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ARTICLE

Utilizing the weak P–Cr bond in $[\{Cp^*Cr(CO)_3\}_2(\mu,\eta^{1:1}-P_4)]$ for the generation of different P_4 butterfly compounds

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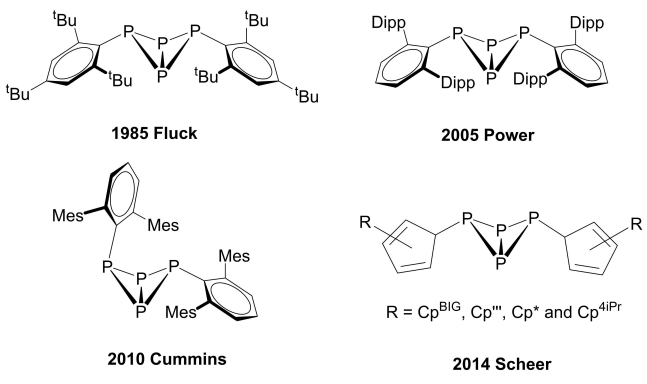
Dedicated to Professor Dr. Peter Klüfers on the Occasion of his 70th Birthday

A novel reactivity of $[\{Cp^*Cr(CO)_3\}_2(\mu,\eta^{1:1}-P_4)]$ ($Cp^* = C_5Me_5$; **1**) is reported, which utilizes the selective cleavage of the two P–Cr bonds and subsequently initiates a substituent exchange yielding P_4 butterfly compounds. By means of NMR and IR spectroscopy studies, the successful implementation of **1** to obtain $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}-P_4)]$ ($Cp''' = C_5H_2{}^tBu_3$; **2**) and Cp'''_2P_4 (**3**) could be confirmed, by reacting **1** with 2.0 eq. of $K[Cp'''Fe(CO)_2]$ or NaCp‴, respectively. Hereby, a quantitative conversion could be detected alongside the formation of 2.0 eq. of the $[Cp^*Cr(CO)_3]^-$ anion. Moreover, various syntheses of novel organometallic and organo-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 P_4 tetrahedron.[1] The generation of unprecedented so called P_4 butterfly compounds could therefore provide more insight in the mechanisms behind the first essential steps of P_4 activation. Due to the expanding understanding of these processes, the generation of phosphorus containing compounds directly from P_4 phosphorus is expected to become more economical, less hazardous and more selective. Most commonly, P_4 butterfly molecules are stabilized by unsaturated organometallic fragments coordinated via the wing tip P atoms of the P_4 butterfly unit. The first example for a compound incorporating such a structural P_4^{2-} motif was reported by *Lindsell* and *Ginsberg* in 1971: $[(PPh_3)_2RhCl(\eta^{1:1}-P_4)]$.[2] At first it was reported that the P_4 moiety in this compound remained intact upon coordination, however subsequent ^{31}P NMR experiments specified a complete cleavage of the P–P bond. Later on, the groups of *Krossing* and *Russell* successfully characterized $[M(\eta^2-P_4)_2]^+$ (M = Ag, Cu, Au), the first homoleptic cations incorporating an intact P_4 moiety.[3] However, the most used P_4 butterfly compound is $[\{Cp^RFe(CO)_2\}_2(\mu,\eta^{1:1}-P_4)]$ ($Cp^R = Cp''$ ($C_5H_3{}^tBu_2$) or Cp''' ($C_5H_2{}^tBu_3$)), 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 $[Cp'''Fe(CO)_2]_2$ with elemental P_4 at ambient conditions.[5] The vast reaction potential of $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}-P_4)]$ has been intensively studied under photolytic[4a] and thermolytic[4b] reaction conditions and the improved generation of $[\{Cp'''Fe(CO)_2\}_2(\mu,\eta^{1:1}-P_4)]$ prompted the study towards its coordinative behavior.[5,6]

Next to the generation of unprecedented organometallic P_4 butterfly compounds, the scientific community shares great interest in the synthesis of 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-P_4 butterfly" complexes is obvious (Scheme 1). After mere theoretical suggestions that a $[P_4C_2]$ motif is thermodynamically stable,[7] Fluck *et al.* were the first to report on the successful synthesis of the bright orange $[Mes^*_2P_4]$ ($Mes^* =$



Scheme 1. Overview of neutral organo-P_4 butterfly compounds.

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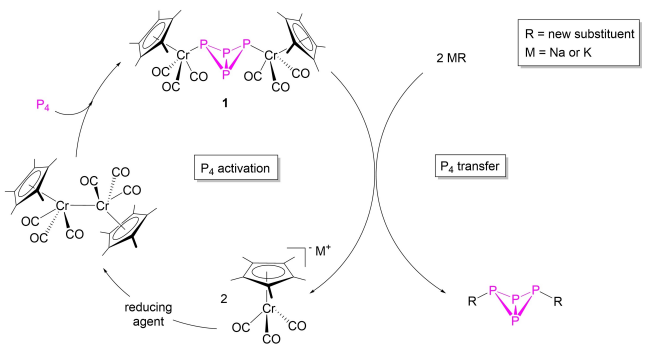
2,4,6-$^{t}Bu_3C_6H_2$) in 1985.[8] Implying different sterically demanding ligands the group of Power was able to isolate [$Ar^{Dipp}{}_2P_4$] (Ar^{Dipp} = C_6H_3-2,6-(C_6H_3-2,6-$^{i}Pr_2$)$_2$) while Cummins reported on the synthesis of [Dmp_2P_4] (Dmp = 2,6-$Mes_2C_6H_3$).[9] One feature all these compounds share is the fact that the P_4 unit is connected to an aromatic ligand via a sp^2 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 synthetizing various $P_4Cp^R{}_2$ compounds (Cp^R = Cp^{BIG} (C_5(4-$^{n}BuC_6H_4$)$_5$), Cp* (C_5Me_5), Cp‴ ($C_5H_2{}^{t}Bu_3$), Cp^{4iPr} ($C_5H^{i}Pr_4$)).[10] [$Cp^{BIG}{}_2P_4$] was obtained by reacting Cp^{BIG} radicals, generated by the reaction of $NaCp^{BIG}$ with CuBr, with P_4. For cyclopentadienyl ligands that do not generate comparingly stable radical species (e.g. Cp*, Cp‴ and Cp^{4iPr}), another reaction pathway starting from $FeBr_3$, MCp^R (M = Li or Na) and P_4 was implied as the supporting Fe^{II}/Fe^{III} redox system enables the reduction from a Cp^R anion to a Cp^R radical.

As the Cr–P bonds in [{Cp*Cr(CO)$_3$}$_2$(μ,η$^{1:1}$–P_4)] (**1**) tested out to be rather weak compared to the corresponding Fe–P bonds in [{Cp‴Fe(CO)$_2$}$_2$(μ,η$^{1:1}$–P_4)] (**2**), the question arose whether it is possible to utilize this remarkable feature of **1**. Therefore, the idea to specifically break this bond and attach new substituents on the P_4 butterfly unit came to mind. This ligand exchange might grant a foothold in the generation of a plethora of unprecedented P_4 butterfly containing compounds that might even be too sensitive to be obtained by a more classical approach (e.g. reacting the corresponding dimer of the substituent with P_4 like it is the usual approach for **2**). Moreover, the released chromium substituent of **1** could perhaps be isolated and used to restore the chromium dimer [Cp*Cr(CO)$_3$]$_2$ with the help of a suitable reducing agent. [Cp*Cr(CO)$_3$]$_2$ could once again be reacted with P_4 to obtain **1**, which could be implemented in another cycle of the P_4 activation procedure (Scheme 2). Consequently, **1** could open up a pathway not only towards the generation of unprecedented P_4 butterfly compounds but also in terms of chemical efficiency as it might eventually enable a cyclic reaction transfer of P_4 butterfly moieties.



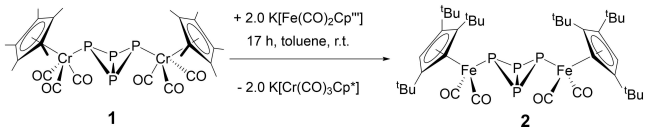
Scheme 2. Proposed P_4 activation/transfer reaction mechanism starting from compound **1**.

Results and Discussion

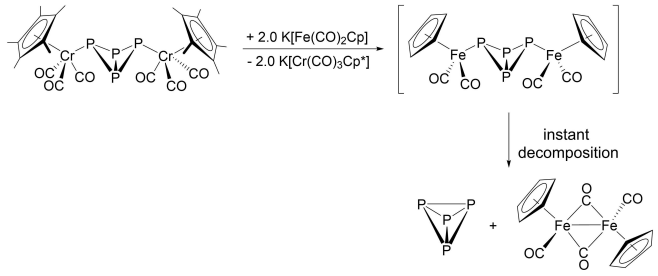
To test out the proposed substituent transfer, **1** was reacted successfully with 2.0 eq. K[Cp‴Fe(CO)$_2$] yielding the well-known [{Cp‴Fe(CO)$_2$}$_2$(μ,η$^{1:1}$–P_4)] (**2**) and 2.0 eq. of K[Cp*Cr(CO)$_3$] quantitatively after 17 hours at room temperature (Scheme 3). NMR as well as IR spectroscopic studies confirmed the quantitative formation of **2** without any side reactions (Figure 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)$_3$]$_2$, obtained after oxidation of K[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 where reacted with **1** according to an analog reaction procedure. Starting from the successful reaction of **1** with K[Cp‴Fe(CO)$_2$] one approach was to imply smaller cyclopentadienyl rings like the unsubstituted Cp and the symmetrical Cp* ligand.[11] Another approach was the exchange of the metal ion, reacting K[Cp'Mo(CO)$_3$], K[CpW(CO)$_3$] and Na[Cp‴W(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 ^{31}P 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 affording P_4 was recorded alongside the occasional formation of small amounts of [Cp*Cr(CO)$_2$(η^3–P_3)], 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 [$Cp^RM(CO)_x$]$_2$ (Scheme 4; exemplified for CpFe(CO)$_2$-fragments), which have been unambiguously identified by spectroscopic methods.

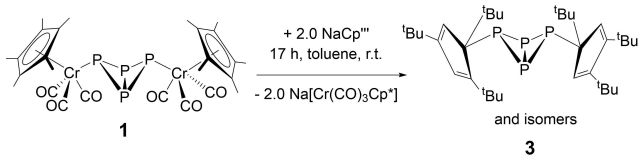
Most likely is the steric demand of the smaller cyclopentadienyl ligands (Cp, Cp* and Cp') compared to the steric hindrance of the Cp‴ ligand of the Fe(CO)$_2$Cp‴ fragment, which is apparently essential for the stability of **2**, not sufficient enough. Therefore, P_4 butterfly compounds incorporating the smaller Cp derivatives appear to be not accessible via this P_4



Scheme 3. Reaction of **1** with K[Fe(CO)$_2$Cp‴].



Scheme 4. Proposed reaction of **1** with K[CpFe(CO)$_2$] as an example of the instant decomposition of the newly obtained P_4 butterfly compounds of the substituent transfer experiments.



Scheme 5. Reaction of **1** with NaCp'''.

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 P_4 butterfly compounds as well. For molybdenum and tungsten no P_4 butterfly compounds are known so far. [{CpM(CO)$_2$}$_2${μ,η^2−P$_2$}] and [CpM(CO)$_2$(η^3−P$_3$)] (M = Mo, W) are the only species obtained from reacting P_4 with [CpM(CO)$_2$]$_2$ or [CpM(CO)$_3$]$_2$ under thermolytic conditions.[12] Hence, the suggestion that molybdenum and tungsten substituted P_4 butterfly compounds are not thermodynamically stable is very likely.

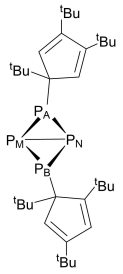
The immediate decomposition of the newly afforded P_4 butterfly complexes also explains the quantitative amount and exclusive record of P_4 as the only phosphorus species in the ^{31}P NMR spectrum of the reaction solution. Moreover, IR spectroscopic investigations confirmed that for the reactions of **1** with K[CpFe(CO)$_2$] and K[Cp*Fe(CO)$_2$] the corresponding [Cp^{R}Fe(CO)$_2$]$_2$ dimers (Cp: $\tilde{\nu}_{CO}$ [cm^{-1}] = 1952, 1937, 1783; Cp*: $\tilde{\nu}_{CO}$ [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 $\tilde{\nu}_{CO}$ [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 P_4 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)$_3$], [CpM(CO)$_x$]$_2$ and P_4.

Next to the formation of novel organometallic P_4 butterfly complexes, the unique reactivity of **1** could be the ideal starting point for an alternative pathway in the generation of *organo*-P_4 butterfly compounds. To test this hypothesis, **1** was reacted with two equivalents of NaCp''', proposing the formation of the already known Cp'''$_2$P$_4$ (**3**) by means of the above discussed P_4 butterfly transfer processes. With the implementation of ^{31}P NMR spectroscopy it was determined that the reaction was successful and moreover an improved selectivity in comparison to the original synthesis, incorporating $FeBr_3$, NaCp''' and P_4, 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 ^{t}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 ^{31}P NMR spectrum, which could be further examined by simulation. In comparison to the ^{31}P NMR chemical shifts given in literature,[10] the signals in the ^{31}P 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-P_4 butterfly complexes as well. Surprisingly, an immediate decomposition of **1** along with the formation of P_4 could be observed in the ^{31}P NMR spectrum suggesting that if a Cp*$_2$P$_4$ 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 P_4 signal in the VT ^{31}P{^{1}H} NMR spectra of the reaction of **1** with 2.0 eq. NaCp* stating that the comprised amount of P_4 (probably caused by decomposition during the transfer of the probe) is consistent below 223 K. Above this temperature only an increase in the P_4 signal (accompanied by a decrease of the signals corresponding to **1**) with no detection of an intermediate (P_4 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-P_4 butterfly compounds. Consequently, a different class of reactive organic substituents was examined. Therefore, Ph_3CCl and Ph_2CHCl, respectively, were reacted with $AlCl_3$ to afford the reactive cations Ph_3C^+ and Ph_2CH^+, 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 P_4 butterfly species could be detected in the ^{31}P NMR spectra of both reactions ([Ph$_3$C]$^+$: δ [ppm] = 16.2 (t, $^1J_{PP}$ = 238 Hz, 2P), −313.6 (t, $^1J_{PP}$ = 238 Hz, 2P); [Ph$_2$CH]$^+$: δ [ppm] = 25.4 (t, $^1J_{PP}$ = 273 Hz, 2P), −301.2 (t, $^1J_{PP}$ = 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_6D_6).



		P_A	P_B	P_M	P_N
δ [ppm]	reported[10]	−154.6	−162.5	−324.8	−352.1
	recorded	−126.6	−132.0	−312.4	−343.2
J [Hz]	reported[10]	191 (AM)	175 (BN)	191 (AM)	175 (BN)
		175 (AN)	191 (BM)	175 (BM)	191 (AN)
		317(AB)	317 (AB)	173 (MN)	173 (MN)
	recorded	187 (AM)	169 (BN)	187 (AM)	169 (BN)
		208 (AN)	195 (BM)	195 (BM)	207 (AN)
		348 (AB)	348 (AB)	177 (MN)	177 (MN)

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*.

T	193 K	213 K	233 K	253 K	273 K	300 K
Integral (P_4)	19.4%	19.3%	19.7%	23.0%	30.0%	55.6%

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 $[Cr(CO)_3Cp^*X]$ (X = CO or Cl) and $[Cp^*_2Cr_2Cl_3]$ 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 $Ph_2CHCl/AlCl_3$. This suggest that after the deprotonation a dimerization forming $Ph_2C{=}CPh_2$ 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 $[Ph_3C][BF_4]$ instead of utilizing Ph_3CCl and $AlCl_3$. Hereby, a different $^{31}P\{^1H\}$ NMR spectrum compared to the one obtained after the reaction of **1** with $Ph_3CCl/AlCl_3$ was recorded (Figure 1). Instead of two triplets assignable to a new P_4 butterfly species, the reaction of **1** with $[Ph_3C]^+[BF_4]^-$ afforded two multiples at δ = 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_4R_2 ligand (R = Cp‴$Fe(CO)_2$) found in $[\{(Cp'''Fe(CO)_2)_2(\mu_3,\eta^{1:1:4}{-}P_4)\}_2Fe][PF_6]_2$ (δ($^{31}P\{^1H\}$ NMR) = 91.7 ppm and 114.3 ppm).[6c]

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

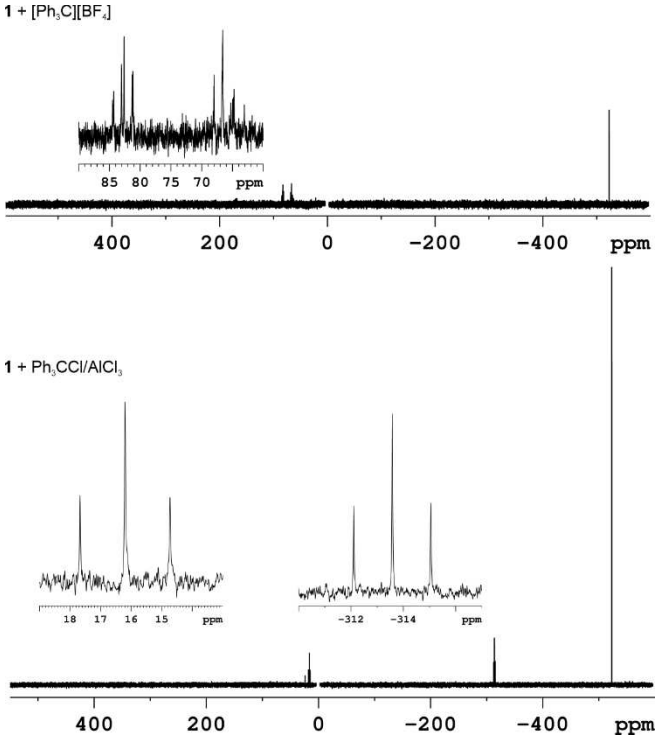
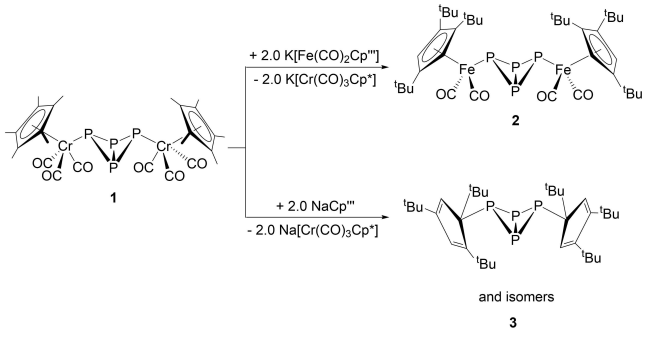


Figure 1. $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures of the reaction of **1** with 2.0 eq. $[Ph_3C]^+[BF_4]^-$ (top) and the reaction of **1** with 2.0 eq. $Ph_3CCl/AlCl_3$ (bottom). Both recorded in CD_2Cl_2.

increase the accessibility of the product an excess of [Cr(CO)$_4$(nbd)] (nbd = norbornadiene) was added to the reaction mixture assuming that a coordination of the newly formed P_4 ligand unit towards [Cr(CO)$_4$] fragments facilitate crystallization. $^{31}P\{^1H\}$ 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 $\delta = -57.3$ ppm. However, the resulting product appears to be a brown oil not feasible for further investigation. Furthermore, the reaction was performed analogously with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in order to promote crystallization by anion exchange. However, only a quantitative conversion to P_4 could be detected in the ^{31}P NMR spectrum of this reaction. Additionally, the reaction was performed with **2** as well. However, the reaction of **2** with $[Ph_3C]^+[BF_4]^-$ apparently does not take place under the same reaction conditions as the reaction with **1**, as no conversion could be detected by NMR experiments. Consequently, **1** is once again the more intriguing starting material due to its increased and more unique reactivity. However, the insufficiency of means to isolate the obtained products is a major drawback.

Conclusions

In conclusion the rather weak P–Cr bonds in **1** give rise to an unprecedented reactivity pathway for P_4 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 P_4 butterfly compounds could be obtained by this reaction pathway is affirming (Scheme 6). [{Cp‴Fe(CO)$_2$}$_2$($\mu,\eta^{1:1}$–P$_4$)] (**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 substituents or the implementation of more thermodynamically stable substituents could promote the successful generation of novel P_4 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 P_4 butterfly compound **2**. Moreover, the clean separation of **2** and K[Cp*Cr(CO)$_3$] is the first step to recover the released chromium substituent and eventually retrieve [Cp*Cr(CO)$_3$]$_2$ starting another cycle in the P_4 activation/transfer process.



Scheme 6. Successful substituent transfer reactions starting from **1**.

Experimental Section

General remarks

All experiments were performed under an inert gas atmosphere of dry argon or nitrogen using standard Schlenk and Glovebox techniques. Residues of oxygen and water were removed from the inert gas by passing it over a BASF R 3–11 (CuO/MgSiO$_3$) catalyst, concentrated H_2SO_4 and finally granulated silica gel. Dry solvents were collected from a Braun SPS Apparatus and degassed prior to use. The deuterated solvents C_6D_6 and CD_2Cl_2 were degassed and dried by stirring with Na/K alloy and CaH_2, respectively, followed by distillation. After the distillation, CD_2Cl_2 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 (^1H, ^{13}C) or 85 % H_3PO_4 (^{31}P) 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.[13] IR spectra were recorded on a FT-IR spectrometer from DIGILAB (FTS 800) for diluted solutions sealed between KBr plates.

The starting materials [{Cp*Cr(CO)$_3$}$_2$($\mu,\eta^{1:1}$–P$_4$)] (**1**),[14] NaCp*,[15] NaCp‴,[16] [Cr(CO)$_4$(nbd)][17] were prepared according to literature procedures. For Na[Cp‴Fe(CO)$_2$], K[CpFe(CO)$_2$], K[Cp*Fe(CO)$_2$] K-[Cp'Mo(CO)$_3$], K[CpW(CO)$_3$] and Na[Cp‴W(CO)$_3$] a variation of the instructions for the preparation of the Cp compounds was implied.[18] $[Ph_3C][BF_4]$, $[Ph_3C][B(C_6F_5)_4]$, Ph_3CCl, Ph_2CHCl, $AlCl_3$, $TlPF_6$ and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) are commercially available and were used without further modification.

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^{R}M(CO)$_x$] (M' = Na, K; Cp^R = 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 C_6D_6 capillary. For NMR and IR spectra of the reactions see SI.

For the reaction with Na[Cp‴Fe(CO)$_2$] the solvent was removed from the reaction mixture under reduced pressure affording a mixture of yellow and red solid. By extraction with *n*-hexane a red solution ([{Cp‴Fe(CO)$_2$}$_2$($\mu,\eta^{1:1}$–P$_4$)] (**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)$_2$]: $^{31}P\{^1H\}$ NMR (toluene with C_6D_6 capillary) δ[ppm] = −82.5 (t, $^1J_{AB}$ = 186 Hz, 2P, P$_A$), −324.7 (t, $^1J_{AB}$ = 186 Hz, 2P, P$_B$); **IR** (toluene) $\tilde{\nu}_{CO}$ [cm^{-1}] = 2000 (s), 1990 (s), 1949(s), 1942 (s), 1765 (w).

Reaction with K[CpFe(CO)$_2$]: ^{31}P{^{1}H} NMR (toluene with C_6D_6 capillary) δ[ppm] = −512.6 (s, P_4); **IR** (toluene) $\tilde{\nu}_{CO}$ [cm^{-1}] = 1995 (s), 1952 (w), 1936 (s), 1914 (m), 1874 (s), 1782 (s), 1726 (m, br).

Reaction with K[Cp*Fe(CO)$_2$]: ^{31}P{^{1}H} NMR (toluene with C_6D_6 capillary) δ[ppm] = −512.6 (s, P_4); **IR** (toluene) $\tilde{\nu}_{CO}$ [cm^{-1}] = 1994 (m), 1972 (w), 1959 (w), 1924 (s), 1873 (s), 1755 (m), 1727 (w).

Reaction with K[Cp'Mo(CO)$_3$]: ^{31}P{^{1}H} NMR (toluene with C_6D_6 capillary) δ[ppm] = −95.0 (t, $^1J_{AB}$ = 196 Hz, 2P, P_A), −273.6 (s, 1.2P, [Cp*Cr(CO)$_2$(η^3−P_3)]), −327.2 (t, $^1J_{AB}$ = 196 Hz, 2P, P_B), −522.6 (s, 21.7 P, P_4).

Reaction with K[CpW(CO)$_3$]: ^{31}P{^{1}H} NMR (toluene with C_6D_6 capillary) δ[ppm] = −273.6 (s, 1.2P, [Cp*Cr(CO)$_2$(η^3-P_3)]), −522.8 (s, 21.7 P, P_4).

Reaction with Na[Cp'''W(CO)$_3$]: ^{31}P{^{1}H} NMR (toluene with C_6D_6 capillary) δ[ppm] = −95.0 (t, $^1J_{AB}$ = 196 Hz, 2P, P_A), −273.5 (s, 0.5P, [Cp*Cr(CO)$_2$(η^3−P_3)]), −327.4 (t, $^1J_{AB}$ = 196 Hz, 2P, P_B), −522.2 (s, 2.7P, P_4).

Reactions with organic nucleophiles

Reaction of 1 with NaCp^R: 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. NaCp^R (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 at room temperature. Subsequently, the solvent was removed *in vacuo* yielding a yellow and a brown solid, respectively.

Reaction with NaCp''': ^{1}H NMR (C_6D_6): δ[ppm] = 1.07 (s, 19.9H, Cp*), 1.15 (s, 14.0H, ^{t}Bu), 1.17 (s, 20.6H, ^{t}Bu), 1.25 (s, 22.9H, ^{t}Bu), 1.30 (s, 14.1H, ^{t}Bu), 1.35 (s, 18.4H, ^{t}Bu), 1.36 (s, 18.3H, ^{t}Bu), 1.71 (s, 12.8H, ^{t}Bu), 2.96 (s, 2.4H, CH), 3.09 (s, 3.0H, CH), 3.89 (q, $^1J_{HH}$ = 6.8 Hz, 3.4H, CH), 5.76 (m, 1.0H, CH), 5.96 (t, $^1J_{HH}$ = 1.8 Hz, 2.3H, CH), 6.42 (m, 4.7H, CH); **^{31}P{^{1}H} NMR** (C_6D_6): δ[ppm] = −99.1 (t, $^1J_{PP}$ = 193 Hz, 0.04P), −123.6 to −135.4 (m, 2P, P_A and P_B), −157.8 (m, 0.1P), −269.4 (s, [Cp*Cr(CO)$_2$(η^3-P_3)], 0.3P), −312.4 (dt, $^1J_{MN}$ = 170 Hz, $^1J_{AM}$ = $^1J_{BM}$ = 190 Hz, 1P, P_M), −328.5 (t, $^1J_{PP}$ = 194 Hz, 0.1P), −332.0 (t, $^1J_{PP}$ = 190 Hz, 0.5P), −334.8 (t, $^1J_{PP}$ = 183 Hz, 0.1P), −343.1 (dt, $^1J_{MN}$ = 170 Hz, $^1J_{AN}$ = $^1J_{BN}$ = 206 Hz, 1P, P_N), −520.6 (s, 3P, P_4)

Reaction with NaCp*: ^{31}P{^{1}H} NMR (C_6D_6): δ[ppm] = −269.9 (s, 1P, [Cp*Cr(CO)$_2$(η^3−P_3)]), −520.4 (s, 17P, P_4)

Reaction of 1 with NaCp* for VT NMR experiments: An orange-brown solution of **1** (25 mg, 0.04 mmol, 1.0 eq.) in 2 mL CD_2Cl_2 and a yellow suspension of NaCp* (12 mg, 0.08 mmol, 1.0 eq.) in 2 mL CD_2Cl_2 were cooled to −80 °C. Subsequently, **1** was added to the suspension of NaCp* dropwise, the resulting mixture was transferred to a chilled NMR tube and placed in a tempered NMR spectrometer recording ^{1}H and ^{31}P{^{1}H} NMR spectra in intervals of 20 °C. (see SI)

Reaction of 1 with Ph$_2$CXCl/AlCl$_3$ (X=Ph or H): A colorless solution of 2.0 eq. Ph$_2$CXCl (X=Ph: 10 mg, 0.04 mmol; X=H 0.06 mL of a 1:10 diluted solution in toluene, 0.04 mmol) in toluene (5 mL) was added dropwise to a colorless suspension of 2.0 eq. $AlCl_3$ (5 mg, 0.04 mmol). The solution turned orange immediately and was stirred for 5 min before adding a brownish solution of 1.0 eq. **1** (12 mg, 0.02 mmol) in 5 mL toluene. No immediate color change could be observed and the resulting mixture was stirred overnight during which a color change to green occurred. The solvent was removed *in vacuo* yielding greenish-brown solids.

Reaction with Ph$_2$CHCl/AlCl$_3$: ^{31}P{^{1}H} NMR (CD_2Cl_2): δ[ppm] = 25.4 (t, $^1J_{PP}$ = 273 Hz, 2P), −301.2 (t, $^1J_{PP}$ = 273 Hz, 2P), −522.8 (s, 0.2P, P_4)

Reaction with Ph$_3$CCl/AlCl$_3$: ^{31}P{^{1}H} NMR (CD_2Cl_2): δ[ppm] = 16.2 (t, $^1J_{PP}$ = 238 Hz, 2P), −313.6 (t, $^1J_{PP}$ = 238 Hz, 2P), −522.8 (s, 7.5P, P_4)

Reaction of 1 with [Ph$_3$C][BF$_4$] and subsequent addition of [Cr(CO)$_4$(nbd)]: An orange-brown solution of 1.0 eq. **1** (12 mg, 0.02 mmol) in toluene (5 mL) was added to a yellow suspension of 2.0 eq. [Ph$_3$C][BF$_4$] (12 mg, 0.04 mmol) in toluene (5 mL). No immediate color change could be observed and the reaction mixture was stirred overnight. The solvent was removed from the now greenish brown solution under reduced pressure affording a brownish solid. **^{31}P NMR** (CD_2Cl_2): δ[ppm] = 82.8 (m, 2P), 66.6 (m, 2P), −522.9 (s, P_4); **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ[ppm] = 82.8 (m, 2P), 66.6 (m, 2P), −522.9 (s, P_4)

In a second step the obtained brownish solid was taken up in CH_2Cl_2 (5 mL) and a solution of 1.0 eq. [Cr(CO)$_4$(nbd)] (39 mg, 0.02 mmol) in CH_2Cl_2 (5 mL) was added to the reaction mixture. No immediate color change was observed and the solution was stirred overnight. The solvent was removed *in vacuo* yielding a green solid. **^{31}P{^{1}H} NMR** (CD_2Cl_2) δ[ppm] = −53.9 to −60.6 (m, 4P), −522.1 (s, 4P, P_4).

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