figure 4. (There have been x-ray structural determinations of μ-chloro-bridged dimers[28] $Pd_2(C_2H_4)Cl_4$ and Pd(norbornadiene)Cl_2.) The Pd complex does exist in solution and has been postulated as the first intermediate formed in the Wacker process[30] of olefin oxidation. Again the upright form is more stable, but by only 7 kcal/mol compared to the planar form and by only 12 kcal/mol compared to dissociation. This finding of a more weakly bound Pd complex does appear to be consistent with greater stabilities observed for organometallic compounds involving olefins, alkyls, and carbenes as one proceeds from second-row to third-row transition-metals. The weaker coordination of ethylene is also reflected in less distortion of the complexed ligand compared to uncoordinated ligand, since one might associate increased metal–ligand interaction with greater π donation to the olefin and hence greater distortion of the ligand. This greater lability of ethylene in $Pd(C_2H_4)Cl_3^-$ may explain the apparent activity of Pd in carrying out olefin oxidations. While the C–C bond may be activated (weakened) to a greater extent in the Pt complex, the stronger platinum–ethylene bond may render the species overall less reactive than the Pd complex.

A detailed analysis of the origin of the barrier to rotation will not be presented here, partly because of the usual difficulties associated with decomposing nuclear repulsion energy and the 1- and 2-electron components of ab initio electronic energies into conceptual terms. However, a qualitative inspection of the orbital energies of the upright and planar forms shows significant changes only in the two highest orbitals of a_1 symmetry, of which one shows significant C–Cl antibonding character in the planar form. This would then lend support to the earlier analysis at the extended Hückel level by Albright, Hoffmann, Thibeault, and Thorn[11] that the barrier is essentially steric in nature arising from olefin–chlorine repulsions, since in unhindered $ML_nC_2H_4$ molecules the

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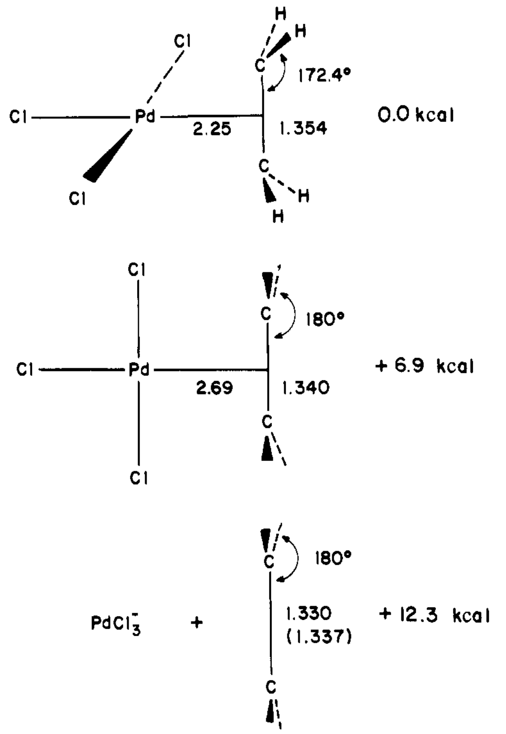

Figure 4. Calculated geometries for $PdCl_3(C_2H_4)^-$ for the upright and planar forms of coordinated ethylene along with uncoordinated ethylene.

d orbitals would preferentially stabilize the planar form.

These qualitative findings can be reinforced by examining the changes in electronic structure within the framework of the Dewar–Chatt–Duncanson model[5,6] of metal–olefin bonding. In Tables II and III we examine the changes in metal orbital population in the upright form of the complex and in the fragments. The MCl_3 fragment is located in the xy plane with the Cl's lying along the $\pm x$ and $-y$ axes and the C_2H_4 along the $+y$ axis. In this coordinate system the "filled" d_{yz} orbital has the proper symmetry to interact with the empty π^* orbital of C_2H_4 ("π donation") and the "empty" $d_{x^2-y^2}$, s, and p_y orbitals can interact with the occupied π orbital of C_2H_4 ("σ acceptance"). In addition the nominally filled d_{z^2} orbital can be influenced by the σ interactions.

The population analysis has been carried out both in terms of standard Mulliken populations[25] and in terms of a modified Mulliken populations scheme due to Noell.[26] In the latter scheme some population normally attributed to the metal but arising from diffuse (mainly s and p) basis functions extending beyond the covalent radius of the metal are assigned to the ligands in that region of space. As far as this discussion is concerned, the *changes* in population are very similar in both approaches and hence similar conclusions are reached. The absolute populations do differ substantially, however, since the Pt in Zeise's salt is described as essentially neutral (+0.02) in Mulliken population analysis compared to quite positive (+1.40) in the modified analysis.

The results of the population analysis (Tables II and III) show both the cooperative effects of σ acceptance and π donation in the metal and the decreased magnitude of such effects in Pd compared to Pt. The latter result was also reflected in the decreased overall binding of C_2H_4 to Pd. Overall a net increase of 0.24 electron was transferred from the olefin to the σ orbitals of Pt while 0.22 electron was "back-donated" from the $5d_{yz}$ orbital into the ligand with very little overall change of the charge on the Pt. For Pd the changes of the σ and π-orbital populations were +0.12 and −0.07, respectively.

Whether the origin of the greater stability of the platinum–ethylene bond compared to palladium–ethylene can be ascribed to more favorable overlap between ligand and metal orbitals remains problematical at this point. Chatt and Shaw[31] suggested greater stability of platinum–alkyl bonds compared to palladium–alkyl was reflected in the larger ligand field splitting, ΔE, in Pt complexes (where ΔE is the difference in energy between highest occupied and lowest unoccupied molecular orbitals). In the parent $PtCl_4^{2-}$ and $PdCl_4^{2-}$ complexes themselves, it is not clear there is much difference in the values of ΔE since recent studies[32] do not reveal significant shifts in the d–d excitation energies.

The relativistic lowering of the 6s orbital energy and raising of the 5d orbital energy in Pt may be contributing to the stability, since both effects place the orbitals in more favorable positions for interaction with the ethylene. The lower 6s orbital could then serve as a better σ acceptor and the 5d orbital could function as a better π donor. Obviously the factors affecting thermodynamic and kinetic stability of transition-metal complexes need further theoretical studies on a variety of ligands and metals.

Summary

The calculated geometry of C_2H_4 complexed to Pt in $PtCl_3(C_2H_4)^-$ agrees closely with the recent neutron study of Love et al. Results for the Pd complex, for which no structural data yet exist, show less distortion of the C_2H_4 ligand from free C_2H_4 and less overall metal–olefin interaction. The calculated barrier to rotation (15 kcal/mol) about Pt lies near the range of 10–14 kcal/mol normally found for platinum–olefin complexes, while a smaller barrier (8 kcal/mol) is obtained for Pd. Analysis of orbital populations shows equal importance of σ acceptance and π donation by the metal atom.

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Supplementary Material Available: Tables IV–VII, the valence basis sets and Gaussian expansions of the effective potentials for Pd, Pt, and Cl (4 pages). Ordering information is given on any current masthead page.

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