

Electronic Supplementary Information

Reactivity of P₄ butterfly complexes towards NHCs: Generation of a metal-bridged P₂ dumbbell complex

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1. General remarks

All experiments were carried out under an atmosphere of dry argon or nitrogen using glovebox and Schlenk techniques. Residues 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 thf-d₈ and toluene-d₈ were degassed and dried by stirring with Na/K alloy, followed by distillation.

The starting materials [$\{\text{Cp}^{\text{***}}\text{Fe}(\text{CO})_2\}_2(\mu, \eta^{1:1}\text{-P}_4)$] (**A**)^[1], [$\{\text{Cp}^*\text{Cr}(\text{CO})_3\}_2(\mu, \eta^{1:1}\text{-P}_4)$] (**B**)^[2a-d], IMe^[3], IDipp^[4] and KCHPh₂^[5] were prepared according to literature procedures. LiNMe₂ and LiCH₂SiMe₃ are commercially available and were used without further modification.

NMR spectra were recorded at the NMR department of the University Regensburg using a Bruker Advance 300 or 400 spectrometer. Samples are referenced against TMS (¹H) or 85% H₃PO₄ (³¹P) as external standards. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. The spectra were processed using the TopSpin 3.5 software (Bruker) and the WIN-DAISY module of this software was used to perform simulations.^[6]

Mass spectrometry was performed by the MS department of the University Regensburg. ESI-MS spectra were recorded on a Q-TOF 6540 UHD (Agilent) spectrometer. The observed fragments were assigned according to the mass/charge (m/z) ratio and the isotope pattern.

2. Synthesis

Synthesis of [P(IMe)₂][Cp^{***}Fe(CO)₂] (**1**)

A colourless solution of IMe (149.0 mg, 1.2 mmol, 4.0 eq) in 10 mL thf is added to a red solution of **A** (244.3 mg, 0.3 mmol, 1.0 eq) in 10 mL thf. Thereby, the red colour intensified and a red solid is formed. The solution is stirred for one hour and subsequently the solvent is removed under reduced pressure. The orange residue is washed with cold toluene (3 x 10 mL, -30 °C), dissolved again in thf and stored at room temperature. Compound **1** is obtained in the form of dark orange plates suitable for single crystal X-ray diffraction analysis after three days.

Analytical data for **1**

Yield	255.2 mg (0.41 mmol, 68 %).
¹H NMR (thf-d ₈ , 300 K):	δ [ppm] = 1.12 (s, 9H, C ₅ H ₂ ^t Bu ₃), 1.30 (s, 18H, C ₅ H ₂ ⁱ Bu ₃), 2.25 (s, 12H, N-CH ₃), 3.44 (s, 12H, C-CH ₃), 3.93 (s, 2H, C ₅ H ₂ ^t Bu ₃).
³¹P{¹H} NMR (thf-d ₈ , 300 K):	δ [ppm] = -114.9 (s, 1P, [P(IMe) ₂] ⁺).
³¹P NMR (thf-d ₈ , 300 K):	δ [ppm] = -114.9 (s, 1P, [P(IMe) ₂] ⁺).
ESI⁻-MS (dme)	m/z = 345.15 [Fe(CO) ₂ Cp ^{***}] (100%).
ESI⁺-MS (dme)	m/z = 279.18 [P(IMe) ₂] ⁺ (100%).
IR (solid)	$\tilde{\nu}_{\text{CO}}$ [cm ⁻¹] = 1836.63 (m), 1767.95 (m)

Synthesis of $[P(IME)_2][\{Cp^*Fe\}_2(\mu, \eta^{3:3}-P_3)]$ (**2**)

A red solution of **A** (760.6 mg, 0.8 mmol, 1.0 eq) in thf is cooled to -80°C . A -80°C cold solution of IME (198.7 mg, 1.6 mmol, 2.0 eq) in 10 mL thf is added. The mixture is stirred overnight and allowed to reach room temperature. Thereby, the colour changes to reddish-purple. The solvent is removed *in vacuo*. A dark red solution is extracted with toluene (3 x 10 mL) from the residue. The solvent is reduced under reduced pressure and stored at 8°C . Compound **2** can be obtained in the form of dark red blocks suitable for single crystal X-ray diffraction analysis after one week.

Analytical data for **2**

Yield	720.0 mg (0.76 mmol, 95 %).
$^1\text{H NMR}$ (tol- d_8 , 300 K)	δ [ppm] = 1.43 (s, 9H, $C_5H_2^tBu_3$), 1.58 (s, 18H, $C_5H_2^tBu_3$), 1.84 (s, 12H, N- CH_3), 2.88 (s, 12H, C- CH_3), 3.82 (s, 2H, $C_5H_2^tBu_3$).
$^{31}\text{P}\{^1\text{H}\}$ NMR (tol- d_8 , 300 K)	δ [ppm] = 638.6 (d, 2P, $^1J_{AX} = 352.6$ Hz, P_A), -114.2 (s, 1P, $[P(IME)_2]^+$), -348.1 (t, 1P, $^1J_{AX} = 352.6$ Hz, P_X).
$^{31}\text{P NMR}$ (tol- d_8 , 300 K)	δ [ppm] = 638.6 (d, 2P, $^1J_{AX} = 352.6$ Hz, P_A), -114.2 (s, 1P, $[P(IME)_2]^+$), -348.1 (t, 1P, $^1J_{AX} = 352.6$ Hz, P_X).
ESI⁻-MS (dme)	$m/z = 671.24$ $[\{Cp^*Fe\}_2(\mu, \eta^{3:3}-P_3)]^-$ (100%).
ESI⁺-MS (dme)	$m/z = 279.18$ $[P(IME)_2]^+$ (100%).
Elemental Analysis	calcd. for $[C_{48}H_{82}N_4P_4Fe_2]$ (950.78 g·mol $^{-1}$) C 60.64, H 8.69, N 5.89; found: C 61.08, H 8.05, N 5.97.

Synthesis of $[P(IME)_2][Cr(CO)_3Cp^*]$ (**3**) and $[\{Cp^*Cr(CO)_2\}(\eta^2-P_2IME_2)][Cr(CO)_3Cp^*]$ (**4**)

An orange-brown solution of **B** (66 mg, 0.1 mmol, 1.0 eq.) in thf (5 mL) and a colorless solution of IME (30 mg, 0.24 mmol, 2.4 eq.) in thf (5 mL) are cooled to -90°C . Slowly, the solution of IME is added to the solution of **B** while stirring. The solution is brought to room temperature overnight and hereby a color change to a dark brown solution and the formation of yellow precipitate is observed. The brown solution is filtered via a canula, diluted with additional 5 mL of thf and layered with n-pentane. After a few days two kinds of crystals suitable for single crystal X-ray diffraction are obtained: small yellowish blocks of **3** and dark brown blocks of **4**.

Crystalline Yield of the mixture of **3 and **4**** 14.0 mg

For product ratio of 3:1 (as found in by NMR spectroscopic studies): **3**: 11.2 mg (0.009 mmol, 9%).

4: 2.8 mg (0.003 mmol, 3%).

Analytical data for **3**

$^1\text{H NMR}$ (thf- d_8 , 300K) δ [ppm] = 1.83 (s, 15H, Cp*), 2.24 (s, 12H, N- CH_3), 3.44 (s, 12H, C- CH_3).

^{31}P NMR (thf- d_8 , 300K)	δ [ppm] = -114.8 (s, 1P, [$\underline{\text{P}}(\text{IMe})_2$] $^+$).
$^{31}\text{P}\{^1\text{H}\}$ NMR (thf- d_8 , 300K)	δ [ppm] = -114.8 (s, 1P, [$\underline{\text{P}}(\text{IMe})_2$] $^+$).
ESI-MS (CH_3CN)	m/z = 271.04 [$\text{Cr}(\text{CO})_3\text{Cp}^*$] $^-$ (100%).
ESI $^+$ -MS (CH_3CN)	m/z = 279.18 [$\text{P}(\text{IMe})_2$] $^+$ (100%).

Analytical data for 4

^1H NMR (thf- d_8 , 300K)	δ [ppm] = 1.83 (s, 15H, Cp *), 2.18 (s, 6H, N- $\underline{\text{CH}}_3$), 2.24 (s, 12H, N- $\underline{\text{CH}}_3$), 3.85 (s, 6H, C- $\underline{\text{CH}}_3$), 4.06 (br, s, 6H, C- $\underline{\text{CH}}_3$).
^{31}P NMR (thf- d_8 , 300K)	δ [ppm] = -52.0 (d, $^1J_{\text{PP}}$ = 388 Hz, 1P), -82.1 (d, $^1J_{\text{PP}}$ = 388 Hz, 1P).
$^{31}\text{P}\{^1\text{H}\}$ NMR (thf- d_8 , 300K)	δ [ppm] = -52.0 (d, $^1J_{\text{PP}}$ = 388 Hz, 1P), -82.1 (d, $^1J_{\text{PP}}$ = 388 Hz, 1P).
ESI-MS (CH_3CN)	m/z = 271.04 [$\text{Cr}(\text{CO})_3\text{Cp}^*$] $^-$ (100%).
ESI $^+$ -MS (CH_3CN)	m/z = 533.20 [$\{\text{Cp}^*\text{Cr}(\text{CO})_2\}(\eta^2\text{-P}_2\text{IMe}_2)$] $^+$ (100%).

3. NMR spectroscopic experiments

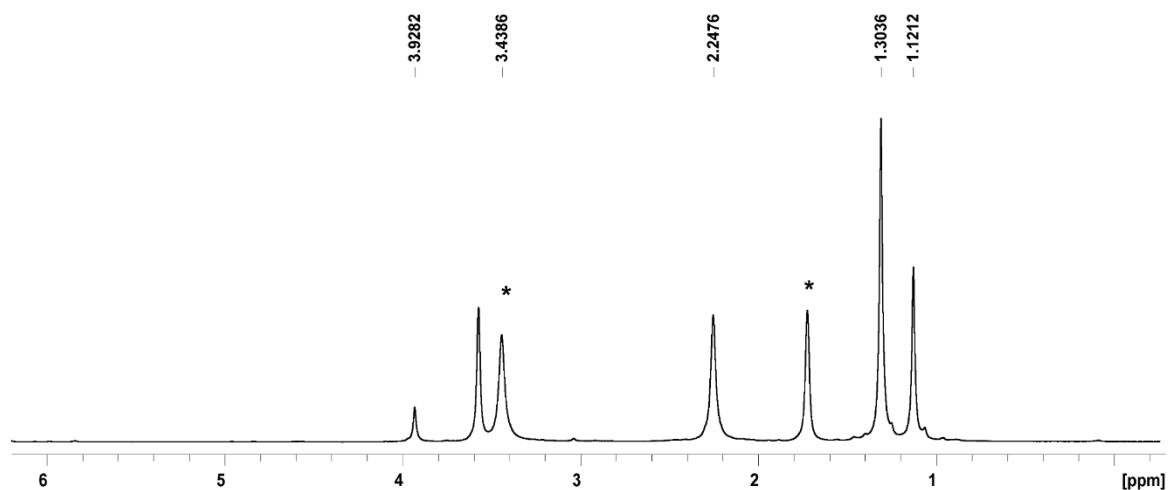


Figure S1. ^1H NMR spectrum of 1 (recorded in thf- d_8 * at 300 K).

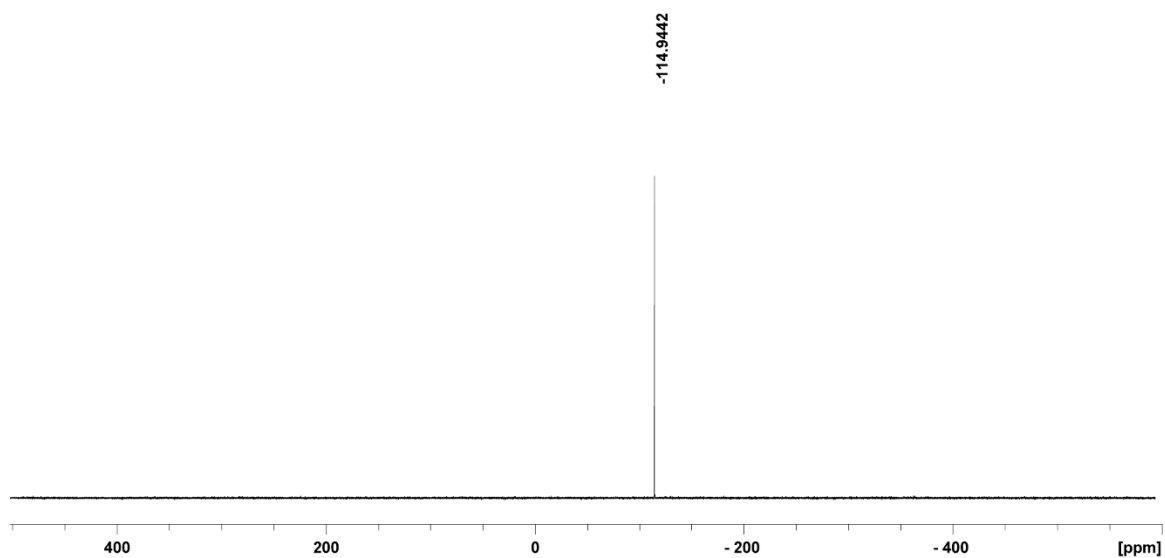


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** (recorded in thf-d_8 at 300 K).

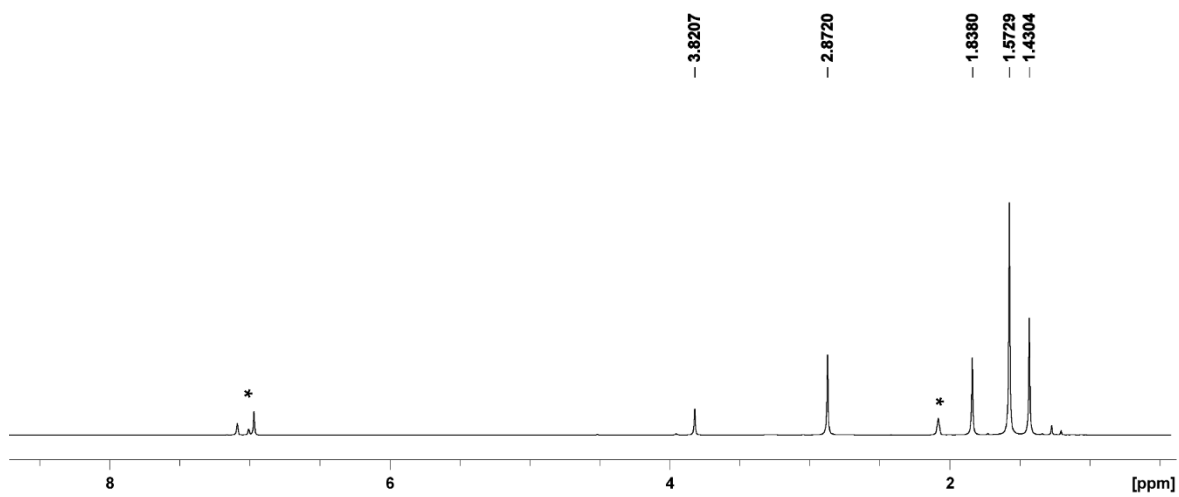


Figure S3. ^1H NMR spectrum of **2** (recorded in tol-d_8^* at 300 K).

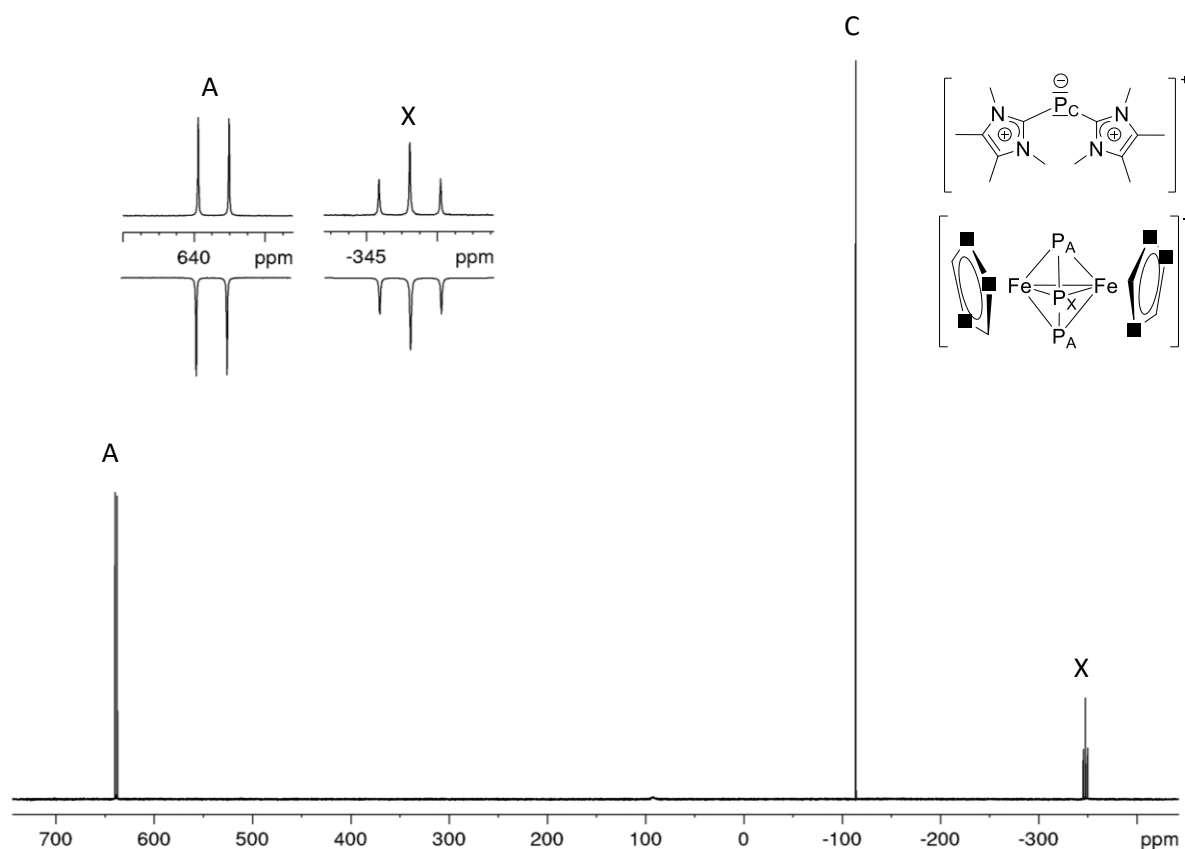


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** (recorded in tol-d_8 at 300 K); inset: comparison of experimental (top) and simulated (bottom) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the anionic entity of **2**.

The simulation of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the anionic entity of **2** was carried out on the basis of an A_2X spin system with a C_1 symmetry.

Table S1. Experimental and simulated values for the chemical shifts and coupling constants in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** (recorded in tol-d_8 at 300 K).

experimental values				simulated values			
δ_{A}	638.6 ppm	$^1J_{\text{AX}}$	353 Hz	δ_{A}	638.6 ppm	$^1J_{\text{AX}}$	352.6 Hz
δ_{X}	-384.1 ppm			δ_{X}	-348.1 ppm		

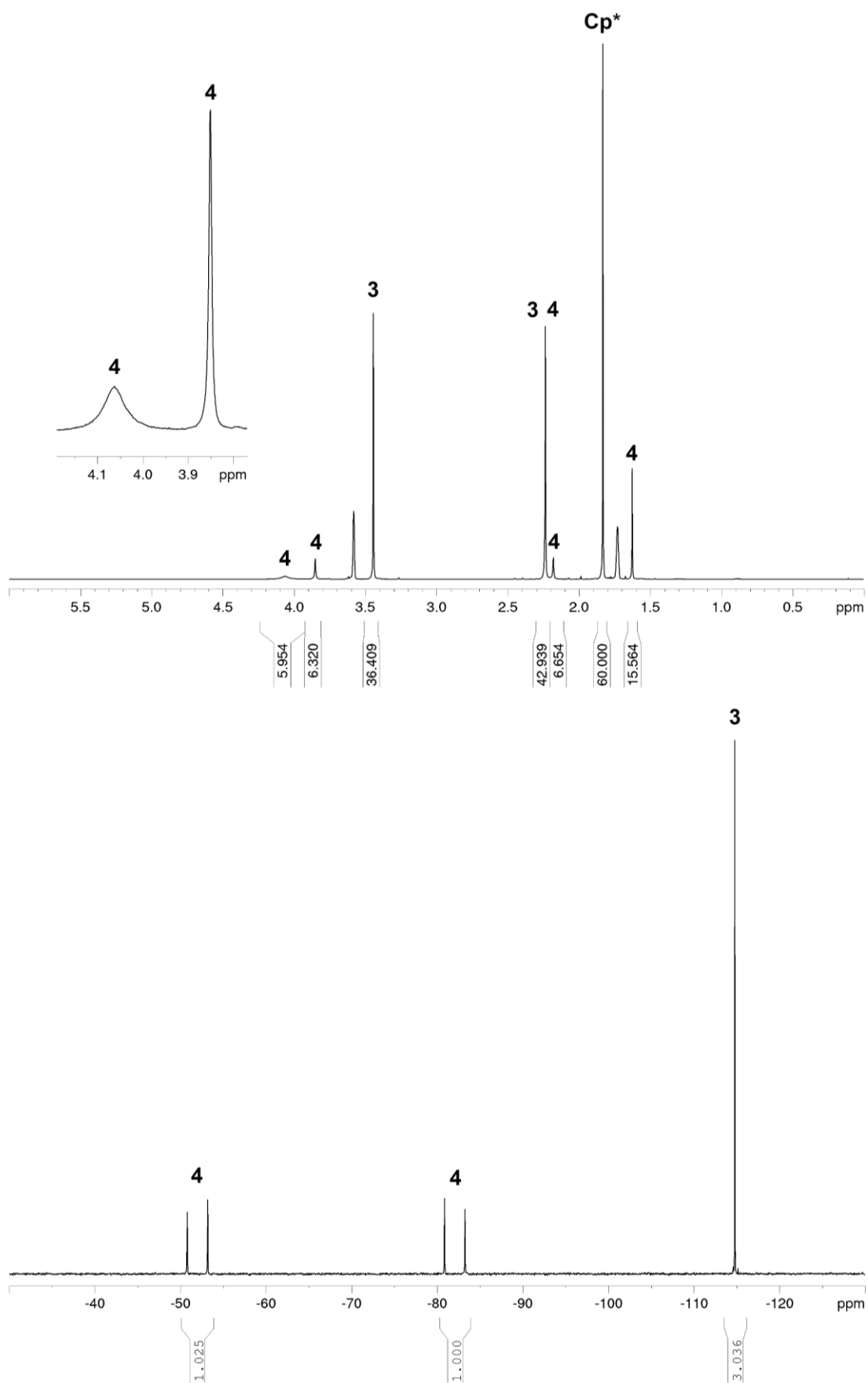


Figure S5. Experimental ¹H NMR (top) and ³¹P NMR (bottom) spectrum of the crystal mixture of **3** and **4** (ratio 3/1, recorded in thf-d₈ at 300 K).

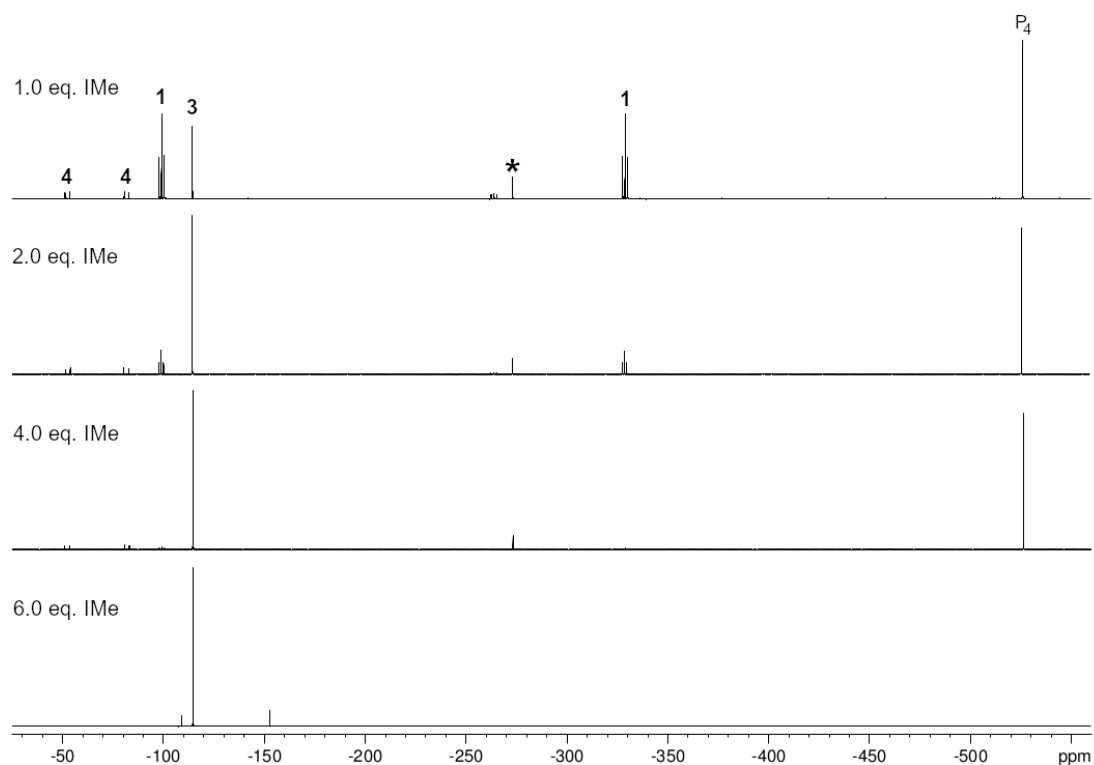
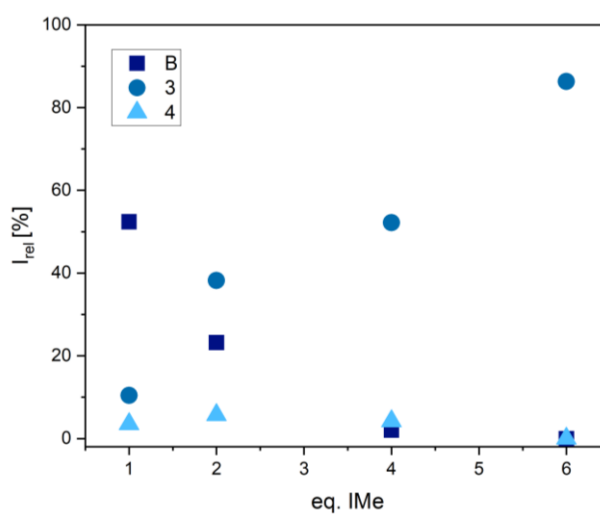


Figure S6. Experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction solution obtained from the reaction of **B** with various equivalents of IMe in thf (recorded with C_6D_6 capillary at 300 K; peak marked with asterisk is attributed to the common side product $[\text{Cp}^*\text{Cr}(\text{CO})_2(\eta^3\text{-P}_3)]$).

Table S2. Relative integrals of the signals obtained from the experimental ^{31}P NMR spectra (Fig. S6) of reactions of **B** with varying equivalents of IMe (recorded in thf with C_6D_6 capillary at 300 K).

eq. IMe	relative integrals I_{rel}		
	B	3	4
1.0	52.4%	10.4%	3.5%
2.0	23.2%	38.2%	5.7%
4.0	2.0%	52.2%	4.2%
6.0*	-	86.3%	-

* formation of reasonable amounts of side products is detected.



4. DFT calculations

The geometry of the molecules has been optimized using the TURBOMOLE program package^[7a-d] at the RI-[8a-b]B3LYP^[9a-e] level together with the def2-TZVP basis set for all atoms.^[10a-d] To speed up the calculations, the Coulomb part was evaluated by using the Multipole Accelerated Resolution of Identity method (MARI-J)^[11a-b] along with optimized auxiliary basis sets on all atoms.^[12] The natural bond orbital analysis (NBO) has been performed with NBO 6.0^[13] on the wave function obtained at the B3LYP/def2-TZVP level of theory. The topological analysis of the electron density obtained from the DFT calculations, according to the Atoms in Molecules theory^[14a-b] has been performed with the MultiWFN program (version 3.6).^[15a-b] The reaction energies have been calculated using the SCF energies without further corrections.

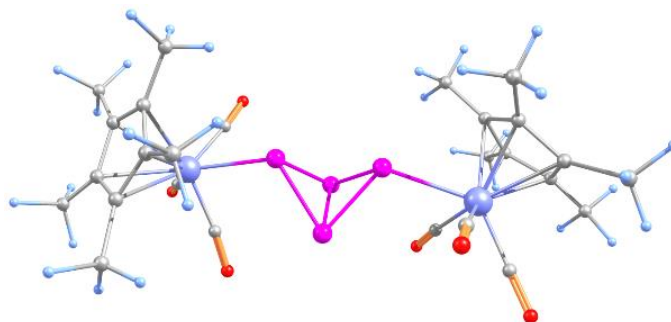
In order to clarify, why the reaction of **4** with nucleophiles leads to the cleavage of the Cr–P bonds, DFT calculations have been performed by Dr. Gábor Balázs (University Regensburg) for the uncoordinated P₄ butterfly ligand [(Cp*Cr(CO)₃)₂(μ,η¹⁻¹-P₄)] (**1**) on the BP86/def2-TZVP level. The calculations show that the homolytic cleavage of one Cr–P bond in **1** leads to a spontaneous dissociation of the second Cp*Cr(CO)₃ fragment which results in the formation of two Cp*Cr(CO)₃ radicals and P₄ with an endothermic dissociation energy of 67.47 kJ·mol⁻¹. With a dissociation energy of 142.91 kJ·mol⁻¹ the dissociation of the iron analogue [(Cp^{''}Fe(CO)₂)₂(μ,η¹⁻¹-P₄)] into two Cp^{''}Fe(CO)₂ radicals and P₄ is considerably more endothermic. Consequently, the assumption that the Fe–P bond in **A** is more stable than the corresponding Cr–P bond in **B** based on the different reactivities towards Grignard reagents, could be confirmed. Moreover, [(Cp^{''}Cr(CO)₃)₂(μ,η¹⁻¹-P₄)], the hypothetical Cp^{''} derivative of **B**, possesses an even less stable P–Cr bond with a corresponding dissociation energy of 32.64 kJ·mol⁻¹. Consequently, this compound is expected to be even more likely to dissociate in the presence of a nucleophile.

Table S3. Total SCF energies of **A**, **B**, [Cp^{''}Cr(CO)₃]₂P₄ and its corresponding fragments.

Compound	Total SCF energies [Hartree]
[Cp ^{''} Fe(CO) ₂] ₂ P ₄	-5678.390385
[Cp*Cr(CO) ₃] ₂ P ₄	-4916.068238
[Cp ^{''} Cr(CO) ₃] ₂ P ₄	-5466.561083
Cp ^{''} Fe(CO) ₂	-2156.323069
Cp*Cr(CO) ₃	-1775.176361
Cp ^{''} Cr(CO) ₃	-2050.429417
P ₄	-1365.689817

Table S4. Cartesian coordinates of the optimized geometry of **B** at the B3LYP/def2-TZVP level (E = -4916.068238 a.u.).

Atom	x	y	z
Cr	1.606012700	-2.263775500	-2.754572600
Cr	-1.818973700	3.037472000	1.649977500
P	0.637885700	-0.911879400	-0.792755700
P	-0.659942400	0.924895200	0.753211700
P	-1.164431100	0.273110500	-1.344413500
P	0.722629000	1.334948800	-0.942681700
C	-0.050459100	-2.958632400	-2.318251500

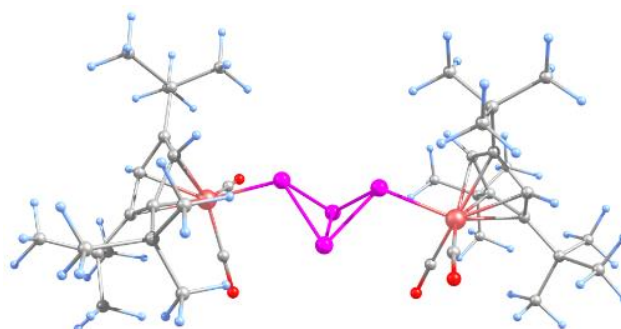


C	0.928419700	-2.601260400	-4.421549800
C	1.518555200	-0.538422500	-3.423369300
C	-0.008630500	3.160450600	2.003689200
C	-1.519590800	4.806641000	1.285936700
C	-2.214663300	3.064347000	-0.159665100
O	-1.064861100	-3.480493800	-2.080377100
O	0.499967800	-2.826933000	-5.481850500
O	1.538260200	0.502666100	-3.944276800
O	1.109933500	3.296580800	2.300837900
O	-1.329238500	5.935280300	1.065409600
O	-2.552087800	3.175366400	-1.268465600
C	3.858914800	-2.121168600	-2.658089800
C	3.469976100	-3.218889800	-3.494835900
C	2.732516400	-4.157164300	-2.689183500
C	2.673571700	-3.634152200	-1.350255800
C	3.389097200	-2.388923300	-1.330603700
C	-3.594843500	3.740146800	2.785613200
C	-2.525124700	3.436175700	3.699900300
C	-2.245904000	2.028583200	3.595807900
C	-3.154425200	1.468052900	2.634655100
C	-3.969620300	2.527772100	2.117929300
C	4.742547100	-0.978993200	-3.061013500
H	5.801357600	-1.235550600	-2.892712900
H	4.526890700	-0.071964200	-2.482466100
H	4.628678400	-0.730850600	-4.123603900
C	3.903138600	-3.424599300	-4.915903100
H	4.892144500	-3.910534600	-4.943235400
H	3.987600400	-2.474684400	-5.459181500
H	3.206162700	-4.064541700	-5.470883900
C	2.249757600	-5.506435800	-3.130307500
H	3.036544000	-6.264576900	-2.982248000
H	1.979784900	-5.515744000	-4.193959500
H	1.368994200	-5.830480700	-2.561459600
C	2.111966200	-4.325846100	-0.144871200
H	2.910332500	-4.847009600	0.408351000
H	1.357246000	-5.073261900	-0.419512500
H	1.642072100	-3.612315900	0.545907300
C	3.738141600	-1.603598000	-0.105188800
H	4.636847100	-2.033811300	0.367724900

H	2.932210200	-1.620269600	0.640756700
H	3.955744300	-0.553942900	-0.338076900
C	-4.308748300	5.053799000	2.667473800
H	-5.167311200	5.081136000	3.358305800
H	-4.695890400	5.218917900	1.653927800
H	-3.657838300	5.900690000	2.917151100
C	-1.919538800	4.384399400	4.691007500
H	-2.493235600	4.376262700	5.632578200
H	-1.914480600	5.416437600	4.317828800
H	-0.884062400	4.114105600	4.933801000
C	-1.293443500	1.241024500	4.443964300
H	-1.826320200	0.764922700	5.283255400
H	-0.506643100	1.876566700	4.869118000
H	-0.805656400	0.443569300	3.866474900
C	-3.338970500	0.008919200	2.357372800
H	-4.002835000	-0.432690800	3.119336600
H	-2.389027900	-0.541528700	2.387938900
H	-3.796200400	-0.168093900	1.376029000
C	-5.120729700	2.365963800	1.171123900
H	-6.041980900	2.123279400	1.725735300
H	-4.946745000	1.556842000	0.450634800
H	-5.311446700	3.283694500	0.601055700

Table S5. Cartesian coordinates of the optimized geometry of **A** at the B3LYP/def2-TZVP level ($E = -5678.390385$ a.u.).

Atom	x	y	z
Fe	3.6563096	-0.0573871	-0.5344296
Fe	-3.5734605	0.0642978	-0.4911500
P	1.4346193	-0.0654399	0.2647336
P	0.0423094	-1.0594926	-1.1801880
P	0.0415403	1.1307841	-1.0388112
P	-1.3489100	-0.0406703	0.2657766
O	2.8109966	0.6288459	-3.2347408
O	3.3927000	-2.8855592	-1.1742666
O	-3.3668258	2.9682208	-0.5831879
O	-2.6867526	-0.1596906	-3.2559047
C	5.5102127	1.0350403	-0.6010401
C	4.5086423	1.8167075	0.1559351
C	4.1304033	0.9963559	1.2720522
C	4.8289777	-0.2409639	1.2718196



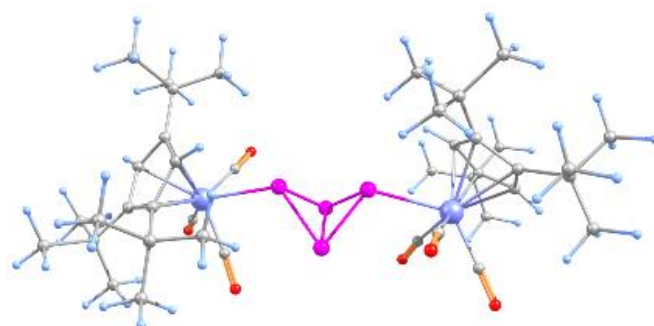
C 5.6617437 -0.2020968 0.1037312
C -4.7127112 -1.7776976 -0.4803460
C -5.6180990 -0.6223178 -0.6132905
C -5.3989513 0.1760080 0.5583415
C -4.4397767 -0.4243692 1.4361342
C -4.0204704 -1.6087487 0.7701563
C 6.4837770 1.3450573 -1.7587498
C 7.7968236 1.8612014 -1.1138994
C 6.0084302 2.3725379 -2.7996436
C 6.8180991 0.0549650 -2.5451511
C 3.4730836 -1.7579433 -0.9018176
C 3.1198023 0.3824773 -2.1415637
C -3.4183000 1.8080024 -0.5349206
C -3.0194488 -0.0880064 -2.1445757
C 4.0139968 3.2765072 0.0584701
C 5.2192597 4.2314600 0.2340569
C 3.2505116 3.6038173 -1.2412143
C 3.0364269 3.5865582 1.2161150
C 4.8767901 -1.2604866 2.4029248
C 5.7989346 -0.6650447 3.4980009
C 3.4825907 -1.5096892 3.0051671
C 5.4728452 -2.6007301 1.9365130
C -4.5625208 -3.1191714 -1.2285756
C -5.5495885 -4.1136225 -0.5620716
C -4.8311948 -3.0913229 -2.7429043
C -3.1341998 -3.6854571 -1.0509118
C -6.7373342 -0.2551977 -1.6128545
C -7.8199530 -1.3606072 -1.6060930
C -7.4438476 1.0464173 -1.1671987
C -6.2385368 0.0039946 -3.0497165
C -4.1407382 0.0091335 2.8667694
C -5.4366332 -0.2090204 3.6878872
C -3.7484030 1.4975101 2.9384466
C -3.0170797 -0.8418571 3.4844882
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H 5.8471505 3.3681932 -2.3737814
H 5.0870636 2.0499933 -3.3009071
H 7.3352290 -0.6948350 -1.9324396
H 7.4898786 0.3059170 -3.3783840
H 5.9127854 -0.4046799 -2.9636918
H 5.9367037 4.1649204 -0.5919544
H 5.7572355 4.0176707 1.1692580
H 4.8615185 5.2707712 0.2795022
H 2.9807581 4.6707130 -1.2462119
H 2.3195471 3.0230693 -1.2954248
H 3.8271194 3.4015196 -2.1467764
H 2.6899265 4.6250201 1.1179420
H 3.5149461 3.4894502 2.2012933
H 2.1487486 2.9386790 1.1871007
H 5.8911864 -1.3700029 4.3377614
H 5.3939735 0.2796575 3.8877167
H 6.8071465 -0.4675789 3.1056735
H 2.8002232 -1.9516453 2.2666923
H 3.0202808 -0.5828058 3.3718845
H 3.5635348 -2.2006666 3.8573883
H 5.5142523 -3.3004139 2.7837633
H 6.4993007 -2.4831566 1.5600557
H 4.8658777 -3.0650574 1.1481827
H -6.5934491 -3.7909561 -0.6688380
H -5.3363035 -4.2194209 0.5111276
H -5.4500268 -5.1048754 -1.0292124
H -5.8597797 -2.8098966 -2.9903965
H -4.6679604 -4.1010278 -3.1473749
H -4.1449514 -2.4133092 -3.2660181
H -3.0469792 -4.6213463 -1.6207549
H -2.8991709 -3.9243773 -0.0056567
H -2.3715230 -2.9883253 -1.4236062
H -8.6706415 -1.0485071 -2.2299937
H -8.1946882 -1.5367034 -0.5871796
H -7.4536480 -2.3146521 -2.0012323
H -8.2306953 1.2896249 -1.8949907

H	-6.7516595	1.8996080	-1.1353807
H	-7.9239280	0.9427621	-0.1835729
H	-5.6870027	-0.8376556	-3.4757343
H	-5.5799140	0.8824708	-3.0725129
H	-7.0992093	0.2087608	-3.7045329
H	-5.7591044	-1.2596361	3.6487168
H	-6.2610666	0.4145341	3.3131417
H	-5.2629214	0.0557806	4.7415912
H	-3.6225188	1.8021326	3.9881379
H	-4.5180015	2.1450145	2.4944692
H	-2.8014818	1.6799189	2.4124878
H	-3.2899000	-1.9071261	3.5191295
H	-2.8312844	-0.5145814	4.5179538
H	-2.0787274	-0.7395847	2.9208763

Table S6. Cartesian coordinates of the optimized geometry of $[\text{Cp}^{\text{III}}\text{Cr}(\text{CO})_3\text{P}_4]$ at the B3LYP/def2-TZVP level ($E = -5678.390385$ a.u.).

Atom	x	y	z
Cr	3.1458758	-2.5049025	-0.4663258
Cr	-2.1239157	3.1003545	-1.2984781
P	1.2402315	-0.7813435	-0.1712300
P	-0.6928364	1.0784640	-0.4857389
P	0.1531819	-0.3003237	-2.0558393
P	1.4345590	1.2384199	-1.1461223
C	1.5627692	-3.3674565	-0.8841603
C	3.6487683	-3.4331418	-1.9645366
C	3.4436006	-1.1685455	-1.7046147
C	-0.6727071	3.7303537	-0.3437112
C	-1.5845611	4.5505345	-2.2768021
C	-1.5767303	2.2681390	-2.8584445
O	0.6098060	-3.9674480	-1.1817343
O	3.9672273	-3.9880837	-2.9378351
O	3.7331548	-0.4045538	-2.5375284
O	0.2057572	4.2260891	0.2414095
O	-1.2096895	5.4746789	-2.8804256
O	-1.2861639	1.8377359	-3.9011770
C	4.9866375	-1.9015318	0.7141117
C	4.9906514	-3.2973135	0.4480604
C	3.8866115	-3.9598429	1.0926161



C 3.1361783 -2.9088086 1.7851934
C 3.8236442 -1.6773133 1.5013358
C -4.2957576 3.5472909 -1.7021866
C -3.8286218 4.2524040 -0.5341020
C -3.4718730 3.3461176 0.5045819
C -3.6661473 2.0522588 -0.0478172
C -4.1894525 2.1229575 -1.3843154
C 6.1250390 -0.9217631 0.4552710
C 3.8748608 -5.5046179 1.1491797
C 2.0096806 -2.9434863 2.8497147
C -4.9572461 4.3215865 -2.8679292
C -3.2280354 3.6820205 1.9719444
C -4.7480707 0.8299438 -2.0231835
C 1.7551935 -1.5234999 3.4095737
H 1.4119182 -0.8285698 2.6308228
H 0.9633173 -1.5836691 4.1697715
H 2.6485492 -1.1042970 3.8947821
C 2.4744793 -3.7936323 4.0569600
H 1.7427470 -3.6946495 4.8724318
H 2.5617228 -4.8597016 3.8222681
H 3.4473134 -3.4450611 4.4336897
C 0.6496454 -3.4547145 2.3308930
H 2.0366689 -5.9173171 2.3082965
H -0.0570381 -3.5235362 3.1719524
H 0.2279385 -2.7519704 1.5993424
C 2.4970152 -6.1601672 1.3455548
H 1.8006081 -5.8794457 0.5443715
H 2.6165879 -7.2531353 1.3124508
H 0.7084017 -4.4394140 1.8604301
C 4.8154725 -5.9220346 2.3111562
H 4.4775000 -5.5333043 3.2793007
H 4.8572682 -7.0194167 2.3796094
H 5.8370203 -5.5539609 2.1384089
C 4.4532269 -6.1209447 -0.1454723
H 5.4791294 -5.7944156 -0.3584641
H 4.4838558 -7.2140705 -0.0320310
H 3.8286485 -5.8943521 -1.0180371
C 5.6351434 0.5371900 0.4393518
H 4.9183964 0.7211529 -0.3709223

H	5.1598458	0.8173485	1.3902028
H	6.4903405	1.2122063	0.2908639
C	6.8648887	-1.2343615	-0.8583658
H	7.7161079	-0.5481662	-0.9757653
H	7.2668067	-2.2575721	-0.8668044
H	6.2122674	-1.1132293	-1.7320879
C	7.1185525	-1.0940123	1.6344387
H	6.6346040	-0.8755961	2.5971567
H	7.5140322	-2.1190428	1.6761308
H	7.9671375	-0.4044435	1.5135735
H	3.5133439	-0.7059770	1.8693087
H	5.7517304	-3.8068385	-0.1333303
C	-2.7312710	5.1275549	2.1531628
H	-3.4537139	5.8577219	1.7610677
H	-2.6005931	5.3408669	3.2239587
H	-1.7661515	5.2947016	1.6583172
C	-2.2351470	2.7086201	2.6319423
H	-2.1519551	2.9359316	3.7049585
H	-2.5628407	1.6636967	2.5404885
H	-1.2333223	2.7878087	2.1908345
C	-4.6015947	3.5434616	2.6797538
H	-5.3470280	4.2200903	2.2377731
H	-4.9862312	2.5163715	2.6049143
H	-4.5011385	3.7943823	3.7461842
C	-4.8231405	0.8000474	-3.5591474
H	-3.8350916	0.9349920	-4.0173385
H	-5.1994733	-0.1845662	-3.8729616
H	-5.5070641	1.5492572	-3.9705221
C	-6.1743768	0.6306994	-1.4440866
H	-6.6074329	-0.2997535	-1.8407628
H	-6.1454396	0.5519489	-0.3479966
H	-6.8469806	1.4572761	-1.7052141
C	-3.9100280	-0.4014464	-1.6100415
H	-3.9050422	-0.5726139	-0.5259530
H	-4.3442019	-1.2989169	-2.0730517
H	-2.8693053	-0.3185380	-1.9494429
C	-6.4643483	3.9686467	-2.9151006
H	-6.9700814	4.6210894	-3.6421719
H	-6.6482084	2.9324307	-3.2190837

H -6.9367698 4.1258279 -1.9344364
 C -4.8867465 5.8456976 -2.6120569
 H -3.8538214 6.2098876 -2.5346934
 H -5.3531637 6.3663472 -3.4603085
 H -5.4348262 6.1382127 -1.7050329
 C -4.3133721 4.0828293 -4.2502763
 H -3.3055142 4.5136497 -4.2925940
 H -4.2368122 3.0260827 -4.5156991
 H -4.9189651 4.5807531 -5.0227304
 H -3.4755957 1.1249065 0.4823527
 H -3.7900245 5.3317937 -0.4459988

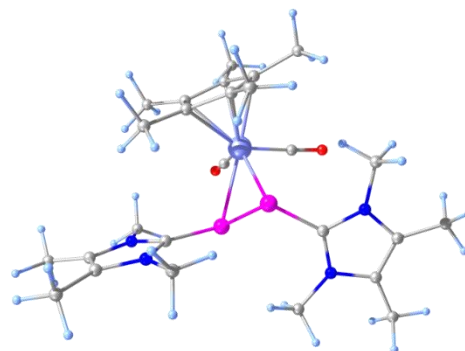


Table S7. Cartesian coordinates of the optimized geometry of **4** at the B3LYP/def2-TZVP level ($E = -3110.31259080507$ a.u.).

Atom	x	y	z	Atom	x	y	z
Cr	2.169143400	0.017355100	1.185933300	H	1.574044000	1.563552900	-2.466059400
P	-0.061701000	-0.001879400	2.237046400	H	0.275974300	1.683664200	-3.670178800
P	-0.052956500	0.034879300	0.083201200	H	0.328345700	0.310336400	-2.554672800
N	-1.453430900	2.666767800	0.034608300	C	2.756086700	1.578064000	2.799516300
N	-0.250691400	-2.444639900	3.649602500	C	-2.906015100	-4.632987000	2.370336000
N	-1.728437900	-2.410116400	2.078091400	H	-3.925860900	-4.264946900	2.508870000
N	-0.322523100	2.118529900	-1.721696400	H	-2.794044400	-5.523257400	2.985616600
O	2.516394500	-2.829156100	2.010026900	H	-2.799395600	-4.937252800	1.326689600
O	2.776562500	-1.100895200	-1.528502600	C	2.644441100	2.234659500	1.542602000
C	-0.630184900	1.710997500	-0.462395300	C	-2.605639500	-1.993149500	0.989414000
C	-0.706333600	-1.700086000	2.614728100	H	-2.659084200	-0.910852700	0.964051000
C	-1.647815600	3.678659300	-0.905401500	H	-3.599075600	-2.397227300	1.168941600
C	-0.933144800	3.334277600	-2.009191600	H	-2.234823300	-2.348836800	0.029151700
C	-1.886860100	-3.618712600	2.754836500	C	-0.768343600	4.036517200	-3.311380700
C	-0.958814700	-3.635480100	3.748129600	H	0.282179400	4.234754500	-3.535477300
C	4.283693500	0.611921100	1.364548700	H	-1.286223100	4.993030100	-3.287857800
C	3.754509300	0.566798600	2.688876500	H	-1.183180500	3.459145600	-4.141399100
C	2.351721000	-1.730017900	1.687230600	C	4.312787700	-0.249574800	3.815947000
C	-2.502398000	4.866512000	-0.634008100	H	3.582732600	-0.410604500	4.609077600
H	-3.534581100	4.583333600	-0.414188400	H	5.167509400	0.263540700	4.267544000
H	-2.519857800	5.521844700	-1.502137400	H	4.661080300	-1.226251200	3.481415600
H	-2.132113100	5.449439000	0.212896900	C	2.080649600	2.009602700	4.064036900
C	2.512417900	-0.677422900	-0.488803500	H	1.063819000	2.361233500	3.891222800
C	-2.126323200	2.672529000	1.327530600	H	2.639662300	2.831366200	4.523420300
H	-1.772011300	1.837343500	1.922046100	H	2.031093400	1.206542500	4.798515200
H	-3.204830200	2.591707800	1.185477000	C	3.975123900	2.177611900	-0.695200100
H	-1.908420900	3.601339900	1.853514100	H	4.307442100	1.390528100	-1.371580800
C	3.594921600	1.647841200	0.654631900	H	4.798563900	2.892607200	-0.601013900
C	0.783475800	-2.047808000	4.596230500	H	3.148395000	2.705366200	-1.171317800
H	1.278478200	-1.157856300	4.223835800	C	5.477269000	-0.150253100	0.872199400
H	1.517779500	-2.843966500	4.695111500	H	5.546256700	-1.136540400	1.330642400
H	0.337094200	-1.834084600	5.568112800	H	6.400095300	0.387504100	1.112593900
C	-0.652263900	-4.662916000	4.779351900	H	5.455617000	-0.291799300	-0.208060400
H	0.362267600	-5.053087500	4.667355600	C	1.842381400	3.473114400	1.280979500
H	-1.340604700	-5.500797300	4.692767300	H	1.577014600	3.576675700	0.229113200
H	-0.745234700	-4.261835800	5.791402300	H	2.414651200	4.365005400	1.557230900
C	0.518711300	1.376589300	-2.657150700	H	0.922010300	3.492217300	1.865208000

The AIM analysis of the electron density in **4** allowed the detection of bond critical points (BCPs) along the P–P and Cr–P bonds (**Figure S7**). The locations of BCPs corresponding to the Cr–P bonds point towards a metallacyclopropane-like

bonding. However, the relatively high ellipticity at the BCPs 1-3 (P₂Cr core) indicates a deformation of the electron density in this plane, hence the presence of a P–P double bond.

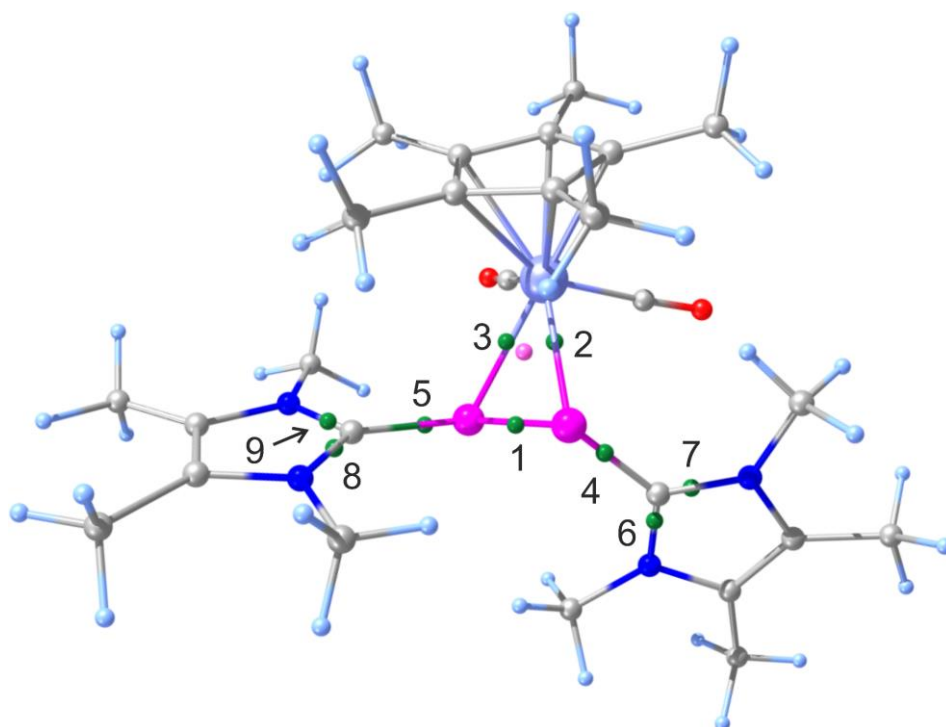


Figure S7. Locations and labeling of selected Bond Critical Points (BCP, green) and Ring Critical Points (RCP, violet) in the electron density of **4**.

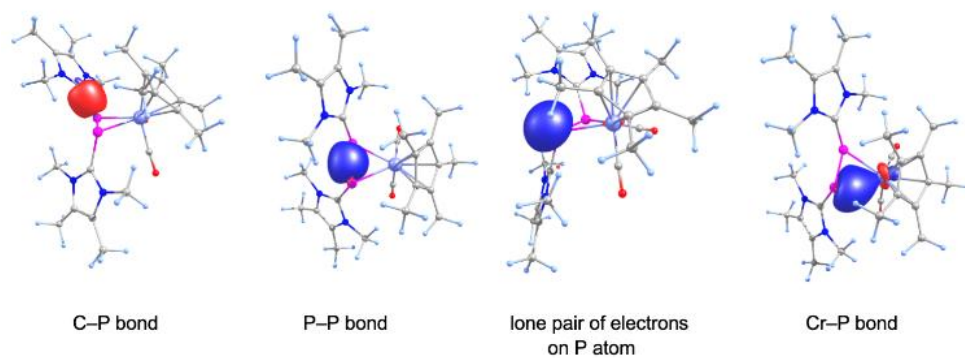
Table S8. Properties of selected critical points in the electron density of **4**. $\rho(r)$ = electron density at CP; $\nabla^2\rho(r)$ = Laplacian of electron density; $H(r)$ = energy density; $G(r)$ = Lagrangian kinetic energy; $V(r)$ = potential energy density; $\epsilon(r)$ = ellipticity of electron density at CP ($\epsilon(r) = [\lambda_1(r)/\lambda_2(r)] - 1$; where λ_1 and λ_2 are the lowest and the second lowest eigenvalues of Hessian matrix of ρ , respectively); $\eta(r)$ = eta index ($\eta(r) = |\lambda_1(r)|/\lambda_3(r)$, where λ_1 and λ_3 are the lowest and the highest eigenvalues of Hessian matrix of ρ , respectively); Bond degree, $BD = H(\text{BCP})/\rho(\text{BCP})$ (the more positive the BD, the weaker the interaction).

	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$G(r)$	$V(r)$	$ V /G$	$\epsilon(r)$	$\eta(r)$	BD (H/R)
BCP-1	0.122	-0.145	-0.069	0.033	-0.101	3.118	0.399	1.548	-0.566
BCP-2	0.059	0.098	-0.016	0.040	-0.056	1.390	0.331	0.263	-0.265
BCP-3	0.055	0.117	-0.013	0.042	-0.055	1.306	0.334	0.182	-0.235
BCP-7	0.331	-1.009	-0.511	0.259	-0.769	2.975	0.224	1.962	-1.542
BCP-6	0.330	-1.002	-0.505	0.254	-0.759	2.985	0.223	1.972	-1.532
BCP-4	0.142	0.003	-0.119	0.119	-0.238	1.993	0.185	0.537	-0.838
BCP-5	0.141	0.001	-0.117	0.118	-0.235	1.998	0.234	0.551	-0.835
BCP-8	0.329	-0.998	-0.502	0.253	-0.755	2.987	0.216	1.968	-1.528
BCP-9	0.329	-1.008	-0.499	0.247	-0.746	3.020	0.212	1.997	-1.519
RCP	0.051	0.114	-0.011	0.040	-0.051	1.284	-	-	-

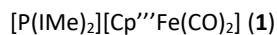
To gain further insight in the electronic structure of **4**, the compound has been investigated by DFT calculations at the B3LYP/def2-TZVP level. The natural population analysis (NPA) shows that the Cr atom is negatively charged (-0.86), while the Cp* ligand and the CO groups are slightly positively charged (0.15 and 0.36, respectively) resulting in an overall negative charge of -0.35 for the $\{\text{Cp}^*\text{Cr}(\text{CO})_2\}$ fragment. The central P₂ unit and the two NHC fragments bear a positive charge of 0.37, 0.51 and 0.47, respectively, resulting in a $\{\text{P}_2\text{Ime}_2\}$ fragment with an overall positive charge of

1.35. The Wiberg Bond Index (WBI) of the P–P bond (1.14) confirms only a weak double bond character, while the WBIs of the C–P bonds (0.98 and 1.01) are characteristic for single bonds. The NBO analysis illustrates the presence of only one lone pair of electrons on each P atom in an approximate $sp^{0.5}$ hybrid orbital, alongside to two weakly polarized Cr–P bonds in which the P atoms participate with almost pure p orbitals (sp^{11} and $sp^{7.2}$). This description of the electronic structure of **4** is in line with the localized molecular orbitals. In Figure S7 the localized molecular orbitals corresponding to the C–P bond, the P–P bond, the lone pair of electrons on the P atom and the Cr–P bond are depicted.

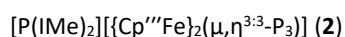
Figure S8. Selected localized molecular orbitals of **4**.



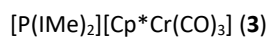
5. Crystallographic details



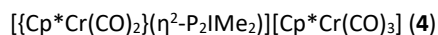
Compound **1** crystallizes in the form of dark orange plates from a saturated solution in thf at room temperature after 3 days. A suitable crystal with dimensions $0.29 \times 0.20 \times 0.08 \text{ mm}^3$ was selected and mounted on a Xcalibur, AtlasS2, Gemini ultra diffractometer. The crystal was kept at a steady $T = 123(1) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2 . The asymmetric unit contains one molecule of **1**.



Compound **2** crystallizes in the form of dark red blocks from a saturated solution in toluene after one week. A suitable crystal with dimensions $0.42 \times 0.16 \times 0.05 \text{ mm}^3$ was selected and mounted on a GV50, TitanS2 diffractometer. The crystal was kept at a steady $T = 123.01(10) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2 . The asymmetric unit contains one molecule of **2**.



Compound **3** crystallizes in the form of clear yellow blocks after layering a saturated reaction solution in thf with n-pentane after a few days. A suitable crystal with dimensions $0.10 \times 0.05 \times 0.04 \text{ mm}^3$ was selected and mounted on a GV50, TitanS2 diffractometer. The crystal was kept at a steady $T = 123.1(3) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2 . Due to poor quality of the obtained crystals only preliminary values can be given for the structural parameters (table S9). The asymmetric unit contains two anionic and cationic fragments of **3**.



Compound **4** crystallizes in the form of dark brown blocks after layering a saturated reaction solution in thf with n-pentane after a few days. A suitable crystal with dimensions $0.17 \times 0.14 \times 0.10 \text{ mm}^3$ was selected and mounted on a GV50, TitanS2 diffractometer. The crystal was kept at a steady $T = 123.00(16) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2 . The asymmetric unit contains one molecule of **4**.

CCDC-2060507 (**1**), CCDC-2060508 (**2**) and CCDC-2060509 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html

Table S9. Selected parameters for the single crystal X-ray diffraction experiments of **1**, **2**, **3** and **4**.

Compound	1	2	3	4
CCDC	2060507	2060508		2060509
Formula	C ₃₃ H ₅₃ FeN ₄ O ₂ P	C ₄₈ H ₈₂ Fe ₂ N ₄ P ₄	C ₅₄ H ₇₈ Cr ₂ N ₈ O ₆ P ₂	C ₃₉ H ₅₄ Cr ₂ N ₄ O ₅ P ₂
<i>D</i> _{calc.} / g cm ⁻³	1.203	1.269	1.266	1.318
<i>m</i> /mm ⁻¹	4.198	6.156	4.047	5.399
Formula Weight	624.61	950.75	1101.18	824.80
Colour	orange	dark pink	yellow	dark brown
Shape	plate	block	plate	block
Size/mm ³	0.29×0.20×0.08	0.42×0.16×0.05	0.10×0.05×0.04	0.17×0.14×0.10
<i>T</i> /K	123(1)	123.01(10)	123.1(3)	123.00(16)
Crystal System	triclinic	monoclinic	triclinic	monoclinic
Space Group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	10.8194(4)	13.7995(2)	8.9241(12)	14.7956(3)
<i>b</i> /Å	12.5965(6)	22.0551(3)	18.0574(17)	8.60807(16)
<i>c</i> /Å	15.1388(6)	16.5807(2)	18.8286(14)	32.9425(6)
α /°	106.563(4)	90	106.662(7)	90
β /°	98.875(3)	99.5490(10)	91.003(9)	97.7244(16)
γ /°	113.707(4)	90	95.628(9)	90
<i>V</i> /Å ³	1723.64(14)	4976.40(12)	2889.4(5)	4157.52(13)
<i>Z</i>	2	4	2	4
<i>Z'</i>	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	CuK α	CuK α	CuK α	CuK α
<i>Q</i> _{min} /°	4.151	3.365	4.035	3.467
<i>Q</i> _{max} /°	72.873	74.005	62.387	75.267
Measured Refl's.	12167	20961	49308	35858
Ind't Refl's	6639	9772	9187	8355
Refl's with <i>I</i> > 2(<i>I</i>)	6295	9039	3895	7041
<i>R</i> _{int}	0.0194	0.0395	0.3119	0.0616
Parameters	387	579	676	679
Restraints	0	57	0	314
Largest Peak	0.530	0.713	0.809	0.479
Deepest Hole	-0.232	-1.177	-0.775	-0.459
Goof	1.030	1.063	1.088	1.040
<i>wR</i> ₂ (all data)	0.0887	0.1239	0.4240	0.1261
<i>wR</i> ₂	0.0871	0.1203	0.3433	0.1180
<i>R</i> ₁ (all data)	0.0363	0.0520	0.2256	0.0548
<i>R</i> ₁	0.0339	0.0488	0.1401	0.0456

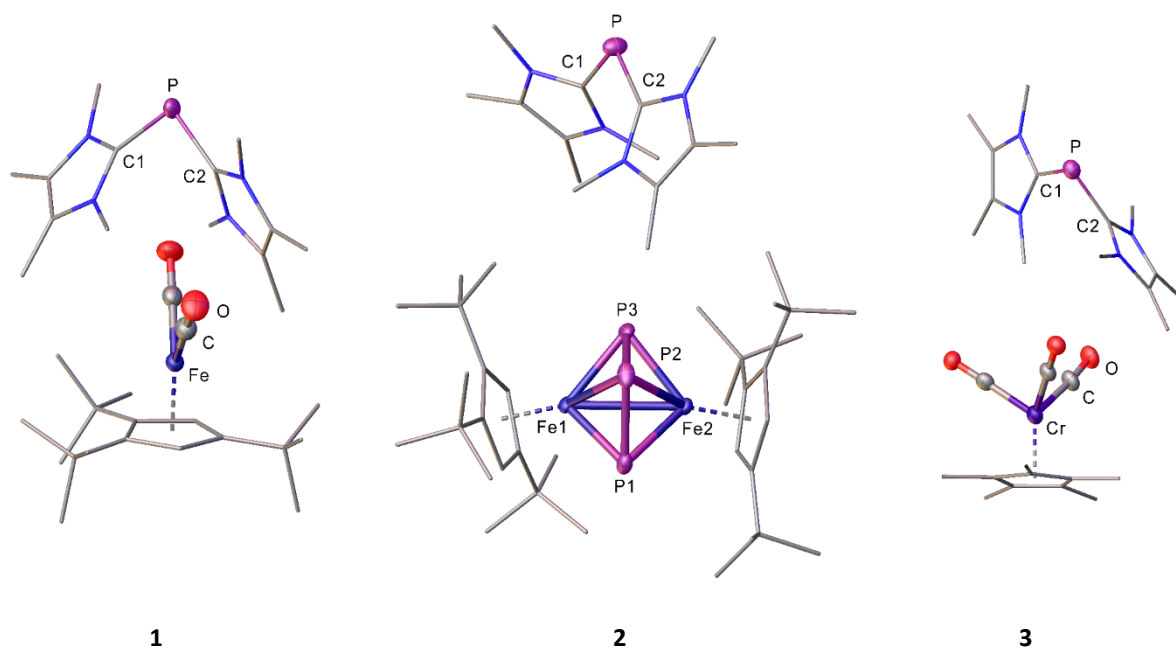


Figure S9. Molecular structure of **1**, **2** and **3** in the solid state; H atoms are omitted for clarity and CO as well as Cp ligands are drawn in the wire frame model; thermal ellipsoids are drawn at 50% probability.

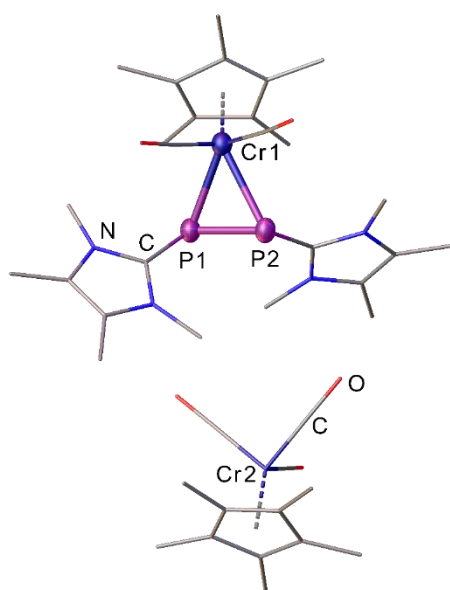


Figure S10. Molecular structure of **4** in the solid state; H atoms are omitted for clarity and CO as well as Cp* ligands are drawn in the wire frame model (only one part of the disordered Cp* ligand is depicted); thermal ellipsoids are drawn at 50% probability.

Table S10. Selected bond lengths [Å] and angles [°] of the [P(IME)₂]⁺ cation of **1**, **2** and **3** in the solid state.

	P–C [Å]		C–P–C [°]	Twist angle [°] ^[1]	
1	1.8049(17)	1.8054(18)	95.79(8)	42.10(8)	44.75(8)
2	1.802(2)	1.797(2)	102.65(10)	26.08(10)	49.42(10)
3 ^[2]	1.805(13)	1.787(11)	98.3(6)	35.9(7)	44.9(7)
	1.817(13)	1.792(12)	96.9(6)	36.3(7)	46.7(7)

^[1] Distortion angle between the PC^{Carbene}₂ plane and the planes spanned by the NHC ring systems.

^[2] Preliminary values due to poor single crystal X-ray diffraction data.

Table S11. Selected bond lengths [Å] and angles [°] of the [(Cp^{'''}Fe)₂(μ,η^{3:3}-P₃)]⁻ anion of **2** in the solid state.

	<i>d</i> / Å		<i>α</i> / °		
Fe1–P1	2.1942(6)	Fe2–P3	2.1971(6)	Fe1–P1–Fe2	79.94(2)
Fe1–P2	2.4221(6)	P1–P2	2.1601(8)	Fe1–P2–Fe2	71.315(18)
Fe1–P3	2.1931(6)	P2–P3	2.1897(8)	Fe1–P3–Fe2	80.06(2)
Fe2–P1	2.2015(6)	Fe1–Fe2	2.8236(4)	P1–P2–P3	95.21(3)
Fe2–P2	2.4217(6)				

Table S12. Selected bond lengths [Å] and angles [°] of **4** in the solid state.

	<i>d</i> / Å		<i>α</i> / °		
Cr1–P1	2.3954(7)	P1–Cr1–P2	52.02(2)	P1–Cr1–P2–C8	93.98(8)
Cr1–P2	2.4480(7)	P2–P1–Cr1	65.26(3)	P2–Cr1–P1–C1	93.37(8)
P1–P2	2.1246(8)	P1–P2–Cr1	62.71(2)		
P1–C	1.842(3)	C1–P1–Cr1	114.09(8)		
P2–C	1.835(3)	C8–P2–Cr1	112.90(8)		

6. Additional Information

Initial studies showed that reactions of the P₄ butterfly compounds **A** and **B** with nucleophiles like LiNMe₂, LiCH₂SiMe₃, KCHPh₂ at various reaction conditions result in either uncontrollable decomposition of the starting materials or no conversion at all.

Table S13. Comparison of structural parameters of the $[\{\text{Cp}^{\text{III}}\text{Fe}\}_2(\mu, \eta^{3:3}\text{-P}_3)]^-$ anion found in **2** and the neutral $[\{\text{Cp}^{\text{III}}\text{Fe}\}_2(\mu, \eta^{3:3}\text{-P}_3)]$ (**C**)^[16] in the solid state.

	d / Å				α / °			
	2	C	2	C	2	C		
Fe1–P1	2.1942(6)	2.225(1)	P1–P2	2.1601(8)	2.148(1)	Fe1–P1–Fe2	79.94(2)	71.51(4)
Fe1–P2	2.4221(6)	2.2446(1)	P2–P3	2.1897(8)	2.148(1)	Fe1–P2–Fe2	71.315(18)	63.92(4)
Fe1–P3	2.1931(6)	2.225(1)	Fe1–Fe2	2.8236(4)	2.589(1)	Fe1–P3–Fe2	80.06(2)	71.51(4)
Fe2–P1	2.2015(6)	2.225(1)				P1–P2–P3	95.21(3)	100.71(7)
Fe2–P2	2.4217(6)	2.2446(1)						
Fe2–P3	2.1971(6)	2.225(1)						

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