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A Melt Approach to the Synthesis of *catena*-Phosphorus Dications To Access Derivatives of $[P_6Ph_4R_4]^{2+}$**

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Dedicated to Hartmut S. Huhn

catena-Phosphorus chemistry is underdeveloped in the context of the diagonal relationship between carbon and phosphorus.[1] Oligophosphines[2,3] such as hexaphenylcyclohexaphosphine $(PPh)_6$[4] provide analogies with cycloalkanes as the CR_2 methylene unit is isolobal with the phosphine (PR) unit. The familiar cationic phosphonium center is also isolobal to these units; however, while extensive series of *catena*-phosphide anions are well-known,[5,6] *catena*-phosphorus cations represent a newly developing family of compounds achieved through homoatomic coordination chemistry.[7–9] Examples of phosphinophosphonium dications are rare and are represented by the unique derivatives of **1**,[10–15] **2**,[16] **3**,[17] and **4**[18] (Scheme 1). Larger polyphosphorus frameworks such as **5** and **6**, which have not been reported so far, are expected to be more viable for the accommodation of multiple charges. We have now prepared the first cyclotetraphosphinodiphosphonium salts, **6a**-$[GaCl_4]_2$ and **6b**-$[GaCl_4]_2$, from molten mixtures of a cyclopolyphosphine, a chlorophosphine, and gallium chloride. This is a versatile potentially synthetic approach to a new direction in phosphorus chemistry using a melt medium.

Stirred mixtures of $^4/_5\,(PhP)_5$, $2\,Ph_2PCl$, and $2\,GaCl_3$ were gradually heated ($5\,^\circ C\,min^{-1}$) over a period of 30 minutes and

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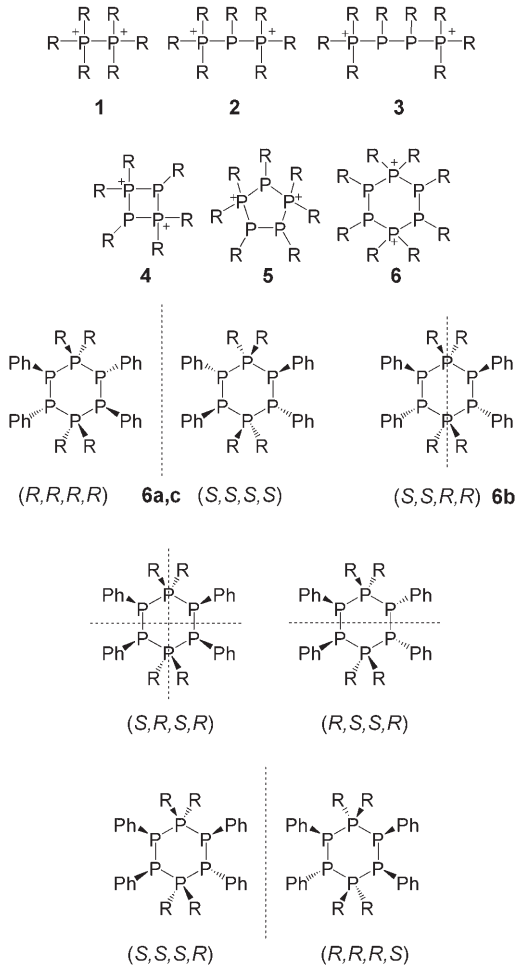


Scheme 1. Cyclic *catena*-phosphinodiphosphonium dications. Seven possible stereoisomers of **6** (**6a**: R = Ph; **6b**,**c**: R = Me) are shown. Dotted lines define mirror relationships or planes of symmetry.

gave a yellow melt between 70 and 125 °C, which became turbid and gradually solidified with increasing temperature up to about 165 °C.[19] The recrystallized solid, which has a decomposition point above 190 °C, was identified by X-ray crystallography as **6a**-$[GaCl_4]_2$,[19] which contains a P_6 homocycle composed of two phosphonium centers (1,4-positions) and four phosphine centers. The cation **6a** is conveniently named a 2,3,5,6-tetraphosphino-1,4-diphosphonium compound and represents the first example of a *catena*-hexaphosphorus dication. The racemic crystalline material contains only the *R,R,R,R* and *S,S,S,S* isomers of cation **6a**, which represent two of seven possible configurational isomers (two enantiomeric pairs and three *meso* forms) imposed by four phosphine stereocenters, as illustrated in Scheme 1. Consistently, the ^{31}P NMR spectrum of **6a**-$[GaCl_4]_2$ in CH_2Cl_2 at room temperature shows a rare and complex AA′A″A‴BB′ spin system.[20] At a field strength of 5.87 T, ^{31}P NMR spectra of **6a**-$[GaCl_4]_2$ show no evidence of dynamic behavior over the temperature range 190–300 K, suggesting preservation of the *R,R,R,R* and *S,S,S,S* configurations in solution within this temperature range based on molecular symmetry.[20]

In the solid state, (±)-**6a**-$[GaCl_4]_2$ (Figure 1)[19] adopts a twist-boat (TB) conformation (the P1−P4 vector represents the axis with P2, P3, P5, and P6 as the twisted plane) with the phenyl groups attached at the phosphino centers in an all-*trans* configuration, as defined by the Cremer and Pople puckering parameters ($Q = 1.7194(8)$ Å, $\theta = 89.84(3)°$ and $\varphi = 88.76(3)°$; ideal values: $\theta = 90°$ and $\varphi = 90°$).[21] The P−P and P−C bond lengths (P−P 2.231(2)–2.242(2) Å, P−C 1.792(3)–1.835(3) Å) are similar to those of phosphinophosphonium monocations[8] and are comparable with those of polyphosphines such as, for example, trigonal hexaphosphine $(PhP)_6$ (P−P 2.237(5) Å, P−C 1.843(7) Å).[4] The TB conformation of (±)-**6a**-$[GaCl_4]_2$ contrasts the chair conformation of $(PhP)_6$,[4] likely owing to the steric demand of the eight phenyl groups. Nevertheless, in comparison with cyclohexane analogues, the twisted-boat conformation of **6a** appears to be relatively strain-free because of the greater flexibility of the phosphorus ring and the larger bond lengths.

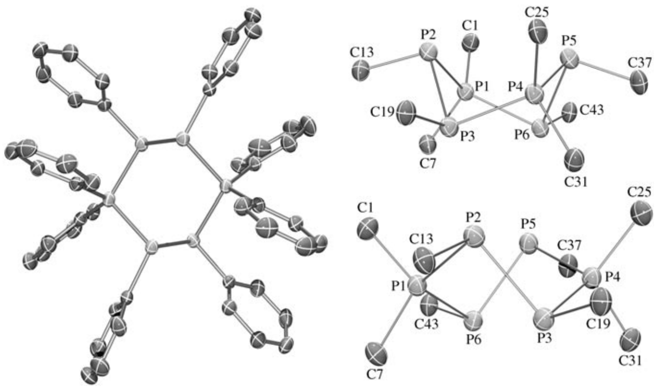
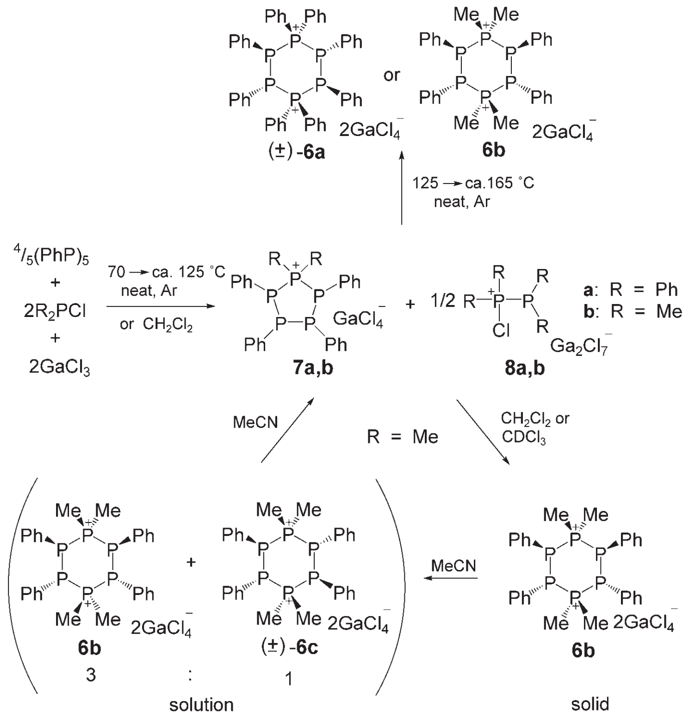


Figure 1. Left side: ORTEP plot of the solid-state structure of the cation in (±)-**6a**-$[GaCl_4]_2$ (H atoms are omitted). Right side: two different side views of the core structure showing the cyclohexane-like geometry in a twist-boat conformation (only the *ipso*-C atoms of the phenyl groups are shown). Thermal ellipsoids are set at 50% probability at 173(2) K. Selected bond lengths [Å] and angles [°]: P1-P2 2.242(2), P2-P3 2.231(2), P3-P4 2.217(2), P4-P5 2.233(2), P5-P6 2.227(1), P1-C1 1.792(3), P1-C7 1.801(3), P2-C13 1.835(3), P3-C19 1.826(3), P4-C25 1.801(3), P4-C31 1.788(3), P5-C37 1.835(3), P6-C43 1.827(3); P1-P2-P3 92.09(5), P2-P3-P4 95.64(6), P3-P4-P5 109.27(4), P4-P5-P6 93.16(6), P5-P6-P1 95.10(6), P6-P1-P2 109.93(4), C1-P1-C7 110.9(1), C1-P1-P2 106.6(1), C1-P1-P6 113.0(1), C7-P1-P2 110.3(1), C7-P1-P6 106.2(1), C25-P4-C31 110.3(1), C25-P4-P3 114.7(1), C25-P4-P5 106.2(1), C31-P4-P3 105.1(1), C31-P4-P5 111.4(1), P1-P6-C43 98.7(1), P4-P3-C19 101.39(9), P4-P5-C37 94.8(1), P1-P6-C43 987(1).

Interestingly, when the temperature of the reaction mixture did not exceed 100 °C and the melt was quenched to room temperature within seconds, ^{31}P NMR spectra of the resulting yellow oil in CH_2Cl_2 showed the presence of the cyclotetraphosphinophosphonium salt **7a**-$[GaCl_4]$,[8] the phosphinophosphonium salt **8a**-$[Ga_2Cl_7]$[7] (Scheme 2), and small amounts of **6a**-$[GaCl_4]_2$. Solutions of **6a**-$[GaCl_4]_2$ in CH_2Cl_2 at room temperature decompose ($t_{1/2} \approx 24$ h) to **7a**-$[GaCl_4]$, **8a**-$[Ga_2Cl_7]$, and $Ph_2(Cl)P{\cdot}GaCl_3$ (s, $\delta = 41$ ppm).[22]

A molten mixture of $^4/_5(PhP)_5$, $2\,Me_2PCl$, and $2\,GaCl_3$ at about 165 °C was cooled and extracted with CH_2Cl_2, thereby



Scheme 2. Formation of (±)-**6a**-$[GaCl_4]_2$ and **6b**-$[GaCl_4]_2$, isomerization of **6b**-$[GaCl_4]_2$, and decomposition of **6b**-$[GaCl_4]_2$ and (±)-**6c**-$[GaCl_4]_2$ in MeCN solution. Only one enantiomer is depicted for (±)-**6a**-$[GaCl_4]_2$ and (±)-**6c**-$[GaCl_4]_2$.

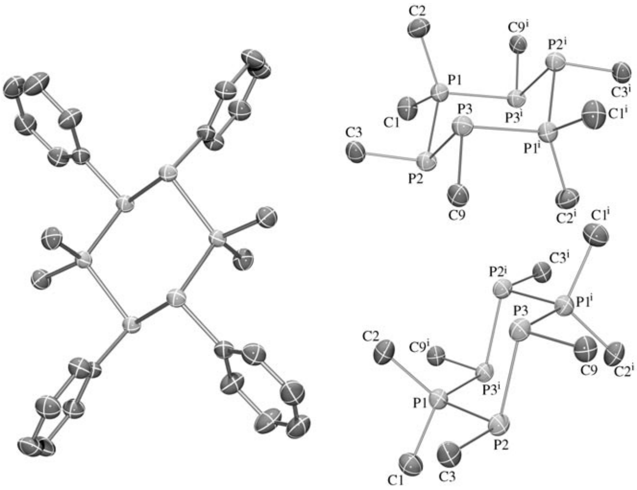


Figure 2. Left side: ORTEP plot of the solid-state structure of **6b**-$[GaCl_4]_2$·2 $CDCl_3$ (H atoms are omitted). Right side: two different side views of the core structure showing the cyclohexane-like chair conformation (only the *ipso*-C atoms of the phenyl groups are shown). Thermal ellipsoids are set at 50% probability at 173(2) K. Selected bond lengths [Å] and angles [°]: P1-P2 2.2014(9), P2-P3 2.2308(9), P3-$P1^i$ 2.2081(9), P1-C1 1.802(3), P1-C2 1.795(2), P2-C3 1.839(2), P3-C9 1.837(2); P1-P2-P3 98.22(3), P2-P3-$P1^i$ 97.31(3), P2-P1-$P3^i$ 105.10(3), C1-P1-C2 108.9(1), C1-P1-P2 104.9(1), C1-P1-$P3^i$ 104.4(1), C2-P1-P2 115.8(1), C2-P1-$P3^i$ 116.7(1), P1-P2-C3 99.30(8), P2-P3-C9 97.65(8), $P1^i$-P3-C9 99.59(8).

leaving a colorless solid in low yield that was spectroscopically characterized as **6b**-$[GaCl_4]_2$. The same reaction mixture in CH_2Cl_2 solution slowly precipitated **6b**-$[GaCl_4]_2$ over about 48 hours (Scheme 2), and crystals grown from the mother liquor by slow removal of solvent at room temperature were identified crystallographically as **6b**-$[GaCl_4]_2$·3 CH_2Cl_2 with disorder in the solvent molecules. Recrystallization of **6b**-$[GaCl_4]_2$ from $CDCl_3$ yielded high-quality crystals of **6b**-$[GaCl_4]_2$·2 $CDCl_3$, and the solid-state structure of the dication **6b** is shown in Figure 2.[19] The observed P–P (2.231(2)–2.242(2) Å) and P–C bond lengths (1.792(3)–1.835(3) Å) are comparable to those of (±)-**6a**-$[GaCl_4]_2$. The side views of the structure show that the ring adopts a chair conformation similar to that of cyclohexane. While the internal C-C-C angle of cyclohexane is 111.4°,[23] the internal P-P-P angles at the phosphonium centers of **6b** (105.10(3)°) are smaller and comparable to those in S_6 (102.61°).[24] The internal P-P-P angles at the phosphine centers (98.22(3)°) are predictably smaller and are comparable to those in $(PhP)_6$. Owing to the longer bonds and flexibility of the P_6 ring, the chair form is indicated by the dihedral angle between the planes of the chair (101.55(5)° vs. 133° in cyclohexane).[25] This form is also reflected by the torsion angles $\tau_1 = -73.5(4)°$ and $\tau_2 = 79.4(1)°$,[26] which are larger than the ideal value in cyclohexane (55.9(2)°)[25] and are consistent with the observed puckering parameters ($Q = 1.2547(8)$ Å, $\theta = 0.37(1)°$ and $\varphi = 0°$),[21] which are very close to those of the chair conformation of cyclohexane (nearest ideal values: $\theta = 0°$ and $\varphi = 0°$).

The ^{31}P MAS NMR spectrum of **6b**-$[GaCl_4]_2$ as a microcrystalline precipitate confirmed the presence of only one symmetric isomer in the solid state with two broad multiplets at $\delta = 11.7$ and -50.1 ppm in the approximate ratio of 1:2.[20] Two complicated AA′A″A‴BB′ spin systems were observed in MeCN solution. Iterative analysis of the complex spectrum, performed at two external field strengths, revealed chemical shifts for one isomer at $\delta = 11.2$ and -53.5 ppm (Table 1), which are similar to those observed in the solid state for **6b**-$[GaCl_4]_2$, thus indicating retention of the solid-state configuration in solution. The other AA′A″A‴BB′ pattern with chemical shifts observed at $\delta = 12.4$ and -63.6 ppm is

Table 1: $^{31}P\{^1H\}$ NMR parameters[a] obtained from a simulated match of experimental spectra of (±)-**6a**-$[GaCl_4]_2$, **6b**-$[GaCl_4]_2$, and (±)-**6c**-$[GaCl_4]_2$ in $[D_3]$MeCN at two different external magnetic field strengths.

	4[b,c,d]	(±)-**6a**-$[GaCl_4]_2$	(±)-**6c**-$[GaCl_4]_2$	**6b**-$[GaCl_4]_2$
$\delta_A = \delta_{A'} = \delta_{A''} = \delta_{A'''}$	+2.2	−60.8	−63.6	−53.5
$\delta_B = \delta_{B'}$	+41.2	+29.8	+12.4	+11.2
$^1J_{AB} = {}^1J_{A'''B} = {}^1J_{A'B'} = {}^1J_{A''B'}$	−287.0	−310.5	−306.2	−295.2
$^1J_{AA'} = {}^1J_{A''A'''}$	–	−80.9	−85.8	−4.0
$^2J_{A'B} = {}^2J_{A''A} = {}^2J_{AB'} = {}^2J_{A'''B'}$	–	+89.4	+79.1	+54.9
$^2J_{AA'''} = {}^2J_{A'A''}$	–	−12.2	−11.1	−71.4
$^3J_{AA''} = {}^3J_{A'A'''}$	–	+98.5	+100.2	+92.5
$^3J_{BB'}$	–	+5.1	+10.2	+7.4

[a] The relative signs of the coupling constants result from the iterative fitting of the spectrum assuming negative values for the $^1J_{PP}$ constants.[27] [b] A_2B_2 spin system. [c] See reference [18]. [d] R = 2,6-dimethoxyphenyl.

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assigned to (±)-**6c**-$[GaCl_4]_2$ (see Table 1). Consistently, the $^1H\{^{31}P\}$ NMR spectrum shows three singlets corresponding to three different methyl groups for the two different stereoisomers **6b**-$[GaCl_4]_2$ and (±)-**6c**-$[GaCl_4]_2$. These compounds decompose in solution at room temperature ($t_{1/2} \approx 30$ min) to give **7b**-$[GaCl_4]$, **8b**-$[Ga_2Cl_7]$,[22] and traces of $Me_2(Cl)P\cdot GaCl_3$ (s, $\delta = 57$ ppm),[22] as shown in Figure 3.

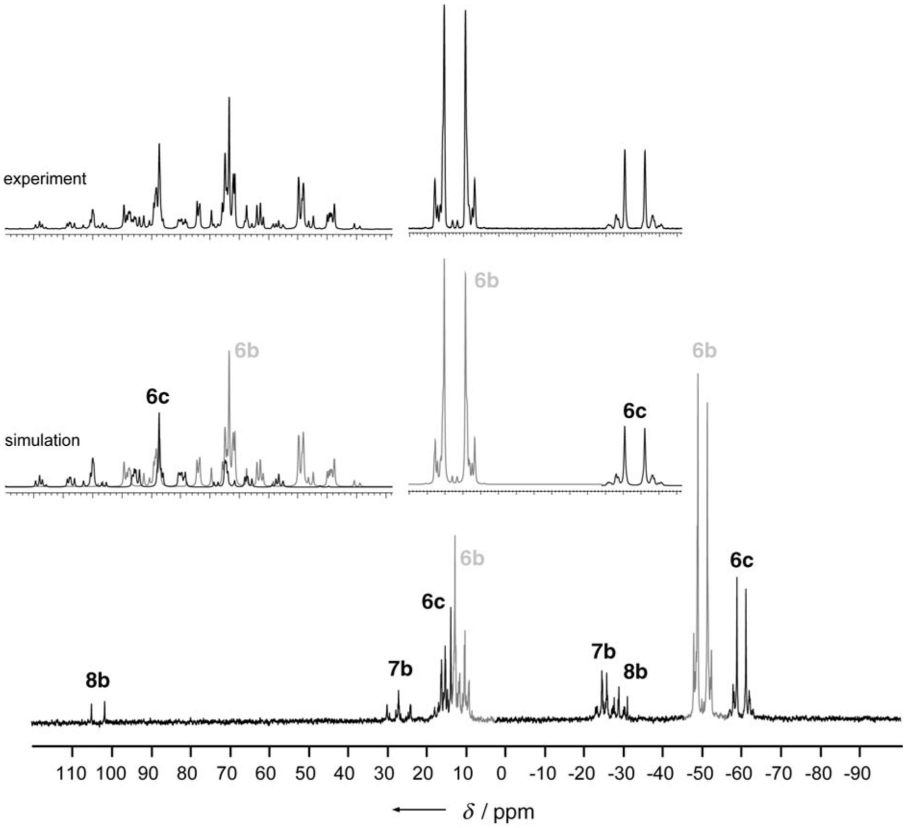

Figure 3. $^{31}P\{^1H\}$ NMR spectrum of **6b** at room temperature, 10 min after being dissolved in MeCN. Assignments: **6b** and (±)-**6c**, **7b** (complex multiplet, $\delta_A = 26$ ppm, $\delta_B = -29$ ppm);[8] **8b** (dd, $\delta(P_A) = +103$ ppm, $\delta(P_B) = -29$ ppm, $J_{PP} = 340$ Hz);[22] experimental (upper) and simulated (lower) for **6b** and (±)-**6c**.

Two peaks of equal integration at $\delta = 1.85$ and 2.25 ppm are tentatively assigned to the axial and equatorial methyl groups, indicating that **6b**-$[GaCl_4]_2$ (*meso*, *S,S,R,R*) exists as a chair conformer, and the sharp singlet at $\delta = 1.88$ ppm is assigned to (±)-**6c**-$[GaCl_4]_2$ (enantiomeric pair *R,R,R,R* and *S,S,S,S*) consistent with a twist-boat conformation.[20]

The $^{31}P\{^1H\}$ NMR data for (±)-**6a**-$[GaCl_4]_2$, **6b**-$[GaCl_4]_2$, and (±)-**6c**-$[GaCl_4]_2$ have been simulated and are summarized in Table 1. Chemical shifts at low field ($\delta = 30$ to 10 ppm) are assigned to the phosphonium centers, and the trivalent phosphorus centers have shifts at higher field ($\delta = -50$ to -60 ppm), in accordance with those for phosphinophosphonium monocations.[7,8]

In conclusion, molten mixtures of organophosphines and diorganochlorophosphines together with gallium trichloride provide a new synthetic approach to *catena*-phosphorus cations and represent a versatile method for the preparation of dications that do not form in solution (**6a**). The new hexaphosphorus dications highlight the potential to develop a diverse *catena*-phosphorus chemistry that parallels *catena*-carbon chemistry (organic chemistry).

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[19] For experimental details, see the Supporting Information; Crystal data: X-ray quality crystals of (±)-**6a**-$[GaCl_4]_2$ were obtained by diffusion of Et_2O vapors into a colorless solution of the dication in fluorobenzene at room temperature over about 6 h. In the case of **6b**-$[GaCl_4]_2$ suitable crystals for the structure

determination were obtained from the mother liquor after 5 days at room temperature in solvated form as **6b**-[GaCl$_4$]$_2$·3CH$_2$Cl$_2$ or **6b**-[GaCl$_4$]$_2$·2CDCl$_3$, depending on the solvent used during the preparation. Single crystals of (±)-**6a**-[GaCl$_4$]$_2$ and **6b**-[GaCl$_4$]$_2$·2CDCl$_3$ were coated with Paratone N oil, mounted using a 20-micron cryoloop, and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and exposure times of 30 s for (±)-**6a**-[GaCl$_4$]$_2$ and 10 s for **6b**-[GaCl$_4$]$_2$·2CDCl$_3$. The detector distance was 5 cm. The data were reduced using SAINT (SAINT 6.02, 1997–1999, Bruker AXS, Inc., Madison, Wisconsin, USA) and corrected for absorption with SADABS (SADABS, George Sheldrick, 1999, Bruker AXS, Inc., Madison, Wisconsin, USA). The structure was solved by direct methods and refined by full-matrix least squares on F^2 with SHELXTL (SHELXTL 6.14, 2000–2003, Bruker AXS, Inc., Madison, Wisconsin, USA). All non-hydrogen atoms were refined anisotropically. For (±)-**6a**-[GaCl$_4$]$_2$ hydrogen atoms were included in calculated positions and refined using a riding model. In the case of **6b**-[GaCl$_4$]$_2$·2CDCl$_3$ hydrogen atoms were found in Fourier difference maps and refined isotropically. (±)-**6a**-[GaCl$_4$]$_2$: $C_{48}H_{40}Cl_8Ga_2P_6$, colorless, irregular, crystal size $0.45 \times 0.35 \times 0.10$ mm^3, monoclinic, space group Cc, $a = 11.396(9)$, $b = 25.90(2)$, $c = 18.73(2)$ Å, $\beta = 104.57(1)°$, $V = 5349(8)$ Å^3, $Z = 4$, $\mu = 1.620$ mm^{-1}; $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $2\theta_{max} = 55.0°$, 18192 collected reflections (8670 independent), $R_{int} = 0.0314$, 577 refined parameters, $R_1 = 0.0291$, $wR_2 = 0.0561$ for all data, max/min residual electron density $= 0.404/-0.265$ e Å^{-3}. **6b**-[GaCl$_4$]$_2$·2CDCl$_3$: $C_{15}H_{16}Cl_7DGaP_3$, colorless, irregular, crystal size $0.40 \times 0.30 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, $a = 12.914(3)$, $b = 11.688(2)$, $c = 17.770(4)$ Å, $\beta = 111.189(4)°$, $V = 2500.8(9)$ Å^3, $Z = 4$, $\mu = 2.041$ mm^{-1}; $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $2\theta_{max} = 55.00°$, 16914 collected reflections (5629 independent), $R_{int} = 0.0294$, 303 refined parameters, $R_1 = 0.0462$, $wR_2 = 0.0830$ for all data, max/min residual electron density $= 0.838/-0.611$ e Å^{-3}. CCDC-607203 ((±)-**6a**-[GaCl$_4$]$_2$), -607204 ((±)-**6b**-[GaCl$_4$]$_2$·2CDCl$_3$), and -607205 (**6b**-[GaCl$_4$]$_2$·3CH$_2$Cl$_2$) contain the supplementary crystallographic data for this paper (excluding structure factors, which are included in the Supporting Information). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] For NMR spectroscopic details, see the Supporting Information.

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[26] The torsion angles τ_1 and τ_2 are defined by the Newman projection of **6b**-[GaCl$_4$]$_2$ down the P1–P2 and P2–P3 bonds (symmetry code: (i) $-x$, $-y$, $-2+z$), respectively (see the Supporting Information).

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