# Facile Synthesis of Dibenzo-7λ³-phosphanorbornadiene Derivatives Using Magnesium Anthracene

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**S** *Supporting Information*

**ABSTRACT:** Unprotected dibenzo-7λ³-phosphanorbornadiene derivatives RP**A** (**A** = $C_{14}H_{10}$ or anthracene; R = $^tBu$, dbabh = N**A**, HMDS = $(Me_3Si)_2N$, $^iPr_2N$) are synthesized by treatment of the corresponding phosphorus dichloride $RPCl_2$ with Mg**A**·3THF, in cold THF (~20% to 30% isolated yields). Anthracene and the corresponding cyclic phosphane $(RP)_n$ form as coproducts. Characteristic NMR features of the RP**A** derivatives include a doublet near 4 ppm in their $^1H$ NMR spectra and a triplet peak in the 175−212 ppm region of the $^{31}P$ NMR spectrum ($^2J_{PH}$ ~14 Hz). The X-ray structures of the **A**N−P**A** and (HMDS)P**A** derivatives are discussed. Thermolysis of RP**A** benzene-$d_6$ solutions leads to anthracene extrusion. This process has a unimolecular kinetic profile for the $^iPr_2N$P**A** derivative. The 7-phosphanorbornene *anti*-$^iPr_2NP(C_6H_8)$ could be synthesized (70% isolated yield) by thermolysis of $^iPr_2N$P**A** in 1,3-cyclohexadiene.

H erein we report a facile synthesis of previously elusive, unprotected dibenzo-7λ³-phosphanorbornadiene derivatives. Long attractive as synthetic targets, 7-phosphanorbornadienes are especially interesting for their potential to serve as phosphinidene precursors under mild conditions *via* concerted loss of an aromatic moiety.[1] The early view that "it was quite obvious that the only reasonable way to prepare 7-phosphanorbornadienes remained the [2 + 4] cycloadditions between electrophilic acetylenic dienophiles and phospholes"[1] has been unchallenged and not fruitful in terms of delivering valuable derivatives that bear an unprotected lone pair of electrons at phosphorus. This status quo fostered a prevailing sensibility that the lone electron pair at phosphorus and the strained CPC angle impart inherent instability to the 7-phosphanorbornadiene architecture.[1,2] Protection of the phosphorus lone pair by either metal complexation[3−6] or by utilizing the corresponding phosphine oxide[7,8] allowed the isolation of stabilized derivatives. In 2000, the first unprotected 7λ³-phosphanorbornadiene derivative was generated (by decomplexation of a protected 7-phosphanorbornadiene) as a species not sufficiently stable for isolation in which the cheletropic loss of the aromatic moiety was disfavored by incorporation of a highly strained metacyclophane subunit.[2]

Against the foregoing backdrop, we were surprised to find that uncoordinated 7λ³-phosphanorbornadiene derivatives can be synthesized directly from the reaction of Mg**A**·3THF (**A** = $C_{14}H_{10}$ or anthracene) with phosphorus dichlorides, $RPCl_2$ (R

= $^tBu$, dbabh (2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene), HMDS ($(Me_3Si)_2N$), $^iPr_2N$; see Scheme 1). In the

**Scheme 1. General Procedure to Synthesize Unprotected 7λ³-Phosphanorbornadiene Derivatives RP A (R = $^tBu$, dbabh, HMDS, $^iPr_2N$) in ~20% to 30% Isolated Yields from the Corresponding Phosphorus Dichloride $RPCl_2$ and Mg A·3THF$^a$**
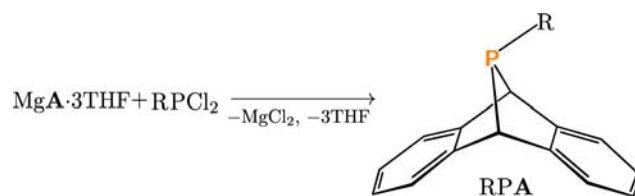


$^a$Anthracene and the corresponding cyclic phosphane $(RP)_n$ are formed as coproducts in this reaction.

context of the previously reported cumbersome, multistep syntheses of *protected* 7-(heteroatom)norbornadienes, the one-step procedure illustrated in Scheme 1 is a model of efficiency despite the fact that competing formation of $(RP)_n$ cyclic oligomers obviates achieving a high yield; we note that some prior discussion has been devoted to the reduction of aryl-dichlorophosphines by magnesium including mechanistic proposals involving phosphinidene intermediates.[9]

Why was the title reaction not already known? A thorough search of the chemical literature for clues or precedent revealed several noteworthy reports of analogous syntheses of group 14 7-(heteroatom)norbornadienes, themselves widely studied as sources of heavy carbene analogues upon thermolysis.[10−13] In 1967 Ramsden, the first to introduce magnesium anthracene as a reducing agent, reported the direct synthesis of $Bu_2Sn$**A** from Mg**A** and the corresponding tin dichloride, $Bu_2SnCl_2$,[14,15] and also made claims on similar syntheses of the other group 14 (Si to Pb) dibenzo-7-(heteroatom)norbornadiene derivatives.[16] Almost a decade later, Smith and Pounds independently reported the direct synthesis of $(Ph_2Si)_2$**A** from a mixture of $Ph_2SiCl_2$, Mg, and anthracene,[17] and yet another decade later Appler et al. reported the synthesis of another dibenzo-7-silanorbornadiene derivative from $Li_2$**A** and the corresponding silyl dichloride.[11] These early organometallic syntheses of dibenzo-7-(heteroatom)norbornadiene architectures were later

overshadowed by the more popular [2 + 4] cycloaddition synthetic routes[3,4,10,11,18−20] and were seemingly forgotten in the annals of the burgeoning chemical literature.

While exploring chemical reduction of the new dichlorophosphine dbabhPCl$_2$, we found serendipitously that treatment of a cold THF solution of dbabhPCl$_2$ with solid MgA·3THF led to formation of **AN−PA** and the cyclic phosphine [(dbabh)P]$_4$, in an ∼2:1 ratio (based on P), together with anthracene. The reduction of dichlorophosphines to cyclophosphines of different ring sizes has been well documented, and was not surprising to us.[22] Positive evidence of **AN−PA** formation was signaled in the $^1$H NMR spectrum of the crude mixture by a characteristic doublet ($^2J_{PH}$ = 14.9 Hz) at 3.89 ppm. Upon consumption of the bright orange MgA·3THF, all volatile materials were removed *in vacuo* from the reaction mixture, and the residue was extracted with the minimum amount of *n*-hexane. The resulting slurry was filtered through a short charcoal plug, and from the colorless filtrate **AN−PA** was selectively crystallized and isolated in 22% yield.

Eager to explore the scope of this synthetic route, we turned to less exotic dichlorophosphine reagents. Treatment of (HMDS)PCl$_2$ with MgA·3THF in THF produced an ∼1:1.4 ratio (based on P) of **(HMDS)PA** and the new *cyclo*-triphosphane [(HMDS)P]$_3$, along with anthracene. **(HMDS)-PA** was isolated in 20% yield as a white powder. Interestingly, when the reaction was carried out in diethyl ether only [(HMDS)P]$_3$ was formed. Similarly, treatment of $^iPr_2NPCl_2$ with MgA·3THF in THF produced a mixture of the previously characterized cyclic phosphane ($^iPr_2NP)_4$[23] and $^iPr_2NPA$. We have not yet been able to obtain pure samples of $^iPr_2NPA$, as the anthracene contaminant has proven difficult to separate in the case of this derivative. Reduction of $^tBuPCl_2$ with MgA·3THF in THF also produced a mixture of the previously characterized cyclic phosphanes ($^tBuP)_n$ ($n$ = 3,4) together with the desired $^tBuPA$, which could be isolated in 20% yield. Carried out under similar conditions, the reduction of the aromatic dichlorophosphines PhPCl$_2$ and MesPX$_2$ (X = Cl, Br; Mes = mesityl) with MgA·3THF led only to the formation of cyclic phosphane oligomers.

The bridgehead protons in the RPA derivatives are characterized by a doublet near 4 ppm in their $^1$H NMR spectra, with large $^2J_{PH}$ coupling constants to phosphorus of ∼14 Hz. Strongly deshielded, the phosphorus bridge gives rise to a triplet peak in the 175−212 ppm region of the $^{31}$P NMR spectrum, 63 to 100 ppm downfield with respect to the value previously reported for a 7λ$^3$-phosphanorbornadiene,[2] but in the same region where complexed 7-phosphanorbornadienes display phosphorus shifts.[3,5,6]

Crystals of suitable quality for X-ray diffraction studies of **AN−PA** and **(HMDS)PA** were grown upon cooling a warm, saturated *n*-pentane solution of **AN−PA**, or from a saturated *n*-pentane solution of **(HMDS)PA** that had been stored at −35 °C (thermal ellipsoid drawings are presented in Figure 1). The two structures are not remarkable with regard to the observed metrical parameters; indeed, they compare well to structures previously reported for lone-pair protected 7-phosphanorbornadiene derivatives.[3,5,6] The acute CPC angle, imposed by the 7-phosphanorbornadiene architecture, has a value of 79.10(6)° in **AN−PA** and 78.97(6)° in **(HMDS)PA**. Consistent with computational predictions,[2] the plane defined by phosphorus and the two bridgehead carbon atoms is inclined away from the benzo ring situated on the same side as the R substituent on phosphorus by ca. 5°. The P−N interatomic distance in AN−
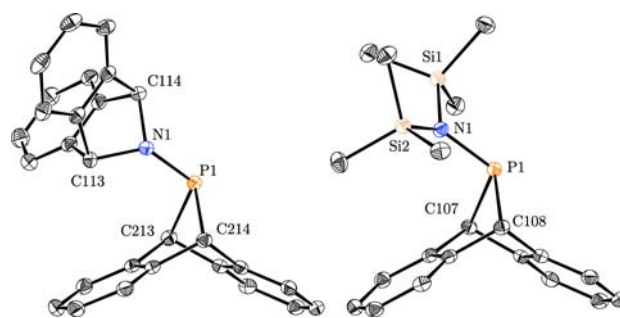


**Figure 1.** Solid-state molecular structure of **AN−PA** (left) and **(HMDS)PA** (right) with ellipsoids at the 50% probability level and rendered using PLATON.[21] Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): (a) for **AN−PA** (left) P1−N1 1.691(1) P1−C213 1.927(1), P1−C214 1.906(1), C113−N1−P1 131.5(1), C114−N1−P1 118.6(1), C113−N1−C114 95.7(1), N1−P1−C214 105.95(6), N1−P1−C213 112.15(6), C214−P1−C213 79.10(6); (b) for **(HMDS)PA** (right): P1−N1 1.726(1), P1−C107 1.917(1), P1−C108 1.912(1), Si1−N1−P1 107.74(6), Si1−N1−Si2 121.44(7), Si1−N1−P1 129.28(7), N1−P1−C107 107.52(6), N1−P1−C108 112.75(6), C107−P1−C108 78.97(6).

PA and **(HMDS)PA** is slightly shorter than 1.82 Å, the sum of the covalent single-bond radii of the two elements.[24] In accord with Bent's rule,[25] the nitrogen atom is slightly pyramidalized in **AN−PA**, with the sum of the angles around N being 345.8(3)°. In **(HMDS)PA**, where the electropositive silyl substituents are more effective at maximizing the involvement of the nitrogen 2s orbital in the N−Si interactions, the nitrogen atom is practically planar.

When benzene-$d_6$ solutions of the RPA derivatives were heated, the RPA species were found to undergo thermal extrusion of anthracene. Potentially susceptible to loss of 2 equiv of anthracene, the **AN−PA** derivative converted upon thermolysis to anthracene as the only soluble species (52% yield) as measured by $^1$H NMR spectroscopy and referenced to $^tBuCN$ as an external standard. Also formed in the reaction was a pale yellow solid that was not soluble in common organic solvents; characterization of this material is in progress. Thermolysis of benzene solutions of **(HMDS)PA**, $^tBuPA$, and $^iPr_2NPA$ led to formation of anthracene, together with the corresponding cyclic phosphanes [(HMDS)P]$_3$, ($^iPr_2NP)_4$, and ($^tBuP)_n$.

The thermal release of an aromatic moiety from 7-phosphanorbornadiene complexes (commonly with W(CO)$_5$) has been shown to be a unimolecular process that proceeds *via* cheletropic elimination of a terminal phosphinidene complex, e.g. [RPW(CO)$_5$].[4,26] The carbene-like chemical reactivity of the transient phosphinidene complexes so generated has been extensively studied, in particular with olefins, 1,3-dienes, and alkynes as the reaction partners.[27] In order to determine whether unprotected 7-phosphanorbornadienes behave similarly upon thermolysis, the disappearance of $^iPr_2NPA$ was monitored in benzene-$d_6$ in the temperature range 72−89 °C using $^1$H NMR spectroscopy. Indeed, plots of ln[$^iPr_2NPA$] versus time were linear and values of the first-order rate constant $k$ extracted therefrom were in the range (2−42) × 10$^{-5}$ s$^{-1}$ corresponding to an Arrhenius activation barrier of 40 ± 2 kcal/mol.

In order to intercept the proposed transient [$^iPr_2NP$] phosphinidene intermediate and compete with its oligomerization channel, the thermolysis of $^iPr_2NPA$ was carried out in

neat 1,3-cyclohexadiene (1,3-CHD). When a solution of $^i$Pr$_2$NP**A** in neat 1,3-CHD was heated at 80 °C for 12 h, only *anti-*$^i$Pr$_2$N-7-phosphanorbornene and anthracene were observed to form (Scheme 2), as measured by $^1$H and $^{31}$P

**Scheme 2. (i) Thermolysis of $^i$Pr$_2$NPA in 1,3-CHD Leading to Quantitative Formation of *anti-*$^i$Pr$_2$NPC$_6$H$_8$; (ii) A Model of *anti-*$^i$Pr$_2$NPC$_6$H$_8$ Built and Optimized Using DFT Methods[28,29] and Visualized Using PLATON[21]$^a$**
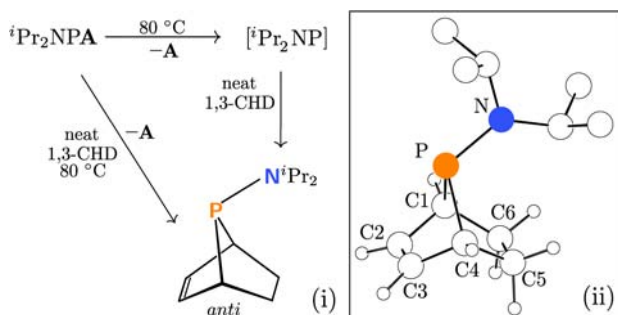


$^a$Hydrogen atoms on the $^i$Pr$_2$N group have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): P–N 1.714, P–C4 1.952, C5–C6 1.555, C2–C6 1.356, C1–P–C4 77.18.

NMR spectroscopy. Upon complete consumption of the $^i$Pr$_2$NP**A** starting material, all volatile materials were removed *in vacuo* from the reaction mixture. The resulting oily residue was suspended in a minimum amount of cold pentane, whereupon the mixture was filtered to remove all precipitated solids. The filtrate was brought to constant mass and was analyzed as spectroscopically pure *anti-*$^i$Pr$_2$NP(C$_6$H$_8$) (yield 69%). The stereochemistry of the product was established based on the large $^2J_{PC}$ coupling constant of the olefinic carbon atoms of 26.6 Hz, diagnostic for a proximal arrangement of the phosphorus lone pair with respect to the C=C bond.[30] A cationic P-chloro derivative of *syn,anti-*$^i$Pr$_2$NP(C$_6$H$_8$) has been reported previously; it was obtained by reaction of the highly electrophilic phosphenium salt [$^i$Pr$_2$NPCl][AlCl$_4$] with 1,3-CHD.[31] In contrast to its $7\lambda^3$ relative reported herein, [$^i$Pr$_2$NP(Cl)C$_6$H$_8$][AlCl$_4$] was produced as a mixture of *syn* and *anti* isomers.[31]

P-trivalent 7-phosphanorbornene derivatives previously have been synthesized from the [2 + 4] Diels–Alder cycloaddition of a phosphole to a dienophilic alkene,[30,32] and enantiopure chiral 7-phosphanorbornenes can also be synthesized using metal templation.[33] Recently, 7-phosphanorbornanes and 7-phosphanorbornenes have been used as ligands in rhodium-catalyzed asymmetric hydrogenations.[34]

In conclusion, we have discovered a simple, direct synthesis of several dibenzo-$7\lambda^3$-phosphanorbornadienes that consists of a magnesium anthracene reaction with dichlorophosphine, RPCl$_2$; within the scope of our limited survey the reaction was successful except for the case of an aryl substituent. The new dibenzo-$7\lambda^3$-phosphanorbornadiene derivatives so obtained were found to extrude anthracene smoothly upon heating, and as such, they very likely give rise thermally to transient phosphinidene intermediates consistent with the observed product mixtures. Along with phosphanylidene-$\sigma^4$-phosphoranes,[35] protected 7-phosphanorbornadienes, and terminal phosphinidene complexes,[1] the class of dibenzo-7-phosphanorbornadiene molecules introduced herein adds to the growing list of species that may serve as facile phosphinidene

sources. A further implication of the results reported herein is the new-found ability to introduce the −PA substituent, making it possible to envision thermal access to unsaturated P-containing intermediates well beyond the phosphinidene subset.

## ■ ASSOCIATED CONTENT

**S** **Supporting Information**
Provided are full details of experimental procedures for the synthesis of all new substances together with characterization data including details of X-ray diffraction studies and Cartesian coordinates for structures optimized by computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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