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

Liesa Eickhoff,[a] Leon Ohms,[a] Jonas Bresien,[a] Alexander Villinger,[a] Dirk Michalik,[a, b] and Axel Schulz*[a, b]

Abstract: Formal coordination of phosphorus(III) by a calix[4]pyrrole Schiff base ligand was achieved through the reaction of this ligand with PCl_3 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 intra-molecular 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).[4,6,15–19,7–14] 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).[25–30] To the best of our knowledge, Pacman com-
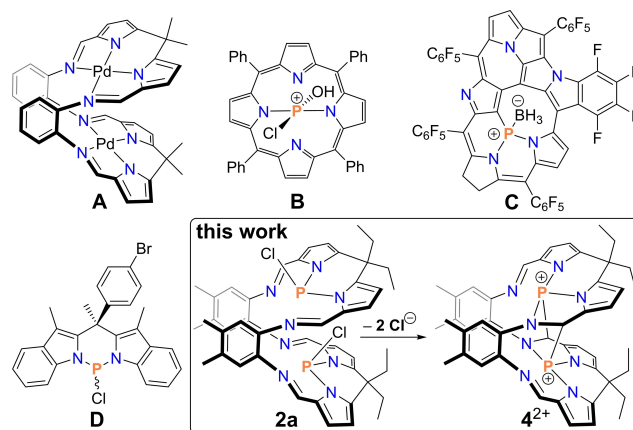
Figure 1. Literature examples for a calix[4]pyrrole Schiff base complex (**A**) and P containing compounds **B** - **D** related to the molecules presented in this work.

plexes 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.[4,15,16,32]
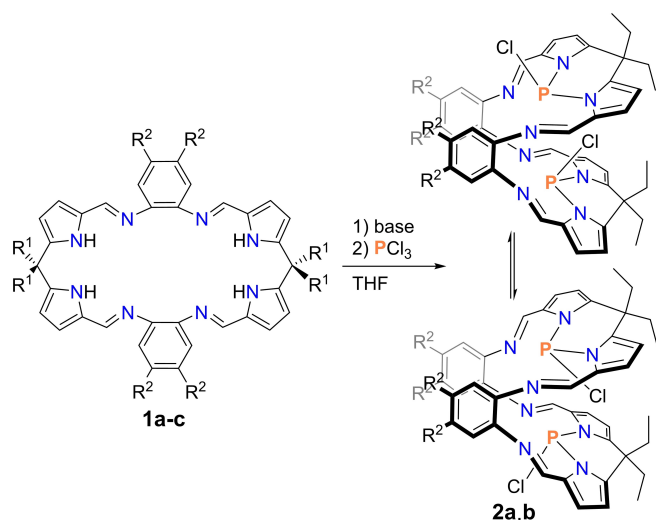
If only one half of Pacman ligands is regarded, porphyrins are structurally closely related and can therefore be seen as model substances. Several P(V) containing porphyrins were reported, mostly cations (e.g. **B**, Figure 1).[33–35] The first P(III) porphyrinoid (**C**, Figure 1) was synthesized in 2012 by Osuka and coworkers[36] and, to our knowledge, Latos-Grażyński, Pawlicki and coworkers reported the only two further examples.[37,38] Both types of P(III) porphyrinoids were structurally characterized but due to missing leaving groups on the P(III) 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

[a] L. Eickhoff, L. Ohms, Dr. J. Bresien, Dr. A. Villinger, Dr. D. Michalik, Prof. Dr. A. Schulz
Institut für Chemie
Universität Rostock
Albert-Einstein-Str. 3a, 18059 Rostock (Germany)
E-mail: jonas.bresien@uni-rostock.de
axel.schulz@uni-rostock.de
Homepage: http://www.schulz.chemie.uni-rostock.de/

[b] Dr. D. Michalik, Prof. Dr. A. Schulz
Leibniz-Institut für Katalyse e. V.
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202103983

Chemistry Europe
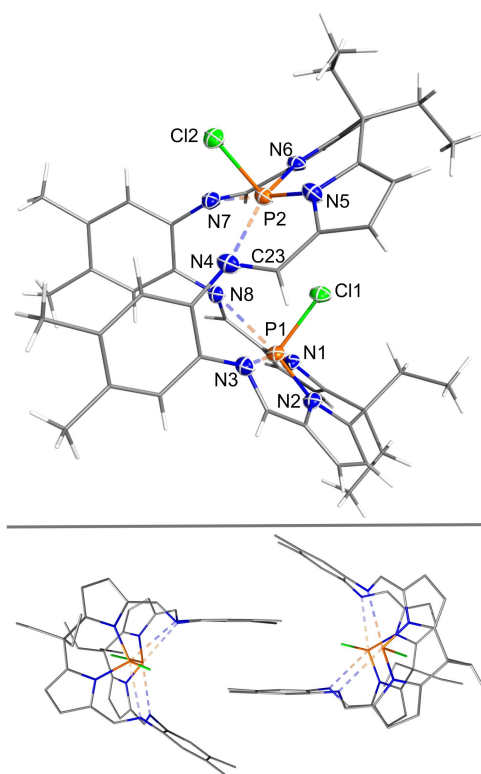European Chemical
Societies Publishing

Scheme 1. Synthesis of **2** and its equilibrium with respect to the *exo/endo* Cl positions (**a**: R^1=Et, R^2=Me, **b**: R^1=Et, R^2=H, **c**: R^1=Ph, R^2=H; base = KH, NEt$_3$).

Figure 2. Top: Molecular structure of **2a** (crystallized from benzene) in the solid state. Ellipsoids are drawn at 50% probability at 123(2) K. Solvent omitted for clarity. Selected distances (Å) and angles (°): P1–Cl1 2.0965(8), P1–N1 1.743(2), P1–N2 1.736(2), P1–N3 2.866(2), P1–N8 2.874(2), P2–Cl2 2.1016(8), P2–N4 2.881(2), P2–N5 1.741(2), P2–N6 1.746(2), P2–N7 2.743(3), N4–C23 1.277(3); N1–P1–Cl1 98.90(6), N2–P1–N1 94.86(8), N1–P1–N3 165.62(8) N5–P2–Cl2 100.18(6), N5–P2–N6: 94.18(9), N5–P2–N7 167.06(8). Bottom: π-stacking between two molecular entities of **2a** in the crystal. Hydrogen atoms omitted for clarity.

Pacman compound binding *two* P–Cl moieties as a promising synthon for versatile reactive species containing P atoms in an enforced neighborhood.[40] The concept of cooperative reactivity is demonstrated by the synthesis of a P based Pacman dication.

For the synthesis, we started from calix[4]pyrrole Schiff base ligands **1a–c** (Scheme 1) of which **1b** has not been reported before (see Supporting Information).[4,14] **1a–c** were synthesized according to modified literature procedures.[4,5,14,16,41–43] Base assisted HCl elimination upon treatment of **1** with PCl$_3$ allowed for the introduction of P–Cl moieties and led to the isolation of the first metal-free Pacman complexes **2a,b** (Scheme 1). Due to severe solubility problems, a reaction product of **1c** (R^1=Ph, R^2=H) could never be isolated. The replacement of the Ph substituents in R^1-position by Et groups enabled us to isolate **2b** but low yields and bad reproducibility prevented further investigations. Only the introduction of additional methyl groups on the phenylene linkers (R^2) allowed for the reliable synthesis of **2a** as yellow to orange crystals. Here, using KH as base (the potassium complex **3** was also isolated and fully characterized, Figure S7) entailed an easier separation of the product from the byproduct (KCl) but only the less reactive NEt$_3$ led to reasonable yields of 26% for crystalline **2a** (raw product 54%).

Inserting two P–Cl moieties in a Pacman ligand can theoretically lead to three different isomers - *endo-endo*, *exo-endo* and *exo-exo* - depending on the position of the Cl substituents outside or inside the cavity of the complex. In single crystals received from benzene and dichloromethane, respectively, **2a** and **2b** reveal the *exo-endo* orientation of the P–Cl moieties within the Pacman structure (Figure 2; due to the resemblance of the structural parameters, only **2a** is discussed here, for **2b** see Figures S5 and S6).[44] Each P$^{(III)}$ atom in **2a** is embedded in a distorted trigonal pyramidal coordination environment including one Cl atom and two pyrrolic N atoms

($d_\varnothing$(P–N$_{pyr}$) = 1.742(3) Å). Additionally, the distances between the P atoms and iminic N atoms $d_\varnothing$(P–N$_{imin}$) = 2.86(3) Å (Table S4) are significantly shorter than the sum of the van der Waals radii (Σr_{vdW}(N···P) = 3.35 Å).[45] This interaction was examined by NBO (Natural bond orbital)[46,47] 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–N$_{pyrrole}$ bonds. Although these interactions are rather weak (the values correspond to the strength of typical hydrogen bonds),[48] they indicate that the structural motif is capable of stabilizing reactive compounds in follow-up reactions. Regarding the N$_4$ planes formed by the pyrrolic and iminc 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 **2a** is not planar but bent away from the respective P–Cl bond.

Both P–Cl bonds are in the expected range for covalent single bonds ($d_\varnothing$(P–Cl) = 2.099(3) Å, cf. Σr_{cov}(P–Cl) = 2.04 Å).[49] In contrast, the intramolecular distance between the *endo* Cl atom

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202103983

Chemistry
Europe

European Chemical
Societies Publishing

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, Σr_{vdW}(P···Cl) = 3.55 Å)[45] but still longer than previously reported distances for Cl atoms bridging two P atoms (e.g. d(P···Cl) = 2.602(1) Å).[50] The overall coordination around the P$^{(III)}$ 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 pyramidally 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 **2a** indicates significant face-to-face π-π-interactions between four phenyl rings of two neighboring **2a** molecules (Figure 2, bottom).

^{31}P{^{1}H} NMR spectra of the reaction solution and isolated **2a** 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 **2a**, too (Figure 4a). Interestingly, the C*H* protons of the phenylene backbone seem to be most influenced by the orientation of the P–Cl moieties, showing the largest chemical
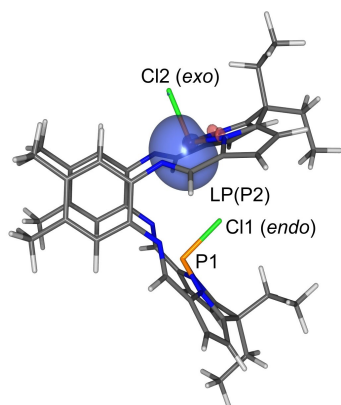
shift difference between their two signals ($\delta = 6.34$, 6.81 ppm; Figure 4a, blue dots). This is explained by their spatial proximity to either the *exo* Cl atom or the lone pair of electrons of the *endo* substituted P atom. Due to the additional *exo* and *endo* orientation of the ethyl groups 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 **2a** in solution. High temperature NMR spectra confirmed this assumption, showing only a single set of signals for **2a** at 100 °C (Figure 4b; Figures S20 and S21). On the other hand, cooling down a solution of **2a** 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 **2a** 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 **2a** to form the corresponding dication. Therefore, 2 equivalents of AgOTf were added to **2a** in the dark, resulting in a red suspension. Extraction with acetonitrile gave the dark red salt [**4**][OTf]$_2$ (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[51] and silicon,[52] 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]$_2$ ring with P in the oxidation state +V. Only few examples for the synthesis of [PNC]$_2$ rings

Figure 3. Natural Localized Molecular Orbital (NLMO) of the lone pair (LP) localized at the *exo*-substituted P2 atom in **2a** (PBE-D3/*m*TZVP).
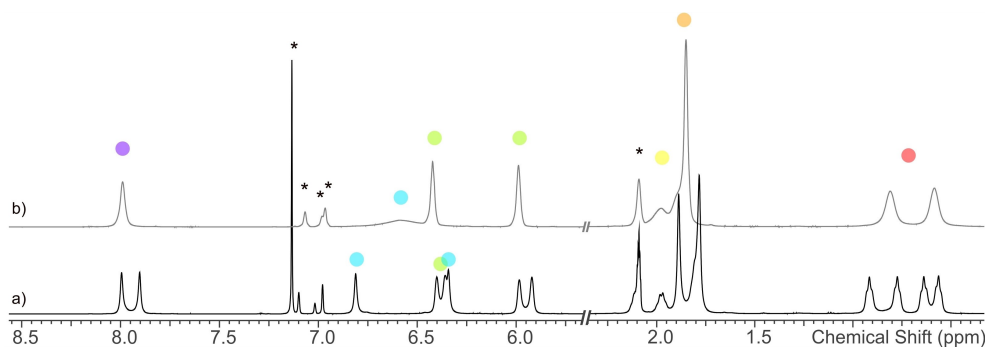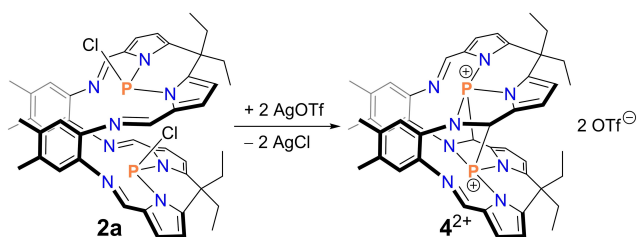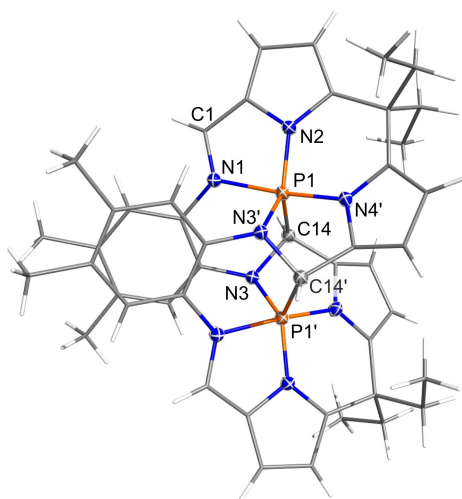

Figure 4. ^{1}H NMR spectra of crystalline **2a** dissolved in toluene-d_8; a) at 25 °C, b) at 100 °C (solvent signals indicated by asterisks).

Chem. Eur. J. **2022**, *28*, e202103983 (3 of 6)

© 2021 The Authors. Chemistry - A European Journal published by Wiley-VCH GmbH

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202103983

Chemistry Europe
European Chemical
Societies Publishing

Scheme 2. Synthesis of [4][OTf]₂.

Figure 5. Molecular structure of 4^{2+} in the solid state. Ellipsoids are drawn at 50% probability at 173(2) K. Counterions and solvent omitted for clarity. Symmetry code: 1-x, y, ½-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' 172.85(4), N1–P1–N2 84.43(4), N2–P1–C14 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 intra-molecular reaction.[53–55] In 4^{2+} 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^{2+} in the mixture with excess **2a**.

The crystal structure of [4][OTf]₂ reveals a C_2 symmetric macrocyclic dication with two monocationic, trigonal bipyrami-dally 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^{2+}, 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 ($d_{\varnothing}$(P–N) = 1.71(2) Å, cf. Σr_{cov}(P–N) = 1.76 Å; d(P1–C14) = 1.889(2) Å, cf. Σr_{cov}(P–C) = 1.87 Å).[49] The N3–C14 distance in 4^{2+} (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.

According to NBO analysis, electron localization function (ELF) and the Laplacian of the electron density,[57] 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^{2+} ion ("closed" structure, **min0**), quantum chemical calculations were performed at the DLPNO-CCSD(T)[58–62]/mTZVP//PBE-D3/mTZVP level of theory, including correction terms for the solvation in MeCN (SMD[63] 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⁻¹ for the reverse "opening" reaction becomes hardly accessible, which is in accord with our experimental observations. NMR spectra of [4][OTf]₂ show only one product: one singlet in the ³¹P{¹H} NMR spectrum and sharp signals including several ¹H,³¹P couplings in the ¹H NMR spectrum (Figure S26). Also, upon heating neither additional nor signifi-cantly broadened signals are observed (Figure S27). Never-theless, 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 $P^{(III)}$ 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.
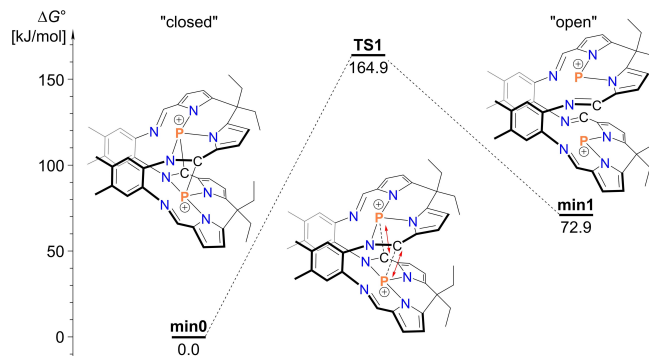
Figure 6. Energy profile of the P–C bond dissociation in 4^{2+} in MeCN (DLPNO-CCSD(T)/mTZVP//PBE-D3/mTZVP) (see also Figure S28).

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202103983

Chemistry
Europe
European Chemical
Societies Publishing

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]$_2$.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: activation · macrocyle · Pacman · phosphorus cation · redox reaction

[1] C. K. Chang, I. Abdalmuhdi, *J. Org. Chem.* **1983**, *48*, 5388–5390.

[2] J. P. Collman, C. M. Elliott, T. R. Halbert, B. S. Tovrog, *Proc. Natl. Acad. Sci. USA* **1977**, *74*, 18–22.

[3] C. K. Chang, in *Advances in Chemistry - Inorganic Compounds with Unusual Properties-II* (Eds.: R. F. Gould, R. B. King), American Chemical Society, Washington, DC, **1979**, pp. 162–177.

[4] G. Givaja, A. J. Blake, C. Wilson, M. Schröder, J. B. Love, *Chem. Commun.* **2003**, 2508–2509.

[5] J. L. Sessler, W.-S. Cho, S. P. Dudek, L. Hicks, V. M. Lynch, M. T. Huggins, *J. Porphyrins Phthalocyanines* **2003**, *07*, 97–104.

[6] V. M. Lynch, J. L. Sessler, U. Mirsaidov, J. M. Veauthier, J. T. Markert, E. Tomat, *Inorg. Chem.* **2005**, *44*, 6736–6743.

[7] P. L. Arnold, A. J. Blake, C. Wilson, J. B. Love, *Inorg. Chem.* **2004**, *43*, 8206–8208.

[8] P. L. Arnold, N. A. Potter née Jones, C. D. Carmichael, A. M. Z. Slawin, P. Roussel, J. B. Love, *Chem. Commun.* **2010**, *46*, 1833.

[9] J. B. Love, *Chem. Commun.* **2009**, 3154–3165.

[10] S. D. Reid, M. Volpe, J. B. Love, C. Wilson, A. J. Blake, *Inorg. Chim. Acta* **2006**, *360*, 273–280.

[11] P. L. Arnold, N. A. Potter, N. Magnani, C. Apostolidis, J. C. Griveau, E. Colineau, A. Morgenstern, R. Caciuffo, J. B. Love, *Inorg. Chem.* **2010**, *49*, 5341–5343.

[12] J. W. Leeland, F. J. White, J. B. Love, *J. Am. Chem. Soc.* **2011**, *133*, 7320–7323.

[13] N. L. Bell, P. L. Arnold, J. B. Love, *Dalton Trans.* **2016**, *45*, 15902–15909.

[14] J. W. Leeland, A. M. Z. Slawin, J. B. Love, *Organometallics* **2010**, *29*, 714–716.

[15] G. Givaja, M. Volpe, J. W. Leeland, M. A. Edwards, T. K. Young, S. B. Darby, S. D. Reid, A. J. Blake, C. Wilson, J. Wolowska, et al., *Chem. Eur. J.* **2007**, *13*, 3707–3723.

[16] E. Askarizadeh, A. M. J. Devoille, D. M. Boghaei, A. M. Z. Slawin, J. B. Love, *Inorg. Chem.* **2009**, *48*, 7491–7500.

[17] E. A. Connolly, J. W. Leeland, J. B. Love, *Inorg. Chem.* **2016**, *55*, 840–847.

[18] C. J. Stevens, G. S. Nichol, P. L. Arnold, J. B. Love, *Organometallics* **2013**, *32*, 6879–6882.

[19] G. Givaja, M. Volpe, M. A. Edwards, A. J. Blake, C. Wilson, M. Schröder, J. B. Love, *Angew. Chem. Int. Ed.* **2007**, *46*, 584–586; *Angew. Chem.* **2007**, *119*, 590–592.

[20] P. D. Harvey, C. Stern, C. P. Gros, R. Guilard, *Coord. Chem. Rev.* **2007**, *251*, 401–428.

[21] A. Osuka, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, N. Tamai, Y. Nishimura, *Chem. Phys. Lett.* **1991**, *181*, 413–418.

[22] J. P. Collman, P. S. Wagenknecht, J. E. Hutchison, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1537–1554.

[23] P. Lang, M. Schwalbe, *Chem. Eur. J.* **2017**, *23*, 17398–17412.

[24] P. Lang, M. Pfrunder, G. Quach, B. Braun-Cula, E. G. Moore, M. Schwalbe, *Chem. Eur. J.* **2019**, *25*, 4509–4519.

[25] M. Abe, *Chem. Rev.* **2013**, *113*, 7011–7088.

[26] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[27] J. Lam, K. M. Szkop, E. Mosaferi, D. W. Stephan, *Chem. Soc. Rev.* **2019**, *48*, 3592–3612.

[28] S. Ito, *Tetrahedron Lett.* **2018**, *59*, 1–13.

[29] J. Bresien, L. Eickhoff, A. Schulz, E. Zander, in *Comprehensive Inorganic Chemistry III* (Eds.: J. Reedijk, K. Poeppelmeier), Elsevier, **2021**, https://doi.org/10.1016/B978-0-12-823144-9.00029-7.

[30] S. González-Gallardo, F. Breher, in *Comprehensive Inorganic Chemistry II* (Eds.: J. Reedijk, K. Poeppelmeier), Elsevier, **2013**, pp. 413–455.

[31] J. M. Veauthier, W.-S. Cho, V. M. Lynch, J. L. Sessler, *Inorg. Chem.* **2004**, *43*, 1220–1228.

[32] C. Finn, J. B. Love, J. R. Pankhurst, D. Betz, T. Cadenbach, *Dalton Trans.* **2015**, *44*, 2066–2070.

[33] P. Sayer, M. Gouterman, C. R. Connell, *J. Am. Chem. Soc.* **1977**, *99*, 1082–1087.

[34] C. J. Carrano, M. Tsutsui, *J. Coord. Chem.* **1977**, *7*, 79–83.

[35] R. Sharma, M. Ravikanth, *J. Porphyrins Phthalocyanines* **2016**, *20*, 895–917.

[36] T. Higashino, A. Osuka, *Chem. Sci.* **2012**, *3*, 103–107.

[37] M. Pawlicki, A. Kędzia, D. Bykowski, L. Latos-Grażyński, *Chem. Eur. J.* **2014**, *20*, 17500–17506.

[38] A. Idec, J. Skonieczny, L. Latos-Grażyński, M. Pawlicki, *Eur. J. Org. Chem.* **2016**, *2016*, 3691–3695.

[39] H. Spinney, D. Richeson, T. Burchell, S. Jurca, S. Gorelsky, I. Mallov, *Inorg. Chim. Acta* **2012**, *392*, 5–9.

[40] A. Schulz, *Dalton Trans.* **2018**, *47*, 12827–12837.

[41] A. J. F. N. Sobral, N. G. C. L. Rebanda, M. Da Silva, S. H. Lampreia, M. Ramos Silva, A. Matos Beja, J. A. Paixão, A. M. D. A. Rocha Gonsalves, *Tetrahedron Lett.* **2003**, *44*, 3971–3973.

[42] T. Dubé, G. P. A. Yap, S. Gambarotta, D. M. M. Freckmann, C. D. Bérubé, *Organometallics* **2002**, *21*, 1240–1246.

[43] J. B. Love, A. J. Blake, C. Wilson, S. D. Reid, A. Novak, P. B. Hitchcock, *Chem. Commun.* **2003**, 1682–1683.

[44] Deposition Number(s) https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.202103983 2095503 (for **1b**·4 HCl), 2095504 (for **2a**·benzene), 2095506 (for **2a**·THF), 2095505 (for **2b**), 2095507 (for **3**), 2095508 (for **4**$^{2+}$), 2095509 (for **5b**), 2095510 (for **6a**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe http://www.ccdc.cam.ac.uk/structures Access Structures service.

[45] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806–5812.

[46] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2013**.

[47] F. Weinhold, C. R. Landis, E. D. Glendening, *Int. Rev. Phys. Chem.* **2016**, *35*, 399–440.

[48] K. Bläsing, J. Bresien, R. Labbow, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2018**, *57*, 9170–9175; *Angew. Chem.* **2018**, *130*, 9311–9316.

[49] A. F. Holleman, N. Wiberg, E. Wiberg, *Holleman Wiberg, Lehrbuch Der Anorganischen Chemie, 102. Aufl.*, Walter De Gruyter, Berlin, **2007**.

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202103983

Chemistry
Europe
European Chemical
Societies Publishing

[50] F. D. Henne, E.-M. Schnöckelborg, K.-O. Feldmann, J. Grunenberg, R. Wolf, J. J. Weigand, *Organometallics* **2013**, *32*, 6674–6680.

[51] F. Ebner, H. Wadepohl, L. Greb, *J. Am. Chem. Soc.* **2019**, *141*, 18009–18012.

[52] F. Ebner, L. Greb, *Chem* **2021**, *7*, 2151–2159.

[53] N. K. Maidanovich, S. V. Iksanova, Y. G. Gololobov, *Zh. Obshch. Khim.* **1982**, *52*, 930–931.

[54] A. M. Kibardin, T. K. Gazizov, K. M. Enikeev, A. N. Pudovic, *Izv. Akad. Nauk SSSR Ser. Khim.* **1983**, 432–434.

[55] A. M. Arif, A. H. Cowley, R. M. Kren, D. L. Westmoreland, *Heteroat. Chem.* **1990**, *1*, 117–122.

[56] J. C. Gilhula, A. T. Radosevich, *Chem. Sci.* **2019**, *10*, 7177–7182.

[57] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.

[58] F. Neese, J. Wiley, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.

[59] F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327.

[60] C. Riplinger, F. Neese, *J. Chem. Phys.* **2013**, *138*, 034106.

[61] D. G. Liakos, M. Sparta, M. K. Kesharwani, J. M. L. Martin, F. Neese, *J. Chem. Theory Comput.* **2015**, *11*, 1525–1539.

[62] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2016**, *144*, 024109.

[63] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.