A Phosphorus-Based Pacman Dication Generated by Cooperative Self-Activation of a Pacman Phosphane

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Abstract: Formal coordination of phosphorus(III) by a calix[4]pyrrole Schiff base ligand was achieved through the reaction of this ligand with PCl₃ under basic conditions. The reaction product adopts a Pacman conformation with two P–Cl moieties, one in exo and one in endo position. It represents the first non-metal compound of calix[4]pyrrole Schiff base ligands and of Pacman ligands in general. The spatial neighborhood of the two phosphorus atoms enables cooperative reactions. As a first example, the chloride abstraction with AgOTf is presented, yielding a macrocyclic dication with two embedded phosphorus(III) monocations, which both undergo a cooperative, internal activation reaction with an adjacent C=N double bond. This intramolecular redox process affords two pentacoordinated phosphorus(V) centers within the Pacman dication. All reaction products were fully characterized and all results are supported by computations.

So-called Pacman ligands and their transition metal complexes have been known since 1983.[1] They are related to cofacial ligands,[2,3] however, in contrast to the latter, the parallel arrangement of the two chelating units in Pacman ligands is enforced by a rigid connection on only one side of the molecule, resulting in a more flexible metal-metal distance. In 2003, the groups of Love and Sessler independently introduced calix[4]pyrrole Schiff base ligands (1, cf. Scheme 1), a new type of Pacman ligands easily synthesized in high yields.[4,5] Ever since, numerous metal complexes have been reported (e.g., A, Figure 1).[6,15–19,7–14] Due to the spatial proximity of two metal centers, Pacman complexes are used to investigate and mimic highly efficient reaction centers of enzymes, for example by using energy and electron transfer upon irradiation for molecule activation.[20–24]

The concept of two cooperative reaction centers is also widely spread in metal-free molecule activation (e.g., in FLPs or biradicals).[4,5] To the best of our knowledge, Pacman complexes of phosphorus or non-metals in general have not yet been described, except for the free ligands with hydrogen atoms on the pyrrolic nitrogen atoms.[37,38] If only one half of Pacman ligands is regarded, porphyrins are structurally closely related and can therefore be seen as model substances. Several P(V) containing porphyrins were reported, mostly cations (e.g., B, Figure 1).[33–35] The first P(II) porphyrinoid (C, Figure 1) was synthesized in 2012 by Osaka and coworkers[36] and, to our knowledge, Latos-Grażyński, Pawlicki and coworkers reported the only two further examples.[37,38] Both types of P(V) porphyrinoids were structurally characterized but due to missing leaving groups on the P(II) atoms, they are not predestined for follow up chemistry. A calix[2]pyrrole binding a P–Cl moiety (D, Figure 1) was synthesized by the group of Richeson in 2012.[39] In contrast to these examples containing only one P center, here, we present a
the first metal-free Pacman complexes suffer from severe solubility problems, a reaction product of the benzene and dichloromethane, substituted outside or inside the cavity of the complex. In endo and exo orientation with respect to the respective chlorine atom by 0.140(1) Å (Scheme 1). Due to severe solubility problems, a reaction product of 1 c (R2=Ph, R3=H) could never be isolated. The replacement of the Ph substituents in R2-position by Et groups enabled us to isolate 2 b but low yields and bad reproducibility prevented further investigations. Only the introduction of additional methyl groups on the phenylene linkers (R2) allowed for the reliable synthesis of 2 a as yellow to orange crystals. Here, using KH as base (the potassium complex was also isolated and fully characterized, Figure S7) entailed an easier separation of the potassium complex 1 b (Scheme 1) of which 2 a was synthesized according to modified literature procedures. Assisted HCl elimination upon treatment of 2 a with PCl3 before (see Supporting Information). Ligands 1 b, 2 a, and its equilibrium with respect to the dication. This interaction was examined by NBO (Natural bond orbital) analysis (see Supporting Information, p. S62 ff). It reveals donor-acceptor energies of about 30 and 60 kJ mol⁻¹ (endo and exo half, respectively; Table S6) for the donation of the lone pairs of the iminic N atoms into the σ* orbitals of the opposite P–Cl bonds. Although these interactions are rather weak (the values correspond to the strength of typical hydrogen bonds), they indicate that the structural motif is capable of stabilizing reactive compounds in follow-up reactions. Regarding the N3 planes formed by the pyrrolic and iminic N atoms in each half of the molecule, the P atoms are slightly bent out of the plane towards the respective chlorine atom by 0.140(1) Å (exo) and 0.190(1) Å (endo). Moreover, the carbon-nitrogen framework in the upper and lower half of the molecule of 2 a is not planar but bent away from the respective P–Cl bond.

Both P–Cl bonds are in the expected range for covalent Cl bonds. Additionally, the distances between the P atoms and iminic N atoms d(2 a–Npyr) = 2.86(3) Å (Table S4) are significantly shorter than the sum of the van der Waals radii (Σr(2 a–Npyr) = 3.35 Å). This interaction was examined by NBO (Natural bond orbital) analysis (see Supporting Information, p. S62 ff). It reveals donor-acceptor energies of about 30 and 60 kJ mol⁻¹ (endo and exo half, respectively; Table S6) for the donation of the lone pairs of the iminic N atoms into the σ* orbitals of the opposite P–Cl bonds. Although these interactions are rather weak (the values correspond to the strength of typical hydrogen bonds), they indicate that the structural motif is capable of stabilizing reactive compounds in follow-up reactions. Regarding the N3 planes formed by the pyrrolic and iminic N atoms in each half of the molecule, the P atoms are slightly bent out of the plane towards the respective chlorine atom by 0.140(1) Å (exo) and 0.190(1) Å (endo). Moreover, the carbon-nitrogen framework in the upper and lower half of the molecule of 2 a is not planar but bent away from the respective P–Cl bond.
Cl1 and the exo substituted P2 atom is slightly smaller than the sum of the van der Waals radii (d(P2–Cl1) = 3.3552(8) Å, \(\Sigma_{vdw}(P–Cl) = 3.55 \, \text{Å}\)) but still longer than previously reported distances for Cl atoms bridging two P atoms (e.g. \(d(P–Cl) = 2.602(1) \, \text{Å}\)).\(^{38}\) The overall coordination around the P\(^{35}\) atom could also be regarded as strongly distorted square pyramidal. The lone pair of the P2 atom, however, does not point away from the base of an imagined square pyramid but rather intersects it while sitting on top of the trigonal pyramid formed by the P atom and the Cl as well as pyrrolic nitrogen atoms (Figure 3). Therefore, the P atoms are better described as trigonal pyramidal surrounded with additional stabilization by two weak interactions with the iminic N atoms (3 \(+\) 2 coordination). A close look at the intermolecular distances in crystalline \(2\,a\) indicates significant face-to-face \(\pi\)-\(\pi\)-interactions between four phenyl rings of two neighboring \(2\,a\) molecules (Figure 2, bottom).

\(^{31}\)P\(^{1}\)H NMR spectra of the reaction solution and isolated \(2\,a\) show two singlets at \(\delta = 80.8\) ppm and \(\delta = 82.6\) ppm, proving that the exo-endo isomer is formed selectively. Due to the inequivalency of the exo and endo halves of the molecule, each half produces a separate set of signals in the \(^{1}\)H NMR spectra of \(2\,a\), too (Figure 4a). Interestingly, the \(CH\) protons of the phenylene backbone seem to be most influenced by the orientation of the P–Cl moieties, showing the largest chemical shift difference between their two signals (\(\delta = 6.34, 6.81\) ppm; Figure 4a, blue dots). This is explained by their spatial proximity to either the exo Cl atom or the lone pair of electrons of the endo substituted P atom. Due to the additional exo and endo orientation of the ethyl groups in each half of the molecule, all ethyl groups are inequivalent. The broad linewidth, both in \(^{1}\)H and \(^{31}\)P\(^{1}\)H NMR spectra, already indicated a dynamic behavior of \(2\,a\) in solution. High temperature NMR spectra confirmed this assumption, showing only a single set of signals for \(2\,a\) at 100°C (Figure 4b; Figures S20 and S21). On the other hand, cooling down a solution of \(2\,a\) led to sharp signals (Figure S22). In the \(^{31}\)P\(^{1}\)H spectrum at \(-40\)°C even a small coupling of 3.2 Hz between the exo and endo P atom could be observed (Figure S23). The dynamic behavior is explained by the exchange of the exo and endo orientation of the P–Cl moieties, which can be regarded as their formal inversion. The addition of [PPh\(_4\)]Cl to an NMR sample of \(2\,a\) in dichloromethane (Figures S24 and S25) had the same effect as heating, leading to only a single set of signals in the NMR spectra. This makes us propose a central role of chloride ions in the inversion of the P–Cl orientation. Further investigations concerning the mechanism are in progress and will be published separately.

After observing the dynamic behavior of the P–Cl bonds and the interactions between the iminic N atoms and the P atoms, we decided to attempt the abstraction of chloride ions from \(2\,a\) to form the corresponding dication. Therefore, 2 equivalents of AgOTf were added to \(2\,a\) in the dark, resulting in a red suspension. Extraction with acetonitrile gave the dark red salt [4]\([\text{OTf}]\) (Scheme 2). We expected each P\(^{+}\) cation in 4\(^{2+}\) to be surrounded by the two pyrrolic and two iminic N atoms in a square planar coordination mode, by analogy with related square planar calix[4]pyrrole complexes of aluminum\(^{31}\) and silicon\(^{32}\) recently published by the group of Greb. Instead, the P\(^{+}\) atoms in 4\(^{2+}\) undergo an internal redox reaction with two of the adjacent iminic C–N double bonds, affording a cationic cage compound as depicted in Figure 5. In each half of dication 4\(^{2+}\), the N atom of one former iminic C–N moiety is now covalently bound to the P atom in the same half of the molecule. The carbon atom of the same C–N moiety is also covalently bound to a P atom, however, of the opposite half, creating a six-membered [PNC]\(_4\) ring with P in the oxidation state +V. Only few examples for the synthesis of [PNC]\(_4\) rings
According to NBO analysis, electron localization function (ELF) and the Laplacian of the electron density, all four P–N interactions can be described as strongly polarized bonds while the P–C bond is almost non-polarized (see Supporting Information, p. S67 ff). Furthermore, as expected for a formal P(V) center, no lone pair was found at either P atom. For the elongated P1–N1 distance, the Wiberg bond index is smallest (0.52), whereas the values for all other P–N and P–C bonds range from 0.64 to 0.78 (Table S7). Together, they add to a total Wiberg bond index of 3.79 for each P center in accord with tetravalent P(V).

To address the question of why the N-tetracoordinated dication (“open structure” min1 in Figure 6) is not observed experimentally but internal oxidation occurs to the 4+ ion (“closed” structure, min0), quantum chemical calculations were performed at the DLPNO-CCSD(T)/mTZVP//PBE-D3/mTZVP level of theory, including correction terms for the solvation in MeCN (SMD[58] model, computed using DFT, cf. Supporting Information). These computations reveal a concerted reaction mechanism with only one transition state for the intramolecular bond formations, confirming the cooperative nature of the reaction. Furthermore, they indicate that the “open” structure lies significantly higher in energy and the transition state of 164.9 kJ/mol for the reverse “opening” reaction becomes hardly accessible, which is in accord with our experimental observations. NMR spectra of [4][OTf], show only one product: one singlet in the 31P{1H} NMR spectrum and sharp signals indicating several 1H,31P couplings in the 1H NMR spectrum (Figure S26). Also, upon heating neither additional nor significantly broadened signals are observed (Figure S27). Nevertheless, we are confident that the addition of appropriate Lewis bases will facilitate the “opening” (cleavage of the P–C bond) which is part of an ongoing project.

In summary, we were able to synthesize the first Pacman complex of phosphorus by reaction of PCl3 with calix[4]pyrrole Schiff base ligands. The product also represents one of the rare examples of P(V) porphyrinoids. Since the Pacman ligand itself provides steric protection comparable to reaction centers of enzymes, implying high stability and selectivity, chloride abstraction in 2a with AgOTf leads to the formation of a highly reactive macrocyclic dication with two monocationic P centers.

**Scheme 2. Synthesis of [4][OTf].**

![Image of Scheme 2](image-url)

**Figure 5. Molecular structure of 4+ in the solid state. Ellipsoids are drawn at 50% probability at 173(2) K. Counters and solvent omitted for clarity. Symmetry code: 1-x, y, z. Selected distances (Å) and angles (°): P1–N1 1.9019(9), P1–N2 1.687(1), P1–N3 1.7028(9), P1–N4 1.7362(9), P1–C14 1.889(2), N1–C1 1.308(2), N3–C14 1.500(2); N1–P1–N4 124.35(5).**

by the activation of iminic C=N double bonds by P cations have been reported and to our knowledge, never as an intramolecular reaction. In 4+, the oxidative addition of the formal two P+ ions to the C=N double bonds can be regarded as a cooperative process. The reaction of 2a with one equivalent of AgOTf did not lead to the formation of the monocation but also to the dication 4+ in the mixture with excess 2a.

The crystal structure of [4][OTf] reveals a C2 symmetric macrocyclic dication with two monocationic, trigonal bipyramidally surrounded P(V) atoms (Figure 5). Radosevich and co-workers observed a square pyramidally surrounded P(V) atom in a related corrole monocation.[56] In 4+, the bonds of the P1 atom to the two pyrrolic N atoms (N2, N4') as well as to the former iminic N3 and C14 atoms lie in the expected range for covalent single bonds (d(P–N) = 1.71(2) Å, cf. Σ_CoP(N) = 1.76 Å; d(P1–C14) = 1.889(2) Å, cf. Σ_CoP(C) = 1.87 Å).[49] The N3–C14 distance in 4+ (d(N3–C14) = 1.500(2) Å) is strongly elongated compared to 2a (d(N4–C23) = 1.277(3) Å, double bond) indicating only a N3–C14 single bond. The P–N distance to the iminic N1 atom (d(P1–N1) = 1.9019(9) Å) is approx. 0.2 Å longer than the other P–N bonds.

**Figure 6. Energy profile of the P–C bond dissociation in 4+ in MeCN (DLPNO-CCSD(T)/mTZVP/PBE-D3/mTZVP) (see also Figure S28).**
These undergo self-activation by cooperative internal redox reactions with C=N double bonds, resulting in C=N single bonds and phosphorus atoms in the oxidation state +V. This demonstrates the ideal pre-requirements in 2a, such as the enforced neighborhood of two phosphorus atoms, for cooperative reactions and is part of ongoing reactivity studies of 2a and [4][OTf].

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Conflict of Interest

The authors declare no conflict of interest.

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