

P Ligands | Hot Paper |

The Butterfly Complex $[\{\text{Cp}^*\text{Cr}(\text{CO})_3\}_2(\mu, \eta^{1:1}-\text{P}_4)]$ as a Versatile Ligand and Its Unexpected P_1/P_3 FragmentationRebecca Grünbauer, Gábor Balázs, and Manfred Scheer*^[a]

Abstract: The versatile coordination behavior of the P_4 butterfly complex $[\{\text{Cp}^*\text{Cr}(\text{CO})_3\}_2(\mu, \eta^{1:1}-\text{P}_4)]$ (**1**) towards Lewis acidic pentacarbonyl compounds of Cr, Mo and W is reported. The reaction of **1** with $[\text{W}(\text{CO})_4(\text{nbd})]$ (nbd = norbornadiene) yields the complex $[\{\text{Cp}^*\text{Cr}(\text{CO})_3\}_2(\mu_3, \eta^{1:1:1:1}-\text{P}_4)\{\text{W}(\text{CO})_4\}]$ (**2**) in which **1** serves as a chelating P_4 butterfly ligand. In contrast, reactions of **1** with $[\text{M}(\text{CO})_4(\text{nbd})]$ ($\text{M} = \text{Cr}$ (**a**), Mo (**b**)) result in the stepwise formation of $[\{\text{Cp}^*\text{Cr}(\text{CO})_2\}_2(\mu_3, \eta^{3:1:1}-\text{P}_4)\{\text{M}(\text{CO})_5\}]$ (**3 a, b**) and $[\{\text{Cp}^*\text{Cr}(\text{CO})_2\}_2(\mu_4, \eta^{3:1:1:1}-\text{P}_4)\{\text{M}(\text{CO})_5\}_2]$ (**4 a, b**) which contain a folded cyclo- P_4 unit. Complex **4 a** undergoes an unprecedented P_1/P_3 -fragmentation yielding the cyclo- P_3 complex $[\text{Cp}^*\text{Cr}(\text{CO})_2(\eta^3-\text{P}_3)]$ (**5**) and the as yet unknown phosphinidene complex $[\text{Cp}^*\text{Cr}(\text{CO})_2\{\text{Cr}(\text{CO})_3\}_2(\mu_3-\text{P})]$ (**6**). The identity of **6** is confirmed by spectroscopic methods and by the in situ formation of $[\{\text{Cp}^*\text{Cr}(\text{CO})_2(\text{tBuNC})\}\{\text{Cr}(\text{CO})_3\}_2(\text{tBuNC})]$ (**7**). DFT calculations throw light on the bonding situation of the reported products.

The research of the activation of small molecules is of great importance, as it can improve uneconomical industrial-scale reactions by making them more atom-efficient, clean, sustainable and inexpensive.^[1] In this field, investigations regarding the activation of P_4 describe the subsequent P–P bond cleavage of the tetrahedral P_4 molecule of white phosphorus.^[2] Ultimately, the goal of these studies is to provide insight into controlling the remarkable reactivity of P_4 and to obtain organo-phosphorus compounds in a more sustainable way. The first step of the selective degradation of the P_4 tetrahedron is the formation of the tetraphospha-*bicyclo*[1.1.0]butane moiety (often referred to as P_4 butterfly due to its geometry). This moiety can be used

as a ligand in coordination chemistry, typically displaying small bite angles, like common chelating diphosphine ligands.^[3] This was demonstrated by the synthesis of the transition-metal-stabilized bridging P_4 butterfly complex $[\{\text{Cp}'''\text{Fe}(\text{CO})_2\}_2(\mu, \eta^{1:1}-\text{P}_4)]$ (**A**, $\text{Cp}''' = \eta^5\text{-C}_5\text{H}_5\text{tBu}_3$).^[4]

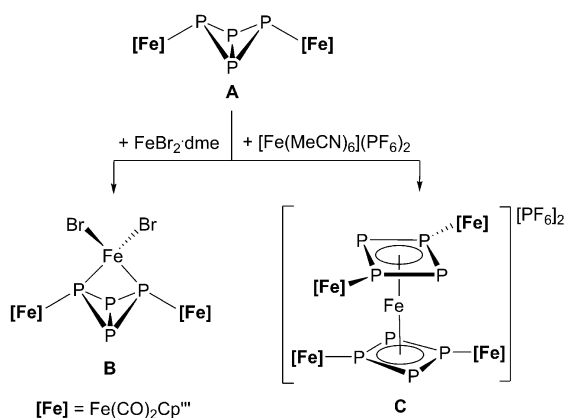
The continuing degradation of white phosphorus via the P_4 butterfly structure has been widely investigated and a plethora of polyphosphorus compounds could be isolated.^[2] However, only very few examples have been reported for a controlled fragmentation of the intact P_4 butterfly moiety affording a P_1 and a P_3 fragment. One of the reported examples originates from the butterfly anion $\text{Li}[\text{Mes}^*\text{P}_4\text{BR}_3]$.^[5] Lammertsma et al. studied its reactivity towards imidazolium salts and phenylisocyanate yielding stabilized phosphinidene adducts and $[\text{Mes}^*\text{P}_3]$ fragments. They succeeded in isolating the P_3 fragment as the respective dimer $[\text{Mes}^*\text{P}_3]_2$ or as the Diels–Alder adduct $[\text{Mes}^*\text{P}_3(\text{C}_6\text{H}_8)]$ after employing the trapping agent 1,3-cyclohexadiene. Starting from elemental phosphorus, Zhang et al. used rare-earth-metal complexes to obtain *bicyclo*[4.1.0]-triphospha-heptanide ligands alongside with phospholyllithium.^[6a–c] Both of these fragmentation routes require additional reactants such as non-innocent ligands in order to induce the P_1/P_3 fragmentation. Very recently, the group of Ghadwal reported on the P_1/P_3 fragmentation of P_4 induced by mesoionic carbenes and anionic dicarbenes affording 1,2,3-triphosphol-2-ides incorporating a *cyclo*- C_2P_3 unit.^[6d,e] A first step towards a more untouched P_1/P_3 fragmentation route was reported by reacting $[\text{Cp}^*\text{Ni}(\mu\text{-CO})_2]$ with P_4 in the presence of stabilizing $[\text{Cr}(\text{CO})_3]$ fragments.^[7] Various steps of irradiation and thermolysis induce the fragmentation process affording a bent *cyclo*- P_4 complex. Finally, the formation of $[\text{Cp}^*\text{Ni}(\eta^3-\text{P}_3)\{\text{Cr}(\text{CO})_3\}_2]$ and a $[\text{Cp}^*\text{Ni} \equiv \text{P}-\text{Cr}(\text{CO})_5]$ intermediate that could be isolated as its corresponding dimer $[\{\text{Cp}^*\text{Ni}\}_2(\mu, \eta^2-\text{P}_2)\{\text{Cr}(\text{CO})_5\}_2]$ was obtained.

DFT calculations predicted that a chelating coordination mode via the lone pairs of the two wing tip P atoms of **A** is energetically most favorable.^[8] Therefore, we studied the coordination behavior of **A** towards monovalent coinage metal salts and different Fe^{II} compounds.^[8,9] As anticipated, chelating coordination products, for example, $[\{\{\text{Cp}'''\text{Fe}(\text{CO})_2\}_2(\mu_3, \eta^{1:1:1:1}-\text{P}_4)\}_2\text{FeBr}_2]$ (**B**, Scheme 1), in which **A** acts as a bidentate ligand could be obtained. With $70.27(3)^\circ$, the bite angle of **B** compares well to the bite angle reported for dppm ($72(2)^\circ$, 1,2-bis(diphenylphosphino)methane).^[3] In contrast, $[\text{Fe}(\text{MeCN})_6]^{2+}$, a Lewis acid containing labile acetonitrile ligands, reacts with **A** by inducing an isomerization of the P_4 butterfly unit forming the 6π -aromatic *cyclo*- P_4 sandwiched dication $[\{\{\text{Cp}'''\text{Fe}(\text{CO})_2\}_2\text{P}_4\}_2\text{Fe}]^{2+}$ (**C**, Scheme 1).^[9]

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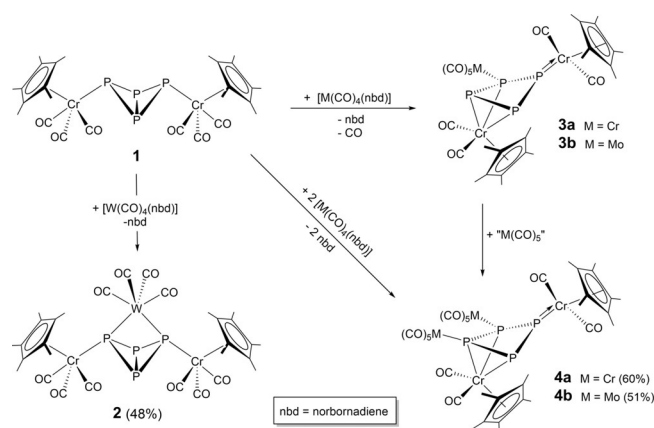
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Scheme 1. Coordination and isomerization obtained from the reaction of **A** with different Fe^{II} Lewis acids.

While the reactivity of **A** under photolytic^[10] and thermolytic^[4] conditions, its reactivity towards alkynes^[11] and its coordination chemistry^[8,9] have been intensively studied, the reactivity of the isostructural chromium-containing complex $[\text{Cp}^*\text{Cr}(\text{CO})_3]_2(\mu_3, \eta^{1:1:1}\text{-P}_4)$ (**1**, $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$) has only been scarcely investigated.^[12] This encouraged us to further study the reactivity of **1** and the question arose whether a simple coordination chemistry as expected for a chelating polyphosphine would occur or a much more diverse reaction pathway would be unraveled. Herein, we report on the reaction of **1** with Lewis acidic group six carbonyl complexes $[\text{M}(\text{CO})_4(\text{nbd})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; nbd = norbornadiene). The weakly coordinating norbornadiene ligand is expected to be replaced by the more strongly donating P₄ butterfly ligand affording new organometallic P₄ coordination compounds. Unexpectedly, in the case of $[\text{Cr}(\text{CO})_4(\text{nbd})]$ an unprecedented reactivity occurs leading to a final P₃/P₁ fragmentation.

The reaction of **1** with 1.0 equiv. $[\text{W}(\text{CO})_4(\text{nbd})]$ selectively yields the chelating complex $[\text{Cp}^*\text{Cr}(\text{CO})_3]_2(\mu_3, \eta^{1:1:1:1}\text{-P}_4)\{\text{W}(\text{CO})_4\}$ (**2**, Scheme 2). The formation of the tetraphosphatungsten-*tricyclo*[1.1.1.0^{2,4}]pentane compound could be verified by single crystal X-ray diffraction analysis^[13] and only little influence of the bidentate coordination on the overall structure of the P₄ scaffold could be detected in comparison to **1** (Figure 1). While for **2** bond lengths and



Scheme 2. Reactions of **1** with Lewis acidic $[\text{M}(\text{CO})_4(\text{nbd})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Yields are given in parentheses.

angles similar to those for **1** are given, the central P₄ unit in **2** is slightly distorted, whereas, in **1**, this moiety is more symmetrical. Due to the distortion which probably perseveres in solution, **2** displays an AA'BB' spin system with a relatively large $\delta_{\text{AA}'}/\delta_{\text{BB}'}$ separation affording two multiplets at $\delta = -168.8$ ppm (bridgehead P atoms) and $\delta = -153.8$ ppm (wing tip P atoms) in the ³¹P{¹H} NMR spectrum. The outstanding feature of **2** is the extremely small P1-W-P2 bite angle of 64.21(11)° again highlighting the structural similarity with the dppm ligand.^[13]

Surprisingly, the reactions of **1** with $[\text{M}(\text{CO})_4(\text{nbd})]$ ($\text{M} = \text{Cr}$ (**a**), Mo (**b**)) do not result in P₄ butterfly-Lewis acid adducts, but afford the mono-substituted $[\text{Cp}^*\text{Cr}(\text{CO})_3]_2(\mu_3, \eta^{3:1:1}\text{-P}_4)\{\text{M}(\text{CO})_3\}$ (**3**) and the bis-substituted derivative $[\text{Cp}^*\text{Cr}(\text{CO})_2]_2(\mu_4, \eta^{3:1:1:1}\text{-P}_4)\{\text{M}(\text{CO})_3\}_2$ (**4**) (Scheme 2). During the formation of **3** and **4**, a cleavage of the P-P bond between the former bridgehead P atoms of **1** is observed affording a folded deltoid *cyclo*-P₄ unit as the central structural moiety. This is a direct result of an initial CO shift from the $[\text{Cp}^*\text{Cr}(\text{CO})_3]$ substituents of **1** to the $[\text{M}(\text{CO})_4]$ fragments yielding $[\text{Cp}^*\text{Cr}(\text{CO})_2]$ substituents and $[\text{M}(\text{CO})_5]$ units. The consequential electron deficit on Cr2 is balanced by an additional coordination of the two former bridgehead phosphorus atoms towards Cr2, leading to the cleavage of the P-P bond (labeling according to Figure 1).

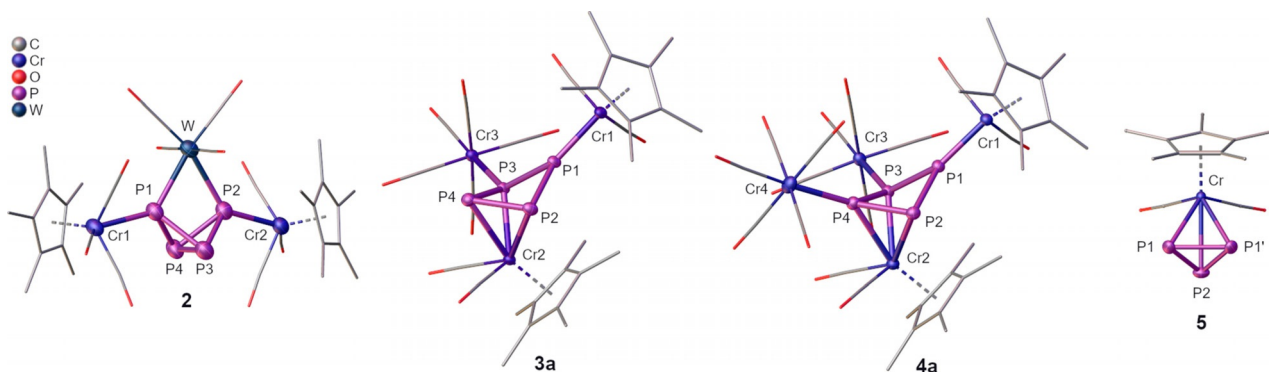


Figure 1. Molecular structures of **2**, **3a**, **4a** and **5** in the solid state. H atoms and solvent molecules are omitted for clarity and CO as well as Cp* ligands are drawn in the wire frame model; thermal ellipsoids are drawn at 50% probability level.

The electron deficit of the Cr1 fragment is balanced by the formation of a formal double bond between Cr1 and the adjacent P1 atom, and the former wing tip atom P1 reaches a planar coordination environment. The formal P=Cr double bond can be viewed as an additional coordination of the P lone pair to the Cr1 atom since the [Cp*Cr(CO)₂] fragment requires three additional electrons according to the 18 VE rule. Various terminal or bridging, square planar or distorted *cyclo*-P₄ ligands have been reported either as bare polyphosphorus units or stabilized by different Lewis acids.^[2] However, the folded deltoid *cyclo*-P₄ unit of **3** and **4** represents a novel structural motif due to the adjacent P=Cr double bond that can be interpreted as the tail of the *cyclo*-P₄ kite. The closest related compound, from a structural perspective, to **3** and **4** is [(CH₃CN)₂(CO)₂WCl](η³-P₃{W(CO)₅}₂P{(X)W(CO)₃})] (X = Cl, OH) for which no phosphorus metal double bond but an additional stabilization with a chloride or hydroxy group, respectively, on the P1 atom is observed.^[14]

According to DFT calculations, the reaction of **1** with [Cr(CO)₄(nbd)] is slightly endothermic (1.34 kJ mol⁻¹) while the reaction of **1** with [W(CO)₄(nbd)] yielding **2** is exothermic (-6.49 kJ mol⁻¹), which reinforces that a stable complex such as [(Cp*Cr(CO)₃)₂(μ_{3,η}^{1:1:1}-P₄){Cr(CO)₄}] (**2a'**) is not formed, but rather a CO shift from a [Cp*Cr(CO)₃] unit to the [Cr(CO)₄] moiety occurs.

When the reaction of **1** with [M(CO)₄(nbd)] (M = Cr (**a**), Mo (**b**)) is performed in a 1:1 stoichiometry, the mono-substituted compound **3** is the main product in the reaction solution alongside with traces of **4**. However, the conversion of **1** is limited to 50% due to the mismatched CO count. Two CO ligands are abstracted from each molecule of **1**, but only one CO ligand is needed to obtain an [M(CO)₅] fragment from [M(CO)₄(nbd)] (M = Cr, Mo). In contrast, **4** is formed almost quantitatively (besides some impurities of **3**), when the reaction of **1** with [M(CO)₄(nbd)] (M = Cr, Mo) is performed in a 1:2 ratio. Attempts to isolate **3** from a 1:1 reaction by crystallization lead to a rearrangement to **4**, which exclusively crystallizes from the solution. This process was monitored by ³¹P{¹H} NMR spectroscopy (vide infra).

Therefore, reasonable amounts of pure **3** could not be isolated, although different isolation methods and alternative synthetic pathways were examined. Yet, a few single crystals of **3a** could be obtained from the reaction mixture after storage at -78 °C, whereas **4a** already crystallizes at -28 °C (Figure 1). Unfortunately, no single crystals could be obtained for **3b**, but a similar structure as compared to **3a** can be proposed based on NMR spectroscopic data.^[15] Compounds **3a**, **4a** and **4b** all crystallize readily in the form of stacked plates from saturated solutions in CH₂Cl₂ at -28 °C (**3a**: P₂/c; **4a** and **4b**: P $\bar{1}$). The central deltoid *cyclo*-P₄ structural motif of **3a**, **4a** and **4b** is very similar. The distances for the P1–P2 bond (**3a**: 2.2181(7) Å, **4a**: 2.2265(13) Å, **4b**: 2.2259(13) Å) and the P1–P3 bond (**3a**: 2.1973(7) Å, **4a**: 2.2013(14) Å, **4b**: 2.1938(13) Å) comply well with the value for a P–P single bond (2.209(5) Å).^[16] In contrast, the P2–P4 bond (**3a**: 2.1606(7) Å, **4a**: 2.1390(15) Å, **4b**: 2.1427(13) Å) and P3–P4 bond (**3a**: 2.1705(7) Å, **4a**: 2.1583(12) Å, **4b**: 2.1560(13) Å) are noticeably

shortened indicating a delocalized electron system between P2, P3 and P4 (labeling according to Figure 1). The Cr1–P1 bond attached to the rearranged *cyclo*-P₄ unit (**3a**: 2.1258(6) Å, **4a**: 2.1129(11) Å, **4b**: 2.1169(11) Å) is significantly shortened in comparison to the corresponding P–Cr bond length in **1** (2.529(2) Å) and the Cr3–P3 as well as Cr4–P4 distance in **3a** (Cr3–P3 2.3664(5) Å) and **4a** (Cr3–P3 2.3564(12) Å, Cr4–P4 2.3517(11) Å), respectively, revealing a Cr1–P1 multiple bond character. Moreover, the degree of folding of the *cyclo*-P₄ unit is independent of the nature of the substituent pattern as **3a**, **4a** and **4b** display nearly identical folding angles (**3a**: 135.50(8)°, **4a**: 135.92(6)°, **4b**: 136.18(8)°).

The ³¹P{¹H} NMR spectra of **3** and **4** are very similar displaying an AMNX spin system.^[15] The chemical shift of the signal attributed to P_A (δ = 515.4 ppm (**3a**), 515.4 ppm (**3b**), 489.1 ppm (**4a**), 487.8 ppm (**4b**); P1 in Figure 1) is in the typical range for a phosphorus atom in the planar environment that is part of a formal phosphorus metal multiple bond. In comparison to the formal [Cr=P(P)₂] structural motif in **3** and **4**, the ³¹P NMR chemical shift of the trigonal planar [Mn=P(Fe)₂] moiety of [(CpMn(CO)₂)(μ_{3,η}^{1:1:1}-P)₂]{Fe₂(CO)₆} is even more downfield shifted (δ(³¹P) = 977 ppm).^[17]

The ³¹P{¹H} NMR spectrum of the reaction mixture after stirring **1** with 1.0 equiv. of [Cr(CO)₄(nbd)] in thf for 3 days shows the signal set characteristic for **3a** (Figure S6a in SI) as the main product, as well as traces of **4a**. In contrast, the ³¹P{¹H} NMR spectrum of the crystals obtained from storing the concentrated reaction mixture at -28 °C displays exclusively the signals of **4a** (Figure S6b in Supporting Information). Obviously, **3a** coordinates to an excess of [Cr(CO)₅] units present in the solution during the crystallization process. Consequently, **4a** is formed, which crystallizes due to its lower solubility. The ³¹P{¹H} NMR spectrum of the supernatant of the obtained crystals exhibits signals for both major compounds **3a** and **4a**. However, the intensity of the signals corresponding to **3a** decreased significantly in comparison to the signals corresponding to **4a**, now promoting **4a** to the primary component in solution after crystallization (Figure S6c in Supporting Information). In summary, storing the concentrated reaction solution at low temperatures leads to the formation of **4a** from **3a** and excess [Cr(CO)₅] in the form of crystalline **4a** as well as in solution. The same observations can be reported for **3b** and **4b**, but in the ³¹P{¹H} NMR spectrum of crystalline **4b**, minor amounts of **3b** can be detected indicating partial degradation after re-dissolving.

In order to elucidate the electronic structure of **4a**, DFT calculations at the B3LYP/def2-TZVP level were performed.^[18] The DFT optimized geometry of **4a** compares well with the experimental geometry. According to the NBO analysis, the Cr1–P1 bond is a double bond built from a σ-type and a π-type bond (Figure 2). The σ-bond is realized over a sp^{0.9} hybrid orbital on phosphorus and a sd^{2.2} hybrid orbital on chromium, while the π-orbital is realized over a pure p-orbital on P and a pure d-orbital on Cr. The partial double bond character is also reflected in the Wiberg Bond Index (WBI) of 1.16, while the WBI of the Cr3–P3 bond is 0.39.^[15] The WBIs of the P1–P2 and P1–P3

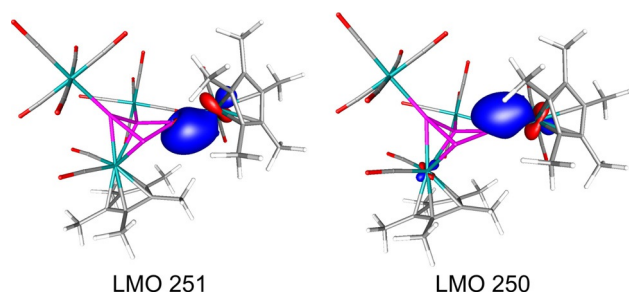


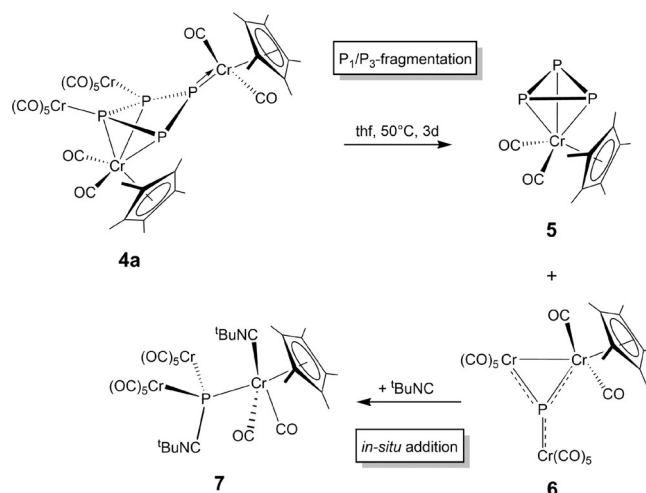
Figure 2. Localized molecular orbitals of **4a** representing the Cr1–P1 multiple bond.

bonds are slightly lower (0.91 and 0.93) than the WBLs of the P2–P4 and P3–P4 bonds (1.06 and 0.99).

A common observation for all experiments performed with **1** is the sensitivity of **1** towards temperature and light causing slow decomposition even at mild reaction conditions. In nearly all manipulations starting from **1**, one characteristic singlet at approx. -270 ppm can be detected in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

By comparison with literature data for similar compounds, Scherer et al. attributed this chemical shift to $[\text{Cp}^*\text{Cr}(\text{CO})_2(\eta^3\text{-P}_3)]$ (**5**),^[19] and within this work, we were able to confirm this proposal by the first single crystal X-ray diffraction of the isolated compound **5** (Figure 1).^[20] Alongside **5**, an insoluble solid (probably a mixture of various polyphosphides) is obtained after the quantitative decomposition of **1**. Remarkably, after stirring a solution of **4a** in thf for three days at 50°C , a distinct second degradation product can be detected. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, an additional singlet at $\delta = 1123.7$ ppm is recorded next to the characteristic singlet at $\delta = -273.3$ ppm corresponding to **5**. The drastic low field shift of this novel signal indicates a planar coordination sphere of the corresponding P atom, as it is typical for planar phosphinidene complexes as for instance the μ_3 -bridging complex $[[\text{Cp}^*\text{W}(\text{CO})_2](\mu_3\text{-P})\{\text{Cr}(\text{CO})_5\}_2]$ (**B**, $\delta(^{31}\text{P NMR}) = 945$ ppm).^[21] Hence, we propose the structurally analog $[[\text{Cp}^*\text{Cr}(\text{CO})_2](\mu_3\text{-P})\{\text{Cr}(\text{CO})_5\}_2]$ (**6**) as the second compound obtained from the degradation of **4a** attributable to the second signal at $\delta = 1123.7$ ppm) observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Although **6** could not be isolated and characterized by single crystal X-ray diffraction analysis, the mutual extreme low field ^{31}P NMR chemical shifts of **6** and **B** validate the proposed structure of **6**. Consequently, an unprecedented type of selective P_1/P_3 -fragmentation of **4a** yielding **5** and **6** can be proposed (Scheme 3). A closer look at the molecular structure of **4a** in the solid state further supports the proposed P_1/P_3 -fragmentation. As discussed above, two different P–P bond lengths can be found in **4a**. The two longest and therefore comparatively weakest P–P bonds (P1–P2 and P1–P3) appear to be the predetermined breaking points of **4a** finally affording **5** and **6**.

Since it was not possible to isolate **6** as a pure compound from the reaction mixture, we attempted to trap **6** with *t*BuNC, as this type of reaction is widely known for phosphinidene complexes. For instance, *t*BuNC reacts with $[\text{Cp}^*\text{P}\{\text{W}(\text{CO})_5\}_2]$ affording the Lewis acid/base (LA/LB) adduct



Scheme 3. P_1/P_3 -fragmentation of **4a** and subsequent phosphinidene adduct formation of the obtained P_1 fragment **6** yielding **7**.

$[\text{Cp}^*\text{P}\{\text{W}(\text{CO})_5\}_2(\text{tBuNC})]$.^[22] Diagnostic is the extreme change in the ^{31}P NMR chemical shift from $\delta = 1076.5$ ppm^[22a] for the phosphinidene complex to $\delta = -73.1$ ppm^[22b] for the LA/LB adduct. Following this strategy, an excess of *t*BuNC was added to a solution of **6**. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy which shows that the characteristic signal for **6** at $\delta = 1124$ ppm disappears while a new signal at $\delta = -166$ ppm appears indicating the full conversion of **6** into the proposed LA/LB adduct $[[\text{Cp}^*\text{Cr}(\text{tBuNC})(\text{CO})_2](\mu_3\text{-P})\{\text{Cr}(\text{CO})_5\}_2]$ (**7**, Scheme 3). In **7**, the planar coordination geometry of the P atom is abrogated by the additional coordination of one *t*BuNC ligand yielding a pseudo-tetrahedral phosphinidene adduct. Consequently, the deshielding of the P atom is strongly reduced leading to the drastic change in the chemical shift. A second *t*BuNC ligand additionally coordinates to the $\text{Cp}^*\text{Cr}(\text{CO})_2$ fragment, compensating the electron deficit that occurred at the Cr atom accordingly. According to DFT calculations, the coordination of one *t*BuNC to the P atom in the center of **6** is exothermic with -48.5 kJ mol $^{-1}$. The addition of the second *t*BuNC molecule to the $\text{Cp}^*\text{Cr}(\text{CO})_2$ fragment is even more exothermic with -53.2 kJ mol $^{-1}$, indicating that the coordination of two *t*BuNC ligands to **6** is to be expected. In order to prove the identity of **6** and **7**, the ^{31}P NMR chemical shifts of **5**, **B**, **6** and **7** were calculated by DFT methods. To this effect, the geometry of the compounds was optimized in the gas phase at the BP86/Def2TZVP level of theory. For the calculation of the ^{31}P NMR chemical shifts, using the GIAO method, the aug-*pc*Sseg-2 basis set for phosphorus was utilized. The values of the calculated chemical shifts are in good agreement with the experimental values (Table 1), validating the proposed identity of **6** and **7**.

It has to be noted that the ^{31}P chemical shifts are very sensitive to geometry changes. In order to evaluate the accuracy of the calculated chemical shifts, we also included the known phosphinidene complex $[\text{Cp}^*\text{W}(\text{CO})_2(\text{Cr}(\text{CO})_5)_2(\mu_3\text{-P})]$ (**B**)^[21] in our calculations. The calculated ^{31}P chemical shift of $\delta = 1046$ ppm is in good agreement with the experimental value of $\delta =$

Table 1. Experimental (δ_{exp}) and calculated (δ_{cal}) ^{31}P NMR chemical shifts of compounds **5**, **B**, **6** and **7**.

	5	B	6	7
δ_{exp} /ppm	−273 ^[a]	945 ^[b]	1124 ^[a]	−166 ^[a]
δ_{cal} /ppm	−242	1046	1221	−111

[a] Recorded in thf with C_6D_6 capillary at room temperature. [b] Recorded in CD_2Cl_2 at -20°C .^[18]

954 ppm. This shows that the electronic structures of **B** and **6** are well described by the applied DFT methods and confirm the identity of **6**.

In conclusion, we were able to illustrate the diverse coordination behavior of the P_4 butterfly complex **1** towards Lewis acidic carbonyl compounds of Cr, Mo and W. On the one hand, a chelating coordination yielding **2**, a complex with a P_4 butterfly ligand that displays an exceedingly small bite angle, was achieved by implying $[\text{W}(\text{CO})_4]$ fragments. On the other hand, **1** turned out to be a promising starting material for rearrangement processes, yielding new compounds with folded *cyclo*- P_4 units (**3** and **4**) when reacted with $[\text{M}(\text{CO})_4]$ moieties ($\text{M} = \text{Cr}$ (**a**), Mo (**b**)). Most importantly, an unprecedented P_1/P_3 -fragmentation route was observed starting from **4a** yielding the *cyclo*- P_3 complex **5** and the novel μ_3 -bridging phosphinidene **6**. The proposed structure of **6** could be verified by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, DFT calculations and the in situ reaction with *t*BuNC, yielding the phosphinidene adduct **7**. These results promote the ongoing implementation of P_4 butterfly complexes as starting materials in the formation of unprecedented polyphosphorus compounds, which represent further steps is the P_4 activation sequence.

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Conflict of interest

The authors declare no conflict of interest.

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