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A unique and novel cyclopropylmethyl cation intermediate: a DFT study

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ABSTRACT

Some physical organic aspects of the intermediates that result from the interaction between phenylmethylenecyclopropane (substituted derivatives are important in synthesizing cyclobutenes) and platinum and palladium halides have been studied using B3LYP. Geometrical aspects, values of atom polarizable tensor charges (APT), effect of substituents, selected transition states activation barriers, and molecular orbital calculations are presented. These calculations suggest a novel organometallic cyclopropylmethyl cation, which is characterized by the presence of a highly polarized and unusually long sigma bond between the benzylic carbon and coordinating halogen atom.

1. Introduction

The chemistry of reactive intermediates is central to a modern mechanistic and quantitative understanding of organic chemistry. Moreover, it underlies a significant portion of modern synthetic chemistry, and is frequently integral to a molecular view of biological chemistry.

Carbocations are a class of reactive intermediates that have been studied for more than a century. Activation of an alkene with a Lewis acid primarily involves disturbing the double bond electron density, as an essential step.[1–4] In other words, a carbon skeleton-based rearrangement catalyzed by a Lewis acid must include generation of an acidic carbon center. Fürstner and Aïssa[5] reported an efficient conversion of alkyl and aryl derivatives of methylenecyclopropane to cyclobutenes using catalytic amounts of various platinum reagents. Shortly after, a similar skeletal rearrangement of methylenecyclopropane using palladium catalysts was reported by Shi's group.[6]

Carbocations can be classical and nonclassical. Nonclassical carbocations (or carbonium ions employing Olah's terminology[7]) are cations in which there is delocalization of sigma electrons. The most extensively studied, and at one time highly controversial, system is the 2-norbornyl cation.[8] This theoretical study detected novel types of carbocations in which there is strong stabilization of the carbocation center by the nonbonding electrons of the halogen (Cl, Br) coordinated to the transition metal (Pd, Pt) through unusually long sigma bonding. This computational study aimed to shed light on the electronic structure of two new intermediates that result from the interaction of the phenyl derivative with the [M–X] unit; the two molecular structures of the $PtCl_2(CO)(olefin)$ and $PdBr_2(CH_3CN)(olefin)$ are shown in Figure 1. In general, studying an intermediate theoretically focuses on its structure, atomic

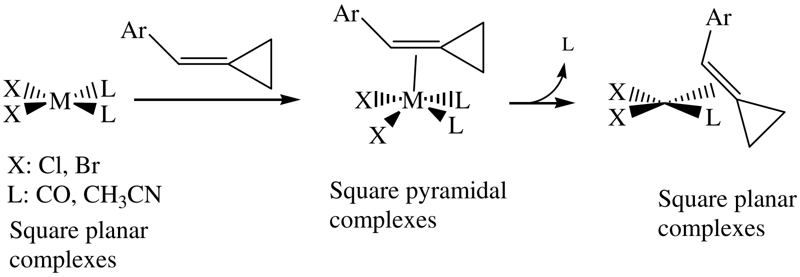

Figure 1. Formation of the olefin complex by an association–dissociation mechanism. M is Pd or Pt.

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charges, chemical reactivity, and its molecular orbital diagram. In this work, we report the geometrical parameters, the atom polarizable tensor charges (APT), and the effect of substituents on the molecular geometry. Some transition state calculations are also reported, which provide a qualitative understanding on the atomic charges and the chemical reactivity. The molecular orbital diagram is discussed qualitatively. A part of the mechanism (catalytic cycle) proposed by Fürstner is cyclopropyl ring expansion via a 1,2-alkyl shift. This is adopted here to evaluate qualitatively and indirectly the partial atomic charge on the benzylic carbon.

2. Computational method

Calculations were carried out by using density functional theory (DFT) employing Becke's three-parameter exchange functional in conjunction with the Lee–Yang–Parr correlation functional (B3LYP)[9,10] as implemented in the GAUSSIAN 03 suite of programs.[11] Calculating the harmonic vibrational frequencies and noting the number of imaginary frequencies confirmed the nature of all the intermediates (number of imaginary frequencies = 0). All the structures in the singlet spin state were calculated using restricted B3LYP (which is the default case in the program). Structure optimization was performed by employing the modified GDIIS algorithm,[12,13] recommended for use with large systems, tight optimizations and molecules with flat potential energy surfaces. The quadratically convergent[14] self-consistent field (SCF) was employed. The geometries of the two complexes were optimized using mixed basis set calculations. The basis set 6-31G*[15] was specified for C, H, O, N, Cl, and Br, and the Stuttgart–Dresden effective-core potentials basis set (SDD)[16,17] was assigned for platinum and palladium. Atom polarizability tensor-based charges (APT)[18] are used throughout the work, qualitatively.

The basis sets 6-31G* and SDD are becoming very popular[19–25] choices for medium size molecular systems. Recently, APT-based atomic charges, compared to Mulliken and natural population analysis (NPA) charges, provided values for atomic charges more consistent with the chemical intuition in many cases of organometallic systems;[26–30] hence, APT were adopted for the followup of some selected partial atomic charges in the absence of a standard method for atomic charge calculations. In this work, APT charges gave results consistent with general chemical intuition and consistent with other calculations. Atom numbering is as used by the graphical interface ChemCraft, and unnecessary atom numbers were deleted for clarity.

The catalytic process in Fürstner's reactions is affected positively by the presence of carbon monoxide; therefore, CO must be an interfering ligand. CO reacts with $PtCl_2$ to form the square planar platinum complex $PtCl_2(CO)_2$, as reported previously.[31] Olefins can replace one or two CO ligands in $PtCl_2(CO)_2$ to form $PtCl_2(CO)$(olefin).[29] Similarly, $PdBr_2(CH_3CN)$(olefin) can be formed by replacing one acetonitrile ligand with the alkene.[32] Figure 1 gives a qualitative mechanism for formation of both $PtCl_2(CO)$(olefin) and $PdBr_2(CH_3CN)$(olefin).

3. Geometry and APT charges for the organoplatinum species

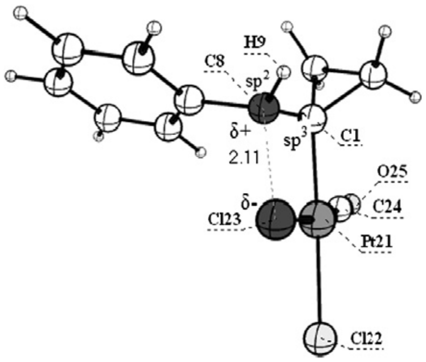


Figure 2. Optimized structure for $PtCl_2(CO)$(olefin) using 6-31G* (C, H, O, Cl) and SDD (Pt). The C8–Cl23 distance is in angstroms.

Table 1
Selected bond lengths and angles of platinum complex **1**[a]

	6-31G*	6-31+G*	6-311G*	6-311+G*
Pt–C1	2.076	2.078	2.076	2.078
Pt–Cl23	2.461	2.461	2.463	2.464
C1–C8	1.504	1.508	1.503	1.505
C8–Cl23	2.059	2.037	2.043	2.030
C1–C8–H9[b]	114.75	114.50	114.50	114.39
C1–C8–C10	121.25	121.02	121.22	121.02
C10–C8–H9	112.11	111.84	112.14	111.91
Cl23–C8–C1–Pt	−22.44	−21.23	−22.09	−21.41

[a] Bond lengths are in Å and bond angles are in degrees.
[b] H9 is the hydrogen atom connected to C8.

The structure of the platinum complex (Fig. 2) was optimized using the 6-31G*, 6-31+G*, 6-311G*, and 6-311+G* basis sets assigned to carbon, hydrogen, oxygen, and chlorine atoms in each case, while the SDD basis set was assigned to platinum in all cases (Table 1). The four basis set groups optimized the complex to nearly the same structure with negligible differences in bond lengths and angles. Qualitatively, carbon atom C1, which coordinates to Pt, has a tetrahedral geometry (sp^3 carbon) while C8 has a planar geometry (a sp^2 carbon). The bond length of Pt–C1 is 2.076–2.078 Å, Pt–Cl23 is 2.461–2.464 Å, C1–C8 is 1.503–1.508 Å, and C8–Cl23 is 2.030–2.059 Å. The considerable change in the bond length of C1–C8 before (1.331 Å) and after (1.503 Å) coordination indicates considerable disturbance of the π-bond and indicates a single C–C bond. The Pt–C1(sp^3) bond is expected to be a slightly polarized covalent bond, and polarization is toward the carbon atom. The carbon atom C8 (sp^2) is best described as a carbocation. Carbon C8 has nearly one unit of positive charge (0.89 and 0.93; Table 2) and Cl23 has a half unit of negative charge (−0.55 and −0.57; Table 2). This charge separation is very similar to that expected between a chloride ion and lithium or sodium ions. Hence, C8···Cl23 is described as an electrostatic interaction that takes place to stabilize the positive charge on C8; so, the interaction between C8 and Cl23 plays an important role in stabilizing the molecular geometry. In Section 7, Molecular Orbital Calculations are discussed, and it is shown that this interaction has sigma bond character..

4. Effect of substituents

To support further the result that the benzylic carbon is an acidic carbon (Lewis definition), an examination of the effect of

Table 2
Selected APT atomic charges of the platinum complex using two basis set groups with the SDD basis set assigned to the Pt atom

Atom	Mixed basis set[a]	6-31G*
C1	−0.07	−0.08
C8	+0.89	+0.93
Pt	+0.20	+0.15
Cl23	−0.55	−0.57

[a] The basis set 6-31+G* was assigned for C and Cl, and 6-31G* was assigned for O and H.

substituents at the *para* position of the phenyl group would make a clearer picture. Platinum complexes with OH and CN groups were chosen. The electron-withdrawing CN group destabilizes the positive charge on C8 (0.881), which resulted in a decrease of the interatomic distance between C8 and Cl23 to 2.005 Å, indicating a stronger electrostatic interaction. The OH group caused an increase in the C8–Cl23 bond length to 3.2 Å. This result qualitatively means that the benzylic carbocation does not need to gain stabilization by interacting with Cl23 because of the better stabilization gained by resonance with OH.

5. Some transition state calculations

As mentioned earlier, ring expansion of the cyclopropyl group (Fig. 3) was adopted from Fürstner's mechanism[5] to examine the effect of substituents (on the phenyl group at the *para* position) on the carbocation. The transition state for cyclopropyl ring expansion to a cyclobutyl ring was determined for OH and CN substituents. The activation free energy for the OH derivative is 18.32 kcal/mol, while that of the CN derivative is 4.45 kcal/mol. In addition, the relative energies of the products of this 1,2-alkyl shift were calculated. For the CN derivative, the product is 4.52 kcal/mol more stable than the cyclopropyl complex. For the OH derivative, the product is 11.91 kcal/mol less stable. This supports the idea that the OH group stabilized the benzylic carbocation by resonance. In the case of the CN substituent, the carbocation center transfers to another carbon not directly affected by CN, which is necessarily a more favored electronic state. Calculating the activation energies is an indirect way to evaluate the partial atomic charges calculated by the APT method, which show that these APT charges are qualitatively in good agreement with chemical intuition and the optimized geometries.

6. Geometry and APT charges for the organopalladium species

In PdBr$_2$(CH$_3$CN)(olefin) (Fig. 4), the benzylic carbon in the palladium complex C10 (0.85 and 0.87, Table 3) has similar atomic charge to C8 in the platinum complex. Carbon C2 has a small negative charge (−0.16) close to that for C1 in the platinum complex. Values of the dihedral angles Cl23–C8–C1–Pt and Br12–C10–C2–Pd are −22.44° and −19.69°, respectively. These values indicate that the carbocation center (the acidic carbon center) is affected greatly, and is stabilized by electrostatic interaction with the partial negative charge present on chlorine or bromine. Thus, it appears that the interaction between C10 and Br12 in the palladium complex also stabilizes the molecular geometry, as in the platinum complex. Primarily, and based on the observed similarity, it might be possible to say that the two rearrangement reactions take place through the same mechanism.

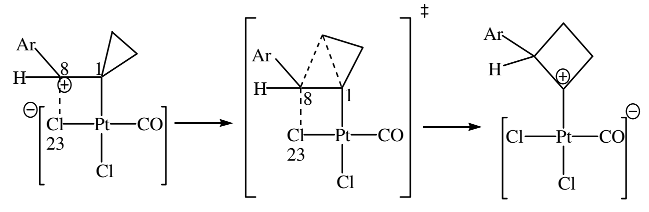


Figure 3. Optimized transition state for OH and CN substituents. Ar is a phenyl group with a substituent at the *para* position.

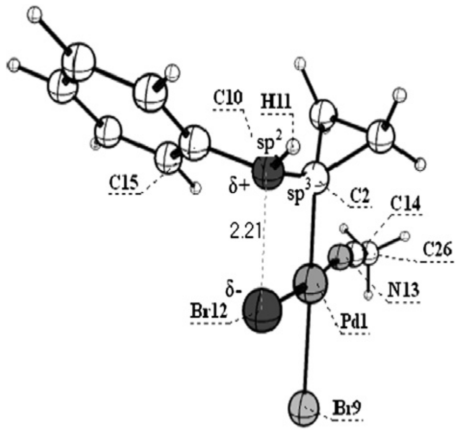


Figure 4. Optimized structure of the palladium complex PdBr$_2$(CH$_3$CN)(olefin) using 6-31G* (C, H, N, Br) and SDD (Pd). Selected bond lengths and angles: Pd–C2 = 2.056 Å; C2–C10 = 1.489 Å; Pd–Br12 = 2.492 Å; C2–C10–H11 = 115.39°; C2–C10–C11 = 112.41°; Br12–C10–C2–Pd = −19.69°. C10–Br12 distance is in Å.

Table 3
ATP atomic charges of the palladium complex using two different basis set groups for atoms other than the metal and the basis set SDD assigned to Pd

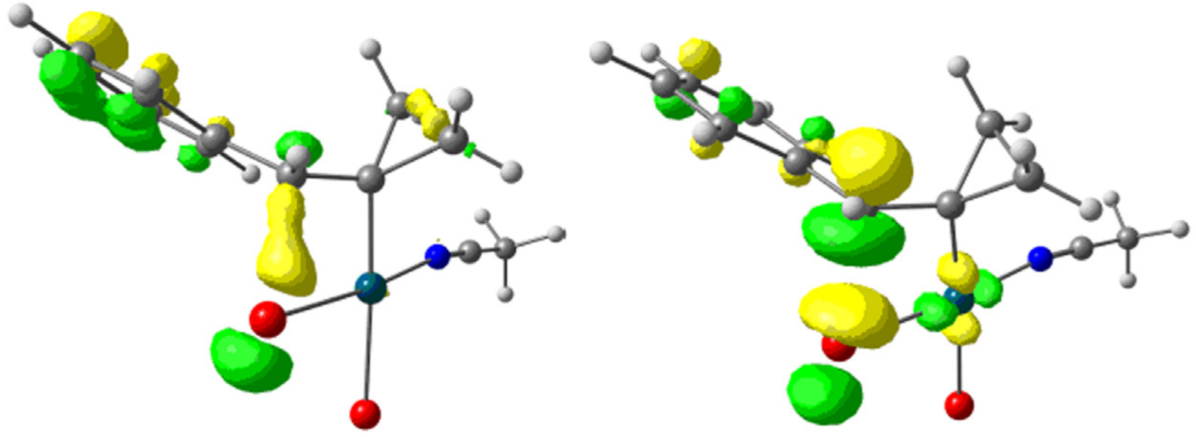
Atom	Mixed basis set[a]	6-31G*
C2	−0.16	−0.16
C10	+0.85	+0.87
Pd	+0.42	+0.33
Br12	−0.41	−0.40

[a] The basis set 6-31+G* was assigned for C and Br, and the basis set 6-31G * was assigned for N and H.

7. Molecular orbital calculations

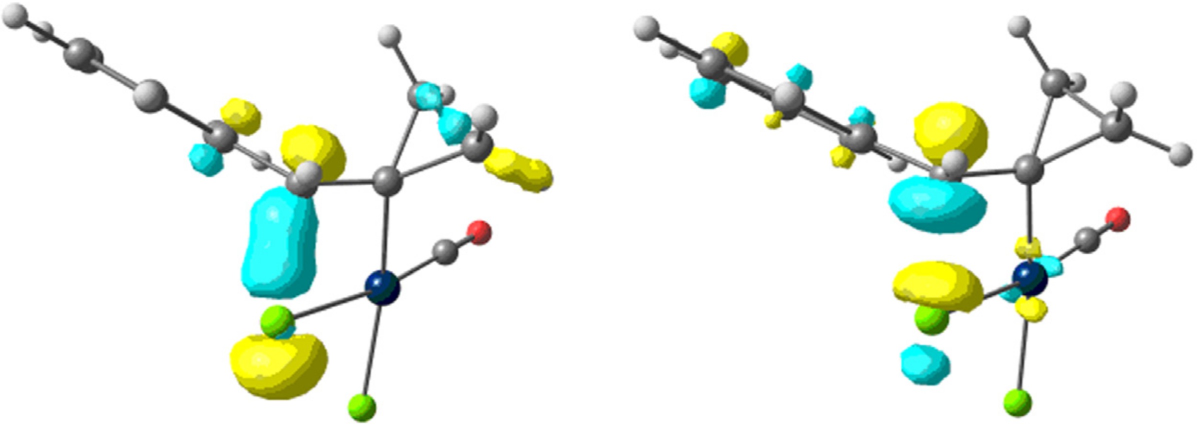
Molecular orbitals developed for the two intermediates can be helpful in further characterizing their nature. The electrophilicity index[33] was calculated for the palladium and the platinum intermediates as 2.30 eV and 2.94 eV, respectively. These values are similar to species of the general formula XY$_3{}^+$,[34] (X = C, Si, Ge, Sn, Pb; Y = CH$_3$, H, F, Cl, Br, I, At; the electrophilicity index values range is 1.7–11.5 eV), which means that they are good electrophiles and can accept electrons in their LUMO orbital. The free carbocation (cyclopropyl)(phenyl)CH(+) has an electrophilicity index value equal to 11.31 eV. Qualitatively, the difference between this value and the values calculated for the palladium and platinum intermediates indicates that the interaction between Cl and Br with the benzylic carbon in the two intermediates is a considerable stabilizing factor. In this regard, it is worth mentioning that the value of the electrophilicity index for the free olefin is 1.02 eV.

Visualizing the molecular orbitals for the two intermediates shows that the benzylic carbon in each has a considerable portion of the LUMO orbital (Fig. 5). The halogen atom in each structure also carries a considerable portion of the LUMO orbital. By investigating the molecular orbital (MO) diagram further we found that MO number 47 mainly represents the electron density between the benzylic carbon and Br in the palladium intermediate (Fig. 5), and MO number 50 is the same for the platinum intermediate (Fig. 5). The source of this electron density can be donation of electron density from the lone pair on the halogen to the electron deficient benzylic carbon. This means that the LUMO orbital is theoretically the antibonding orbital for an unusually long C–X bond. Based on chemical intuition, the carbon in such cases is an electrophilic center, as is the case for alkyl halides. To evaluate qualitatively the strength of this rare case of interaction (see Figs. 2 and 3) these bonds were compared with the C–X bonds in Me–Br and Me–Cl as in the following. The energy difference (ΔE) in the molecular orbital diagram between the sigma bond (σ), C–X, and anti-sigma (denoted as sigma* or σ^*, which is the LUMO orbital



Pd intermediate: MO number 47

Pd intermediate LUMO orbital



Pt intermediate: MO number 50

Pt intermediate LUMO orbital

Figure 5. The LUMO orbital on the benzylic carbon in each intermediate.

in the two cases) was calculated ($\Delta E = E_\sigma - E_\sigma^*$) for the four species (Me–Br, Me–Cl, Pd-intermediate, and Pt-intermediate). Then the following percents were calculated: [(ΔE of Pt-intermediate/ΔE of Me–Cl) × 100%] and [(ΔE of Pd-intermediate/ΔE of Me–Br) × 100%]. For platinum and palladium the values are nearly 86% and 80%, respectively, which indicate that what was described based on the atomic charges as electrostatic interaction actually has considerable sigma-bond character, and is a strong interaction that can cause a considerable stabilization of the benzylic carbon and the molecular geometry. Therefore, these organometallic species have structures intermediate between those proposed by Fürstner[5] and Shi.[6]

These calculations show that Lewis acidity can transfer from the transition metal to the olefin after coordination to generate a positively charged carbon center. The olefin phenylmethylenecyclopropane coordinates to [X–M] and generates an unstable intermediate metalla-hala-cyclobutane segment due to the appreciable interaction between the benzylic carbocation and the negatively charged halide. The characteristics of the organic part in the two complexes resemble that of the cyclopropylmethyl cation, and therefore it can be viewed as an organometallic version of this intermediate. What most makes this intermediate unique and novel is that the interaction between the benzylic carbon and the halogen atom is described as a highly polarized and unusually long sigma bond.

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