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π-Excess σ²P ligands: synthesis of biaryl-type 1,3-benzazaphosphole hybrid ligands and formation of P^P′–M(CO)$_4$ chelate complexes†

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Acid-catalyzed cyclocondensations of 2-phosphanylanilines **1** with substituted benzaldehydes or heteroaryl aldehydes open a convenient route to new biaryl-type 1*H*-1,3-benzazaphosphole hybrid ligands **2a–f** with *o*-phosphanylphenyl, pyridyl, imidazolyl, thienyl or *o*-methoxyphenyl donor groups (in addition to the σ²P donor) and to bromophenyl substituted benzazaphospholes **2g,h**. Excess aldehyde leads to concomitant reductive *N*-alkylation, as shown by formation of **3h** besides **2h**. The reactions proceed *via* dihydrobenzazaphospholes **4**, which can be detected under mild conditions. The aromaticity-driven dehydrogenation does not liberate dihydrogen but is accomplished by transfer hydrogenations, mainly by reduction of some of the aldehyde. *N*-Secondary 2-phosphanylanilines **5** also react with aldehydes to form the corresponding *N*-substituted benzazaphospholes **6**. The formation of (P^P′)M(CO)$_4$-chelate complexes **8a** (M = Cr) and **9a,b** (M = Mo) was demonstrated by reaction with M(CO)$_4$(norbornadiene). The crystal structure of **9a**, determined in addition to the solution structure elucidation by multinuclear NMR spectra, confirms the chelate formation and reveals a trigonal environment for the low coordinated phosphorus, with the P–Mo(0) vector bent out of the benzazaphosphole ring plane by 14.4° (0.57 Å), together with axial chirality of the molecules in the racemic crystals by twisting of the benzazaphosphole and phenyl π-planes around the common C(2)–C(21) bond.

Introduction

In contrast to the large amount of research that has been performed on bidentate biarylphosphanes and their use in homogenous transition metal catalysis,[1,2] our knowledge of biaryl-type σ²P-ligands with additional P-, N- or O-donor sites, and complexes thereof, is limited, being restricted essentially to compounds involving phosphinine moieties, *e.g.* 2,2′-bisphosphinines, pyridylphosphinines, *o*-O-functional 2-phenylphosphinines and single P,N,P or O,P,O pincer ligands.[3,4] The interest in coordination compounds of phosphinines was stimulated by the discovery of highly active *o*-aryl-substituted phosphinine rhodium catalysts for the hydroformylation of styrene and internal or bulky substituted olefins.[5] Additional donor sites, allowing chelate formation, improve the stability of the phosphinine complexes with transition metal cations, which otherwise suffer from the low donor strength of the low-coordinated phosphorus and the loss of aromatic stabilization on coordination of cations. The first MeClPt(II) diphosphinine and pyridylphosphinine chelates were still sensitive to addition of moisture or ROH at the P=C bond[6,7] but combinations with suitable *o*-substituents and electron-rich RuCp* or IrCp* fragments led to stable M(II) complexes, and recently even made possible the isolation of the first Rh(III) and Ir(III) pyridylphosphinine chelate complexes that allowed controlled addition reactions.[8] In the course of our investigations of 1*H*-1,3-azaphospholes[9] we recently isolated the first complexes with d^{10} transition metal cations,[10] but our attempts to synthesize d^8 metal complexes have failed so far. Even the formation of a cationic benzazaphosphole Rh(I)(COD) complex was accompanied by instantaneous addition of traces of moisture,[10,11] whereas phosphinines form stable Rh(I)(COD) complexes.[5,12] Therefore, we searched for routes to 1,3-azaphosphole-based chelate ligands that might provide more stable chelate complexes. 1*H*-1,3-Benzazaphospholes with O-donor groups were obtained recently by catalytic phosphonylation of *o*-methoxybenzoyl or

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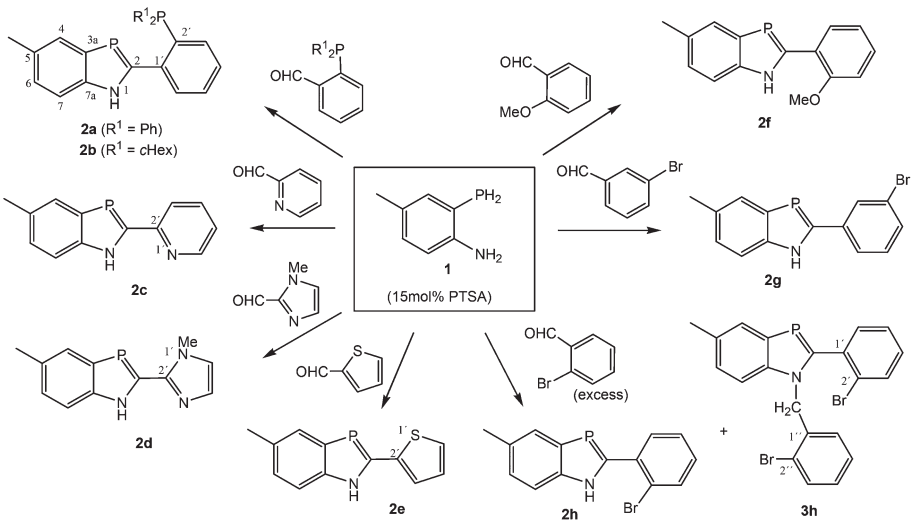
2-furoyl *o*-bromoanilides and reductive cyclization with excess lithium aluminium hydride,[9d] but N- or P-donor substituted benzazaphospholes were not available by this method. Here we present a route to the latter by acid-catalyzed condensation of 2-phosphanyl-4-methylaniline with carbo- or heterocyclic arylaldehydes. We also present the first examples of formation of $M(0)(CO)_4$ chelate complexes with these ligands, whereas reactions with non-zero-valent transition metal compounds are still under investigation and will be reported separately.

Results and discussion

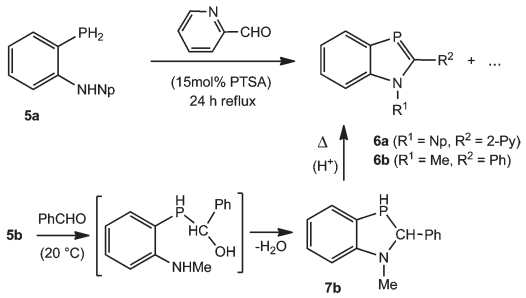
Syntheses

The first 1*H*-1,3-benzazaphospholes were synthesized by cyclocondensation of 2-phosphanylanilines with iminoester hydrochlorides or imidoylchlorides,[13,14] similarly to the related unsaturated As,N-heterocycles.[15] The more stable P-heterocycles were also obtained with acyl chlorides or orthoesters. To introduce additional donor groups into the heterocycles, however, carbonyl compounds must be used that are better compatible with the desired functional groups but still sufficiently reactive to undergo cyclocondensation. Aldehydes are known to tolerate tertiary N- and P-donor groups and to undergo cyclocondensations with 2-phosphanylaniline. Whereas aliphatic aldehydes gave distillable 2-alkyl-2,3-dihydro-1,3-benzazaphospholes in good yields, benzaldehyde provided 2-phenyl-2,3-dihydrobenzazaphosphole in low yield (12%) only,[16] but decomposed on heating at 180 °C partly to 2-phenyl-1,3-benzazaphosphole. The yield was again very low (15%).[13b] Nevertheless, we were interested to find out if this potential route to 2-arylbenzazaphospholes could be improved to function as a general access to functionally substituted 2-aryl-1,3-benzazaphospholes. Therefore, we screened the reactions of various aldehydes with 4-methyl-2-phosphanylaniline **1**, which is more advantageous for NMR monitoring than unsubstituted phosphanylaniline, under different conditions. It was found that 1*H*-benzazaphospholes can be synthesized in reasonable to good yields (33–68%) by heating aldehydes with **1** in toluene or xylene in the presence of 10–15 mol% of *p*-toluenesulfonic acid hydrate (PTSA). An equimolar amount of PTSA, tested in one example, did not improve the yield. Nafion(H^+) and Me_3SiCl were much less efficient and led to only partial conversion, mainly to dihydrobenzazaphospholes. Depending on the molar ratio, NH-functional derivatives **2** (molar ratio 1 : 1) or mixtures with *N*-CH_2R-derivatives **3** (molar ratio 1 : 1–1 : 2) were formed (Scheme 1). Clean reaction to *N*-CH_2R-substituted benzazaphospholes can be achieved with a greater excess of aldehyde, as demonstrated by the acid-catalyzed reaction of **1** with 4–5 equivalents of paraformaldehyde to 1,5-dimethyl-1,3-benzazaphosphole (62% yield) or, more efficiently, with *o*-diformylarenes, both recently published by us.[17] The aforementioned tolerance of tertiary P- and N-Lewis-basic groups to aromatic aldehydes, combined with their convenient synthetic or commercial availability, allowed us to synthesize the bidentate *o*-phosphanylphenyl and N-heterocyclic-substituted benzazaphospholes **2a–d**. Likewise, 2-thienyl- and *o*-methoxyphenyl substituents were introduced (**2e**, **f**), whereas attempts to synthesize a 2-(*o*-hydroxyphenyl)-1,3-benzazaphosphole from **1** and salicylaldehyde failed and gave a mixture with an unidentified main product with $\delta^{31}P$ = 134.5 ppm. Bromophenyl-substituted derivatives **2g**, **h** and **3h** were obtained by condensation of **1** with excess 2- and 3-bromobenzaldehyde, respectively, and may be useful for insertions of zerovalent metals or cross-coupling reactions, but these aspects were not investigated within this study.

The formation of *N*-substituted benzazaphospholes of type **3** inspired us to look for ways to introduce substituents from different aldehydes in the 1- and 2-position. However, attempts at cross-condensation of **1** with pyridine-2-carboxaldehyde and formaldehyde (molar ratio 1 : 1 : 1) furnished mixtures, and *N*-methylation of **2c** by formaldehyde failed. Only acid-



Scheme 1 Acid-catalyzed syntheses of the benzazaphospholes **2** and **3** from **1** and aldehydes in boiling toluene (or xylene for **2e**).



Scheme 2 Reactions of *N*-secondary 2-phosphanylanilines with aldehydes.

catalyzed conversions of *N*-secondary phosphanylanilines with aldehydes RCHO produced *N*-substituted benzazaphospholes with substituents other than CH_2R at nitrogen. Examples are the condensation of **5a** with pyridine-2-carboxaldehyde to the *N*-neopentyl-2-pyridylbenzazaphosphole **6a** and the NMR-monitored reaction of **5b** with benzaldehyde to the already known *N*-methyl-benzazaphosphole **6b**.[14] The reaction of **5b** with benzaldehyde was slow without catalysts at 20 °C and led *via* diastereoisomers of a primary addition product (δ = −34.1 and −38.9 ppm, *ca.* 20% each after 15 h) to the diastereoisomeric dihydrobenzazaphospholes **7a**. After one week at 20 °C the latter were the main products (δ = −53.5, −64.9 ppm, *ca.* 80 : 20%). In the presence of PTSA, the conversion of **5b** to **7b** was complete within less than 3 h, and much less side products (δ = 3.0, 4.0, −11.1, −0.5 ppm) were formed. The benzazaphosphole **6b**, however, was obtained only on heating to reflux (Scheme 2).

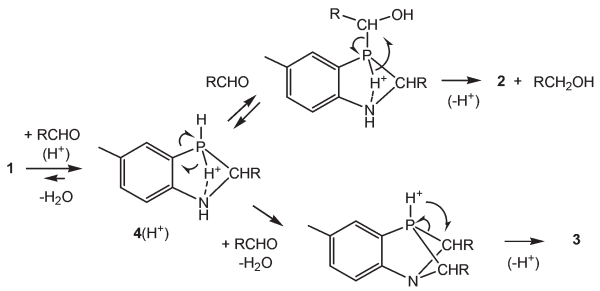
Mechanistic aspects

The above NMR experiment showed that the acid-catalyzed reaction of 2-phosphanylanilines with aldehydes to benzazaphospholes comprises two principal steps, (*i*) cyclocondensation and (*ii*) dehydrogenation, the latter driven by the aromaticity of the 1*H*-1,3-benzazaphospholes.[18] The same was observed in the condensations of **1** with pyridine- and thiophene-2-carboxaldehyde, monitored by ^{1}H and ^{31}P NMR. After combining the reactants at room temperature each two pairs of diastereoisomeric dihydrobenzazaphospholes **4** were formed as the main products, identified by the typical coupling pattern of the PH and PCHN protons and phosphorus resonances in the range of secondary phosphanes (**4c** at δ = −46.5 and −63.0 ppm and **4e** at δ = −48.4 and −58.5 ppm). On heating, these signals depleted and finally disappeared in favour of the signals of the benzazaphospholes **2c** and **2e**, respectively, as the main products. To obtain information as to the fate of the two hydrogen atoms eliminated in the conversion of **4** to **2** under inert conditions, the volume and the composition of the gas liberated during heating of crude **4e** were determined. It was less than 10% of the amount calculated for cleavage of H_2 and contained only about 1% H_2. The main part was N_2, liberated by heating the N_2-saturated solution. This shows that a transfer hydrogenation with **4e** as the hydrogen donor must have occurred. Indeed, in the solution thiophene-2-methanol was detected by GCMS. The formation of thiophene-2-methanol might suggest that two equivalents of aldehyde should be used in the reaction, one for the cyclocondensation and one to trap the hydrogen. The isolation of **3h** along with **2h** in the conversion of **1** with an excess of 2-bromobenzaldehyde shows, however, that excess aldehyde not only traps hydrogen by formation of the alcohol, but also, at least in part, leads to formation of *N*-CH_2R groups, *e.g.* by reductive alkylation at nitrogen of the 1*H*-1,3-benzazaphosphole. It is proposed that the transfer of hydrogen proceeds with P–C bond cleavage *via* equilibrium amounts of P-protonated species. Benzazaphospholes of type **2** might be formed *via* the monocondensation products **4** through equilibrium amounts of aldehyde addition products. Benzazaphospholes of type **3**, observed only in the case of excess aldehyde, might be generated *via* unstable condensation products with two molecules of aldehyde (Scheme 3). If reduction of a primarily formed imine to $MeC_6H_3(PH_2)NHCH_2R$, which could condense with RCHO to **3**, were to play a major role in the hydrogen transfer, as observed for the similarly complex conversion of benzimidazolines to benzimidazoles,[19] then **3** should be observed also in the 1 : 1 condensation. A small amount of not completely identified *p*-toluidyl species, detected by the characteristic AA′BB′ proton multiplets in the upfield aryl region, showed in addition minor cleavage of the P–aryl bond. The fate of the phosphorus is not clear in this case but reductive cleavage of PH_3, in the presence of PTSA fixed as a PH_4^+ salt (not detected in the gas phase), appears to be possible and to make a further contribution to the aromatization of the dihydro-precursors **4**.

Attempts to improve the yields of **2c** by dehydrogenation of crude **4c** with CCl_4/Et_3N failed and led to increased amounts of impurities, as did attempts at dehydrogenation by heating in the presence of Pd/charcoal (5 mol%), a normal method in the aromatization of classical air-stable heterocycles.[20]

Properties

The new functionally substituted 2-(hetero)aryl-benzazaphospholes are thermally and hydrolytically stable aromatic compounds, in the solid state slightly, in solution more sensitive to air oxidation. They are well soluble in THF, dichloromethane or ethyl acetate but only moderately to sparingly soluble in toluene, diethyl ether or methanol and insoluble in

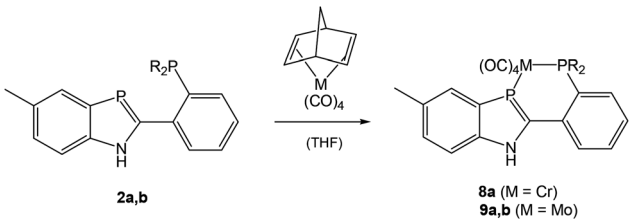


Scheme 3 Proposed mechanism.

n-hexane. This allows purification by precipitation from concentrated THF or ether solutions with hexane or MeOH or by column chromatography on silica gel under a nitrogen atmosphere. The lack of N-basic properties of the azaphosphole ring by involvement of the N lone-pair in the aromatic π-system enables the separation of dihydrobenzazaphosphole impurities by extraction with dilute acids except for derivatives with a basic group in the 2-(hetero)aryl substituent. The NH-function exhibits weakly acidic properties and displays the proton NMR signals of **2a**, **2e**, **2g** and **2h** in the range δ = 9.10–9.62 ppm. Particularly strong downfield shifts in the presence of the more P-basic *o*-dicyclohexylphosphanyl group of **2b** (δ = 12.06 ppm), the N-basic 2-pyridyl and 2-imidazolyl groups of **2c** (δ = 10.80 ppm) and **2d** (δ = 11.37 ppm), respectively, or the *o*-methoxy group of **2f** (δ = 10.95 ppm) indicate the formation of hydrogen bonds and preference for a conformation of the 2-aryl-substituents with the donor atom close to NH. The opposite orientation of the 2-aryl group is enforced in chelate complexes involving coordination at the low-coordinated phosphorus and the donor function of the 2-(hetero)aryl group. Annulated 1,3-azaphospholes, like other σ^2P-compounds, are rather π-acidic and known to form metal(0) pentacarbonyl complexes.[9a–c,21] Chelate complexes, however, are not yet known. Such complexes are formed from **2a** and **2b** with M(CO)$_4$(nbd) (M = Cr, Mo; nbd norbornadiene) in THF, as detected by conclusive NMR data of **8a** and **9a,b** (Scheme 4). Detailed structural information was obtained by crystal structure analysis of the molybdenum complex **9a** (Fig. 1).

Structure elucidation

The structure elucidation of the new ligands and metal(0) carbonyl complexes was based on conclusive solution NMR and HRMS data. The assignments are supported by characteristic shift ranges and H–H, P–H and P–C coupling constants.[9,11,13–15] The coordination of the M(CO)$_4$ fragments in the six-membered M(0) chelate complexes is evident from the coordination chemical shifts of both phosphorus resonances and the signals of adjacent ^{13}C nuclei, particularly of C-2, but also of C-3a and C-2′. In addition, marked changes of the $^1J_{PC}$ coupling constants are observed, even if the $\Delta\delta^{13}$C values are small (C3a, C2′ and C-i), so that Δ^1J_{PC} is a useful probe for metal coordination of the low-coordinated phosphorus (Table 1). Compared to the coordination chemical shifts of the phosphorus resonance in 1,3-azaphosphole Cr(CO)$_5$ and Mo(CO)$_5$ complexes ($\Delta\delta_{complex\text{-}ligand}$ *ca.* 4–8 and *ca.* −7 ppm[21]) the coordination chemical shifts for the low-coordinated phosphorus of **8a** and **9a,b** are considerably greater. The complex **9b** with the more P-basic dicyclohexylphosphanyl group displays however a smaller downfield shift than the diphenylphosphanyl complex **9a**. This suggests that the downfield drift of the signals of low-coordinated



Scheme 4 Formation of chelate complexes with **2a**.

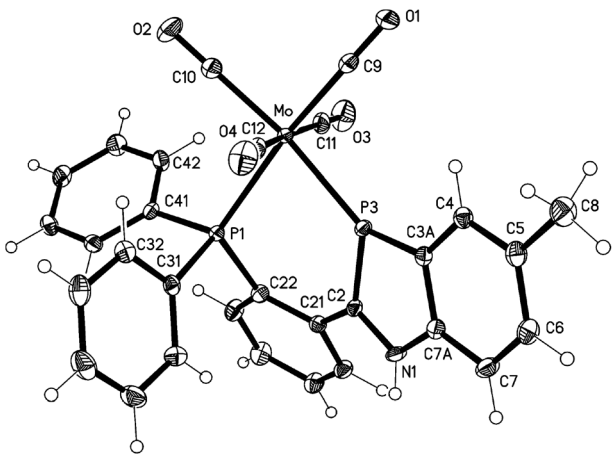


Fig. 1 Structure of **9a** (enantiomer with an *R*-configuration) in the crystal (ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): Mo–P(1) 2.5442(5), Mo–P(3) 2.4219(5), Mo–C(9) 1.973(2), Mo–C(10) 2.011(2), Mo–C(12) 2.039(2), Mo–C(11) 2.050(2), C(2)–P(3) 1.7173(17), P(3)–C(3A) 1.7574(18), N(1)–C(2) 1.369(2), N(1)–C(7A) 1.381(2); P(3)–Mo–P(1) 79.598(13), C(2)–P(3)–Mo 126.51(6), C(3A)–P(3)–Mo 136.83(6), C(9)–Mo–P(1) 174.05(6), C(10)–Mo–P(3) 171.81(7), *cis*-C–Mo–C 87.31(9) to 93.81(9), C(12)–Mo–C(11) 173.79(8), C(2)–P(3)–C(3A) 92.17(8), N(1)–C(2)–P(3) 110.84(13).

Table 1 Characteristic coordination chemical shifts and changes of $^1J_{PC}$ coupling constants in the (P^P′)M(CO)$_4$ complexes (δ in ppm, J_{PX} in Hz)

	2a ($CDCl_3$)	**8a** ($CDCl_3$)	**9a** ($CDCl_3$)	**2b** ($CDCl_3$)	**9b** (CD_2Cl_2)
$\delta^{31}P_{ring}$ (J_{PP}),	83.1 (16.1),	108.5 (65.5),	88.4 (41.2),	85.5 (s),	80.5 (44),
$\delta^{31}P_{PR2}$ (J_{PP})	−12.0 (16.1)	53.2 (65.5)	33.4 (41.2)	−11.7 (s)	28.4 (44)
$\Delta\delta^{31}P$ (ΔJ_{PP})	—	25.4, 65.2 (49)	5.3, 45.4 (25)	—	−5.0, 40.1 (44)
δ^{13}C-2 ($^1J_{PC}$)	174.1 (50.6)	160.0 (27) (noise level)	161.0 (25.2)	177.0 (49)	160.9 (22.6)
$\Delta\delta^{13}$C-2 (ΔJ)	—	−14.1 (−23.6)	−13.9 (−25.4)	—	−16.1 (−26.4)
δ^{13}C-3a ($^1J_{PC}$)	141.9 (42.3)	136.2 (10.6)	138.1 (11.9)	141.6 (40.0)	138.6 (10.6)
$\Delta\delta^{13}$C-3a (ΔJ)	—	−5.7 (−31.7)	−3.8 (−30.4)	—	−3.0 (−29.4)
δ^{13}C-2′ ($^1J_{PC}$)	135.2 (15.1)	130.7 (31.2)	130.3 (33.2)	130.4 (vbr 20)	127.1 (19)
$\Delta\delta^{13}$C-2′ (ΔJ)	—	−4.5 (16.1)	−4.9 (18.1)	—	−3.3 (–)
δ^{13}C-i/α ($^1J_{PC}$) of R_2P	136.2 (9)	135.3 (34.4)	135.1 (33.1)	33.7 (9.4)	37.4 (14.6)
$\Delta\delta^{13}$C-i/α (ΔJ)	—	−0.9 (25.4)	−1.1 (24.1)	—	3.7 (5.2)

phosphorus is caused by steric rather than electronic effects on replacement of a π-accepting CO with a σ-donor P-ligand.

More detailed information on the constitution and geometry of the chelates is provided by the crystal structure analysis of **9a** (Fig. 1). The compound crystallizes in the orthorhombic space group $Pna2_1$ with four molecules in the unit cell. Molybdenum displays a distorted octahedral coordination, the coordinated phosphanyl group is essentially tetrahedral and the low-coordinated phosphorus has a trigonal geometry. The metal lies 0.57 Å out of the benzazaphosphole ring plane, corresponding to an angle of 14.4° between the ring plane and the P–Mo vector. The π-planes of the benzazaphosphole and 2-phenyl-ring are mutually rotated around the C(2)–C(21) axis by 33° (*cf.* torsion angle P(3)–C(2)–C(21)–C(22) −37°) by the steric demands within the chelate ring. This generates axial asymmetry and consequently there are two molecules each with *R*- and *S*-configuration in the unit cell. The Mo–P(3) bond (2.4219(5) Å) is shorter than the Mo–P(1) bond (2.5442(5) Å), consistent with the smaller radius of formally sp^2- compared to sp^3-hybridized phosphorus. The P(3)–C(2) and P(3)–C(3a) bonds are slightly shortened and the C(3a)–P(3)–C(2) angle is slightly increased by the coordination, compared to the values in free benzazaphospholes.[9,11] Other bond lengths and angles are not significantly altered and indicate preservation of aromaticity[18] in the 1,3-benzazaphosphole ring.

Conclusions

Biaryl-type 1,3-benzazaphosphole hybrid ligands with *o*-phosphanylphenyl, heterocyclic imine, thienyl or *o*-alkoxyphenyl donor groups can be synthesized in moderate to good yields by PTSA-catalyzed cyclocondensation of *o*-phosphanylanilines with the respective functionally substituted (hetero)aryl aldehydes in boiling toluene or xylene. A larger excess of aldehyde (RCHO) leads to the additional introduction of a CH_2R substituent at nitrogen by reductive N-alkylation. Benzazaphospholes with other *N*-substituents can be obtained by condensation of the corresponding *N*-secondary *o*-phosphanylanilines with aldehyde. As demonstrated for 2-*o*-phosphanylphenyl-1,3-benzazaphospholes, chelate complexes are formed with suitable M(0) carbonyl complexes. The potential for stabilization of the generally quite labile benzazaphosphole complexes with nonzerovalent transition metals by the chelate effect still has to be explored but the synthetic accessibility of suitable 1,3-benzazaphosphole hybrid ligands reported in this study paves the way to such investigations.

Experimental section

General considerations

All reactions with air- or moisture-sensitive compounds were carried out under a nitrogen atmosphere using Schlenk techniques and deoxygenated dry solvents. 4-Methyl-2-phosphanylaniline **1**,[17] *N*-neopentyl-*o*-phosphanylaniline **5a**[11a] and *N*-methyl-*o*-phosphanylaniline **5b**[14,22] were prepared as reported earlier. Commercially available reagents were used as received unless indicated otherwise. NMR spectra were measured on a multinuclear FT-NMR spectrometer Bruker ARX300 at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. ^{1}H, ^{13}C and ^{31}P chemical shifts are δ values and given in ppm relative to Me_4Si and H_3PO_4 (85%), respectively. Assignment numbers are indicated in Scheme 1. Coupling constants refer to H–H (^{1}H NMR) or P–C couplings (^{13}C NMR) unless stated otherwise. Assignments of ^{1}H, ^{13}C and ^{31}P NMR signals are based on typical shift ranges and coupling constants of known benzazaphospholes and their $M(CO)_5$ complexes, tentative assignments of 2-aryl, 1-CH_2-aryl and cyclohexyl carbon nuclei in addition by using 135 DEPT spectra and increment methods. UV-Vis spectra were measured on a Perkin-Elmer spectralphotomer Lambda 800 in MeOH. Melting points were determined in sealed capillaries. Detection of thiophen-2-methanol by GCMS was carried out using a GC Agilent 6890N and an MS Agilent 5973 with Software MS-Chemstation. HRMS measurements were performed in Göttingen using a double focusing sector-field instrument MAT 95 (Finnigan) (EI 70 eV) or a 7T Fourier transform ion cyclotron resonance mass spectrometer APEX IV (Bruker Daltonics) (ESI).

2-(2-Diphenylphosphanylphenyl)-5-methyl-1*H*-1,3-benzazaphosphole (2a). *o*-Diphenylphosphanyl-benzaldehyde[23] (815 mg, 2.81 mmol) and *p*-toluenesulfonic acid hydrate (PTSA) (80 mg, 15 mol%) were added to **1** (390 mg, 2.80 mmol) in toluene (10 mL) and heated to reflux for 24 h. NMR monitoring displayed **2a** as the main product (60% by integration of the methyl signals). Removal of toluene in a vacuum, treatment of the crude product with degassed 5% aq. NaOH–diethyl ether, drying of the organic phase with Na_2SO_4, concentration of the solution and crystallization from dry methanol gave *ca.* 0.6 g (52%) pale-yellow **2a**. ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 3 H, Me), 6.98 (ddd, ^3J = 7.6, $^4J_{PH}$ = 4.2, ^4J = 1 Hz, H-6′), 7.03 (d br, ^3J = 8.4, $^4J \approx J_{PH} \approx$ 1.5, 0.7 Hz, aryl), 7.12 (d br, ^3J = 8.4 Hz, 1 H, aryl), 7.19–7.31 (m, 11 H, aryl), 7.34 (td, ^3J = 7.5, ^4J = 1.4 Hz, H-4′ or H-5′), 7.68 (dt, $^3J_{PH}$ = 4.3, ^4J = 1 Hz, 1 H, H-4), 7.70 (m, 1 H, aryl), 9.31 (br, 1 H NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.25 (s, Me), 113.25 (s, C-7), 126.81 (d, ^4J = 2.6 Hz, C-6), 127.88 (d, ^2J = 20.1 Hz, C-4), 128.59 (s, C-4′), 128.81 (d, ^3J = 6.7 Hz, 4 C-*m*), 129.11 (s, C-5′), 129.17 (s, 2 C-*p*), 129.58 (d, ^3J = 11.9 Hz, C_q-5), 131.33 (dd, ^3J = 11.8, 5.2 Hz, C-6′), 134.06 (d, ^2J = 18.6 Hz, 4 C-*o*), 134.11 (s, C-3′), 135.17 (dd, ^1J = 15.1, ^3J = 5.9 Hz, C_q-2′), 136.24 (d, ^1J = 9.3 Hz, 2 C_q-i), 140.47 (dd, ^2J = 26.4, 16.0 Hz, C_q-1′), 140.50 (d, ^2J = 6.5 Hz, C_q-7a), 141.89 (d, ^1J = 42.3 Hz, C_q-3a), 174.11 (dd, ^1J = 50.6, ^3J = 3.9 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −12.0 (d, $^4J_{PP}$ = 16.1 Hz, PPh_2), 83.1 (d, $^4J_{PP}$ = 16.2 Hz, P_{ring}) ppm. MS (EI 70 eV, 350 °C): *m*/*z* (%) = 410 (29), 409 (100) [M^+], 408 (96), 332 (18), 254 (45), 183 (21), 137 (51), 98 (32). HRMS (ESI, MeOH–FA): $C_{26}H_{21}NP_2$ (409.11) calcd for $[M + H]^+$ 410.1222; found 410.1218.

2-(2-Dicyclohexylphosphanyl-phenyl)-5-methyl-1*H*-1,3-benzazaphosphole (2b). 2-Dicyclohexylphosphanyl-benzaldehyde[24] (774 mg, 2.56 mmol) and PTSA (73 mg, 15 mol%) were added

to **1** (356 mg, 2.56 mmol) in toluene (10 mL) and heated to reflux for 48 h. Replacement of toluene by ether, extraction of the catalyst with degassed 5% aq. NaOH from the ethereal solution of the product and purification by column chromatography using 1% Et_2O–*n*-hexane gave *ca.* 0.6 g (51%) of pale yellow viscous **2b**. ^{1}H NMR ($CDCl_3$): δ = 1.03–1.35 (m br, 10 H, *c*Hex), 1.58–1.78 (m br, 10 H, *c*Hex), 1.91–2.06 (m br, 2 H, *c*Hex), 2.45 (s, 3 H, Me), 7.17 (d br, ^3J = 8.5 Hz, H-6), 7.25–7.42 (m br, 2 H, aryl), 7.51–7.62 (m br, 2 H, aryl), 7.82 (dt, $^3J_{PH}$ = 2.8, ^4J = 1, ^5J = 0.7 Hz, 1 H, H-4), 8.17 (br dt-shape, 1 H, H-6′), 12.06 (vbr, 1 H, NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.30 (Me), 26.18 (C-δ), 26.89 (d, ^3J = 8.5 Hz, C-γ), 27.04 (d, ^3J = 13.3 Hz, C-γ′), 28.81 (d, ^2J = 6.7 Hz, C-β), 29.86 (d, ^2J = 15.6 Hz, C-β′), 33.68 (d, ^1J = 9.4 Hz, C-α), 113.85 (br s, C-7), 126.72 (br s, C-6), 127.41 (br s, C-4′), 127.60 (d, ^2J = 21.0 Hz, C-4), 129.23 (br s, C-5′), 129.51 (d, ^3J = 12.1 Hz, C_q-5), 130.4 (vbr d, $^1J \approx$ 20 Hz, halfwidth each 23 Hz, C_q-2′), 131.34 (vbr d, ^2J = 22 Hz, halfwidth each 23 Hz, C-3′), 133.56 (br s, C-6′), 140.79 (vbr d, halfwidth 24 Hz, C_q-1′), 141.34 (d, ^2J = 5.3 Hz, C_q-7a), 141.55 (dd, ^1J = 40.0, ^5J = 2.8 Hz, C_q-3a), 177.0 (br d, ^1J = 49 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): −11.7 (s, P*c*Hex$_2$), 85.5 (s, P_{ring}) ppm. HRMS (ESI, MeOH–FA): $C_{26}H_{33}NP_2$ (421.49), calcd for $[M + H]^+$ 422.2161; found 422.2163.

5-Methyl-2-(pyrid-2-yl)-1*H*-1,3-benzazaphosphole (2c). Pyridine-2-carboxaldehyde (0.62 mL, 6.52 mmol) and PTSA (150 mg, 13 mol%) were added to **1** (850 mg, 6.11 mmol) in toluene (10 mL) and refluxed for 24 h. Removal of the solvent, extraction of the catalyst with degassed 5% aq. NaOH from the ethereal solution and purification of the resulting orange oil by column chromatography using dry 50% CH_2Cl_2–*n*-hexane gave 830 mg (60%) of **2c** as a yellow solid. UV (3.8×10^{-5} M in MeOH): λ_{max} (ε) = 367 (sh, 7.400), 336 (12.000), 262 (14.300), 228 (20.000) nm. ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H, Me), 7.14 (d, partly superimposed, ^3J = 8.5, ^4J = 1 Hz, 1 H, H-6), 7.16 (m, partly superimposed, $^3J \approx$ 7.2, 4.9, $^4J \approx$ 1 Hz, 1 H, H-5′), 7.49 (d br, ^3J = 8.5 Hz, 1 H, H-7), 7.64 (td, ^3J = 7.8, 7.7, J = 1.8 Hz, 1 H, H-4′), 7.78 (ddd, $^3J_{PH}$ = 4.2, ^4J = 1.5, ^5J = 0.7 Hz, 1 H, H-4), 8.03 (ddt, ^3J = 8.0, $^4J_{PH}$ = 2.1, $^4J \approx {}^5J$ = 1 Hz, 1 H, H-3′), 8.49 (d br, ^3J = 4.9 Hz, 1 H, H-6′), 10.80 (br, 1 H, NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$, ref. solv.): δ = 21.26 (s, Me), 114.10 (s, C-7), 121.69 (d, $^3J_{PC}$ = 14.2 Hz, C-3′), 122.94 (d, ^5J = 2.7 Hz, C-5′), 128.18 (d, ^4J = 3.4 Hz, C-6), 128.45 (d, ^2J = 21.2 Hz, C-4), 129.99 (d, ^3J = 13.3 Hz, C_q-5), 137.71 (s, C-4′), 141.05 (d, ^2J = 7.5 Hz, C_q-7a), 142.55 (d, ^1J = 40.1 Hz, C_q-3a), 147.71 (br, C-6′), 151.79 (d, ^2J = 20.1 Hz, C_q-2′), 169.05 (d, ^1J = 50.0 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 80.0 ppm. MS (EI 70 eV, 280 °C): *m*/*z* (%) = 227 (14), 226 (94) [M^+], 225 (17), 199 (20), 167 (41), 149 (100), 78 (47), 57 (65). HRMS (ESI, MeOH–FA): $C_{13}H_{11}N_2P$ (226.07), calcd for $[M + H]^+$ 227.0733; found 227.0733.

5-Methyl-2-(*N*-methyl-imidazol-2-yl)-1*H*-1,3-benzazaphosphole (2d). 1-Methyl-imidazole-2-carboxaldehyde (960 mg, 8.72 mmol) and chlorotrimethylsilane (0.11 mL, 10 mol%) were added to **1** (1.21 g, 8.70 mmol) in toluene (10 mL) and refluxed for 24 h. Then the solvent was removed in a vacuum and the acid was extracted with degassed 5% aq. NaOH–diethyl ether. A slightly yellow precipitate was obtained when dry *n*-hexane was poured into a concentrated solution of the crude product in THF. Separation of the precipitate, washing with THF–hexane (1 : 2) and drying in a vacuum gave 659 mg (33%) of **2d** as a nearly colourless solid, mp. 197–199 °C. UV (9.0×10^{-5} M in MeOH): λ_{max} (ε) = 331 (7.700), 272 (sh, 6.200), 261 (7.500), 220 (10.300) nm. ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, Me), 4.03 (d, $^5J_{PH}$ = 2.4 Hz, 3 H, NMe), 7.05 (s, 1 H, H-4′ or H-5′), 7.17 (d, $^5J_{PH}$ = 1.2 Hz, 1 H, H-4′ or H-5′), 7.21 (d br, ^3J = 8.4 Hz, 1 H, H-6), 7.54 (d br, ^3J = 8.5 Hz, 1 H, H-7), 7.86 (ddd, $^3J_{PH}$ = 4.1, $^4J \approx$ 1.5, ^5J = 0.7 Hz, 1 H, H-4), 11.37 (br, 1 H, NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.25 (s, Me), 36.11 (d, $^4J_{PC}$ = 26.0 Hz, NMe), 113.79 (s, C-7), 123.74 (s, C-6), 127.14 (s, C-4′ or C-5′), 127.99 (d, ^2J = 22.3 Hz, C-4), 127.99 (d, ^4J = 2.6 Hz, C-4′ or C-5′), 129.93 (d, ^3J = 12.6 Hz, C_q-5), 140.24 (d, ^2J = 7.7 Hz, C_q-7a), 141.66 (d, ^1J = 39.6 Hz, C_q-3a), 144.01 (d, ^2J = 16.0 Hz, C_q-2′), 158.67 (d, ^1J = 56.4 Hz, C_q-2) ppm. ^{31}P NMR ($CDCl_3$): δ = 76.1 ppm. MS (EI 70 eV, 260 °C): *m*/*z* (%) = 230 (17), 229 (100) [M^+], 228 (35), 201 (13), 161 (11), 160 (12), 95 (17), 77 (13). HRMS (ESI, MeOH–FA): $C_{12}H_{12}N_3P$ (229.22), calcd for $[M + H]^+$ 230.0842; found 230.0842.

5-Methyl-2-(thien-2-yl)-1*H*-1,3-benzazaphosphole (2e) and detection of 4e. Thiophene-2-carboxaldehyde (0.56 mL, 6.09 mmol) was added to a solution of **1** (830 mg, 5.97 mmol) and PTSA (103 mg, 10 mol%) in xylene (7 mL). The solution became warm and turbid. NMR-monitoring showed strong signals for the diastereoisomers of **4e**, four weak signals in the region δ = −56.3 to −53.8 ppm and some in the region δ = −1.9 to 4.5 and at 11.8 ppm. After heating the mixture at reflux for 12 h the ^{31}P NMR spectrum showed a very strong peak for **2e** and several weak signals. GC analysis of the volatiles, separated in a vacuum at 50 °C/2 Torr, displayed a peak for thiophene-2-methanol, confirmed by comparison with pure thiophene-2-methanol and additionally by GCMS. The sticky residue was dissolved in diethyl ether and purified by extraction of N-basic and acid impurities with cold aqueous H_2SO_4 and NaOH solution and final column chromatography (*n*-hexane, followed by 25% Et_2O–hexane), yielding 700 mg (50%) of a pale yellow powder, mp. 160–164 °C. The compound is easily soluble in methanol, moderately soluble in cold and much more readily in hot $CHCl_3$. Crystals in the form of yellow platelets formed on cooling. UV (2.1×10^{-5} M in MeOH): λ_{max} (ε) = 357 (6.200), 268 (sh, 7.700), 256 (sh, 11.500), 240 (14.500), 211 (12.700) nm. ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 3 H, Me), 7.01 (ddd, ^3J = 5.2, 3.6, $^5J_{PH}$ = 1.5 Hz, 1 H, H-4′), 7.09 (dt, ^3J = 8.2, $^4J \approx {}^5J_{PH} \approx$ 1.0 Hz, 1 H, H-6), 7.23 (dd, ^3J = 5.2, ^4J = 1.1 Hz, 1 H, H-5′), 7.34 (ddd, ^3J = 3.7, ^4J = 1.1, $^4J_{PH}$ = 1.8 Hz, 1 H, H-3′), 7.39 (d br, ^3J = 8.3 Hz, 1 H, H-7), 7.71 (m, $^3J_{PH}$ = 4.0, $^4J \approx$ 1.5, ^5J = 0.7 Hz, 1 H, H-4), 9.10 (br, 1 H, NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.21 (s, Me), 113.01 (s, C-7), 123.63 (d, ^3J = 11.4 Hz, C-3′), 125.51 (d, J = 5.3 Hz, C-4′ or C-5′), 127.24 (d, ^4J = 3.4 Hz, C-6), 128.13 (d, ^2J = 21.2 Hz, C-4), 128.23 (s br, C-5′ or C-4′), 130.04 (d, ^3J = 12.0 Hz, C_q-5), 138.46 (d, ^2J = 19.5 Hz, C_q-1′), 140.65 (d, ^2J = 7.6 Hz, C_q-7a), 141.78 (d, ^1J = 41.2 Hz, C_q-3a), 166.64 (d, ^1J = 49.3 Hz, C_q-2) ppm. ^{31}P{^{1}H}

NMR ($CDCl_3$): δ = 75.23 ppm. HRMS (ESI, MeOH–FA): $C_{12}H_{10}NPS$ (231.25), calcd for $[M + H]^+$ 232.0344; found: 232.0345.

Characteristic NMR ($CDCl_3$) signals of 5-methyl-2-thienyl-2,3-dihydro-1,3-benzazaphosphole (**4e**): diastereoisomer with P–H and 2-thienyl in the *syn*-position, δ^1H = 4.49 (dd, $^1J_{PH}$ = 188.5, ^3J = 15.0 Hz, PH), 5.55 (dd, $^2J_{PH}$ = 21.3, ^3J = 15.0 Hz, H-2), δ^{31}P = −47.0 ppm; diastereoisomer with P–H and 2-thienyl in the *anti*-position, δ^1H = 4.95 (dd, $^1J_{PH}$ = 185.8, ^3J = 6.6 Hz, PH), 5.67 (d, ^3J = 6.6 Hz, $^2J_{PH}$ very small, H-2), δ^{31}P = −58.5 ppm; *syn* : *anti* ratio 2 : 1 (based on PH integrals).

2-(2-Methoxyphenyl)-5-methyl-1*H*-1,3-benzazaphosphole (2f). *o*-Methoxybenzaldehyde (318 mg, 2.32 mmol) and PTSA (64 mg, 15 mol%) were added to **1** (310 mg, 2.23 mmol) in toluene (10 mL) and heated to reflux for 48 h. Toluene was removed in a vacuum, and the ethereal solution of the residue extracted with degassed 5% aq. NaOH. Drying with Na_2SO_4 and evaporation of ether furnished 525 mg brown oil, still displaying aryl impurities in the NMR spectrum. Column chromatography (*n*-hexane, followed by 25% Et_2O–hexane) gave *ca.* 250 mg (44%) of a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3 H, Me), 4.04 (s, 3 H, OMe), 7.03 (superimposed dd, ^3J = 8.4–7, ^4J = 1–2.5 Hz, 1 H, H-6), 7.13 (superimposed t, ^3J = 7–8 Hz, 1 H, H-5′), 7.17 (superimposed d, $^3J \approx$ 7.5 Hz, 1 H, H-3′), 7.32 (tdd ^3J = 8.3, 7.2, ^3J = 1.6, J = 0.8 Hz, 1 H, H-4′), 7.52 (d br, ^3J = 8.3 Hz, 1 H, H-7), 7.85 (ddd, $^3J_{PH}$ = 3.8, ^4J = 1.7, ^5J = 0.7 Hz, 1 H, H-4), 8.21 (ddd, ^3J = 8.0, $^4J_{PH}$ = 4.2, J = 1.6 Hz, 1 H, H-6′), 10.95 (br, 1 H, NH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, ref. solv): δ = 21.28 (Me), 55.27 (OMe), 112.02 (s, CH-3′), 113.47 (s, CH-7), 121.80 (s, CH-5′), 123.17 (d, ^2J = 14.5 Hz, C_q-1′), 126.58 (d, ^4J = 2.5 Hz, CH-6), 127.65 (d, ^2J = 21.4 Hz, CH-4), 129.46 (superimposed d, ^3J = 10.7 Hz, C_q-5), 129.68 (superimposed d, ^3J = 22 Hz, CH-6′), 129.73 (d, ^5J = 3.4 Hz, CH-4′), 141.07 (d, ^1J = 40.0 Hz, C_q-3a), 140.76 (d, ^2J = 5.5 Hz, C_q-7a), 154.66 (d, ^3J = 8.3 Hz, C_q-2′), 172.97 (d, ^1J = 50.6 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 76.1 ppm. HRMS (ESI, MeOH–FA): $C_{15}H_{14}NOP$ (255.25), calc. for $[M + H]^+$ 256.0886; found: 256.0886.

2-(3-Bromophenyl)-5-methyl-1*H*-1,3-benzazaphosphole (2g). *m*-Bromobenzaldehyde (1.06 ml, 9.09 mmol) and PTSA (1.56 g, 8.20 mmol) were added to **1** (1.13 g, 8.12 mmol) in toluene (10 mL) and heated to reflux for 72 h. Toluene was removed in a vacuum, the residue dissolved in dichloromethane and the catalyst extracted with 5% aq. NaOH solution. The organic phase was dried with Na_2SO_4 and concentrated. The crude product **2g** was purified by column chromatography, eluting with 20% CH_2Cl_2–*n*-hexane, to give 1.68 g (68%) of a pale brownish-yellow viscous oil. ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, Me), 7.20 (d br, ^3J = 8 Hz, H-6), 7.30 (t, ^3J = 7.9 Hz, 1 H, H-5′), 7.48 (dtd, ^3J = 7.9, ^4J = 1.8, $^6J_{PH}$ = 0.8 Hz, 1 H, H-4′), 7.52 (d, ^3J = 8.5 Hz, 1 H, H-7), 7.71 (dtd, ^3J = 7.8, ^4J = 1.8, $^4J_{PH}$ = 1.2 Hz, 1 H, H-6′), 7.83 (d br, $^3J_{PH}$ = 4.1 Hz, 1 H, H-4), 7.91 (q, $^4J_{PH} \approx {}^4J$ = 1.8 Hz, 1 H, H-2′), 9.32 (br, 1 H, NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.23 (s, Me), 113.29 (s, C-7), 123.24 (s, C_q-3′), 123.96 (d, ^3J = 13.0 Hz, C-6′), 127.55 (d, ^4J = 2.6 Hz, C-6), 127.86 (d, ^3J = 12.2 Hz, C-2′), 128.30 (d, ^2J = 21.1 Hz, C-4), 130.12 (d, ^3J = 12.9 Hz, C_q-5), 130.64 (s, C-5′), 131.48 (d, ^5J = 2.6 Hz, C-4′), 137.09 (d, ^2J = 15.5 Hz, C_q-1′), 141.29 (d, ^2J = 6.9 Hz, C_q-7a), 141.79 (d, ^1J = 40.6 Hz, C_q-3a), 171.81 (d, ^1J = 50.5 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 79.0 ppm. MS (EI 70 eV, 350 °C): *m*/*z* (%) = 306 (5), 305 (34), 304 (8), 303 (29) [M^+], 226 (19), 149 (18), 121 (28), 91 (17), 77 (19), 57 (17), 44 (100). HRMS (ESI, MeOH–FA): $C_{14}H_{11}BrNP$ (304.12), calcd for $[M(^{79}Br) + H]^+$ 303.9885; found 303.9888.

Synthesis of 2-(2-bromophenyl)-5-methyl-1*H*-1,3-benzazaphosphole (2h) and 1-(2-bromobenzyl)-2-(2-bromophenyl)-5-methyl-1,3-benzazaphosphole (3h). *o*-Bromobenzaldehyde (0.95 mL, 8.14 mmol), **1** (750 mg, 5.39 mmol) and PTSA (1.02 g, 5.36 mmol) were heated in toluene (10 mL) to reflux for 72 h, and the mixture was worked up as described for **2g**. The resulting oil was separated into two products by column chromatography. The 1,2-disubstituted product **3h** was obtained as a brownish yellow solid as the first fraction using dry 10% CH_2Cl_2–*n*-hexane as an eluent, yield 381 mg (15%). The second fraction using dry 20% CH_2Cl_2–*n*-hexane for elution gave 652 mg (40%) of **2h** as a brownish yellow oil.

Data of **2h**: ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, Me), 7.21 (d br, superimposed, ^3J = 8.3 Hz, 1 H, H-6), 7.21–7.28 (m, superimposed, 1 H, H-4′), 7.38 (td, ^3J = 7.5, ^4J = 1.2 Hz, 1 H, H-5′), 7.54 (br d, ^3J = 8.4 Hz, 1 H, H-7), 7.69 (dd, ^3J = 8.0, ^4J = 1.1 Hz, 1 H, H-3′), 7.76 (dt, ^3J = 7.7, $^4J \approx {}^4J_{PH}$ = 1.7, 1.6 Hz, 1 H, H-6′), 7.86 (ddd, $^3J_{PH}$ = 3.7, ^4J = 1.6, ^5J = 0.8 Hz, 1 H, H-4), 9.62 (br, 1 H, NH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.25 (s, Me), 113.43 (s, C-7), 120.85 (d, $^3J_{PC}$ = 6.7 Hz, C_q-2′), 127.31 (d, ^4J = 3.2 Hz, C-6), 127.79 (s, C-5′), 128.00 (d, ^2J = 20.3 Hz, C-4), 129.85 (d superimposed, $^3J \approx$ 11 Hz, C_q-5), 129.89 (s, C-4′), 132.43 (d, ^3J = 12.1 Hz, C-6′), 133.91 (s, C-3′), 135.59 (d, ^2J = 17.1 Hz, C_q-1′), 140.71 (d, ^2J = 6.7 Hz, C_q-7a), 141.65 (d, ^1J = 42.4 Hz, C_q-3a), 172.30 (d, ^1J = 50.4 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 84.3 ppm. MS (EI 70 eV, 320 °C): *m*/*z* (%) = 306 (17), 305 (100), 304 (22), 303 (99) [M^+], 224 (90), 121 (64), 77 (25). HRMS (ESI, MeOH–FA): $C_{14}H_{11}BrNP$, calcd for $[M(^{79}Br) + H]^+$ 303.9885, found 303.9889.

Data of **3h**: ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3 H, Me), 5.15, 5.55 (2 d, ^2J = 17.4 Hz, 2 H, NCH_AH_B), 6.21 (m, 1 H, aryl), 7.01–7.04 (m, superimposed, 2 H, aryl), 7.15 (dt, ^3J = 8.6, $^4J \approx {}^5J_{PH}$ = 0.7 Hz, 1 H, H-6), 7.27–7.28 (m, br, 3 H, aryl), 7.33–7.39 (m, 1 H, aryl), 7.45–7.50 (m, 1 H, aryl), 7.65–7.70 (m, 1 H, aryl), 7.91 (br dt, $^3J_{PH}$ = 4.1, $^4J \approx {}^5J$ = 0.7 Hz, 1 H, H-4) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.14 (s, Me), 50.29 (d, $^3J_{PC}$ = 3.5 Hz, NCH_2), 113.45 (s, C-7), 121.55 (s, C_q-2″), 124.72 (d, $^3J_{PC}$ = 6.8 Hz, C_q-2′), 127.14, 127.30 (C-4″, C-5″), 127.72 (s, C-5′), 128.45 (d, ^2J = 22.1 Hz, C-4), 128.80 (s, C-6″), 130.24 (d, ^3J = 11.2 Hz, C_q-5), 130.47 (s, C-4′), 132.56 (s, C-3″), 132.74 (d, ^3J = 12.0 Hz, C-6′), 132.82 (s, C-3′), 135.49 (d, ^2J = 17.4 Hz, C_q-1′), 135.73 (s, C_q-1″), 141.02 (d, ^2J = 6.5 Hz, C_q-7a), 141.83 (d, $^1J_{PC}$ = 41.0 Hz, C_q-3a), 175.66 (d, $^1J_{PC}$ = 48.7 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 79.4 ppm. MS (EI 70 eV, 170 °C): *m*/*z* (%) = 475 (19), 474 (9), 473 (37), 471 (29) [M^+], 394 (11), 392 (11.5), 304 (13), 302 (14), 222 (51), 171 (72), 169 (74), 149 (100), 71 (48), 57 (68). HRMS (ESI, MeOH–FA): $C_{21}H_{16}Br_2NP$ (473.14), calcd for $[M(^{79}Br_2) + H]^+$ 471.9460, found 471.9463.

1-Neopentyl-2-(pyrid-2′-yl)-1,3-benzazaphosphole (6a). Pyridine-2-carboxaldehyde (0.31 mL, 3.26 mmol) and PTSA (81 mg, 15 mol%) were added to **5a** (557 mg, 2.85 mmol) in toluene (10 mL) and were heated to reflux for 24 h. NMR-monitoring showed **6a** as the main product (*ca*. 55% relative intensity). The catalyst was removed with degassed 5% aq. NaOH. Drying on Na_2SO_4, evaporation of toluene in a vacuum and repeated precipitation from the concentrated solution in THF with hexane (THF–*n*-hexane *ca.* 1 : 3) furnished pale yellow **6a**, yield 400 mg (50%). ^{1}H NMR ($CDCl_3$): δ = 0.67 (s, 9 H, Me), 4.31 (vbr, 1 H, NCH_A), 5.53 (vbr, 1 H, NCH_B), 7.16 (tdd, ^3J = 7.9, 7.0, $^4J_{PH}$ = 1.9, ^4J = 1.0 Hz, H-5), 7.25 (tt, ^3J = 7.5, 4.9, ^4J = 1.3, $J \approx$ 1.1 Hz, 1 H, H-5′), 7.38 (tt, ^3J = 8.4, 7.0, ^4J = 1 Hz, 1 H, H-6), 7.71 (br dd, ^3J = 8.6, ^4J = 1 Hz, 1 H, H-7), 7.75 (td, ^3J = 7.8, 7.5, ^4J = 1.8 Hz, 1 H, H-4′), 7.87 (dq, ^3J = 7.8, $^4J_{PH} \approx {}^4J \approx {}^5J$ = 1 Hz, 1 H, H-3′), 8.07 (dddd, ^3J = 7.9, $^3J_{PH}$ = 4.5, ^4J = 1.3, ^5J = 0.6 Hz, 1 H; H-4), 8.69 (dq, ^3J = 4.9, ^4J = 1.8, ^5J = 1 Hz, 1 H; H-6′) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 28.65 (s, C*Me*$_3$), 35.44 (s, C_q), 54.92 (d, $^3J_{PC}$ = 2.6 Hz, NCH_2), 115.08 (s, C-7), 120.14 (d, $^3J_{PC}$ = 11.9 Hz, C-5), 122.29 (br s, C-5′), 124.76 (d, ^4J = 4.0 Hz, C-6), 125.36 (d, ^3J = 11.9 Hz, C-3′), 128.73 (d, ^2J = 22.6 Hz, C-4), 137.04 (s, C-4′), 141.36 (d, ^1J = 37.2 Hz, C_q-3a), 146.09 (d, ^2J = 6.6 Hz, C_q-7a), 148.80 (s, C-6′), 155.73 (d, ^2J = 23.8 Hz, C_q-2′), 175.26 (d, ^1J = 47.8 Hz, C_q-2) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 89.4 ppm. HRMS (ESI, MeOH–FA): $C_{17}H_{19}N_2P$ (282.32), calcd for $[M + H]^+$ 283.1359; found 283.3159.

Detection of 1-methyl-2-phenyl-1,3-benzazaphosphole (6b). The reaction of **5b** with benzaldehyde in toluene with and without PTSA (15 mol%) was carried out on the NMR scale to obtain information about the effect of PTSA and about the reaction intermediates (see *mechanistic aspects* and ^{31}P NMR spectra in the ESI†). The final formation of **6b** was confirmed by good accordance of the ^{31}P and ^{1}H NMR data with **6b**, obtained by cyclocondensation of **5b** with benziminomethylester hydrochloride.[14]

Detection of chromium(0)(tetracarbonyl)(2-(2-diphenylphosphanyl)phenyl-5-methyl-1,3-benzazaphosphole-*P*,*P*′) (8a). Excess $Cr(CO)_4$(nbd) (128.26 mg, 0.45 mmol) was added to a solution of **2a** (90 mg, 0.22 mmol) in THF (5 mL). ^{31}P NMR reaction monitoring after 2 h displayed a mixture of **2a** and **8a**. After 24 h colourless crystals of $Cr(CO)_6$ had separated and the filtrate was concentrated to give 118 mg of orange solid **8a**, contaminated by unconverted $Cr(CO)_4$(nbd). The compound was identified by characteristic NMR data. ^{1}H NMR (CD_2Cl_2): δ = 2.43 (s, 3 H, Me), 6.69 (t, ^3J = 8.4 Hz, 1 H, aryl-H), 7.20, 7.22 (2 superimposed br t, 2 H, aryl-H), 7.15–7.75 (m, 13 H, aryl-H), 7.71 (br d, ^3J = 8.4 Hz, 1 H, aryl-H), 9.44 (br, 1 H, NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.20 (s, Me), 114.44 (d, ^3J = 4.0 Hz, C-7), 123 (vbr, C-4′), 126.28 (d, ^2J = 13.3 Hz, C-4), 128.02 (dd, ^3J = 6, 4.5 Hz, C-6′), 128.38 (d, ^3J = 9.3 Hz, 4 C-*m*), 128.87 (d, ^4J = 4.6 Hz, C-6), 129.87 (d, ^4J = 2.0 Hz, 2 C-*p*), 130.35 (d, ^3J = 15.3 Hz, C_q-5), 131.13 (br s, C-5′), 132.95 (d, ^2J = 11.3 Hz, 4 C-*o*), 134.64 (τ, $|{}^2J + {}^4J|$ = 6.6 Hz, C-3′), 135.32 (d, ^1J = 33.2, ^3J = 5.3 Hz, 2 C_q-i), 136.23 (d, ^1J = 10.6 Hz, C_q-3a), 141.25 (d, ^2J = 2.7 Hz, C_q-7a); nearly noise level: 130.72 (dd, ^1J = 31.2, ^3J = 5.3 Hz, C_q-2′), 159.97 (dd, ^1J = 27.2, ^3J = 11.3 Hz, C_q-2), 218.5 (dd, $^2J_{cis\text{-}PC}$ = 20, 12 Hz, 2 CO), 226.8 (dd, $^2J_{cis\text{-}PC}$ = 13, $^2J_{trans\text{-}PC}$ = 6.6 Hz, 2 CO) ppm; C_q-1′ in noise. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 53.2 (d, $^2J_{PP}$ = 65.5 Hz, PPh_2), 108.5 (d, $^2J_{PP}$ = 65.5 Hz, P_{ring}) ppm.

Molybdenum(0)(tetracarbonyl)(2-(2-diphenylphosphanyl)-phenyl-5-methyl-1,3-benzazaphosphole-*P*,*P*′) (9a). THF (10 mL) was added to a Schlenk flask, charged with **2a** (58.9 mg, 0.144 mmol) and excess $Mo(CO)_4$(nbd) (51.6 mg, 0.172 mmol). Within a few minutes the colour changed from pale yellow to yellow-orange. NMR monitoring after stirring at room temperature for 20 h showed incomplete reaction, but after heating at 40 °C for 4 h it was complete. The mixture was filtered and the solvent and volatiles were removed in a vacuum (10 h, 10^{-3} Torr) to give 63 mg (71%) of orange-brown **9a**. Crystals were formed from a concentrated solution in C_6D_6/CH_3OH, single crystals by slow partial evaporation of a concentrated solution in $CDCl_3$ (crystal data, Table 2). ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 3 H, Me), 6.62 (br t, J = 8.7, 8.4 Hz, 1 H, aryl-H), 7.07, 7.09 (2 superimposed br t, J = 7–8 Hz, 2 H, aryl-H), 7.20–7.61 (br m, 13 H, aryl-H), 7.58 (br d, J = 7.9, 1 H, aryl-H), 9.49 (s br, 1 H, NH) ppm. ^{13}C{^{1}H} and DEPT135 NMR ($CDCl_3$): δ = 21.15 (s, Me), 114.41 (br s, C-7), 125.30 (vbr, C-4′), 126.34 (d, ^2J = 14.6 Hz, C-4), 128.14 (dd, ^3J = 5.5, 3.3 Hz, C-6′), 128.35 (d, ^3J = 9.3 Hz, 4 C-*m*), 128.58 (d, ^4J = 4.5 Hz, C-6), 129.89 (br s, 2 C-*p*), 130.31 (dd, ^1J = 33.2, ^3J = 6.6 Hz, C_q-2′), 130.47 (d, ^3J = 14.6 Hz, C_q-5), 130.87 (br s, C-5′), 133.23 (d, ^2J = 13.3 Hz, 4 C-*o*), 133.95 (τ, $|{}^2J + {}^4J|$ = 6.6 Hz, C-3′), 135.13 (dd,

Table 2 Crystal data and structure refinement for **9a**

Compound	**9a**
Empirical formula	$C_{30}H_{21}MoNO_4P_2$
Formula weight	617.36
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	a = 15.5796(4) Å b = 9.4484(2) Å c = 19.0086(4) Å
Volume	2798.11(11) Å^3
Z	4
Density (calculated)	1.465 Mg m^{-3}
Absorption coefficient	0.619 mm^{-1}
F(000)	1248
Crystal size	0.40 × 0.25 × 0.10 mm^3
ϑ range for data collection	2.41 to 30.51°
Index ranges	$-21 \le h \le 22$, $-13 \le k \le 13$, $-25 \le l \le 27$
Reflections collected	70 559
Independent reflections	8221 [R(int) = 0.0433]
Completeness	98.4% to ϑ = 30.51°
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.96238
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8221/2/349
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0242, wR_2 = 0.0497
R indices (all data)	R_1 = 0.0290, wR_2 = 0.0521
Absolute structure parameter	0.392(18)
Largest diff. peak and hole	0.363 and −0.433 e Å^{-3}

^1J = 33.1, ^3J = 4.0 Hz, 2 C_q-i), 137.95 (dd, ^2J = 11.9, 10.6 Hz, C_q-1′), 138.10 (dd, ^1J = 11.9, ^3J = 4.0 Hz, C_q-3a), 141.07 (d, ^2J = 2.7 Hz, C_q-7a), 160.96 (dd, ^1J = 25.2, ^3J = 10.6 Hz, C_q-2), 207.26 (dd, $^2J_{cis\text{-PC}}$ = 12.6, 8.6 Hz, 2 CO), 215.83 (dd, $^2J_{trans\text{-PC}}$ = 23.9, $^2J_{cis\text{-PC}}$ = 9.3 Hz, CO), 216.22 (dd, $^2J_{trans\text{-PC}}$ = 15.9, $^2J_{cis\text{-PC}}$ = 9.3 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.4 (d, $^2J_{PP}$ = 41.2 Hz, PPh_2), 88.4 (d, $^2J_{PP}$ = 41.2 Hz, P_{ring}) ppm. Elemental analysis, calcd for $C_{30}H_{21}MoNO_4P_2$ (617.38): C 58.36, H 3.43, N 2.27; found: C 58.15, H 3.57, N 2.14%. MS (ESI in MeOH–FA): calcd for $[M(^{98}Mo) - 2CO]^+$ ($C_{28}H_{21}MoNO_2P_2^+$) 563.01, found: 563.01 (and other peaks for the correct isotopic pattern).

Detection of molybdenum(0)(tetracarbonyl)(2-(2-dicyclohexylphosphanyl)phenyl-5-methyl-1,3-benzazaphosphole-*P*,*P*′) (9b). Reaction of **2b** (51 mg, 0.121 mmol) and $Mo(CO)_4$(nbd) (36.3 mg, 0.121 mmol) in THF (10 mL) as described for **9a** furnished 37 mg (73%) of yellow-brown viscous **9b**. ^1H NMR ($CDCl_3$): δ = 1.05–1.45 (m, 11 H, *c*Hex), 1.57–1.85 (m, 9 H), *c*Hex), 2.08–2.23 (m, 2 H, *c*Hex), 2.48 (s, 3 H, 5-Me), 7.23 (d, ^3J = 8.1 Hz, 1 H, aryl-H), 7.40 (t, ^3J = 7.2 Hz, 1 H, aryl-H), 7.47–7.63 (br m, 3 H, aryl-H), 7.69 (br m, 1 H, aryl-H), 7.79 (d, ^3J = 8.1 Hz, 1 H, aryl-H), 9.99 (s br, 1 H, NH) ppm. $^{13}C\{^1H\}$ and DEPT135 NMR ($CDCl_3$): δ = 21.38 (s, Me), 26.34 (C-δ), 27.24 (d, ^3J = 9.3 Hz, C-γ), 27.58 (d, ^3J = 11.9 Hz, C-γ′), 27.94 (d, ^2J = 13.3 Hz, C-β), 27.96 (d, ^2J = 10.6 Hz, C-β′), 37.39 (d, ^1J = 14.6, ^3J = 2.6 Hz, C-α), 114.98 (br s, C-7), 126.36 (vbr, C-4′), 126.34 (d, ^2J = 14.6 Hz, C-4), 127.05 (dd, ^1J = 19, ^3J = 7 Hz, C_q-2′), 127.94 (dd, $^3J \approx {}^3J \approx 4$ Hz, C-6′), 128.81 (d, ^4J = 4.0 Hz, C-6), 130.95 (d, ^3J = 15.6 Hz, C_q-5), 130.70 (br s, C-5′), 133.95 (d, ^2J = 2.7 Hz, C-3′), 138.64 (dd, ^1J = 10.6, ^3J = 4.0 Hz, C_q-3a), 139.44 (t, ^2J = 10 Hz, C_q-1′), 141.46 (d, ^2J = 2.7 Hz, C_q-7a), 160.90 (dd, ^1J = 22.6, ^3J = 8.0 Hz, C_q-2), 208.34 (dd, $^2J_{cis\text{-PC}}$ = 11.9, 9.3 Hz, 2 CO), 216.30 (dd, $^2J_{trans\text{-PC}}$ = 22.6, $^2J_{cis\text{-PC}}$ = 10.6 Hz, CO), 218.53 (dd, $^2J_{trans\text{-PC}}$ = 33.2, $^2J_{cis\text{-PC}}$ = 8.0 Hz, CO *trans* to P*c*Hex$_2$) ppm. ^{31}P NMR ($CDCl_3$): δ = 28.4 (d, $^2J_{PP}$ = 43 Hz, P*c*Hex$_2$), 80.5 (d, $^2J_{PP}$ = 44 Hz, P_{ring}) ppm. HRMS (ESI in THF): $C_{30}H_{33}MoNO_4P_2$ (629.47); **9b** in THF is rapidly oxidized by air and displays peaks for $[M + 2O]^-$ and $[M + 3O]^-$ (half intensity), stronger peaks for $[M + nO - CO]^-$ and strong peaks for $[M + nO - 2CO]^-$ (n = 2, 3) with correct isotopic pattern; calcd for $[M + nO - 2CO]^-$ 606.0861, found: 606.0849.

Crystal structure analysis

Crystals of **9a** were mounted on a glass fiber in an inert oil. Data were recorded at low temperature on a Bruker SMART 1000 CCD using MoK_α-radiation (λ = 0.71073 Å). *Crystal data* are summarized in Table 2. The structures were solved by direct methods and refined by full-matrix least-squares on F^2.[25] Hydrogen atoms were included using a riding model or rigid methyl groups.

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