From the Parent Phosphinidene-Carbene Adduct NHC=PH to Cationic P_4-Rings and P_2-Cycloaddition Products

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Supporting Information

Preparations and Experiments

1. General Considerations

Starting material ^{Dipp}NHC=PH **1**[1] was synthesised from sodium phosphaethynolate[2, 3] and 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium chloride[4] according to literature procedures. Dichloro(diisopropylamino)phosphane[5] and chlorobis(dimethylamino)phosphane[6] was synthesised as described in literature. Precursors described herein (**2a**-**c**) have been applied as obtained from hexane extraction of crude material without further purification. All other reagents and solvents have been purchased from commercial suppliers. 2,3-Dimethylbuta-1,3-diene was distilled from $NaBH_4$ and degassed. Cyclopentadiene was distilled from dicyclopentadiene over copper powder and stored over molecular sieve 3 Å at -30 °C. Solvents have been degassed and purified using an INNOVATIVE TECHNOLOGIES PURE SOLV solvent purification system prior to use. All syntheses and manipulations have been performed in argon under the exclusion of air and moisture using standard SCHLENK technique or a M. BRAUN glovebox.

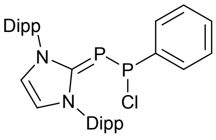
Single crystal X-ray diffraction measurements were performed on BRUKER SMART APEX, SMART APEX2 or D8 VENTURE systems. Data analysis were performed using BRUKER APEX2 and OLEX2 1.2 software.[7] CCDC numbers (1415566-1415574) are listed in the crystallographic tables. Powder diffraction measurements were performed on a STOE system. From single crystal data, powder patterns have been calculated using MERCURY 3.3 and plotted together with the measured data using ORIGIN PRO 9.1 in order to prove the identity of the bulk product. Due to the extreme sensitivity of these compounds to oxidation, we were only able to obtain analytical pure material of **2a**.

NMR spectra have been recorded on BRUKER 250, 300, 400 and 500 MHz spectrometers. Deuterated solvents have been degassed and dried prior to use. Chemical shifts are reported in ppm relative to $SiMe_4$ (for ^1H and ^{13}C) and 85 % phosphoric acid (for ^{31}P) using the solvent deuterium signals as internal standards. Signal multiplicities are described as singlet (s), doublet (d), triplet (t), quartet (q), septet (sept), multiplet (m) and broad singlet (bs). For ^{13}C signals overlapping with solvent residual signals, shifts have been taken from DEPT 135 spectra. Data analysis has been carried out using BRUKER TOPSPIN 3.1.

MALDI-TOF mass spectra were recorded at the ETH Zürich MS department on a BRUKER ULTRAFLEX II system. Elemental analyses have been carried out at the ETH Zürich Mikrolabor.

2. Carbene Stabilised Chlorodiphosphanes

Synthesis of DippNHC=PPClPh (**2a**)

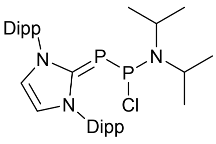


2a

Dichlorophenylphosphane (63.8 mg, 0.36 mmol, 1 eq.) is dissolved in 0.2 mL of dry THF. A solution of **1** (149.7 mg, 0.36 mmol, 1 eq.) in 2 mL of dry THF and DABCO (41.3 mg, 0.37 mmol, 1.03 eq.) in 1 mL of dry THF are added. The colour changes from pale to deep yellow and a colourless solid precipitates immediately. The reaction mixture is filtered over a PTFE syringe filter and evaporated *in vacuo*. The obtained orange foam is extracted 6 × with 10 mL of hexane. Evaporation of the combined yellow hexane fractions yields ^{Dipp}NHC=PPClPh (**2a**) as yellow solid (74.3 mg, 0.13 mmol, 36 %). Single crystals suitable for X-ray crystallography have been obtained by slow evaporation of a hexane solution of **2a**. A minimum amount of analytically pure material has been obtained from hexane at -30 °C.

^{1}H NMR (500 MHz, THF-d_8, 298 K) $\delta = 7.48$ (t, $J_{HH} = 7.8$ Hz, 2H, p-Dipp), 7.45-7.40 (m, 2H, Ph), 7.38 (s, 2H, CH=CH), 7.33 (m, 4H, m-Dipp), 7.09 (t $J_{HH} = 7.5$ Hz, 2H, Ph), 7.07-7.02 (m, 1H, Ph), 2.93 (sept., $J_{HH} = 7.0$ Hz, 2H, Dipp-CH(CH$_3$)$_2$), 2.85 (sept., $J_{HH} = 6.9$ Hz, 2H, Dipp-CH(CH$_3$)$_2$), 1.41 (d, $J_{HH} = 6.9$ Hz, 12H, Dipp-CH_3), 1.23 (d, $J_{HH} = 6.9$ Hz, 12H, Dipp-CH_3); **^{13}C{^{1}H} NMR** (125.8 MHz, THF-d_8, 298 K) $\delta = 169.9$ (dd, $J_{PC} = 119.0$ Hz, $J_{PC} = 20.8$ Hz, C$_{carbene}$), 146.18 (d, $J = 33.9$ Hz, ipso-Dipp), 124.0 (m-Dipp), 123.1 (d, $J_{PC} = 3.6$ Hz, CH=CH), 29.0 (Dipp-CH(CH$_3$)$_2$), 28.9 (Dipp-CH(CH$_3$)$_2$), 24.2 (CH$_3$), 24.1 (CH$_3$), 22.4 (CH$_3$), 22.2 (CH$_3$); **^{31}P{^{1}H} NMR** (202.5 MHz, THF-d_8, 298 K) $\delta = 157.6$ (d, $J_{PP} = 374.5$ Hz), -17.3 (d, $J_{PP} = 377.9$ Hz); **EA** calc. for $C_{33}H_{41}N_2P_2Cl$: C 70.39, H 7.34, N 4.97, found: C 70.67, H 7.57, N 4.95

Synthesis of ^{Dipp}NHC=PPCl(N^{i}Pr$_2$) (**2b**)



2b

Dichloro(diisopropylamino)phosphane (130.6 mg, 0.646 mmol, 1 eq.) is dissolved in 0.5 mL of THF and a solution of DABCO (76 mg, 0.68 mmol, 1.05 eq.) in a minimum amount of THF is added. Upon addition of this solution to a pale yellow solution of ^{Dipp}NHC=PH (271.7 mg, 0.646 mmol, 1 eq.) in a minimum amount of THF, the colour changes to bright green and a colourless solid precipitates immediately. The crude reaction mixture is evaporated *in vacuo*, ca. 50 mL of dry hexane are added and the mixture is sonicated for 10 min yielding a greenish suspension.

Filtration over a PTFE syringe filter results in a bright yellow solution, which is evaporated *in vacuo* yielding ^{Dipp}NHC=PPCl(N^{i}Pr$_2$) (**2b**) as yellow solid (323 mg, 0.551 mmol, 85 %). Single crystals suitable for X-ray crystallography have been obtained by slow evaporation of a hexane solution of **2b**.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ = 7.24 (m, 2H, p-*Ar*), 7.13 (d, J_{HH} = 7.8 Hz, 4H, m-*Ar*), 6.28 (s, 2H, C*H*=C*H*), 3.02 (sept., J_{HH} = 6.8 Hz, 4H, Dipp-C*H*(CH$_3$)$_2$), 1.55 (d, J_{HH} = 6.8 Hz, 12H, Dipp- CHC^a*H*$_3$C^{b}H$_3$), 1.34—1.19 (m, 2H, NC*H*(CH$_3$)$_2$), 1.10 (d, J_{HH} = 6.9 Hz, 12H, Dipp-CHC^{a}H$_3$C^b*H*$_3$), 1.06—0.92 (m, 12H, NCH(C*H*$_3$)$_2$); **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K) δ = 171.6 (dd, J_{PC} = 110.4 Hz, J_{PC} = 31.3 Hz, $C_{carbene}$), 146.6 (o-Dipp), 134.5 (d, J = 1.8 Hz, ipso-Dipp), 130.3 (p-Dipp), 124.5 (m-Dipp), 121.6 (d, J_{PC} = 3.2 Hz, *C*H=*C*H), 28.9 (Dipp-*C*H(CH$_3$)$_2$), 24.7 (Dipp-CHC^{a}H$_3$*C*^{b}H$_3$), 23.2 (Dipp-CH*C*^{a}H$_3$C^{b}H$_3$), 22.7 (NCH(*C*H$_3$)$_2$), not found: (N*C*H(CH$_3$)$_2$); **^{31}P{^{1}H} NMR** (162.0 MHz, C_6D_6, 298 K) δ = 213.0 (d, J_{PP} = 337.0 Hz), -16.7 (d, J_{PP} = 336.1 Hz); **^{31}P{^{1}H} NMR** (202.5 MHz, THF-d$_8$, 298 K) δ = 215.1 (d, J_{PP} = 342.2 Hz), -18.4 (d, J_{PP} = 342.1 Hz)

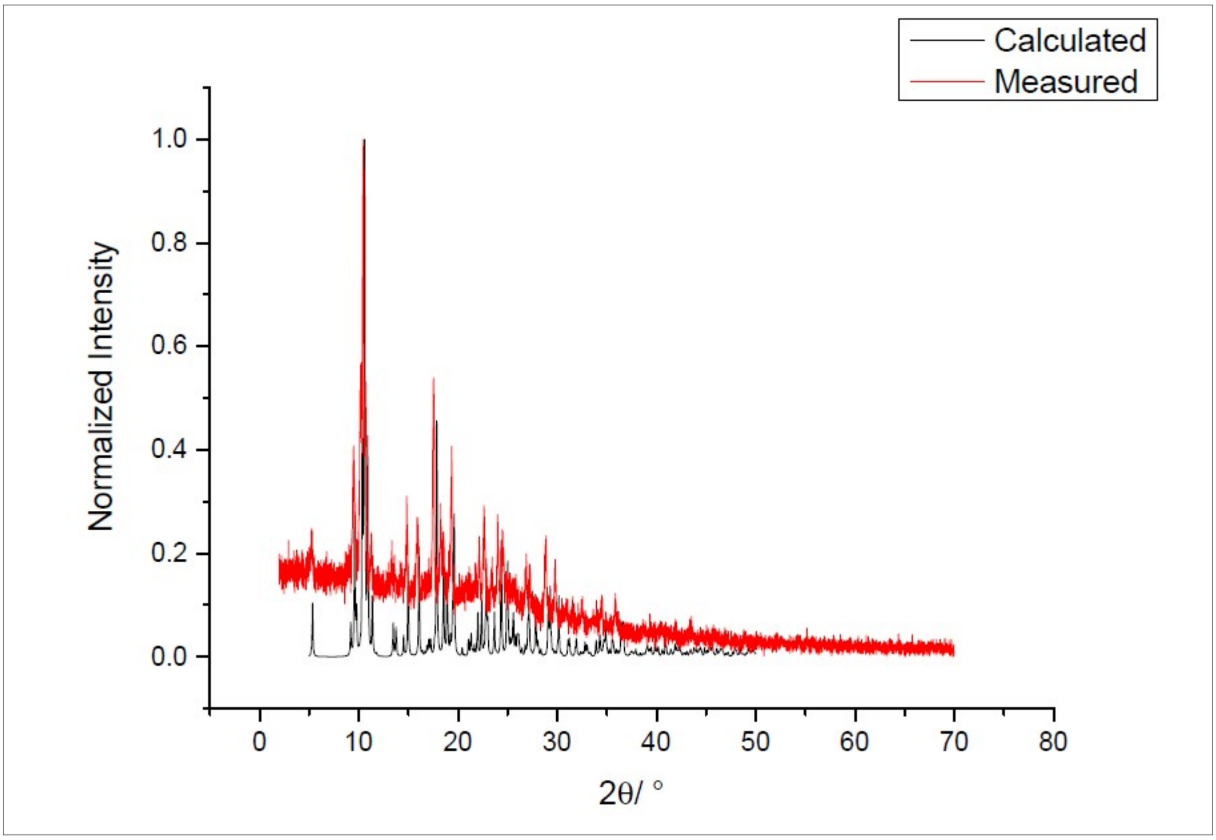
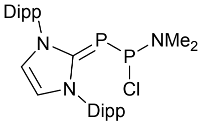


Figure S 1 Calculated and measured powder diffractograms of **2b**

Synthesis of $^{\text{Dipp}}$NHC=PPCl(NMe$_2$) (**2c**)



2c

Chlorobis(dimethylamino)phosphane (257.6 mg, 1.67 mmol, 2.2 eq.) is dissolved in 2 mL of THF and a solution of DABCO (86.6 mg, 0.772 mmol, 1.01 eq.) in 2 mL of THF is added. While stirring at r.t., a solution of **1** (320.0 mg, 0.761 mmol, 1.0 eq.) in 10 mL of THF is added dropwise over 10 min. The solution turns from pale to intense yellow and a solid precipitates. After stirring the reaction mixture for 2 h at r.t., the solvent is removed *in vacuo*. An olive green mass is obtained, which is treated with dry hexane (2 × 100 mL) upon sonication. The yellow hexane solution is filtered off. Evaporation *in vacuo* gives **2c** as dirty orange crystalline solid (278.2 mg, 0.525 mmol, 69 %), which is used for further conversions.

We were not able to obtain a publishable structure of **2c**. However, for the calculation of a powder pattern a low quality molecular structure (data not shown) of **2c** has been used. The measured powder pattern shows good accordance with the calculated (Figure S 2).

^{1}H NMR (400 MHz, THF-d$_8$, 298 K) δ = 7.47 (t, J_{HH} = 7.8 Hz, 2H, p-Dipp), 7.31 (d, J_{HH} = 7.8 Hz, 4H, m-Dipp), 7.18 (s, 2H, C*H*=C*H*), 2.89 (sept., J_{HH} = 6.9 Hz, 4H, Dipp-C*H*(CH$_3$)$_2$), 2.39 (d, J_{PH} = 13.5 Hz, 6H, PN(CH_3)$_2$), 1.39 (d, J_{HH} = 6.8 Hz, 12H, Dipp-CH_3), 1.21 (d, J_{HH} = 6.9 Hz, 12H, Dipp-C‘H_3); **^{13}C{^{1}H} NMR** (100.6 MHz, THF-d$_8$, 298 K) δ = 170.7 (dd, , J_{PC} = 113.7 Hz, J_{PC} = 24.6 Hz, C$_{\mathrm{carbene}}$), 147.1-146.2 (m, ipso-Dipp), 130.0 (p-Dipp), 134.2 (d, J = 3.3 Hz, o-Dipp), 124.1 (m-Dipp), 121.9 (d, J_{PC} = 3.5 Hz, *C*H=*C*H), 40.3-39.7 (m, PN(*C*H$_3$)$_2$), 28.8 (Dipp-*C*H(CH$_3$)$_2$), 24.0 (Dipp-CH*C*‘H$_3$CH$_3$), 22.2 (Dipp-CHC‘H$_3$*C*H$_3$); **^{31}P{^{1}H} NMR** (162.0 MHz, THF-d$_8$, 298 K) δ = 214.1 (d, J_{PP} = 349.2 Hz), -33.5 (d, J_{PP} = 351.0 Hz); **^{31}P NMR** (162.0 MHz, THF-d$_8$, 298 K) δ = 215.6-212.8 (m), -33.6 (d, J_{PP} = 346.8 Hz)

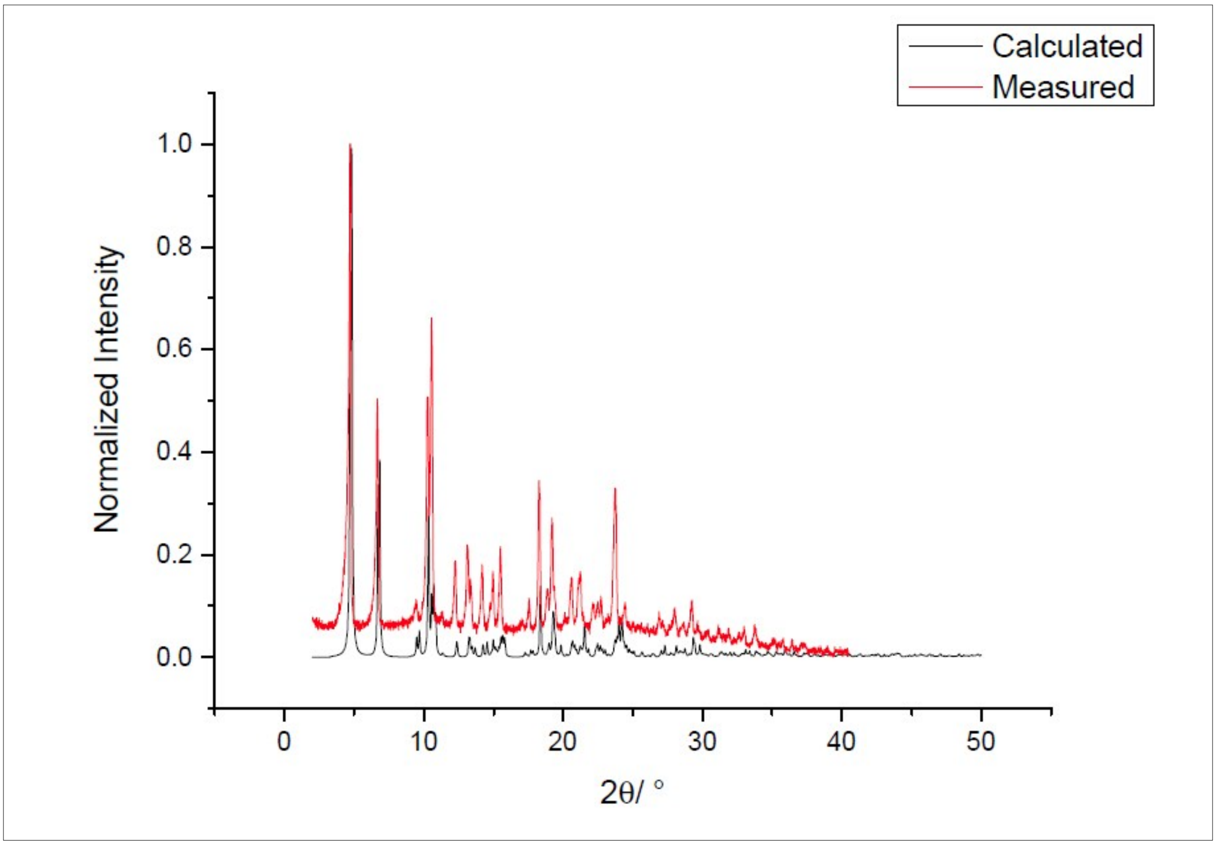


Figure S 2 Calculated and measured powder diffractograms of **2c**

3. Cationic Derivatives

Mass and NMR Data of the Postulated [2+2] Cycloadduct (**3a**)$_2$

$^{\text{Dipp}}$NHC=PPClPh (**2a**) (14.7 mg, 0.026 mmol) and GaCl$_3$ (5.3 mg, 0.030 mmol, 1.15 eq.) are dissolved in 0.5 mL of purified THF-d$_8$. A clear orange solution is obtained from which NMR spectra are recorded at a BRUKER 400 MHz spectrometer (**Figure S 3**). **^{31}P NMR** (162.0 MHz, THF-d$_8$, 298 K) δ = -24.2 (t, J_{PP} = 111.9 Hz), -69.3 (t, J_{PP} = 112.1 Hz). A small triplet with J = 107.3 Hz and δ = -66.0 ppm might be assigned to a stereoisomer of the described four membered ring **(3a)$_2$** (of which the corresponding coupling triplet might be located under the strong triplet at δ = -24.2 ppm), while signals around 48 and -126 ppm remain unassigned. MALDI-TOF data of a sample prepared similarly are depicted in **Figure S 4**. The postulation of this structure is also supported by the NMR data of **(3c)$_2$** (δ = 16.6 (t, J_{PP} = 163.3 Hz), -6.9 (t, J_{PP} = 162.9 Hz)), of which the structure is proven by single crystal X-ray diffraction (*vide infra*).

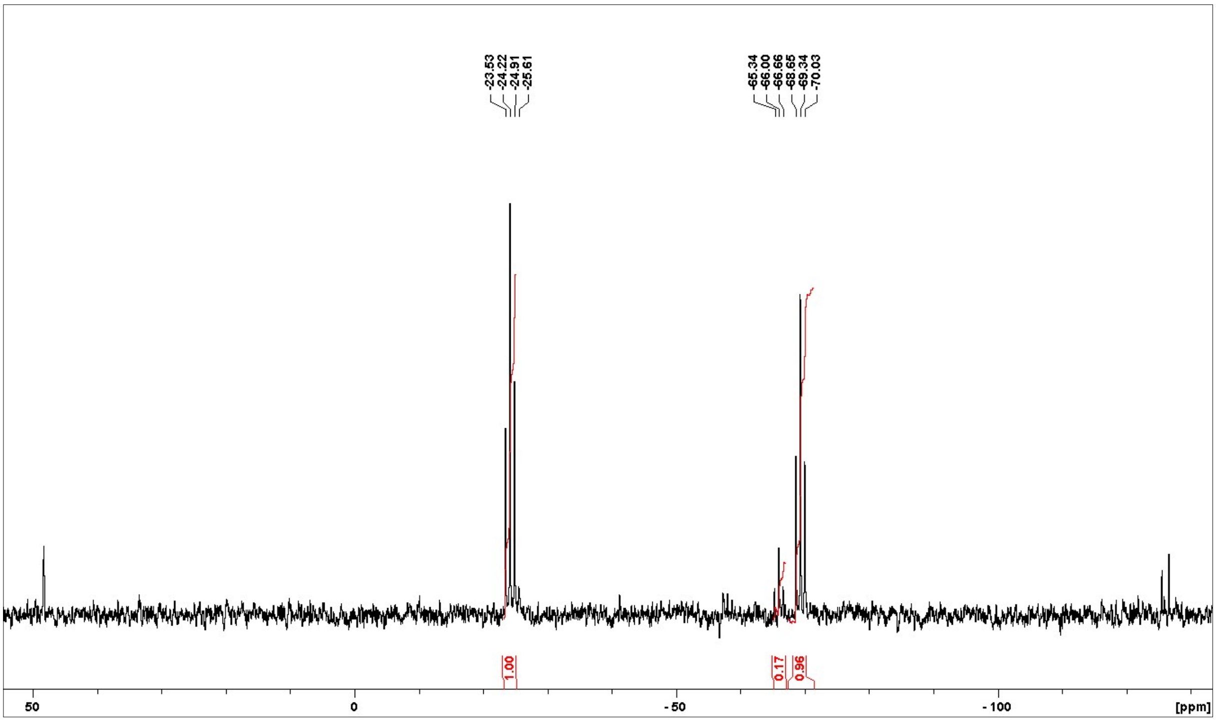
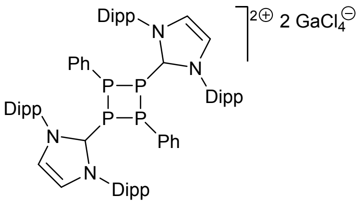
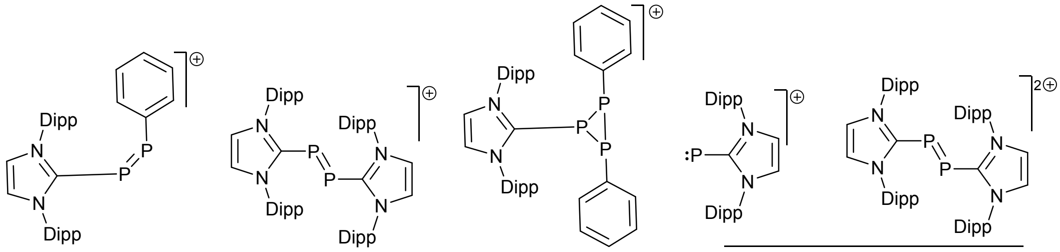


Figure S 3 ^{31}P NMR spectrum of the postulated species **(3a)$_2$**



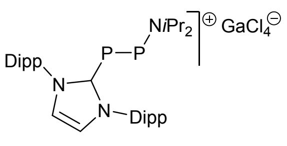
$(3a)_2$



100 %	46.6 %	41.5 %	3.4 %
$C_{33}H_{41}N_2P_2^+$	$C_{54}H_{72}N_4P_2^+$	$C_{39}H_{46}N_2P_3^+$	$C_{27}H_{36}N_2P^+$ or $C_{54}H_{72}N_4P_2^{2+}$
m/z calc. = 527.2745	m/z calc. = 838.5232	m/z calc. = 635.2874	m/z calc. = 419.2616
m/z found = 527.2738	m/z found = 838.5227	m/z found = 635.2869	m/z found = 419.2611

Figure S 4 MALDI-TOF (positive mode) data of a sample prepared similarly to the method described above and assignment of the main signals

Synthesis of ^{Dipp}NHC=PP(N^{i}Pr$_2$)(GaCl$_4$) (**3b**)



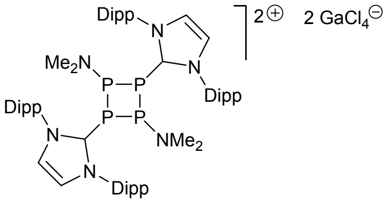
3b

Dipp$_2$NHC=PPCl(N^{i}Pr$_2$) (38.3 mg, 0.07 mmol, 1 eq.) is dissolved in 1 mL of dry DME. Anhydrous $GaCl_3$ (12.3 mg, 0.07 mmol, 1 eq.) in a minimum amount of hexane is added yielding a deep yellow solution.

By layering this solution with hexane, crystals suitable for single crystal X-ray crystallography have been obtained which have also been used for NMR spectroscopy. Yield has not been determined.

^{1}H NMR (500 MHz, THF-d$_8$, 298 K) δ = 8.31 (s, 2H, C*H*=C*H*), 7.68 (t, J_{HH} = 7.8 Hz, 2H, p-*Ar*), 7.52 (d, J_{HH} = 7.9 Hz, 4H, m-*Ar*), 4.70 – 3.76 (m, 2H, NC*H*(CH$_3$)$_2$), 2.56 (sept., J_{HH} = 6.8 Hz, 4H, Dipp-C*H*(CH$_3$)$_2$), 1.34 (d, J_{HH} = 6.9 Hz, 12H, Dipp-C*H*$_3$), 1.30 (d, J_{HH} = 6.9 Hz, 12H, Dipp-C*H’*$_3$), 1.16 (d, J_{HH} = 6.6 Hz, 12H, NCH(C*H*$_3$)$_2$); **^{13}C{^{1}H} NMR** (125.8 MHz, THF-d$_8$, 298 K) δ = 145.4 (ipso-Ar), 132.2 (p-Ar), 131.8 (o-Ar), 128.1 (*C*H=*C*H), 125.1 (m-Ar), 29.4 (Dipp-*C*H(CH$_3$)$_2$), 25.9 (NCH(C*H*$_3$)CH’$_3$, only in HSQC), 24.3 (Dipp-CH$_3$), 22.0 (Dipp-CH’$_3$), 19.0 (NCH(CH$_3$)C*H’*$_3$, only in HSCQ), not found: (*C*$_{carbene}$, N*C*H(CH$_3$)$_2$); **^{31}P{^{1}H} NMR** (202.5 MHz, THF-d$_8$, 298 K) δ = 492.1 (d, J_{PP} = 527.2 Hz), 158.1 (d, J_{PP} = 523.7 Hz)

Synthesis of $(^{Dipp}NHC{=}PPNMe_2)_2(GaCl_4)_2$ **(3c)$_2$**



(3c)$_2$

To the yellow solution of **2c** (40.9 mg, 0.077 mmol) in 1 mL of dry THF, a solution of $GaCl_3$ (13.7 mg, 0.077 mmol, 1 eq.) in 0.7 mL of dry hexane is added. Upon evaporating the obtained milky reaction mixture *in vacuo*, a green foam is obtained, which is dissolved in 0.5 mL of dry DME. Covering this solution with dry diisopropyl ether gives **(3c)$_2$** as large colourless crystals (38.5 mg, 0.027 mmol, 70 %) suitable for X-ray diffraction.

^{1}H NMR (500 MHz, THF-d_8, 298 K) δ = 8.18 (s, 4H, C*H*=C*H*), 7.75 (t, J_{HH} = 7.8 Hz, 4H, p-Dipp), 7.59 (d, J_{HH} = 7.9 Hz, 8H, m-Dipp), 2.51 (sept., J_{HH} = 7.1 Hz, 8H, Dipp-C*H*(CH_3)$_2$), 2.30-1.60 (m, 12H, N(CH_3)$_2$), 1.44 (d, J_{HH} = 6.9 Hz, 24H, Dipp-CH_3), 1.24 (d, J_{HH} = 6.8 Hz, 24H, Dipp-C'H_3), **^{13}C{^{1}H} NMR** (125.8 MHz, THF-d_8, 298 K) δ = 145.0 (ipso-Dipp), 133.2 (p-Dipp), 130.6 (o-Dipp), 129.9 (*C*H=*C*H), 126.2 (m-Dipp), 29.7 (Dipp-*C*H(CH_3)$_2$), 24.7 (Dipp-CH(*C*H_3)$_2$), 22.1 (Dipp-CH(*C*H_3)$_2$), not found: N(*C*H_3)$_2$, $C_{carbene}$; **^{31}P{^{1}H} NMR** (202.5 MHz, THF-d_8, 298 K) δ = 16.6 (t, J_{PP} = 163.3 Hz), -6.9 (t, J_{PP} = 162.9 Hz)

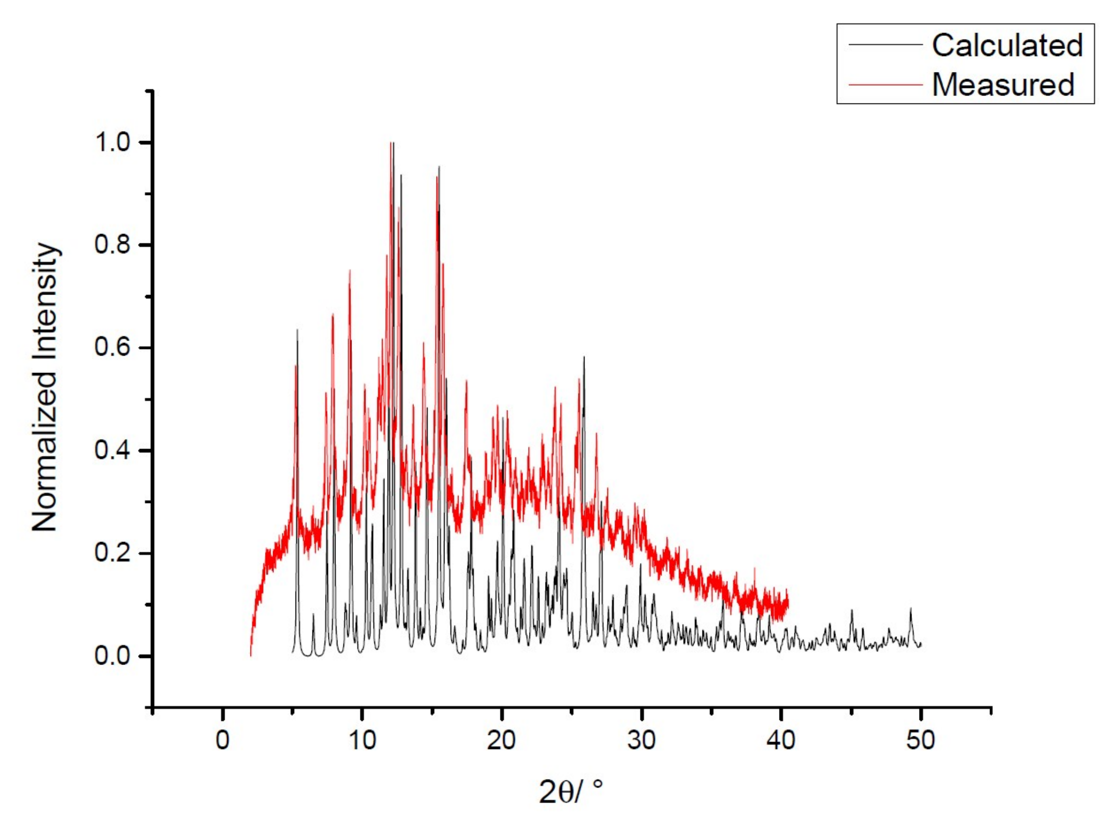


Figure S 5 Calculated and measured powder diffractograms of **(3c)$_2$**

Cycloreversion Reaction of **$3c_2$** upon Heating

The 121.5 MHz ^{31}P NMR spectrum of a solution of **(3c)$_2$** (7.0 mg, 0.005 mmol) and 2,3-dimethylbuta-1,3-diene (45 mg, 0.55 mmol, 220 eq. relative to the monomer) in 0.45 mL of THF in a J. YOUNG type NMR tube equipped with a sealed glass capillary containing 0.85 % D_3PO_4 in D_2O as external NMR standard is recorded. This spectrum (Figure S 6a) shows the signals reported for **(3c)$_2$** (17.0 ppm, t, *J* = 165.5 Hz and -6.7 ppm, t, *J* = 164.5 Hz). Subsequently, the sample is heated to 60 °C for 20 h. The spectrum recorded afterwards (Figure S 6b) shows the NMR signals of the cycloadduct **4c** (65.5 ppm, d, *J* = 228.0 Hz and -41.8 ppm, d, *J* = 229.4 Hz, *vide infra*) indicating the full conversion of **(3c)$_2$** to **4c**. This proves that **(3c)$_2$** exists monomeric at elevated temperature.

All 121.5 MHz ^{31}P NMR spectra are recorded with 30 s relaxation delay and apodization is applied (a = 10 Hz).

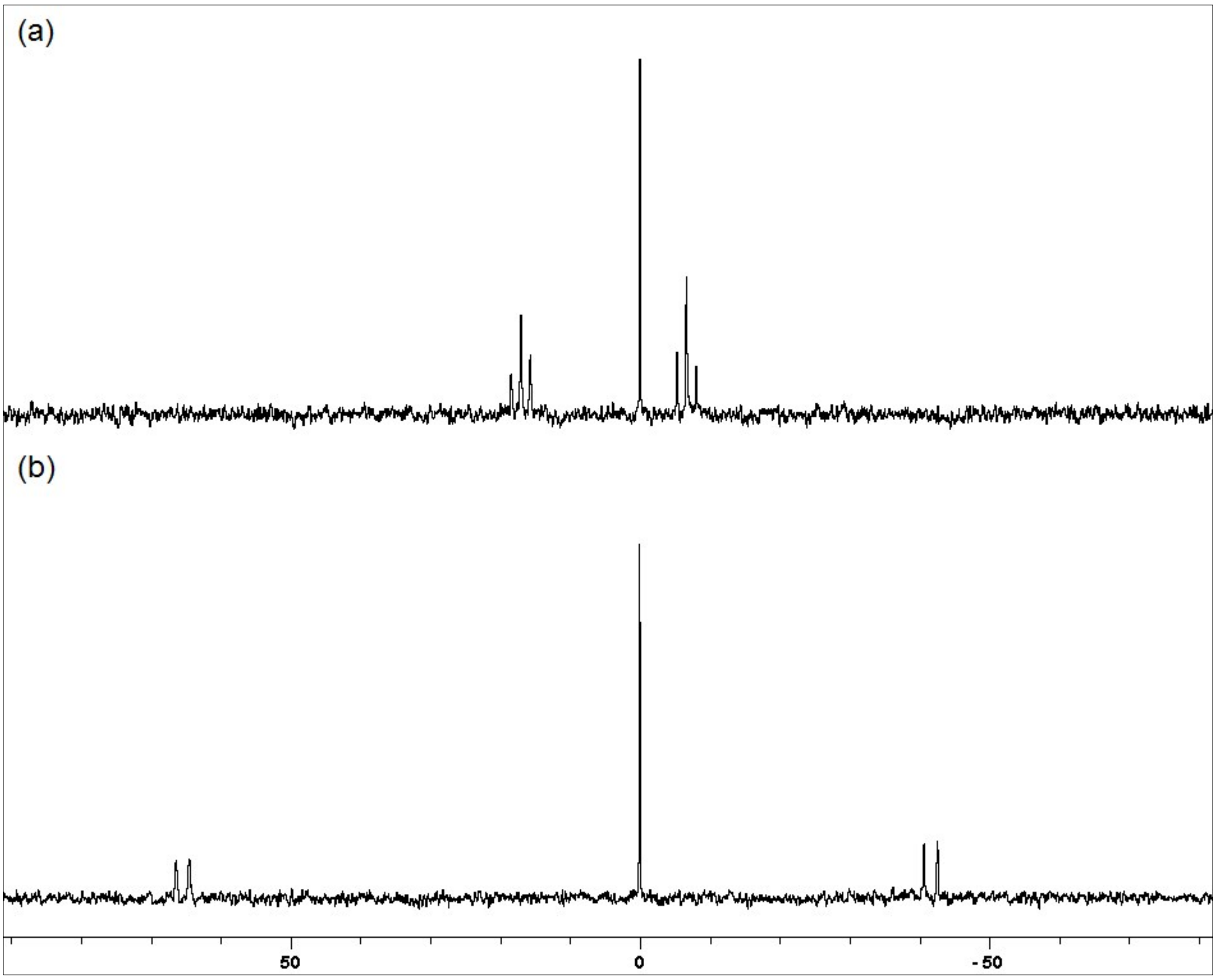
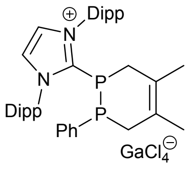


Figure S 6 ^{31}P NMR spectra showing the conversion of **(3c)$_2$** into **4c** upon heating to 60 °C in the presence of 2,3-dimethylbuta-1,3-diene. The signal at 0 ppm is 0.85 % D_3PO_4 in D_2O as external NMR standard

4. Cycloadducts with 2,3-Dimethylbuta-1,3-diene

Synthesis of Cycloadduct **4a**



4a

To the deep yellow solution of **2a** (51.6 mg, 0.092 mmol) and 2,3-dimethylbuta-1,3-diene (0.2 mL, ca. 2.4 mmol, ca. 26 eq.) in 3 mL of dry THF, $GaCl_3$ (17.4 mg, 0.099 mmol, 1.08 eq.) in 1 mL of dry hexane is added dropwise while stirring at r.t. After 30 min, the reaction mixture is evaporated *in vacuo* yielding an off-white foam, which is recrystallized twice from a DME solution layered with hexane. **4a** is isolated as off-white crystals suitable for X-ray crystallography (34.7 mg, 0.042 mmol, 46 %).

It is necessary to abstract the Cl atom in presence of the trapping agent as otherwise the *in situ* formed cation dimerises and therefore would not be accessible for a cycloaddition reaction with DMB.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 7.84 (s, 2H, C*H*=C*H*), 7.47 (t, J_{HH} = 7.9 Hz, 2H, p-Dipp), 7.30-7.23 (m, 1H, Ph), 7.29 (dd, J_{HH} = 7.8 Hz, J_{HH} = 1.1 Hz, 2H, m-Dipp), 7.25 (dd, J_{HH} = 7.8 Hz, J_{HH} = 1.2 Hz, 2H, m‘-Dipp), 7.16-7.11 (m, 2H, Ph), 6.99-6.93 (m, 2H, Ph), 2.58 (sept., J_{HH} = 7.0 Hz, 2H, Dipp-C*H*(CH_3)$_2$), 2.51 (sept., J_{HH} = 7.1 Hz, 2H, Dipp-C*H*(CH_3)$_2$), 2.24 (dt, J_{HH} = 14.4 Hz, J_{HH} = 6.7 Hz, 1H, C‘*H*H), 2.03-1.92 (m, 2H, C‘*H*H, CH*H*), 1.82 (td, J_{HH} = 11.9 Hz, J_{HH} = 3.5 Hz, 1H, CH*H*), 1.62 (bs, 3H, C*H*$_3$), 1.37 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.37 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.28 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.22 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.19 (d, 3H, J_{PH} = 6.75 Hz, C*H*$_3$); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K) δ = 151.6 (dd, J_{PC} = 81.8 Hz, J_{PC} = 28.2 Hz, $C_{carbene}$), 145.7 (ipso-Dipp), 145.1 (ipso-Dipp), 134.3 (dd, J_{PC} = 262 Hz, J_{PC} = 16 Hz, ipso-Ph), 132.8-132.5 (several signals, p-Dipp, Ph), 130.6 (o-Dipp), 129.3 (Ph), 128.6 (*C*H=*C*H), 128.0 (d, J_{PH} = 6.2 Hz, Ph), 125.0 (m-Dipp), 124.9 (m-Dipp), 33.0 (dd, , J_{PC} = 29.6 Hz, J_{PC} = 3.8 Hz, *C*‘HH), 29.7-29.5 (several signals, Dipp-*C*H(CH_3)$_2$), 26.2 (Dipp-CH(*C*H$_3$)$_2$), 25.7 (Dipp-CH(*C*H$_3$)$_2$), 24.1 (d, J_{PC} = 25.8 Hz, *C*HH), 22.4-22.2 (several signals, Dipp-CH(*C*H$_3$)$_2$), 21.6 (d, J_{PC} = 3.5 Hz, *C*H$_3$), 18.5 (*C*H$_3$); **^{31}P{^{1}H} NMR** (202.5 MHz, $CDCl_3$,, 298 K) δ = -19.4 (d, J_{PP} = 211.4 Hz), -44.7 (d, J_{PP} = 211.7 Hz)

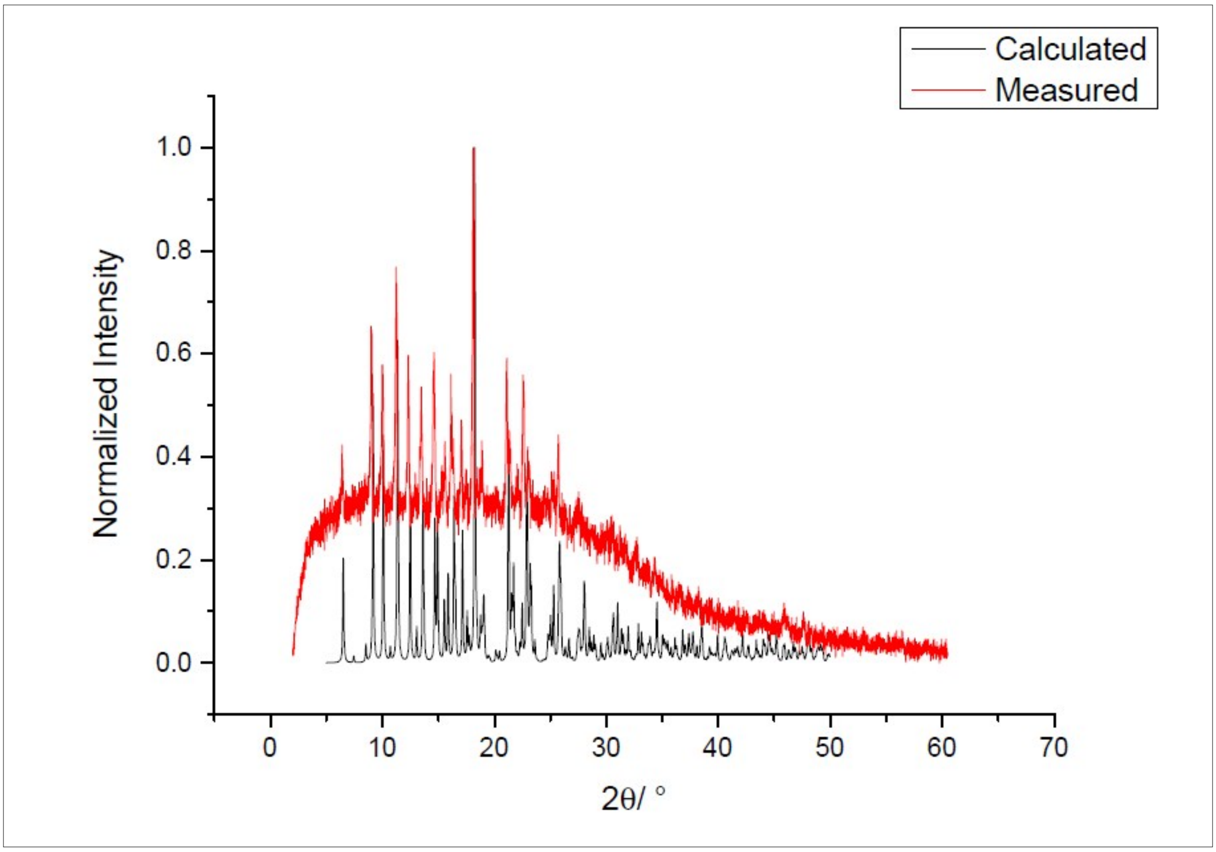
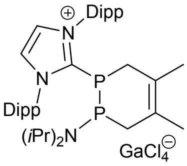


Figure S 7 Calculated and measured powder diffractograms of **4a**

Synthesis of Cycloadduct **4b**



4b

To the deep yellow solution of **2b** (196.7 mg, 0.336 mmol) and 2,3-dimethylbuta-1,3-diene (0.4 mL, ca. 10 eq.) in 4 mL of dry THF, $GaCl_3$ (59.2 mg, 0.336 mmol, 1.0 eq.) in a minimum amount of dry hexane is added while stirring. After concentrating the reaction mixture to one half, 10 mL of dry hexane are added yielding the precipitation of a solid and the formation of an oil. Subsequent evaporation of the whole batch *in vacuo* yields **4b** as a yellow solid (242.8 mg, 0.288 mmol, 86 %). Single crystals suitable for X-ray crystallography have been obtained from a solution of **4b** in DME layered with hexane at r.t.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 7.90 (s, 2H, C*H*=C*H*), 7.63 (t, J_{HH} = 7.8 Hz, 2H, p-Dipp), 7.45 (dd, J_{HH} = 7.8 Hz, J_{HH} = 1.1 Hz, 2H, m-Dipp), 7.37 (dd, J_{HH} = 7.8 Hz, J_{HH} = 1.1 Hz, 2H, m‘-Dipp), 3.06 (d sept., J_{PH} = 11.8 Hz, J_{HH} = 6.4 Hz, 2H, $N(CH(CH_3)_2)_2$), 2.57 (sept., J_{HH} = 6.7 Hz, 2H, Dipp-$CH(CH_3)_2$), 2.36 (sept., J_{HH} = 7.1 Hz, 2H, Dipp-$CH(CH_3)_2$), 2.30-2.22 (m, 2H, CH*H,* C*H*H), 2.00 (ddd, *J* = 14.8 Hz, *J* = 6.0 Hz, *J* = 3.0 Hz, 1H, C‘H*H*), 1.73 (d, 3H, J_{PH} = 5.0 Hz, CH_3), 1.69 (bs, 3H, CH_3), 1.54 (d, J_{HH} = 6.8 Hz, 6H, Dipp-CH_3), 1.32 (d, J_{HH} =

6.8 Hz, 6H, Dipp-CH_3), 1.25 (d, J_{HH} = 6.5 Hz, 6H, Dipp-CH_3), 1.24 (d, J_{HH} = 6.6 Hz, 6H, Dipp-CH_3), 1.02 (d, J_{HH} = 6.6 Hz, 6H, N(CH(CH_3CH$_3$))$_2$), 0.95-0.87 (m, 1H, C‘*H*H), 0.83 (d, J_{HH} = 6.6 Hz, 6H, N(CH(CH$_3$CH_3))$_2$), some shifts and coupling constants from 300 MHz and 400 MHz spectra; **^{13}C{^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K) δ = 150.9 (dd, , J_{PC} = 85.1 Hz, J_{PC} = 31.4 Hz, C$_{\mathrm{carbene}}$), 145.7 (ipso-Dipp), 145.2 (ipso-Dipp), 133.1 (d, J_{PC} = 11.2 Hz, *C*CH$_3$=CH$_3$C), 132.4 (p-Dipp), 131.6 (o-Dipp), 129.4 (d, *C*H=*C*H), 124.9 (m-Dipp), 124.6 (m’-Dipp), 121.1 (d, J_{PC} = 4.1 Hz, CCH$_3$=*C*CH$_3$), 49.8-48.9 (m, N(*C*H(CH$_3$CH$_3$))$_2$), 39.1 (d, J_{PC} = 37.1 Hz, *C‘*HH), 27.9 (d, J_{PC} = 21.4 Hz, *C*HH), 30.0-29.5 (several signals, Dipp-*C*H(CH$_3$)$_2$), 26.4 (Dipp-*C*H$_3$), 26.2 (Dipp-*C*H$_3$), 24.3 (d, J_{PC} = 4.4 Hz, N(CH(*C*H$_3$CH$_3$))$_2$), 22.8 (d, J_{PC} = 8.0 Hz, N(CH(CH$_3$*C*H$_3$))$_2$), 22.7-22.3 (several signals, Dipp-CH(*C*H$_3$)$_2$), 21.7 (d, J_{PC} = 2.5 Hz, *C*H$_3$), 19.5 (d, J_{PC} = 16.3 Hz, *C*H$_3$); **^{31}P{^{1}H} NMR** (202.5 MHz, CDCl$_3$,, 298 K) δ = 32.9 (d, J_{PP} = 239.9 Hz), -56.5 (d, J_{PP} = 238.7 Hz); impurities observed in NMR

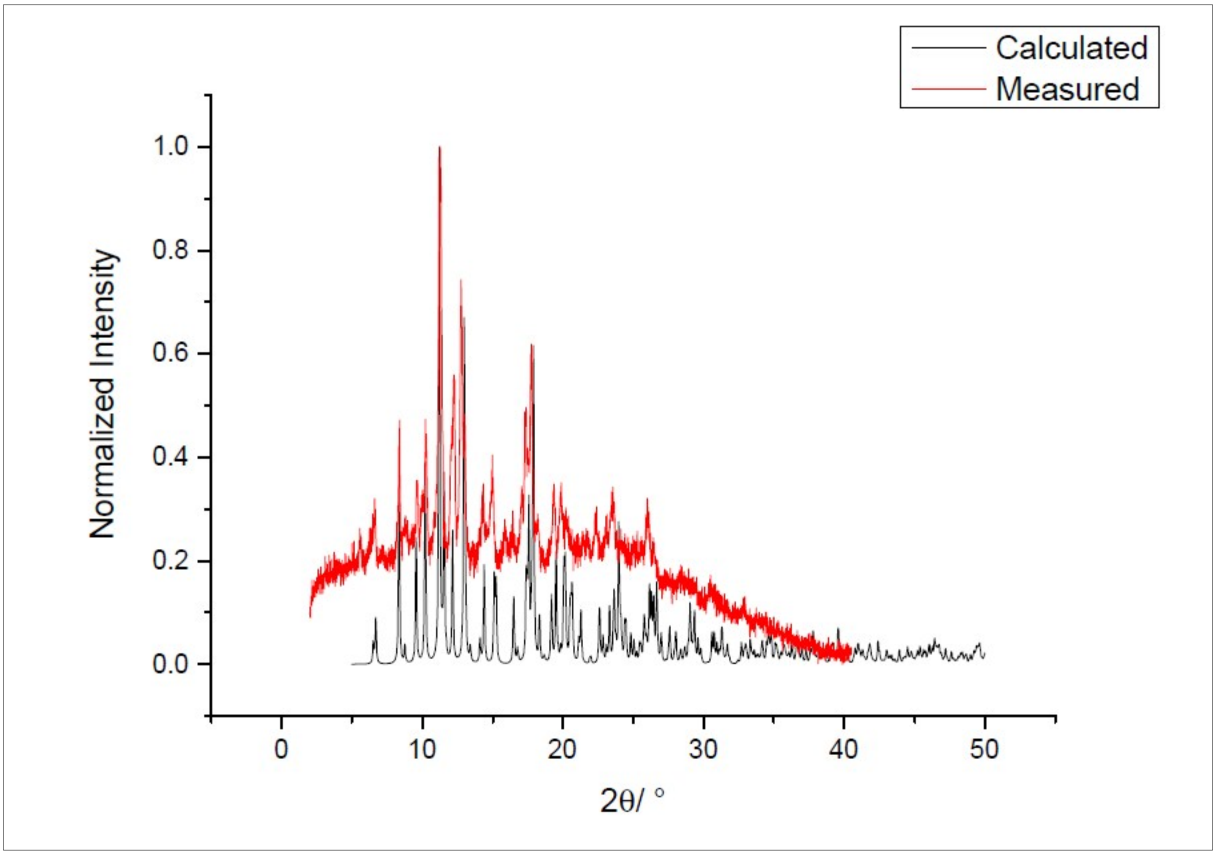
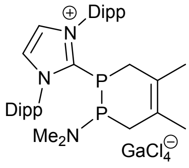


Figure S 8 Calculated and measured powder diffractograms of **4b**

Synthesis of Cycloadduct **4c**



4c

To a stirred solution of **2c** (86.4 mg, 0.163 mmol) and 2,3-dimethylbuta-1,3-diene (0.1 mL, ca. 0.9 mmol, ca. 5.5 eq.) in 3 mL of DME, a solution of $GaCl_3$ (29.2 mg, 0.166 mmol, 1.02 eq.) in 1.5 mL of hexane is added dropwise. After stirring for 30 min at r.t., the reaction mixture is evaporated *in vacuo*. The residue is dissolved in 5 mL of DME, filtered over a PTFE syringe filter, covered with 5 mL of hexane and left for crystallisation. **4c** is obtained as pale green crystals suitable for X-ray diffraction (52.5 mg, 0.067 mmol, 41 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.76 (s, 2H, C*H*=C*H*), 7.64 (t, J_{HH} = 7.8 Hz, 2H, p-Dipp), 7.41 (d, J_{HH} = 7.8 Hz, 2H, m-Dipp), 7.38 (d, J_{HH} = 7.8 Hz, 2H, m‘-Dipp), 2.56 (sept., J_{HH} = 6.9 Hz, 2H, Dipp-C*H*(CH_3)$_2$), 2.48 (sept., J_{HH} = 7.0 Hz, 2H, Dipp-C*H*(CH_3)$_2$), 2.29 (ddd, J_{HH} = 14.9 Hz, J_{HH} = 6.8 Hz, J_{HH} = 2.5 Hz, 1H, C*H*H), 2.16 (d, J_{PH} = 9.6 Hz, 6H, N(C*H*$_3$)$_2$), 2.02-1.91 (m, 1H, C’*H*H), 1.72 (d, J_{PH} = 6.3Hz, 3H, C*H*$_3$), 1.70-1.61 (m, 2H, CH*H*, C’H*H*), 1.58 (bs, J_{PH} = 6.3Hz, 3H, C*H*$_3$), 1.42 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.38 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.29 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.23 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 298 K) δ = 152.1 (dd, J_{PC} = 83.9 Hz, J_{PC} = 30.0 Hz, $C_{carbene}$), 145.7 (ipso-Dipp), 145.3 (ipso-Dipp), 133.3 (d, J_{PC} = 13.8 Hz, *C*CH_3), 132.6 (p-Dipp), 131.1 (o-Dipp), 128.6 (bs, *C*H=*C*H), 125.1 (m-Dipp), 125.0 (m-Dipp), 121.8 (d, J_{PC} = 4.8 Hz, *C*CH_3), 42.9 (dd, , J_{PC} = 42.9 Hz, J_{PC} = 8.1 Hz, N(*C*H$_3$)$_2$), 37.1 (d, J_{PC} = 36.7 Hz, *C*HH), 29.7-29.5 (several signals, Dipp-*C*H(CH_3)$_2$), 26.0 (Dipp-CH(*C*H$_3$)$_2$), 25.6 (Dipp-CH(*C*H$_3$)$_2$), 24.9 (d, J_{PC} = 23.2 Hz, *C’*HH), 22.5-22.3 (m, Dipp-CH(*C*H$_3$)$_2$), 20.6 (d, J_{PC} = 3.7 Hz, *C*H$_3$), 19.0 (d, J_{PC} = 2.3 Hz, *C*H$_3$); **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$,, 298 K) δ = 65.4 (d, J_{PP} = 227.7 Hz), -41.2 (d, J_{PP} = 230.0 Hz)

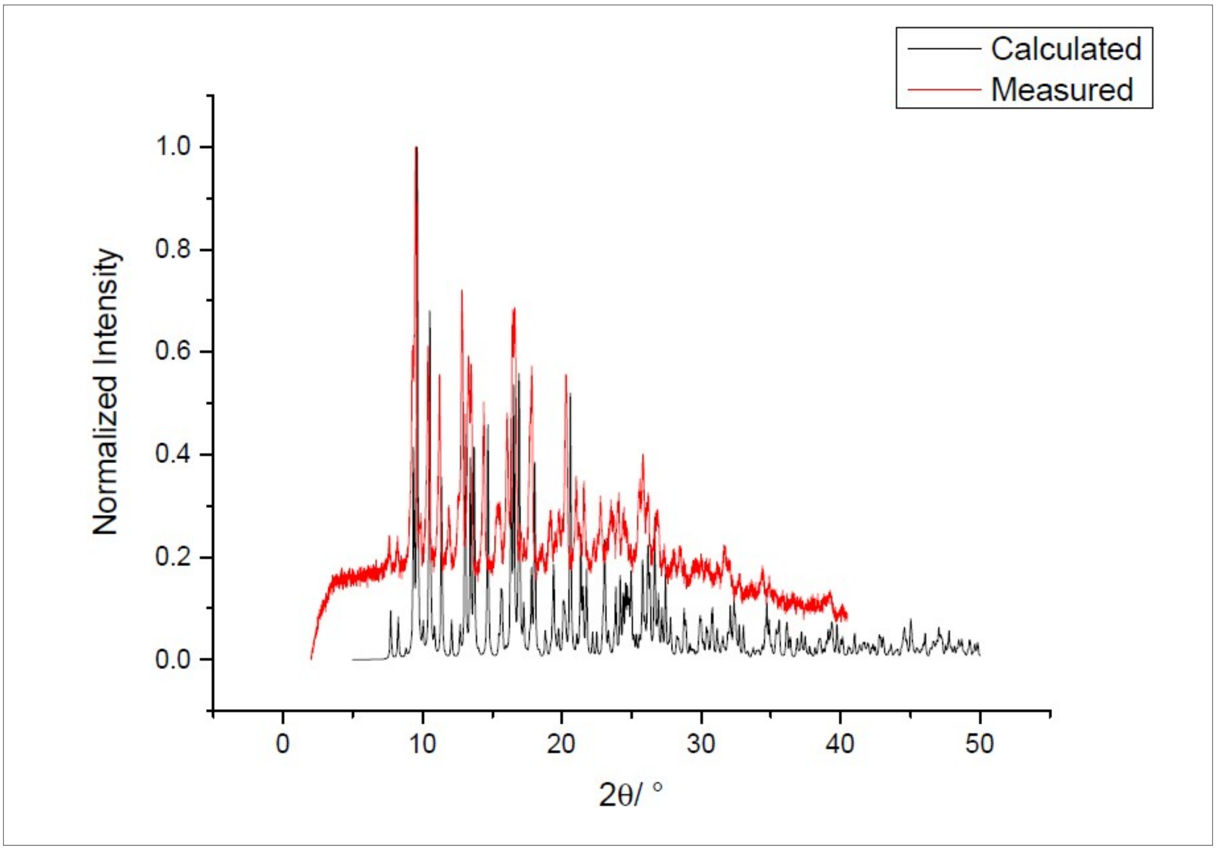
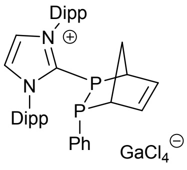


Figure S 9 Calculated and measured powder diffractograms of **4c**

5. Cycloadducts with Cyclopentadiene

Synthesis of Cycloadduct **5a**



5a

To a solution of **2a** (127.7 mg, 0.227 mmol) in a minimum amount of THF 0.5 mL of cyclopentadiene (ca. 27 eq.) are added followed by the addition of a solution of $GaCl_3$ (40.0 mg, 0.227 mmol, 1.0 eq.) in a minimum amount of hexane over 1 min while stirring at r.t. The obtained orange solution is evaporated *in vacuo* and dissolved in DCM. An unidentified solid is removed by syringe filtration. Covering the obtained yellow solution with hexane and subsequent cooling to -30 °C overnight yields **5a** as pale orange to colourless crystals suitable for x-ray crystallography (54.2 mg, 0.067 mmol, 30 %).

^{1}H NMR (400 MHz, THF-d$_8$, 298 K) δ = 8.28 (s, 2H, NC*H*=C*H*N), 7.63 (t, J_{HH} = 7.8 Hz, 2H, p-Dipp), 7.58-7.52 (m, 2H, m-Dipp), 7.45-7.40 (m, 2H, m-Dipp), 7.29-7.23 (m, 1H, Ph), 7.18-7.11 (m, 2H, Ph), 6.95-6.88 (m, 2H, Ph), 5.78-5.71 (m, 1H, CC*H*=CHC), 5.62-5.56 (m, 1H, CCH=C*H*C), 3.82-3.69 (m, 1H, PC*H*), 2.92-2.85 (m, 1H, PC'*H*), 2.69 (sept., J_{HH} = 6.8 Hz, 2H, Dipp-C*H*(CH$_3$)$_2$), 2.57 (sept., J_{HH} = 7.0 Hz, 2H, Dipp-C*H*(CH$_3$)$_2$), 1.56 (d, J_{HH} = 6.8 Hz, 6H, Dipp-C*H*$_3$), 1.32 (d, J_{HH} = 6.9 Hz, 6H, Dipp-C*H*$_3$), 1.30 (d, J_{HH} = 7.0 Hz, 6H, Dipp-C*H*$_3$), 1.25 (d, J_{HH} = 6.9 Hz, 6H, Dipp-C*H*$_3$), not found: methylene-H, regions 1.93-1.77 ppm and 1.45-1.34 ppm show ^{1}H-^{13}C-HSQC crosspeaks to CH$_2$; **^{13}C{^{1}H} NMR** (100.6 MHz, THF-d$_8$, 298 K) δ = 145.9 (ipso-Dipp), 145.1 (ipso-Dipp), 139.6 (d, J_{PC} = 12.3 Hz, C*C*=CC), 133.2-132.7 (m, Ph), 132.6 (p-Dipp), 131.5 (o-Dipp), 129.2 (Ph), 128.6 (N*C*H=*C*HN), 127.8-127.6 (m, Ph), 125.4-124.7 (multiple signals, m-Dipp, CC=*C*C), 47.6 (d, J_{PC} = 14.8 Hz, *C*H$_2$), 46.3 (dd, J_{PC} = 26.9 Hz, J_{PC} = 3.4 Hz, P*C'*H), 43.7 (dd, J_{PC} = 27.5 Hz, J_{PC} = 8.0 Hz, P*C*H), 29.8-29.4 (several signals, *C*H(CH$_3$)$_2$), 25.3 (Dipp-*C*H$_3$), 25.1 (Dipp-*C*H$_3$), 21.6-21.4 (m, Dipp-*C*H$_3$), 21.2 (Dipp-*C*H$_3$), not found: C$_{carbene}$, ipso-Ph; **^{31}P{^{1}H} NMR** (162.0 MHz, THF-d$_8$, 298 K) δ = -13.0 (d, J_{PP} = 240.8 Hz), -15.1 (d, J_{PP} = 242.2 Hz); **^{31}P{^{1}H} NMR** (162.0 MHz, CD$_2$Cl$_2$, 298 K) δ = -14.7 (s); impurities observed in NMR

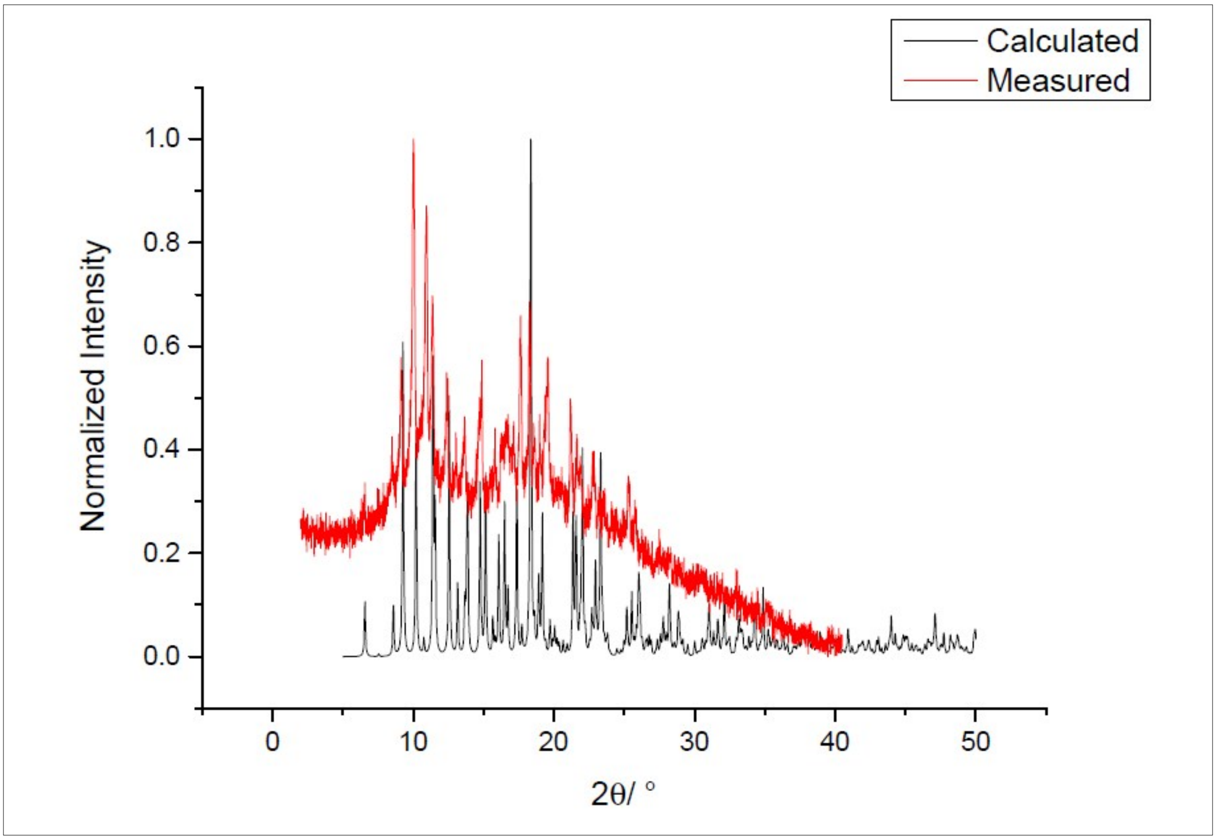
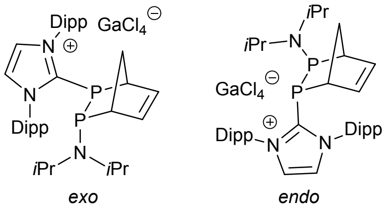


Figure S 10 Calculated and measured powder diffractograms of **5a**

The Reaction of **3b** with Cyclopentadiene – Proof of Reversibility



Both diastereomers

In an argon atmosphere, a solution of **2b** (18.8 mg, 0.032 mmol) in 0.5 mL of THF is added to a J. Young type NMR tube containing dry $GaCl_3$ (5.9 mg, 0.034 mmol, 1.06 eq.) yielding a deep orange clear solution. A sealed glass capillary containing 0.85 % D_3PO_4 in D_2O is added as external NMR standard. The 121.5 MHz ^{31}P spectrum (**Figure S 11**a) of this solution shows the signals of **3b** (492.4 ppm, d, $J = 520$ Hz and 158.3 ppm, d, $J = 525$ Hz) and the singlet of phosphoric acid at 0 ppm.

Subsequently, cyclopentadiene (0.05 mL, 0.44 mmol, ca. 14 eq.) is added and spectra are recorded directly after the addition (**Figure S 11**b) and 12 h later (c). Both spectra now show two sets of signals in addition to trace signals of **3b** and phosphoric acid. These signals are assigned to the two diastereomers obtained in the [4+2] cycloaddition reaction between **3b** and cyclopentadiene (*cf.* shifts of other cycloaddition products): **5b** (42.5 ppm, d, $J = 282$ Hz and -24.3 ppm, d, $J = 289$ Hz) and **5b’** (35.7 ppm, d, $J = 279$ Hz and -19.0 ppm, d, $J = 278$ Hz). In the spectrum recorded immediately after the addition of cyclopentadiene, the signals of **5b’** are stronger than the signals of **5b**, while it is the other way round in the spectrum recorded 12 h later (**Figure S 12** shows a magnification). Hence, we assume that **5b’** is the kinetic product isomerising to the thermodynamic product **5b**.

Finally, the solution is carefully evaporated *in vacuo* forming an orange foam, which is left under rotary vane pump vacuum for 1 h. A final NMR spectrum is recorded after the dissolution of the foam in 0.5 mL of THF again showing the signals of **3b** besides traces of the cycloaddition products (**Figure S 11**d).

All 121.5 MHz ^{31}P NMR spectra are recorded with 30 s relaxation delay and apodization is applied (a = 30 Hz).

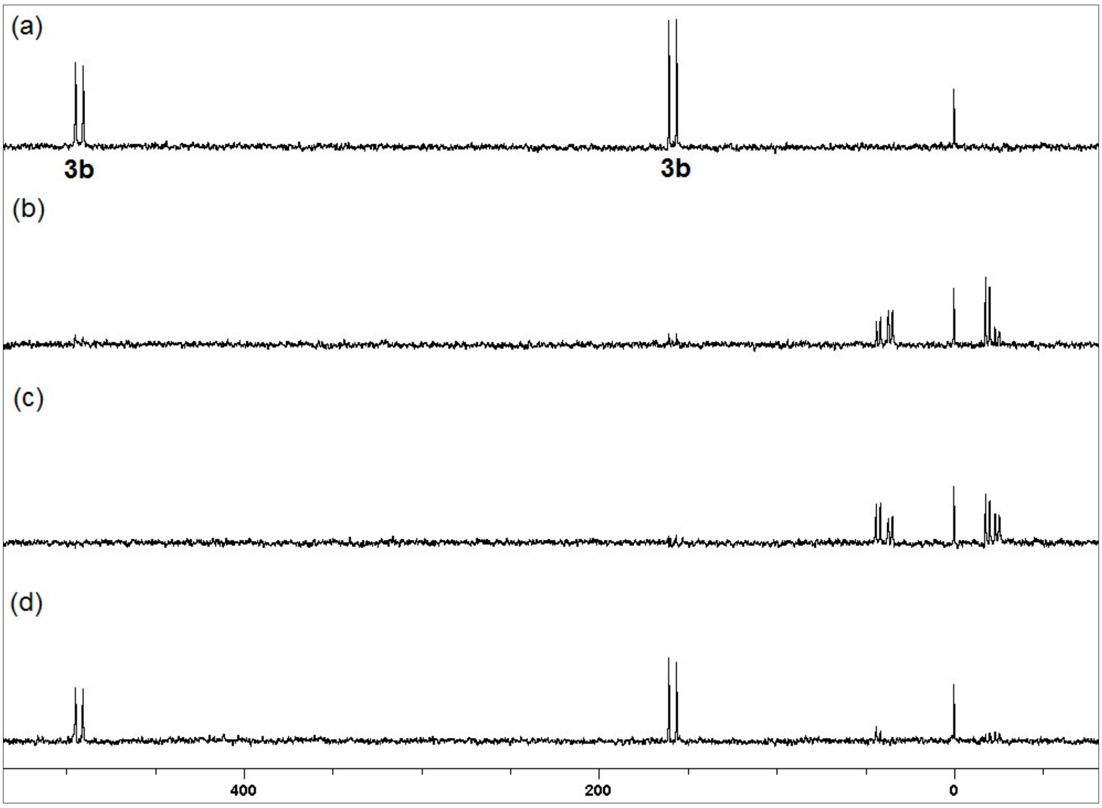


Figure S 11 ^{31}P NMR spectra showing the reversibility of the reaction of cation **3b** with cyclopentadiene. (a) without cyclopentadiene, (b) directly after the addition of cyclopentadiene, (c) 12 h later, (d) after evaporation *in vacuo* and dissolution in THF

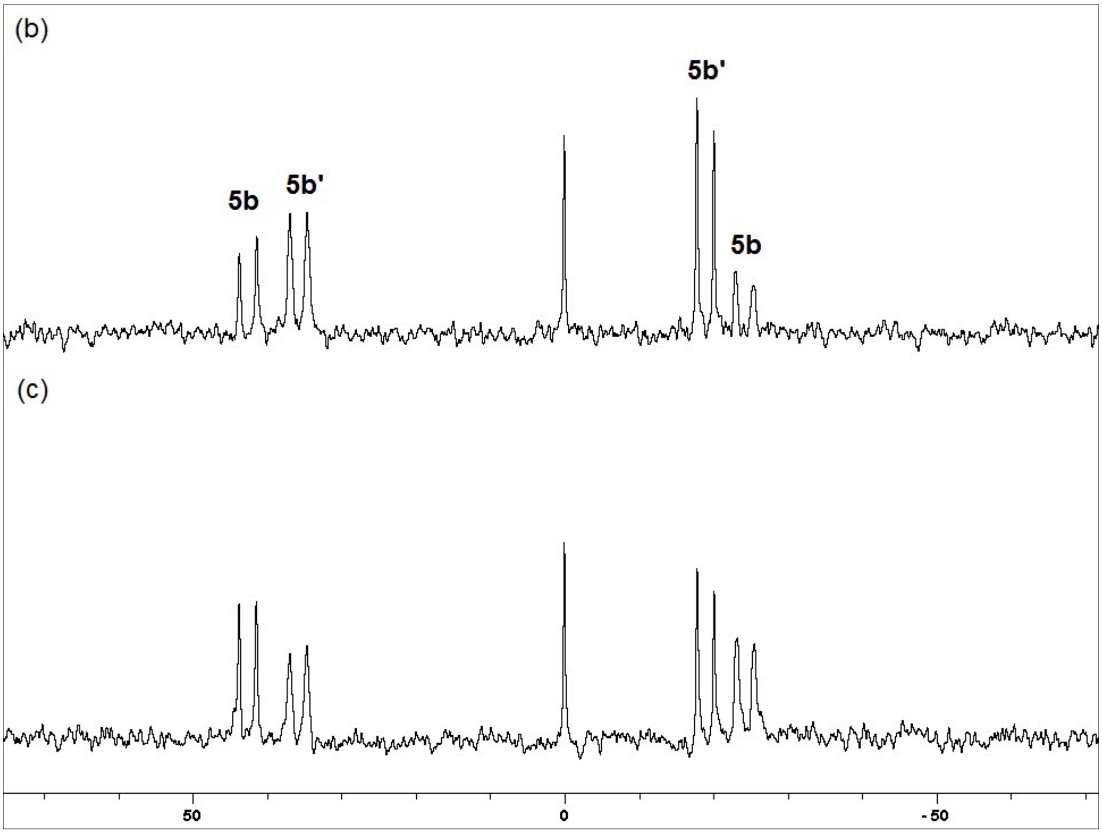
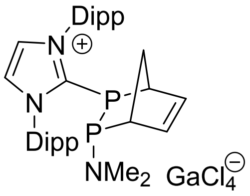


Figure S 12 Detail of the ^{31}P NMR spectrum shown in **Figure S 11**. Spectrum (b) measured directly after the addition of cyclopentadiene, spectrum (c) 12 h later. Two sets of signals are observed, which are assigned to cycloaddition products

Synthesis of Cycloadduct **5c**



5c

To a solution of **2c** (85.8 mg, 0.162 mmol) and 0.1 mL of cyclopentadiene (ca. 1.2 mmol, 7.5 eq.) in 2 mL of dry THF, a solution of $GaCl_3$ (29.9 mg, 0.170 mmol, 1.05 eq.) in 1 mL of dry hexane is slowly added while stirring. Upon evaporation *in vacuo*, an off-white foam is obtained, which is dissolved in a minimum amount of dry DME. Covering the filtered solution with dry hexane, **5c** is obtained as colourless crystals suitable for XRD (19.1 mg, 0.025 mmol, 15 %). Note that **5c** is extremely sensitive to vacuum as cycloreversion reactions occur. This leads to major impurities, which are observed in NMR spectra (Figure S 14). Therefore, the assignment of NMR signals must be regarded as rough estimation in comparison with similar compounds.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ/ppm = 7.74 (s, 2H, NCH=CHN), 7.67 (t, J_{HH} = 7.9 Hz, 2H, p-Dipp), 7.49-7.46 (m, 2H, m-Dipp), 7.42-7.37 (m, 2H, m-Dipp), 6.16-6.11 (m, 1H, CCH=CHC), 5.52-5.48 (m, 1H, CCH=CHC), 3.39-3.25 (m, 1H, PCH), 1.74-1.58 (m, 1H, PCH), 2.57-2.38 (m, Dipp-CH(CH_3)$_2$), 2.14-2.10 (m, 6H, N(CH_3)$_2$), 1.48 (d, J_{HH} = 6.8 Hz, 6H, Dipp-CH_3), 1.35-1.18 (m, Dipp-CH_3), 1.10-1.00 (m, 2H, CH_2); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K) δ/ppm = 146.0 (ipso-Dipp), 145.2 (ipso-Dipp), 137.9 (d, J_{PC} = 15.6 Hz, CC=CC), 132.6 (p-Dipp), 131.5 (o-Dipp), 128.3 (NCH=CHN), 125.7-124.9 (multiple signals, m-Dipp, CC=CC), 48.4 (d, J_{PC} = 39.1 Hz, PCH), 44.7-44.4 (m, CH$_2$), 44.0 (dd, J_{PC} = 16.5 Hz, J_{PC} = 6.2 Hz, N(CH_3)$_2$), 29.9-29.2 (several signals, CH(CH_3)$_2$), 26.4-22.2 (several signals, Dipp-CH$_3$), not found: $C_{carbene}$, second PCH; **^{31}P{^{1}H} NMR** (162.0 MHz, $CDCl_3$, 298 K) δ/ppm = 66.5 (d, J_{PP} = 258.6 Hz), -25.2 (d, J_{PP} = 258.3 Hz), beside major impurities

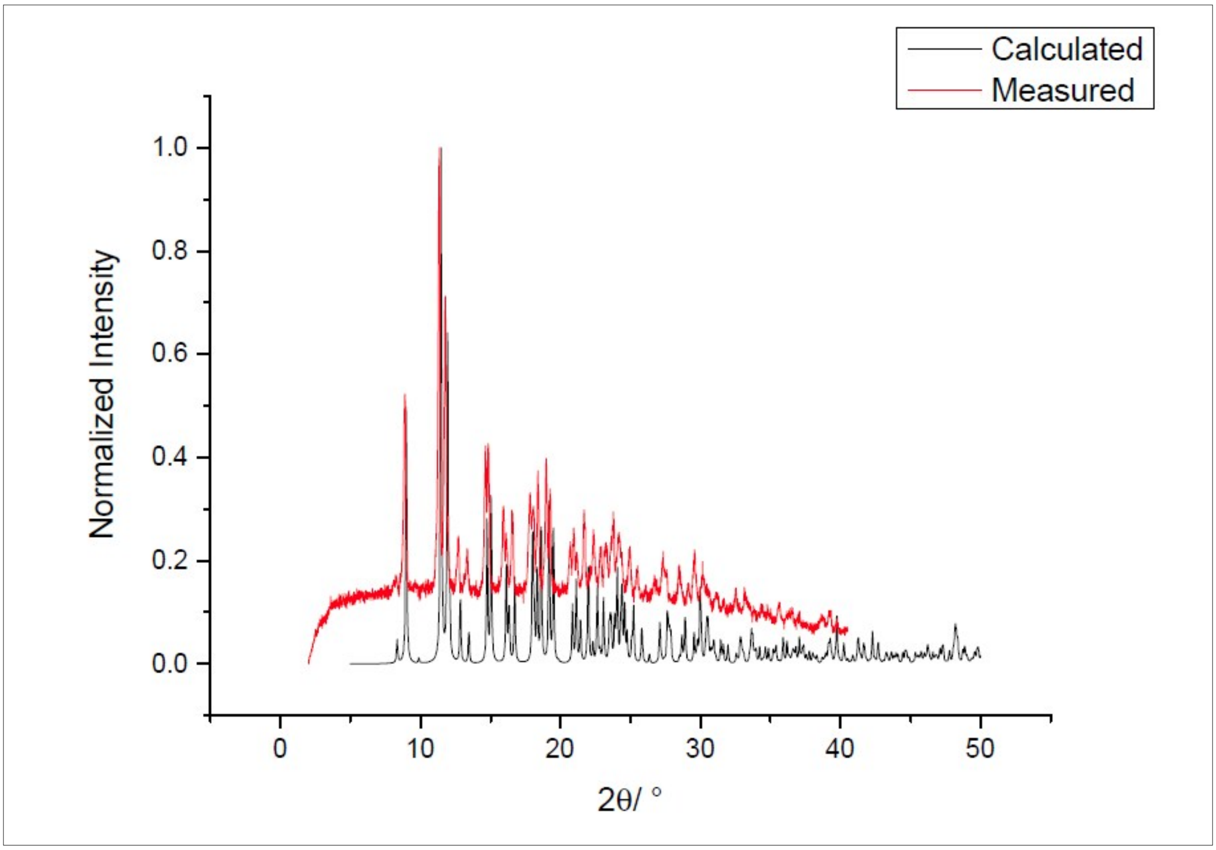


Figure S 13 Calculated and measured powder diffractograms of **5c**

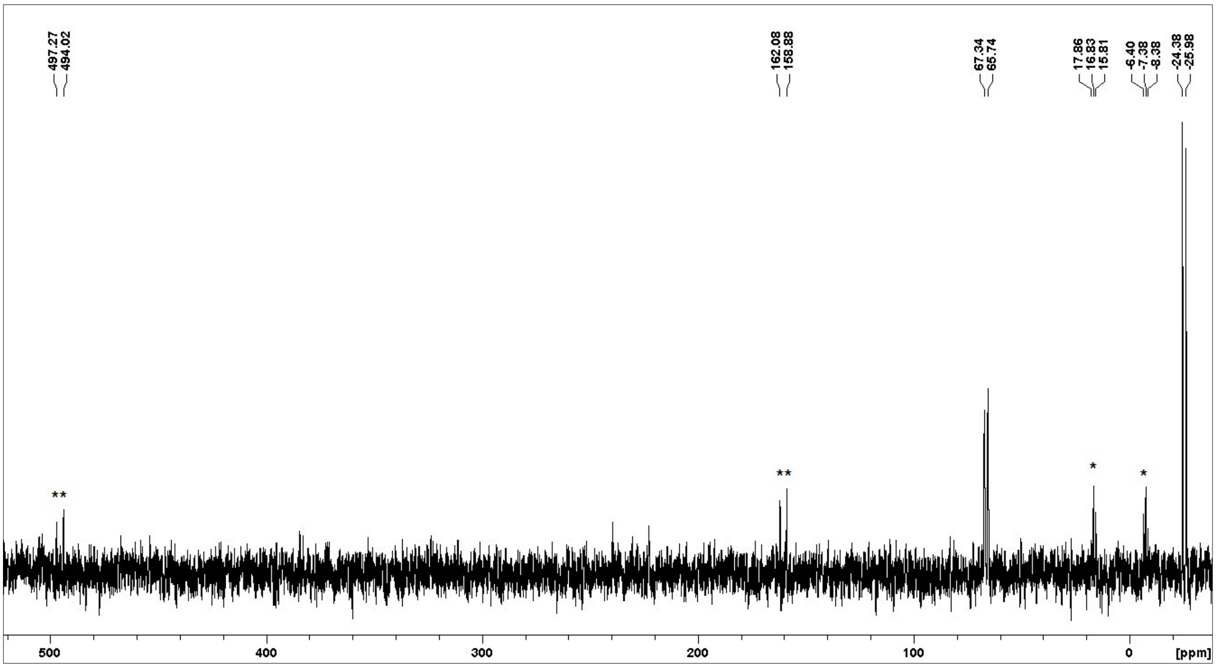


Figure S 14 162.0 MHz $^{31}P\{^{1}H\}$ NMR spectrum of **5c**. Beside the signals of **5c**, signals assigned to **(3c)$_2$** (*) and the monomeric cation **3c** (**), which has not been observed otherwise, are detected

Crystallographic Tables

Table S 1 Crystal data and structure refinement for **2a**

CCDC number	1415566
Empirical formula	$C_{33}H_{41}N_2P_2Cl$
Formula weight	563.07
Temperature/K	102.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.0682(3)
b/Å	12.4824(3)
c/Å	24.4361(6)
α/°	90
β/°	93.0570(10)
γ/°	90
Volume/Å^3	3066.64(14)
Z	4
ρ_{calc}g/cm^3	1.220
μ/mm^{-1}	2.262
F(000)	1200.0
Crystal size/mm^3	0.19 × 0.164 × 0.097
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.246 to 157.984
Index ranges	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-31 \leq l \leq 31$
Reflections collected	65434
Independent reflections	6607 [$R_{int} = 0.0581$, $R_{sigma} = 0.0270$]
Data/restraints/parameters	6607/0/351
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	$R_1 = 0.0445$, $wR_2 = 0.1129$
Final R indexes [all data]	$R_1 = 0.0513$, $wR_2 = 0.1175$
Largest diff. peak/hole / e Å^{-3}	0.53/-0.35

Table S 2 Crystal data and structure refinement for **2b**

CCDC	1415567
Empirical formula	$C_{33}H_{50}N_3P_2Cl$
Formula weight	586.15
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	10.4571(2)
b/Å	10.8862(2)
c/Å	16.6912(3)
α/°	83.6921(8)
β/°	82.8084(8)
γ/°	62.1884(8)
Volume/Å^3	1664.52(5)
Z	2
ρ_{calc}g/cm^3	1.169
μ/mm^{-1}	0.236
F(000)	632.0
Crystal size/mm^3	0.297 × 0.176 × 0.083
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.464 to 54.228
Index ranges	$-13 \leq h \leq 13, -10 \leq k \leq 13, -21 \leq l \leq 21$
Reflections collected	25555
Independent reflections	7359 [R_{int} = 0.0346, R_{sigma} = 0.0483]
Data/restraints/parameters	7359/0/364
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.0792
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.0867
Largest diff. peak/hole / e Å^{-3}	0.37/-0.29

Table S 3 Crystal data and structure refinement for **3b**

CCDC	1415568
Empirical formula	$C_{33}H_{50}Cl_4GaN_3P_2$
Formula weight	762.22
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.3933(8)
b/Å	24.7035(17)
c/Å	15.9464(12)
α/°	90
β/°	105.836(4)
γ/°	90
Volume/Å^3	3938.9(5)
Z	4
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	1.077
F(000)	1592.0
Crystal size/mm^3	0.185 × 0.132 × 0.083
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.126 to 52.742
Index ranges	$-12 \leq h \leq 12$, $-30 \leq k \leq 30$, $-19 \leq l \leq 19$
Reflections collected	51773
Independent reflections	8040 [R_{int} = 0.0423, R_{sigma} = 0.0319]
Data/restraints/parameters	8040/0/421
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0343, wR_2 = 0.0708
Final R indexes [all data]	R_1 = 0.0511, wR_2 = 0.0769
Largest diff. peak/hole / e Å^{-3}	0.67/-0.54

Table S 4 Crystal data and structure refinement for **(3c)$_2$**

CCDC	1415569
Empirical formula	$C_{62}H_{94}Cl_8Ga_2N_6O_2P_4$
Formula weight	1502.35
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbcn
a/Å	32.9377(6)
b/Å	23.6356(4)
c/Å	19.1985(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	14946.1(5)
Z	8
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	1.136
F(000)	6256.0
Crystal size/mm^3	0.452 × 0.224 × 0.222
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.686 to 61.102
Index ranges	$-47 \leq h \leq 38, -33 \leq k \leq 33, -27 \leq l \leq 13$
Reflections collected	103106
Independent reflections	22865 [R_{int} = 0.0493, R_{sigma} = 0.0449]
Data/restraints/parameters	22865/155/895
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.0893
Final R indexes [all data]	R_1 = 0.0755, wR_2 = 0.1023
Largest diff. peak/hole / e Å^{-3}	0.51/-0.67

Table S 5 Crystal data and structure refinement for **4a**

CCDC	1415570
Empirical formula	$C_{39}H_{51}N_2P_2Cl_4Ga$
Formula weight	821.28
Temperature/K	101.1
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5864(5)
b/Å	16.4856(8)
c/Å	24.2540(11)
α/°	90
β/°	102.366(2)
γ/°	90
Volume/Å^3	4134.7(3)
Z	4
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	1.030
F(000)	1712.0
Crystal size/mm^3	0.992 × 0.541 × 0.526
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.642 to 61.126
Index ranges	$-15 \leq h \leq 15$, $-23 \leq k \leq 23$, $-34 \leq l \leq 34$
Reflections collected	78415
Independent reflections	12547 [R_{int} = 0.0763, R_{sigma} = 0.0426]
Data/restraints/parameters	12547/0/443
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.0859
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.0917
Largest diff. peak/hole / e Å^{-3}	0.83/-0.49

Table S 6 Crystal data and structure refinement for **4b**

CCDC	1415571
Empirical formula	$C_{39}H_{60}N_3P_2Cl_4Ga$
Formula weight	844.36
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.7703(2)
b/Å	15.0762(3)
c/Å	27.5758(5)
α/°	90
β/°	101.0720(10)
γ/°	90
Volume/Å^3	4394.28(14)
Z	4
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.972
F(000)	1776.0
Crystal size/mm^3	0.297 × 0.255 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.044 to 52.744
Index ranges	$-13 \leq h \leq 5$, $-18 \leq k \leq 18$, $-34 \leq l \leq 34$
Reflections collected	34737
Independent reflections	8936 [R_{int} = 0.0272, R_{sigma} = 0.0290]
Data/restraints/parameters	8936/0/461
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0908
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.0981
Largest diff. peak/hole / e Å^{-3}	0.85/-0.37

Table S 7 Crystal data and structure refinement for **4c**

CCDC	1415572
Empirical formula	$C_{35}H_{52}N_3P_2Cl_4Ga$
Formula weight	788.25
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a/Å	20.036(3)
b/Å	18.337(2)
c/Å	21.409(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7865.6(18)
Z	8
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	1.081
F(000)	3296.0
Crystal size/mm^3	0.396 × 0.32 × 0.264
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.562 to 58.374
Index ranges	$-27 \le h \le 27$, $-24 \le k \le 20$, $-29 \le l \le 29$
Reflections collected	55940
Independent reflections	10591 [R_{int} = 0.0281, R_{sigma} = 0.0224]
Data/restraints/parameters	10591/18/464
Goodness-of-fit on F^2	1.199
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1456
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1520
Largest diff. peak/hole / e Å^{-3}	0.85/-0.52

Table S 8 Crystal data and structure refinement for **5a**

CCDC	1415573
Empirical formula	$C_{38}H_{47}Cl_4GaN_2P_{2.07}$
Formula weight	807.32
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4962(7)
b/Å	16.4244(11)
c/Å	23.8724(15)
α/°	90
β/°	101.7157(11)
γ/°	90
Volume/Å^3	4029.7(5)
Z	4
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	1.059
F(000)	1676.0
Crystal size/mm^3	0.49 × 0.34 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.03 to 58.438
Index ranges	$-14 \leq h \leq 14$, $-22 \leq k \leq 22$, $-32 \leq l \leq 32$
Reflections collected	44260
Independent reflections	10899 [R_{int} = 0.0312, R_{sigma} = 0.0287]
Data/restraints/parameters	10899/0/440
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0915
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.0970
Largest diff. peak/hole / e Å^{-3}	0.72/-0.40

Table S 9 Crystal data and structure refinement for **5c**

CCDC	1415574
Empirical formula	$C_{34}H_{48}N_3P_2Cl_4Ga$

Formula weight	772.21
Temperature/K	100
Crystal system	monoclinic
Space group	Cc
a/Å	19.7393(3)
b/Å	13.1426(2)
c/Å	16.1564(2)
α/°	90
β/°	115.0700(10)
γ/°	90
Volume/Å^3	3796.52(10)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	1.118
F(000)	1608.0
Crystal size/mm^3	0.331 × 0.125 × 0.094
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.846 to 66.186
Index ranges	$-30 \leq h \leq 30, -19 \leq k \leq 20, -23 \leq l \leq 22$
Reflections collected	24678
Independent reflections	11114 [R_{int} = 0.0340, R_{sigma} = 0.0684]
Data/restraints/parameters	11114/28/431
Goodness-of-fit on F^2	0.953
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0731
Final R indexes [all data]	R_1 = 0.0464, wR_2 = 0.0764
Largest diff. peak/hole / e Å^{-3}	0.75/-0.29

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