On the Circumambulatory Rearrangement of Cyclopentadienylphosphanes — Retention versus Inversion at the Migration Phosphorus

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Circumambulatory Rearrangement, Cyclopentadienylphosphanes. MNDO Calculations

According to a quantum chemical analysis based on energy optimized MNDO calculations the 1.5-sigmatropic reaction of cyclopentadienylphosphanes can occur via a transition state either with retention or inversion of configuration at phosphorus, depending on the ligands within the PR2 fragment. Electropositive R favour inversion and electronegative R retention of configuration at phosphorus. In addition, given the same ligand R, retention (over inversion) comes to the fore with increasing atomic number of the central atom at the MR unit, i.e. in the order M = N<P<As<Sb.

Experimental studies [1] on the 1.5-sigmatropic reactions of pentamethylcyclopentadienylphosphanes 1a and -boranes 1b have led to a systematic classification of ligand effects on the rate of migration [2].

In the former case, 1a, a low energy barrier for the walk reaction is expected if (a) radical stabilizing groups are attached to the cyclopentadienyl unit, (b) the fragment M = PR2 (migrating group) exerts a strong radical stabilizing ability and (c) possesses energetically high lying frontier orbitals. For comparison, in 1b, the degenerate rearrangement retards with electron donating ligands (e.g. amino groups) at the boron atom and/or electron withdrawing substituents at the cyclopentadienyl (cp) unit.

According to the quantum chemical studies for the 1.5-sigmatropic reaction of 1a the transition states with retention or inversion of configuration at the migrating phosphorus atom are almost equal in energy [2a]. On the contrary for the circumambulatory reaction of the boranes, 1b, strong preference of inversion over retention is predicted [2b].

Results and Discussion

a. Bonding in the alternative transition state geometries

Following the previous theoretical studies [2], the bonding situation in the transition state geometries (η2-structures) can be viewed as mutual interaction of two fragment orbital systems, (a) the cyclopentadienyl system and (b) a PR2 unit, where R refer to the various ligands (R = H, alkyl, halogen, amino) attached to the migrating phosphorus atom. In other words the orbital system of the PR2 fragment (radical) is isolobal [3] to the corresponding carbene [4] anion radical.

In the case of inversion of configuration at phosphorus mutual interaction takes place with (a) the α-orbital at the PR2 fragment and (b) its p-orbital and the two degenerate π-orbitals at the cp-unit. The situation can be depicted as follows:
In the case of retention of configuration the former overlap (σ at PR₂ with a' at cp) is offset. Hence this type of interaction determines the preference of inversion over retention of configuration at the migrating phosphorus atom. It increases with lifting the energy level of σ. As analyzed for the case of the isolobal carbene fragments [4] electropositive ligands decrease and electronegative ligands increase the ionization potential of the σ-orbital. In other words, the more the ligand R becomes electropositive, the more inversion over retention is promoted at the migrating atom.
b. Numerical calculations for \( Cp-PR_2 \) and \( Cp-NR_2 \)

In order to put these arguments on firmer ground we first performed energy optimized MNDO calculations [5] on the two transition state geometries of the (parent) system \( Cp-PR_2 \), with \( R = H, CH_3, SiH_3, Cl, F \) and \( CF_3 \). These substituents should model the whole variety of ligands at phosphorus. The bonding parameters thus obtained are similar to those reported in the previous theoretical study [2a]. Therefore, they will not be listed here. However, a plot of the energy differences of the two transition states versus the energies of the \( \sigma \)-orbitals of the corresponding \( PR_2 \) fragments (radicals [6]) is shown in Fig. 1. For the computations of the transition state geometries \( C_s \) symmetry was imposed throughout.

Positive values for \( \Delta E \) here correspond to predominance of inversion over retention of configuration at phosphorus, and negative values to the opposite.

Accordingly, for \( R = SiH_3, CH_3 \) a transition state geometry with inversion is favoured, while for \( R = F \) the opposite holds true. The ligands \( R = CF_3, Cl \) present borderline cases. For all cases the trends correlate well with the trends in the energies of the \( \sigma \)-orbitals.

Corresponding energy optimized MNDO calculations were also performed for the \( \eta^2 \)-structures of cyclopentadienylamines, with various ligands \( R \) at nitrogen. As before the same variety of substituents was chosen. The obtained results are summarized in Fig. 2. In agreement with the previous considera-

Fig. 2. Energies (in eV) for the \( \sigma \)-orbitals of the \( NR_2 \) radicals versus the energy differences (in kcal per mole) for the corresponding transitions states of the \( cp-NR_2 \) systems, obtained from energy optimized MNDO calculations (\( C_s \) symmetry imposed).
tions electropositive ligands \((R = SiH_3)\) promote inversion and electronegative ligands \((R = F)\) retention of configuration at the nitrogen. The picture which emerges for the amines (Fig. 2) parallels that for the phosphanes (Fig. 1). However, there is one essential difference between both cases. For the latter (phosphanes) the overall tendency to favour retention rather than inversion is stronger pronounced. Compared to the former. This is the more surprising, since for a given ligand \(R\) the \(\sigma\)-orbital in the corresponding \(PR_2\) fragment results at lower ionization potentials in comparison with the corresponding \(NR_2\) fragment [7]. On this basis inversion over retention in the transition state geometries should be facilitated in the opposite order.

What is the reason for this unexpected observation? Consider the orbital system which emerges from the mutual interaction of the \(p\) (or \(\sigma\)) orbital at a \(PH_2\) fragment with the (degenerate) set of \(\pi\)-orbitals at the \(Cp\)-unit. Their bonding combinations shows as follows:

With increasing principal quantum number of the central atom in the \(MR_2\) fragment \((M = N < P < As < Sb)\) its \(p\)-orbital is enlarged, \(\text{i.e.}\) it becomes more diffuse. On the other hand the \(\sigma\)-orbital gains more \(s\)-character, due to the stronger contraction of the valence \(s\)-orbital compared with its valence \(p\)-orbital [8]. On this basis overlap in the transition state with retention of configuration comes to the fore with increasing principal quantum number of the central atom in the \(MR_2\) fragment, \(\text{i.e.}\) in the order \(N < P < As < Sb\) [9].

c. \textit{Substituent effects at the Cp-unit}

Our discussion is not complete without an analysis of the substituent effects at the \(Cp\)-unit on the stereochemistry in the transition state. According to the MNDO calculations for the simplest case, \(cp-PH_2\), the two alternative transition states are polarized as follows:

For comparison we also included in our considerations an analysis of the charge distribution in the ground state geometry. In the transition state geometries negative charge at phosphorus is either depleted (retention) or accumulated (inversion). Concomitantly the cyclopentadiene units are differently polarized. Accordingly, \(\pi\)-donating or \(\pi\)-accepting substituents attached to the \(Cp\)-system should exert various effects on the magnitude of the energy splitting between both transition state geometries.

In order to test these predictions again energy optimized MNDO calculations were performed on

<table>
<thead>
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<th>Substituent(s)</th>
<th>position(s)</th>
<th>(\Delta E)</th>
</tr>
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<tbody>
<tr>
<td>(NH_2)</td>
<td>3</td>
<td>-9.9</td>
</tr>
<tr>
<td>(BH_2)</td>
<td>3</td>
<td>-13.8</td>
</tr>
<tr>
<td>(NH_2, NH_2)</td>
<td>2.4</td>
<td>-25.5</td>
</tr>
<tr>
<td>(BH_2, BH_2)</td>
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<td>-2.3</td>
</tr>
<tr>
<td>(NH_2, BH_2)</td>
<td>1.5</td>
<td>-0.8</td>
</tr>
<tr>
<td>(BH_2, BH_2)</td>
<td>1.5</td>
<td>-32.9</td>
</tr>
</tbody>
</table>
differently substituted cp-systems, with PH$_2$ as the migrating fragment. As a typical $\pi$-donor ($\pi$-acceptor) a NH$_2$ (BH$_2$) group was chosen. The results from these calculations are collected in Table I.

The various substitution patterns were tested for all positions at the cp-ring. The values for $\Delta E$ refer to the energy differences of the two possible $\eta$-structures. As before negative values correspond to the preference of retention over inversion, and vice versa for the positive values. Only in two cases inversion is preferred; either a $\pi$-donating (NH$_2$) group at C(3) or $\pi$-accepting substituent (BH$_2$) at C(2) and C(4) is required. Overall the observed trends are in accord with the predicions obtained from the analyses of charge densities.

Conclusions

In the traditional picture [10] on circumambulatory 1.5-sigmatropic rearrangements the stereochemistry at the migrating atom (group) is retained. Here we present theoretical evidence for the case of cyclopentadienylphosphanes that both stereochemical alternatives, retention and inversion of configuration at the migrating atom, are feasible. In detail the following conclusions emerge from the present study:

1) Retention over inversion is promoted with increasing atomic number of the central atom in the isolobal MR$_2$ fragment, i.e. in the order N<P<As<Sb. (2) For a given central atom in the MR$_2$ fragment, e.g. P, inversion over retention is favoured with increasing electropositive character of the ligands R. It must be noted that these trends parallel the trends observed for the inversion barriers [11]. Although an experimental investigation of the stereochemistry in the circumambulatory reaction of cyclopentadienylphosphanes has not been reported so far, the detailed dynamical studies [1a] on the related pentamethylcyclopentadienylphosphanes indicate no unique mechanism for the reaction [12] which is in favour of our theoretical analysis.

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[7] This is due to the more electropositive character of phosphorus compared with nitrogen; see also ref. [4].
[12] In fact the data reported by Jutzi and Saleske [1a] indicate no "extrathermodynamic" relationship (for the definition and evaluation of this criterium see G. W. Klumpp, “Reaktivität in der organischen Chemie II”, Thieme Verlag, Stuttgart 1978) among the activation parameters which alludes the existency of more than one transition state in the 1.5-sigmatropic reaction.