Studies of Allylic Substitution Catalysed by a Palladium Complex of a C_2-Symmetric Bis(aziridine): Preparation and NMR Spectroscopic Investigation of a Chiral π-Allyl Species

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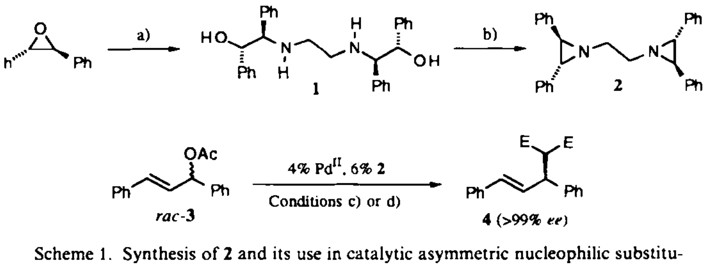
Abstract: The chiral palladium π-allyl intermediate for the catalytic asymmetric synthesis shown in Scheme 1 has been isolated as the PF_6^- salt. MM2 calculations have been performed and the structure of the palladium complex in solution has also been investigated by means of NMR spectroscopy. Both the computational and spectroscopic results suggest that in the complex the bidentate bis(aziridine) ligand adopts a conformation that forces the π-allyl moiety out of the normally preferred square-planar geometry. This nicely explains the very high enantioselectivity observed in the title reaction.

Keywords
asymmetric catalysis · aziridines · chiral ligands · palladium compounds

Introduction

We recently reported the synthesis of the C_2-symmetric bis(aziridine) **2**[1] and applications to a number of asymmetric transformations mediated by transition metals. In this paper we provide experimental procedures for the preparation of **2** and describe its use as a ligand in a palladium-catalysed asymmetric allylic alkylation (Scheme 1). Furthermore, we have prepared the putative catalytic intermediate and determined its structure by a combination of molecular mechanics calculations and NMR spectroscopic studies.



Scheme 1. Synthesis of **2** and its use in catalytic asymmetric nucleophilic substitution: $Pd^{II} = (\pi\text{-allyl})_2Pd_2Cl_2$, $E = CO_2Me$; a) 0.5 equiv $H_2N(CH_2)_2NH_2$, reflux; b) PPh_3, diethyl azodicarboxylate, THF, RT, 74% for two steps; c): 1.5 equiv $CH_2(CO_2Me)_2$, 1.5 equiv *N,O*-bis(trimethylsilyl)acetamide, 0.1 equiv KOAc, THF, RT, 77%; d): 1.2 equiv $NaCH(CO_2Me)_2$, THF, RT, 89%.

Results and Discussion

Ligand synthesis, structure and dynamics: The synthesis of chiral ligand **2** (Scheme 1) begins with (*S,S*)-1,2-diphenyloxirane[2] (itself available from *trans*-stilbene via (*S,S*)-stilbene diol),[2] which is subjected to a "double" ring opening by ethylenediamine to give **1**, followed by a twofold Mitsunobu reaction[3] to give **2** in good overall yield. The C_2 symmetry of the ligand is apparent from its ^1H NMR spectrum (see Experimental Procedure). Pyramidal inversion at nitrogen is fairly rapid at room temperature on the NMR time scale, and the aziridine ring protons give rise to a broad singlet, which becomes very sharp at 60 °C. At −40 °C the singlet splits into a sharp AB pattern ($J = 3.5$ Hz, $\Delta\nu = 58$ Hz, $T_c = 294$ K), and a simple calculation of the barrier to nitrogen inversion gives a value of approximately 60 kJ mol^{-1} ($k = 130\ s^{-1}$).[4] This barrier is substantially lower than might be expected for an *N*-alkylaziridine, an effect that is ascribed, in part, to "pseudo-conjugation" between the phenyl rings and the nitrogen lone pairs.[5]

Palladium-catalysed asymmetric allylic substitution: The ligand **2** was then used in the catalytic asymmetric synthesis shown in Scheme 1. The key intermediate is a π-allyl Pd^{II} species, and such complexes normally adopt a square-planar geometry.[6] This has been shown[7] or assumed[7] for several Pd^{II} complexes with chiral bidentate nitrogen ligands related to **2**. However, the molecular models of the putative intermediate for the reaction shown in Scheme 1 suggest that steric interactions between phenyl groups on the ligand and those on the π-allyl moiety force the complex to deviate considerably from square-planar geometry.[8] It also appears that the termini of the π-allyl could be sufficiently differentiated to allow some asymmetric induction during subsequent attack of the nucleophile. Support for these ideas came from MM2 calculations (see Experimental Procedure), which provided the optimized structure **5** shown in

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Figures 1 and 2. It is significant that this geometry was obtained by relaxation from a symmetrical structure. Rings B and D of the ligand define a chiral cleft which accommodates the π-allyl moiety. The terminal carbons C-1 and C-3 of the π-allyl group reside in very different steric environments: C-3 lies close to ring B of the ligand, and the phenyl group at C-3 is twisted considerably out of the π-allyl plane (59°). It is known that nucleophilic attack on such complexes occurs *anti* to palladium and, for the above-mentioned steric reasons, one would predict preferential attack at C-1. This should lead to predominant formation of the (*S*) enantiomer of the product, and this is indeed observed. Moreover, the enantioselectivity of the process is impressive (>99%, Scheme 1, Fig. 3). It should also be noted that the chromatographic purification of the product did not enhance the *ee* to any observable extent.[9]

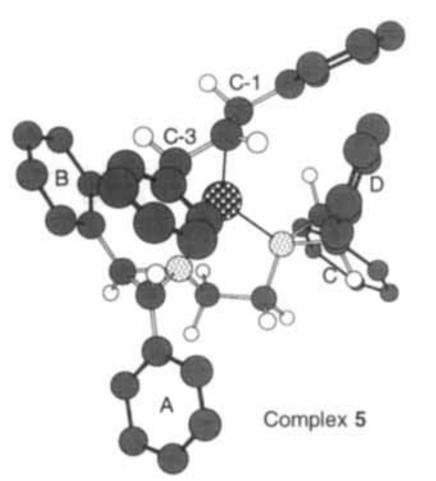

Fig. 1. MM2-optimized structure of the 1,3-diphenylallyl–palladium complex **5** formed from ligand **2**. Hydrogen atoms on the phenyl groups have been omitted for clarity.

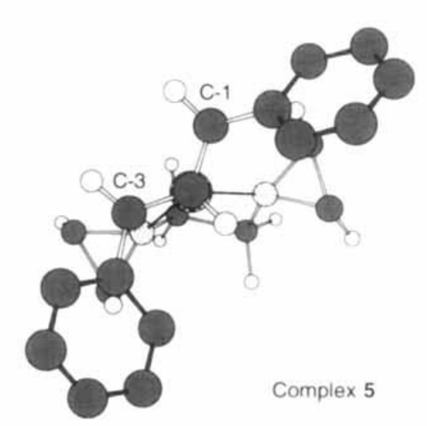

Fig. 2. View of complex **5** along the Pd–C(2) axis. The phenyl groups on the bis(aziridine) ligand have been omitted for clarity.

Synthesis, structure and dynamics of the chiral π-allyl species: The putative π-allyl intermediate was then prepared according to a general literature procedure,[10] and the complex isolated as the PF_6^- salt. So far we have been unable to obtain crystals suitable for X-ray crystallography,[11] and we thus decided to study the structure and dynamics of the complex in solution by means of ^1H and ^{13}C NMR spectroscopy. The results are actually in very good agreement with the calculated structure and will now be described in detail. Since the actual reaction was performed in tetrahydrofuran, $[D_8]$THF was used as the solvent in all the NMR studies. The lettering/numbering system shown in Figure 4 will be used in the following discussion.

The ^1H and ^{13}C NMR spectra for **5**·PF_6 are summarized in Tables 1 and 2, and both sets of data are indicative of a single, conformationally rigid,[12] and unsymmetrical complex. That the π-allyl system adopts the expected *syn,syn* geometry is apparent from the vicinal coupling constants and is further confirmed by a NOE between H_I and H_K (10.2%). The most striking features of the ^1H and ^{13}C NMR spectra are the unexpectedly large shift differences between the terminal atoms of the π-allyl system ($\Delta\delta$ = 2.78 for ^1H and 18.4 for ^{13}C). In the ^1H NMR spectrum the doublet at δ = 2.19 is assigned to H_K. The unusual high-field shift can be explained from the models and on the basis of Figure 1: H_K is expected to suffer anisotropic shielding by ring B of the ligand. In the calculated structure, the distance between H_K and the centre of ring B is approximately 2.7 Å, which, according to Johnson and Bovey,[13] should lead to an upfield shift of approximately 2.6 ppm. A HETCOR experiment then allows the assignment of the terminal π-allyl carbons

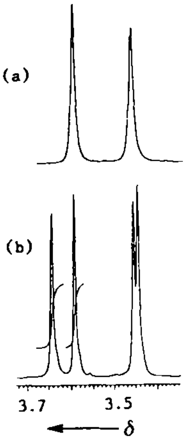

Fig. 3. Methyl region in the ^1H NMR spectrum of **4** (300 MHz, C_6D_6) in the presence of Eu(hfc)$_3$: a) (*S*)-**4** prepared as shown in Scheme 1; b) racemic material.

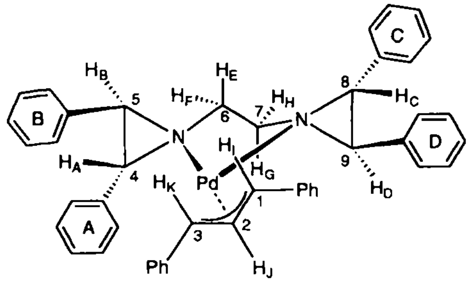

Fig. 4. Schematic representation of the π-allyl complex **5**.

Table 1. ^1H NMR data for complex **5**·PF_6 in $[D_8]$THF (300 MHz, 23 °C).

atom	δ	multiplicity	J / Hz
H_A	2.54	d	5.0
H_B	4.15	d	5.0
H_C	2.65	d	5.0
H_D	3.48	d	5.0
H_E	2.50	app. t	12.0
H_F	2.28	app. d	12.0
H_G	3.25	app. t	12.0
H_H	2.00	app. d	12.0
H_I	4.97	d	12.5
H_J	5.44	dd	12.5, 10.0
H_K	2.19	d	10.0
"aromatic H"	7.83 (2H)	d	7.0
	7.72 (2H)	t	8.2
	7.66 (2H)	m	
	7.56 (2H)	m	
	7.50-7.29 (16H)	m	
	7.21 (4H)	m	
	7.04 (2H)	d	6.6

Table 2. Selected ^{13}C NMR data for 5·PF$_6$ in [D$_8$]THF (75 MHz, 23 °C).

atom	δ	atom	δ
C-1	88.1	C-6	57.3
C-2	104.9	C-7	56.8
C-3	69.7	C-8	48.4
C-4	49.8	C-9	50.2
C-5	53.4		

as shown in Table 2 (C-1 at $\delta = 88.1$ and C-3 at $\delta = 69.7$). The ^{13}C chemical shifts are expected to be much less sensitive to ring current effects exerted by neighbouring aromatic rings, and the observed values thus indicate that the two centers C-1 and C-3 might show substantial differences in reactivity. If the downfield shift of C-1 is taken to imply increased electrophilicity, than the nucleophile should attack preferentially at C-1. This agrees with the earlier prediction based on steric arguments. Such "electronic activation" of C-1 is also in line with results obtained with other C_2-symmetric nitrogen ligands.[7b, 7c]

Homonuclear decoupling, NOEDIF, and two-dimensional NMR techniques (HETCOR, COSY, NOESY) were used to assign the signals due to the nonaromatic part of the chiral ligand (see Tables 1 and 2, Fig. 5). Of particular importance was the observed NOEs between the *ortho* protons ($\delta = 7.04$) of the phenyl ring attached to C-3 and H_J (15%) and H_K (9.7%) as well as the aziridine signal at $\delta = 2.54$ (2.2%), which thus can be assigned as H_A. This allows assignment of H_B (decoupling, COSY), which in turn can be related to H_F as follows: In the five-membered ring formed between palladium and the bidentate ligand, H_F and H_H are "equatorial", and H_E and H_G "axial". As a consequence, H_F and H_H appear as "doublets", while H_E and H_G give rise to "triplets". The models and the calculated structure show that H_B is in close proximity to H_F, and this is confirmed by a NOE (4.9%) between the two protons. The same type of argument was used to assign H_D (6% NOE to H_H) and thus H_C (by decoupling and COSY).

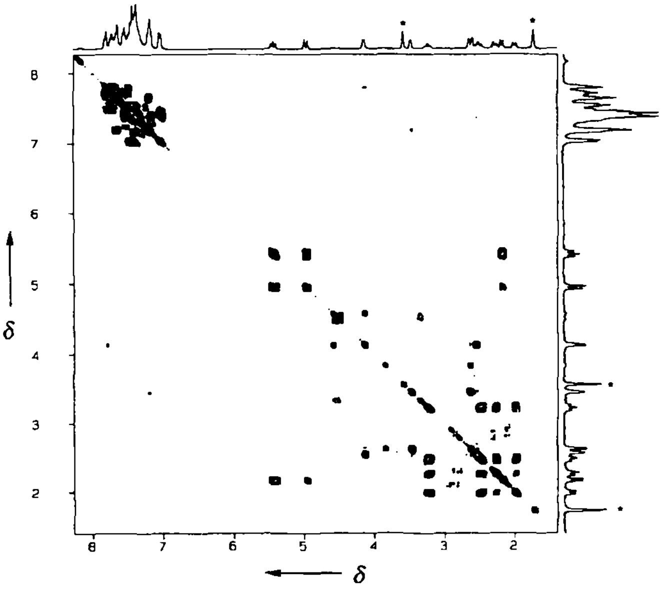

Fig. 5. COSY spectrum of 5 ([D$_8$]THF, residual solvent signals are marked by an asterisk).

As for the dynamic structure of the complex, site exchange in the nonaromatic portion is obviously slow on the NMR time scale at or below 23 °C. However, at 23 °C exchange between the proton pairs H_A/H_C, H_B/H_D, H_E/H_G and H_F/H_H is rapid on the NOE time scale,[14] as indicated by negative signals in the NOEDIF and NOESY spectra. These experiments were repeated at −20 °C. At this temperature the exchange process is no longer observed, and the assignments shown in Tables 1 and 2 are based on the low-temperature NOE data. At 65 °C modest but clearly discernible exchange broadening was observed for the ^{1}H NMR signals derived from the ligand, while the signals from the π-allyl unit remained unchanged. A DNMR 5[15] simulation with the EFGH spin system suggests that the temperature dependence of the spectra is consistent with a process that exchanges the two nitrogens with a calculated barrier of approximately 72 kJ mol^{-1} ($k = 15\,s^{-1}$, $\Delta G^{\neq} = 72.7$ kJ mol^{-1} at 53 °C; $k = 40\,s^{-1}$, $\Delta G^{\neq} = 72.3$ kJ mol^{-1} at 63 °C).

The important dynamic processes characteristic of π-allyl palladium species were summarized in 1975 by Vrieze.[16] Since then, a recurring question has been the mechanism of the "apparent π-allyl rotation" process,[17, 18, 19] which is common in complexes with bidentate nitrogen ligands. It is this process that is responsible for the exchange phenomena described above for complex **5**. Of the mechanistic possibilities, we consider two to be most likely in the present case: 1) a pseudo-rotation mechanism,[18] which does not require cleavage of N–Pd bonds and involves a pentacoordinated palladium intermediate in which the fifth coordination site is occupied by a solvent molecule (THF); and 2) a dissociative process[17, 19] involving scission of one N–Pd bond at a time, followed by rotation about the intact N–Pd bond, rearrangement of a T-shaped intermediate and finally reformation of the N–Pd linkage. Both these processes would lead to the observed exchange between H_A/H_C, H_B/H_D, H_E/H_G and H_F/H_H. Exchange of H_A/H_B and H_C/H_D would in addition require pyramidal inversion at nitrogen, but this is not observed. The pseudo-rotation mechanism obviously precludes nitrogen inversion. If the dissociative mechanism is operative, the sequence of events following initial N–Pd dissociation must occur faster than the pyramidal inversion process (the barrier to inversion is presumably similar to the 60 kJ mol^{-1} found for the free ligand). Addition of LiCl to the NMR sample resulted in an increase in the rate of the observed exchange process;[18, 19] however, since this behaviour is consistent with either of the two proposed mechanisms and since added LiCl did not cause any observable exchange between H_A/H_B or H_C/H_D, a clear-cut mechanistic distinction cannot be made at present. Finally, there is no evidence for a π–σ–π isomerization process[20] that could alter the *syn,syn* geometry of the π-allyl ligand, nor was there any exchange between the terminal π-allyl positions, a process which would require a "flipping" of the π-allyl moiety (i.e., exchange of the face that is bound to palladium).

Conclusion

The structure of complex **5** in solution appears to be in good agreement with the structure calculated by means of the MM2 force field. The proposed structure also provides a plausible explanation for the excellent enantioselectivity[21] induced by chiral ligand **2** in the palladium-catalysed allylic alkylation process: at ambient temperature the malonate anion attacks the sterically less hindered and more electrophilic terminus of a rigid, well-defined π-allyl complex in which the two possible reaction sites are differentiated.

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Experimental Procedure

^{1}H NMR and ^{13}C NMR spectra were run on a Varian XL300 or Varian Unity400 spectrometer. IR spectra were obtained for thin films or CH_2Cl_2 solutions on a Perkin-Elmer 1600 FT-IR instrument, and only the strongest/structurally most important peaks are listed. Optical rotations were measured at the indicated temperature on a Perkin-Elmer 241 polarimeter. THF was distilled under nitrogen from purple solutions of Na/benzophenone immediately before use. Merck silica gel 60 (240–400 mesh) was used for flash chromatography. (*S,S*)-1,2-diphenyloxirane [2] was prepared from (*S,S*)-stilbenediol [2a] in > 70% overall yield, without extensive purification of intermediates, by the general method described in ref. [2b]. There was no detectable epimerization, and the spectral and physical properties of our material were in excellent agreement with those reported for the (*R,R*) enantiomer [2c].

1: A mixture of (*S,S*)-1,2-diphenyloxirane (2.35 g, 12 mmol) and ethylenediamine (0.4 mL, 6 mmol) was heated with stirring under nitrogen at 90–95 °C for 60 h. Remaining volatile material was removed in vacuo, and the crude product (which usually contained a small amount of unreacted epoxide) was normally used directly in the next step. For purposes of characterization, a small portion of the crude product was purified by flash chromatography (silica gel, ethyl acetate/methanol) to yield pure **1** as a highly viscous oil: $[\alpha]_D^{25} = -24.6°$ ($c = 0.93$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.41-7.23$ (m, 16H; ArH), 7.09 (m, 4H; ArH), 4.71 (d, $^3J(H,H) = 6.5$ Hz, 2H; CH), 3.78 (d, $^3J(H,H) = 6.5$ Hz, 2H; CH), 2.53–2.39 (AA'BB' m, 4H; CH_2) 1.57 (brs, 4H; OH, NH); IR: $\tilde{\nu} = 3688$, 3629, 3383, 3321, 3065, 3021, 2944, 2839 cm^{-1}; $C_{30}H_{32}N_2O_2$ (452.6): calcd C 79.61, H 7.13; found C 79.28, H 7.09.

2 [29]: The crude product from above was dissolved with stirring under nitrogen in dry THF (30 mL), and the solution was cooled to 0 °C. Triphenylphosphine (3.46 g, 13.2 mmol) and diethyl azodicarboxylate (2.30 g, 13.2 mmol) were added, and the resultant solution was stirred for 2 h at room temperature. The reaction mixture was then poured into diethyl ether (100 mL), and the solution was washed with water (25 mL). The organic phase was dried ($MgSO_4$), and the solvents were removed in vacuo to yield a residue, which was purified by flash chromatography (silica gel, 20% diethyl ether in pentane). Compound **2** was obtained pure as a clear colorless oil which crystallized upon standing (1.85 g, 74% for two steps): M.p. 94–95 °C; $[\alpha]_D^{25} = +117°$ ($c = 1.03$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.44-7.15$ (brm, 20H; ArH), 3.16 (brs, 4H; CH) 2.60–2.42 (AA'BB' m, 4H; CH_2); ^{1}H NMR (400 MHz, $CDCl_3$, −40 °C, TMS): $\delta = 7.39-7.17$ (m, 20H; ArH), 3.21 (d, $^3J(H,H) = 3.5$ Hz, 2H; CH), 3.08 (d, $^3J(H,H) = 3.5$ Hz, 2H; CH), 2.53–2.39 (AA'BB' m, 4H; CH_2); $C_{30}H_{28}N_2$ (416.6): calcd C 86.50, H 6.78; found C 86.32 H 6.69.

Palladium-catalysed allylic alkylation: Conditions c), Scheme 1: Dimethylmalonate (72 mg, 0.54 mmol), acetate **3** (100 mg, 0.45 mmol), ligand **2** (11.3 mg, 0.027 mmol), *N,O*-bis(trimethylsilyl)acetamide (111 mg, 0.54 mmol) and potassium acetate (4.5 mg, 0.045 mmol) were dissolved with stirring under argon in dry THF (5 mL). Allylpalladium chloride dimer (4.2 mg, 0.011 mmol) was added, and the resultant solution was stirred at room temperature overnight. Diethyl ether (10 mL) was added, and the mixture was washed with water (5 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residue was purified by flash chromatography (silica gel, 10% diethyl ether in pentane) to yield **4** as a clear colourless oil (113 mg, 77%): $[\alpha]_D^{23} = -18.7°$ ($c = 1.1$ in ethanol), ref. [22] (for 99% *ee*): $[\alpha]_D^{23} = -18.4°$ ($c = 1.1$ in ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.32-7.09$ (m, 10H; ArH), 6.60 (d, $^3J(H,H) = 16$ Hz, 1H; CH), 6.49 (dd, $^3J(H,H) = 16$ Hz, 8.9 Hz, 1H; CH), 4.65 (dd, $^3J(H,H) = 11$ Hz, 8.9 Hz, 1H; CH), 4.23 (d, $^3J(H,H) = 11$ Hz, 1H; CH), 3.36 (s, 3H; CH_3), 3.18 (s, 3H; CH_3).

Conditions d), Scheme 1: Dimethylmalonate (72 mg, 0.54 mmol) and sodium hydride (80% suspension in oil, 12 mg, 0.5 mmol) were dissolved with stirring under argon in dry THF (5 mL) at room temperature. When gas evolution had ceased, ligand **2** (11.3 mg, 0.027 mmol) was added followed by allylpalladium chloride dimer (4.2 mg, 0.011 mmol) and acetate **3** (100 mg, 0.45 mmol). The resultant solution was stirred at room temperature overnight and then worked up as described above to give **4** (89% yield, > 99% *ee*). The *ee* value was confirmed by ^{1}H NMR spectroscopy with the chiral shift reagent Eu(hfc)$_3$, according to ref. [23] (See Fig. 3).

5: The general method described in ref. [10] was used to prepare di-μ-chlorobis(1,3-diphenyl-π-allyl)dipalladium. This complex (120 mg, 0.18 mmol) was slurried in methanol (8 mL), and ligand **2** (150 mg, 0.36 mmol) was added. The resultant mixture was stirred at room temperature until a clear yellow solution was obtained (ca. 3 h). Silver hexafluorophosphate (91 mg, 0.36 mmol) was added and a white precipitate formed immediately. After 15 min the mixture was filtered through a pad of Celite, and the yellow filtrate was evaporated to dryness. The residue was recrystallized from chloroform/diethyl ether, and 260 mg (84%) of **5**·PF_6 was obtained as a yellow microcrystalline solid, which was air-stable, but slowly decomposed above 130 °C: $[\alpha]_D^{22} = -179°$ ($c = 1.0$ in CH_2Cl_2); for ^{1}H NMR and ^{13}C NMR data, see Tables 1 and 2; $C_{45}H_{41}F_6N_2PPd$ (861.2): calcd C 62.76, H 4.80; found C 62.47, H 4.72.

Computational details: The calculations were performed with MM2(91) for the Macintosh [24]. A parameter set [25] for the (π-allyl)palladium moiety has been published previously, and parameters for phenyl substituents on the allyl moiety were also available [26]. For the aziridine ligand, tentative parameters were assigned, which allowed reproduction of known structural features of aziridines [27]. We had no data suitable for determination of force constants, so values were assigned by analogy with similar values in the existing force field. A tentative parameter set obtained in this way will not give reliable predictions about energetics (e.g., vibrations, relative conformational energies), but is well suited for modelling tasks and determination of gross structural features. The predictive power of this approach is demonstrated by the close correspondence between the calculated and observed NOEs for complex **5** (Table 3).

Table 3. Calculated and observed NOEs for complex **5**.

irradiated-observed	calculated NOE (%)	observed
H_I - H_K	11	10.2
C-3 phenyl (*ortho*) H_K	8	9.7
H_A	4	2.2
H_B - H_F	4	4.9
H_D - H_H	5	6.0
H_E - H_H	2	2.8
H_E - H_G	0	0

The previously unpublished parts of the parameter set used in this work and a parameter list suitable for use in MM2 calculations can be obtained through e-mail from P.-O. N upon request [28].

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[28] Please send requests for parameters to peon@medchem.dfh.dk (Per-Ola Norrby).

[29] Note added in proof (February 10, 1995): Recently, Wang and Sharpless have published a procedure for the kilogram-scale preparation of the enantiomerically pure stilbene diol required for the synthesis of ligand **2** (Z. M. Wang, K. B. Sharpless, *J. Org. Chem.* **1994**, *59*, 8302).