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The Binary $Ph_2PCl/GaCl_3$ System: A Room-Temperature Molten Medium for P–P Bond Formation

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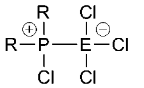
Dedicated to Professor Heinrich Nöth on the occasion of his 80th birthday

Keywords: Melt reaction / Phosphorus cations / Structure elucidation / Coordination complexes

An equimolar reaction mixture of Ph_2PCl and $GaCl_3$ at room temperature results in the formation of a melt **M** consisting of the donor–acceptor complex $Ph_2PCl{\rightarrow}GaCl_3$ (**1a**), the chloro(diphenylphosphanyl)diphenylphosphonium cation (**2a**), and the counteranions $[Ga_nCl_{3n+1}]^-$ ($n = 1, 2, 3$). The melt has been characterized by Raman and NMR spectroscopy and is compared with the reaction mixture of Ph_2PCl and $GaCl_3$ observed in solution (CH_2Cl_2). The melt provides a facile and reactive source of the diphenylphosphenium cation, as demonstrated with use for P–P bond insertion into $(PhP)_5$, to give the 2,3,4,5-tetraphosphanyl-1,4-diphosphonium dication (**3**), and reductive coupling with gallium metal to give the diadduct $Cl_3GaPPh_2PPh_2GaCl_3$ (**5**).

Introduction

The reaction between halophosphanes and ECl_3 (E = Al, Ga) Lewis acids in organic solvents has been extensively investigated.[1a–1f] Whereas the expected E–P Lewis acid–base complex **1** is observed, other structural alternatives are also formed,[1f] including coordination complexes of the phosphenium cation, also described as phosphanylphosphonium cations **2**, which contain P–P bonds.[2a–2c] We have exploited the reactivity of phosphanylphosphonium cations to develop new *catena*-phosphorus cations;[2c] however, a more diverse chemistry is becoming apparent for the $Ph_2(Cl)P/GaCl_3$ system in the absence of solvent, which is a molten mixture at room temperature.



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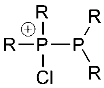

a: R = Ph
E = Al, Ga

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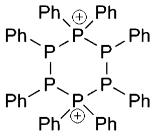

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A heated mixture of 2 Ph_2PCl, 2 $GaCl_3$, and 4/5 $(PhP)_5$ results in the quantitative formation of $[Ph_8P_6][GaCl_4]_2$ containing the new cyclotetraphosphanyldiphosphonium dication **3**.[3] The melt medium provides a potentially versatile approach to a wide range of new phosphanylphosphonium salts. This melt is observed to react with elemental gallium which affects a new reductive coupling P–P bond-forming reaction. Herein we describe the characterization of the $Ph_2(Cl)P/GaCl_3$ system using Raman and NMR spectroscopy.

Results and Discussion

Room-temperature molten salts (RTMS), also known as ionic liquids, have been media of interest for a number of years. The equimolar mixture of Ph_2PCl and $GaCl_3$ at room temp. (Scheme 1, **I**) gives an analogous homogeneous liquid (melt) that has some features in common with RTMS.[4] The mixture is essentially identical to that resulting from an equimolar mixture of solid $GaCl_3$ and solid **2a**$[GaCl_4]$ (Scheme 1, **II**) by stirring at room temp. over 20 min (Figure 1).

The melt has been characterized by $^{31}P\{^1H\}$ NMR (Figure 2) and Raman spectroscopy (Figure 3) as a mixture (**M**) of the Lewis acid–base complex $Ph_2(Cl)P{-}GaCl_3$ (**1a**) and the gallate, digallate, and trigallate salts of the chloro(diphenylphosphanyl)diphenylphosphonium cation (**2a**). The room-temperature melt **M** is indefinitely stable but is extremely moisture-sensitive.

The Raman spectra of **2a**$[GaCl_4]$ and of the melt **M** are essentially identical in the region from 3200 to 500 cm^{-1} and show only bands that belong to the phosphanylphosphon-

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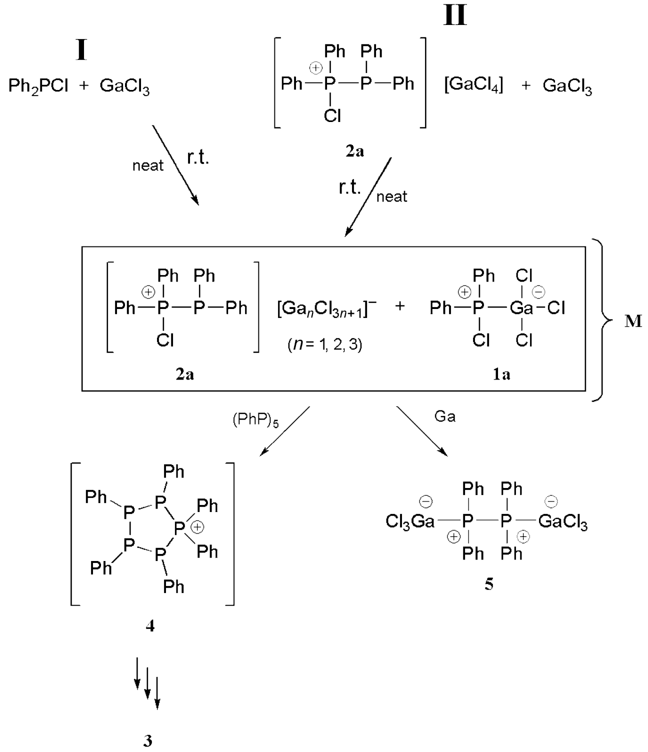


Scheme 1. Reactions of Ph_2PCl or phosphanylphosphonium cation **2a** with $GaCl_3$ and subsequent reactions of the molten mixture with $(PPh)_5$ or Ga.

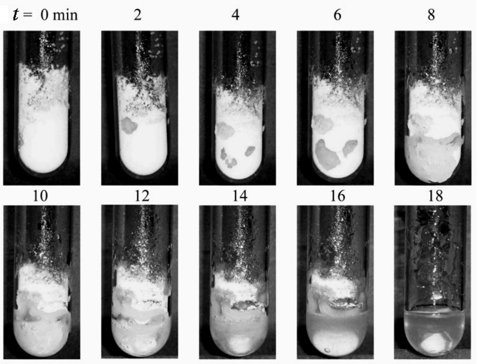


Figure 1. Formation of the melt composition **M**.

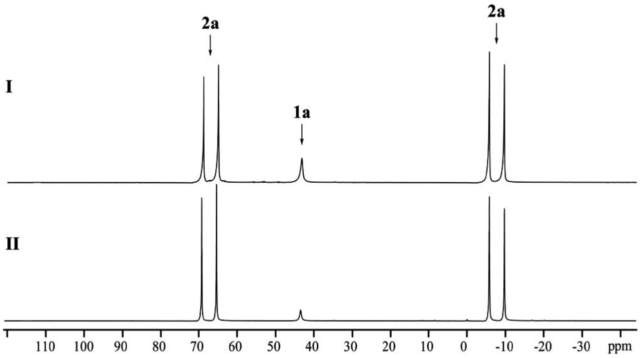


Figure 2. The $^{31}P\{^1H\}$ NMR spectra of the melt **M** obtained by the reactions **I** and **II** according to Scheme 1.

ium cation **2a**. Figure 3 shows the Raman spectra below 500 cm^{-1} of **2a**[$GaCl_4$] and **M** (**I**, **II**) (Table 1). Salt **2a**[$GaCl_4$] exhibits a band at 348 cm^{-1}, corresponding to the A_1 vibration of the tetrahedral $GaCl_4^-$ species, which is very weak in the spectra of the melts. Other features in the spectrum of **2a**[$GaCl_4$] at 153 cm^{-1} and in the region of 379–390 cm^{-1} belong to the T_2 mode of the anion and are not evident in the spectra of the melts. In contrast, the Raman spectra for the melts show weak broad features at 431 cm^{-1} and strong bands at 363 cm^{-1} and 139 cm^{-1}, assigned to $Ga_2Cl_7^-$, as well as a broad band at approximately 322 cm^{-1} which is assigned to $Ga_3Cl_{10}^-$. The most substantial spectroscopic proof of the separate existence of $Ga_3Cl_{10}^-$ are the broad bands at approximately 360–390 cm^{-1} and at 120–140 cm^{-1} as well as the observation of $GaCl_4^-$, which is consistent with an equilibrium such as that outlined in Equation (1).[5]

$$2\,Ga_2Cl_7^- \rightleftharpoons Ga_3Cl_{10}^- + GaCl_4^- \tag{1}$$

All assignments are in agreement with experimental data from the literature.[5,6] As the heptachlorodigallate and decachlorotrigallate ions, $Ga_2Cl_7^-$ and $Ga_3Cl_{10}^-$, are observed

Table 1. Comparison of Raman bands observed in the **2a**[$GaCl_4$], **M** (**I**), and **M** (**II**) systems.[5,6]

2a[$GaCl_4$][a]	**M** (**I**)[a]	**M** (**II**)[a]	Assignment[b]
	ca. 430 (w, sh, vbr)	ca. 430 (w, sh, vbr)	$Ga_2Cl_7^-$
	395 (m)	394 (m)	$Ga_3Cl_{10}^-$, $\nu_{asym}[Ga–(Cl_t)_3]$
	385 (m)	385 (m)	$Ga_2Cl_7^-$, $\nu_{asym}[Ga–(Cl_t)_3]$
380vw(sh)	–[c]	–[c]	$GaCl_4^-$, $\nu_3[T_2]$
	363 (vs)	363 (vs)	$Ga_2Cl_7^-$, $\nu_{sym}[Ga–(Cl_t)_3]$
	363 (vs)	363 (vs)	$Ga_3Cl_{10}^-$, $\nu_{sym}[Ga–(Cl_t)_3]$
348vs	348 (w)	348 (w)	$GaCl_4^-$, $\nu_1[A_1]$
	322 (w, br)	322 (w, br)	$Ga_3Cl_{10}^-$
	ca. 274 (w, br)	ca. 274 (w, br)	$Ga_2Cl_7^-$, $\nu[Ga–Cl_b–Ga]$
	ca. 274 (w, br)	ca. 274 (w, br)	$Ga_3Cl_{10}^-$, $\nu[Ga–Cl_b–Ga]$
149m	–[c]	–[c]	$GaCl_4^-$, $\nu_4[T_2]$
	138 (m)	137 (m)	$Ga_2Cl_7^-$, $\delta[Ga–(Cl_t)_3]$
	129 (m)	130 (m)	$Ga_3Cl_{10}^-$, $\delta[Ga–(Cl_t)_3]$

[a] Intensity and appearance of bands are indicated by the following abbreviations: s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder. [b] Assignments of bands for $GaCl_4^-$, $Ga_2Cl_7^-$, and $Ga_nCl_{3n+1}^-$ are based on data from the Ga/$GaCl_3$ system from ref.[6] [c] Not observed due to overlapping of bands.

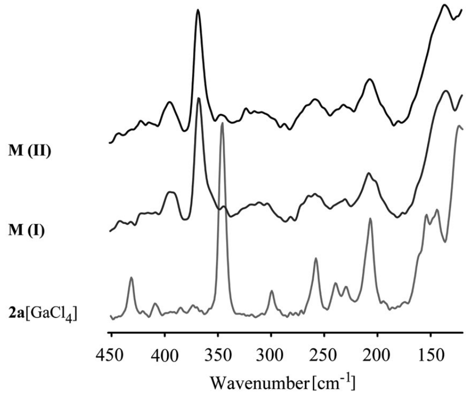
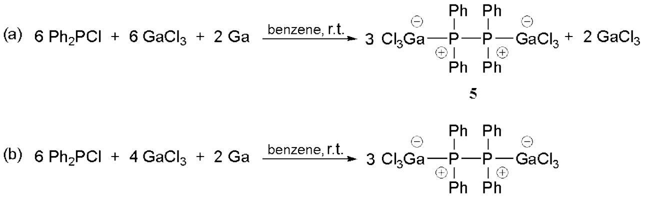


Figure 3. Raman spectra below 500 cm^{-1} for **2a**[$GaCl_4$] and of the melt **M** obtained by the reactions **I** and **II** according to Scheme 1.

in the molten mixture, **M** is considered to be an acidic medium.

The $^{31}P\{^1H\}$ NMR spectra of the melt **M** at room temp. (Figure 4a) indicate the presence of the phosphanylphosphonium salt **2a** (two doublets, δ_{iso} = 75.5, –0.9 ppm, $^1J_{PP}$ = –381.0 Hz) and the complex **1a** (δ_{iso} = 49.0 ppm). A temperature profile up to 400 K (Figure 4a) results in a broadening of the signals, which is reversible upon cooling, implying an equilibrium process. Introduction of $(PhP)_5$ into the melt **M** (Figure 4b) has no influence on the $^{31}P\{^1H\}$ NMR spectrum at room temperature as $(PhP)_5$ does not dissolve in the melt. At slightly elevated temperatures (ca. 320 K), signals corresponding to cation **4** are observed (δ_{iso} ≈ 22 and –38 ppm).[7,8] At 340 K and above, signals distinctively characteristic of the hexaphosphorus dication **3** (δ_{iso} ≈ 12 and –60 ppm)[3] are observed, demonstrating **3** as the thermodynamic sink for this medium.[3] In CD_2Cl_2, the same reaction mixture quantitatively produces cation **4**, presumably due to a kinetic barrier in solution.[7] From the cooled NMR sample, rod-like crystals were recovered from the clear melt **M** and were identified as **3**. The $^{31}P\{^1H\}$ NMR spectrum of the dissolved crystals in CD_2Cl_2 showed the same complex AA′A′′A′′′BB′ spin system as previously reported; consistent with the P_6 homocycle composed of two phosphonium centers (1,4-positions) and four phosphane centers.[3]

A further illustration of the synthetic value of the new melt medium for use in P–P bond formation is demonstrated by the reaction of the melt **M** with gallium metal. Addition of benzene and stoichiometric amounts of gallium metal to **M** [Scheme 2 (a)] produces a two-phase liquid system. After stirring for 48 h, a white precipitate is formed that has been isolated and characterized as **5**, representing a donor–acceptor complex of Ph_2PPPh_2 with two $GaCl_3$ acids. Excess $GaCl_3$ was removed by washing the precipitate with benzene. Adjustment of the reaction according to Scheme 2 (b) provides the same product; however, a higher yield (isolated 94%) is obtained by using excess $GaCl_3$. The $^{31}P\{^1H\}$ NMR signal for **5** in CD_2Cl_2 (δ = –2.1 ppm) is shifted downfield relative to that of Ph_2PPPh_2 (δ = –14.4 ppm).[7]



Scheme 2. Formation of diphosphanes through a coordination (formation of a donor–acceptor complex) and reduction process.

Compound **5** crystallizes in the orthorhombic space group, *Pbca*, with four formula units in the unit cell. The solid-state structure of **5** is shown in Figure 5, and crystallographic details are summarized in the Experimental Section. In the solid state, the P–P^i [2.2400(9) Å; symmetry code: (i) –*x* + 2, –*y* + 1, –*z* +1] and P–C [1.806(2) and 1.814(2) Å] bonds are in the typical range for P–P [2.17–2.24 Å] and P–C [1.78–1.83 Å] single bonds.[9] The P–Ga

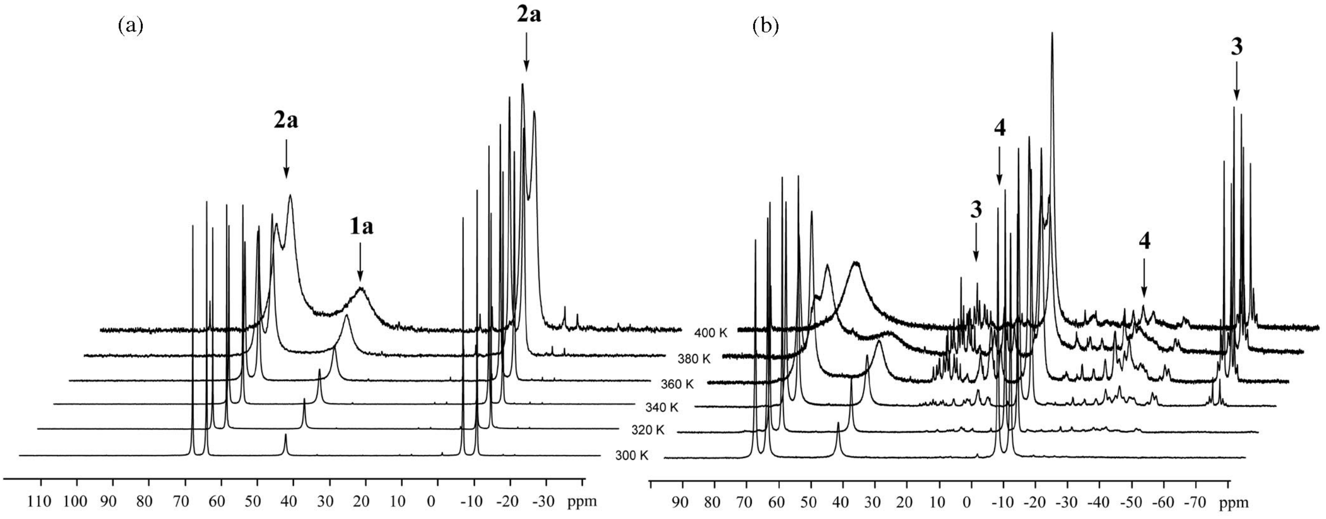


Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of the melt **M** without (a) and with the reactant $(PhP)_5$ (b).

bond length [2.4285(6) Å] in **5** is typical of phosphane–gallane complexes (2.35–2.68 Å),[10] and is comparable to those of symmetrically alkylated complexes, such as $Me_3P{\rightarrow}GaCl_3$ [2.353(2) Å][11] and $Me_3P{\rightarrow}GaMe_3$ [2.455(4) Å].[12] Moreover, the environments for the phosphorus centres in **5** are essentially tetrahedral, adopting a perfectly staggered conformation with the $GaCl_3$ moieties which are in a *trans* disposition.

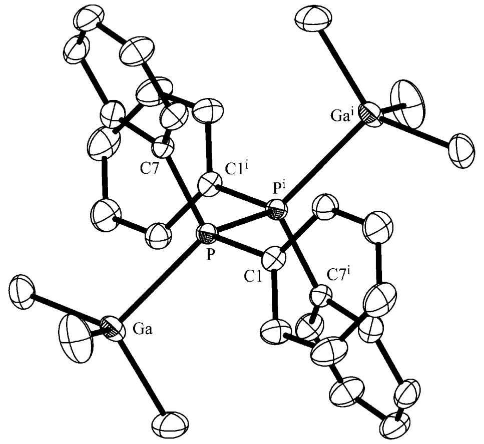


Figure 5. ORTEP plot of the solid-state structure of the diadduct **5**. Thermal ellipsoids with 50% probability (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P1^i 2.2400(9), P–Ga 2.4285(6), P–C1 1.806(2), P–C7 1.814(2), C1–P–C7 109.37(8), C1–P–P^i 104.20(6), C1–P–Ga 111.08(6), C7–P–Ga 109.09(6), P^i–P–Ga 116.43(3); symmetry code: (i) $-x + 2$, $-y + 1$, $-z + 1$.

Conclusions

A room-temperature melt medium **M** was readily prepared by the stoichiometric combination of Ph_2PCl and $GaCl_3$, and characterized by Raman and NMR spectroscopy which show the presence of complex **1a** and cation **2a** with a variety of complex anions ($Ga_2Cl_7^-$ and $Ga_3Cl_{10}^-$). The melt **M** is an excellent medium for cyclophosphane P–P insertion reactions and a reduction reaction to give a Lewis acid–base diadduct. Furthermore, this approach opens a new route to form diphosphanes through a coordination (formation of a donor–acceptor complex) and reduction process.

Experimental Section

General Considerations: All reactions were carried out in either a glove box or by using standard Schlenk techniques under argon. Dichloromethane, benzene and pentane were dried in an MBraun solvent purification system, degassed with three freeze-pump-thaw cycles and stored under nitrogen and over molecular sieves prior to use. $(PhP)_5$[13] and $[Ph_2PPh_2Cl][GaCl_4]$ (**2a**$[GaCl_4]$)[2a] were prepared as previously reported. Ph_2PCl was freshly distilled prior to use. Reagent-grade $GaCl_3$ and Ga (99.999%) were used as received from commercial suppliers. All new compounds, unless otherwise stated, were fully characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. Measurements were performed at 25 °C. Bruker AVANCE 500 [^1H (500.13 MHz), ^{13}C (125.76 MHz) chemical shift referenced to $\delta_{TMS} = 0.00$ ppm; ^{31}P (202.46 MHz) to $\delta_{H3PO4(85\%)} = 0.00$ ppm]. J values are reported in Hz. Melting points were recorded with an electrochemical melting-point apparatus in sealed capillaries under dinitrogen and are uncorrected. Raman spectra were obtained for powdered and liquid samples with a Bruker RFS 100 instrument equipped with an Nd:YAG laser (1064 nm, 172 mW, 1000 scans, 90° geometry). Elemental analyses were performed with a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster, Germany.

NMR Studies of the Reaction of Ph_2PCl or $[Ph_2P(Cl)PPh_2][GaCl_4]$ (2a$[GaCl_4]$) with $GaCl_3$: In a typical experiment, $GaCl_3$ (5 mmol) was added to Ph_2PCl (5 mmol) or $[Ph_2P(Cl)PPh_2][GaCl_4]$ (**2a**$[GaCl_4]$) (5 mmol) with stirring under argon at room temp. In both cases, pale yellow viscous liquids were obtained within 20 min. The ^{31}P NMR spectra were recorded for the liquids by using H_3PO_4 as external standard. $^{31}P\{^1H\}$ NMR (300 K): $\delta = -73.62$ (d, 1 P), –0.90 (d, $^1J_{PP} = 381.0$ Hz, 1 P, AX spin system) ppm.

NMR Studies of the Reaction of Ph_2PCl, $GaCl_3$ and $(PhP)_5$: To 1.0 mL of the room-temperature melt medium **M** was added $(PhP)_5$ (70 mg) in a glove box. The mixture was transferred to an NMR tube and sealed. The variable-temperature $^{31}P\{^1H\}$ NMR spectra of the melt **M** and the mixture were recorded from room temp. up to 400 K (see text).

Preparation of $Ph_4P_2Ga_2Cl_6$ (5): Benzene (5 mL) and Ga (0.33 mmol, 23 mg) were added to a freshly prepared molten salt mixture from Ph_2PCl (1 mmol, 221 mg) and $GaCl_3$ (1 mmol, 176 mg) under argon. The mixture was stirred for 48 h, and the white precipitate formed was separated by filtration. The precipitate was washed with benzene (3 × 5 mL) to remove excess $GaCl_3$ and pentane (2 × 5 mL), dried under vacuum, and recrystallized from a minimal amount of CH_2Cl_2 by pentane diffusion at –32 °C to yield **6** as very moisture-sensitive X-ray quality crystals; 680 (450) mg (94%); m.p. 120–126 °C (dec.) ($GaCl_3$ sublimes off). ^1H NMR (CD_2Cl_2, 300 K): $\delta = 7.49$–7.59 (m, 8 H, Ph), 7.69–7.79 (m, 12 H, Ph) ppm. ^{13}C NMR (CD_2Cl_2, 300 K): $\delta = 117.8$ (t, $^1J_{PP} = 20.0$ Hz, 4 C), 130.7 (t, $^3J_{PP} = 5.3$ Hz, 8 C), 134.7 (s, 4 C), 135.9 (t, $^2J_{PP} = 7.8$ Hz, 8 C) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 300 K): $\delta = -2.08$ (br, 1 P) ppm. $C_{24}H_{20}Cl_6Ga_2P_2$ (722.53): calcd. C 39.90, H 2.49; found C 39.62, H 1.87. The same reaction with 2/3 mmol (117 mg) of $GaCl_3$ gave 450 mg (62%) of **5**.

Crystal Data: A suitable single crystal was coated with Paratone-N oil, mounted by using a 20-micron cryo-loop and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected with a Bruker AXS P4/SMART 1000 diffractometer (Mo-K_a radiation, $\lambda = 0.71073$ Å) by using ω and θ scans with a scan width of 0.3° and 10 s time. The detector distance was 5 cm. The data were reduced (SAINT 7.23A, Bruker AXS, Inc., Madison, Wisconsin, USA, 2006) and corrected for absorption (G. Sheldrick, SADABS 2004, Bruker AXS, Inc., Madison, Wisconsin, USA, 2004). The structures were solved by direct methods and refined by full-matrix least squares on F^2 (G. Sheldrick, SHELXTL 6.14, Bruker AXS, Inc., Madison, Wisconsin, USA, 2000). All non-hydrogen atoms were refined first by using isotropic and later anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were added to the structure models in calculated position and refined by using a riding model. $Ph_4P_2Ga_2Cl_6$, $FW = 722.48$, orthorhombic, space group $Pbca$, $Z = 4$, $a = 15.893(3)$, $b = 9.922(2)$, $c = 18.239(4)$, $V = 2876(1)$, $F(000) = 1432$, $T = 173(1)$, $\mu = 2.556$ cm^{-1}, 18575 reflections collected, 3273 reflections unique ($R_{int} = 0.0322$). The final R_1 value was 0.0231 and $wR_2 = 0.0606$ (all data). CCDC-695825 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[8] When the temperature of the reaction mixture did not exceed 330 K and the melt was quenched to room temperature within seconds, $^{31}P\{^1H\}$ NMR spectra of the resulting yellow oil in CH_2Cl_2 showed the presence of only cation **4**,[7] the phosphanylphosphonium cation **2a**, and small amounts of dication **3**.

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