Supporting Information

Gallium phosphaketenes derived from bis(imino)acenaphthenes (bian): synthesis and reactivity towards trityl radical and bian-gallylene

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1. General information

The newly obtained compounds **1-4** are sensitive to oxygen and air moisture, so all manipulations for their synthesis, isolation and identification were carried out in a vacuum or under argon/nitrogen using standard Schlenk technique or under argon atmosphere in MBraun glovebox. All reaction were carried out under natural light conditions. Toluene, tetrahydrofuran (thf), 1,2-dimethoxyethane (dme), diethyl ether and *n*-hexane were distilled from sodium/benzophenone and stored over 3 Å molecular sieves under nitrogen. Toluene-d_8 and thf-d_8 were dried over sodium/benzophenone at ambient temperature and condensed just prior to use under vacuum into the NMR tubes, which contained the analyzed sample. The halid $[(\mathrm{Ar^{BIG}}\text{-bian})\mathrm{GaI_2}]$[1], gallylene $[(\mathrm{Ar^{BIG}}\text{-bian})\mathrm{Ga}]$[1], dimer of trityl radical[2] and $[\mathrm{Na(PCO)(diox)_{0.5}}]$[3] were obtained according to a published procedure. The NMR spectra were obtained on Bruker Avance III (400 MHz) instruments. ESR spectra were recorded on a Magnettech ESR 5000 (9.48 GHz). A ESR signals were simulated using EasySpin (v. 6.0.6) software.[4] The simulation was performed using the "*garlic*" function to computes isotropic EPR spectra. The Hamiltonian of the electron Zeeman interaction ($H_{EZ}(i)$) and the hyperfine interaction ($H_{HF}(i,k)$) have been used. The error of the obtained data was determined using least-squares fitting algorithms.[4] IR spectra (4000-450 $\mathrm{cm^{-1}}$) were obtained on FSM-1201 instrument in mineral oil. The C,H,N analysis was conducted with an Elementar Vario EL Cube elemental analyzer.

2. Experimental section

2.1. Synthesis of [(Ar^{BIG}-bian)Ga(PCO)$_2$] (1)

To a solution of [(Ar^{BIG}-bian)GaI$_2$] (0.6 g, 0.4 mmol)) in toluene, [Na(PCO)(diox)$_{0.5}$] (0.1 g, 0.9 mmol) was added. The reaction mixture was stirred for 24 h at 90 °C. The resulting brown solution was filtered and concentrated under vacuum. The solution was allowed to stand for 12 h at ambient temperature. Precipitated brown crystals of compound **1** were separated from the solution by decantation, washed with cold toluene and dried in vacuum. Yield 0.28 g (56 %). Found: C, 79.61; H, 5.09; N, 2.21. $C_{83.50}H_{64}GaN_2O_2P_2$ (1259.02). Calculated: C, 79.66; H, 5.12; N, 2.23.

EPR (toluene, 340 K): $a_i(2 \times {}^{14}N) = 0.454$, $a_i(2 \times {}^{1}H) = 0.090$, $a_i(2 \times {}^{1}H) = 0.120$, $a_i({}^{69,71}Ga) = 1.511$, $a_i({}^{31}P) = 0.716$, $a_i({}^{31}P) = 0.717$ mT; $g = 2.0051$.

IR (mineral oil, cm^{-1}): 3083 w, 3061 w, 3025 w, 1926 s, 1909 s, 1599 s, 1525 s, 1338 w, 1309 w, 1265 s, 1220 w, 1208 w, 1154 m, 1077 m, 1031 s, 1003 w, 985 w, 949 w, 918 m, 875 s, 819 m, 791 m, 762 s, 740 s, 698 s, 650 w, 635 m, 623 w, 605 s, 562 s, 546 s.

2.2. Reaction of 1 with gallylene [(Ar^{BIG}-bian)Ga]. Preparation of 2.

To a solution of (Ar^{BIG}-bian)Ga(PCO)$_2$ (0.6 g, 0.4 mmol)) in toluene, (Ar^{BIG}-bian)Ga (0.46 g, 0.4 mmol) was added. The reaction mixture was stirred for 24 h at 90 °C. The resulting brown solution was concentrated under vacuum. The solution was allowed to stand for 24 h at ambient temperature. Precipitated brown crystals of compound **2** were separated from the solution by decantation, washed with cold toluene and dried in vacuum. Yield 0.47 g (44 %). Found: C,83.61; H, 5.76; N, 2.11. $C_{93}H_{76}GaN_2OP$ (1338.24). Calculated: C, 83.46; H, 5.72; N, 2.09.

^{1}H NMR (400 MHz, thf-d$_8$, 295.7 K, δ, ppm, *J*/Hz): 7.32 (s, 2H, C$\underline{H}$ *meta* Ar^N), 7.00 (m, 22H, C$\underline{H}$ arom), 6.94 (m, 10H, C$\underline{H}$ arom), 6.87 (m, 12H, C$\underline{H}$ arom), 6.71 (ps.t, 2H, C$\underline{H}$ napht), 6.07 (s, 4H, C$\underline{H}$(Ph)$_2$), 5.69 (d, 2H, C$\underline{H}$ napht, $J_1 = 6.78$), 2.26 (s, 6H, C$\underline{H}_3$).^{31}P{^{1}H} (161.99 MHz, thf-d$_8$, 295.6 K): – 368.8 (PCO).

IR (mineral oil, cm^{-1}): 3083 w, 3060 w, 3024 m, 1975 s, 1960 s, 1928 s, 1599 s, 1494 s, 1383 s, 1353 s, 1333 m, 1291 m, 1277 s, 1252 m, 1216 m, 1198 w, 1188 w, 1177 w, 1155 m, 1147 w, 1127 w, 1077 s, 1031 s, 1002 m, 982 w, 969 w, 931 s, 920 s, 885 m, 856 m, 829 m, 811 s, 799 m, 763 s, 749 m, 698 s ,681 m, 656 w, 645 m, 635 w, 623 m, 606 s, 555 s.

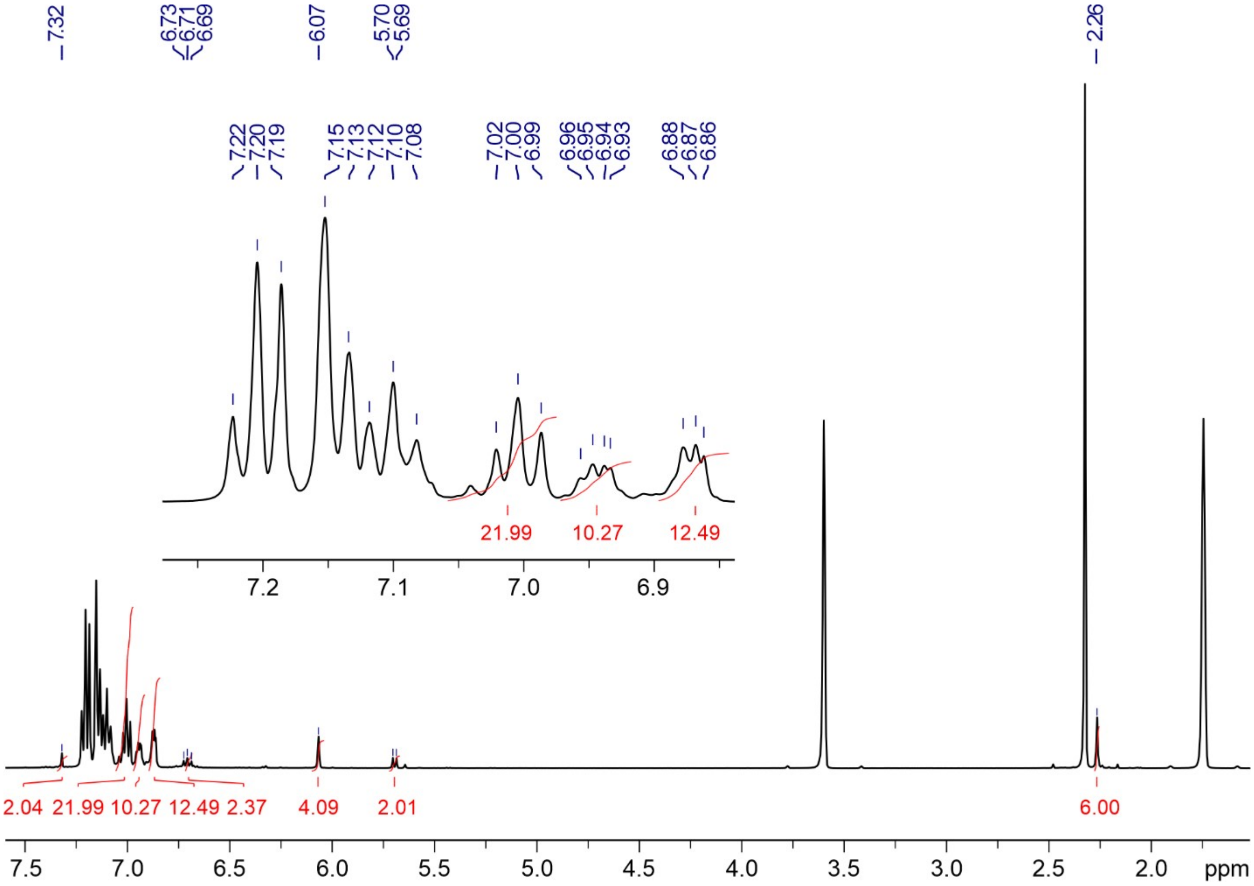

Figure S1. ^{1}H NMR spectrum of complex **2** (400 MHz, thf-d$_8$, 295.7 K).

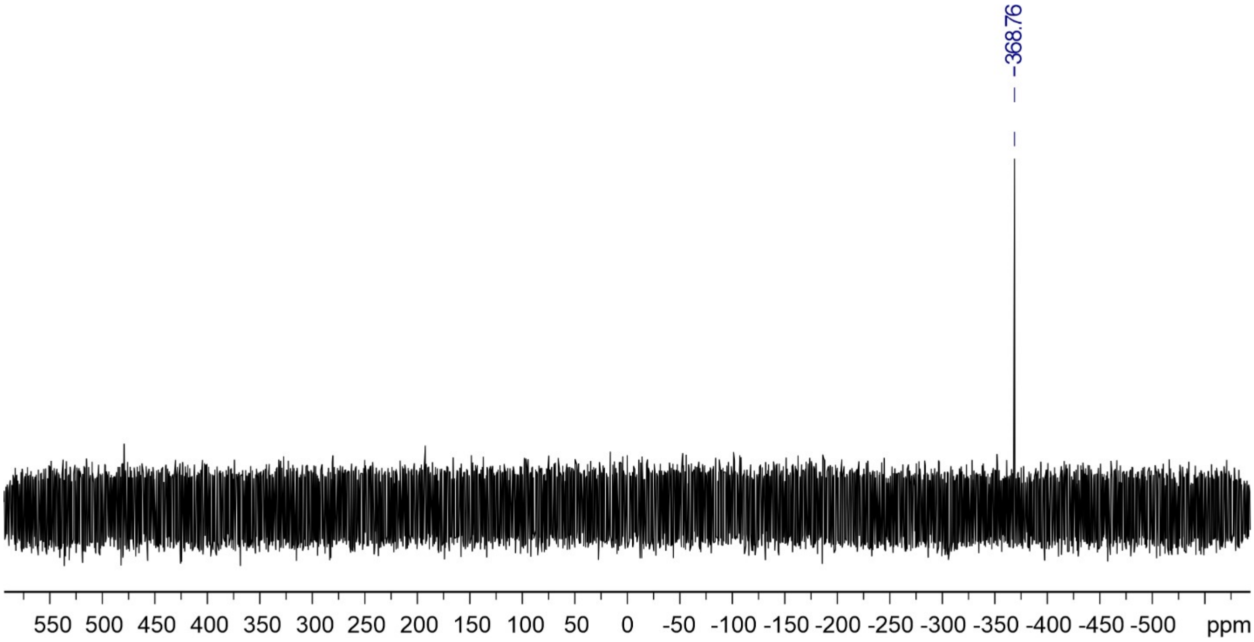

Figure S2. ^{31}P{^{1}H} NMR spectrum of complex **2** (161.99 MHz, thf-d$_8$, 295.6 K).

2.3. Synthes of [(Ar^{BIG}-bian)Ga(Py)(PCO)] (3).

To a solution of Ar^{BIG}-bian (0.5 g, 0.5 mmol) and excess of gallium (ca. 0.3 g, 4.3 mmol) in pyridine, $GaCl_3$ (0.03 g, 0.17 mmol) was added. The reaction mixture was stirred for 24 h at 130 °C. The resulting blue solution of [(Ar^{BIG}-bian)Ga(Py)Cl] was filtered, pyridine was evaporated and changed to dme, then [Na(PCO)(diox)$_{0.5}$] was added. The color of the reaction mixture changed to green. The solution was decanted from NaCl. The green crystals of compound **3** were separated from the dme/Et_2O mixture and characterized by IR, NMR-spectroscopy and elemental analysis. Yield 0.41 g (59 %). Found: C, 81.69; H, 5.92; N, 3.05.

^{1}H NMR (400 MHz, toluene-d$_8$, 222.4 K, δ, ppm, *J*/Hz): 7.63 (m, 18H, C$\underline{H}$ arom), 7.28 (m, 10H, C$\underline{H}$ arom), 6.88 (m, 16H, C$\underline{H}$ arom), 6.43 (m, 2H, C$\underline{H}$ napht), 5.26 (m, 2H, C$\underline{H}$ napht), 1.99 (br. s, 6H, C$\underline{H}_3$). ^{31}P{^{1}H} (161.99 MHz, toluene-d$_8$, 223.2 K, δ, ppm): – 346.1 (PCO). The NMR signals (Fig. S4) are broadened, which is assigned to dynamic processes in solution. Unfortunately, the peaks of Py can not be identified among overlapping signals of aromatic protons.

IR (mineral oil, cm^{-1}): 3083 w, 3059 m, 3025 m, 1940 s, 1924 s, 1912 s, 1598 s, 1508 s, 1493 s, 1341 m, 1333 s, 1317 s, 1290 m, 1267 s, 1246 m, 1215 m, 1196 w, 1180 w, 1154 m, 1146 w, 1137 w, 1124 w, 1076 s, 1067 s, 1043 s, 1031 s, 1015 m, 1003 m, 987 w, 971 w, 950 w, 925 s, 911 m, 890 w, 882 m, 851 m, 831 m, 820 w, 812 s, 794 m, 784 m, 761 s, 698 s, 648 w, 639 m, 632 m, 618 w, 606 s, 569 w, 552 s.

The crystals suitable for x-ray analysis were prepared from a toluene/hexane mixture (Table 1S).

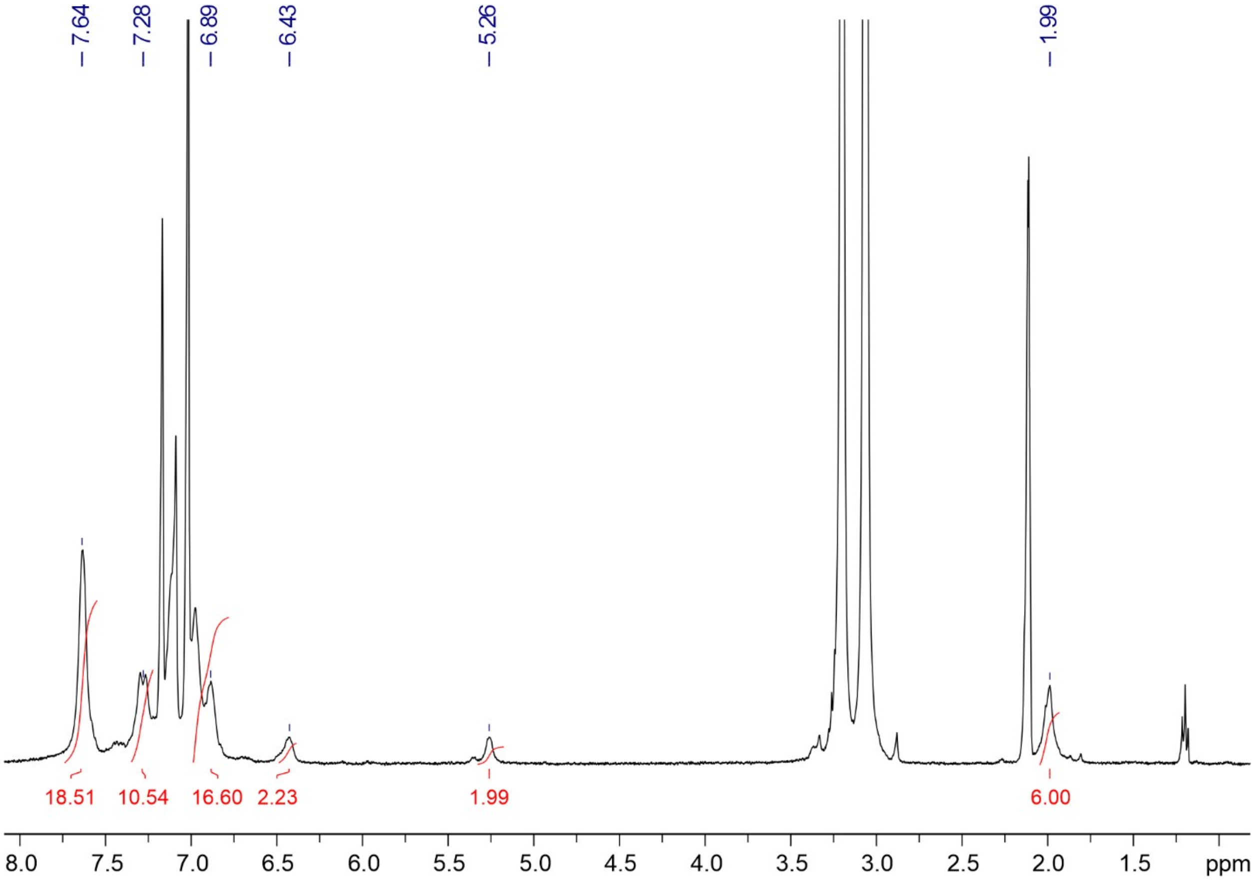

Figure S3. ^{1}H NMR spectrum of complex **3** (400 MHz, toluene-d$_8$, 222.4 K).

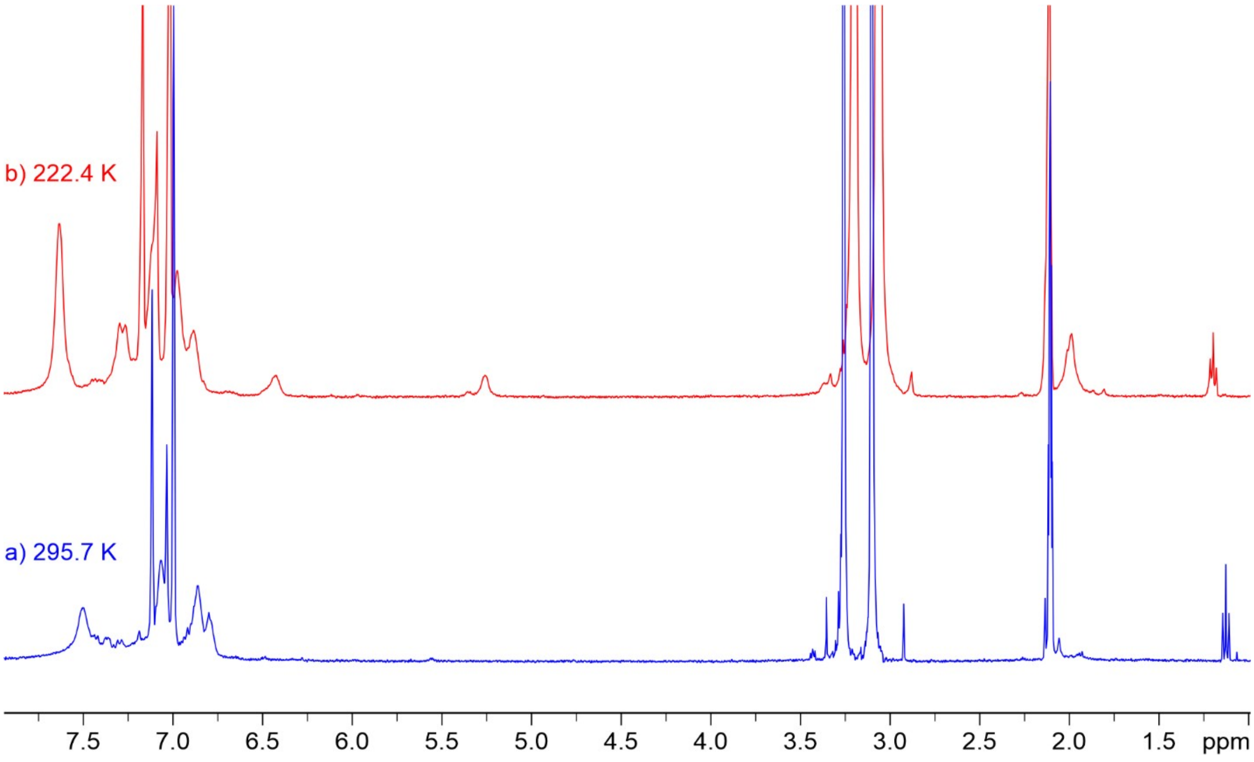

Figure S4. ^{1}H NMR spectrum of complex **3** (400 MHz, toluene-d$_8$) at 295.7 (a) and 222.4 (b) K.

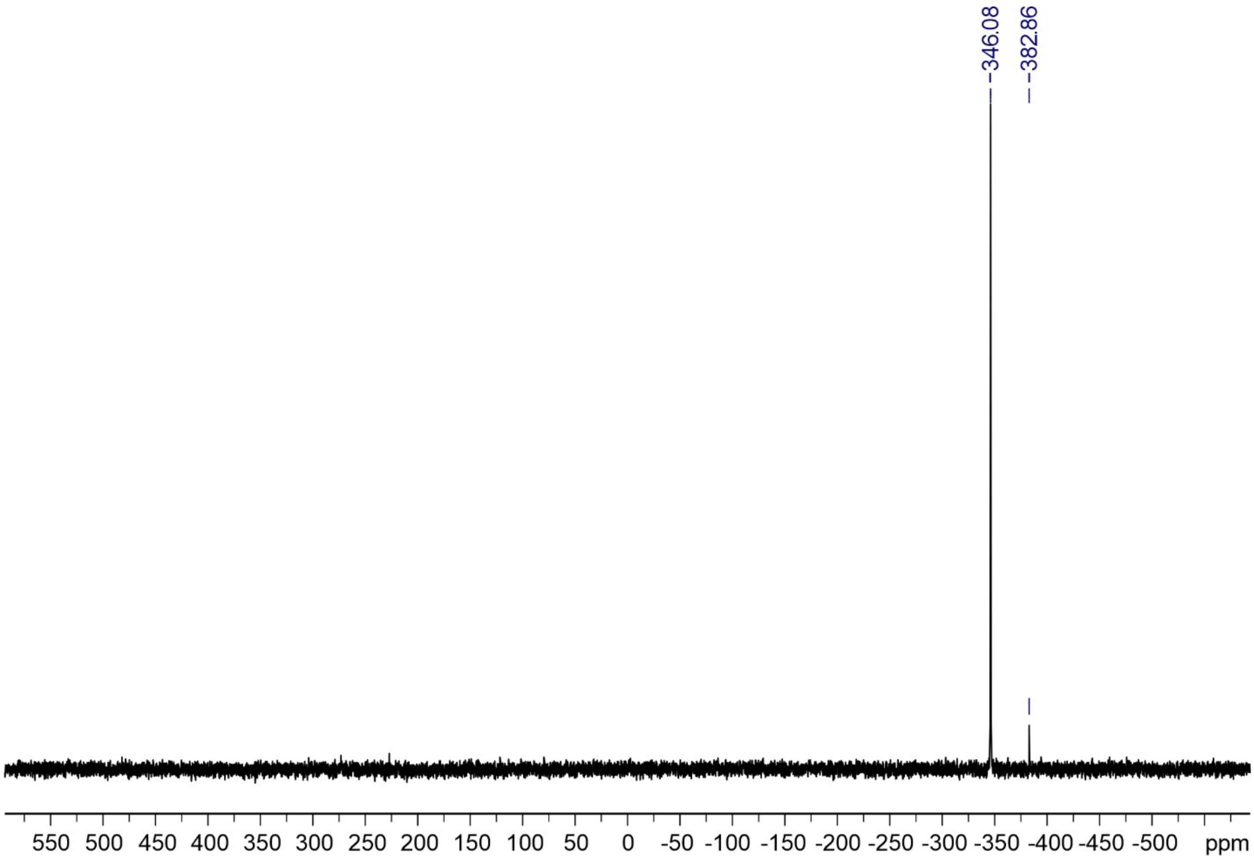

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** (161.99 MHz, toluene-d$_8$, 223.2 K).

2.4. Reaction of 3 and bian-gallylene with trityl radical. Preparation of [(Ar^{BIG}-bian)Ga(CPh$_3$)] (4).

Method 1. To a solution of [(Ar^{BIG}-bian)Ga(Py)(PCO)] (*in situ*, 0.5 mmol) in thf, the dimer of trityl radical (0.25 mmol, 0.12 g) was added. The reaction mixture was stirred for 24 h at 90 °C. The resulting dark brown solution was filtered, thf was evaporated and changed to a mixture of dme and hexane. The solution was allowed to stand for 24 h at ambient temperatures. Precipitated brown crystals of compound **4** were separated from the solution by decantation, washed with cold hexane and dried in vacuum. Yield 0.47 g (24 %). Found: C,85.96; H, 5.91; N, 2.00. $C_{99.50}H_{81.25}GaN_2O_{1.25}$ (1394.63). Calculated: C, 85.69; H, 5.87; N, 2.01.

^{1}H NMR (400 MHz, thf-d_8, 296.6 K, δ, ppm, J/Hz): 7.19 (s, 4H, C$\underline{H}$ *meta* Ar^N), 6.98 – 6.83 (m, 23H, C$\underline{H}$ arom), 6.79 (t, 6H, C$\underline{H}$ arom, J_1 = 7.53, J_2 = 7.53), 6.74 (d, 2H, C$\underline{H}$ napht, J_1 = 8.28), 6.68 (d, 8H, C$\underline{H}$ arom, J_1 = 7.53), 6.66 – 6.55 (m, 18 H, C$\underline{H}$ arom), 6.21(ps. t, 2H, C$\underline{H}$ napht), 5.97 (s, 4H, C$\underline{H}$(Ph)$_2$), 5.02 (d, 2H, C$\underline{H}$ napht), 2.39 (s, 6H, C$\underline{H}_3$). ^{13}C{^{1}H} NMR (100.6 MHz, thf-d_8, 296 K): 144.5 (4C, arom), 144.4 (3C, C$\underline{Ph}_3$), 143.5 (2C, arom), 142.3 (4C, arom), 142.0 (4C, arom), 134.6 (2C, arom), 132.6 (2C, napht), 131.8 (2C, arom), 130.4 (6C, C$\underline{Ph}_3$), 130.0 (4C, $\underline{C}$H *meta* Ar^N), 129.7 (8C, arom), 129.5 (8C, arom), 128.5 (6C, C$\underline{Ph}_3$), 127.8 (8C, arom), 127.2 (8C, arom), 126.0 (3C, C$\underline{Ph}_3$), 125.8 (1C, napht), 125.3 (4C, arom), 125.3 (4C, arom), 125.2 (2C, $\underline{C}$H napht), 124.8 (1C, napht), 122.3 (2C, $\underline{C}$H napht), 119.4 (2C, $\underline{C}$H napht), 68.8 (1C, $\underline{C}$Ph$_3$) 51.6 (4C, $\underline{C}$H(Ph)$_2$), 20.6 (2C, $\underline{C}$H$_3$).

IR (mineral oil, cm^{-1}): 3084 w, 3059 m, 3026 m, 1598 s, 1517 w, 1494 s, 1341 m, 1296 w, 1271 m, 1245 m, 1214 w, 1199 w, 1180 w, 1155 w, 1144 w, 1136 m, 1128 w, 1010 m, 1033 s, 1003 m, 979 w, 964 w, 926 m, 919 m, 882 w, 866 m, 853 m, 829 m, 812 m, 798 w, 780 m, 765 s, 760 s, 745 s, 740 s, 699 s, 636 w, 624 w, 606 s, 570 w, 558 m, 552 w.

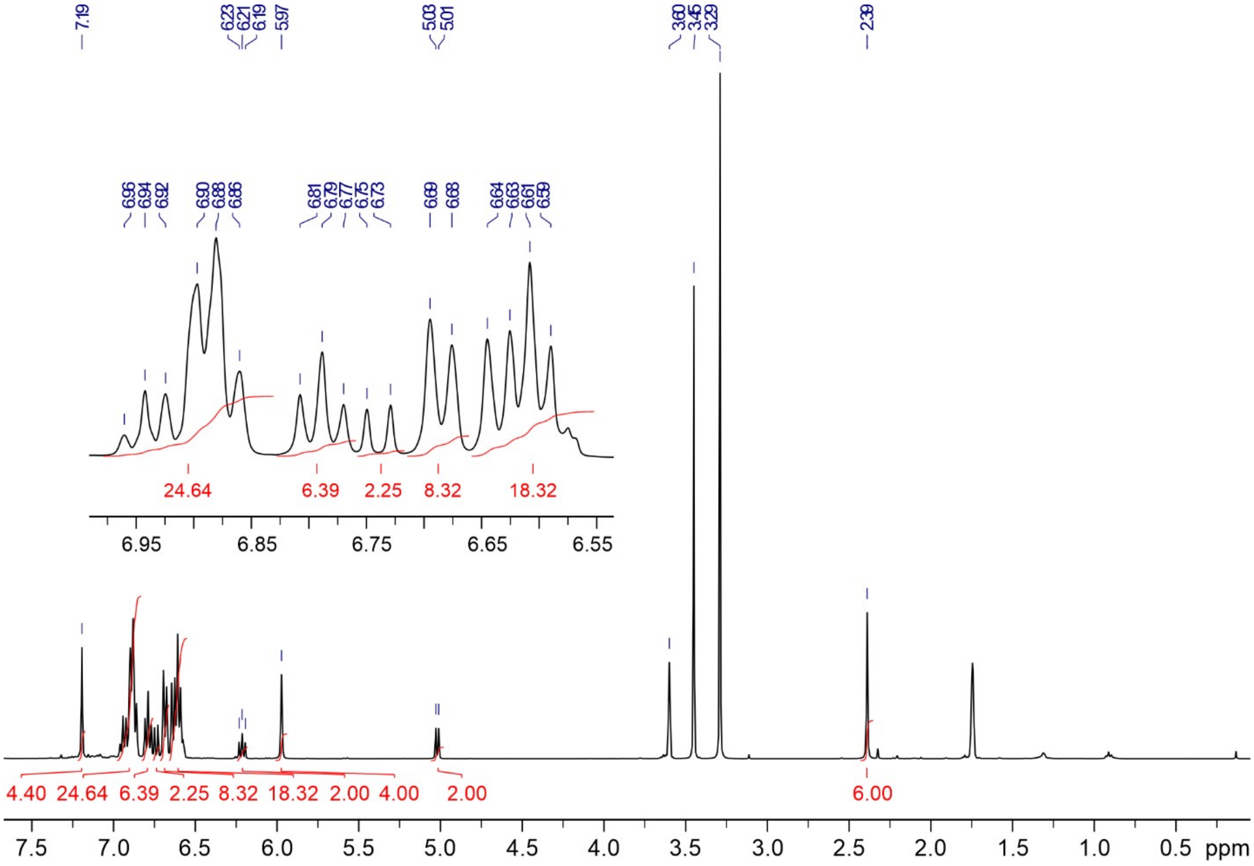

Figure S6. ^{1}H NMR spectrum of complex **4** (400 MHz, thf-d$_8$, 296.6 K).

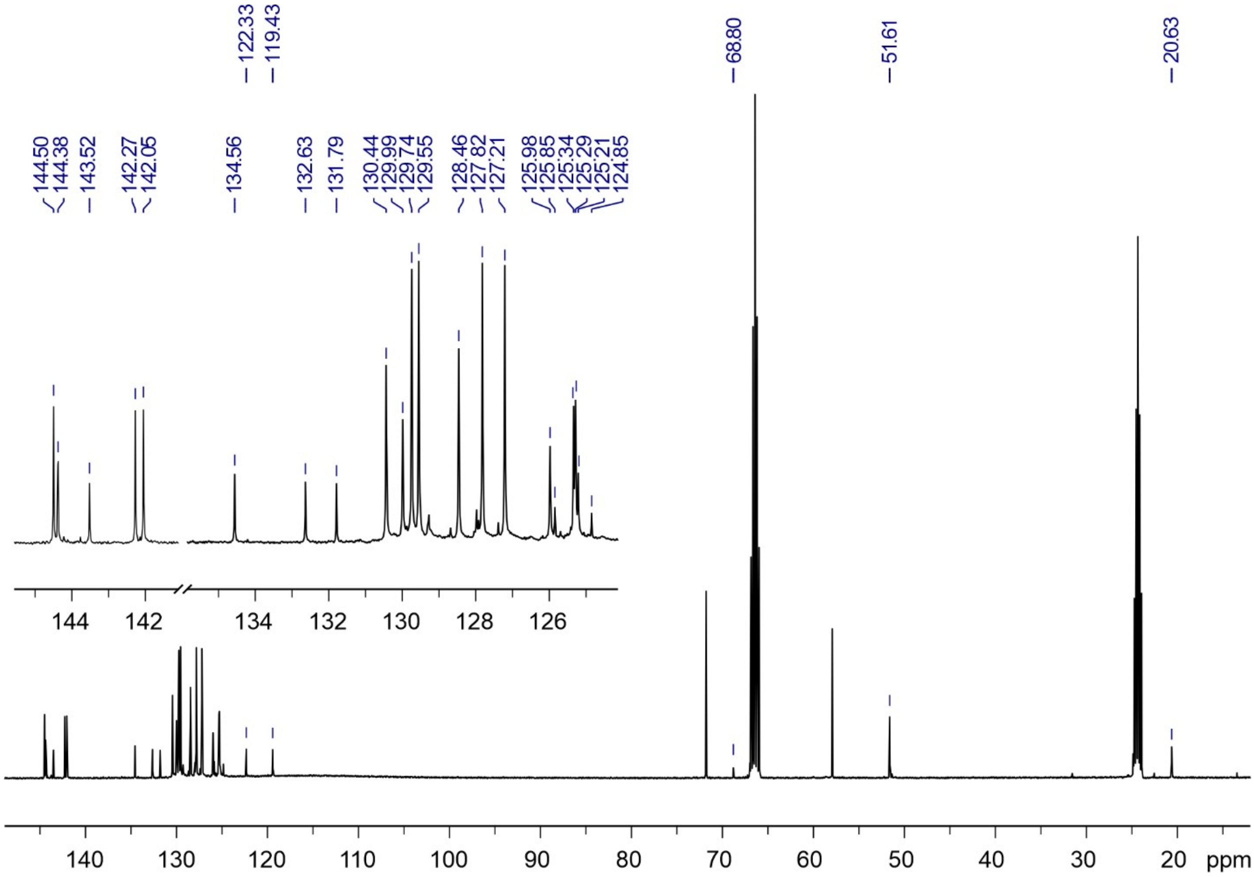

Figure S7. ^{13}C{^{1}H} NMR spectrum of complex **4** (100.6 MHz, thf-d$_8$, 296 K).

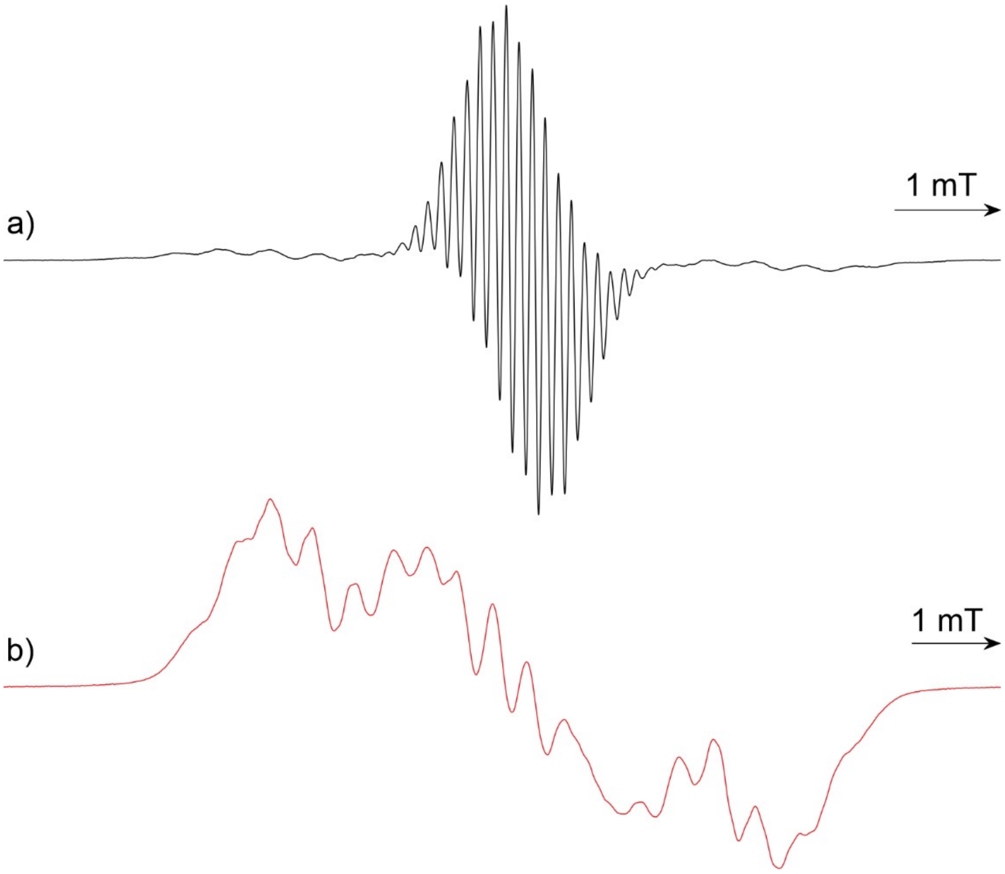

Figure S8. ESR spectrum of a reaction mixture of [Ar^{BIG}-bianGa(Py)PCO] (**3**) + Ph$_3$C in thf: initial mixture (a) and after 72 h (b).

Method 2. Manipulations were carried out in a glove box under argon atmosphere. The crystals of Ar^{BIG}-bianGa (0.031 g, 0.027 mmol) and $(Ph_3C)_2$ (0.0065 g, 0.027 mmol) were placed into NMR tube. The reaction mixture was dissolved in thf-d_8. In the course of the reaction, the color of the mixture in the tube changed from brown to red. Before the reaction, the ^1H NMR spectrum was recorded.

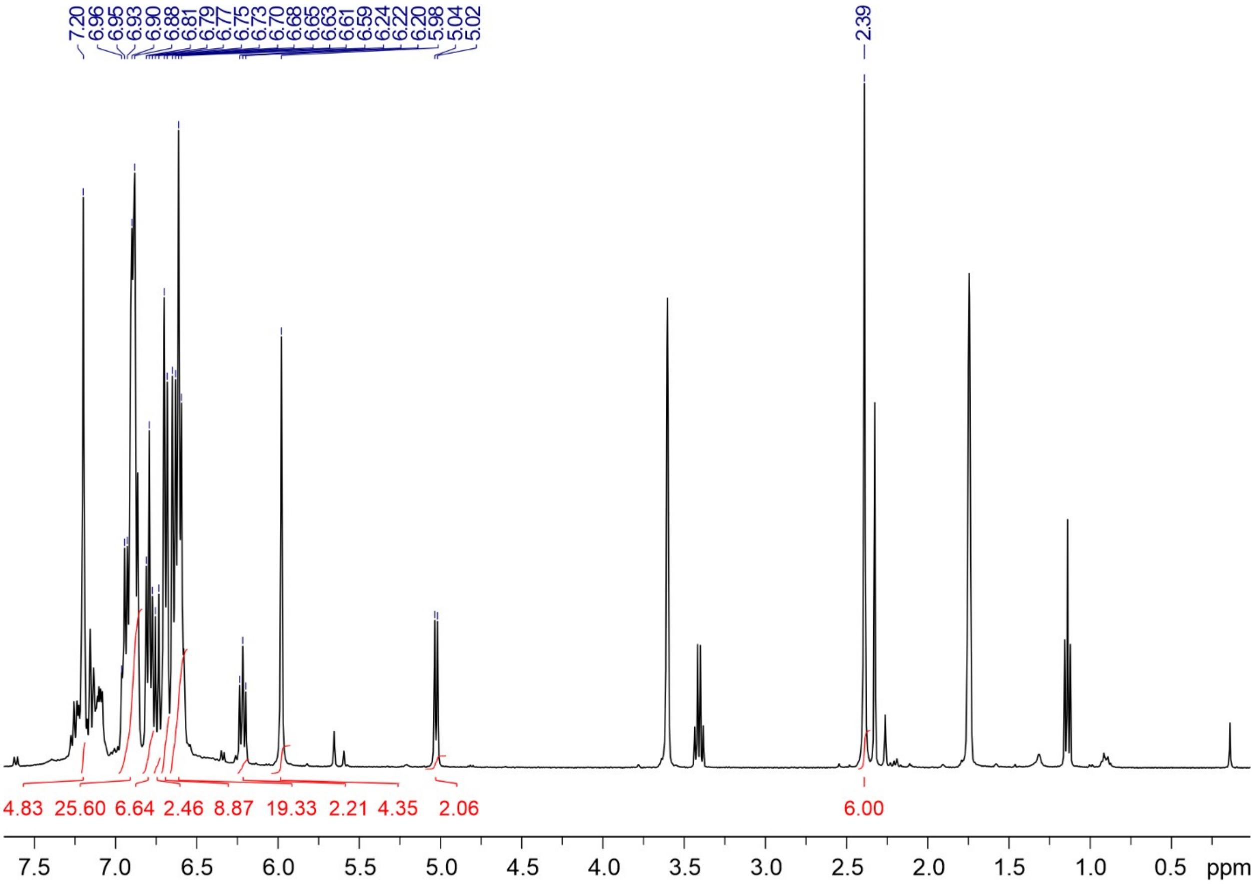

Figure S9. ^1H NMR spectrum of reaction mixture [Ar^{BIG}-bianGa] + trityl radical (100.6 MHz, thf-d_8, 296 K).

3. X-ray crystallography

3.1. General methods. The X-ray diffraction data were collected on an Agilent Xcalibur Eos (for **1** and **2**) and Bruker D8 Venture (for **3**, **4**) diffractometers (Mo-K_α radiation, φ- and ω-scan techniques, λ = 0.71073 Å). The collection of data, the initial reflection indexing and the refinement of the unit cell parameters were performed using the CrysAlisPro[5] (for **1**, **2**) and APEX3[6] (for **3, 4**) software packages. The intensity data were integrated by the CrysAlisPro[5] and SAINT[7] programs respectively. Empirical absorption corrections for **1** and **2** were performed using the SCALE3 ABSPACK scaling algorithm[8], implemented in CrysAlisPro[5]. Absorption corrections for **3** and **4** were carried out by SADABS[9, 10]. All structures were solved by the dual-space method using the SHELXT[11] software and refined by full-matrix least squares on F_{hkl}^2 with SHELXL[12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions and refined using a riding model ($U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for other groups). Crystals of **1-4** contain disordered solvate molecules of toluene and DME correspondingly. The ratios of these molecules to one Ga complex are different: 0.5:1 in **1**; 2:1 in **2**; 1:1 in **3** and 0.625:1 in **4**. One Ph-group of the Ar^{BIG} fragment in the Ar^{BIG}-bian ligand of **3** is dirordered over two positions. The Py molecule in **3** coordinated to the Ga atom, are disordered with the chlorine substutient of initial gallium(III) chloride in an occupancy ratios of approx. 0.73:0.27.

The main crystallographic data and structure refinement details for complexes **1-4** are presented in Table 1. CCDC 2479698 (**1**), 2479699 (**2**), 2479700 (**3**) and 2479701 (**4**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures

3.2. Summary of crystal data

Table 1S. Crystal data and structure refinement details for **1-4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{83.50}H_{64}GaN_2O_2P_2$	$C_{93}H_{76}GaN_2OP$	$C_{89.64}H_{71.64}Cl_{0.28}GaN_{2.73}OP$	$C_{99.50}H_{81.25}GaN_2O_{1.25}$
Formula weight	1259.02	1338.24	1313.47	1394.63
Temperature [K]	100(2)	100(2)	150(2)	150(2)
Crystal system	orthorhombic	triclinic	triclinic	triclinic
Space group	$Pbca$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a [Å]	20.6204(4)	12.2228(4)	11.8992(6)	13.327(4)
b [Å]	24.5542(5)	14.9094(4)	14.8576(5)	13.562(4)
c [Å]	25.5396(5)	20.3396(6)	19.8172(7)	21.365(10)
α [°]	90	68.618(3)	85.634(1)	90.675(15)
β [°]	90	86.435(3)	82.537(2)	102.827(14)
γ [°]	90	83.840(2)	89.968(2)	97.442(7)
Volume [$Å^3$]	12931.1(5)	3430.45(19)	3463.6(2)	3730(2)
Z	8	2	2	2
ρ_{calc} [gcm^{-3}]	1.293	1.296	1.259	1.242
μ [mm^{-1}]	0.527	0.478	0.483	0.422
$F(000)$	5248	1404	1375	1466
Crystal size [mm^3]	0.49×0.21×0.18	0.47×0.28×0.10	0.22×0.18×0.08	0.18×0.16×0.01
2θ range [°]	4.18 − 60.07	3.94 − 50.05	3.57 − 58.00	3.54 − 60.00
Index ranges	$-29 \le h \le 29$ $-34 \le k \le 34$ $-35 \le l \le 35$	$-14 \le h \le 14$ $-17 \le k \le 17$ $-24 \le l \le 24$	$-16 \le h \le 16$ $-20 \le k \le 19$ $-24 \le l \le 27$	$-17 \le h \le 18$ $-19 \le k \le 19$ $-29 \le l \le 30$
Reflections collected	159357	70217	55038	33442
Independent Reflections (R_{int})	18904 (0.0966)	12113 (0.0744)	18270 (0.2491)	20973 (0.0945)
Completeness to θ = 25.242°, %	99.9	100.0	99.8	97.8
Data / Restraints / Parameters	18904/0/838	12113/192/886	18270/208/959	20973/131/1059
Absorption correction T_{min}/T_{max} (method)	0.694/0.925 (analytical)	0.842/0.959 (analytical)	- / - (none)	0.4984/0.7465 (multi-scan)
Gof on F^2	1.013	1.082	0.913	1.007
Final R_1 and wR_2 indexes [$I \geq 2\sigma(I)$]	0.0461 0.0952	0.0737 0.1830	0.0700 0.1476	0.0813 0.1549
Final R_1 and wR_2 indexes [all data]	0.0862 0.1105	0.1163 0.2167	0.1545 0.1654	0.2146 0.1821
Largest peak/hole, [$eÅ^{-3}$]	0.81/−0.56	0.86/−0.87	0.60/−0.66	0.67/−1.11

Table 2S. Selected bond lengths [Å] and angles [°] for complexes **1-4.**

Bond	**1**	**2**	**3**	**4**
Ga(1)–N(1)	1.9696(15)	1.850(4)	1.914(3)	1.871(3)
Ga(1)–N(2)	1.9576(15)	1.865(4)	1.923(2)	1.870(3)
Ga(1)-N(3)	-	-	2.051(9)	-
Ga(1)–P(1)	2.3363(6)	2.2321(16)	2.295(1)	-
Ga(1)–P(2)	2.3922(6)	-	-	-
Ga(1)-C(79)	-	-	-	1.991(4)
N(1)–C(1)	1.342(2)	1.379(6)	1.396(4)	1.379(4)
N(2)–C(2)	1.339(2)	1.392(6)	1.372(4)	1.403(4)
C(1)–C(2)	1.433(2)	1.372(6)	1.393(4)	1.376(4)
P(1)–C(79)	1.646(2)	1.630(7)	1.610(5)	-
P(2)–C(80)	1.626(2)	-	-	-
C(79)-O(1)	1.167(3)	1.160(7)	1.158(5)	-
C(80)-O(2)	1.171(3)	-	-	-
Angle	**1**	**2**	**3**	**4**
N(1)–Ga(1)–N(2)	86.13(6)	91.31(17)	90.37(11)	90.02(12)
P(1)–Ga(1)–P(2)	114.63(2)	-	-	-
P(1)–Ga(1)–N(3)	-	-	110.05(18)	-
P(1)–Ga(1)–H(1)	-	-	-	-
N(1)-Ga(1)-P(1)	116.96(5)	145.72(13)	118.34(8)	-
N(2)-Ga(1)-P(1)	112.16(5)	122.94(13)	127.41(8)	-
N(1)-Ga(1)-P(2)	111.16(5)	-	-	-
N(2)-Ga(1)-P(2)	112.62(5)	-	-	-
N(1)-Ga(1)-N(3)	-	-	107.3(3)	-
N(2)-Ga(1)-N(3)	-	-	100.3(4)	-
N(1)-Ga(1)-C(79)	-	-	-	130.58(13)
N(2)-Ga(1)-C(79)	-	-	-	138.36(12)
Ga(1)–P(1)–C(79)	85.78(8)	90.9(2)	91.50(16)	-
Ga(1)–P(2)–C(80)	83.26(8)	-	-	-
P(1)–C(79)–O(1)	175.1(2)	172.6(5)	176.1(5)	-
P(2)–C(80)–O(2)	177.5(2)	-	-	-

4. Computational details.

DFT calculations of molecules **1-4** as well as the relevant reactants and reaction products were carried out at the B3LYP/6-31G(d) level of theory.[13-16] The solvation effects in toluene were taken into account by the polarizable continuum model (PCM).[17] Computations were performed using the Gaussian 09 program suit.[18] The molecular structures were optimized and then the harmonic frequencies were calculated to confirm true energy minima and to produce the H^0 and G^0 values at 298K. The number of atoms in complex **1** is too large to obtain isotropic Fermi couplings so we used a simplified dpp-bian model. The QTAIM analysis was carried out using the AIM ALL package.[19]

Table 3S. Calculated Gibbs free energies (kcal mol^{-1}) of selected reactions of (Ar^{BIG}-bian)Ga(PCO)(Py) (**3**) with the trityl radical dimer $Ph_2C(C_6H_5)CPh_3$ in thf solution.

No	Reaction	ΔG^0_{298}
1	(Ar^{BIG}-bian)Ga(PCO)(Py)+ 0.5 $Ph_2C(C_6H_5)CPh_3$ = (Ar^{BIG}-bian)GaPCPh$_3$+CO+Py	16.5
2	2 (Ar^{BIG}-bian)Ga(PCO)(Py)+ 0.5 $Ph_2C(C_6H_5)CPh_3$ = (Ar^{BIG}-bian)GaCPh$_3$ + (Ar^{BIG}-bian)Ga(PCO)$_2$ + 2 Py	-9.6
3	5 (Ar^{BIG}-bian)Ga(PCO)(Py)+ 2 $Ph_2C(C_6H_5)CPh_3$ = 3 (Ar^{BIG}-bian)GaCPh$_3$ + (Ar^{BIG}-bian)GaPCPh$_3$ + (Ar^{BIG}-bian)GaP$_4$ + 5 Py +5 CO	-16.5
4	4 (Ar^{BIG}-bian)Ga(PCO)(Py) + 1.5 $Ph_2C(C_6H_5)CPh_3$ = 3 (Ar^{BIG}-bian)GaCPh$_3$ + (Ar^{BIG}-bian)GaP$_4$+4 Py +4 CO	-27.2

Table 4S. Selected interatomic distances (Å) in optimized structures of complexes **1-4** in toluene solution.

Bond	**1**	**2**	**3**	**4**
Ga–N(Ar^{BIG}-bian)	2.003 [a]	1.887 [a]	1.925 [a]	1.914 [a]
Ga–N(Py)			2.088	
Ga–P	2.378 [a]	2.300	2.363	-
Ga-C	-	-	-	2.026
N–C	1.344 [a]	1.393 [a]	1.405 [a]	1.397 [a]
C(1)–C(2)	1.444	1.390	1.391	1.386
P–C	1.668 [a]	1.686	1.667	-
C-O	1.172 [a]	1.164	1.175	-

[a] – The distance averaged over two bonds.

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