

Teaching Bonding in Organometallic Chemistry Using Computational Chemistry

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Since the major breakthroughs in the 1950s, organometallic compounds of transition metals have found widespread use as homogeneous catalysts in organic synthesis (1) and a fast-increasing number of both bulk- and fine-chemical industrial processes (2). In our group, much effort has been devoted to the development of homogeneous catalysts for a variety of reactions. Rational design of ligands by adjusting electronic and steric properties (3) has led to the development of catalysts that display high (enantio, regio, chemo) selectivity in many reactions. For bidentate ligands, the so-called *bite angle* of the ligand (see below) can be another important ligand parameter (4).

Palladium is often used as a homogeneous catalyst and it is possible to use a common palladium compound such as Pd(PPh₃)₄ or Pd(OAc)₂ as catalyst precursor for several very different reactions (1, 3). Substitution of the PPh₃ or the OAc group by specific ligands enables one to fine-tune the catalyst. We have recently found an interesting effect of the P–Pd–P angle (bite angle) of bidentate phosphine ligands on the structure and catalytic activity of cationic (ligand)palladium(η³-allyl) complexes (5). The η³-C₄H₇–Pd complexes used in the work reported here occur as two isomers, syn and anti. It was found that a larger bite angle of the ligand resulted in a different syn:anti ratio and also in a different regioselectivity in the palladium-catalyzed allylic alkylation (5).

In our studies, molecular modeling proved to be a valuable tool. We used the Spartan computation package (6), which, as well as other packages (Macromodel, Hyperchem, Gaussian94, etc.), facilitates calculations on several levels of theory. The relatively straightforward molecular modeling stimulated us to use this approach in a computational chemistry course for undergraduates. It was helpful in introducing important concepts of organometallic chemistry, such as d orbitals, σ donation, π back-donation, and the geometry of organometallic compounds.

Here we report on the example we used during the course, involving two isomeric Pd(1-Me-allyl) complexes (syn

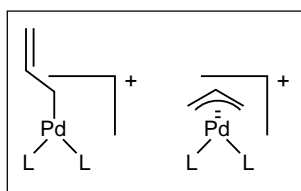


Figure 1. Left: the η¹-allyl-Pd; right: the η³-allyl-Pd bonding mode.

and anti). It is shown by the use of computational chemistry that the isomer ratio is influenced by the bite angle of the ligand. Also included in the course is the design of ligands that favor a high or a low syn:anti ratio, which resulted in some surprisingly good ideas. We hope that this contribution will stimulate the use of molecular modeling in the introduction of organometallic chemistry to undergraduate students.

Palladium–Allyl Complexes

Metal–ligand bonds are characterized by bonding and back-bonding interactions (1, 7). The latter take place from (partially) filled metal d-orbitals to empty low-lying antibonding σ* or π* orbitals on the ligand. Back-bonding is important for the coordination and activation of ligands such as CO, ethene, and H₂.

The allyl ligand is special because it can coordinate in two ways (8): η¹ and η³ (Fig. 1). The η¹ bonding mode is a donating interaction of a lone pair on the α-carbon atom. The η³-bond is more complicated. Each carbon has one unpaired electron in a 2p atomic orbital. Linear combinations of these p orbitals lead to the construction of three new (molecular) orbitals (Fig. 2).

The bonding orbital ψ₁ (all plus) has no nodal plane, the nonbonding ψ₂ has one, and the antibonding combination ψ₃ has two (intersecting both C–C bonds). Filling these orbitals with the three 2p electrons of the carbon atoms shows the interesting properties of the allyl ligand. It is instructive to visualize this process by calculating (single point) the frontier orbitals of the C₃H₅ fragment bearing the charge +1, 0, and -1 (Example 1, p 590).

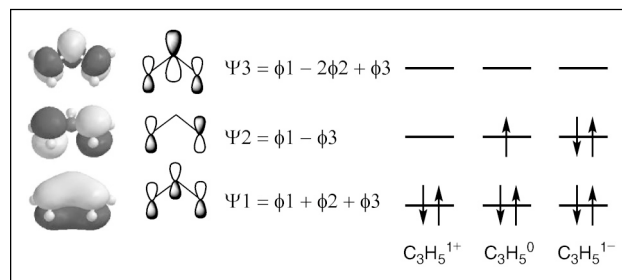


Figure 2. The linear combinations of carbon 2p orbitals in the allyl group (right) and the calculated, delocalized, orbitals (PM3(tm), left). Note that the adjacent atomic 2p orbitals in the ψ₁ orbital overlap (because of the absence of a nodal plane perpendicular to the C–C bond) and form a delocalized molecular orbital).



Figure 3. Ball-and-stick representation of the cationic $(\text{C}_3\text{H}_5)\text{Pd}(\text{PH}_3)_2^+$ model complex. Left: top view; right: side view.

The bonding orbital Ψ_1 can participate in electron donation to the metal. The nonbonding orbital Ψ_2 is occupied by only one electron and can therefore receive electron density from the metal. This occurs via the d-orbital with the appropriate symmetry. For metal-to-allyl π -back-bonding, at least partially filled d_{xy} orbitals are required on the metal center. Therefore, allyl complexes of early transition metals often adopt an η^1 structure, whereas complexes of late transition metals prefer an η^3 structure (8). In this paper, we focus on the η^3 -allyl complexes of palladium.

Inspection of published crystal structures (9) shows that (ligand) $\text{Pd}(\eta^3\text{-allyl})$ complexes are square planar and the counterion is located far from the palladium atom. Calculations for $[\text{Pd}(\eta^3\text{-allyl})(\text{PR}_3)_2\text{X}^-]$ complexes are therefore performed on the 16-electron cationic complex and the nature of the anion is neglected.

Calculations

The smallest complex to start with is $(\text{C}_3\text{H}_5)\text{Pd}(\text{PH}_3)_2^+$, which serves as a model for larger systems (Fig. 3). The geometry of this complex has been calculated using several levels of theory; the required time is shortest for the semiempirical PM3(tm) level (6). The results of a fully optimized structure on the ab initio level were obtained from literature (10). Inspection of the calculated geometry (bond distances, bond angles) reveals that all three methods give similar results (see Table 1).

In all cases, the (Pd–Dummy–Cc) angle, the “leaning-backward” of the allyl moiety, is larger than 90° , which is a result of the back-bonding interaction (10). Since there is no coefficient of the allyl nonbonding orbital ψ_2 on the central carbon atom, the two terminal carbon atoms are expected to

Table 1. Optimized Geometry of $(\text{C}_3\text{H}_5)\text{Pd}(\text{PH}_3)_2^+$ Using Different Levels of Theory

Geometrical Parameter ^a	Level of Theory		
	Semi-empirical PM3(tm)	Density Functional bp86-dn**	Ab Initio (10) MP2/A-LANL2DZ
$d(\text{Pd-Ct}) / \text{\AA}$	2.163	2.260	2.212
$d(\text{Pd-Cc}) / \text{\AA}$	2.198	2.242	2.192
$d(\text{Cc-Ct}) / \text{\AA}$	1.440	1.409	1.422
$\angle \text{Ct-Cc-Ct} / \text{deg}$	115.6	119.3	118.3
$d(\text{Pd-P}) / \text{\AA}$	2.278	2.373	2.392
$\angle \text{P-Pd-P} / \text{deg}$	98.7	100.734	103.5
$\angle \text{Pd-Dummy-Cc} / \text{deg}$	119.6	116.6	not reported

^aCt represents a terminal allylic carbon atom; Cc represents the central allylic carbon atom.

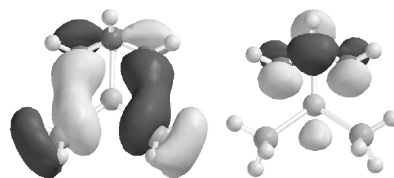


Figure 4. The (left) HOMO and (right) LUMO of the optimized structure of cationic $(\text{C}_3\text{H}_5)\text{Pd}(\text{PH}_3)_2^+$, calculated by the semiempirical PM3(tm) method.

bind more strongly to the metal. The more advanced methods predict that all three carbon atoms are bonded to palladium, probably via back-bonding to a mixed orbital on the allyl ligand (10).

The values used for the parameters in the semiempirical PM3(tm) method are partly based on crystal structures of which many are known for cationic $\text{Pd}(\eta^3\text{-allyl})(\text{ligand})$ complexes. Calculations performed on this level of theory provide satisfactorily reliable results in a very short computing time. Therefore, this method was used for the classroom exercises (see Example 2).

Figure 4 shows the HOMO and LUMO of the optimized structure of cationic $(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{PH}_3)_2^+$. On the allyl moiety the combinations of carbon 2p orbitals can be identified in both the HOMO and the LUMO. Interestingly, the molecular orbitals have coefficients on the allyl moiety, the palladium atom, and the PH_3 groups. The orbitals of the isolated allyl group (Fig. 2) can still be identified easily.

Effect of Substituents and the Bite Angle of the Ligand

The allyl ligand possesses five H atoms that can be substituted with, for example, a CH_3 group (Fig. 5). The results of the calculation of the structures using several substitution patterns are listed in Table 2 and the calculated structures of *syn*-(CH_3 -allyl) $\text{Pd}(\text{PH}_3)_2^+$ (b) and *anti*-(CH_3 -allyl) $\text{Pd}(\text{PH}_3)_2^+$ (a) are presented in Figure 6. The energy of formation of complexes with anti substituents is higher than that of the analogous complexes with syn substituents (Table 2) because the anti substituent is closer to the Pd atom (Fig. 6). Apart from increased steric hindrance, the cis conformation of the allylic C–C bond further destabilizes the anti complex as compared to the syn complex.

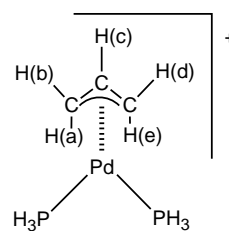


Figure 5. The designation of the five H positions in the $[\text{C}_3\text{H}_5]$ fragment.

The influence of the P–Pd–P angle on the relative stability of the syn and anti complexes can be calculated by using a geometrical constraint on the P–Pd–P angle. The energies of formation of syn and anti ($\eta^3\text{-1-CH}_3\text{-C}_3\text{H}_5$)Pd(PH₃)₂⁺ complexes as a function of the P–Pd–P angle are plotted in Figure 7. The energy of the syn complex is always lower than that of the anti complex. Both curves show a minimum energy at a bite angle of around 100°. When the bite angle is larger, a smaller energy difference is calculated. The Boltzmann equation thus predicts that an equilibrium mixture of syn and anti complexes will always contain a higher fraction of the syn isomer, but the fraction of anti isomer is expected to increase when larger bite angles are applied. This is indeed what is observed experimentally (see below) (5).

The origin of this effect is both steric and electronic. A larger value of the bite angle will bring the phosphine ligands closer to the substituent on the allyl group. The steric effect will be more pronounced when the phosphine ligand bears large groups such as a phenyl ring or a cyclohexyl ring.

Ligand Design

A ligand with a bite angle of around 85° can easily be obtained by linking the two PH₃ ligands with a –CH₂– or a –CH₂–CH₂– bridge. From Tables 1 and 2 and Figure 7, however, it is clear that the optimum value of the P–Pd–P angle for a Pd(allyl) complex is around 100°. Thus, the real challenge is to design a ligand that enforces a bite angle larger than 100°. The backbone needs to be rigid, as otherwise it will twist in such a way that the bite angle assumes the optimal value of 100°. Our research group developed a series of ligands based on a xanthene backbone that have this property (4) (Fig. 8). In this exercise, students designed ligands on the computer with similar structures (see Example 3).

Link to Experiment

We used the semiempirical PM3(tm) calculation to study the steric effect of the bite angle (5). A series of cationic (1-CH₃-C₃H₅)Pd(P–P) complexes bearing a bidentate phosphine ligand was prepared and the structures of the syn and anti isomers were calculated. The ligand was varied in such a way that the P–Pd–P angle in the complex ranged from 85° to 110°. The complexes are formed as equilibrium mixtures of syn and anti isomers. In all cases, the syn isomer is thermodynamically favored, but when the bite angle of the ligand is larger, the syn:anti ratio decreases from 9 (dppe), to 1.3 (Sixantphos) (Table 3). The modeling data predict the same trend, since the energy difference between the syn and the anti isomer is smaller for the ligands with a larger bite angle.

Examples

Example 1: Calculation of the Frontier Molecular Orbitals of the Allyl Fragment

The allyl group can be obtained from the “expert” builder menu. After deleting the dummy atom, which is used to attach the allyl group via its gravicenter to a metal atom, a single-point calculation can be carried out. For the calculation of transition metal compounds, the lowest level of theory



Figure 6. Ball-and-stick representations of the calculated structures (PM3) of (left) *syn*- η^3 -(CH₃-allyl)Pd(PH₃)₂⁺ and (right) *anti*- η^3 -(CH₃-allyl)Pd(PH₃)₂⁺.

Table 2. Selected Data from the PM3 Geometry Optimization of CH₃-Substituted [((CH₃)_n-C₃H₅)Pd(PH₃)₂⁺ X⁻] Complexes

Substitution Pattern	<i>E</i> /(kcal mol ⁻¹)	β/deg
None	67.994	98.72
a (anti isomer)	62.278	98.75
b (syn isomer)	56.910	98.12
c	53.606	98.62
ac	48.264	98.63
bc	43.557	97.95
ad	51.190	98.07
bd	46.199	97.45
ae	58.597	97.94

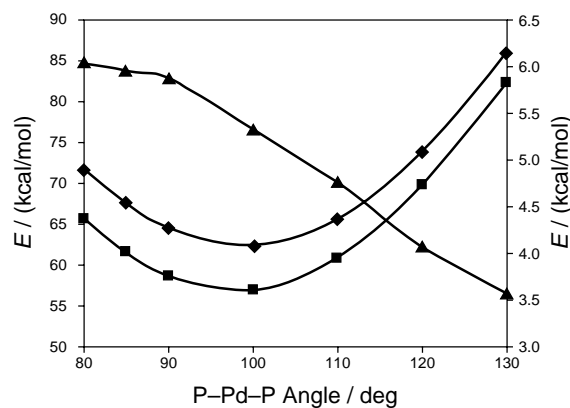


Figure 7. Calculated energy of formation of *syn*- and *anti*-(1-CH₃-allyl)Pd(PH₃)₂⁺ complexes with different bite angle; (■): *syn*, (◆): *anti*, (▲): energy difference (right axis).

required is the semiempirical PM3 method. To visualize the filling of the orbitals of the allyl with electrons, the allyl fragment can be calculated bearing the charges -1, 0, and +1. As can be seen in Figure 2, the spin multiplicity of the allyl fragment bearing a charge -1 or +1 is 1 (singlet) and the neutral fragment has a spin multiplicity of 2 (doublet). Calculate the following molecular orbitals: HOMO-1, HOMO, LUMO, LUMO+1. The results of the calculation (allyl, charge 1+) are presented in Figure 2.

In the cationic fragment, the “all plus” combination is the HOMO and the combination with one nodal plane is the LUMO. In the neutral C₃H₅ fragment, the latter orbital

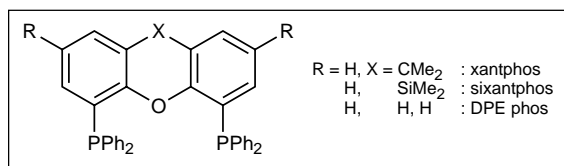


Figure 8. Generic xantphos structure.

Table 3. Experimental Results: Effect of Ligand Bite Angle on Syn:Anti Ratio in Cationic (1-CH₃-C₃H₅)Pd(P-P) Complexes (5)

Ligand	\angle P-Pd-P/ deg ^a	Syn (%)	Anti (%)	ΔE (syn - anti)/ (kcal mol ⁻¹) ^b
dppe	85	90	10	-5.7
dppp	95	92	8	-5.2
dppb	99	86	14	-4.8
dppf	106	78	22	-4.5
DPEphos	108	72	28	-3.7
Sixantphos	110	57	43	-3.0

^aValue obtained from optimized structure of syn complex (PM3(tm)).

^bDetermined from semiempirical PM3(tm) calculations.

is occupied with one electron and becomes the HOMO. The LUMO is now formed by the combination with two nodal planes.

Example 2: Geometry Optimization of (C₃H₅)Pd(PH₃)₂⁺

The molecule is again constructed in the “expert” builder menu, using a trigonal planar palladium atom. Both the allyl group and the phosphine ligands can be obtained from the “ligand” menu. The calculation is set up with the complex bearing a charge +1 and a singlet spin multiplicity and is performed on the semiempirical PM3(tm) (not just PM3) level, which is the lowest level of theory required for this calculation.

Example 3: Rational Ligand Design

Construct a new ligand starting from a selected backbone (e.g. -CH₂-CH₂-) and attach two or more -PH₂ groups. Connect the trigonal planar Pd atom (expert builder menu) to two of the phosphorus atoms. Add an allyl fragment to the vacant site of the palladium atom. Optimize the geometry using the PM3 method, with the charge of the complex set to +1 and a singlet spin multiplicity. Determine the bite angle of the ligand. Add a methyl group on the allyl moiety and calculate the energy of the optimized structure of the syn and the anti isomers.

Concluding Remarks

We have shown that semiempirical calculations can help in the understanding of experimentally observed phenomena in organometallic chemistry and the rational design of ligands. The approach is straightforward and the methods used can easily be adapted to classroom exercises for undergraduate students. The choice of (allyl)palladium fragments allows for the introduction of important concepts such as the geometry of organometallic complexes, σ -donation, π -back-donation, and the bite angle of bidentate phosphine ligands.

The level and the scope of the exercises can easily be extended by using substituents other than a CH₃ group, other ligand donor atoms, and bidentate ligands.

Acknowledgments

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