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P−P Bond Activation of P_4 Tetrahedron by Group 13 Carbenoid and its Bis Molybdenum Pentacarbonyl Adduct

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Activation of white phosphorus with Ga(DDP) (DDP = 2-di*iso*-propylphenylamino-4-di*iso*-propylphenylimino-2-pentene) afforded [(DDP)Ga(P_4)] (**1**) by insertion of the Ga(I) center at one of the six P−P bonded edges of the P_4 tetrahedron. Further reaction of **1** with three equivalents of $Mo(CO)_6$ results in the formation of [(DDP)Ga($\eta^{2:1:1}$-P_4){Mo-$(CO)_5$}$_2$]·2toluene (**2**). Compounds **1** and **2** are characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and single crystal X-ray structural analysis. The solid-state structure of molecule **1** reveals the first example of a structurally characterized GaP_4 core stabilized by a β-diketiminate ligand. Compound **2** represents a rare type of coordination mode of a gallium supported P_4 butterfly structure.

Introduction

The interest in selective activation of a P−P bond in highly reactive white phosphorus is deeply rooted in phosphorus chemistry.[1] Especially transition metal-mediated P−P bond activation has a promising future to produce phosphorus transfer reagents for organic reactions, while this type of reaction is still at an early stage of development with main group metals.[2−10] The main group metal mediated P−P bond activation of the P_4 tetrahedron can be classified as either activation or insertion of the P_4 core by main group elements.[3−10]

Fragmentation reactions are the most common pathways of P_4 with main group precursors. Recently G. Bertrand et al. have documented the fragmentation of P_4 by a N-heterocyclic carbene (NHC) and related carbene ligands.[3b−d] A similar type of reaction is observed with σ-donor low-valent main group elements. For example, the reaction between P_4 and (DDP)Al (DDP = 2-di*iso*-propylphenylamino-4-di*iso*-propylphenylimino-2-pentene) resulted in the formation of [{(DDP)Al}$_2$$P_4$] (**A**) by the attack of two P−P bonds leading to double insertion.[4] Interestingly, the series of related carbenoid ER reactants, i.e., $[Cp^*Al]_4$ ($Cp^* = C_5Me_5$), $[\{(Me_3Si)_3C\}Ga]_4$ and $[ArTl]_2$ ($Ar = C_6H_3(2,6\text{-}i Pr_2\text{-}C_6H_3)_2$) afford $[(Cp^*Al)_6P_4]$ (**B**),[5] $[\{(Me_3Si)_3CGa\}_3P_4]$ (**C**),[6] and $[(ArP)_2P_2Tl_2]$ (**D**),[7] respectively, by dissipation of the P_4 tetrahedron (Chart 1). It is most often difficult to predict the fate of P_4 in these reactions, and random distribution of metal centers in the phosphorus core is observed.

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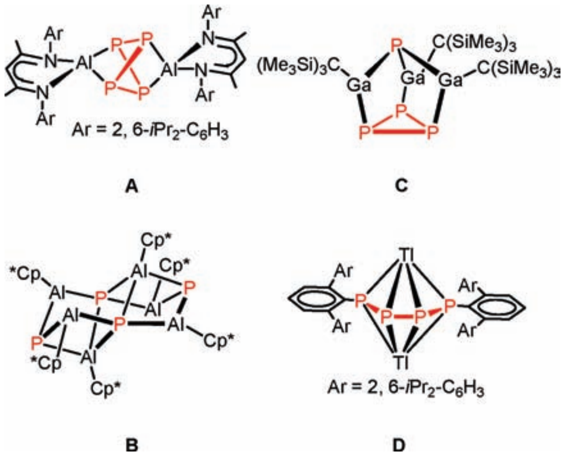
Chart 1. Molecular Species Obtained from the Reaction of Monovalent Group 13 Ligands[a]



[a] RE(I) [R; bulky organic group, E: Al, Ga, Tl] with white phosphorus.

Interestingly, the P_4 molecule also shows addition reactions with Lewis acids, such as tBu$_3$Ga,[8] or dissipation reactions with strong bases, such as tBu$_3$SiNa and [(Me$_3$Si)$_3$-SiK][18-crown-6].[9] However, stable molecules with single insertion of low-valent main group elements at P_4 core are limited, and such types of molecules can provide four naked phosphorus centers for further reactions. The only reported example with a low-valent main group metal is a P_4 unit supported by the NHC analog DDP″Si [DDP″ = HC-(CMeNC$_6$H$_3$-2,6-iPr$_2$)(H$_2$C=CNC$_6$H$_3$-2,6-iPr$_2$)].[10] Hereby we report the synthesis, spectroscopic, and structural characterization of the first example of a tetraphosphabicyclobutane molecule [(DDP)Ga(P$_4$)] (**1**) which is supported by a group 13 metal center and its bis-molybdenum pentacarbonyl adduct [(DDP)Ga($\eta^{2:1:1}$-P$_4$){Mo(CO)$_5$}$_2$]·2toluene (**2**).

Experimental Section

General Procedures. All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glovebox techniques. Hexane and toluene were dried using an MBraun solvent purification system. The final H_2O content in all solvents was checked by Karl Fischer titration and did not exceed 5 ppm. Ga(DDP) was prepared as previously described procedure.[11] Unless otherwise stated, chemicals used in this work were purchased from commercial sources. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer in C_6D_6 or toluene-d_8 at 25 °C. Chemical shifts are given relative to tetramethylsilane (TMS) and were referenced to the solvent resonances as internal standards. Chemical shifts are described in parts per million, downfield shifted from TMS, and are consecutively reported as position (δ_H or δ_C), relative integral, multiplicity (s = singlet, d = doublet, sept = septet, m = multiplet), coupling constant (J in Hz), and assignment. IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer.

X-ray Crystallography. Crystals of **1** and **2** were obtained from mixtures of toluene/n-hexane at −30 °C. X-ray data for compounds **1** and **2** were collected on an Oxford Excalibur 2 diffractometer. The crystals were coated with a perfluoropolyether, picked up with a glass fiber, and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final R values are provided in Supporting Information (Table S1). The structural solution and refinement were performed using the programs SHELXS-97 and SHELXL-97.[12a,b] Molecules **1** and **2** were refined with distance restraints and restraints for the anisotropic displacement parameters. The disordered solvent molecule toluene in **2** was "squeezed" out with the program Platon 1.13.[12c]

Synthesis of 1. Toluene (1.5 mL) was added to a Schlenk tube charged with Ga(DDP) (0.1 g, 0.209 mmol) and P_4 (0.026 g, 0.209 mmol) at room temperature under vigorous stirring. Slowly the P_4 was consumed within 30 min, and the reaction mixture color changed from yellow to orange. The clear orange solution was stirred for 24 h, volatiles were removed under vacuum, and the yellow-orange solid was dissolved in n-hexane/toluene mixture (2:1) under warm condition, filtered, and stored at −30 °C to afford bright yellow crystals of **1**. Yield: 83% (0.106 g, based on P_4). Mp: 232−234 °C. ^{1}H NMR (C_6D_6, 250 MHz), δ: 7.17−7.04 (m, 6H, Ar CH), 4.58 (s, 1H, γ-CH), 3.19 (sept, 4H, CH(Me)$_2$), 1.42 (s, 12H, CH_3), 1.49 (d), 0.94 (d) (24H, CH(Me)$_2$) ppm. ^{13}C NMR (C_6D_6, 62.8952 MHz), δ: 168.6 (C(Dipp)−N), 144.0 (CMe), 140.3 [o-C(Dipp)], 129.3 [p-C(Dipp)], 125.0 [m-C(Dipp)], 96.1 (γ-C), 29.4 (CHMe$_2$), 25.3 (CHMe_2), 25.2 (CMe), 23.7 (CHMe_2) ppm. ^{31}P NMR (C_6D_6, 101.2545 MHz), δ: −328.7 ($^1J_{PP}$ = 152 Hz, 2P, $P-P$), 212.7 ($^1J_{PP}$ = 152 Hz, 2P, Ga−P) ppm. Anal. calcd (%) for $C_{43}H_{57}GaN_2P_4$ (795.56): C, 64.92; H, 7.22; N, 3.52. Found: C, 64.89; H, 7.17; N, 3.50.

Synthesis of 2. To a mixture of Mo(CO)$_6$ (0.129 g, 0.490 mmol) and **1** (0.1 g, 0.163 mmol), dry toluene (4 mL) was added, stirred for 5 min, and heated at 80 °C for 1day. The resultant brown solution was evaporated in order to remove all volatiles. The brown residue was then redissolved in toluene (5 mL), layered with n-hexane and placed at −30 °C for 1day to give pale yellow crystals of compound **2**. The crystals were washed with n-hexane (2 × 4 mL) and dried under vacuum. Yield (0.070 g, 41%, based on [(DDP)Ga(P$_4$)]. Decomp. range >160 °C. IR ($\bar{\nu}$, cm^{-1}): 2966(w), 2929(w), 2871(w), 2064(s), 1995(w), 1934(vs), 1912(vs), 1888(vs), 1588(m), 1437(w), 1312(w), 1254(w), 1019(w), 871(w), 799(m), 789(m), 758(w), 600(vs), 581(vs), 559(w), 532(w), 442(w). ^{1}H NMR (toluene-d_8, 250 MHz), δ: 7.19−6.99 (m, 6H, Ar CH), 4.50 (s, 1H, γ-CH), 3.09 (sept, 4H, CH(Me)$_2$), 1.64 (d, 12H, CH(Me)$_2$), 1.37 (s, 6H, CH$_3$), 1.07 (d, 12H, CH(Me)$_2$) ppm. ^{13}C NMR (toluene-d_8, 62.8952 MHz), δ: 204.8 (Mo−CO), 170.55 (C(Dipp)−N), 143.7 (CMe), 138.7 [o-C(Dipp)], 137.9 [p-C(Dipp)], 128.2 [m-C(Dipp), overlapped with solvent resonances], 98.3 (γ-CH), 29.5 (CHMe$_2$), 26.5 (CHMe_2), 24.8 (CMe), 23.8 (CHMe_2) ppm. ^{31}P NMR (C_6D_6, 101.2545 MHz), δ: −315.2 ($^1J_{PP}$ = 174 Hz, 2P, $P-P$), 51.6 ($^1J_{PP}$ = 175 Hz, 2P, Ga−P) ppm. Anal. calcd (%) for $C_{53}H_{57}N_2O_{10}GaP_4Mo_2$ (1267.53): C, 50.22; H, 4.53; N, 2.21. Found C, 51.09; H, 4.99; N, 2.43.

Results and Discussion

The activation of P_4 using gallium reagents was first investigated by A. R. Barron et al. in 1991. The tBu and gallium addition of tBu$_3$Ga into P_4 led to the isolation of [tBu$_2$Ga{(P)(PtBu)(PGatBu)(P)}].[8] In contrast, the threefold insertion of gallium into the P−P bond of P_4 was observed when 3/4 [{(Me$_3$Si)$_3$C}Ga]$_4$ was treated with P_4.[6] However, a single or double insertion of a gallium center into P_4 has not been reported yet. Since the sterically encumbered Ga(DDP) is known to stabilize the unusual Zintl-type cluster,

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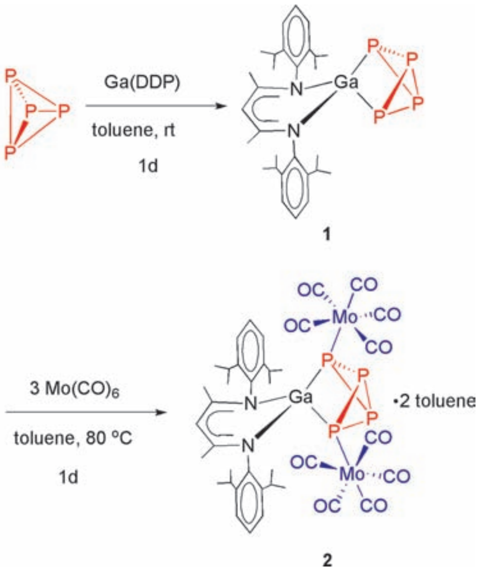
Scheme 1. Synthesis of **1** and **2**



[{(DDP)Ga(Cl)}$_4$(Sn$_{17}$)][13] and dibismuthenes, [{(DDP)Ga(OR^f)}(Bi)]$_2$ (R^f = SO$_2$CF$_3$, C$_6$F$_5$),[14] we anticipated a mild reaction between Ga(DDP) and P$_4$.

Synthesis and Structural Characterization of 1. Reaction of P$_4$ with one equivalent of Ga(DDP)[11] in toluene at room temperature resulted in the formation of **1** (Scheme 1). Bright yellow crystals of **1** were obtained in a good yield (83%) when a solution of the crude product in a mixture of toluene and *n*-hexane was cooled from room temperature to −30 °C and stored at this temperature for 12 h. It is highly soluble in common organic solvents, such as benzene, toluene, and THF. Moreover, it is stable both in solution as well as in the solid state at room temperature in an inert atmosphere (Ar). Molecule **1** has been characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and single crystal X-ray structural analysis. The ^{1}H and ^{13}C NMR spectra of **1** exhibit the expected resonances for a DDP ligand, well comparable with known metal complexes of Ga(DDP). The ^{31}P NMR spectrum shows two triplets at δ +212.7 and −328.7 ppm. The signal at δ +212.7 ppm with a large coupling constant ($^1J_{PP}$ = 152 Hz) can be assigned to the phosphorus atoms linked to the gallium center. The same coupling constant is also observed for the remaining two phosphorus atoms with a upfield chemical shift value at δ −328.7 ppm. The chemical shift value for *P*−Ga is nearly δ 47−95 ppm downfield shifted, while that for *P*−P−Ga is δ 110−122 ppm upfield shifted compared to [(Cp″)$_2$M(P$_4$)] (Cp″ = η^5-1,3-*t*Bu$_2$-C$_5$H$_3$) [M = Zr (δ +166.1 and −206.5 ppm), Hf (δ +117.5 and −219.3 ppm)].[15] Moreover, a considerable downfield shift of *P*−Ga (δ 80 ppm) and *P*−P−Ga (δ 16 ppm) in **1** is observed compared to [(DDP″)Si(P$_4$)], which is well acceptable since the electron delocalization in C$_3$N$_2$Si and C$_3$N$_2$Ga backbones are distinctly different.[10]

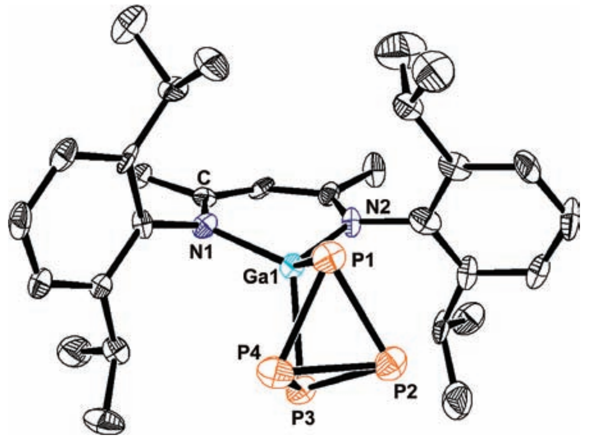


Figure 1. Molecular structure of **1** (50% ellipsoids). The H atoms attached to carbon are omitted for clarity. Important bond lengths (Å) and angles (°): Ga(1)−N(2) 1.907(6), Ga(1)−N(1) 1.968(6), Ga(1)−P(3) 2.340(2), Ga(1)−P(1) 2.346(2), P(2)−P(4) 2.154(3), P(2)−P(3) 2.239(3), P(2)−P(1) 2.242(3), P(3)−P(4) 2.245(3), P(4)−P(1) 2.229(3), P(3)−P(2)−P(1) 90.14(11), P(4)−P(2)−P(1) 60.88(10), P(2)−P(3)−P(4) 57.41(10), P(2)−P(4)−P(1) 61.53(10), P(2)−P(4)−P(3) 61.15(10), P(1)−P(4)−P(3) 90.34(11), P(4)−P(1)−P(2) 57.60(10), P(4)−P(2)−P(3) 61.44(10), P(2)−P(3)−Ga(1) 83.38(9), N(2)−Ga(1)−N(1) 97.1(3), N(2)−Ga(1)−P(3) 119.03(19), N(1)−Ga(1)−P(3) 119.71(17), N(2)−Ga(1)−P(1) 115.82(18), N(1)−Ga(1)−P(1) 122.03(18), P(3)−Ga(1)−P(1) 85.21(8), P(4)−P(3)−Ga(1) 85.11(9), P(2)−P(1)−Ga(1) 83.17(9), P(4)−P(1)−Ga(1) 85.34(9).

Molecule **1** crystallizes in the tetragonal space group, *P*4$_3$2$_1$2 (Figure 1). Compound **1** can be regarded as a single insertion product of (DDP)Ga into one of the P−P bonds of a P$_4$ tetrahedron. Therefore, the molecular structure of **1** is comparable with that of [(DDP″)Si(P$_4$)].[10] The tetraphosphabicyclobutane fragment in **1** shows a typical butterfly shape structure. Atoms Ga(1), P(1), and P(3) are in the same plane, while the atoms P(2), P(4), and the six-membered GaN$_2$C$_3$ ring are perpendicular to the former plane. The Ga−P bond distances in **1** are almost equal within the range of the accuracy to the measured data: 2.346(2) Å for Ga(1)−P(1) and 2.340(2) Å for Ga(1)−P(3). Consequently, the remaining five P−P bond distances are different and fall within the range of 2.154(3)−2.245(3) Å. Although such types of bonding features were reported for [Cp*(CO)Co(P$_4$)] (Co−P = 2.261(1) and 2.255(1) Å; P−P range = 2.158(2)−2.217(2) Å)[2j] and [(DDP″)Si(P$_4$)] (Si−P = 2.250(1) and 2.246(1) Å; P−P range = 2.159(2)−2.235(2) Å),[10] compound **1** draws near to the higher end of the P−P bond distances. The P(2)−P(4) bond distance in **1** is approximately 0.056(3)Å shorter than that of the P−P bond distance found in P$_4$ (2.21(2) Å), while P(2)−P(3) (0.029 Å), P(2)−P(1) (0.032 Å), P(3)−P(4) (0.035 Å), and P(4)−P(1) (0.019 Å), are slightly elongated.[16] The P(1) and P(3) separation in **1** is 3.173(3) Å, which is somewhat larger than that of [Cp*(CO)Co(P$_4$)][2j] (P···P = 2.606(1) Å) and [(DDP″)Si(P$_4$)] (P···P = 3.103 Å).[11] Furthermore, the value of the angle P(1)−Ga(1)−P(3) is 85.21(8)°, which compares with P−Si−P angle (87.32(5)°) of [(DDP″)-Si(P$_4$)].[11] The widening of the P−P−P angles reveals the distorted tetrahedral geometry for the phosphorus centers. The sum of P−P−P angle around P(2) (Σ P(2) = 212.46(10)°) and P(4) (Σ P(4) = 213.02(10)°) and the sum of Ga−P−P and P−P−P angle around P(1) (Σ P(1) = 226.11(9)°) and P(3) (Σ P(3) = 225.9(9)°) are comparable.

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The P(2)−P(3)−P(4) bond in the P_4 core exhibits the lowest P−P−P angle (57.41(10)°), while the P(1)−P(4)−P(3) depicts the highest angle (90.34(11)°).

The shortening of the Ga−N bond (Ga(1)−N(2) 1.907(6) and Ga(1)−N(1) 1.968(6) Å) and elongation of N(1)−Ga−N(2) angle (97.1(3)°) in **1**, as compared to free Ga(DDP) (av. Ga−N = 2.0544 Å; N−Ga−N = 87.53°), demonstrates the increased electrophilic nature of Ga(DDP) upon coordination to the P_4 moiety.[11] As shown in the space-filling representation of **1** (Supporting Information, Figure S4), the sterically crowded DDP group effectively protects the extremely reactive P_4 moiety of **1** and thereby prevents its oligomerization.

Synthesis and Structural Characterization of 2. Furthermore, the coordinating ability of **1** was investigated with hexacarbonylmolybdenum. Compound **2** was prepared from a mixture of $[Mo(CO)_6]$ and **1** in a ratio of approximately 3:1 in toluene at 80 °C. Elimination of one carbonyl group in $[Mo(CO)_6]$ led to the formation of **2**. Pale yellow crystals of **2** are soluble in polar organic solvents and stable at room temperature. Compound **2** is an air- and moisture-sensitive compound and stable only under inert atmosphere. It has been characterized by elemental analysis, IR, multinuclear NMR (^{1}H, ^{13}C, and ^{31}P), and single crystal X-ray diffraction techniques. As indicated by elemental analysis, **2** has the composition of $[(DDP)Ga(P_4)\{Mo(CO)_5\}_2]\cdot$2toluene (**2**) and is sufficiently pure to be used directly for further characterization. IR spectroscopy confirms the presence of five carbonyl bands ($\bar{\nu}_{CO}$ 2064(s), 1995(w), 1934(vs), 1912(vs), 1888(vs) cm^{-1}), all attributable to the $Mo(CO)_5$ fragment.[17] The ^{13}C NMR spectrum of **2** in toluene-d_8 shows only one peak in the carbonyl region (δ 204.8 ppm) (see Supporting Information, Figure S6 and references there). The ^{31}P NMR spectrum of **2** in C_6D_6 displays two triplets at δ −315.2 and 51.6 ppm. The triplet at δ −315.2 ppm corresponds to the uncoordinated phosphorus atoms, which is slightly shifted downfield with respect to **1** ($\Delta\delta$ 13.5 ppm). The lower field triplet at δ 51.6 ppm can be attributed to the phosphorus atoms of $[P{-}Mo(CO)_5]$ moiety, and upon coordination, a very strong upfield shift ($\Delta\delta$ 161.1 ppm) is observed. Although compound **2** is isolated exclusively from this reaction, the ^{31}P NMR spectrum of the mother liquor clearly indicates the presence of more than one complex with different coordination modes (Supporting Information).

The molecular structure of **2** is shown in Figure 2. Compound **2** crystallized from toluene/*n*-hexane mixture in the monoclinic space group $P2_1/n$ (Figure 2) with two solvent molecules of toluene per asymmetric unit. Compound **2** consists of a Ga, Mo, and P based heteronuclear $[Ga(\eta^{2:1:1}\text{-}P_4)Mo_2]$ core. Two $Mo(CO)_5$ fragments are attached to the phosphorus atoms of **1** in monodendate (η^1) fashion. Interestingly, each $Mo(CO)_5$ fragment is tethered to the phosphorus atoms that are linked to the gallium center, which is a rather rare type of coordination mode observed for metal complexes bearing a tetraphosphorus ligand.[2,17b,18] However, the reaction of DDP″Si with $[(NiDDP)_2\cdot$toluene] or $[(NiDDP')_2\cdot$toluene] (DDP′ = 2-di-ethylphenylamino-4-diethylphenylimino-2-pentene) results in molecules consisting of a $[Si(\mu,\eta^{2:2}\text{-}P_4)Ni]$ core similar to **2**.[19] The molybdenum center in **2** is in distorted octahedral geometry, surrounded by five CO ligands and one P atom. Interestingly, the $Mo(CO)_5$ fragment prefers coordination at the more nucleophilic P centers (as suggested by VB formulas of the P_4^{2-} anion), despite the sterically less favorable situation at this positions.

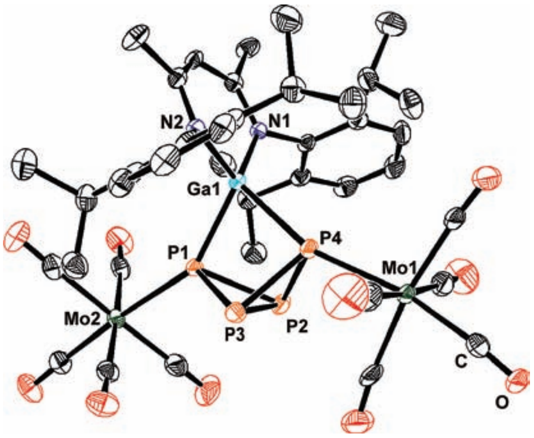

Figure 2. Molecular structure of **2** (50% ellipsoids). The H atoms attached to carbon and toluene molecules are omitted for clarity. Important bond lengths (Å) and angles (°): Mo(2)−P(1) 2.5458(8), P(4)−Mo(1) 2.5856(8), Ga(1)−P(1) 2.3746(8), Ga(1)−P(4) 2.4051(8), Ga(1)−N(2) 1.927(2), Ga(1)−N(1) 1.931(2), P(4)−P(3) 2.2163(11), P(4)−P(2) 2.2195(11), P(3)−P(2) 2.1818(11), P(3)−P(1) 2.2174(11), P(2)−P(1) 2.2244(11), N(2)−Ga(1)−N(1) 98.71(10), P(1)−Ga(1)−P(4) 79.03(3), P(3)−P(4)−P(2) 58.93(4), P(3)−P(4)−Ga(1) 88.73(3), P(2)−P(4)−Ga(1) 88.12(3), P(3)−P(4)−Mo(1) 107.06(4), P(2)−P(4)−Mo(1) 107.85(4), Ga(1)−P(4)−Mo(1) 161.66(3), P(2)−P(3)−P(4) 60.61(4), P(2)−P(3)−P(1) 60.74(3), P(4)−P(3)−P(1) 86.62(4), P(3)−P(2)−P(4) 60.47(4), P(3)−P(2)−P(1) 60.42(3), P(4)−P(2)−P(1) 86.38(4), P(3)−P(1)−P(2) 58.84(4), P(3)−P(1)−Ga(1) 89.48(3), P(2)−P(1)−Ga(1) 88.77(3), P(3)−P(1)−Mo(2) 115.73(4), P(2)−P(1)−Mo(2) 116.61(4), Ga(1)−P(1)−Mo(2) 150.59(3).

The Mo−P bond lengths (Mo(2)−P(1), 2.5458(8) Å and Mo(1)−P(4), 2.5856(8) Å) in **2** are not equal, and it is comparable with $[Cp'Mo(CO)_2(\eta^3\text{-}P_4)\{Cr(CO)_5\}_4(H)]$ (Cp′ = C_5H_4tBu).[17b] The Ga(1)−P(1) distance (2.3746(8) Å) is distinctly shorter than that of Ga(1)−P(4) (2.4051(8) Å). The average Ga−P bond distances (2.3899(8) Å) in **2** are slightly longer than the same bond distances of **1** (2.343(2) Å). As shown in Figure S9 (Supporting Information), a negligible elongation of P−P bond lengths with respect to **1** (except P(2)−P(3)) is observed. The P−P bond distance of **2** falls in the range of 2.1818(11)−2.2244(11) Å. The P(1)−Ga(1)−P(4) bond angle is 79.03(3)°, which is nearly 6° lower than **1** (P(1)−Ga(1)−P(3), 85.21(8)°). As expected, a slight change in the bond angle of GaP_4 core is observed in **2** as compared to **1**. The central GaN_2C_3 ring atoms of Ga(DDP) are essentially coplanar.

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Conclusions

In summary, the activation of a single P−P bond in white phosphorus (P_4) by Ga(DDP) (DDP = 2-di*iso*-propylphenylamino-4-di*iso*-propylphenylimino-2-pentene) led to the isolation of molecular gallium-tetraphosphabicyclopentane (**1**) with open access to the phosphorus core. The butterfly shape P_4 unit coordinated to the Ga(DDP) framework is the first example of a single insertion of a monovalent group 13 element at the P_4 tetrahedron. Further reaction of [(DDP)-Ga(P_4)] with excess of $Mo(CO)_6$ afforded **2** consisting of a heteronuclear [Ga($\eta^{2:1:1}$-P_4)Mo_2] core, which is an example of a rare coordination mode observed in metal supported P_4 molecules.

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Supporting Information Available: Figures S1−S9, Table S1, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.