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Rich Coordination Chemistry of π -Acceptor Dibenzoarsole Ligands

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S Supporting Information

ABSTRACT: A series of dibenzoarsole (also known as 9arsafluorene) derivatives have been prepared, and their coordination chemistry has been investigated. The different ligand topology and the arsenic substituents govern the reactivity of the ligands. We report various crystal structures of palladium and platinum complexes derived from this family of ligands. The biphenyl backbone of the bridged bidentate ligands allows very flexible coordination. We have also studied the application of an allylic Pd complex in nucleophilic substitution reactions, revealing that the benzoarsole substituent is susceptible to metal insertion.



INTRODUCTION

Arsoles, the heavier analogues of pyrroles and phospholes, make up a scarcely explored class of compounds. These fivemembered heterocycles share great similarities with their phosphorus analogues, such as the pyramidalization at the heteroatom, contrasting the planar situation found in pyrrole derivatives. Consequently, the electronic structure differs greatly between the lightest and all other heavier analogues. While pyrroles are highly aromatic,¹ their heavier analogues are significantly less aromatic.² The observed pyramidalization in the heavier heteroles inhibits cyclic electron delocalization between the butadiene fragment and the pnictogen lone pair; however, partial aromaticity is regained from a $\pi^* - \sigma^*$ hyperconjugation with the exocyclic substituent.³ As a consequence, these pyramidal heteroles are π -acceptor ligands because of the stabilization of the lowest unoccupied orbital (LUMO) levels.⁴ Despite the discovery of arsoles in the middle of the last century $^{5-8}$ and the possibility of utilizing the versatile Fagan–Nugent route, $^{9-11}$ only very few reports have dealt with the synthesis and characterization of these systems.¹²⁻¹⁴ Phospholes, on the other hand, have received a great deal of attention over the past decade as interesting ligands for catalysis,¹⁵ coordination compounds,^{16,17} and building blocks for supramolecular assemblies^{18,19} but also as fascinating compounds for optoelectronic materials and organic electronic applications.^{4,20-25} Common to all these phospholes is their facile derivatization, such as oxidation with chalcogens and their coordination to Lewis acids.²⁶ Only very recently has some work discussing the optical properties of arsoles been published.²⁷⁻³² Remarkably, even reports of simple coordination compounds of arsoles are very rare.^{33,34} Recently, very interesting examples of emissive and responsive arsole complexes have been reported.^{35–37} Consequently, a deeper understanding of their coordination properties and their solid

state packing motifs will be essential to tapping the full potential of this class of heavier group 15 heteroles as Lewis bases. The intrinsic differences of phosphorus and arsenic, i.e., their oxo- and thiophilicity, respectively, open new possibilities toward novel ligand systems in catalytic applications³⁸ as well as organic electronics.²⁹

Interesting flexible frameworks have been derived from the 2,2'-biphenyl-bridged bidentate phosphorus ligand frameworks toward dinuclear gold,³⁹ mononuclear palladium,⁴⁰ ruthe-nium,⁴¹ or platinum.⁴² On the other hand, analogous biphenyl-bridged diarsine complexes are rare,^{43,44} and no arsole derivatives have been reported to date.

In this work, we have explored easily accessible dibenzoarsole, also known as 9-arsafluorene, ligands that possess monoand ditopic ligand geometry as well as their coordination to transition metals, such as Pd and Pt (Figure 1). Finally, possible application of an allylic palladium complex is demonstrated for the nucleophilic substitution of benzyl acetate. Crystallographic



Figure 1. Known biphenyl-bridged bidentate ligand systems based on phosphines and arsines. Bis-dibenzoarsole and mixed arsine-arsole ligand frameworks are from this work.

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analysis of the catalyst revealed an unexpected arsenic-carbon bond cleavage and formation of an arsa-palladacycle.

EXPERIMENTAL SECTION

General Remarks. All reactions, unless otherwise specified, were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried over sodium [tetrahydrofuran (THF) or diethyl ether] or calcium hydride [dichloromethane (DCM)]. All chemicals were obtained from Sigma-Aldrich or Fluorochem and used as received. Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol 400 MHz spectrometer operating at 400.13 MHz for ¹H NMR and 100.62 MHz for ¹³C{¹H} NMR. Spectra are referenced internally to residual solvent peaks (¹H and ¹³C). Biphenyl-bridged dibenzoarsole 1 is obtained following a literature procedure (Scheme 1),⁴⁵ and NMR data of phenyl-9-dibenzoarsole (3) are in agreement with previously published data.³⁰

Scheme 1. Synthetic Route for the Formation of Arsole Derivatives $1-4^{a}$



^aDetails and synthetic procedure found in the Experimental Section.

Synthesis of 2. First, 0.51 g of 2,2'-dibromo-biphenyl (1.63 mmol) was dissolved in ~20 mL of THF and the mixture cooled to -78 °C. Subsequently, 1.6 mL of *n*-BuLi (2.5 M in hexane, 4.0 mmol) was added and the mixture stirred for 30 min at this temperature until AsCl₃ (0.30 g, 1.65 mmol) was quickly added. The mixture was slowly allowed to reach room temperature (rt), and 1.0 mL of *n*-BuLi (2.5 M, 2.5 mmol) was added. The reaction was quenched with water and the mixture extracted with DCM giving 150 mg (0.53 mmol, 33%) of arsole **2**: ¹H NMR (400 MHz, CDCl₃) δ 7.89 (m, 2H), 7.69 (m, 2H), 7.43 (m, 2H), 7.30 (m, 2H), 1.67 (t, *J* = 8.0 Hz, 2H), 1.43 (m, 2H), 1.31 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.4, 145.6, 131.2, 128.1, 127.3, 122.3, 30.3, 29.0, 24.7, 13.6; ESI-HRMS calcd for C₁₆H₁₇As [M + H]⁺ 301.05681, found 301.05625.

Synthesis of 3 and 4. First, 1.07 g of 2,2'-dibromo-biphenyl (3.43 mmol) was dissolved in ~20 mL of THF and the mixture cooled to -78 °C. Subsequently, 2.88 mL of *n*-BuLi (2.5 M in hexane, 7.2 mmol) was added and the mixture stirred for 30 min at this temperature until AsCl₃ (700 mg, 3.86 mmol) was quickly added. The mixture was slowly allowed to reach rt, and 2.5 mL of Ph-Li (1.8 M, 4.5 mmol) was added. The reaction was quenched with water and the mixture extracted with DCM giving 730 mg (2.4 mmol, 70% based on 2,2'-dibromo-biphenyl) of arsole **3** and 120 mg of **4** (0.2 mmol, 7%). **4** after column chromatography (silica, 9:1 hexane/ethyl acetate): ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.48 (m, 3H), 7.18–7.31 (m, 8H), 7–34–7.42 (m, 7H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.90 (d *J* = 7.3 Hz, 2H),

6.57 (d, J = 7.7 Hz, 1H); $^{13}\mathrm{C}$ NMR (100 MHz, CDCl₃) δ 122.1, 122.3, 127.5, 127.8, 128.0, 128.4, 128.6, 128.8, 130.5, 131.1, 131.4, 131.6, 132.3, 134.1, 139.5, 139.5, 139.9, 145.1, 146.4, 147.1, 147.9, 147.9; ESI-HRMS calcd for $\mathrm{C_{36}H_{26}As_2}$ [M + O₂ + H]⁺ 641.04375, found 641.04375.

5. Solid PdCl₂ (120 mg, 0.68 mmol) was added to a solution of 2 (80 mg, 0.28 mmol in MeCN). The resulting mixture was stirred for 48 h. The solvent was allowed to completely evaporate, which afforded two types of crystals, identified as $[PdCl_2(MeCN)_2]$ and complex **5**: ¹H NMR (400 MHz, CDCl₃) δ 8.08 (br s, 2H), 7.86 (br s, 2H), 7.52 (br s, 2H), 7.37 (br s, 2H), 7.26 (m, 2H), 7.05 (br s, 2H), 2.52 (br s, 2H), 2.36 (br s, 2H), 1.50 (br s, 2H), 1.36 (br s, 2H), 1.05 (br s, 2H), 0.92 (br s, 2H), 0.81 (br s, 3H), 0.59 (br s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.25, 142.65, 134.84, 131.11, 130.64, 128.83, 128.32, 122.24, 30.23, 28.91, 27.56, 26.48, 24.03, 23.70, 13.53, 13.38.

6. Ligand **2** (110 mg, 0.38 mmol) and $[PdCl_2(MeCN)_2]$ (50 mg, 0.19 mmol) were mixed in DCM (5 mL) and stirred for 2 h. The resulting mixture was filtered with through a Celite pad and kept for crystallization. Orange crystals were obtained by slow evaporation of dichloromethane (121 mg, 0.16 mmol, 84%): ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 7.3 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H) 7.38–7.33 (m, 6H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.0 Hz, 2H), 2.52 (m, 2H), 2.36 (m, 2H), 1.50 (m, 2H), 1.35 (m, 2H) 1.05 (m, 2H), 0.91 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H), 0.59 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.19, 142.63, 134.85, 133.62, 132.76, 131.11, 130.78, 130.65, 128.83, 128.26, 122.25, 122.16, 30.25, 28.83, 27.62, 26.49, 24.18, 23.67, 13.54, 13.35; ESI-HRMS calcd for C₃₂H₃₄As₂Cl₂Pd [M – Cl]⁺ 710.98113, found 710.98004.

7. A solution of $[Pd(CH_3CN)_2Cl_2]$ (29 mg, 0.11 mmol, MeCN, 1 mL) was added to a solution of **1** (67 mg, 0.11 mmol in DCM, 10 mL). The resulting mixture was stirred for 48 h and kept for crystallization by slow evaporation of the solvent: 74 mg yield (0.09 mmol, 86%); ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 7.7 Hz, 2H), 8.14 (d, *J* = 7.5 Hz, 2H), 8.07 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.60–7.72 (m, 8H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 2H), 5.80 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 143.88, 142.80, 142.08, 135.69, 135.57, 134.38, 133.20, 132.69, 131.86, 130.01, 129.43, 129.01, 123.84, 123.62; ESI-HRMS calcd for C₃₆H₂₄As₂Cl₂Pd [M + Na]⁺ 806.86109, found 806.86086.

8. Compound **1** (50 mg, 0.08 mmol) and PtCl₂ (31 mg, 0.08 mmol) were supended in dichloromethane. The resulting mixture was stirred for 2 h and kept for crystallization by slow evaporation of the solvent: 58 mg yield (0.06 mmol, 83%); ¹H NMR (400 MHz, CDCl₃) δ 8.26 (m, 4H), 7.85 (m, 8H), 7.74 (d, *J* = 7.7 Hz, 4H), 7.62 (m, 8H), 7.52 (m, 8H), 7.37 (t, *J* = 7.7 Hz, 4H), 7.01 (m, 4H), 6.92 (t, *J* = 7.7 Hz, 4H), 5.63 (d, *J* = 7.3 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 144.17, 144.03, 135.05, 134.84, 131.82, 131.66, 131.37, 129.32, 128.74, 128.20, 123.04, 122.54; ESI-HRMS calcd for $C_{36}H_{24}As_2Cl_2Pt$ [M + Na]⁺ 895.92215, found 895.92058.

9. A solution of **1** (35 mg, 0.06 mmol, 2 mL of $CHCl_3$) was added to a suspension of excess $PdCl_2$ (70 mg, 0.4 mmol) in acetonitrile (2 mL). The resulting suspension was stirred for 48 h and kept for crystallization letting all volatiles evaporate, yielding a mixture of 7 (minor), **9** (major), and $[PdCl_2(MeCN)_2]$ (major) by visual inspection of the predominately crystalline material. Because of the heterogeneous mixture, no satisfactory NMR data of compound **9** could be obtained. The identity of all three crystalline components was proven by X-ray crystallography.

10. Compound 4 (50 mg, 0.08 mmol) and PdCl₂ (21 mg, 0.08 mmol) in acetonitrile were stirred for 2 h and kept for crystallization by evaporation: 39 mg yield (0.05 mmol, 60%); ¹H NMR (400 MHz, CDCl₃) δ 8.29 (m, 1H), 7.78 (ps d, J = 8.0 Hz, 2H), 7.72 (d + s, J = 7.9 Hz, 2H + 1H), 7.56 (m, 3H), 7.52–7.42 (m, 6H), 7.40–7.26 (m, 6H), 6.99 (m, 2H), 6.86 (t, J = 7.3 Hz, 1H), 6.71 (dd, J = 7.0, 2.3 Hz, 1H), 5.65 (d, J = 7.3 Hz, 1H). Because of contamination with an unidentified side product, insufficient ¹³C NMR data were obtained (see the Supporting Information). ESI-HRMS calcd for C₃₆H₂₆As₂Cl₃Pd [M + Na]⁺ 808.87674, found 808.87474.



Figure 2. Molecular structure of arsole ligands (a) 2,2'-biphenyl-bis-dibenzoarsole, $[(AsC_{12}H_8)_2(C_{12}H_8)]$, 1; (b) phenyl dibenzoarsole, 3; and (c) mixed 2-diphenylarsine-2'-dibenzoarsole biphenyl, 4.

11. Palladium precursor $[Pd(allyl)Cl]_2$ (25 mg) and ligand 1 (100 mg) were stirred in DCM (10 mL) for 90 min and left for slow crystallization: ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, J = 7.3 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.78–7.89 (m, 3H), 7.76 (d, J = 7.7 Hz, 1H), 7.64 (t, J = 7.1 Hz, 1H), 7.59 (d, J = 7.1 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.48 (m, 1H), 7.37–7.44 (m, 2H), 7.26–7.35 (m, 3H), 7.09–7.23 (m, 4H), 6.98–7.03 (m, 2H), 6.86 (t, J = 7.3 Hz, 1H), 6.73 (t, J = 7.3 Hz, 1H), 5.56 (d, J = 7.6 Hz, 1H), 5.42 (m, 1H), 4.67 (d, J = 16.8 Hz, 1H), 4.62 (br s, 1H), 3.15 (br s, 1H), 2.97 (br s, 1H). We were unable to obtain ¹³C NMR data for complex 11 because of its low solubility. ESI-HRMS calcd for C₃₉H₂₉As₂ClPd [M-Cl]⁺ 752.97449, found 752.97386.

Catalysis. A flame-dried Schlenk tube containing a stir bar was charged with [Pd(allyl)Cl]₂ (5 mg, 2.5% mol), biphenyl bisarsole 1 (19 mg, 5.5% mol), and DCM (1 mL). The mixture was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 1 h, after which the solvent was removed under vacuum. A solution of 1phenylallyl acetate (100 mg, 0.57 mmol) and aniline (0.1 mL, 1.14 mmol) in toluene (2 mL) was added to the complex. The slurry was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 2 h. The solvent was removed, and the crude product was purified by column chromatography on silica gel eluting with a pentane/EtOAc mixture (25:1) to give the desired product (94 mg, 79% yield) as a light yellow oil: ¹H NMR (CDCl₃, 400 MHz) δ 7.48– 7.17 (m, 7H), 6.78 (tt, J = 7.3, 1 Hz, 1H), 6.75-6.63 (m, 3H), 6.37 (dt, I = 15.9, 5.8 Hz, 1H), 3.98 (dd, I = 5.8, 1.6 Hz, 2H), 3.88 (br s, 1.6 Hz, 2H), 3.88 (br1H); ¹³C NMR (CDCl₂, 100 MHz) δ 148.0, 136.9, 131.5, 129.3 (2), 128.6 (2), 127.6, 127.1, 126.3 (2), 117.6, 113.1 (2), 46.2; IR (neat) 3413, 3052, 3023, 2919, 2835, 1602, 1505, 1430, 1448, 1322, 1250, 967, 748, 692 cm⁻¹; ESI-HRMS calcd for $C_{15}H_{16}N [M + H]^+$ 210.1277. found 210.1264

Crystallography. Reflections were collected on a Bruker APEXII CCD diffractometer using graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. Crystals were mounted on the loop. Data reduction was performed with SAINT.⁴⁶ Absorption corrections for the area detector were performed using SADABS.47 Structures were determined by direct methods and refined by least-squares methods on F^2 using the SHELX suit of programs.⁴⁸ The data collections for all crystals were performed at 100(2) K. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained in geometrical positions to their parent atoms. The solvated atoms located in the packing cavities of 11 were treated as a diffuse contribution to the overall scattering without specific atom positions using the SQUEEZE algorithm implemented in PLATON. The crystal quality of 7 was poor, and partial twinning was observed. While the overall connectivity is not in doubt, attention should be taken during evaluation of bond lengths and angles. Consequently, we do not discuss the metric parameters of 7. Crystallographic data for all the complexes and selected bond length and bond angles are listed in Tables S1 and S2.

RESULTS AND DISCUSSION

In this study, we have synthesized and investigated a series of dibenzoarsoles and studied their coordination properties. Monotopic dibenzoarsoles 2 and 3 are obtained through chloride substitution of As-chloro-dibenzoarsole with n-BuLi and Ph-Li, respectively. In the preparation of 3, a side product of up to 10% of mixed arsine-arsole bidentate ligand 4 is also obtained. Intrigued by the formation of the biphenyl-bridged bidentate arsine-arsole ligand, we have prepared biphenylbridged bis-dibenzoarsole 1, which was obtained through the reaction of 2,2'-dilithio-biphenyl with stoichiometric amounts of arsenic trichloride (3:2 ratio) in excellent yields following literature procedures.⁴⁵ Surprisingly, the lighter phosphole derivative is unknown, while the Sb49 and Bi derivatives50 have been described previously. We were able to obtain crystals suitable for X-ray analysis of ligands 1, 3, and 4, whereas no solid state structure of butyl dibenzoarsole 2 could be obtained. The crystal structure of bisdibenzoarsole 1 was determined in monoclinic space group P2(1)/n. From the crystal structure analysis, it is evident that the arsole moieties are bridged by 2,2'-biphenyl. The steric demand of the arsole moieties induces a considerable twist of the central biphenyl linker, resulting in a $61.2(4)^{\circ}$ angle between the least-squares planes (Figure 2a), which is significantly smaller than that of the bismuth analogue $[80(1)^{\circ}]^{41}$ Consequently, the As atoms are separated by 3.248(6) Å. The structure of mixed diphenylarsine-dibenzoarsole 4 was determined in monoclinic space group P2(1)/c(Figure 2c). The increased steric demand of the diphenyl arsine moiety results in a larger twist angle of $86.10(3)^{\circ}$ and an increased through space As...As distance of 4.277(7) Å.

The crystal structure of phenyldibenzoarsole (3) has previously been reported in the monoclinic space group from data obtained at room temperature.⁵¹ Our crystallographic analysis (performed at 100 K) indicates that 3 crystallizes in orthorhombic space group P2(1)2(1)2(1), confirming the previous molecular structure (Figure 2b). The arsoles all exhibit typical metric parameters as expected for this class of dibenzoheteroles. Interestingly, the arsoles show C–As–C angles between 98.8° and 102.0°, which are only slightly reduced compared to those of the corresponding phenyl-dibenzophospholes, ^{52,53} indicating similar hybridization of the As atom and a comparable s-contribution to the lone pair.

Coordination Studies. With these ligands in hand, we started to explore the coordination of these arsoles toward heavy metals, especially palladium, which is one of the most important metals in catalysis. Recent studies of the coordination of arsole to Pd explored the [4+2] cycloaddition reactivity

of these complexes to form arsa-norbornene derivatives.^{54,55} First, we have reacted monodentate arsole 2 with $[PdCl_2]$ in acetonitrile (MeCN) (Scheme 2). Structures of single crystals

Scheme 2. Synthesis of Various Arsole Complexes Using Ligands 1, 2, and 4



of complex **5** were determined in trigonal space group $R\overline{3}$. Surprisingly, we found that two ligands coordinate in a *trans* fashion to a planar Pd dimer having two bridging and two terminal chloride ligands (Figure 3a), which was also found for



Figure 3. Single-crystal X-ray structures of (a) 5 and (b) 6.

other phosphole,⁵⁶ phosphite,⁵⁷ and regular phosphine ligands. The As–Pd₂Cl₄–As fragment forms an almost perfect plane with maximal deviations from the least-squares planes of only 0.082(5) Å for Cl1. There is only one structural report of an arsine-coordinated Pd₂Cl₄ dinuclear complex, which however shows significant distortion from planarity adopting an envelope shape of the central Pd₂(μ -Cl₂ unit.⁵⁸

Utilizing a different palladium source {[PdCl₂(MeCN)₂]} and a strict 1:2 metal:ligand ratio, mononuclear complex **6** was obtained as orange crystals. The structure was determined in monoclinic space group P2(1)/n with half a molecule in the asymmetric unit. As expected for nonbridged systems, the ligands adopt a *trans* configuration. Because of the *transoid* square planar geometry of the two dibenzoarsole systems, no intramolecular π - π actions are observed (Figure 3b). Proton

and carbon NMR data, however, display two sets of signals, which points toward the presence of two stable conformers in solution, i.e., a transoid and a cisoid species. The reaction of biphenyl-bridged bisdibenzoarsole 1 with suitable Pd(II) and Pt(II) salts gives expected mononuclear complexes 7 and 8, respectively.

Because of the lack of good quality crystallographic data for complex 7, we have focused the structural discussion on isostructural platinum complex 8, which crystallizes in monoclinic space group C2/c with half of the molecule in asymmetric unit (Figure 4a and Figure S1). The Pt(II) complex



Figure 4. Single-crystal X-ray structures of (a) 8 and (b) 9.

shows a fully planar geometry and a cis arrangement imposed by the ligand topology with an As-Pt-As angle of $91.06(2)^{\circ}$. The angle between the least-squares planes of the biphenyl bridge decreased to 58.39°(10) [from 61.2(4)° in 1], although with a slight increase in the As…As distance to 3.338(1) Å [from 3.248(6) Å in 1] upon coordination. If bidentate ligand 1 is treated with an excess of PdCl₂ in MeCN, crystals of a dinuclear Pd complex (9) are obtained. Compound 9 crystallizes in monoclinic space group P2/c with a halfmolecule in the asymmetric unit. The dibenzoarsole units act as independent donor sites coordinating each to a trans-PdCl₂ center (Figure 4b). The coordination environment of the square planar metal center is completed with one MeCN molecule trans to the As donor. Two further solvent molecules are in the packing cavity (Figure S2). In the case of 9, the two metal centers maximize their distance and the biphenyl twist angle becomes $121.6(1)^{\circ}$. We observe a large intermolecular As...As separation of 5.283(0) Å in this complex.

The structural analysis of these coordination compounds demonstrates the flexibility of the ligand framework to adjust to variable coordination modes. Ultimately, we have prepared a Pd complex of mixed arsine-arsole ligand 4. Compound 10 crystallizes in monoclinic space group P2(1)/c along with four chloroform solvents in the asymmetric unit (Figure 5 and Figure S3). The *cis*-Pd(II) center shows only a small deviation from a perfectly square planar coordination mode. The calculated Pd-As bond lengths for the arsine and arsole are 2.359(2) and 2.337(4) Å, respectively, exemplifying their similar donor properties. The torsion of the biphenyl linker is also reduced to $67.53(3)^{\circ}$ compared to $86.10(3)^{\circ}$ in 4 but still significantly larger than in Pt complex 8; however, the As-Pd-As angles are quite similar [94.1(1)°]. The solid state structure



Figure 5. Single-crystal X-ray structure of 10. Solvent molecules have been omitted for the sake of clarity.

shows large cavities that are solvated by chloroform molecules in a zigzag manner. These show intermolecular H···Cl interactions between the three solvated chloroforms and one chloride of complex 10 (Figure S4).

Catalysis. From our theoretical comparison of group 15 heteroles (1 and its phosphorus analogue, 1-P) with triphenyl phosphine and triphenyl arsine, we clearly see stabilized LUMO (lowest unoccupied molecular orbitals) levels for the heteroles. The arsole is less sensitive to oxidation by air and also has a LUMO ($\Delta = 0.04 \text{ eV}$) at a level lower than that of the phosphorus analogue (for details, see pages 21–25 of the Supporting Information). This fueled our interest in investigating the presented bidentate ligands in palladium-catalyzed nucleophilic substitution reactions, which are known to benefit from strongly π -accepting ligands.^{59,60} On the other hand, the lower oxophilicity of the arsole ligands should make these systems less prone to undergoing oxidative decomposition reactions.

For this purpose, we have investigated the reaction of anillin with the phenyl allyl alcohol and activated, i.e., acetate-

Scheme 3. Attempted Nucleophilic Substitution Reactions^a

derivatized, allylic alcohol (reaction 1; for details see also Table S3, the Supporting Information, and Scheme 3). The catalytically active species was generated in situ by mixing ligand 1 with a suitable palladium source, i.e., $[Pd(allyl)Cl]_2$, in DCM for 1.5 h. We observed no conversion of the free alcohol (E1a) and only moderate reactivity of the acetate derivative (E1b) in reaction 1. Surprisingly, longer reaction times (24 h) and higher temperatures did not significantly improve the reactivity, and the best results were obtained after 6 h (37% conversion). As a comparison, we used triphenyl arsine as a ligand (11 mol %), which showed almost no conversion after 6 h (10%). Similar reactivity was observed for the slightly more hindered substrate E2 to give product P2 in 77% yield after 18 h and higher catalyst loadings. In contrast, substrate E3 showed almost full conversion to isomerized product P3 at room temperature within 2 h as the sole product, while P3' was not observed. In this case, similar reactivity was observed with AsPh₃ as a ligand, requiring slightly longer reaction times (2.5 h) to reach completion. In addition, the reactivity of the simple allyl acetate E4 with aniline was tested and proved to give moderate results (74% conversion after 4 h). Similarly, monodentate phospholes⁶¹ and bidentate 1,1'-bisphosphole systems⁶² have been used in allylic substitutions using anionic malonitrile, giving satisfactory results. Other nucleophiles (thiophenol, benzylic alcohol, and indole) were tested but gave unsatisfactory results (Table S3). Surprised by this reactivity, we opted to investigate the catalytically active species to gain further insights into the reactivity of this catalyst.

We were able to grow crystal from the reaction mixture of ligand 1 with palladium dimer $[Pd(allyl)Cl]_2$ in DCM layered by hexane upon prolonged standing. The structure of complex 11 was determined in trigonal space group $R\overline{3}$. To our great surprise, we found that the ligand framework did not stay intact,



 ${}^{a}R = H$ (a) or COCH₃ (b). Possible formation of cyclometalated complex 11 via a π -allyl complex 11'.

but the Pd inserted into the biphenyl-As bond, giving the cyclo-metalated arsapalladacycle (Figure 6). Consequently, a



Figure 6. Single-crystal X-ray structure of the resulting cyclometalated complex 11.

migration of the allyl moiety to the released As center is observed, affording an allyl-dibenzoarsole ligand. The coordination environment of the Pd center is completed with one chloride trans to the carbon ligand with typical Pd-Cl and Pd-C distances of 2.381(0) and 2.012(0) Å, respectively. The biphenyl shows a twist of $44.0(3)^\circ$, which is the smallest angle observed in this series of compounds. Although the formation of cyclometalated species is reported through a methyl C-H activation with Pt⁶³ and Pd,⁶⁴ Ru⁶⁵ having arsine and imine ligands, respectively, an allyl migration with concomitant As-CArvl bond cleavage has not been observed previously. We assume that the lack of catalytic activity in reaction 1 can be at least partially ascribed to the observed catalyst rearrangement, while fast catalytic reactions such as the transformation of activated substrates E2 reach completion. Presumably, the first and catalytically active species is complex 11' possessing a weakly coordinating chloride ligand, which slowly rearranges to isolated rearrangement product 11.

Conclusions. We describe the facile synthesis of electron deficient ligand systems based on easily accessible dibenzoarsole fragments. Coordination studies reveal the flexible nature of these ligand frameworks to from a variety of mono- and dinuclear metal complexes. Possible application of these ligands in the nucleophilic substitution of activated allylic alcohols is demonstrated. In summary, we report the synthesis and extensive structural investigations of metal complexes demonstrating the rich coordination chemistry and unique reactivity of these dibenzoarsole ligands. Moreover, an unusual rearrangement of an allylic intermediate is observed to give an arsapalladacycle as an off-cycle catalyst species. The coordination chemistry of this ligand framework and comparison with their phosphorus analogues with respect to other transition metals are currently under investigation in our lab, along with further catalytic studies.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00100.

Synthetic procedures, product characterization, and spectral data (PDF)

- Crystallographic tables for 1 (CIF)
- Crystallographic tables for 3 (CIF)
- Crystallographic tables for 4 (CIF)

Crystallographic tables for 5 (CIF) Crystallographic tables for 6 (CIF) Crystallographic tables for 7 (CIF) Crystallographic tables for 8 (CIF) Crystallographic tables for 9 (CIF) Crystallographic tables for 10 (CIF) Crystallographic tables for 11 (CIF)

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The authors declare no competing financial interest.

CCDC 1512678–1512687 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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