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Molecular Mechanics (MM2) Parameters for the (η^3-Allyl)palladium Moiety

Per-Ola Norrby,[*,†] Björn Åkermark,[*,†] Fredrik Hæffner,[†] Sverker Hansson,[†] and Margareta Blomberg[*,‡]

Contribution from the Royal Institute of Technology, Department of Organic Chemistry, Stockholm, Sweden, and Stockholm University, Department of Physics, Stockholm, Sweden

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Abstract: Molecular mechanics parameters have been developed that allow calculation of (η^3-allyl)palladium complexes with the MM2 force field. Virtual (dummy) atoms have been used to simulate the bond between palladium and the ligands. The parameterization was based upon selected X-ray structures together with ab initio calculations for different geometries of unsubstituted (η^3-allyl)palladium. For comparison, a few complexes with auxiliary ligands were also calculated. All ab initio calculations were performed with electron correlation of all valence electrons. The parameter set is used to calculate syn–anti equilibrium data for substituted (η^3-crotyl)palladium complexes with 2,9-disubstituted phenanthrolines as ligands. The equilibrium calculations are correlated with experimental data. The problems of adding parameters for atoms bound to more than four ligands to the MM2 force field are discussed.

Background

During recent years, a large number of highly regio- and stereoselective reactions have been developed where transition metal complexes act as catalysts.[1] The outcome of these reactions is generally the result of delicately balanced steric and electronic interactions between the auxiliary ligands, the metal, and the substrate. Reliable predictions, therefore, require accurate methods for calculating these interactions. In organic chemistry and enzyme catalysis, molecular mechanics calculations have proven useful for this purpose, and some advances have been made in development of force fields suitable for calculation of organometallic complexes.[2–4] In the present work, we have developed a methodology for molecular mechanics calculations on (η^3-allyl)palladium systems, which are intermediates in a number of useful synthetic reactions.[5] In these systems, the ligands play an important role in regulating stereo- and regioselectivity in nucleophilic addition to the η^3-allyl. For instance, we have recently shown that the syn–anti ratio (Scheme I), which determines the product structure after nucleophilic addition, can be strongly influenced by phenanthroline-type ligands.[6]

Scheme I

We have chosen to work with the MM2 force field, because MM2-type programs[7] are the most thoroughly tested of available programs and also because many researchers have access to various implementations and can include new parameters relatively easily. The parameterization was initialized by using a range of known structures to screen a number of different bonding models for their potential of structural prediction. The majority of the structures are normal square-planar (η^3-allyl)palladium complexes with either one bidentate or two monodentate auxiliary ligands (**3–21**, Figure 1). However, there appears to be no reliable

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[†] Royal Institute of Technology.

[‡] Stockholm University.

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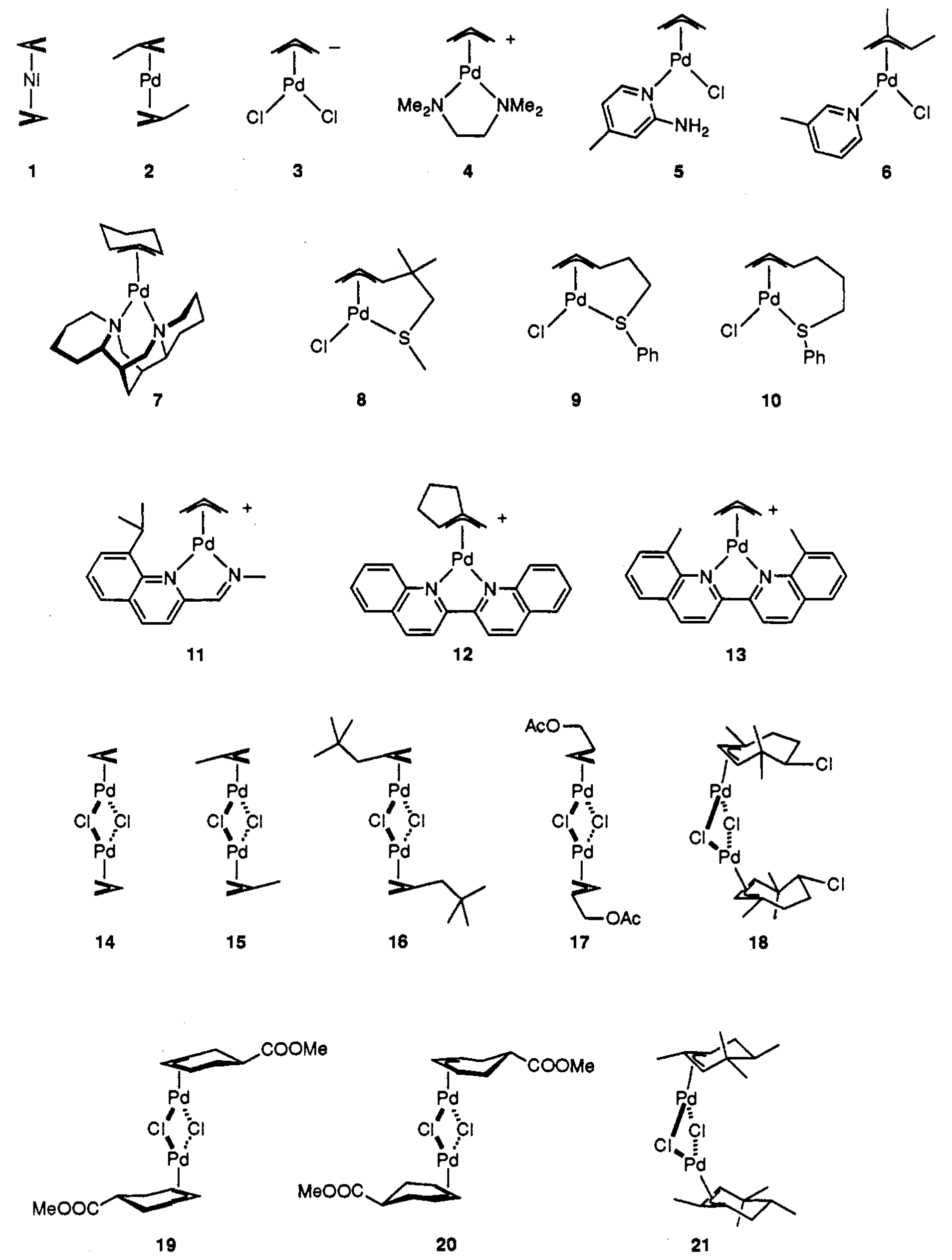

Figure 1. The structures used for parameterization.[8]

determinations of the hydrogen positions in the η^3-allyl group within this class. We therefore also included bis(2-methyl-η^3-allyl)palladium (**2**) where a very good low-temperature X-ray structure gives reliable hydrogen positions. Because X-ray structures give a picture of the electron density, not the nuclear positions needed for MM2 and ab initio calculations, we also wanted to include some neutron diffraction data in the parameterization. To our knowledge, no such data are available for palladium allyl compounds, but data for bis(η^3-allyl)nickel (**1**) showed an allyl group very similar to the one in compound **2**. We therefore felt it was justified to include the geometry of the allyl group from nickel compound **1** in the present work.

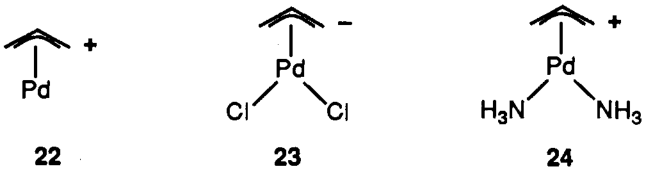

Figure 2. Symmetrized structures used for ab initio calculations. The geometry of the allyl group is taken from structure **1**. The initial position of palladium relative to the allyl group is taken from structure **2**. The positions of chlorine and nitrogen in structures **23** and **24** are taken from structures **3** and **4**, respectively.

In order to obtain a completely independent measure of the energy surface of the η^3-allyl–palladium bond, we also performed ab initio calculations on a few model complexes sufficiently small to permit accurate calculations (**22–24**, Figure 2). For the smallest complex (**22**), the potential energy surface for the movement of palladium relative to the η^3-allyl group was calculated (Figure 3). The molecular mechanics model was then refined until both the structures of Figure 1 and the calculated potential surface were reproduced with an acceptable level of accuracy. Finally, experimental data for syn–anti equilibria of a few phenanthroline type complexes (**27–31**, Figure 9) were utilized in a further refinement of the force field.

Bonding Models

The bond between an allyl group and palladium is best described in terms of orbital overlap, but in order to make calculations with MM2, a classical valence bond model must be used. In the most straightforward model, the three carbon atoms of the allyl group

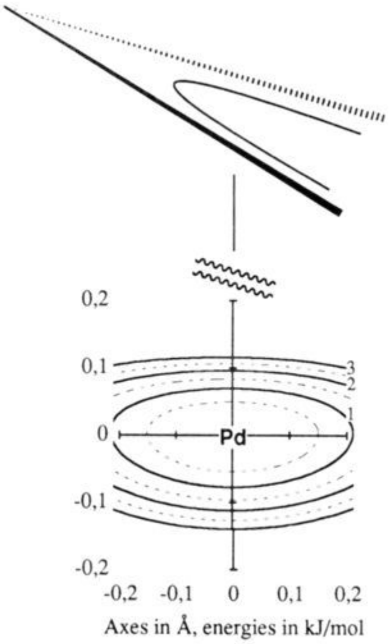

Figure 3. The potential surface generated when palladium is moved in the mirror plane of the symmetrized structure **22**.

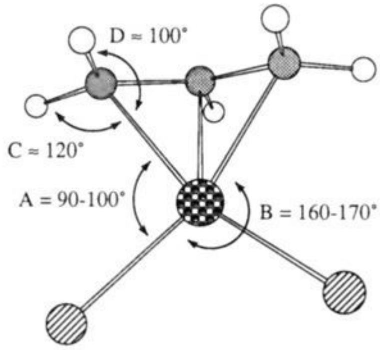

Figure 4. Dichloro(η^3-allyl)palladate (**3**) with pentavalent palladium. Important angles are noted.

are considered to be bound to palladium with single bonds. The other ligands, such as chloride or amines, would then also be bound to palladium with single bonds, making in all five bonds to palladium. Unfortunately, this model cannot be used for several reasons.

The first is the inability of the present MM2 program to handle more than four bonds to one atom. A second, more serious problem lies in the low symmetry at the palladium center. The MM2 program can only accept one ideal angle value for one type of angle. As is evident from the representative structure **3** (Figure 4), the chlorides have two different angles *A* and *B* to the terminal allyl carbons, and also the two angles *C* and *D* are of the same type but have different values. These limitations in the MM2 program raise the question whether another computational package should be used for this system. However, the advantages of the MM2 force field prompted us to try to find a working model.

A second model can be derived from the quantum chemical calculations performed on the hypothetical (η^3-allyl)palladium cation (**22**) and the two complexes **23** and **24**. The calculations show that the main contribution to the η^3 bond comes from overlap between palladium and the terminal allyl carbons, while the bond from palladium to the central carbon is weak. This is in complete accordance with the IR spectrum of (η^3-allyl)palladium chloride dimer (**14**) which, when solved with the assumption of a planar allyl group, shows a ratio of approximately 4/1 between the force constants of these two bonds.[9] The same conclusion can also be reached from simple frontier molecular orbital considerations since the HOMO of the allyl anion has a node at the central carbon. Based on these observations, we decided to investigate a bonding model similar to the one depicted in Figure 4, but lacking the bond between the central carbon and palladium (Figure 5).

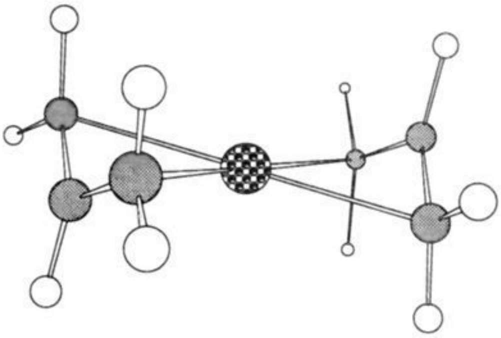

Figure 5. Palladium with a square-planar geometry bound to the terminal carbons, exemplified by bis(η^3-allyl)Pd.

The distance from palladium to the central carbon can easily be adjusted using strong angle bending force constants and selected torsional parameters. Initially we pursued this approach. The model contains a square-planar palladium atom. Other workers have ensured the planarity of such systems by introducing an energy penalty for deviations from a least-squares plane.[4] We decided instead to use proper torsional functions in order to avoid changing the original program. The final parameter set could reproduce most of the known structures fairly well. However, the worst problem with this model is the small deviation of the terminal allyl carbons from the coordination plane of palladium in experimental structures. In unstrained complexes, it is the centroid of the allyl, not the terminal carbons, that lies in or close to the coordination plane of palladium. Parameters were developed that displaced the terminal carbons slightly from the coordination plane defined by palladium and the two ligands, but it was impossible to avoid creating a false energy minimum with the allyl displaced equally far on the other side of the coordination plane. As a result, certain strained structures would yield the false minimum as the only answer, even when the starting structure in the calculation was the X-ray structure. Additionally, molecular dynamics would cause all structures to fluctuate between the false and real structures. This parameter set, which we believe is close to optimum for simple bonding models in MM2, is unacceptable. We therefore had to search for a way to extend the scope of MM2, preferably without reprogramming. We found that this could be done by introducing so called "dummy atoms" (Du).

The Dummy Atom Bonding Model

Dummy atoms are mathematical objects that need not have any physical reality. Basically, they allow an extension of the force field without reprogramming. A well-known example of such virtual atoms in molecular mechanics is the lone pairs used by MM2 to model anisotropic van der Waals interactions.[3a,7] Dummy atoms have been used previously in an attempt to model an (η^3-allyl)palladium complex,[3b] and in another application to model a distorted square-planar Cu complex.[3c] In our case, the dummy atom serves a dual purpose. It is used as a branching point in a bond, enabling the central atom to bind to more than four ligands while maintaining a semitetrahedral symmetry, and also extending the number of variable parameters associated with

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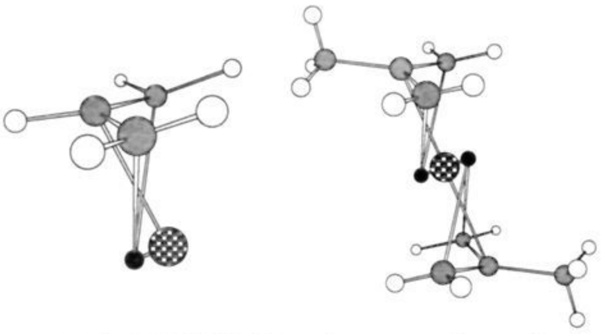

Figure 6. (η^3-Allyl)Pd$^+$ (**22**) with one dummy atom. Structure **2**, using the same bond model.

the bond. By making the palladium–dummy bond approximately perpendicular to the coordination plane, the ligand atoms are more easily held in a planar arrangement. Because addition of more atoms requires more parameters to be determined and also slows down computation somewhat, the number of dummy atoms should be as low as possible. However, as will be shown below, the correct use of dummy atoms solves the problems with allyl–palladium bonding models mentioned above without an excessive increase in parameters or computation time.

In the current implementation of the MM2 force field, palladium with two auxiliary ligands can only utilize two valences for bonding to the allyl group. The carbons in the allyl group have only one bond each available for bonding to palladium. To simplify the model, the dummy atom should be bound both to palladium and to the allyl group. The palladium then has only one valence free for bonding to an allyl carbon. For symmetry reasons, this should be the central carbon. The terminal carbons can then be bound to the dummy atom, which ends up with a total of three bonds (Figure 6). Note that this formally creates a fused bicyclic [1.1.1] system, making the allyl atoms members of four-membered rings. These rings receive special treatment in many programs.

In diallyl palladium molecules, palladium binds two central allyl carbons at 180° from each other. The optimal position for the dummy atoms here is along a line in the mirror plane approximately perpendicular to the Pd–C bonds. The only decision left to make is exactly where along this line to put the dummy atom. Because MM2 will allow specification of only one Du–C–H angle, the dummy atom should be positioned to give it the same angle to both the syn and anti hydrogens of the allyl. Only one point fits the requirements. The resulting model is shown in Figure 6.

A limitation of this model must be pointed out. If, while building new structures, the dummy atom is positioned on the wrong side of palladium, a false, strained minimum may be created. Structures resulting from such a misplacement might look reasonable on casual inspection and are stable in molecular dynamics, so this situation must be avoided when creating structures.

Another obstacle which is unavoidable when introducing dummy atoms into MM2 is that additional van der Waals interactions might result between palladium and certain other atoms. MM2 is programmed to calculate van der Waals forces between atoms that are not connected by a shared bond or bond angle (i.e., separated by at least three bonds). Because the model includes no bonds from palladium to the terminal allyl carbons, such unwanted interactions will result between palladium and 1- and 3-substituents on the allyl, especially groups in the anti position. This force is countered by including selected torsional constants. When new parameters are added to the model, care must be taken so that dihedral angles including all three allyl carbons always have torsional parameters that reproduce correctly both syn and anti substituents on the allyl group.

Table I. Atom Type Parameters

new atom type	van der Waals parameters r^* (Å)	ϵ (kcal/mol)	atomic wt
C_{allyl}	1.940	0.044	12.000
$Cl_{bridging}$	2.030	0.240	34.969
Du_{allyl}	0.002	0	0.500
Du_{ligand}	0.002	0	0.500
Pd_{allyl}	2.300	0.030	106.400

Table II. Bond-Stretching Parameters

bond type	k_s (mdyn/Å)	l_0 (Å)	μ (D)	rms dev (Å)
C_{alkane}–C_{allyl}	5.000	1.492	0.300	0.017
C_{alkene}–$S_{sulfonium}$	3.500	1.772		0.002
H–C_{allyl}	4.600	1.100		
Cl–Pd_{allyl}	2.000	2.383	−2.000	0.011
$S_{sulfonium}$–Du_{ligand}	2.000	1.108	1.000	0.003
N_{sp^3}–Du_{ligand}	2.000	0.821	1.000	0.009
$N^+_{sp^3}$–Pd_{allyl}	1.800	2.121	3.000	0.024
$Cl_{bridging}$–Pd_{allyl}	2.000	2.415	−1.000	0.012
C_{allyl}–C_{allyl}	7.000	1.395		0.024
C_{allyl}–Du_{allyl}	1.200	2.285		0.024
C_{allyl}–Pd_{allyl}	1.600	2.147	−4.500	0.024
Du_{allyl}–Pd_{allyl}	1.700	0.506	0.900	0.006
Du_{ligand}–Pd_{allyl}	2.000	1.257	1.000	0.006

The Parameter Set

The initial force field developments reported in this paper were performed using the Chem3D Plus™ program[10a] on Macintosh computers. The final parameter set was developed for the MacMimic/MM2(91)[10b] package for Macintosh. In all the calculations, the dielectric constant was set to 9 in order to simulate a chlorinated solvent or a crystal. A virtual "dummy" atom is added to the (η^3-allyl)palladium moiety, bound to palladium and the terminal allyl carbons. Palladium is only bound to this dummy atom and the central allyl carbon. Two additional ligands are bound to palladium in a plane approximately perpendicular to the palladium–dummy atom bond. In some cases, palladium is not bound directly to the ligand, but rather to another dummy atom, which in turn binds to the respective ligands (see below).

The atomic weight of atoms in the MM2 force field is only used to calculate a stretch–bend interaction constant. Our available data do not motivate the determination of stretch–bend constants for either dummy atoms or palladium. The atomic weight of palladium is outside the range where MM2 assigns a nonzero stretch–bend constant. The atomic weight of the dummy atoms was given an arbitrary value below the range used by MM2. We have found no reason to calculate van der Waals interactions to the dummy atoms. Therefore the hardness (ϵ) of dummy atoms is set to zero (Table I).

The sum of the van der Waals radii (r^*) of two atoms is used in the denominators of energy functions. To avoid division-by-zero errors, van der Waals radii must be nonzero, but the value should be as low as possible to gain computation speed in systems with a van der Waals cutoff at long distances (Table I, the dummy atoms). The parameters for the allyl carbons were taken from corresponding values for alkene carbons.

The equilibrium values for bond lengths and angles not involving hydrogen have been adjusted to give a good agreement with X-ray structures. The rms (root-mean-square) difference between the parameter values in X-ray and minimized structures are given for all relevant parameters (Tables II, IV, and VI). The dipole moments for bonds are nonoptimized values chosen to reproduce

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(10) (a) *Chem3D Plus™ 3.0* for Macintosh, Cambridge Scientific Computing Inc., 875 Massachusetts Ave., Suite 61, Cambridge, MA 02139. The three-dimensional drawings in this paper were created with Chem3D. (b) *MacMimic/MM2(91)* for Macintosh, InStar Software AB, IDEON Research Park, S-223 70 Lund, Sweden. MM2 versions for platforms other than Macintosh are available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405.

Table III. Electronegativity Constants for the $\mathrm{C_{allyl}-Pd_{allyl}}$ Bond

$\mathrm{Pd_{allyl}}$ substituent	correction to $\mathrm{C_{allyl}-Pd_{allyl}}$ l_0 (Å)	$\mathrm{Pd_{allyl}}$ substituent	correction to $\mathrm{C_{allyl}-Pd_{allyl}}$ l_0 (Å)
Cl	−0.040	$\mathrm{Cl_{bridging}}$	−0.045
$\mathrm{N^{+}{}_{sp^3}}$	−0.058	$\mathrm{Du_{ligand}}$	−0.034

Table IV. Four-Membered Ring Angle Bending Parameters

angle type	k_b (mdyn Å/rad^2)	θ_0 (deg)	rms dev (deg)
$\mathrm{Pd_{allyl}-Cl_{bridging}-Pd_{allyl}}$	0.450	91.500	1.2
$\mathrm{C_{allyl}-C_{allyl}-C_{allyl}}$	0.450	117.500	2.2
$\mathrm{C_{allyl}-C_{allyl}-Du_{allyl}}$	0.200	67.500	1.3
$\mathrm{C_{allyl}-C_{allyl}-Pd_{allyl}}$	2.000	71.100	1.6
$\mathrm{C_{allyl}-Du_{allyl}-C_{allyl}}$	0.300	62.000	0.9
$\mathrm{C_{allyl}-Du_{allyl}-Pd_{allyl}}$	0.300	63.000	1.4
$\mathrm{Cl_{bridging}-Pd_{allyl}-Cl_{bridging}}$	5.000	91.500	0.7
$\mathrm{C_{allyl}-Pd_{allyl}-Du_{allyl}}$	0.360	89.400	1.1

Table V. Four-Membered Ring Torsional Parameters

dihedral angle type	v_1 (kcal/mol)	v_2 (kcal/mol)	v_3 (kcal/mol)
$\mathrm{C_{allyl}-C_{allyl}-C_{allyl}-Du_{allyl}}$	−2.500	0.750	0
$\mathrm{C_{allyl}-C_{allyl}-Pd_{allyl}-Du_{allyl}}$	2.000	0	0

the dipole moments for **22**, **23**, and **24** obtained in the quantum chemical calculations (Table II).

The distance from palladium to the allyl group varies with the substituents on palladium. This can be accounted for by addition of selected electronegativity constants. All constants in Table III concern corrections to the $\mathrm{C_{allyl}-Pd_{allyl}}$ bond when a substituent is added to palladium. These have been varied in order to optimize the allyl geometry in selected subgroups of the structure set.

In the present model, the (η^3-allyl)palladium moiety is, in fact, a bicyclic [1.1.1] system. For this reason, angles and dihedrals including only atoms with the index "allyl" must have four-membered-ring parameters (Tables IV and V). The chloride dimers also contain a four-membered ring. This presents a problem in some current MM2 implementations that do not allow addition of enough four-membered-ring parameters.

Initially, torsional parameters were copied from similar dihedrals in the existing parameter set. Where no closely related values could be found, the parameters were set to zero. In many cases, no changes were made during refinement. Only dihedrals with at least one nonzero value are listed (Tables V and VII).

Some of the angle bending parameters were copied from similar values in the MM2 force field. In the cases where the original approximations gave good agreement with X-ray structures, no optimization was done (Table VI). Some of the parameters are only used with one of the structures. These are therefore less reliable and have been noted with an asterisk (*). Most out-of-plane parameters in the existing parameter set have a value of 0.05 md Å/rad^2.[10] We found no reason to assign different values to any parameters in our set (Table VIII).

It must be stressed that the MM2 force field is developed to calculate gas-phase structures. In crystals the molecules are affected by packing forces which distort the structure. The calculated steric energy of the X-ray structure is therefore expected to be higher than the energy of the global minimum by up to a few kcal/mol. In order to evaluate our parameter set, we compared two different calculations on each X-ray structure. In the first minimization, all heavy atoms were fixed, while the positions of hydrogens and dummy atoms were optimized. In the second step, a full minimization was performed. The difference in steric energy between these calculations is given in Table IX for each structure. Some of the highest energy differences could be attributed to parts of the structures unaffected by our parameters. These are noted in the table and discussed below.

Table VI. Angle Bending Parameters

angle type	k_b (mdyn Å/rad^2)	θ_0 (deg)	rms dev (deg)
$\mathrm{C_{alkane}-C_{alkane}-C_{allyl}}$	0.450	109.400	1.3
$\mathrm{H-C_{alkane}-C_{allyl}}$	0.360	109.470	
$\mathrm{O_{carboxyl}-C_{alkane}-C_{allyl}}$	0.400	105.300	*
$\mathrm{C_{alkene}-C_{alkene}-S_{sulfonium}}$	0.450	120.100	2.3
$\mathrm{N_{sp^2}-C_{alkene}-N_{enamine}}$	0.450	114.800	*
$\mathrm{C_{alkane}-S_{sulfonium}-C_{alkene}}$	0.400	103.100	2.7
$\mathrm{C_{alkane}-S_{sulfonium}-Du_{ligand}}$	0.300	102.300	0.6
$\mathrm{C_{alkene}-S_{sulfonium}-Du_{ligand}}$	0.320	105.400	2.1
$\mathrm{C_{alkane}-N_{sp^2}-Du_{ligand}}$	0.500	117.000	*
$\mathrm{C_{alkene}-N_{sp^2}-Du_{ligand}}$	0.500	119.800	1.0
$\mathrm{C_{alkane}-N^{+}{}_{sp^3}-Pd_{allyl}}$	0.450	112.900	2.8
$\mathrm{H_{ammonium}-N_{enamine}-H_{ammonium}}$	0.450	120.000	*
$\mathrm{C_{alkane}-C_{allyl}-C_{alkane}}$	0.450	123.600	*
$\mathrm{C_{alkane}-C_{allyl}-H}$	0.360	120.000	
$\mathrm{C_{alkane}-C_{allyl}-C_{allyl}}$	0.450	123.300	1.6
$\mathrm{C_{alkane}-C_{allyl}-Du_{allyl}}$	0.320	114.100	2.1
$\mathrm{C_{alkane}-C_{allyl}-Pd_{allyl}}$	0.370	117.900	0.9
$\mathrm{H-C_{allyl}-H}$	0.360	118.000	
$\mathrm{H-C_{allyl}-C_{allyl}}$	0.360	120.000	
$\mathrm{H-C_{allyl}-Du_{allyl}}$	0.300	110.000	
$\mathrm{H-C_{allyl}-Pd_{allyl}}$	0.300	106.500	
$\mathrm{S_{sulfonium}-Du_{ligand}-Pd_{allyl}}$	0.100	180.000	2.5
$\mathrm{N_{sp^2}-Du_{ligand}-Pd_{allyl}}$	0.100	180.000	0.9
$\mathrm{Cl-Pd_{allyl}-Cl}$	0.400	98.000	*
$\mathrm{Cl-Pd_{allyl}-C_{allyl}}$	0.150	131.000	3.4
$\mathrm{Cl-Pd_{allyl}-Du_{allyl}}$	0.200	82.400	2.2
$\mathrm{Cl-Pd_{allyl}-Du_{ligand}}$	0.300	94.400	1.6
$\mathrm{N^{+}{}_{sp^3}-Pd_{allyl}-N^{+}{}_{sp^3}}$	0.450	89.500	0.7
$\mathrm{N^{+}{}_{sp^3}-Pd_{allyl}-C_{allyl}}$	0.300	134.500	0.8
$\mathrm{N^{+}{}_{sp^3}-Pd_{allyl}-Du_{allyl}}$	0.500	80.600	0.5
$\mathrm{Cl_{bridging}-Pd_{allyl}-C_{allyl}}$	2.900	139.100	2.2
$\mathrm{Cl_{bridging}-Pd_{allyl}-Du_{allyl}}$	0.500	68.000	1.6
$\mathrm{C_{allyl}-Pd_{allyl}-C_{allyl}}$	0.500	180.000	*
$\mathrm{C_{allyl}-Pd_{allyl}-Du_{allyl}}$	2.000	94.000	*
$\mathrm{C_{allyl}-Pd_{allyl}-Du_{ligand}}$	0.150	130.400	1.9
$\mathrm{Du_{allyl}-Pd_{allyl}-Du_{allyl}}$	1.000	180.000	*
$\mathrm{Du_{allyl}-Pd_{allyl}-Du_{ligand}}$	0.240	82.100	1.4
$\mathrm{Du_{ligand}-Pd_{allyl}-Du_{ligand}}$	0.600	91.900	1.0

Palladium Atom van der Waals Parameters

Determination of new van der Waals parameters to be added to the MM2 force field is not completely straightforward. One of the best ways of doing this is to calculate the total interactions in a crystal from heats of sublimation. Another way is to find strained X-ray structures where the distortion is due to van der Waals repulsion. The coordinatively unsaturated palladium poses a special problem here. The coordination can be viewed as an octahedron with two unoccupied sites. It has been speculated that palladium can accept weakly bound ligands in these positions, and we have recently observed[11] that such a complex is an intermediate in the syn–syn, anti–anti exchange commonly observed for these complexes.[12] This weak coordination may take place with groups able to donate a free electron pair. When determining the van der Waals parameters of palladium, we must be certain to exclude such effects because they are highly directional, whereas the van der Waals interaction in MM2 is isotropic by nature.

Because van der Waals parameters form the foundation for all the other parameters, we must exclude all structures where the group interacting with palladium is also affected by other as yet undetermined parameters. Ideally, we should only use structures where the interacting group is separated by more than three bonds from any part of the molecule containing new atom types. We have not found any structures which fulfill all these requirements, but three acceptable structures were selected for the parame-

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(11) Hansson, S.; Norrby, P.-O.; Sjögren, M.; Akermark, B.; Vitagliano, A. To be published.

(12) For a review, see: Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 441.

Table VII. Torsional Parameters

dihedral angle type	v_1 (kcal/mol)	v_2 (kcal/mol)	v_3 (kcal/mol)
$C_{alkane}-C_{alkane}-C_{alkane}-C_{allyl}$	0.170	0.270	0.093
$H-C_{alkane}-C_{alkane}-C_{allyl}$	0	0	0.500
$S_{sulfonium}-C_{alkane}-C_{alkane}-C_{allyl}$	0	0	0.483
$N^+{}_{sp^3}-C_{alkane}-C_{alkane}-N^+{}_{sp^3}$	−0.400	−1.100	1.200
$C_{alkane}-C_{alkane}-S_{sulfonium}-C_{alkene}$	0	0	0.300
$H-C_{alkane}-S_{sulfonium}-C_{alkene}$	0	0	0.500
$C_{alkane}-C_{alkane}-N^+{}_{sp^3}-Pd_{allyl}$	0	0.120	0.100
$H-C_{alkane}-N^+{}_{sp^3}-Pd_{allyl}$	0	0	0.250
$C_{alkane}-C_{alkane}-C_{allyl}-C_{alkane}$	0.400	0.030	0.500
$C_{alkane}-C_{alkane}-C_{allyl}-H$	0	0	0.010
$C_{alkane}-C_{alkane}-C_{allyl}-C_{allyl}$	−0.440	0.240	0.060
$H-C_{alkane}-C_{allyl}-C_{alkane}$	0	0	0.540
$H-C_{alkane}-C_{allyl}-H$	0	0	0.520
$H-C_{alkane}-C_{allyl}-C_{allyl}$	0	0	−0.240
$C_{alkene}-C_{alkene}-C_{alkene}-S_{sulfonium}$	0	15.000	0
$H-C_{alkene}-C_{alkene}-S_{sulfonium}$	0	15.000	0
$N_{sp^2}-C_{alkene}-C_{alkene}-N_{sp^2}$	0	10.000	0
$C_{alkane}-C_{alkene}-N_{sp^2}-Du_{ligand}$	0	3.000	0[a]
$C_{alkene}-C_{alkene}-N_{sp^2}-C_{alkane}$	0	10.000	0
$C_{alkene}-C_{alkene}-N_{sp^2}-Du_{ligand}$	0	3.000	0
$H-C_{alkene}-N_{sp^2}-Du_{ligand}$	0	3.000	0[a]
$N_{enamine}-C_{alkene}-N_{sp^2}-C_{alkene}$	0	10.000	0
$N_{enamine}-C_{alkene}-N_{sp^2}-Du_{ligand}$	0	3.000	0
$N_{sp^2}-C_{alkene}-N_{enamine}-H_{amine}$	0	15.000	0
$C_{alkane}-C_{allyl}-C_{allyl}-C_{alkane}$	0	3.000	0
$C_{alkane}-C_{allyl}-C_{allyl}-C_{allyl}$	1.300	2.500	0
$H-C_{allyl}-C_{allyl}-C_{allyl}$	1.300	1.300	−0.700

[a] These parameters have not been optimized, but are needed in the calculation of structures **27** and **28**. They are copied from similar optimized values.

Table VIII. Out-of-Plane Bending Parameters

angle type	k_0 (mdyn Å/rad^2)
$C_{alkene}-S_{sulfonium}$	0.050
$N_{sp^2}-Du_{ligand}$	0.050

Table IX. Calculated Energy Excess for the X-Ray Structures

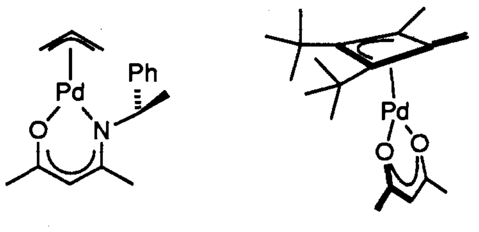
structure	ΔE (kcal/mol)	structure	ΔE (kcal/mol)
2	0.5	**12**	5.3
3	1.6	**13**	12.5
4	68.0[a]	**14**	2.7
5	2.2	**15**	2.9
6	6.3	**16**	4.1
7	11.8[b]	**17**	11.3[d]
8	2.4	**18**	13.1
9	7.5	**19**	9.4
10	5.0	**20**	11.3
11	8.7[c]	**21**	7.0

[a] The ethylenediamine C–C bond is ≈0.3 Å shorter than expected. [b] The main errors come from alkane C–C-bonds, which are longer than expected in the X-ray structure. [c] One of the allyl C–C bonds is 0.07 Å shorter than expected; the other is normal. [d] The main errors are due to bond deviations within the acetoxymethyl moiety.

Table X. A Comparison of Calculated and Experimental Energy Differences between Syn and Anti Forms in a Series of Phenanthroline (η^3-Crotyl)palladium Complexes

complex	anti form (%) calcd	anti form (%) exptl
27	19	10
28	51	69
29	59	65
30	32	40
31	18	41

terization, all containing an sp^3 carbon situated less than 4 Å from palladium (**21**, Figure 1; **25**–**26**, Figure 7).[8] In all examples, errors may arise from crystal packing forces or from unknown torsional parameters. However, the positions of the relevant sp^3 carbons are determined mainly by known through-bond interactions, known van der Waals parameters, and the unknown van der Waals parameters for palladium.



25 **26**

Figure 7. Two of the structures used in van der Waals parameter determination.[8]

There are two van der Waals parameters which need to be determined for a new atom type: the radius and the hardness of the atom (mechanical, not chemical hardness, an energy parameter). Trial values were tested for each structure by locking all heavy atoms (not hydrogens, dummy atoms, or lone pairs) except the interacting carbons and their closest neighbors, then performing a minimization of the structure. The error after minimization was defined as the root-mean-square (rms) deviation from the X-ray structure of the distance from palladium to the moving carbons. A screening of trial parameters showed, not unexpectedly, the structures could be reproduced by a range of different values, from a small, hard palladium to a large, soft one. The possible radii seemed to be in the range 2.0–2.5 Å with the corresponding hardness (ϵ) spanning 0.01–0.1 kcal/mol (0.04–0.4 kJ/mol). The optimum radius was determined for a number of different values of the hardness. In subsequent parameterizations, only the radius was varied while the corresponding hardness was calculated using the optimum values. The final values are shown in Table I.

The (η^3-Allyl)palladium Moiety

It is important for the parameterization to obtain correct positions for the hydrogen atoms. In structures with a heavy metal close to the hydrogens, it is preferable to use neutron diffraction data. As far as we are aware, no such investigations have been performed in the palladium series, but the neutron structure of the very similar diallyl nickel (**1**) is available in the literature.[8] The conformation of the allyl group in **1** is very similar to the few literature X-ray structures of (η^3-allyl)palladium complexes where hydrogen positions were determined. The approximate position of palladium relative to the allyl group was determined from structure **2**,[8] yielding the idealized model structure **22**. Ab initio calculations were performed for structure **22**. By moving the palladium in the mirror plane, energies for 19 different low-energy structures were calculated. A fourth degree polynomial was fitted to the energies to generate a potential surface. This shows the expected oval well structure with a minimum close to the original starting structure. As expected, the steepest ascent is toward the centroid of the allyl. The calculated potential surface was used for the subsequent parameterization.

In principle, any new system can be parameterized by using arbitrary starting values and then refining these iteratively. However, in order to have a reasonable convergence time, it is advisable to start with bond lengths and angles from known, unstrained structures. The starting values for energy parameters such as force constants and torsional parameters are most readily obtained from related systems where molecular mechanics parameters have already been determined. In some cases, values calculated from vibrational spectra may be used. Another possibility, which is used for the palladium–allyl bond in the present study, is to calculate the energy parameters by high-level quantum chemical calculations.

In our case, we first had to find a reasonable position for the dummy atom. As a first approximation, it was positioned in the mirror plane, 0.5 Å from palladium with a C–Pd–Du angle of 90°. Tentative values for the allyl carbons were based on the corresponding existing values for alkene carbons. The bond from the central carbon to palladium was assumed to be weak, and the force constant was set arbitrarily to 1 mdyn/Å. Based upon IR,[9] the force constant for the bond from the dummy atom to the terminal carbons was assumed to be approximately four times as strong and was set to 4 mdyn/Å.

The starting values were refined iteratively by identification and variation of the parameters responsible for large deviations from our basic set of data (the X-ray structures in Figure 1, the quantum chemical potential surface, and the equilibrium data for phenanthroline complexes).

Quantum Chemical Calculations

Quantum chemical calculations on the (η^3-allyl)palladium complex were performed with two goals. The first is to gain a qualitative insight into the type of bonding between palladium and the allyl group, and the second is to obtain a quantitative description of the variation of the interaction energy when the relative positions of the allyl group and the palladium atom are varied. In particular for the second goal, it cannot be expected that simple calculations at the Hartree–Fock level will give sufficiently accurate results since it is known that effects of electron correlation can be very important in describing the metal–ligand interaction in transition metal complexes. For example, in $Fe(CO)_5$ the calculated Fe–C force constants are changed by a factor of 2–5 by the inclusion of correlation effects.[13] Therefore, high-level calculations were performed, including correlation effects from all valence electrons on the (η^3-allyl)palladium cation (**22**). The calculations are described in the Appendix. The two auxiliary ligands on palladium are excluded from the calculations. The main reason for this is to make the size of the calculations more reasonable since a considerable number of points on the potential surface have to be calculated. Of course, the extra ligands on palladium have some effects on the Pd–allyl interaction which are not described by the present calculations. However, as discussed below, a comparison with two ligated complexes shows large similarities in the bonding in the ligated and the unligated systems. The cation is chosen to give the same oxidation state (Pd(II)) as in the ligated complexes to be described by the parameterization.

The bonding in the (η^3-allyl)palladium cation can be described in the following way, starting from the neutral allyl radical and the palladium cation. The allyl radical unpaired electron resides in the π orbital having a nodal plane through the central carbon. The ground state of the palladium cation ($^2D(4d^9)$) has one unpaired electron which, for example, can be placed in the 4d orbital having the same symmetry as the allyl orbital containing the radical electron, that is, the 4d orbital pointing toward the terminal allyl carbons. In the traditional picture, the unpaired electron on palladium is thought to be transferred to the allyl group creating a closed-shell allyl anion interacting with a palladium(II) cation. However, the two unpaired electrons can also be thought to form a covalent bond between the two fragments. The population analysis reveals that an essentially covalent bond is formed between the palladium atom and the two terminal carbons. The bonding orbital, with a total occupation of 1.9 electrons in the correlated calculation, has 1.2 electrons on palladium and 0.6 electron on the terminal carbons. There is also a σ-interaction which occurs between the doubly occupied π orbital on the allyl radical and palladium. This interaction is usually viewed as an attractive force created by a donation into the empty 5s and 5p orbitals on palladium. In the population analysis, this orbital has a total of 1.0 electron on the terminal carbons, 0.7 electron on the central carbon, and 0.2 5s and 5p electron on palladium. The palladium population in this orbital, as well as the total charge of +0.6 electron obtained for palladium, is, however, a bit uncertain since the outermost palladium s and p basis functions are very diffuse and might partly be describing the allyl ligand. The calculated d populations on transition metals are, on the other hand, more reliable, and the 4d population of 9.0 electrons obtained for palladium shows clearly that the $4d^9$ configuration is dominating in the cationic (η^3-allyl)Pd complex.

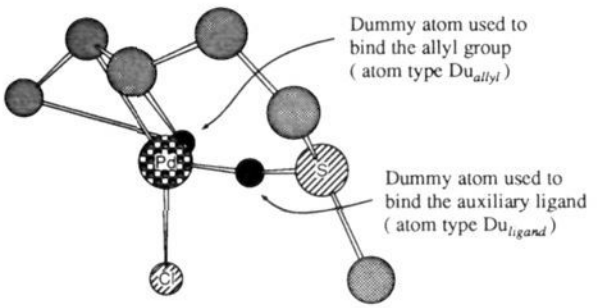


Figure 8. Part of structure **9**, showing the dummy atom needed to reproduce the angle distortion on sulfur. The Du_{ligand} "atom" represents a coordinating lone pair.

To investigate the effects of auxiliary ligands on palladium, the same type of calculations were also performed for single geometries of two ligated complexes, $Cl_2PdC_3H_5^-$ (**23**) and $(NH_3)_2PdC_3H_5^+$ (**24**). Inspection of the bonding orbitals and the results from the population analysis show that the general picture is the same for the ligated complexes as for the ligand-free complex **22**, even if there are minor differences. The added ligands supply electrons to the palladium–allyl fragment, decreasing the total charge on this moiety from +1.0 in the unligated complex to +0.8 in the ammonia complex and +0.1 in the chloride complex. However, the 4d population on palladium is very similar in all complexes (close to 9.0), showing that the main bonding configuration on palladium is the same. Furthermore, the populations in the σ-interacting doubly occupied allyl π orbital are essentially unchanged by the ligands. In the covalently bonding orbital involving the allyl radical electron, the ligands create a minor shift of 0.2–0.3 electron from palladium to the allyl compared to the ligand-free case, leading to populations of 1.0 palladium electron and 0.8 allyl electron in the ammonia case, and 0.9 electron on both palladium and allyl in the chloride case.

Modelling of Ligands

In most real η^3-allyl systems, palladium coordinates two additional ligands in an approximately square-planar arrangement including the terminal allyl carbons. In the current force field, the auxiliary ligands utilize one bond each for bonding to palladium. This gives the effect that, for example, amine ligands are best modelled with an ammonium-type nitrogen.

It is clear from observation of strained structures that the palladium–ligand bond behaves differently from the normal alkane bonds which are the basis of MM2. In a series of sulfide ligands (**8**, **9**, and **10**), we observed that, when the sulfur is forced out from its preferred coordination site, the angles centered on sulfur are distorted. This distortion can be rationalized by assuming that sulfur is not bound to palladium with a single, straight bond, but rather with a coordinating lone pair on the ligand pointing at an angle toward the preferred coordination site on palladium. This phenomenon can easily be modelled by substituting a dummy atom bound to both palladium and sulfur for the palladium–sulfur bond (Figure 8). The strained structures **11**, **12**, and **13** are also more closely reproduced by introduction of this auxiliary dummy atom.

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[13] Barnes, L. A.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1991**, *94*, 2031.

In this case, the dummy atom has a physical reality; that is, it represents a coordinating lone pair. By introduction of an extra dummy atom, the calculations could be made to agree much more closely with the X-ray structures. The ligand–dummy–palladium angle must, of course, have an ideal angle parameter of 180° because any other value would lead to two possible minima with the ligand still in the coordination plane. The ideal bond lengths to ligand dummy atoms from palladium and sulfur were varied until bond angles on sulfur in structures **8–10** were as unstrained as possible. Bond angles for Du–nitrogen bonds were then determined from relatively unstrained structures. Tentative values for all other parameters affected by the ligand–dummy bond were taken from the corresponding nitrogen–lone pair values for the pyridines and from sulfur–hydrogen parameters for the sulfides. Force constants for angles with dummy atoms as the central atom had to be guessed but could be refined by trial minimizations of X-ray structures with different degrees of strain.

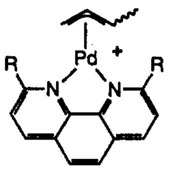
Results and Discussion

To be valid, a force field must be able to correctly reproduce both energies and structures. The ability of the force field to reproduce the quantum chemical potential energy surface shown in Figure 3 was tested by calculating the steric energy of 18 evenly spaced structures with palladium moved up to 0.15 Å from the equilibrium position. The rms error was 0.09 kcal/mol (≈0.4 kJ/mol) which is a remarkably good fit. The calculations of solution equilibria shown below also give very good fits to experimental values.

The MM2 force field is parameterized to generate gas-phase structures. In crystals, distortions of these structures take place due to crystal packing forces. Therefore, the X-ray structures are expected to have an energy higher than the calculated minimum energy. The parameter set can reproduce most of the chosen structures well. Some of the remaining errors could in principle be alleviated by addition of more parameters. For example, the ligand atoms might have their own atom types instead of using similar atom types in the existing parameter set. However, this has two serious drawbacks. First, the number of new parameters would be much larger. Second, the amount of experimental data is fairly limited. Variation of more parameters would certainly lead to a closer reproduction of the structures, but the validity of such a good fit would be questionable. If too many unknowns are varied, systematic errors may easily cancel each other.

The most flagrant discrepancy in the energy calculation is for the ethylenediamine complex **4**. Inspection of the detailed output from the MM2 calculation of the energy for the X-ray structure shows that most of the excess steric energy comes from an abnormal C–C bond in the ethylenediamine (found, 1.25 Å; expected, 1.52 Å). Also, the two N–C–C angles are severely distorted (found, 122° and 125°; expected, 104°). Actually, compound **4** has two enantiomeric MM2 minima. It can be easily seen that the X-ray structure of **4** is an average between the two minima. The resulting distortions give the X-ray structure a very high MM2 energy.

Compound **13** gives an uncomfortably high MM2 energy for the X-ray structure (ΔE = 12.5 kcal/mol). However, inspection of the energy calculations shows that this mainly is due to anomalous C–C bond lengths in the aromatic rings. This may be caused by an incorrect conjugated system calculation (not unreasonable, since the pyridine-type nitrogens are severely distorted). Structures **7** and **17** also gives high MM2 energies for the X-ray structures due to bonds that we have not attempted to optimize. In all three cases, part of the problem may be that no good atom types are available for some of the atoms in the structure. In structure **11**, one of the allyl C–C bonds is much shorter than any other such bond in the structure set. We have made no attempt to differentiate between the two allyl C–C bonds in any calculation.



27: R = H
28: R = Me
29: R = t-Bu
30: R = Ph

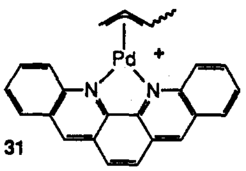


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Figure 9. The phenanthroline complexes used for correlation with anti–syn equilibria.

The largest remaining errors are calculated for structures where the allyl lies in a carbocyclic ring (**7**, **18–21**). This is a little worrying, since these are the only anti-substituted allyls in the structure set. However, the position of the anti carbons relative to palladium seem to be only slightly affected during minimization, and the energy difference between anti and syn crotyl complexes is well reproduced (see below).

Calculations on Phenanthroline Complexes of η^3-Crotylpalladium. We have recently shown the syn–anti equilibrium in substituted (η^3-allyl)palladium complexes can be shifted toward the anti form by 2,9-disubstituted phenanthroline ligands.[6] Already the nonrefined early calculations were useful in guiding the development of new, more efficient ligands. Because small energy differences are involved, only qualitative correspondence between experimental and calculated values was initially obtained. Comparison between calculated and experimental structures for compounds **11–13** revealed some problems with our early force fields. The force field would not allow the large observed out-of-plane bending of palladium from the plane of the aromatic system of the ligand. Instead, steric interaction was reduced by rotation of the allyl group about an axis through palladium and the allyl centroid. The out-of-plane bending was facilitated by the introduction of the ligand dummy atoms, spreading the angle distortion over one more bond angle. The insufficient barrier against allyl rotation was mainly observed in compound **11** where the two termini of the allyl group experience a large difference in steric interaction without any large observed rotation of the allyl group in the X-ray structure. A larger barrier against rotation could be imposed by raising the force constant of the four-membered ring angles involving the palladium–dummy bond. The complete allyl–palladium moiety was then recalibrated to reproduce both the ab initio energy surface and the observed rotation in compounds **8–11** as closely as possible.

With the present refinement, calculated and experimental values agree well (Table X, Figure 9). The calculations for the phenanthroline ligand itself give a slight bias toward the anti conformation, whereas the opposite phenomenon is observed for the more bulky phenanthroline derivatives. Here the palladium is displaced out of the aromatic plane of the ligands, resulting in large angle distortions in angles including the ligand dummy atom. The MM2 force field gives a rapidly increasing angle energy when angle distortions exceed ≈15°, due to a sextic factor in the bond angle function. Angle distortions of this magnitude are seldom seen in hydrocarbon molecules, but in strained metal complexes deviations are often large (e.g., complexes **8–13**). The use of ligand dummy atoms alleviates part of this problem by distributing the distortion over more angles, but the angles are still not soft enough. We have avoided changing any of the original MM2 parameters, but in order to refine our model further the sextic factor should probably be reduced or abolished when a metal atom is participating in the angle.

The displacement of palladium and the allyl group out of the plane of the aromatic system observed and calculated for bulky ligands gives rise to an interesting phenomenon in the crotyl complexes **28–31**. Only one low-energy minimum can be found for each syn isomer. In these minima the methyl group is pointed away from the plane of the phenanthroline. However, the calculations for the anti isomers show two distinctly different low-energy conformations for each anti isomer. In one of these the methyl group is pointing away from the plane of the phenanthroline, but in the other the allyl group is rotated around an axis through palladium and the allyl centroid, with the methyl group positioned almost in the plane of the phenanthroline.

Conclusions

The force field is accurate enough to aid in the development of new auxiliary ligands to be used in selective transformations. Most of the results obtained by using dummy atoms could have been reached by reprogramming existing molecular mechanics programs. The great advantages of the dummy atom concept are the ease of implementation and the generality obtained. The parameters developed here can be used in many existing programs. The concept of dummy atoms as branching atoms for bonds can be expanded to more areas. We are currently working on parameters for calculation on coordinated olefins using this basic idea. We are also working on a method to calculate metal complexes with octahedral and higher coordination in MM2 using dummy atoms to represent coordinating lone pairs as described above.

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Appendix: Computational Details for the ab Initio Calculations

The potential surface around the optimal structure of the $PdC_3H_5^+$ moiety (**22**) was calculated using fairly large basis sets and size-consistent correlation methods where all valence electrons were correlated. A few calculations were also performed for the ligated systems $Cl_2PdC_3H_5^-$ (**23**) and $(NH_3)_2PdC_3H_5^+$ (**24**).

The basis set used for palladium is the Huzinaga (17s, 11p, 8d) primitive basis,[14] augmented with one diffuse d function, two p functions in the 5p region, and three f functions, yielding a (17s, 13p, 9d, 3f) primitive basis. A generalized contraction scheme[15] is used leading to a [8s, 7p, 4d, 1f] contraction. In the calculations on the ligated systems, the f functions were deleted from the basis set. For carbon and nitrogen, the Huzinaga (9s, 5p) set[16] was generally contracted to a [3s, 2p] set. On carbon, one d function with exponent 0.63 was added leading to a [3s, 2p, 1d] contraction. For chlorine, a (12s, 9p) uncontracted basis[17] was used, generally contracted to [4s, 3p] and with one diffuse p function (exponent 0.044) added, leading to a [4s, 4p] contracted basis. The hydrogens were described by a [4s] basis[16] contracted to [2s] and with the exponents scaled by a factor of 1.2.

The zeroth-order wave function is generated at the SCF level, and electron correlation is accounted for by using the size-consistent modified coupled pair functional (MCPF) method.[18] All valence electrons on both palladium and C_3H_5 are correlated (i.e., 26 electrons for **22**), yielding a configuration expansion of about 190 000 terms. When chloride or ammonia ligands are added, the valence electrons on these ligands are also correlated (i.e., a total of 42 correlated electrons for both **23** and **24**), yielding configuration expansions of up to about 800 000 terms. The relativistic contribution to the energy is obtained by means of first-order perturbation theory where the mass–velocity and the Darwin terms are retained in the perturbation operator.[19] The calculations were performed on CRAY using the MOLECULE-SWEDEN[20] package.

For a judgment on the quality of the calculations, it is useful to know the splitting between the two lowest states of the palladium atom calculated with the present basis set and methods. The experimental energy difference between the ^1S (d^{10}) ground state and the ^3D (d^9s^1) excited state is 0.95 eV and the calculated value is 0.88 eV. The palladium atom is thus very well described in the present calculations.

The potential surface of the $PdC_3H_5^+$ moiety was described by the calculation of the energy of 19 different structures. The geometry of C_3H_5 was taken from the neutron structure **1** enforcing one plane of symmetry (C_s symmetry). The starting position of palladium relative to the allyl carbons was taken from structure **2**. From this structure stepwise displacements of the palladium atom orthogonal and parallel to the plane of the allyl carbons were made with a magnitude of 0.0529 Å (0.1 a_0) retaining the C_s symmetry. The calculated optimal structure has a distance of 2.15 Å from the palladium atom to the central carbon and 2.16 Å from the palladium atom to the terminal carbons. This is in the range of values from X-ray structures (2.05–2.15 Å and 2.10–2.20 Å, respectively). Calculations on the ligated systems (**23** and **24**) were only performed for a single structure each in which the initial geometry of the $PdC_3H_5^+$ moiety was used. The positions of the two ligands (two chlorides or two ammonia) were taken from structures **3** and **4** and symmetrized, yielding a pseudo-square-planar structure around palladium.

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