

VIP Very Important Paper

Enhancing the Reactivity of an Aromatic *cyclo*-P₅ Ligand via Electrophilic ActivationChristoph Riesinger,^[a] Philip M. Blank,^[b] Christian Scholtes,^[c] Ruth M. Gschwind,^[c] and Manfred Scheer^{*[a]}

In memoriam of Ian Manners.

Electrophilic activation of the aromatic *cyclo*-P₅ ligand in [Cp*Fe(η⁵-P₅)] is demonstrated to drastically enhance its reactivity towards weak nucleophiles. Unprecedented functionalized, contracted as well as complexly aggregated polyphosphorus compounds are accessed utilizing [Cp*Fe(η⁵-P₅Me)][OTf] (**A**), highlighting the great potential of this underexplored mode of reactivity. Addition of carbenes to **A** affords novel 1,2- or 1,1-difunctionalized *cyclo*-P₅ complexes [Cp*Fe(η⁴-P₅(1-L)(2-Me)][OTf] (L = IDipp (**1**), ^{Et}CAAC (**2**), ⁱPr (**3 b**)) and [Cp*Fe(η⁴-P₅(1-ⁱPr)(1-Me)][OTf] (**3 a**). For the first time, the much smaller IMe₄ leads to the contraction of the *cyclo*-P₅ ligand and formation of

[Cp*Fe(η⁴-P₄(1-IMe)(4-Me)] (**4**). DFT calculations shed light on the delicate mechanism of this type of reaction, which is reinforced by the experimental identification of key intermediates. Even the comparably weak nucleophile IDippCH₂ reacts with **A** to form [Cp*Fe(η⁴-P₅(1-IDippCH₂)(1/2-Me)][OTf] (**6 a/b**), highlighting its explicitly more reactive nature. Moreover, exposure of **A** to IDippEH (E = N, P) leads to a unique aggregation reaction affording [(Cp*Fe)₂{μ₂η^{4:3:1}-P₁₀Me₂(IDippN)}][OTf] (**8**) and [(Cp*Fe)₂{μ₂η^{4:1:1:1}-P₁₁Me₂(IDipp)}][OTf] (**9**), respectively.

Introduction

The concept of aromaticity originates from classic organic chemistry, explaining the outstanding stability of cyclic, planar and unsaturated molecules with 4n + 2 π-electrons.^[1] While the development of this concept towards phenomena such as σ-, φ- or spherical aromaticity^[2] is a matter of ongoing research^[3] and debate,^[4] aromatic molecules are ubiquitous in all fields of organic chemistry. Their unique optoelectronic properties are utilized in applications such as OLED manufacturing,^[5] their synthetic utility is exploited in the synthesis of modern pharmaceuticals,^[6] and their geometrical constraints (e.g. *p*-terphenyls) are employed in the design of new ligands for transition metals and catalysis.^[7] However, the aromatic stabilization within these species (e.g. benzene) also presents the biggest obstacle in their transformation. Textbook electrophilic substitution benefits from the restoration of aromaticity.^[8] In contrast, many apparently simple transformations such as reduction reactions of benzene derivatives, actually pose a

significant challenge in contemporary organic chemistry. While modern developments towards photochemical dearomatization are flourishing,^[9] the majority of synthetic approaches require harsh reaction conditions (cf. Birch-reduction),^[10] or the utilization of powerful reagents. For example, the insertion of an aluminyl anion into the C=C double bond of benzene could recently be accomplished.^[11]

Interestingly, cyclic polyphosphorus (P_n) compounds are intimately related to organic aromatics via the isolobal relationship between the P atom and the CH fragment.^[12] These P_n ligands are stabilized by coordination to a transition metal (TM) permitting their isolation. Prominent examples are the recently accomplished side-on stabilization of P₂^[13] or the trapping of its lighter homolog NP.^[14] Moreover, cyclic P_n scaffolds^[15] may experience additional aromatic stabilization, in analogy to their isolobal organic counterparts.^[12] Consequently, the reductive^[16] and nucleophilic^[17] functionalization of such highly stabilized and aromatic TM-coordinated P_n ligands equally requires undesirable harsh conditions and powerful reagents. Commonly, this relies on reactive species such as ^tBuLi or KC₈ and is reminiscent of approaches developed earlier in (organo-)phosphorus chemistry, e.g. by Baudler *et al.*^[18] One particularly stable P_n framework is the *cyclo*-P₅ ligand. It occupies a special position among cyclic P_n scaffolds, as it is isolobal to the aromatic cyclopentadienide anion,^[12] a ubiquitous aromatic organometallic ligand. In analogy to these,^[19] the reactivity of the *cyclo*-P₅ moiety is modulated by the coordination to a TM. It can be found in organometallic sandwich compounds,^[16d,20] pure inorganic sandwich complexes,^[21] and even multi-decker arrangements.^[22] However, the transformation of the *cyclo*-P₅ ligand is extremely challenging, accentuat-

[a] C. Riesinger, M. Scheer
Institute of Inorganic Chemistry, University of Regensburg, Regensburg 93040, Germany
E-mail: manfred.scheer@chemie.uni-regensburg.de

[b] P. M. Blank
Laboratory of Organic Chemistry, ETH Zürich, Vladimir-Prelog-Weg 3, HCI, Zürich 8093, Switzerland

[c] C. Scholtes, R. M. Gschwind
Institute of Organic Chemistry, University of Regensburg, Regensburg 93040, Germany

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202402675>

ing the outstanding similarity between cyclic P_n ligands and organic aromatic compounds. For example, functionalization of prototypical pentaphosphaferrocene $[Cp^*Fe(\eta^5-P_5)]$ (I, Scheme 1a)^[19] is limited to strong nucleophiles such as organolithium reagents. These are needed to overcome the aromatic stabilization of the *cyclo*- P_5 ligand yielding strongly bent, non-aromatic *cyclo*- P_5R moieties (II, Scheme 1a).^[17a] Further functionalization (III) and even the release of asymmetrically substituted phosphines could be achieved using BnK (Bn = benzyl).^[23] However, less powerful nucleophiles such as NHCs (N-heterocyclic carbenes) undergo addition to I only in an equilibrium with the dissociated species,^[17d,h] indicating the strong aromatic stabilization within the *cyclo*- P_5 ligand. Its direct transformation to more complex structural arrangements is only observed when I is exposed to extremely reactive species such as Al(I) compounds (IV),^[24] disilylenes (V)^[25] or iodine^[26] under partly forcing conditions (Scheme 1b).

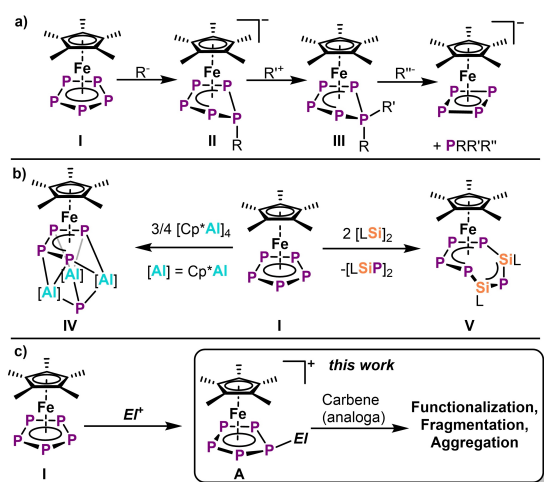
The discussion above highlights the similarities between aromatic organic compounds and *cyclo*- P_n compounds and the mutual interest in developing novel synthetic tools for their functionalization, transformation and dearomatization. While nucleophilic and reductive functionalization have been explored extensively (*vide supra*), progress in the complementary electrophilic^[27] and oxidative^[28] functionalization of P_n frameworks has primarily been made only recently. This left the reactivity of the resulting polyphosphorus cations strikingly underexplored.^[29] Besides others,^[30] our group contributed significantly to the field of TM-stabilized polyphosphorus cations by introducing unprecedented P_2^- to P_{16}^+ -cations via oxidation and especially the electrophilic functionalization of neutral P_n ligand complexes.^[16f,i,31] Intriguingly, electrophilic addition to I proceeds under very mild conditions affording unprecedented pentaphosphole (*cyclo*- P_5R) complexes, strictly contrasting the harsh conditions and the limited scope established for the nucleophilic functionalization of I. Notably, the aromaticity within the resulting *cyclo*- P_5R (pentaphosphole) ligands is preserved (Scheme 1c).^[31d,f] With this in mind, one can

speculate that the electrophile addition and coinciding transfer of positive charge would enhance the reactivity of the aromatic *cyclo*- P_5 ligand in I towards even weaker nucleophiles. A successful realization of this concept would open a plethora of new synthetic avenues for the transformation of the aromatic *cyclo*- P_5 ligand in I far beyond known P_n architectures,^[17a,23] and avoid the use of harsh reagents.^[24–26] Furthermore, establishing this reactivity enhancement by electrophilic activation of the robust I would infer its transferability to other aromatic, highly stabilized P_n ligands and main group species in general.

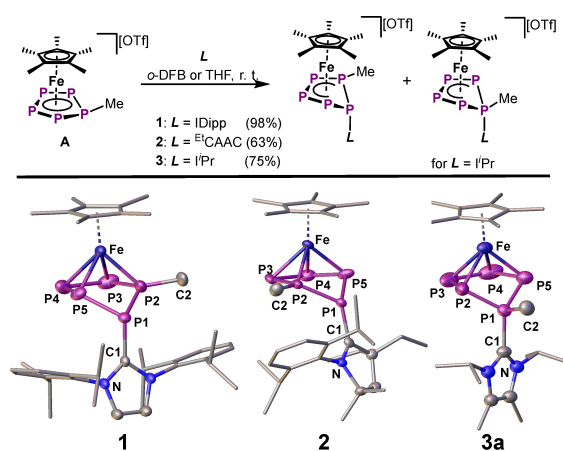
Herein, we report the drastic reactivity enhancement of the aromatic *cyclo*- P_5 ligand in I by reacting it with MeOTf. Thus, the resultant electrophilic activation permits its reaction even with weak nucleophiles, leading to the easy degradation of its aromaticity and yielding new substitution patterns at the *cyclo*- P_5 ligand. The yet unachieved contraction of the *cyclo*- P_5 ring in I can be realized for the first time using a simple carbene. Moreover, the addition of carbene-derived imines or their P-analogs even leads to distinct aggregation reactions and the formation of unprecedented P_{10}^- and P_{11}^- -scaffolds, opening uncharted chemical transformations in this field.

Results and Discussion

Previous studies have shown that singlet carbenes such as NHCs or CAACs (Cyclic Alkyl Amino Carbenes) only form labile adducts with I, which is attributed to the robustness of its aromatic *cyclo*- P_5 ligand.^[17d,h] In contrast, we now found that electrophilically activated A (Figure 1), in which the aromaticity of the P_5 ring is still preserved, undergoes rapid addition reactions with IDipp (1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene) as well as $^t\text{CAAC}$ ((2,6-diisopropylphenyl)-4,4-diethyl-2,2-dimethyl-pyrrolidin-5-ylidene) without showing any equilibria. Interestingly, both resulting products $[Cp^*Fe(\eta^4-P_5(1-L)(2-Me))][OTf]$ (1: L = IDipp, 98%; 2: L = $^t\text{CAAC}$, 63%; Figure 1) feature novel η^4 -bound 1,2-difunctionalized *cyclo*- P_5R_2 ligands without any signs of carbene dissociation in solution, contrast-



Scheme 1. Selected examples of the functionalization and conversion of coordinated *cyclo*- P_5 ligands: a) R = alkyl/aryl, R' = alkyl, R'' = benzyl (Bn); b) L = $PhC(N^tBu)_2$; c) El = p-block electrophile.



ing the reactivity of **1**.^[17d] Notably, the synthetic access to 1,2-disubstituted *cyclo*-P₅ ligands has so far been extremely limited and unselective.^[32] Thus, **1** and **2** constitute the first complexes in which such a new structural motif could be realized via a selective addition reaction. When **A** is exposed to the smaller *i*Pr (1,4-diisopropyl-2,3-dimethylimidazol-5-ylidene), a mixture of both products, the 1,1- and 1,2-substituted isomers [Cp*Fe(η⁴-P₅(1-*i*Pr)(1-Me))] [OTf] (**3a**) and [Cp*Fe(η⁴-P₅(1-*i*Pr)(2-Me))] [OTf] (**3b**), is obtained in 75 % yield (Figure 1). While **3a** can be obtained spectroscopically pure from CH₂Cl₂/*n*-hexane mixtures, it slowly equilibrates with **3b** to a final ratio **3a**:**3b** of 0.23:1 in solution (cf. SI). Experimentally, this corresponds to **3b** being only 3.6 kJ/mol more stable than **3a** and is in line with the computational data (ωB97X-D4/def2-TVPPD), suggesting an energetic difference of 1.5 kJ/mol. Overall, this points towards the steric demand of the used carbene to govern the regioselectivity of this addition reaction. Moreover, dispersive interaction in **1** and **2** could reinforce this selectivity (*vide infra*).

For the isomerization of **3**, two mechanisms are conceivable: (I) a dissociative/associative one, in analogy to the one observed for [Cp*Fe(η⁴-P₅IMe)],^[17d] or (II) a unimolecular one which occurs via a 1,2-ligand shift. Due to the slow isomerization rate, the prevailing mechanism was not spectroscopically accessible via EXSY NMR (cf. SI). To prove that **A** is involved in the isomerization mechanism three kinetic experiments were carried out using different concentrations of **A** (0 mM, 55 mM and 110 mM) while keeping the initial concentration of **3a** constant at 110 mM (Figure 2). The kinetics shown in Figure 2 display that the isomerization of **3a** into **3b** is independent of the concentration of **A** within the experimental error. This strongly indicates that **A** is not involved in the isomerization mechanism and suggests a unimolecular mechanism. This can be seen as the result of the increased electrophilicity of **A** and thus underlines the drastic change in reactivity compared to **1**.

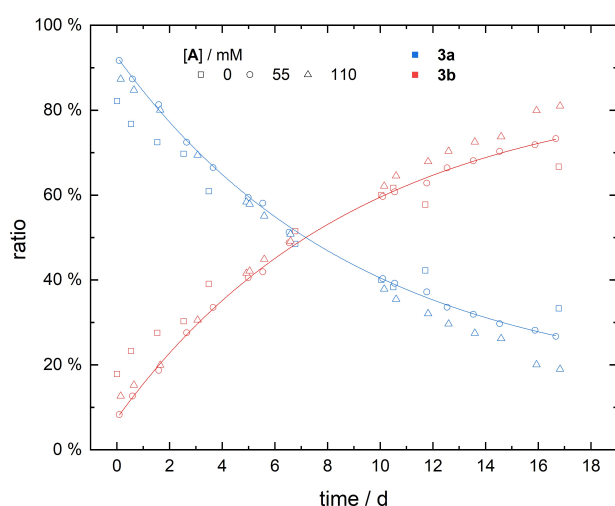


Figure 2. The isomerization of **3a** (blue) into **3b** (red) is independent of the concentration of **A**. The kinetic profiles obtained by the integration of the ³¹P NMR spectra starting from **3a** (110 mM) in DCM-d₂ show similar rates at concentrations of **A** of 0 mM (squares), 55 mM (circles) and 110 mM (triangles). The data set with 55 mM of **A** was exponentially fitted to function as guide line. To compensate for partial degradation the ratio of **3a** and **3b** of the sum of both is depicted.

Spectroscopically, **1** and **2** reveal their 1,2-difunctionalization as they show ABMQX and AMNQX spin systems in the respective ³¹P NMR spectra (see SI). While solutions of **3** always contain both isomers **3a** and **3b**, the respective AMM'XX' spin system of **3a** is indicative of its 1,1-disubstitution allowing the assignment of signals to both compounds **3a** and **3b**. Structurally, the most striking feature of these complexes is the rare 1,2-difunctionalized *cyclo*-P₅ ligand in **1**, **2** and **3b** with a bent P1 atom and a Me substituent at P2. While the P–P bond lengths (**1**: 2.112(3)–2.155(1) Å, **2**: 2.049(1)–2.252(1) Å, **3b**: 2.057(9)–2.223(9) Å) and angles are similar to those observed in other complexes featuring envelope-shaped *cyclo*-P₅ ligands,^[17a,23] the P1–C1 (**1**: 1.836(4) Å, **2**: 1.827(3) Å, **3b**: 1.834(5) Å) as well as the P2–C2 (**1**: 1.737(7) Å, **2**: 1.643(7)/1.743(1) Å, **3b**: 1.785(18)/1.890(30) Å) bond lengths are in agreement with their formulation as single bonds.^[33] Notably, the imidazolyl substituent in **3b** is rotated perpendicular to the position it occupies in **1** and **2**. This may be the result of the smaller steric demand of *i*Pr but also prohibits any dispersive interaction of the *i*Pr groups with the Me substituent. Thus, the latter dispersive interactions may be responsible for the high regioselectivity in the formation of **1** and **2**, respectively. In contrast, the solid-state structure of **3a** reveals a more common 1,1-disubstituted *cyclo*-P₅ ligand. The P–P bond lengths (2.114(3)–2.159(2) Å) and angles in **3a** are similar to reported derivatives with both P1–C bond lengths (1.811(7)/1.867(5) Å) in the range of single bonds.^[33]

While the even smaller IMe₄ (IMe₄ = 1,2,3,4-tetramethylimidazol-5-ylidene) can lead to ring contraction reactions with several P_n ligand complexes,^[17c] it only affords labile adducts in combination with **1**.^[17d] In contrast, exposing the aromatic but electrophilically activated **A** to an excess of three equivalents of IMe₄ yields the tetraphosphorus complex [Cp*Fe(η⁴-P₄(1-IMe₄)(4-Me))] (**4**, 52 %, Figure 3), in which one P atom is extruded. Thus, **4** represents the first compound in which the *cyclo*-P₅ ligand of **1** could be opened without the use of harsh reagents such as BnK.^[23] Accordingly, the formation of the cation [(IMe₄)₂P]⁺^[34] can be observed spectroscopically (see SI). Interestingly, cobalt complexes featuring non-aromatic *cyclo*-P₅R₂ ligands (similar to **III**) also show further reactivity towards comparably weak nucleophiles. Their reactivity, however, strongly depends on the utilization of redox non-innocent co-ligands^[35] and often yields simple addition products.^[36] While carbene(oid)-induced fragmentation/rearrangement reactions are known for polyphosphorus compounds,^[37] a mechanistic understanding has rarely been obtained.^[38] When **A** is reacted with equimolar amounts or a twofold excess of IMe₄, respectively, complicated product mixtures are monitored by NMR spectroscopy, which is attributed to the instability of the corresponding intermediates formed in these reactions. However, subjecting a 1:1 mixture of **A** and IMe₄ to ³¹P{¹H} NMR spectroscopy at –80 °C reveals the immediate formation of the anticipated first intermediate [Cp*Fe(η⁴-P₅(1-IMe₄)(1-Me))] [OTf] (**4_{INT1}**). Interestingly, no trace of the respective 1,2-regioisomer is observed, which agrees with the higher stability of the 1,1-isomer (5.9 kJ/mol) bearing the small IMe₄ substituent (see Figure 4 and SI). Exposing **A** to two equivalents of IMe₄ under the same conditions shows more

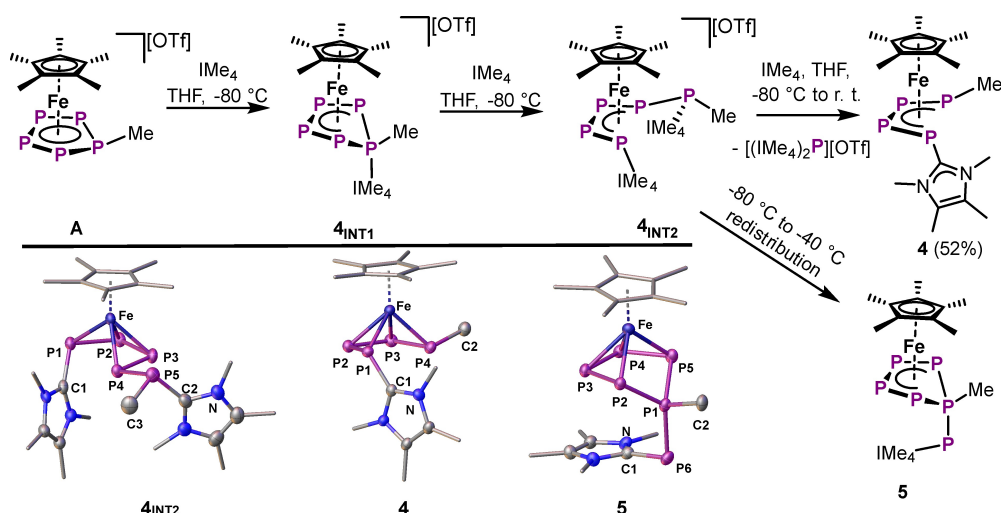


Figure 3. Synthetic pathway for obtaining **4** including both experimentally observed intermediates **4_{INT1}** and **4_{INT2}** as well as the decomposition product **5** (top) and the corresponding molecular structures of **4_{INT2}**, **4** and **5** in the solid state (bottom); H atoms and anions are omitted for clarity and ellipsoids are drawn at the 50% probability level.

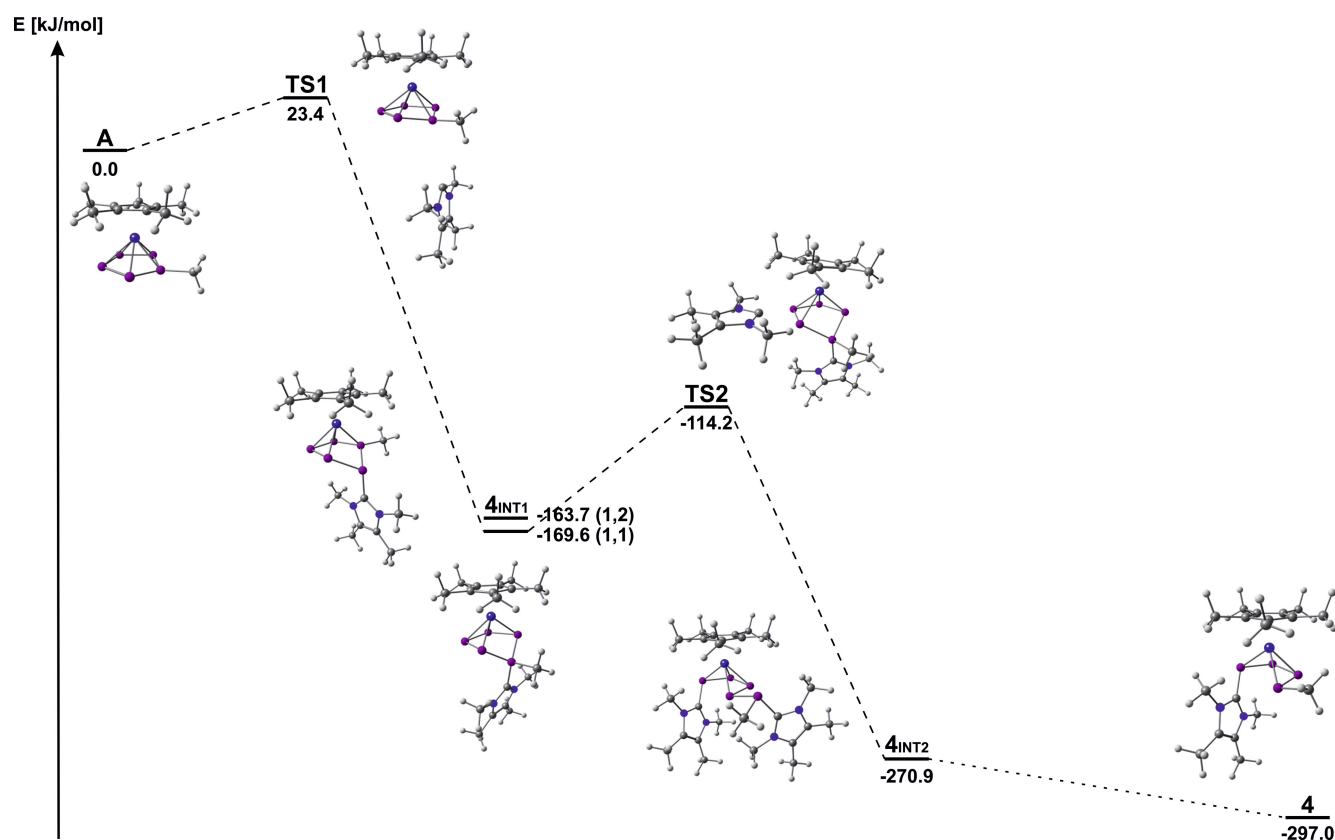


Figure 4. Stepwise reaction of **A** with three equivalents of IMe_4 computed at the $\omega\text{B97X-D4/def2-TZVPPD}$ level of theory and PCM solvent correction for THF.

complicated ^{31}P NMR spectra (see SI). However, a second intermediate, formed already at -80°C , could now be identified from these spectra and assigned to $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5(1\text{-IMe}_4)(1\text{-Me})(5\text{-IMe}_4))][\text{OTf}]$ (**4_{INT2}**), featuring an opened *catena*- P_5 ligand. More importantly, it was even possible to grow a single crystal of this key intermediate at low temperatures, corroborating the structural assignment of **4_{INT2}** (Figure 3). Upon warming to room

temperature, *in situ* generated **4_{INT2}** rapidly converts to $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5(1\text{-PIMe}_4)(1\text{-Me}))]$ (**5**, 45% based on Fe, **4** is observed as a side product in this transformation, see SI), possessing a phosphinidenido substituent. While this transformation/redistribution could not be traced further spectroscopically, it highlights the delicate reaction pathway during the formation

of **4**. Finally, adding three or more equivalents of IMe_4 to **A** results in the formation of **4** and unreacted IMe_4 , respectively.

Obtaining structural information on the highly reactive intermediates involved in the formation of **4** was the key to elucidating the underlying mechanism of its formation. While the molecular structure of $\mathbf{4}_{\text{INT1}}$ is consolidated by its spectroscopic data and the structural information obtained on the derivatives **1–3**, compounds $\mathbf{4}_{\text{INT2}}$, **4** and **5** are highly sensitive and especially $\mathbf{4}_{\text{INT2}}$ decomposes upon warming solutions to temperatures higher than -60°C (see SI). However, the solid-state structure of $\mathbf{4}_{\text{INT2}}$ reveals an opened *catena*- P_5 ligand attached to the Fe center in η^4 -binding mode (Figure 3). Additionally, the *catena*- P_5 ligand bears an IMe_4 and an Me group at the uncoordinated P5 atom as well as another IMe_4 substituent at P1. This structural motif arises from the nucleophilic attack of the second IMe_4 at the P5 atom (in $\mathbf{4}_{\text{INT1}}$), which is followed by the cleavage of the P1–P5 bond and the formation of the *catena*- P_5 ligand observed in $\mathbf{4}_{\text{INT2}}$. While the P4–P5 bond length (2.234(1) Å) agrees with a single bond, the residual P–P bonds (2.131(1) – 2.160(1) Å) coordinated to Fe point towards a delocalized double bond character.^[33] Furthermore, the P–C (1.832(3) – 1.845(4) Å) bond lengths are in the range of single bonds.^[33] Interestingly, the final product **4** shows a similar structural core compared to $\mathbf{4}_{\text{INT2}}$, with only the phosphino group in the latter being replaced by a Me group. Accordingly, the P–P bond lengths (2.134(1) – 2.157(1) Å) in **4** are similar to those in $\mathbf{4}_{\text{INT2}}$ and agree with the delocalized double bond character. Again, the P–C bonds (1.841(3) Å – 1.876(3) Å) are best described as single bonds. In contrast, **5** shows a 1,1-disubstituted *cyclo*- P_5 ligand bearing an IMe_4 -stabilized phosphinidenido and a Me group. Thus, the P_6 ligand in **5** displays the rare product of a formal expansion of the former *cyclo*- P_5 ligand. The overall envelope structure of the P_5 ring and the associated P–P bond lengths (2.134(1) – 2.187(1) Å) are similar to those observed in simple alkyl-substituted derivatives **III**.^[23] The newly formed P1–P6 bond (2.124(1) Å) is slightly shorter than the sum of the covalent single bond radii and the P–C bonds (1.822(2) Å) are best described as single bonds.^[33] The IMe_4 substituent is located directly below the plane of the Fe-coordinated P atoms, which may allow for additional stabilization through π – π interactions.

To gain deeper insight into the mechanistic key steps of the contraction reaction leading to **4**, DFT calculations ($\omega\text{B97X-D4/def2-TZVPPD}$, Figure 4) were carried out. The overall reaction of **A** with three equivalents of IMe_4 to **4** and $[(\text{IMe}_4)_2\text{P}]^+$ is strongly exergonic by 297 kJ/mol. However, the first steps of this reaction and especially the ring opening of the *cyclo*- P_5 ligand were of utmost interest, as this reactivity is unprecedented for **I**. The addition of the first equivalent of IMe_4 in **TS1** occurs at P1 with an energy barrier of 23.4 kJ/mol, and the follow-up formation of $\mathbf{4}_{\text{INT1}}$ is exergonic by 169.6 kJ/mol. Interestingly, the structural core of **A** is nearly undeformed within **TS1**. The corresponding 1,2-isomer of $\mathbf{4}_{\text{INT1}}$ is 5.9 kJ/mol higher in energy, which is in line with the exclusive experimental observation of the 1,1-isomer ($\mathbf{4}_{\text{INT1}}$) in solution (*vide supra*). The addition of the second equivalent of IMe_4 then proceeds via the approach to the neighboring P2 in **TS2** which has an energetic barrier of

55.4 kJ/mol. Although P1 shows a Mulliken charge of 0.9, the addition of the second IMe_4 unit to P1 can be discarded on steric arguments.^[23] While the carbene center in **TS2** is located only at 2.6 Å from P2 (as labelled in $\mathbf{4}_{\text{INT1}}$), the respective P1–P2 bond amounts to 2.4 Å and is thus significantly elongated compared to $\mathbf{4}_{\text{INT1}}$. Next, the P1–P2 bond is cleaved in $\mathbf{4}_{\text{INT2}}$ and its computed molecular structure is in good agreement with the parameters observed experimentally (*vide supra*). Finally, the addition of the last equivalent of IMe_4 to $\mathbf{4}_{\text{INT2}}$ leads to the extrusion of $[(\text{IMe}_4)_2\text{P}]^+$ and accordingly to the formation of **4**, which is exergonic by 26.1 kJ/mol (from $\mathbf{4}_{\text{INT2}}$).

To test the boundaries of the electrophilic reactivity enhancement of **I**, **A** was reacted with the weak nucleophile IDippCH_2 (N-heterocyclic olefin, NHO). Surprisingly, even this comparably weak nucleophile rapidly undergoes an addition to the *cyclo*- P_5 ligand of **A** affording the functionalized complex $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5(1\text{-NHO})(1/2\text{-Me}))][\text{OTf}]$ (**6**, Figure 5) in good yields of 74%. The formation of both regioisomers **6a** and **6b** (ratio 1:1.6) is attributed to the diminished steric control invoked by the IDipp substituent due to the incorporation of the methylene moiety in **6**. This is in qualitative agreement with computational data showing **6b** to be 3.0 kJ/mol higher in energy than **6a** (in contrast **1** is 10.2 kJ/mol more stable than its hypothetical 1,1-isomer; $\omega\text{B97X-D4/def2-TZVPPD}$). Both isomers **6a** and **6b** co-crystallize and reveal 1,1- and 1,2-disubstituted *cyclo*- P_5 ligands, respectively (Figure 5). While the P–P bonds (2.040(14)–2.224(19) Å) are close to those observed in simple alkyl-substituted derivatives **III**,^[23] the P–C bonds in **6a** (1.786(9) Å/1.70(4) Å) are shorter than in **6b** (1.914(4) Å/1.833(6) Å). However, the C=C bond (1.465(5) Å) in the IDippCH_2 substituent remains in the range of a double bond.^[33]

Finally, **A** was reacted with the carbene-stabilized parent phosphinidene IDippPH as well as its lighter homolog IDippNH (Figure 6). These reactions lead to the highly complex products $[(\text{Cp}^*\text{Fe})_2\{\mu_2, \eta^{4:3:1}\text{-P}_{10}\text{Me}_2(\text{IDippN})\}][\text{OTf}]$ (**8**) and $[(\text{Cp}^*\text{Fe})_2\{\mu_2, \eta^{4:1:1:1}$

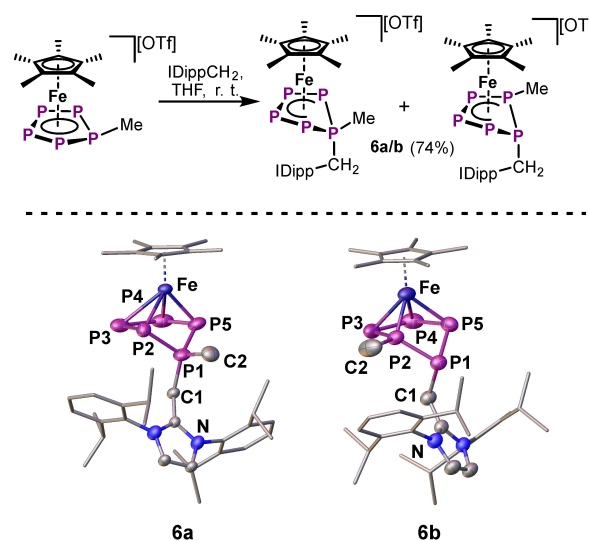


Figure 5. Synthesis of **6a** and **6b** via addition of IDippCH_2 to **A** (top, yield is given in parentheses) and the molecular structure of **6a** and **6b** in the solid state (bottom); H atoms and the anion are omitted for clarity and ellipsoids are drawn at the 50% probability level.

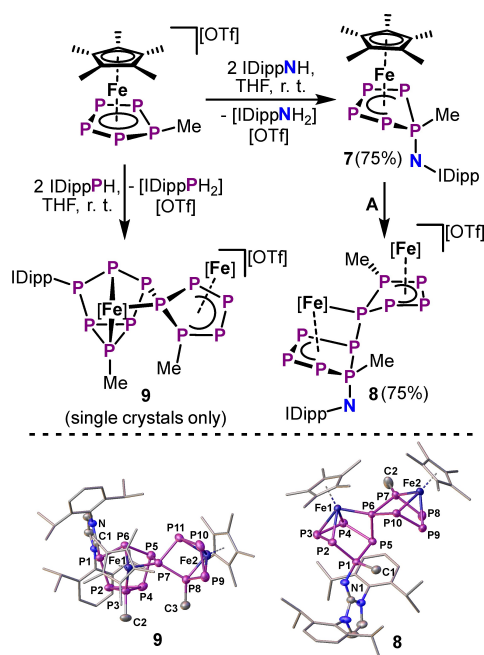


Figure 6. Synthesis of **8** and **9** including formation of **7** (top, isolated yields are given in parentheses) as well as the molecular structures of **8** and **9** in the solid state (bottom); H atoms and anions are omitted for clarity and ellipsoids are drawn at the 50% probability level.

$P_{11}Me_2(IDipp)]][OTf]$ (**9**). Comparably large cationic P_n species of such complex substitution and coordination patterns are entirely unprecedented. Formally, both compounds arise from the addition of $IDippXH$ ($X=N, P$) to **A** followed by deprotonation, the insertion of a second equivalent of **A** and the loss of one equivalent of $[IDippXH_2]^+$ ($X=N, P$). The latter is confirmed as $[IDippPH_2]^+$ in the ^{31}P NMR spectra of the crude reaction mixture of **9**.^[39] To circumvent the formation of the stoichiometric side product $[IDippXH_2][OTf]$, **A** was reacted with two equivalents of $IDippNH$ leading to the rapid formation of $[Cp^*Fe(\eta^4-P_5(1-NIDipp)(1-Me))]$ (**7**). This enables the removal of $[IDippNH_2][OTf]$ via filtration, allowing the isolation of **7** in yields of up to 75%. **7** cleanly reacts with another equivalent of **A**, affording the formation of **8** in 75% yield. Notably however, this approach could not be transferred to **9**, as the respective key intermediate, which would be isostructural to **7**, is inaccessible via this way (see SI).

Both solid-state structures of **8** and **9** reveal extremely complex P_n ligand complexes (Figure 6). While the former $cyclo-P_5$ ligands can still be recognized within the bicyclic P_{10} ligand of **8**, the P_{11} ligand in **9** has partly rearranged to a nortricyclane-type scaffold with an inserted $cyclo-P_5Me$ moiety. The P_{10} ligand in **8** is derived from **7** which underwent the insertion of another equivalent of **A** into the former $P2-Fe$ bond. Notably, this insertion takes place via the $P2$ atom in **A** and results in a strong bend of the $cyclo-P_5$ ligand. This insertion can occur with both Me groups pointing into the same (*cis*) or the opposing (*trans*) direction and, thus, affords two distinct isomers (cf. SI) of which the respective *trans* derivative crystallized. Furthermore, the formation of the isomers of **8** is confirmed by monitoring

their ^{31}P NMR spectra. However, this issue could not be circumvented due to the low steric demand of the Me substituent in **A**. The nortricyclane cage in **9** formally arises from the addition of an $IDippP$ -moiety to **A**, followed by the aggregation with a second equivalent of **A**.^[40] The formation of *cis*- and *trans*- Me isomers can now even be observed in the solid state as a positional disorder of $C3$ (Figure 6). In contrast, the solid-state structure of **7** is incommensurately modulated. Thus, only its heavy atom core could be modelled reliably, which features a 1,1-disubstituted $cyclo-P_5R_2$ ligand with an envelope structure (cf. SI). However, the molecular geometry of **7** is well reproduced by DFT calculations and agrees with its spectroscopic data. Thus, the highly indicative AMM'XX' spin system in the ^{31}P NMR spectrum agrees with the 1,1-disubstituted $cyclo-P_5RR'$ ligand. Interestingly, the Wiberg Bond Index (WBI) of the $N1-C2$ bond is 1.40, while the WBI of the $P1-N1$ bond is 0.91. This is in line with the observation of highly localized NBOs and no π -type orbitals for the $P1-N1$ bond (see SI for details).

Conclusions

In summary, a decisive reactivity enhancement of the $cyclo-P_5$ ligand in **1** by electrophilic activation has been demonstrated, which, for the first time, allowed to overcome its aromatic stabilization without the use of harsh reaction conditions and strongly nucleophilic reagents. It also paved a selective pathway towards novel 1,2-disubstituted $cyclo-P_5R_2$ moieties as found in **1**, **2** and **3b**, respectively. When the small IMe_4 was used, the enhanced reactivity of **A** culminated in an unprecedented contraction reaction affording the *catena*- P_4 complex **4**. DFT calculations provided valuable insight into the underlying stepwise reaction pathway and low temperature NMR spectroscopic studies corroborated the key intermediates **4**_{INT1} and **4**_{INT2}. Crystallization of **4**_{INT2} even provided rare and highly valuable structural insight into the pathway of this reaction. The surprisingly successful reaction with the weak nucleophile $IDippCH_2$ underlined the drastic increase in reactivity of **1** by electrophilic activation and yielded the functionalized complex **6**. Most intriguingly, the imine $IDippNH$ as well as its P analog $IDippPH$ afforded the aggregated compounds **8** and **9**, bearing unprecedented P_{10} and P_{11} ligands, respectively. These findings disclose the electrophilic activation of **1** in **A** as a powerful tool for the functionalization and transformation of its $cyclo-P_5$ ligand. This novel synthetic avenue grants access to unprecedented, complex, and functionalized P_n architectures. As this concept is established for the robust and aromatic $cyclo-P_5$ ligand in **1**, it is expected to be easily transferred to various polypnictogen compounds and supposably even for other aromatic, highly stabilized main group species.

Supporting Information Summary

The authors have cited additional references within the Supporting Information.^[15e,33,35,39,41–57] The supporting Informa-

tion includes details of the syntheses, spectroscopic and crystallographic characterizations of the products as well as detail of the computations.

Deposition Numbers 2368519 (for **A**), 2368520 (for **1**), 2368521 (for **2**), 2368522 (for **3a**), 2368523 (for **3b**), 2368524 (for **4**), 2368525 (for **4_{INT2}**), 2368526 (for **5**), 2368527 (for **6**), 2368528 (for **8**), and 2368529 (for **9**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the projects Sche 384/38-3 and Sche 384/36-2. C. R. is grateful to the Studienstiftung des Deutschen Volkes for a PhD fellowship. P. M. B. is grateful to the Studienstiftung des Deutschen Volkes and the Max Weber-Programm for Bachelor and Master degree fellowships.

Conflict of Interests

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: Aromaticity · Carbene · Cyclo-P₅ · Electrophilic activation · Phosphorus

- [1] E. Hückel, *Z. Phys.* **1931**, *70*, 204–286.
- [2] Selected examples: a) J. T. Boronski, J. A. Seed, D. Hunger, A. W. Woodward, J. van Slageren, A. J. Wooles, L. S. Natrajan, N. Kaltsoyannis, S. T. Liddle, *Nature* **2021**, *598*, 72–75; b) A. R. Eulenstein, Y. J. Franzke, N. Lichtenberger, R. J. Wilson, H. L. Deubner, F. Kraus, R. Clérac, F. Weigend, S. Dehnen, *Nat. Chem.* **2021**, *13*, 149–155; c) B. Peerless, A. Schmidt, Y. J. Franzke, S. Dehnen, *Nat. Chem.* **2023**, *15*, 347–356; d) C.-C. Shu, D. W. Szczepanik, A. Muñoz-Castro, M. Solà, Z.-M. Sun, *J. Am. Chem. Soc.* **2024**, *146*, 14166–14173; e) W. Sheng, T. Rajeshkumar, Y. Zhao, L. Maron, C. Zhu, *J. Am. Chem. Soc.* **2024**, *146*, 12790–12798.
- [3] Selected reviews: a) X. Li, A. E. Kuznetsov, H.-F. Zhang, A. I. Boldyrev, L.-S. Wang, *Science* **2001**, *291*, 859–861; b) I. A. Popov, A. A. Starikova, D. V. Steglenko, A. I. Boldyrev, *Chem. Eur. J.* **2018**, *24*, 292; c) M. Wang, J. Wang, *Molecules* **2024**, *29*, 763.
- [4] a) B. J. R. Cuyacot, C. Foroutan-Nejad, *Nature* **2022**, *603*, E18–E20; b) J. T. Boronski, J. A. Seed, D. Hunger, A. W. Woodward, J. van Slageren, A. J. Wooles, L. S. Natrajan, N. Kaltsoyannis, S. T. Liddle, *Nature* **2022**, *603*, E21–E22; c) D. W. Szczepanik, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204337; d) X. Lin, Y. Mo, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209658; e) J. Tomeček, S. T. Liddle, N. Kaltsoyannis, *ChemPhysChem* **2023**, *24*, e202300366; f) D. W. Szczepanik, *RSC Adv.* **2023**, *13*, 34224–34229.
- [5] G. Hong, X. Gan, C. Leonhardt, Z. Zhang, J. Seibert, J. M. Busch, S. Bräse, *Adv. Mater.* **2021**, *33*, 2005630.
- [6] P. Ruiz-Castillo, S. L. Buchwald, *Chem. Rev.* **2016**, *116*, 12564–12649.
- [7] For example: a) A. Velian, S. Lin, A. J. M. Miller, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* **2010**, *132*, 6296–6297; b) S. Lin, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* **2011**, *133*, 3828–3831; c) S. Lin, D. E. Herbert, A. Velian, M. W. Day, T. Agapie, *J. Am. Chem. Soc.* **2013**, *135*, 15830–15840; d) K. T. Horak, A. Velian, M. W. Daya, T. Agapie, *Chem. Commun.* **2014**, *50*, 4427–4429; e) J. A. Buss, G. A. Edouard, C. Cheng, J. Shi, T. Agapie, *J. Am. Chem. Soc.* **2014**, *136*, 11272–11275.
- [8] For textbook examples: a) R. Brückner, *Reaktionsmechanismen*, Springer, Berlin, Heidelberg **2004**, 203–235; b) P. Y. Bruice, *Organische Chemie*, Pearson Studium, Hallbergmoos **2013**, 627–642.
- [9] For example: P. Ji, K. Duan, M. Li, Z. Wang, X. Meng, Y. Zhang, W. Wang, *Chem. Soc. Rev.* **2024**, DOI: 10.1039/D4CS00137K.
- [10] A. J. Birch, *J. Chem. Soc.* **1944**, 430–436.
- [11] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *J. Am. Chem. Soc.* **2019**, *141* (28), 11000–11003.
- [12] R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711–724.
- [13] S. Wang, J. D. Sears, C. E. Moore, A. L. Rheingold, M. L. Neidig, J. S. Figueroa, *Science* **2022**, *375*, 1393–1397.
- [14] A. K. Eckhardt, M.-L. Y. Riu, M. Ye, P. Müller, G. Bistoni, C. C. Cummins, *Nat. Chem.* **2022**, *14*, 928–934.
- [15] Selected examples of cyclic P_n ligands (n=3–6): a) O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *J. Organomet. Chem.* **1984**, *268*, C9–C12; b) O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 351–353; c) O. J. Scherer, J. Schwalb, G. Wolmershäuser, W. Kaim, R. Gross, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 363–364; d) O. J. Scherer, J. Vondung, G. Wolmershäuser, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1355–1357; e) O. J. Scherer, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1104–1122.
- [16] a) B. M. Cossairt, C. C. Cummins, *Angew. Chem. Int. Ed.* **2008**, *47*, 169–172; b) D. Tofan, B. M. Cossairt, C. C. Cummins, *Inorg. Chem.* **2011**, *50*, 12349–12358; c) T. Li, J. Wiecko, N. A. Pushkarevsky, M. T. Gamer, R. Köppe, S. N. Konchenko, M. Scheer, P. W. Roesky, *Angew. Chem. Int. Ed.* **2011**, *50*, 9491–9495; d) C. M. Knapp, B. H. Westcott, M. A. C. Raybould, J. E. McGrady, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2012**, *51*, 9097–9100; e) T. Li, M. T. Gamer, M. Scheer, S. N. Konchenko, P. W. Roesky, *Chem. Commun.* **2013**, *49*, 2183–2185; f) M. V. Butovskiy, G. Balázs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, J. Sutter, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 2972–2976; g) S. Pelties, A. W. Ehlers, R. Wolf, *Chem. Commun.* **2016**, *52*, 6601–6604; h) S. Pelties, T. Maier, D. Herrmann, B. de Bruin, C. Rebreyend, S. Gärtner, I. G. Shenderovich, R. Wolf, *Chem. Eur. J.* **2017**, *23*, 6094–6102; i) M. Piesch, C. Graßl, M. Scheer, *Angew. Chem. Int. Ed.* **2020**, *59*, 7154–7160; j) R. Yadav, M. Weber, A. K. Singh, L. Münzfeld, J. Gramüller, R. M. Gschwind, M. Scheer, P. W. Roesky, *Chem. Eur. J.* **2021**, *27*, 14128–14137; k) P. Coburger, J. Leitl, D. J. Scott, G. Hierlmeier, I. G. Shenderovich, E. Hey-Hawkins, R. Wolf, *Chem. Sci.* **2021**, *12*, 11225–11235; l) A. Velian, C. C. Cummins, *Chem. Sci.* **2012**, *3*, 1003.
- [17] a) E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7643–7646; b) E. Mädl, G. Balázs, E. V. Peresypkina, M. Scheer, *Angew. Chem. Int. Ed.* **2016**, *55*, 7702–7707; c) M. Piesch, S. Reichl, M. Seidl, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2019**, *58*, 16563–16568; d) F. Riedlberger, S. Todisco, P. Mastorilli, A. Y. Timoshkin, M. Seidl, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 16251–16255; e) F. Riedlberger, M. Seidl, M. Scheer, *Chem. Commun.* **2020**, *56*, 13836–13839; f) M. Piesch, M. Seidl, M. Scheer, *Chem. Sci.* **2020**, *11*, 6745–6751; g) V. Heintz, M. Seidl, G. Balázs, M. Scheer, *Chem. Eur. J.* **2023**, *29*, e202301016; h) S. Reichl, C. Riesinger, R. Yadav, A. Y. Timoshkin, P. W. Roesky, M. Scheer, *Angew. Chem. Int. Ed.* **2024**, *63*, e202316117.
- [18] a) M. Baudler, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 492–512; b) M. Baudler, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 419–441; c) M. Baudler, K. Glinka, *Chem. Rev.* **1993**, *93*, 1623–1667.
- [19] For text book examples: a) A. F. Holleman, N. Wiberg, in *Lehrbuch der Anorganischen Chemie*, De Gruyter, Berlin (DE) **2007**, *102*, 1850–1873; b) C. Elschenbroich, in *Organometallchemie*, Vieweg u. Teubner, Wiesbaden (DE) **2008**, *6*, 443–540.
- [20] O. J. Scherer, T. Brück, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 59.
- [21] E. Urnius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. R. Schleyer, *Science* **2002**, *295*, 832–834.
- [22] a) O. J. Scherer, J. Schwalb, G. Wolmershäuser, W. Kaim, R. Gross, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 363–364; b) C. Riesinger, D. Röhner, I. Krossing, M. Scheer, *Chem. Commun.* **2023**, *59*, 4495–4498.
- [23] S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, *Nat. Commun.* **2021**, *12*, 5774.

- [24] R. Yadav, T. Simler, B. Goswami, C. Schoo, R. Köppe, S. Dey, P. W. Roesky, *Angew. Chem. Int. Ed.* **2020**, *59*, 9443–9447.
- [25] R. Yadav, T. Simler, S. Reichl, B. Goswami, C. Schoo, R. Köppe, M. Scheer, P. W. Roesky, *J. Am. Chem. Soc.* **2020**, *142*, 1190–1195.
- [26] H. Brake, E. Peresyphkina, A. V. Virovets, M. Piesch, W. Kremer, L. Zimmermann, C. Klimas, M. Scheer, *Angew. Chem. Int. Ed.* **2020**, *59*, 16241–16246.
- [27] a) N. Burford, T. S. Cameron, P. J. Ragogna, E. Ocampo-Mavarez, M. Gee, R. McDonald, R. E. Wasylshen, *J. Am. Chem. Soc.* **2001**, *123*, 7947–7948; b) M. Gonsior, I. Krossing, L. Müller, I. Raabe, M. Jansen, L. van Wüllen, *Chem. Eur. J.* **2002**, *8*, 4475–4492; c) J. J. Weigand, N. Burford, M. D. Lumsden, A. Decken, *Angew. Chem. Int. Ed.* **2006**, *45*, 6733–6737; d) J. J. Weigand, M. Holthausen, R. V. Krohlich, *Angew. Chem. Int. Ed.* **2009**, *48*, 295–298; e) M. H. Holthausen, J. J. Weigand, *Chem. Soc. Rev.* **2014**, *43*, 6639–6657; f) A. Wiesner, S. Steinhauer, H. Beckers, C. Müller, S. Riedel, *Chem. Sci.* **2018**, *9*, 7169–7173; g) C. Taube, K. Schwedtmann, M. Noikham, E. Somsook, F. Hennersdorf, R. Wolf, J. J. Weigand, *Angew. Chem. Int. Ed.* **2020**, *59*, 3585–3591.
- [28] a) O. Back, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* **2010**, *2*, 369–373; b) T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing, *Angew. Chem. Int. Ed.* **2012**, *51*, 6529–6531; c) J. Frötschel-Rittmeyer, M. Holthausen, C. Friedmann, D. Röhner, I. Krossing, J. J. Weigand, *Sci. Adv.* **2022**, *8*, eabq8613.
- [29] a) S. S. Chitnis, H. A. Sparkes, V. T. Annibale, N. E. Pridmore, A. M. Oliver, I. Manners, *Angew. Chem. Int. Ed.* **2017**, *56*, 9536–9540; b) S. S. Chitnis, R. A. Musgrave, H. A. Sparkes, N. E. Pridmore, V. T. Annibale, I. Manners, *Inorg. Chem.* **2017**, *56*, 4522–4538; c) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking, J. J. Weigand, *Angew. Chem. Int. Ed.* **2013**, *52*, 11078–11082; d) P. Royla, K. Schwedtmann, Z. Han, J. Fidelius, D. P. Gates, R. M. Gomila, A. Frontera, J. J. Weigand, *J. Am. Chem. Soc.* **2023**, *145*, 10364–10375.
- [30] a) G. Capozzi, L. Chiti, M. Di Vaira, M. Peruzzini, P. Stoppioni, *Chem. Commun.* **1986**, 1799–1800; b) A. Barth, G. Huttner, M. Fritz, L. Zsolnai, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 929–931; c) I. de los Rios, J.-R. Hamon, P. Hamon, C. Lapinte, L. Toupet, A. Romero, M. Peruzzini, *Angew. Chem. Int. Ed.* **2001**, *40*, 3910–3912; d) I. Krossing, *J. Am. Chem. Soc.* **2001**, *123*, 4603–4604; e) P. Barbaro, A. Ienco, C. Mealli, M. Peruzzini, O. J. Scherer, G. Schmitt, F. Vizza, G. Wolmershäuser, *Chem. Eur. J.* **2003**, *9*, 5196–5210; f) M. Peruzzini, R. R. Abdrimova, Y. Budnikova, A. Romero, O. J. Scherer, H. Sitzmann, *J. Organomet. Chem.* **2004**, *689*, 4319–4331; g) P. Barbaro, C. Bazzicalupi, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, *Angew. Chem. Int. Ed.* **2012**, *51*, 8628–8631; h) I. M. Riddellstone, P. Weis, A. Martens, M. Schorpp, H. Scherer, I. Krossing, *Chem. Eur. J.* **2019**, *25*, 10546–10551; i) J. Sun, H. Verplancke, J. I. Schweizer, M. Diefenbach, C. Würtele, M. Otte, I. Tkach, C. Herwig, C. Limberg, S. Demeshko, M. C. Holthausen, S. Schneider, *Chem* **2021**, *7*, 1952–1962.
- [31] a) M. Fleischmann, F. Dielmann, L. J. Gregoriades, E. V. Peresyphkina, A. V. Virovets, S. Huber, A. Y. Timoshkin, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 13110–13115; b) L. Dütsch, M. Fleischmann, S. Welsch, G. Balázs, W. Kremer, M. Scheer, *Angew. Chem. Int. Ed.* **2018**, *57*, 3256–3261; c) C. Riesinger, L. Dütsch, G. Balázs, M. Bodensteiner, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 17165–17170; d) C. Riesinger, G. Balázs, M. Bodensteiner, M. Scheer, *Angew. Chem. Int. Ed.* **2020**, *59*, 23879–23884; e) M. Piesch, S. Reichl, C. Riesinger, M. Seidl, G. Balázs, M. Scheer, *Chem. Eur. J.* **2021**, *27*, 9129–9140; f) C. Riesinger, G. Balázs, M. Seidl, M. Scheer, *Chem. Sci.* **2021**, *12*, 13037–13044; g) M. Piesch, A. Nicolay, M. Haimerl, M. Seidl, G. Balázs, T. Don Tilley, M. Scheer, *Chem. Eur. J.* **2022**, *28*, e202201144; h) C. Riesinger, F. Dielmann, R. Szlosek, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218828; i) L. Zimmermann, C. Riesinger, G. Balázs, M. Scheer, *Chem. Eur. J.* **2023**, e202301974; j) C. Riesinger, A. Erhard, M. Scheer, *Chem. Commun.* **2023**, *59*, 10117–10120; k) M. Widmann, C. Riesinger, R. Szlosek, G. Balázs, M. Scheer, *Chem. Eur. J.* **2024**, *30*, e202304183.
- [32] For a CoP₄ complex as starting material cf.: a) C. G. P. Ziegler, T. M. Maier, S. Pelties, C. Taube, F. Hennersdorf, A. W. Ehlers, J. J. Weigand, R. Wolf, *Chem. Sci.* **2019**, *10*, 1302–1308; b) C. M. Hoidn, K. Trabitsch, K. Schwedtmann, C. Taube, J. J. Weigand, R. Wolf, *Chem. Eur. J.* **2023**, *29*, e202301930; c) S. Reichl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl, M. Scheer, *Chem. Sci.* **2023**, *14*, 7285–7290.
- [33] P. Pykkö, *J. Phys. Chem. A* **2015**, *119*, 2326–2337.
- [34] A. K. Macdonald, J. F. Binder, A. Swidan, J. H. Nguyen, S. C. Kosnik, B. D. Ellis, *Inorg. Chem.* **2016**, *55*, 7152–7166.
- [35] C. M. Hoidn, T. M. Maier, K. Trabitsch, J. J. Weigand, R. Wolf, *Angew. Chem. Int. Ed.* **2019**, *58*, 18931–18936.
- [36] A. K. Adhikari, C. G. P. Ziegler, K. Schwedtmann, C. Taube, J. J. Weigand, R. Wolf, *Angew. Chem. Int. Ed.* **2019**, *58*, 18584–18590.
- [37] C. Yang, X. Jiang, Q. Chen, X. Leng, J. Xiao, S. Ye, *J. Am. Chem. Soc.* **2022**, *144*, 20785–20796.
- [38] a) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 14180–14181; b) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2007**, *46*, 7052–7055; c) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold, G. Bertrand, *Chem. Commun.* **2013**, *49*, 4486–4488.
- [39] L. L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, *Chem. Commun.* **2015**, *51*, 12732–12735.
- [40] A more detailed explanation for the formation of the isomers in the case of **8** and **9**, based on the low steric demand of the Me-substituent in **A**, can be found in the supporting information and within the Schemes S1 and S2.
- [41] <https://omics.pnl.gov/software/molecular-weight-calculator>, (07.08.2023).
- [42] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534.
- [43] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709.
- [44] N. Kuhn, T. Kratz, *Synth.* **1993**, *6*, 561–562.
- [45] S. M. I. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Commun.* **2011**, *47*, 6987–6989.
- [46] M. Tamm, D. Petrovic, S. Randall, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, *Org. Biomol. Chem.* **2007**, *5*, 523–530.
- [47] A. M. Tondreau, Z. Benkö, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545–1554.
- [48] Agilent, *Crysalis PRO*, Agilent Technologies Ltd., Yarnton, Oxfordshire, England **2014**.
- [49] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [50] G. M. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3–8.
- [51] a) G. M. Sheldrick, *Acta Crystallogr. C* **2015**, *71*, 3–8; b) G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112–122.
- [52] a) F. Neese, F. Wennmohs, U. Becker, C. Rieplinger, *J. Chem. Phys.* **2020**, *152*, 224108–224125; b) F. Neese, *WIREs Comput. Mol. Sci.* **2022**, *12*, 1606–1620.
- [53] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [54] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; b) D. Rappoport, F. Furche, *J. Chem. Phys.* **2010**, *133*, 134105–134115.
- [55] a) J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620; b) J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 84106; c) Y.-S. Lin, G.-D. Li, S.-P. Mao, J. D. Chai, *J. Chem. Theory Comput.* **2013**, *9*, 263–272; d) E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth, S. Grimme, *J. Chem. Phys.* **2019**, *150*, 154122–154140.
- [56] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3093.
- [57] NBO 7.0., E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI **2018**.

Manuscript received: July 15, 2024

Accepted manuscript online: September 30, 2024

Version of record online: November 7, 2024