Utilizing the weak P–Cr bond in \([\{\text{Cp}^*\text{Cr(CO)}_3\}_2(\mu_1\eta^{1:1}–\text{P}_4)]\)
for the generation of different \(\text{P}_4\) butterfly compounds


Dedicated to Professor Dr. Peter Kliéners on the Occasion of his 70th Birthday

A novel reactivity of \([\{\text{Cp}^*\text{Cr(CO)}_3\}_2(\mu_1\eta^{1:1}–\text{P}_4)]\) \((\text{Cp}^* = \text{C}_5\text{Me}_5; 1)\) is reported, which utilizes the selective cleavage of the two P–Cr bonds and subsequently initiates a substituent exchange yielding \(\text{P}_4\) butterfly compounds. By means of NMR and IR spectroscopy studies, the successful implementation of 1 to obtain \([\{\text{Cp}'\text{Fe(CO)}_2\}_2(\mu_1\eta^{1:1}–\text{P}_4)]\) \((\text{Cp}' = \text{C}_5\text{H}_3\text{Bu}_2; 2)\) and \(\text{Cp}”’\text{P}_4\) (3) could be confirmed, by reacting 1 with 2.0 eq. of \(\text{K(Cp}’\text{Fe(CO)}_2\}_2\) or \(\text{NaCp}”’\), respectively. Hereby, a quantitative conversion could be detected alongside the formation of 2.0 eq. of the \([\{\text{Cp}’\text{Cr(CO)}_3\}_2]^−\) anion. Moreover, various syntheses of novel organometallic and organo-\(\text{P}_4\) butterfly compounds were examined and first results show that the generation of different compounds should be possible. However, the isolation and stabilization of these sensitive molecules proves to be a major challenge.

Introduction

Compounds incorporating a tetraphospha-bicyclo[1.1.0]butane motif are a good starting point to investigate the reactivity of polyphosphorus ligand complexes as they are formed in the first step of the activation of the \(\text{P}_4\) tetrahedron.[1] The generation of unprecedented so called \(\text{P}_4\) butterfly compounds could therefore provide more insight in the mechanisms behind the first essential steps of \(\text{P}_4\) activation. Due to the expanding understanding of these processes, the generation of phosphorus containing compounds directly from \(\text{P}_4\) phosphorus is expected to become more economical, less hazardous and more selective. Most commonly, \(\text{P}_4\) butterfly molecules are stabilized by unsaturated organometallic fragments coordinated via the wing tip P atoms of the \(\text{P}_4\) butterfly unit. The first example for a compound incorporating such a structural \(\text{P}_4^2−\) motif was reported by Lindsell and Ginsberg in 1971: \([\text{PPH}_3\text{RhCl(}\eta^{1:1}–\text{P}_4)]^+\).[2] At first it was reported that the \(\text{P}_4\) moiety in this compound remained intact upon coordination, however subsequent \(^{31}\text{P}\) NMR experiments specified a complete cleavage of the \(\text{P}–\text{P}\) bond. Later on, the groups of Krossing and Russell successfully characterized \([\text{M(}\eta^{1}–\text{P}_4)\text{]}^+\) \((\text{M} = \text{Ag, Cu, Au}),[3]\) the first homoleptic cations incorporating an intact \(\text{P}_4\) moiety.[3] However, the most used \(\text{P}_4\) butterfly compound is \([\{\text{Cp}’\text{Fe(CO)}_2\}_2(\mu_1\eta^{1:1}–\text{P}_4)]\) \((\text{Cp}’ = \text{C}_5\text{H}_3\text{Bu}_2; \text{Cp}”’; \text{Cp}”’\text{P}_4)^{[4]}\) first obtained by Scherer et al.[4] Interestingly, our group was able to optimize the synthesis of those compounds which can be quantitatively obtained by reacting the dimeric \([\text{Cp}’’\text{Fe(CO)}_2\}_2\) with elemental \(\text{P}_4\) at ambient conditions.[5] The vast reaction potential of \([\{\text{Cp}’’\text{Fe(CO)}_2\}_2(\mu_1\eta^{1:1}–\text{P}_4)]\) has been intensively studied under photolytic[4a] and thermolytic[4b] reaction conditions and the improved generation of \([\{\text{Cp}’’\text{Fe(CO)}_2\}_2(\mu_1\eta^{1:1}–\text{P}_4)]\) prompted the study towards its coordinative behavior.[5a]

Next to the generation of unprecedented organometallic \(\text{P}_4\) butterfly compounds, the scientific community shares great interest in the synthesis of \(\text{P}_4\) butterfly entities with solely organic substituents. Only a few of them are known so far and therefore the need for simple synthetic access to novel “organo-\(\text{P}_4\) butterfly” complexes is obvious (Scheme 1). After more theoretical suggestions that a \([\text{P}_4\text{C}_4]\) motif is thermodynamically stable,[7] Fluck et al. were the first to report on the successful synthesis of the bright orange \([\text{Mes}^*\text{P}_4]\) \((\text{Mes}^* = Spheres.1.png

Scheme 1. Overview of neutral organo-\(\text{P}_4\) butterfly compounds.

[a] Dr. R. Grünbauer, Dr. M. Seidl, Dr. G. Balázs, Prof. Dr. M. Scheer
Institut für Anorganische Chemie
Universität Regensburg
93040 Regensburg (Germany)
E-mail: manfred.scheer@ur.de
Homepage: https://www.uni-regensburg.de/chemie-pharmazie/ anorganische-chemie-scheer/startseite/index.html

Supporting information for this article is available on the WWW under https://doi.org/10.1002/zaac.202000401


DOI: 10.1002/zaac.202000401
2,4,6-^Bu_3C_5H_2 in 1985,[10] implying different sterically demanding ligands the group of Power was able to isolate [Ar^Dppe,P_4] (Ar^Dppe = C_6H_5-2,6-(C_6H_4-2,6-Pr_2)) while Cummins reported on the synthesis of [Dmp,P_4] (Dmp = 2,6-Mes_2C_5H_3).[10] One feature all these compounds share is the fact that the P_4 unit is connected to an aromatic ligand via a sp^3 hybridized carbon atom. However, our group was able to show that a substitution via a sp^3 hybridized carbon atom is possible as well by synthesizing various P_5Cp^3 compounds (Cp^S = Cp^{36iPr} (C_5(4^2-BuC_5H_3)_4), Cp^* (C_5Me_5), Cp^{''''} (C_5H_5^2Bu_2), Cp^{6^6} (C_5H_5^2Pr_4)),[110] [Cp^{36iPr},P_4] was obtained by reacting Cp^{36iPr} radicals, generated by the reaction of NaCp^{36iPr} with CuBr, with P_4. For cyclopentadienyl ligands that do not generate comparably stable radical species (e.g. Cp^*, Cp^{''''} and Cp^{6^6}), another reaction pathway starting from FeBr_2, MCP^S (M = Li or Na) and P_4 was implied as the supporting Fe/Fe^II redox system enables the reduction from n-hexane leaving behind K[Cp*Cr-(CO)_3] as a yellow solid. The clean separation of the two reaction products due to different solubilities is a great starting point for the desired recovery of [Cp*Cr(CO)_3] obtaine after oxidation of [Cp*Cr(CO)_3] to achieve a cyclic P_4 activation/transfer procedure.

The substituent transfer is a success in the investigation of this unique reaction pathway and a compelling incentive to expand the investigations in order to obtain novel P_4 butterfly compounds. Therefore, various organometallic reagents that reacted with 1 according to an analog reaction procedure. Starting from the successful reaction of 1 with K[Cp^{'''}Fe(CO)_3] one approach was to imply smaller cyclopentadienyl rings like the unsubstituted Cp and the symmetrical Cp^* ligand.[111] Another approach was the exchange of the metal ion, reacting K[Cp^{'''}Mo(CO)_3], K[Cp^{'''}W(CO)_3] and Na[Cp^{'''}Mo(CO)_3] with 1 to generate the P_4 butterfly complexes of the heavier homologs of chromium. However, all of the implied reagents gave the same result. In the ^31P NMR spectra of the reaction mixtures no signals corresponding to any P_4 butterfly complexes could be obtained, neither of the starting material 1, nor of a newly formed product. However, an almost quantitative conversion around P_4 was recorded alongside the occasional formation of small amounts of [Cp^{'''}Cr(CO)_3(n)^1-P_4)], a commonly side product of all manipulations of 1. This leads to the assumption that the cleavage of the P–Cr bonds in 1 is achieved, depleting the amount of 1 in the reaction solution. However, the newly obtained P_4 butterfly compounds are likely to be unstable, instantly converting to P_4 and the corresponding organometallic dimer [Cp^{'''}M(CO)_3] (Scheme 4; exemplified for CpFe (CO)_2-fragments), which have been unambiguously identified by spectroscopic methods.

Most likely is the steric demand of the smaller cyclopentadienyl ligands (Cp, Cp^* and Cp^{'''}), compared to the steric hindrance of the Cp^{'''} ligand of the Fe(CO)_3Cp^{'''}-fragment, which is apparently essential for the stability of 2, not sufficient enough. Therefore, P_4 butterfly compounds incorporating the smaller Cp derivatives appear to be not accessible via this P_4

Results and Discussion

To test out the proposed substituent transfer, 1 was reacted successfully with 2.0 eq. K[Cp^{'''}Fe(CO)_3] yielding the well-known [(Cp^{'''}Fe(CO)_3)_{(n)^1-P_4}] (2) and 2.0 eq. of K[Cp*Cr(CO)_3] quantitatively after 17 hours at room temperature (Scheme 3). NMR as well as IR spectroscopic studies confirmed the quantitative formation of 2 without any side reactions (Fig-ure S1/S4). Consequently, it can be stated that the proposed substituent transfer deriving from 1 is generally possible. A red solution of 2 could be isolated from the crude reaction mixture upon the extraction with n-hexane leaving behind K[Cp*Cr-(CO)_3] as a yellow solid. The clean separation of the two reaction products due to different solubilities is a great starting point for the desired recovery of [Cp*Cr(CO)_3], obtained after oxidation of [Cp*Cr(CO)_3] to achieve a cyclic P_4 activation/transfer procedure.

![Scheme 2](image2.png)

Scheme 2. Proposed P_4 activation/transfer reaction mechanism starting from compound 1.

![Scheme 3](image3.png)

Scheme 3. Reaction of 1 with K[Fe(CO)_3Cp^{'''}]].
butterfly transfer reaction pathway. Additionally, the implementation of the heavier transition metal elements Mo and W did not result in the formation of the desired novel P₄ butterfly compounds as well. For molybdenum and tungsten no P₄ butterfly compounds are known so far. [CpM(CO)]₃[μ-P₄] and [CpM(CO)](μ₂-P₄)] (M = Mo, W) are the only species obtained from reacting P₄ with [CpM(CO)]₂ or [CpM(CO)]₃ under thermolytic conditions.[12] Hence, the suggestion that molybdenum and tungsten substituted P₄ butterfly compounds are not thermodynamically stable is very likely.

The immediate decomposition of the newly afforded P₄ butterfly complexes also explains the quantitative amount and exclusive record of P₄ as the only phosphorus species in the ³¹P NMR spectrum of the reaction solution. Moreover, IR spectroscopic investigations confirmed that for the reactions of 1 with K[Cp*Fe(CO)]₂ and K[Cp*Fe(CO)]₃ the corresponding [Cp*Fe(CO)]₂ dimers (Cp*: νCO [cm⁻¹] = 1952, 1937, 1783; Cp*: νCO [cm⁻¹] = 1959, 1924, 1755 cm⁻¹; both recorded in toluene) can be detected in the reaction mixture. Alongside, bands corresponding to K[Cp*Cr(CO)]₃ could be identified as well νCO [cm⁻¹] = 1994, 1873; recorded in toluene). This observation confirms that the initial step in the transfer process, the cleavage of the Cr–P bond, took place. Unfortunately, no method could be established to stabilize, obtain and eventually characterize the proposed novel P₄ butterfly complexes expected from the subsequent substituent transfer processes. In contrast, the instant fragmentation of the newly formed species can be verified by detecting the expected decomposition products K[Cp*Cr(CO)]₂, [CpM(CO)]₃, and P₄.

Next to the formation of novel organometallic P₄ butterfly complexes, the unique reactivity of 1 could be the ideal starting point for an alternative pathway in the generation of organo-P₄ butterfly compounds. To test this hypothesis, 1 was reacted with two equivalents of NaCp*₄, proposing the formation of the already known Cp*₂P₄ (3) by means of the above discussed P₄ butterfly transfer processes. With the implementation of ³¹P NMR spectroscopy it was determined that the reaction was successful and moreover an improved selectivity in comparison to the original synthesis, incorporating FeBr₃, NaCp*™ and P₄ could be achieved.[10] In the previous synthetic approach the compound depicted in Scheme 5 was obtained in approx. 35% ratio alongside three other constitutional isomers varying in the layout of the ’Bu substituents of the Cp™ ligands. In contrast, the depicted molecule could be identified as the main product from the substituent transfer originating from 1 with a relative amount of 84% in respect to all obtained isomers of 3. The ABMN spin system of the major isomer of 3 gives four elaborate multiplets in the ³¹P NMR spectrum, which could be further examined by simulation. In comparison to the ³¹P NMR chemical shifts given in literature,[10] the signals in the ³¹P NMR spectrum recorded for this reaction were slightly shifted (Table 1). This may be explained by the interference of a paramagnetic chromium compound present in the reaction solution.

Motivated by the successful synthesis of 3, the reaction of 1 with NaCp* was analogously studied to investigate, if this reaction pathway is feasible for the synthesis of smaller organo-P₄ butterfly complexes as well. Surprisingly, an immediate decomposition of 1 along with the formation of P₄ could be observed in the ³¹P NMR spectrum suggesting that if a Cp₄P₄ butterfly compound is formed, it decomposes instantly. Performing the reaction at low temperatures could not facilitate the detection of the proposed product. Table 2 depicts the relative integral of the P₄ signal in the VT ³¹P(¹H) NMR spectra of the reaction of 1 with 2.0 eq. NaCp*™ stating that the comprised amount of P₄ (probably caused by decomposition during the transfer of the probe) is consistent below 223 K. Above this temperature only an increase in the P₄ signal (accompanied by a decrease of the signals corresponding to 1) with no detection of an intermediate (P₄ butterfly) species is observed. Consequently, a rapid decomposition of an unstable reaction product which cannot be detected on an NMR time scale can be stated. Hence, the above discussed reaction of 1 with alkali cyclopentadienyl compounds is not a universal reaction pathway for the formation of new organo-P₄ butterfly compounds. Consequently, a different class of reactive organic substituents was examined. Therefore, Ph₃CCl and Ph₃CHCl, respectively, were reacted with AlCl₃ to afford the reactive cations Ph₃C⁺ and Ph₃CH⁺, respectively. In a second step, these activated carbon species were reacted with 1 in order to perform the abstraction of the [Cp*Cr(CO)]₃ fragment and the subsequent P–C bond formation.

First experiments on a NMR scale gave promising results. After stirring the reaction solution overnight, two triplets assignable to new P₄ butterfly species could be detected in the ³¹P NMR spectra of both reactions ([Ph₃C]⁺: δ [ppm] = 16.2 (t, Jₚp = 238 Hz, 2P), −313.6 (t, Jₚp = 238 Hz, 2P); [Ph₃CH]⁺: δ [ppm] = 25.4 (t, Jₚp = 273 Hz, 2P), −301.2 (t, Jₚp = 273 Hz, 2P)). However, the quantitative formation of these new compounds is not reproducible, leading to the formation of variable
**Table 1.** Comparison of the previously reported $^{31}$P NMR spectrum of the depicted isomer of 3 and the corresponding signals in the simulated $^{31}$P NMR spectrum from the reaction of 1 with 2.0 eq. NaCp$^*$ (both recorded in C$_6$D$_6$).

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ [ppm]</th>
<th>J [Hz]</th>
<th>$\delta$ [ppm]</th>
<th>J [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>reported$^{10}$</td>
<td></td>
<td>recorded</td>
<td></td>
</tr>
<tr>
<td>P$_A$</td>
<td>$-154.6$</td>
<td>191 (AM)</td>
<td>175 (BN)</td>
<td>191 (AM)</td>
</tr>
<tr>
<td>P$_B$</td>
<td>$-162.5$</td>
<td>175 (BM)</td>
<td>175 (BM)</td>
<td>191 (AN)</td>
</tr>
<tr>
<td>P$_M$</td>
<td>$-324.8$</td>
<td>317 (AB)</td>
<td>317 (AB)</td>
<td>173 (MN)</td>
</tr>
<tr>
<td>P$_N$</td>
<td>$-352.1$</td>
<td>348 (AB)</td>
<td>177 (MN)</td>
<td>177 (MN)</td>
</tr>
</tbody>
</table>

**Table 2.** Relative integral of the P$_4$ signal in the VT $^{31}$P{¹H} NMR spectra of the reaction of 1 with 2.0 eq. NaCp$^*$.

<table>
<thead>
<tr>
<th>T</th>
<th>Integral (P$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>193 K</td>
<td>19.4 %</td>
</tr>
<tr>
<td>213 K</td>
<td>19.3 %</td>
</tr>
<tr>
<td>233 K</td>
<td>19.7 %</td>
</tr>
<tr>
<td>253 K</td>
<td>23.0 %</td>
</tr>
<tr>
<td>273 K</td>
<td>30.0 %</td>
</tr>
<tr>
<td>300 K</td>
<td>55.6 %</td>
</tr>
</tbody>
</table>

amounts of side products and upscaling of the reaction lead to major difficulties. One was the formation of reasonable amounts of side products as species like [Cr(CO)$_3$Cp$^*$X] (X = CO or Cl) and [Cp$^*$$_2$Cr$_2$Cl$_3$] could be isolated from the reaction mixture and characterized. Additionally, a blue fluorescent oil could be extracted from the crude reaction mixture of the reaction of 1 with Ph$_2$CHCl/AlCl$_3$. This suggest that after the deprotonation a dimerization forming Ph$_2$C=CPh$_2$ occurred. To rule out that AlCl$_3$ is the culprit of the side reactions, alternative chloride abstractors like TlPF$_6$ were implied and the reaction was repeated in the presence of a base (DBU). Unfortunately, no conversion could be detected at all when adding these reagents.

Another approach to eliminate the side effects of AlCl$_3$ on the reaction, was performing the reaction with [Ph$_3$C][BF$_4$] instead of utilizing Ph$_3$CCl and AlCl$_3$. Hereby, a different $^{31}$P{¹H} NMR spectrum compared to the one obtained after the reaction of 1 with Ph$_3$CCl/AlCl$_3$ was recorded (Figure 1). Instead of two triplets assignable to a new P$_4$ butterfly species, the reaction of 1 with [Ph$_3$C][BF$_4$] afforded two multiples at $\delta = 66.6$ ppm and 82.8 ppm in the $^{31}$P{¹H} NMR spectrum. These seem very similar to the signals reported for the 6π-aromatic P$_4$R$_2$ ligand (R = Cp$^*$Fe(CO)$_3$) found in $^{[([Cp]^*Fe(CO)$_3$)$_2$}$($\mu$_{3}$_{-}$-P$_4$)$_2$Fe]$[PF_6]_2$ ($\delta^{(1)}$P{¹H} NMR) = 91.7 ppm and 114.3 ppm.$^{[9c]}

Consequently, it can be proposed that no substituent transfer on the intact P$_4$ butterfly moiety occurred but some sort of rearrangement of the central P$_4$ scaffold arose. Unfortunately, all attempts to crystalize, isolate or further characterize the intriguing reaction product failed. In order to
increase the accessibility of the product an excess of [Cr-(CO)₆(nbd)] (nbd = norbornadiene) was added to the reaction mixture assuming that a coordination of the newly formed P₄ ligand unit towards [Cr(CO)₄] fragments facilitate crystallization. 

³¹P{¹H} NMR experiments confirmed the successful coordination of [Cr(CO)₄] fragments as a remarkable upfield shift of approx. 130 ppm and a change in the splitting pattern of the detected signal could be observed resulting in a very broad multiplet with a chemical shift of δ = −57.3 ppm. However, the resulting product appears to be a brown oil not feasible for further investigation. Furthermore, the reaction was performed analogously with [Ph₂C₆]: [B(C₆F₅)₂] in order to promote crystallization by anion exchange. However, only a quantitative conversion to P₄ could be detected in the 

Conclusions

In conclusion the rather weak P─Cr bonds in 1 give rise to an unprecedented reactivity pathway for P₄ butterfly compounds by allowing selective substituent transfer. Although first results were very promising, the substituent exchange starting from 1 could not produce any new compounds so far. However, the fact that already known P₄ butterfly compounds could be obtained by this reaction pathway is affirming (Scheme 6). [(Cp''Fe(CO)₃)₂(μ₃-η¹−P₄)] (2) and 3 could be obtained from this novel synthetic pathway and in the case of 3 even an increase in selectivity could be observed compared to the literature procedure. Maybe fine-tuning the reaction conditions, improving the steric demand of the substrates or the implementation of more thermodynamically stable substrates could promote the successful generation of novel P₄ butterfly compounds from the novel reactivity we found for 1. Notably, control experiments showed, that 2 does not display this kind of reactivity further manifesting that 1 is the more divers’ reagent compared to the traditional P₄ butterfly compound 2. Moreover, the clean separation of 2 and K[Cp*Cr(CO)₄] is the first step to recover the released chromium substituent and eventually retrieve [Cp*Cr(CO)₄] starting another cycle in the P₄ activation/transfer process.

Experimental Section

General remarks

All experiments were performed under an inert gas atmosphere of dry argon or nitrogen using standard Schlenk and Glovebox techniques. Residue of oxygen and water were removed from the inert gas by passing it over a BASF R 3–11 (CuO/MgSiO₃) catalyst, concentrated H₂SO₄, and finally granulated silica gel. Dry solvents were collected from a Braun SPS Apparatus and degassed prior to use. The deuterated solvents CD₃OD and CDCl₃ were degassed and dried by stirring with Na/K alloy and CaH₂, respectively, followed by distillation. After the distillation, CDCl₃ was additionally stored over molecular sieve (3 Å) which had previously been dried for four hours under high vacuum at 100 °C. NMR spectra were recorded using a Bruker Advance 300 or 400 spectrometer. Samples are referenced against TMS (δH, 13C) or 85% H₃PO₄ (δP) as external standards. Chemical shifts [δ] are reported in ppm and coupling constants [J] in Hz. The spectra were processed using the TopSpin 3.0 software (Bruker) and the WIN-DAISY module of this software was used to perform simulations. IR spectra were recorded on a FT-IR spectrometer from DIGILAB (FTS 800) for diluted solutions sealed between KBr plates.

Reactions with organometallic nucleophiles

Experimental setup: To a solution of 1.0 eq. 1 (20 mg, 0.03 mmol) in 5 mL toluene a solution of 2.0 eq. M'[Cp'M(CO)₃] (M’ = Na, K; Cp' = Cp, Cp', Cp''; M = Fe, Mo, W; X = 2, 3) (0.06 mmol) in toluene (5 mL) was added dropwise. No immediate color change could be observed, and the reaction mixture was stirred over night at room temperature. Subsequently, the solution was concentrated and an NMR sample was prepared with a C₆D₆ capillary. For NMR and IR spectra the reactions see SI.

For the reaction with Na[Cp''Fe(CO)₃] the solvent was removed from the reaction mixture under reduced pressure affecting a mixture of yellow and red solid. By extraction with n-hexane a red solution (([(Cp''Fe(CO)₃)₂(μ₃-η¹−P₄)] (2)) could be separated from the yellow residue [Na(Cp''Cr(CO)₃)]. The solvent from the extract was subsequently removed in vacuo.

For the reaction with Na[Cp''Fe(CO)₃] the solvent was removed from the reaction mixture under reduced pressure affecting a mixture of yellow and red solid. By extraction with n-hexane a red solution [(Cp''Fe(CO)₃)₂(μ₃-η¹−P₄)] (2) could be separated from the yellow residue [Na(Cp''Cr(CO)₃)]. The solvent from the extract was subsequently removed in vacuo.

Reaction with Na[Cp''Fe(CO)₃]: ³¹P{¹H} NMR (toluene with C₆D₆ capillary) δ(ppm) = −82.5 (t, J_H = 186 Hz, 2P, P₄), −324.7 (t, J_H = 186 Hz, 2P, P₄). IR (toluene) ν_CO [cm⁻¹] = 2000 (s), 1990 (s), 1949(s), 1942 (s), 1765 (w).

Scheme 6. Successful substituent transfer reactions starting from 1.
Reaction of 1 with NaCp: An orange-brown solution of 1.0 eq. 1 (17 mg, 0.03 mmol or 25 mg, 0.04 mmol, respectively) in 5 mL toluene was added dropwise to a suspension of 2.0 eq. AlCl₃ (Cp*: 13 mg, 0.05 mmol; Cp: 12 mg, 0.08 mmol) in 5 mL toluene. No immediate color change could be observed and the reaction mixture was stirred overnight. The solvent was removed from vacuo yielding a yellow and a brown solid, respectively.

Reaction of 1 with NaCp*: ¹H NMR (toluene, CDCl₃): δ(ppm) = 1.07 (s, 19.9H, Cp*), 1.15 (s, 14.0H, Bu*), 1.17 (s, 20.6H, Bu*), 1.25 (s, 22.9H, Bu*), 1.30 (s, 14.1H, Bu*), 1.35 (s, 18.4H, Bu*), 1.36 (s, 18.3H, Bu*), 1.71 (s, 12.8H, Bu*), 2.96 (s, 2.4H, CH), 3.09 (s, 3.0H, CH), 3.89 (q, JHH = 6.8 Hz, 3.4H, CH), 5.76 (m, 1.0H, CH), 5.96 (t, JMM = 1.8 Hz, 2.3H, CH), 6.42 (m, 4.7H, CH); ¹³P(¹H) NMR (CDCl₃): δ(ppm) = -99.1 (t, JHP = 193 Hz, 0.04P), -123.6 to -135.5 (m, 2P, P₂), -157.8 (m, 0.1P), -269.4 (s, [Cp*Cr(CO)₅]⁻, P₀), -312.4 (dt, JMM = 170 Hz, JMM = 1.05 Hz, 1P), -332.0 (t, JHP = 190 Hz, 0.5P), -334.8 (t, JHP = 183 Hz, 0.1P), -343.1 (dt, JMM = 170 Hz, JMM = 206 Hz, 1P), -526.0 (s, 3P, P₂).

Reaction of 1 with NaCp*: ¹H NMR (toluene, CDCl₃): δ(ppm) = -269.9 (s, 1P, [Cp*Cr(CO)₅]⁻, P₀), -520.4 (s, 17P, P₂).

Reaction of 1 with NaCp*: ³¹P(¹H) NMR (toluene, CDCl₃): δ(ppm) = 16.2 (t, JHP = 238 Hz, 2P), -313.6 (t, JHP = 238 Hz, 2P), -522.8 (s, 0.2P, P₂).

Reaction with Ph₂CCI/AlCl₃: ³¹P(¹H) NMR (CD₂Cl₂): δ(ppm) = -512.6 (s, P₂), IR (toluene) νCO [cm⁻¹] = 1995 (s), 1952 (w), 1936 (s), 1914 (m), 1874 (s), 1782 (s), 1726 (m, br).

Reaction with K[CpFe(CO)₂]: ³¹P(¹H) NMR (toluene, CD₂Cl₂): δ(ppm) = -512.6 (s, P₂), IR (toluene) νCO [cm⁻¹] = 1994 (m), 1972 (w), 1959 (w), 1924 (s), 1873 (s), 1755 (m), 1727 (w).

Reaction with K[Cp/Mo(CO)₅]: ³¹P(¹H) NMR (toluene, CD₂Cl₂): δ(ppm) = -95.0 (t, JMM = 196 Hz, 2P, P₂), -273.5 (s, 0.5P, [Cp*Cr(CO)₅]⁻, P₀), -272.4 (t, JMM = 196 Hz, 2P, P₂), -522.2 (s, 2.7P, P₂).

Reactions with organic nucleophiles

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sch 384/38-1. RG is grateful for the Fonds der Chemischen Industrie for a PhD fellowship. Open access funding enabled and organized by Projekt DEAL.

Keywords: phosphorus · chromium · P₄ · butterfly · organophosphorus compounds · metathesis


[11] \[[\text{Cp}^*\text{Fe(CO)}_2]_2(\mu_1:1:1\text{P}_4)\] was proposed by $^{31}$P NMR spectroscopy ($\delta$[ppm] = –46.5 (t, $^1J_{AB} = 185$ Hz, 2P, $P_A$), –337.5 (t, $^1J_{AB} = 185$ Hz, 2P, $P_B$); recorded in a THF reaction solution), however it decomposes during workup and could therefore not be structurally characterized yet: L. Weber, U. Sonnenberg, Chem. Ber. 1991, 124, 725–728.


