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Metalated 1,3-Azaphospholes: Structure and Reactivity of 2-Lithio-1-methyl-1,3-benzazaphosphole, an Isolable $-P=C(Li)-NR$ Heterocycle

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The preparation, NMR data, a crystal structure, and the reactivity of isolable 2-lithio-1,3-benzazaphospholes are described. The compounds are or belong to the most stable $P=CLi$ species, although they lack steric congestion. Reactions with organoelement or organometal halides $W(CO)_6$ as well as with CO_2 or benzophenone allow access to various novel functionally substituted 1,3-benzazaphospholes (2-R = $SnMe_3$, $Fe(CO)_2Cp$, $C[=W(CO)_5]OLi(THF)_3$, CPh_2OH, PPh_2, $P(O)Ph_2$). The crystal structure of the tungsten-carbene derivative is described. Attempts to lithiate and functionalize a 1,3-benzazaphosphole $P-W(CO)_5$ complex failed, but reactions of 1-methyl-2-stannyl- and 1-methyl-2-phosphino-1,3-benzazaphosphole with $W(CO)_5(THF)$ furnished examples for a 2-metalated benzazaphosphole $P-W(CO)_5$ complex and the preferred complexation of the phosphino substituent, respectively. The considerable upfield shifts of the ^{31}P NMR signals after complexation of the low-coordinated phosphorus atom by $W(CO)_5$ attest that the ligands are stronger acceptors than donors.

Introduction

α-Lithiated aromatic heterocycles[1] are, like aryllithium compounds, important building blocks for syntheses, but are frequently different from the latter with respect to structure and bonding due to the influence of the heteroatoms[2] or, especially in 2-lithio-1,3-heteroazoles, due to a ring-opening equilibrium underlining their proximity to carbenoids.[3] Whereas the 2-lithio-1-methylindole THF solvate **I** forms a dimer with lithium bound only to the anionic carbon atom,[4] the related dimer 2-lithiobenzofurane *i*Pr_2O solvate **II** is distinguished by the coordination of lithium to the anionic carbon atom as well as to oxygen.[5] Comparative structure investigations on 2-lithio-1,3-heteroazoles from Boche et al.[6] show rearrangement of 2-lithio-1,3-benzoxazoles to *o*-isonitrile-substituted phenolates,[6a] while corresponding 2-lithio derivatives of benzothiazoles and benzimidazoles preferably (but depending on substituents) and of thiazoles and imidazoles exclusively are present in the cyclic form.[6c] The cyclic isomers differ in their structure from simple lithium aryls as well as from **I**. As shown recently by crystal structure analyses, in “2”-lithiated dimer *N*-methyl imidazole **III** and thiazole **IV** lithium is bonded to nitrogen rather than to C-2, which coordinates also to the lithium atom of the neighboring molecule.[6a,b] Thus, the structure resembles that of the dimer diamino carbene LiO-aryl complex **V**.[7] In this context the smooth lithiation of *N*-methyl-1,3-benzazaphosphole **1a**[8] and the quite high stability of solutions of 2-lithio-*N*-methyl-1,3-benzazaphosphole **2a**, a phosphorus homologue of 2-lithiated *N*-alkyl-benzimidazoles or a P→C analogue[9] of 2-lithiated *N*-alkylindoles, raised the question of the structural features of **2a**, particularly since other $P=CLi$ derivatives such as lithiated phosphabenzenes[10] or acyclic aryl-$P=C(X)Li$ derivatives[11] are known to decompose even at low temperatures (ca. −90 and −50 °C, respectively). Only

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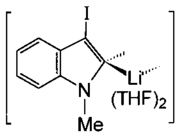
RP=C(Li)Mes* derivatives,[12] protected by steric congestion at carbon, could be characterized at room temperature (by ^{31}P NMR measurements). The unexpected formation and high persistence of **2a** as compared to 2-lithiophosphabenzene might be attributed to the π-donor ability of nitrogen and an increase of the electron density at phosphorus ($N{-}C{=}P \leftrightarrow N^{+}{=}C{-}P^{-}$) in the aromatic 1*H*-1,3-benzazaphospholes,[13] which hinders the addition of $R^{\delta-}Li^{\delta+}$ at the P=C bond and in turn might induce interactions between phosphorus and lithium. Lithio-1-methyl-1,2,4-diazaphosphole, characterized by methylation and stannylation at low temperature,[14] belongs to the same type of π-excess heteroaromatics and may similarly be stabilized. Recent ab initio calculations on various nonsolvated monomeric lithio-1,3-azaphospholes revealed only one minimum structure for the 2-lithio-1*H*-1,3-azaphosphole with lithium in the ring plane but somewhat distorted toward phosphorus.[15] Calculations on lithiated benzazaphospholes could not be done at this level.



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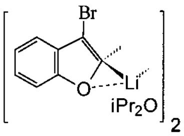

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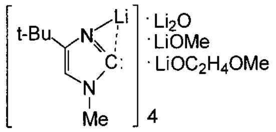

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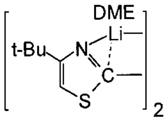

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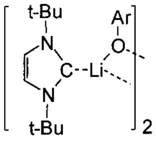

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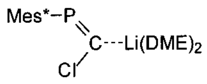


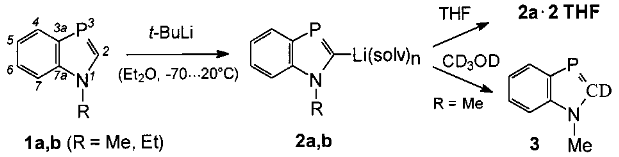
VI

To better understand the nature of 2-lithio-1,3-benzazaphospholes, to indicate prerequisites and demands on the design of stable P=CLi compounds, and to explore the synthetic potential, an earlier preliminary study was continued. This paper reports on the structure of isolated 2-lithio-1,3-benzazaphospholes and their reactions with metallic and nonmetallic electrophiles.

Results and Discussion

Synthesis and Structure of 2-Lithio-1,3-benzazaphospholes. The lithiation of 1-methyl- and 1-ethyl-1,3-benzazaphosphole **1a,b** with *tert*-butyllithium in ether at −70 °C (Scheme 1) affords with high regioselectivity the 2-lithio derivatives **2a**,**b**. Only traces of the corresponding 1,2-addition products of *t*BuLi to the P=C bond (δ^{31}P −61.4) were observed. By quenching **2a** with CD_3OD to give **3** the yield was determined to be about 85%. **2a**,**b** are isolated as orange-yellow powders. The compounds are more stable in the solid state than in solution, but even the latter can be stored without marked decomposition for several hours up to 1 day at room temperature and for several weeks at −20 °C. Single crystals of the dimer **2a**·2THF were grown from THF/hexane at −30 °C. The structure elucidation is based on multinuclear NMR data and on the results of a X-ray structure determination of **2a**·2THF.

Scheme 1



The ^{1}H NMR spectra of **2a** and **2b** are in accordance with lithiation in position 2. The characteristic downfield doublets for H-2 ($^{2}J_{PH} \approx 38$ Hz) disappear while the multiplets for H-4 to H-7 remain present. The downfield resonance of the NCH_3 and NCH_2 protons attributed to the ring current within the benzazaphosphole 10π-system is little affected. Marked changes are observed in the ^{13}C NMR spectra. The C-2 nuclei of **2a**,**b** are strongly deshielded ($\delta = 249.5$ and 248.7, respectively), much more than those in the ring-closed forms of related 2-lithiated *N*-methylindole **I**, *N*-methylbenzimidazole, or benzothiazole ($\delta = 200$, 216, and 221, respectively),[6c] in the amidocarbene-like "2"-lithioimidazole and -thiazole **III** and **IV** ($\delta = 195$ and 215, respectively)[6a,b] and even in benzimidazolin-2-ylidenes ($\delta = 232$),[16] but less than the carbenoid C atom in **VI** ($\delta = 257.4$)[11e] or C-2 in 2-lithio-*N*-methyl-1,3-benzazarsole ($\delta = 275$).[17] In analogy with the effect in phenyllithium[18] ($\Delta\delta = 58$) the observed low-field shift of the NMR signal of C-2 can be brought into agreement with a polarization and shift of the π-charge density that increases considerably with increasing size of the adjacent heteroatoms ($\Delta\delta$ N < C < S < P < As) and reaches $\Delta\delta = 87{-}88$ in **2a**,**b** and $\Delta\delta = 98$ in the As compound, respectively. As with **VI** the decreased π-density at C-2 on lithiation causes a strong increase of the $^{1}J_{PC2}$ coupling constants ($\Delta^{1}J_{PC2} \approx 56$ Hz). Like C-2, phosphorus is deshielded, but to a smaller extent ($\Delta\delta = 31$). For the other carbon nuclei of the azaphosphole ring the deshielding and the increase of P,C coupling constants are much smaller ($\Delta\delta_{C\text{-}3a,C\text{-}7a}$ 7.3, 5.5; $\Delta J_{PC3a,PC7a,NCH3} = 21.0$, 2.4, 4.6 Hz). The other carbon nuclei of the benzene ring exhibit the opposite effect, a small shielding ($\Delta\delta = -3.7$ to -7.3) and a decrease of the P,C coupling constants by 40−50% is observed, indicating a transfer of π-charge

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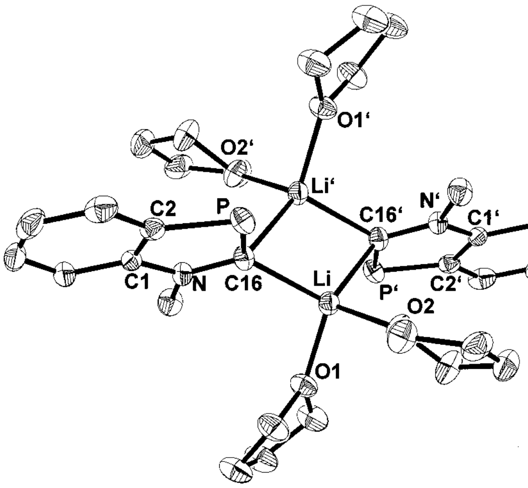


Figure 1. Molecular structure of **2a**·2THF in the crystal (thermal ellipsoids at 30% probability).

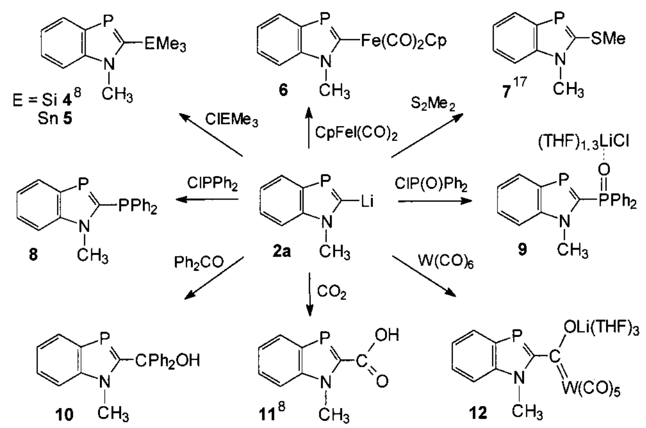
Table 1. Selected Distances (Å) and Angles (deg) for 2a·2THF

	Bond Distances		
P−C2	1.789(3)	C16−Li	2.209(5)
P−C16	1.731(9)	C16−Li′	2.273(4)
N−C1	1.388(3)	P···Li	3.443
N−C16	1.383(3)	P···Li′	3.196
	Bond Angles		
C16−P−C2	92.26(11)	P−C16−Li	121.3(2)
C16−N−C1	116.7(2)	P−C16−Li′	105.1(2)
P−C16−N	109.5(2)	Li−C16−Li′	70.2(2)
P−C2−C1	109.5(2)	C16−Li−C16′	109.8 (2)
N−C1−C2	112.0(2)	O1−Li−O2	98.0(2)

density into the benzene ring. The position of lithium cannot be derived from the NMR data since the polarization effects can be caused by a strongly polar lithium compound as well as a σ-electron lone pair at C-2 of a solvated anion in solution. A splitting of the ^{6}Li signal was not observed on cooling to −60 °C.

The X-ray single-crystal structure investigation of **2a**·2THF (Figure 1, Table 1) shows that in the solid state the lithium is bonded to C-16, forming dimers with a planar Li_2C_2 four-membered ring (Li−C16−Li′ 70.2(2)°, C16−Li−C16′ 109.8 (2)°). The Li−C bond distances of 2.209(5) and 2.273(4) Å correspond better to those in **I** (2.209, 2.269 Å[4]) than to those in **III** (2.31 Å[6a]) and **IV** (2.176 Å[6b]). The P−Li distances (P···Li′, 3.196; P···Li, 3.443 Å) are nonbonding and remarkably longer than P−Li bond lengths in comparably solvated lithium arylphosphides (2.60−2.65 Å)[19] or intramolecular phosphine-coordinated aryllithium compounds (2.60−2.77 Å).[20] Thus **2a**·2THF differs clearly from the *N*-lithiated 1,3-heteroazoles **III** and **IV** and is similar to **I**.[4] However, weak interactions of lithium with the low-coordinated phosphorus may be possible, as indicated by the significantly shorter P···Li distances (3.196 Å) compared to the van der Waals distance (3.65 Å[21]). Additionally the angle between the plane of the C_2Li_2 ring and the plane of the benzazaphosphole ring (average deviation from the best plane 0.0028 Å) is 83°. Finally it should be mentioned that the lithiation causes a decrease of the angle P−C16−N in **2a**·2THF compared to that in the unsubstituted 1*H*-1,3-benzazaphosphole (115.7(7)°)[22] by 6.2°, which is similar to the lithiation-induced increase of the N−C−N angle in **III**(Li/H)[6a] by 6.6−6.9° and of the N−C−S angle in **IV**(Li/H)[6b] by 7.0/7.2° and underlines the electronic relationship of the five-membered benzazoles **I**, **2a**, **III**, and **IV**.

Scheme 2



Reactivity of 2. Due to electron lone pairs at carbon and phosphorus, the anions of 2-lithio-1,3-benzazaphospholes **2** may be regarded as ambident nucleophiles. While 1-lithio-1,3-benzazaphospholes[23,24] with electron lone pairs at nitrogen and phosphorus behave ambident and can be attacked by suitable electrophiles either at nitrogen or at phosphorus, **2a** was found to react with electrophiles with strong preference or even exclusively at the anionic carbon atom (Scheme 2). The reactivity toward methyl iodide, which often prefers reaction at phosphorus, is low and did not result in a defined product, but with more polar organoelement or organometallic halides **2a** undergoes rapid substitution. Me_3SiCl[8] as well as the softer organo main group or transition metal halides Me_3SnCl and $CpFe(CO)_2I$ give regiospecifically the corresponding 2-substituted 1,3-benzazaphosphole derivatives **4**−**6**. The structure is evident from NMR spectra, particularly from the $^2J(^{31}P,^{117/119}Sn)$ and $^1J(^{13}C,^{117/119}Sn)$ coupling constants in the trimethyltin compound **5** and from the ^{13}C chemical shifts and P,C coupling constants typical for the 1*H*-1,3-benzazaphosphole skeleton and with the characteristic metalation effects on $\delta^{13}C$ and $J(P,C)$ for C-2 and C-3a. The deshielding as well as the P,C coupling constants increase with increasing ionic character of the bond to the substituent at C2 in the order **1a** < **4** < **5** < **6** < **2a**, strongly for C-2 (δ = 162.5, 179.4, 179.6, 190.1, 249.5; $^1J_{PC}$ = 53.4, 74.2, 83.9, 94.4, 109.4 Hz, respectively). The same trend, but less pronounced, is observed for C-3a as well.

The enormous potential of organolithium reagents in syntheses and the resistance of the P=C bond in most 1,3-benzazaphospholes toward addition reactions[24,25] allow the introduction of a large variety of functional groups in the 2-position. This is illustrated by some examples in Scheme 2. The cleavage of MeSSMe by **2a**

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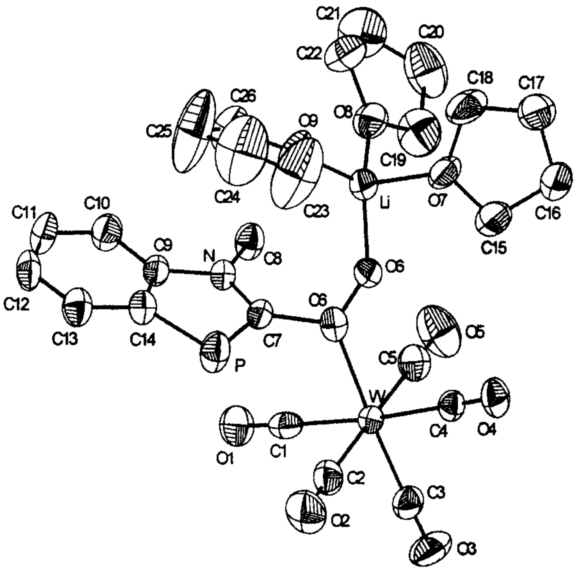

Figure 2. Molecular structure of **12**·3THF in the crystal (thermal ellipsoids at 50% probability).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 12·3THF

Bond Distances			
P−C14	1.786(11)	W−C1	2.047(14)
P−C7	1.728(18)	W−C2	2.036(19)
N−C9	1.389(14)	W−C3	2.019(13)
N−C7	1.354(10)	W−C4	2.033(12)
C6−C7	1.523(14)	W−C5	2.041(19)
C6−W	2.206(12)	Li−O6	1.880(15)
C6−O6	1.261(9)	Li−O(THF)	1.921(17)−1.938(24)
Bond Angles			
C7−P−C14	88.22(25)	P−C7−C6	124.60(36)
C7−N−C9	113.17(45)	N−C7−C6	120.57(47)
P−C7−N	114.84(36)	C7−C6−O6	112.84(43)
P−C14−C9	111.66(40)	C7−C6−W	120.38(41)
N−C9−C14	112.01(42)	O6−C6−W	126.68(43)

affords the methylthio derivative **7**.[17] A phosphino or a phosphoryl group is introduced by reaction of **2a** with $ClPPh_2$ or $ClP(O)Ph_2$ to give **8** and **9**, respectively. The addition of **2a** to carbonyl compounds such as benzophenone, CO_2, or tungsten hexacarbonyl yields the diphenylcarbinol derivative **10**, the carboxylic acid **11**,[8] and the benzazaphospholyl(lithiumoxy)carbene pentacarbonyl tungsten complex **12**·3THF, respectively. The lithium salts resulting in the addition reactions are usually worked up by addition of Me_3SiCl and methanolysis or hydrolysis after removal of LiCl and the excess of chlorosilane. Treatment of the crude addition product of **2a** and $W(CO)_6$ with Me_3SiCl furnishes a red solution, from which, however, only **12**·3THF and an ill-defined red oil can be isolated. **12**·3THF is characterized by an X-ray single-crystal structure determination (Figure 2, Table 2). It crystallizes in the space group $P\bar{1}$ with two molecules in the unit cell. The benzazaphosphole ring is planar, and the P,C und N,C distances within the azaphosphole ring (P−C7 1.728(18) Å, P−C14 1.786(11) Å, N−C7 1.354(10) Å, N−C9 1.389(10) Å) are similar to those in **2a**·2THF and in the unsubstituted 1*H*-1,3-benzazaphosphole,[22] indicating a delocalized aromatic π-system. The tungsten carbon distance W−C6 to the carbene C atom of 2.206(12) Å falls into the same range as those observed for neutral tungsten carbonyl carbene complexes of the Fischer type;[26] the tungsten carbon distances to the carbonyl C atoms (W−C3 2.019(13), $W-C_{cis}$ 2.033−2.047 Å) are considerably shorter. The coordination around the lithium and the tungsten atom is tetrahedral and octahedral, respectively. The coordination around the carbene carbon atom C6 is trigonal planar; this plane (including in addition to C6 also O6, C7, and W) is nearly perpendicular to the plane of the benzazaphosphole ring (dihedral angles P−C7−C6−O6 109.5(5)°, P−C7−C6−W 73.9(5)°, N−C7−C6−O6 71.0(7)°, N−C7−C6−W 106.6(5)°). This indicates that there is almost no conjugative interaction between the π-system of the benzazaphosphole ring and that of the carbene unit, which is supported also by the distance between C6 and C7 of 1.523(14) Å, corresponding to a C,C single bond. The question, if replacement of lithium by low-valent transition metals may allow coordination at phosphorus and formation of chelate complexes, remains to be studied.

Also **7**−**11** and related compounds may be regarded as potentially hybrid or chelate ligands with a low-coordinated phosphorus and a classical donor group. Although some chelate complexes of pyridylphosphaalkenes,[27] functional substituted phosphaferrocenes,[9,28] or four-membered chelate rings of 1-aza-3-phosphaallyl anions[29] are known, such species have received very limited attention compared to those with functionally substituted phosphines. The properties of such ligands will differ considerably from those of analogously functionalized phosphines. Although detailed complex chemical studies have not yet been carried out, this became evident by the different catalytic behavior of nickel complexes prepared in situ from $Ni(COD)_2$ and phosphinoacetic acid, phosphinobenzoic acid,[30] or 2-phosphinophenols[31] on the one side and **10** or **11** on the other side. While the former catalyze the oligomerization or polymerization of ethene, the latter are completely inactive under analogous conditions. This may be due to the lower basicity and dominance of acceptor properties of ligands with two-coordinated phosphorus as well as a lower stability of P,O-chelate complexes with such substructures. The particular ligand properties of 1,3-benzazaphospholes in the $W(CO)_5$ complex **13**, obtained from **1a** and $W(CO)_5(THF)$, are characterized by a strong upfield complexation shift ($\Delta\delta = -45.7$) in comparison with downfield complexation shifts of

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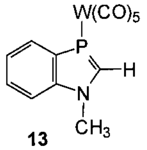
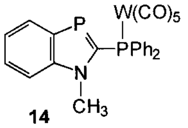
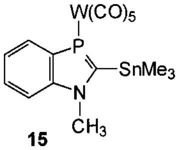
$R_3PW(CO)_5$ complexes (R = alkyl, phenyl) while the $^1J(^{183}W,^{31}P)$ coupling constants remain similar.[32] The stability of complexes with two-coordinated phosphorus is lower compared to that of common phosphino complexes also in the case of metal(0) compounds, as demonstrated by the formation of **14** from **8** and $W(CO)_5$-(THF). An analogous behavior was reported for 2-diphenylphosphino-5-methylphosphabenzene.[10a] The preferred coordination at the diphenylphosphino group is detected by its downfield ^{31}P coordination shift ($\Delta\delta = 26.8$) and particularly by the ^{183}W satellite signals in the ^{31}P NMR spectrum with $^1J(^{183}W,^{31}P) = 246$ Hz. The two-coordinated phosphorus becomes similarly deshielded in this case, and the magnitude of the $^2J(^{31}P,^{31}P)$ coupling constant is significantly enlarged by the changed hybridization of the coordinated phosphorus atom.



13



14



15

Attempts to generate a defined lithium compound from **13** and *t*BuLi at −70 °C failed. Neither subsequent addition of Me_3SiCl nor metalation in the presence of Me_3SiCl to trap instable intermediately formed lithium reagents as applicable in the case of 2-lithio-phosphabenzene-$W(CO)_5$ complexes[10] gave the expected trimethylsilyl compound. This indicates a destabilization of 1,3-benzazaphospholes with (organo)metallic substituents in the 2-position by complexation at phosphorus. The same effect, but to a much smaller degree, is observed for the 2-trimethylstannyl-1,3-benzazaphosphole tungsten pentacarbonyl complex **15** formed from **5** and $W(CO)_5$(THF). Repeated crystallization of crude **15** from hot hexane led to partial decomposition and increasing contamination by the Sn−C cleavage product **13**. **15** was thus not isolated as a pure compound, but it was unambiguously identified in a mixture with **13** (ratio ca. 75:25%) by its characteristic ^{13}C, ^{31}P, and ^{119}Sn NMR data. Like in **13**, the complexation induces a considerable upfield coordination shift ($\Delta\delta = -46.8$). The $^1J(^{31}P,^{13}C)$ coupling constant, however, decreases much more ($\Delta J = -54.5$ Hz) than that in **13** ($\Delta J = -26.5$ Hz). On the other hand the magnitude of the $^2J(^{119}Sn,^{31}P)$ coupling constant significantly decreases by complexation of **5**.

Conclusions

1-Alkyl-1,3-benzazaphospholes **1** can be lithiated in the 2-position by *t*BuLi at low temperature. The resulting lithium compounds **2** can be isolated at room temperature and are or belong to the most stable P═CLi derivatives. This may be attributed to the π-donor effect of nitrogen, which increases the electron density at phosphorus and lowers the polarity of the P═C bond, thus preventing addition of RLi to this bond. Hence the reactivity of **2** is reduced by the effective repulsion of π-density which exceeds that in PhLi, as seen by the much stronger deshielding of C-2. Phosphorus is deshielded by this effect as well. The reduced negative charge and the lower electronegativity of P explain the weak or negligible interactions between lithium and phosphorus, the lack of nucleophilic reactivity at phosphorus, and the similarity to the carbon analogues 2-lithioindoles. The stability of **2** and the failure to detect a 2-lithiated benzazaphosphole $W(CO)_5$ complex are in contrast to the behavior of phosphabenzenes, where P═C−Li reagents could be generated and trapped only in the case of the transition metal complexes. This difference may be explained in terms of a different electronic situation. The increase of electron density at the electron-deficient P atom in phosphabenzenes by complexation, reflected in part by the complexation shift ($\Delta\delta \approx -23.9^{10a}$), will decrease the P═C polarity and raise the resistance toward addition reactions of RLi, whereas the further increase of electron density by complexation of the relatively π-electron rich P atom in **2** (in **1** $\Delta\delta \approx -46$) creates probably a more polar P═C bond with inverse polarity, which induces insufficient kinetic stability. The lithium reagents **2** allow the synthesis of a broad variety of functionally substituted benzazaphospholes. Such benzazaphospholes with additional donor centers are potential candidates for new hybrid or chelate ligands with one low-coordinate phosphorus site besides a classical donor site.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of purified argon using standard Schlenk techniques. THF, ether, hexane, and toluene were dried and deoxygenated by refluxing and distilling from sodium/benzophenone. 1-Methyl- and 1-ethyl-1,3-benzazaphosphole, **1a** and **1b**, were prepared as reported recently.[8,33] Other reagents were purchased and used as received. NMR spectra were recorded on a multinuclear ARX300 (Bruker) FT NMR spectrometer at 300.1 (^1H), 75.5 (^{13}C), 121.5 (^{31}P), 111.9 (^{119}Sn), and 44.2 MHz (^6Li) and referenced to Me_4Si, H_3PO_4 (85%), Me_4Sn, and 1 M LiCl in D_2O, respectively, as external standards unless stated otherwise. The numbering used for the assignment of the ^1H and ^{13}C NMR data of the benzazaphosphole ring is identical with that according to the nomenclature. Coupling constants are quoted for J_{HH} or J_{PC} unless indicated otherwise. Mass spectra were measured on a single focusing AMD40 (Intectra) sector-field mass spectrometer. Elemental analyses were carried out with handling of the samples in air under standard conditions (carbon combustion sometimes incomplete) using an LECO Model CHNS-932 elemental analyzer. Melting points were determined in a sealed capillary and are uncorrected. Procedures for the synthesis of **4** and **11**[8] are given below; for **7** see ref 17.

1-Methyl-1,3-benzazaphosphol-2-yl-lithium(thf)$_2$, 2a·2THF. A solution of **1a** (374 mg, 2.5 mmol) in THF (10 mL) was cooled to −70 °C, and *t*BuLi (1.5 mL, 1.65 M in pentane, 2.5 mmol) was added. After warming to room temperature (4 h) the orange solution was layered with hexane (5 mL). Single crystals were obtained at −30 °C. ^1H NMR (THF-d_8, 25 °C): δ 4.03 (s, 3H, NMe), 6.71 (t, $^3J \approx 6.9$, 7.4 Hz, 1H, H-5), 6.84 (dd, $^3J \approx 6.9$, 8 Hz, 1H, H-6), 7.31 (d, $^3J = 8.1$ Hz, 1H, H-7), 7.70 (d, $^3J = 7.5$ Hz, 1H, H-4). ^{13}C NMR (THF-d_8, 25 °C): δ 42.4 (d, $^3J = 8.5$ Hz, NMe), 110.9 (C-7), 116.5 (d, $^3J = 6.2$ Hz, C-5), 119.0 (C-6), 126.4 (d, $^2J = 11.6$ Hz, C-4), 148.6 (d, $^2J = 8.4$ Hz, C-7a), 150.4 (d, $^1J = 62.2$ Hz, C-3a), 249.5 (d, $^1J = 109.4$ Hz, C-2). ^{31}P NMR (THF-d_8): 25 °C δ 105.2; −60 °C δ 102.4. Crystal structure, see Figure 1, Table 1.

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1-Ethyl-1,3-benzazaphosphol-2-yl-lithium, 2b. 1-Ethyl-1,3-benzazaphosphole (127 mg, 0.8 mmol) dissolved in ether was reacted with *t*BuLi (0.5 mL, 1.7 M in pentane, 0.85 mmol) as above. Evaporation of ether in vacuo gave an orange powder, which dissolved in THF-d_8 with a dark orange-brown color. ^{1}H NMR (THF-d_8): δ 1.08 (t, $^3J = 7.0$ Hz, 3H, CH$_3$), 3.34 (q, $^3J = 7.0$ Hz, 2H, NCH$_2$), 6.69 (t, $^3J = 6.8$, 7.5 Hz, 1H, H-5), 6.83 (t, $^3J = 6.8$, 8.1 Hz, 1H, H-6), 7.35 (d, $^3J = 8.1$ Hz, 1H, H-7), 7.70 (d, $^3J = 7.5$ Hz, 1H, H-4). ^{13}C NMR (THF-d_8): δ 15.9 (CH$_3$), 49.9 (d, $^3J = 8.4$ Hz, NCH$_2$), 111.1 (C-7), 116.3 (d, $^3J = 6.2$ Hz, C-5), 118.8 (C-6), 126.6 (d, $^4J = 11.8$ Hz, C-4), 147.2 (d, $^2J = 8.6$ Hz, C-7a), 150.8 (d, $^1J = 61.6$ Hz, C-3a), 248.7 (d, $^1J = 108.7$ Hz, C-2). ^{31}P NMR (THF-d_8): δ 104.7.

2-Deutero-1-methyl-1,3-benzazaphosphole, 3. A solution of **1a** (520 mg, 3.5 mmol) in ether (10 mL) was treated with *t*BuLi (2.4 mL, l.65 M, 4.0 mmol) as described above and after cooling to −70 °C quenched with CD$_3$OD (0.18 mL, 4 mmol). The solvent was removed in vacuo and the residue extracted with hexane. Yield of **3** determined by NMR was ca. 85%. ^{1}H NMR (C$_6$D$_6$): δ 2.87 (d, $^4J = 0.9$ Hz, 3H, NMe), 6.96 (dm, $^3J = 8.3$ Hz, 1H, H-7), 7.03 (tm, $^3J = 6.8$, $^4J = 0.9$ Hz, 1H, H-5), 7.15 (ddt, $^3J = 7.0$, 8.3, $^4J \approx {}^5J_{\mathrm{PH}} = 1.2$ Hz, 1H, H-6), 8.05 (ddm, $^3J = 7.9$, $^3J_{\mathrm{PH}} = 3.9$ Hz, H-4). ^{13}C NMR (C$_6$D$_6$): δ 34.9 (NMe), 112.2 (C-7), 118.8 (d, $^3J = 11.7$ Hz, C-5), 123.2 (d, $^4J = 2.26$ Hz, C-6), 128.3 (d, $^2J = 21.1$ Hz, C-4), 141.5 (d, $^1J = 41.1$ Hz, C-3a), 141.7 (d, $^2J = 6.0$ Hz, C-7a), 160.6 (dt, $^1J = 53.1$ Hz, $J_{\mathrm{CD}} = 26.6$ Hz, C-2). ^{31}P NMR (C$_6$D$_6$): δ 72.8 (t, $^2J_{\mathrm{PD}} = 5.5$ Hz). Unreacted **1a** ca. 15%, ^{1}H NMR: δ 7.82 (d, $^1J = 38.2$ Hz, H-2).

1-Methyl-2-trimethylsilyl-1,3-benzazaphosphole, 4. Chlorotrimethylsilane (6.3 mL, 49.8 mmol) was added at −70 °C to a solution of **2a**, prepared as above from **1a** (4.9 g, 33 mmol) in ether (10 mL) and *t*BuLi (27.5 mL, 1.2 M, 33 mmol). The mixture was stirred overnight at ambient temperature and filtered. The solvent was removed in vacuo and the residue distilled to give liquid **4** (5.8 g, 80%), bp 98−100 °C/0.01 Torr. ^{1}H NMR (100 MHz, CDCl$_3$, ref H$_2$SO$_4$ ext): δ 0.36 (s, 9H, SiMe$_3$), 3.88 (br, 3H, NMe), 6.90−7.44 (m, 3H, H-5, H-6, H-7), 7.92 (ddm, $^3J \approx 7.5$, $^3J_{\mathrm{PH}} \approx 3$ Hz, 1H, H-4). ^{13}C NMR (50.3 MHz, C$_6$D$_6$): δ 0.89 (d, $^3J = 8.8$ Hz, SiMe$_3$), 36.9 (NMe), 113.0 (C-7), 120.0 (d, $^3J = 11.6$ Hz, C-5), 125.3 (C-6), 129.1 (d, $^2J = 19.0$ Hz, C-4), 143.9 (d, $^1J = 44.8$ Hz, C-3a), 147.8 (d, $^2J = 5.9$ Hz, C-7a), 179.4 (d, $^1J = 74.2$ Hz, C-2). ^{31}P NMR (81 MHz, C$_6$D$_6$): δ 120.5. Anal. Calcd for C$_{11}$H$_{16}$NPSi (221.31): P, 13.96. Found: P, 14.25.

1-Methyl-2-trimethylstannyl-1,3-benzazaphosphole, 5. Trimethyltin chloride (658 mg, 3.3 mmol) dissolved in ether (10 mL) was added at −70 °C to a solution of **2a**, prepared as above from **1a** (432 mg, 2,9 mmol) and *t*BuLi (2.0 mL, 1.65 M, 3.3 mmol) in ether. After 15 h at 20 °C the solution was filtered, and the solvent was removed in vacuo. Distillation of the residue afforded **5** (552 mg, 61%) as a light yellow oil, bp 100 °C/0.03 Torr. ^{1}H NMR (C$_6$D$_6$): δ 0.32 (s sat, $^2J_{\mathrm{HSn}} = 54.2$, 56.6 Hz, 9H, SnMe$_3$), 3.23 (d, $^4J = 0.9$ Hz, 3H, NMe), 7.09−7.15 (m, 2H, H-5, H-7), 7.23 (tt, $^3J = 8.0$, 6.8, $^4J \approx {}^5J_{\mathrm{PH}} = 1.1$ Hz, 1H, H-6), 8.15 (ddq, $^3J = 7.9$, $^3J_{\mathrm{PH}} = 3.6$, $^4J = 1.1$, $^5J = 0.7$ Hz, 1H, H-4). ^{13}C NMR (C$_6$D$_6$): δ −9.1 (d sat, $^3J = 6.2$, $^1J_{\mathrm{SnC}} = 338$, 350 Hz, SnMe$_3$), 36.8 (sat, $^3J_{\mathrm{SnC}} \approx 21$ Hz, NMe), 111.3 (C-7), 118.4 (d, $^3J = 10.8$ Hz, C-5), 123.0 (d, $^4J = 2.6$ Hz, C-6), 127.6 (d, $^2J = 18.6$ Hz, C-4), 143.7 (d, $^1J = 47.9$ Hz, C-3a), 145.8 (d, $^2J = 2.3$ Hz, C-7a), 179.6 (d, $^1J = 83.9$ Hz, C-2). ^{31}P NMR (C$_6$D$_6$): δ 114.0 (sat, $^2J_{\mathrm{PSn}} = 210.2$, 218.7 Hz). ^{119}Sn NMR (C$_6$D$_6$): δ −41.1 (d, $^2J_{\mathrm{PSn}} = 218.6$ Hz). MS (EI, 70 eV): *m*/*z* (%) 313 (64) [M$^+$ for ^{120}Sn], 298 (100), 296 (77), 268 (52), 149 (26), 139 (12), 107 (49), 57 (12). Anal. Calcd for C$_{11}$H$_{16}$NPSn (311.94): C, 42.35; H, 5.17; N, 4.49. Found: 43.43; H, 5.33; N, 4.48.

(1-Methyl-1,3-benzazaphosphol-2-yl)(η^5-cyclopentadienyl)dicarbonyliron, 6. 1a (426 mg, 2.8 mmol) was lithiated with *t*BuLi (2.0 mL, 1.65 M, 3.3 mmol) as above and reacted with CpFe(CO)$_2$I (1.002 g, 3.3 mmol) dissolved in ether (10 mL) at −70 °C. After 15 h the solids were filtered off, and the solvent was removed in vacuo. The red-brown residue was extracted with benzene. The resulting oil, after adding hexane, was chromatographed with toluene using silylated silica 60 (Merck). Removal of the solvent gave 350 mg (27% based on **6**·1/2LiI(THF)$_2$) of an oil which precipitates as solid from THF on adding hexane at −20 °C but melts at room temperature. NMR spectra and elemental analyses fit with a composition **6**·1/2LiI(THF)$_2$. ^{1}H NMR (C$_6$D$_6$, toluene,hexane): 3.50 (s, 3H, NMe), 4.05 (s, 5H, Cp), 6.99−7.16 (m, toluene, H-5 superimposed), 7.20 (t br, partially superimposed, H-6), 7.28 (d br, $^3J \approx 8$ Hz, 1H, H-7), 8.06 (d m, 1H, H-4); (THF-d_8): δ 4.05 (s, 3H, NMe), 5.13 (s, 5H, Cp), 6.89 (t, br, 1H, H-5), 7.01 (t br, 1H, H-6), 7.44 (d br, $^3J \approx 8$ Hz, 1H, H-7), 7.61 (d br, 1H, H-4). ^{13}C NMR (THF-d_8): δ 40.6 (NMe), 88.0 (Cp), 112.1 (C-7), 118.9 (d, $^3J = 8.5$ Hz, C-5), 121.4 (C-6), 124.9 (d, $^2J = 17.3$ Hz, C-4), 148.4 (d, $^1J = 50.6$ Hz, C-3a), 149.2 (C-7a), 190.1 (d, $^1J = 94.4$ Hz, C-2), 215.7 (d, $^3J = 6.9$ Hz, CO). ^{31}P NMR: δ 110.8 (THF-d_8), 115.1 (C$_6$D$_6$). Anal. Calcd for C$_{15}$H$_{12}$FeNO$_2$P·1/2LiI(THF)$_2$ (456.12): C, 50.03; H, 4.42; N, 3.07. Found: C, 48.99; H, 4.88; N, 3.10.

1-Methyl-2-diphenylphosphino-1,3-benzazaphosphole, 8. Chlorodiphenylphosphine (0.73 mL, 4.0 mmol) was added at −70 °C to a solution of **2a** obtained from **1a** (522 mg, 3.5 mmol) and *t*BuLi (2.4 mL, 1.7 M, 4.0 mmol) in ether (10 mL). After stirring overnight the solvent was removed in vacuo, and the viscous residue was distilled in high vacuum at ca. 200−220 °C/4 × 10^{-6} Torr to yield 670 mg (57%) of **8** as a light orange, very viscous oil. ^{1}H NMR (C$_6$D$_6$): δ 3.32 (t, $J+J' = 1.7$ Hz, 3H, NMe), 6.90−7.20 (m, 7H and solvent), 7.48−7.60 (m, 5H, Ph), 7.85−8.00 (m, 2H, H-4, *o*-H). ^{13}C NMR (C$_6$D$_6$): δ 35.1 (dd, $^3J = 19.4$, $^3J = 3.8$ Hz, NMe), 113.3 (C-7), 121.1 (d, $^3J = 11.4$ Hz, C-5), 125.8 (d, $^4J = 2.4$ Hz, C-6), 129.6 (d, $^3J = 7.7$ Hz, C-*m*), 129.7 (d, $^2J = 20$ Hz, C-4), 130.4 (C-*p*), 135.2 (d, $^2J = 20.2$ Hz, C-*o*), 136.7 (t, $J+J' = 15.3$ Hz, C-*i*), 144.3 (d, $^1J = 44.4$ Hz, C-3a), 148.0 (dd, $^2J = 5.0$, $^3J = 2.4$ Hz, C-7a), 177.7 (dd, $^1J = 73.6$, $^1J = 17.6$ Hz, C-2). ^{31}P NMR (C$_6$D$_6$): δ 112.5 (d, $^2J_{\mathrm{PP}} = 15.4$ Hz), −19.5 (d, $^2J_{\mathrm{PP}} = 15.4$ Hz). MS (EI, 70 eV): *m*/*z* (%) 333 (100) [M$^+$], 254 (7), 242 (31), 225 (51), 201 (57), 183 (27), 152 (6), 107 (24), 77 (36), 51 (22). Anal. Calcd for C$_{20}$H$_{17}$NP$_2$ (333.31): C, 72.07; H, 5.14; N, 4.20. Found: C, 71.53; H, 5.07; N, 4.12.

1-Methyl-2-diphenylphosphono-1,3-benzazaphosphole with LiCl·1.3THF, 9. To a stirred solution of **2a**, prepared by lithiation of **1a** (475 mg, 3.18 mmol) with *t*BuLi (2.45 mL, 1.3 M, 3.18 mmol) in ether (15 mL) was added ClP(O)Ph$_2$ (0.547 mL, 2.87 mmol) at −78 °C. After reaching room temperature, the color changed from yellow to brown. The cloudy solution was stirred for 1 day, then the solvent was evaporated. The slightly brown residue was washed with ether to remove unreacted **1a** and ClP(O)Ph$_2$, providing a pale yellow residue, which almost completely dissolves in THF. NMR analysis of the crude product showed a mixture of **1a**, **9**, and Ph$_2$PHO in a ratio 1:2.5:2, crude yield nearly 45%. Repeated crystallization from THF/*n*-hexane gave a fraction of pure **9**, mp 93−95 °C. ^{1}H NMR (CDCl$_3$/CD$_3$OD): δ 3.81 (d, $^4J_{\mathrm{PH}} = 1.3$ Hz, 3H, NMe), 7.03 (dd br, $^3J = 7.9$, 7.3 Hz, 1H, H-5), 7.27−7.35 (m, 5H, H-*m*, H-6), 7.38−7.46 (m, 3H, H-*p*, H-7), 7.54 (dd br, $^3J_{\mathrm{PH}} = 12.6$, $^3J \approx 7$ Hz, 4H, H-*o*), 7.82 (dd br, $^3J = 7.9$, $^4J_{\mathrm{PH}} = 3.9$ Hz, 1H, H-4); 1.79, 3.68 (m, C$_4$H$_8$O). ^{13}C NMR (CDCl$_3$/CD$_3$OD): δ 35.6 (NMe), 112.8 (C-7), 120.5 (d, $^3J = 12.8$ Hz, C-5), 127.1 (d, $^4J = 2.8$ Hz, C-6), 128.2 (d, $^3J = 12.8$ Hz, C-*m*), 128.8 (d, $^2J = 21.3$ Hz, C-4), 130.7 (dd, $^1J = 110.9$, $^3J = 3.8$ Hz, C-*i*), 131.9 (dd, $^2J = 10.4$, $^4J = 1.8$ Hz, C-*o*), 132.5 (d, $^4J = 0.4$ Hz, C-*p*), 141.6 (dd, $^1J = 42.8$, $^3J = 12.6$ Hz, C-3a), 147.2 (dd, $^2J = 7.2$ and $^3J = 9.3$ [uncertain] Hz, C-7a), 163.0 (dd, $^1J_{\mathrm{P(V)}} = 99.6$, $^1J_{\mathrm{P(III)}} = 66.7$ Hz, C-2); 25.0, 67.5 (C$_4$H$_8$O). ^{31}P NMR (CDCl$_3$/CD$_3$OD): δ 25.6 (d, $^2J_{\mathrm{PP}} = 73.3$ Hz, P$^{\mathrm{V}}$), 134.4 (d, $^2J_{\mathrm{PP}} = 73.3$ Hz, P$^{\mathrm{III}}$). MS (EI, 70 eV): *m*/*z* (%) 349 (100) [M$^+$], 334 (2) [M$^+$ − Me], 272 (3) [M$^+$ − Ph], 258 (11), 224 (27), 148 (31) [M$^+$ − OPPh$_2$]. IR (Nujol, selected data): 1638 (vs), 1593 (s); 1190 (vs) cm^{-1}. Anal. Calcd for $C_{20}H_{17}NOP_2 \cdot LiCl \cdot 1.3C_4H_8O$ (485.44): C, 62.35; H, 5.69; N, 2.88; Cl, 7.30. Found: C, 60.15; H, 6.02; N, 2.86; Cl, 7.11.

(1-Methyl-1,3-benzazaphosphol-2-yl)diphenylmethanol, 10. Benzophenone (244 mg, 1.34 mmol) was added at −78 °C with vigorous stirring to a solution of **2a** prepared as above from **1a** (200 mg, 1.34 mmol) and *t*BuLi (0.78 mL, 1.7 M, 1.34 mmol) in THF (20 mL), leading to a color change from orange to green. The solution was allowed to warm to room temperature, and after 3 h its color changed back to orange. Neutralization by solid NH_4Cl (71.7 mg, 1.34 mmol) furnished a pale yellow solution. After 1 day the solvent was removed in vacuo, and the residue was extracted with *n*-hexane followed by ether. Removal of the solvent from the ether fraction gave 166 mg (37%) of yellow **10**, mp 65 °C. On longer contact with air **10** becomes orange, mp 77−79 °C. ^1H NMR ($CDCl_3$): δ 3.43 (s br, 1H, OH), 3.66 (s, 3 H, Me), 7.14 (tdd, $^3J \approx 8$, 7, $^4J_{PH} = 1.7$, $^4J = 1.3$ Hz, 1H, H-5), 7.28−7.39 (m, 11 H), 7.42 (tm, $^3J \approx 8$ Hz, 1H, H-6), 7.91 (ddm, $^3J = 7.8$, $^3J_{PH} = 3.8$ Hz, 1H, H-4). ^{13}C NMR (C_6D_6): δ 35.5 (d, $^3J = 3.6$ Hz, Me), 80.5 (d, $^2J = 20.0$ Hz, C−O), 112.5 (C-7), 120.3 (d, $^3J = 11.5$ Hz, C-5), 125.2 (d, $^4J = 2.9$ Hz, C-6), 127.4 (d, $^4J = 3.2$ Hz, 4C, *o*-C), 127.7 (2 C, *p*-C), 127.9 (4C, *m*-C), 128.8 (d, $^2J = 21.4$ Hz, C-4), 139.7 (d, $^1J = 37.6$ Hz, C-3a), 145.3 (d, $^3J = 4.7$ Hz, 2C, *i*-C), 145.6 (d, $^2J = 6.3$ Hz, C-7a), 182.3 (d, $^1J = 51.6$ Hz, C-2). ^{31}P NMR ($CDCl_3$): δ 88.7. MS (EI, 70 eV, 120 °C): *m*/*z* (%) 331 (100) [M^+], 314 (10) [$M - OH^+$], 184 (69) [Ph_2COH^+], 149 (60) [$\mathbf{1}^+$], 108 (41), 106 (98), 78 (80). Anal. Calcd for $C_{21}H_{18}NOP$ (331.35): C, 76.12; H, 5.48; N, 4.23. Found: C, 74.01; H, 5.64; N, 4.01.

(1-Methyl-1,3-benzazaphosphol-2-yl)carboxylic Acid, 11. Gaseous CO_2 (from dry ice) was introduced to a stirred solution of **2a** prepared as above from **1a** (830 mg, 5.57 mmol) and *t*BuLi (3.24 mL, 1.7 M, 5.57 mmol) in THF (20 mL) over a period of 1 h at −60 °C, leading to a color change from orange to yellow. A slight excess of Me_3SiCl (1 mL) was added at the same temperature. The solution was allowed to warm to room temperature (3 h), and the solvent was removed in a vacuum, leading to a yellow crystalline mush. ^1H and ^{31}P NMR spectra (in C_6D_6) showed the nearly pure silylester,[8] contaminated with small impurities (5%) of **1a** and the hydrolysis product. Recrystallization of the silylester in ethanol lead via alcoholysis in nearly quantitative yield to **11**; 0.6 g (56%) of pale yellow crystals were obtained from a mixture of EtOH and *n*-hexane at −30 °C. **11** is soluble in MeOH and EtOH and sparingly soluble in C_6D_6. ^1H NMR (CD_3OD): δ 4.23 (s, 3 H, Me), 4.87 (s br, OH and OH of solvent), 7.21 (tdd, $^3J \approx 8$, 7, $^4J_{PH}$, $^4J = 1.5$, 0.8 Hz, 1H, H-5), 7.51 (tt, $^3J = 8.4$, 7.0, $^4J \approx {^5J_{PH}} = 1.1$ Hz, 1H, H-6), 7.75 (d br, $^3J \approx 8.7$ Hz, 1H, H-7), 8.05 (dd br, $^3J = 7.9$, $^3J_{PH} = 4.2$ Hz, 1H, H-4). ^{13}C NMR (CD_3OD): δ 34.9 (d, $^3J = 3.8$ Hz, Me), 114.8 (C-7), 121.9 (d, $^3J = 12.8$ Hz, C-5), 128.4 (d, $^4J = 3.8$ Hz, C-6), 130.5 (d, $^2J = 21.9$ Hz, C-4), 143.2 (d, $^1J = 37.7$ Hz, C-3a), 147.3 (d, $^2J = 7.5$ Hz, C-7a), 161.7 (d, $^1J = 52.8$ Hz, C-2), 166.6 ($^2J = 21.9$ Hz, COOH). ^{31}P NMR (CD_3OD): δ 120.2. Anal. Calcd for $C_9H_8NO_2P$ (193.14): C, 55.97; H, 4.17; N, 7.25. Found: C, 56.10; H, 4.33; N, 7.16.

[Lithiumoxy(1-methyl-1,3-benzazaphosphol-2-yl)carbene]pentacarbonyltungsten (3THF), 12·3THF. Tungstenhexacarbonyl (1.33 g, 3.80 mmol) was dissolved in THF (10 mL) and added at −78 °C with vigorous stirring to a solution of **2a** prepared as above from **1a** (566 mg, 3.80 mmol) and *t*BuLi (2.92 mL, 1.3 M, 3.80 mmol) in Et_2O (20 mL), leading to color change from yellow to reddish orange. The solution was allowed to warm to room temperature for 3 h. After cooling again to −78 °C, Me_3SiCl (excess) was added. The color changed immediately to dark red. The mixture was stirred for 12 h at room temperature, the precipitate removed by filtration, and the solution evaporated to dryness and redissolved in a mixture of THF (10 mL) and hexane (15 mL). Storage at −78 °C gave 1.50 g (55%) of orange **12·**3THF, mp 73−76 °C, soluble in C_6D_6, very soluble in THF or $CDCl_3$. Single crystals were obtained from THF/hexane. Removal of the solvent from the red filtrate left an ill-defined viscous oil. ^1H NMR (C_6D_6): δ 3.58 (s, 3H, NMe), 7.04 (tdd, $^3J = 7.8$, 6.9, $^4J_{PH} = 1.7$, $^4J = 1.2$ Hz, 1H, H-5), 7.16 (d br, $^3J = 8.3$ Hz, 1H, H-7), 7.24 (t br, $^3J = 8.3$, 6.9 Hz, 1H, H-6), 7.99 (dd br, $^3J = 7.8$, $^3J_{PH} = 3.8$ Hz, 1H, H-4); 1.83, 3.73 (CH_2, 12H each). ^{13}C NMR (C_6D_6): δ 34.8 (d, $^3J = 2.8$ Hz, Me), 113.7 (C-7), 121.3 (d, $^3J = 11.4$ Hz, C-5), 126.0 (d, $^4J = 2.5$ Hz, C-6), 130.4 (d, $^2J = 21.0$ Hz, C-4), 142.1 (d, $^1J = 42.3$ Hz, C-3a), 144.6 (d, $^2J = 5.5$ Hz, C-7a), 199.6 (d, $^1J = 55.6$ Hz, C-2), 202.8 (d sat, $^4J = 3.5$, $^1J_{WC} = 128.5$ Hz, 4CO), 208.5 (s, 1CO), 298.6 (br, O−C═W); 25.3, 68.2 (C_4H_8O). ^{31}P NMR (C_6D_6): δ 73.6. MS (EI, 70 eV, 200 °C): *m*/*z* (%) 352 (88) [$HOC{=}W(CO)_5^+$], 324 (12) [$HOC{=}W(CO)_4^+$], 296 (70) [$HOC{=}W(CO)_3^+$], 268 (100) [$HOC{=}W(CO)_2^+$], 240 (90) [$HOC{=}WCO^+$], 212 (90) [$HOC{=}W^+$], 149 (60) [$\mathbf{1}^+$], 107 (80), 74 (100). Anal. Calcd for $C_{14}H_7LiNO_6PW \cdot 3(C_4H_8O)$ (723.28): C, 43.18; H, 4.32; N, 1.94. Found: C, 43.55; H, 4.42; N, 2.02.

η^1(P)-(1-Methyl-1,3-benzazaphosphole)pentacarbonyltungsten, 13. To a solution of $W(CO)_5(THF)$, prepared by irradiation of $W(CO)_6$ (1.2 g, 3.42 mmol) in THF (30 mL) with a mercury lamp until 74 mL of CO was liberated, was added a solution of **1a** (0.51 g, 3.42 mmol) in THF (1 mL). After 3 days the solvent was removed, and the residue was crystallized from hexane to yield 1.05 g (65%) of yellow **13**, mp 161 °C. **13** is less soluble in hexane than **1a**. (**13** decomposes on prolonged exposure to sunlight and becomes green.) ^1H NMR (THF-d_8): δ 4.08 (d, $^4J_{PH} = 2.7$ Hz, 3H, NMe), 7.30 (dddd, $^3J = 8.1$, 7.0, $^4J_{PH} = 2.8$, $^4J = 0.8$ Hz, 1H, H-5), 7.50 (ddt, $^3J = 8.5$, $^3J = 7.0$ Hz, $^4J \approx {^5J_{PH}} = 1.3$−1.5 Hz, 1H, H-6), 7.80 (dd, $^3J = 8.6$, $^4J = 0.7$ Hz, 1H, H-7), 7.99 ("tt", $^3J = 8$−8.2 Hz, $^3J_{PH} \approx {^4J} = 1$ Hz, 1H, H-4), 8.71 (d, $^2J_{PH} = 34.0$ Hz, 1H, H-2). ^{13}C NMR (THF-d_8): δ 37.8 (NMe), 114.9 (d, $^3J = 4.0$ Hz, C-7), 122.0 (d, $^3J = 14.8$ Hz, C-5), 126.9 (d, $^4J = 3.7$ Hz, C-6), 127.7 (d, $^2J = 13.4$ Hz, C-4), 138.4 (d, $^1J = 21.6$ Hz, C-3a), 144.4 (s, C-7a), 158.6 (d, $^1J = 27.0$ Hz, C-2), 195.6 (d sat, $^2J = 8.8$, $^1J_{WC} = 124.5$ Hz, 4CO), 200.4 (d, $^2J = 29.0$ Hz, 1CO). ^{31}P NMR (THF-d_8): δ 28.5 (sat, $^1J_{PW} = 240.5$ Hz). MS (EI, 70 eV): *m*/*z* (%) 473 (100) [M^+ for ^{184}W], 417 (85) [$M^+ - 2CO$], 389 (75) [$M^+ - 3CO$], 361 (53) [$M^+ - 4CO$], 333 (69) [$M^+ - 5CO$], 304 (43), 265 (10), 167 (12), 149 (31), 107 (14). Anal. Calcd for $C_{13}H_8NO_5PW$ (473.03): C, 33.01; H, 1.70; N, 2.96. Found: C, 31.94; H, 1.57; N, 2.65.

(2-Diphenylphosphino[η^1]-1-methyl-1,3-benzazaphosphole)pentacarbonyltungsten, 14. **8** (400 mg, 1.2 mmol), dissolved in THF (10 mL), was added to a solution of $W(CO)_5$(THF) prepared by irradiation of $W(CO)_6$ (420 mg, 1.2 mmol) in THF (30 mL) as described above. After 2 days the solvent was removed, and the residue was extracted with hexane. Crystals deposited at −70 °C were filtered off. They melt on warming to room temperature, forming a viscous yellow material. This was extracted with a small portion of hexane to leave 276 mg (35%) of **14**, slightly contaminated by **8**. ^1H NMR (C_6D_6): δ 3.22 (d, $^4J = 0.6$ Hz, 3H, NMe), 6.90−7.11 (m, 10H), 7.53−7.57 (m, 3H), 7.86 (dd br, $^3J = 7.7$, $^3J_{PH} = 3.5$ Hz, 1H, H-4). ^{13}C NMR (C_6D_6): δ 37.9 (t, $J+J' = 8.3$ Hz, NMe), 114.0 (C-7), 122.0 (d, $^3J = 12.1$ Hz, C-5), 127.7 (d, $^4J = 1.9$ Hz, C-6), 129.8 (d, $^3J = 9.9$ Hz, C-*m*), 130.2 (d, superimposed, C-4), 131.5 (C-*p*), 133.3 (d, $^2J = 12.3$ Hz, C-*o*), 135.5 (dd, $^1J = 41.4$, $^3J = 5.8$ Hz, C-*i*), 142.7 (dd, $^1J = 42.5$, $^3J = 12.6$ Hz, C-3a), 149.1 (t, $J+J' = 10.7$ Hz, C-7a), 169.6 (dd, $^1J = 67.0$, $^1J = 27.6$ Hz, C-2), 198.5 (dd sat, $^2J = 6.9$, $^4J = 3.2$, $^1J_{WC} = 126.6$ Hz, 4CO), 200.1 (d, $^2J = 22.3$ Hz, CO). ^{31}P NMR (C_6D_6): δ 132.9 (d, $^2J_{PP} = 90.1$ Hz, P-3), 7.34 (d sat, $^2J_{PP} = 90.6$, $^1J_{PW} = 247.2$ Hz, *P*Ph_2). Anal. Calcd for $C_{25}H_{17}NO_5P_2W$ (657.21): C, 45.69; H, 2.61; N, 2.13. Found: C, 44.12; H, 2.83; N, 2.35.

η^1(P)-(2-Trimethylstannyl-1-methyl-1,3-benzazaphosphole)pentacarbonyltungsten, 15. A solution of **5** (230 mg, 0.73 mmol) in THF (1 mL) was added to $W(CO)_5$(THF) prepared by irradiation of $W(CO)_6$ (260 mg, 0.73 mmol) in THF (30 mL) as above. After 3 days the solvent was removed and the crude product extracted with C_6D_6. NMR spectra revealed formation of a 75:25 mol % mixture (470 mg) of **15** and **13**. By crystallization with hot hexane the content of **13** increased, indicating partial decomposition of **15**. ^{13}C NMR (C_6D_6): δ −5.5 (d sat, ^3J = 6.0, $^1J_{CSn}$ = 366.2 Hz, $SnMe_3$), 39.5 (d sat, ^3J = 3.9, $^3J_{CSn}$ = 20.4 Hz, NMe), 114.4 (d, ^3J = 5.5 Hz, C-7), 121.8 (d, ^3J = 13.5 Hz, C-5), 126.6 (d, ^4J = 3.9 Hz, C-6), 127.6 (d, ^2J = 10.7 Hz, C-4), 141.6 (d, ^1J = 12.6 Hz, C-3a), 147.3 (d, $^2J_{PC}$ = 6.2 Hz, C-7a), 176.6 (d, ^1J = 29.4 Hz, C-2), 196.7 (d sat, ^2J = 8.4, $^1J_{CW}$ = 125.0 Hz, 4CO), 200.7 (d, ^2J = 28.2 Hz, 1CO). ^{31}P NMR (C_6D_6): δ 67.2 (sat, $^2J_{PSn}$ = 148.4 Hz, $^1J_{PW}$ = 236.5 Hz). ^{119}Sn NMR (C_6D_6): δ −33.2 (d, $^2J_{PSn}$ = 149.2 Hz).

X-ray Crystal Structure Analysis of 2a·2THF. The X-ray data of **2a**·2THF were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation, $\lambda = 0.71069$ Å. Crystal data: 0.5 × 0.5 × 0.5, white prisms, space group *Pbca*, orthorhombic, $a = 14.620(3)$ Å, $b = 13.658(3)$ Å, $c = 16.966(3)$ Å, $T = 200$ K, $V = 3388(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.173$ g·cm^{-3}. A total of 9471 reflections were collected, 2715 were independent of symmetry, of which 1946 were observed ($I > 2\sigma I$), R1 = 0.049, wR2 (all data) = 0.149, 190 parameters. The structure was solved by direct methods (SHELXS-86, G. M. Sheldrick) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93, G. M. Sheldrick).[34,35] Structure representation: XP (Siemens). For selected data, see Table 1.

X-ray Crystal Structure Determination of 12·3THF. The X-ray data of **12**·3THF were collected on a STOE-IPDS diffractometer using Mo Kα radiation, $\lambda = 0.71073$ Å. Crystal data: 0.11 × 0.13 × 0.25 orange block, space group $P\bar{1}$, triclinic, $a = 10.5437(10)$ Å, $b = 10.9105(11)$ Å, $c = 15.5675(15)$ Å, $T = 200$ K, $V = 1489.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.6131(3)$ g·cm^{-3}. A total of 11 072 reflections were collected, 5369 were independent of symmetry, of which 4172 were observed ($I > 2\sigma I$), R1 = 0.0466, wR2 (all data) = 0.0554, 352 parameters. The structure was solved by direct methods (SHELXS-97). Structure representation: Diamond 2.1c (Crystal Impact GbR). For selected data, see Table 2.

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Supporting Information Available: Tables of crystal structure parameters and details of data collection, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **2a**·2THF and for **12**·3THF. NMR spectra are deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

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