

Dalton Transactions

An international journal of inorganic chemistry

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Terphenyl(bisamino)phosphines: Electron-rich Ligands for Gold-Catalysis

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Terphenyl(bisamino)phosphines have been identified as effective ligands in cationic gold(I) complexes for the hydroamination of acetylenes. These systems are related to Buchwald phosphines and their steric properties have been evaluated. Effective hydroamination was noted even at low catalyst loadings and a series of cationic gold(I) complexes has been structurally characterized clearly indicating stabilizing effects through gold-arene interactions.

Transition metal catalysis is governed by the influence of multiple factors; however, most crucial are the following three: Metals, substrates and ligands.¹ Among the plethora of ligands used in transition metal catalysis phosphines have been demonstrated to be an invaluable ligand class in a variety of transformations. Buchwald and co-workers have developed the so-called Buchwald-type phosphines, which have been shown to occupy two coordination sites in low-valent Pd-complexes (Figure 1, A).²⁻⁴ In addition to the P-Pd interaction an η^1 -Pd-C_{ipso} bonding interaction was found in the complex LPd(dba) (L = 2-(2',6'-dimethoxybiphenyl)dicyclohexylphosphine; dba = dibenzylidene-acetone).⁵ The 2-biphenyl moiety in this ligand class has allowed to achieve the challenging coupling of aryl chlorides and extremely hindered aryl boronic acids in Suzuki-Miyaura cross-coupling reactions. Since their initial synthesis various Buchwald-type phosphines have been presented and are now commercially available (e.g. JohnPhos).⁶

In order to access the electronic properties of phosphines usually Tolman's cone angle and/or electronic parameter (TPE) are utilized, allowing to measure direct ligand metal interactions.^{7, 8} In contrast to Pd-catalysis (with mostly square planar complexes), in gold(I)-catalysis the linear coordination

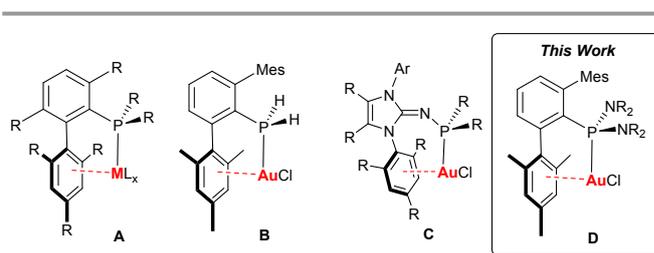


Figure 1. General metal complexes with Buchwald-type ligands (A), related gold complexes from the literature (B, C), and synthetic targets of this study (D).

mode at gold is operational. This forces substrates into transposition of the ligand, which enhances its electronic effects. Cationic gold complexes are well suited for the electrophilic activation of alkynes and their subsequent functionalization with a variety of nucleophiles.⁹⁻¹¹ This preference for alkyne activation has been attributed to the low LUMO energies of Au-alkyne complexes, rendering them more electrophilic.^{12, 13} In Au(I) catalysis a major drawback is the decay of the gold catalyst, which results from reduction of the cationic gold center to Au(0).¹⁴ It has been shown that in many of these transformations electron-rich phosphine ligands outperform their electron-deficient counterparts. For the intermolecular amination of alkynes electron-rich phosphines with a 2-biphenyl moiety are considered superior.¹⁵ Comparing the TEP-values of common Buchwald-type phosphines show that they do not exceed the donor strength of simple ^tBu₃P,⁸ and the prominent class of N-heterocyclic carbenes (NHCs) are stronger σ -donor ligands (Figure 1).¹⁶ Dielmann and co-workers, as well as Sundermayer et al. have recently pushed the electron-donating ability of phosphines beyond their classical endpoint through P-substitution with N-heterocyclic imines (NHIs)¹⁷ or phosphazenes,¹⁸ respectively. In addition, the NHI-functionalization allows the metal center to engage in additional interaction with the aryl-substituents in the N_{NHC}-position of the carbene (Figure 1, C).

Terphenyl-groups, of the general formula 2,6-Ar₂-C₆H₃, have played a leading role in advancing the chemistry of low-valent main group and transition metal species.¹⁹⁻²³ A reagent

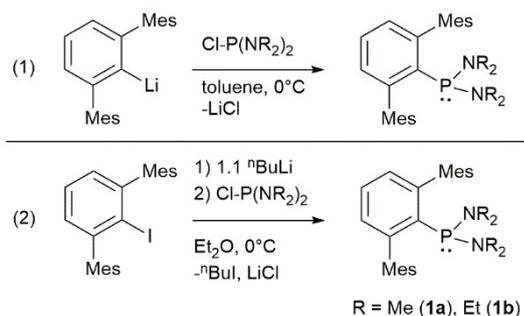
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Electronic Supplementary Information (ESI) available: Synthesis and characterization of compounds, NMR spectra, crystallographic, and computational details. CIFs available from the CCDC, deposition numbers 2014543-2014551. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x{

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Scheme 1. Two synthetic routes towards terphenyl-substituted bisaminophosphines **1a** (R = Me) and **1b** (R = Et).

commonly used to introduce the terphenyl moiety is Ter-Li (Ter = 2,6-Mes₂-C₆H₃),²⁴ which can be treated with element halides to access Ter-EX_n species.^{17, 25, 26} In our hands treatment of Ter-Li with PCl₃ often resulted in trace amounts of Ter-H contaminating the desired Ter-PCl₂ product.²⁷ Thus, we were interested in a way to circumvent the formation of Ter-H. Ragnogna et al. have recently described the successful preparation of [TerPS]₂, a source of monomeric phosphinidene sulfides.²⁸ [TerPS]₂ is synthesized by treating Ter-PCl₂ with S(SiMe₃)₂. In their study the authors outlined an alternative route towards Ter-PCl₂. Additionally, TerPH₂ was shown to form AuCl complexes in which stabilizing arene-interactions with one of the flanking mesityl group are detected (Figure 1, B).²⁹ In this contribution we describe the application of the TerPCl₂ precursors TerP(NR₂)₂ [R = Me (**1Me**), Et (**1Et**)] as Buchwald-type phosphine ligands in gold(I)-catalyzed hydroamination reactions of terminal alkynes (Figure 1, D). The effect of the amino groups was investigated on a theoretical basis and an efficient tool for the estimation of the TEP_{Ni}-value is presented.

Results and discussion

Ragnogna and co-workers have recently described a route towards Ter-PCl₂ through aminolysis of Ter-P(NEt₂)₂ with dry HCl.^{28, 30} Consequently, we prepared Ter-P(NR₂)₂ [R = Me (**1a**), Et (**1b**)] by treatment of isolated Ter-Li with ClP(NR₂)₂ (R = Me, Et; an HCl-free P-source) in toluene at ambient temperature (Scheme 1, reaction 1). In case of **1a**, filtration over a celite-padded frit and removal of the solvent resulted in the isolation of an analytically pure colourless solid in 67% yield. For **1b**, after stirring for 1.5 h, the solvent was removed and the residue was extracted with *n*-hexane, concentrated to incipient crystallization and standing at 5 °C overnight afforded **1b** as an analytically pure colourless crystalline solid, in a moderate yield of 40%. We found that consistently higher yields are obtained by starting from Ter-I. Lithiation of Ter-I with 2.5 M ⁿBuLi (in *n*-hexane) in Et₂O at 0 °C and subsequent treatment with ClP(NR₂)₂ afforded **1a** (79%) and **1b** (89%) in good isolated yields (Scheme 1, reaction 2). In addition, this synthetic approach can be easily scaled and **1b** was prepared on a multigram scale. Ligands **1a** and **1b** are characterized by ³¹P NMR signals at 102.5 and 100.2 ppm, respectively, upfield- shifted compared to their

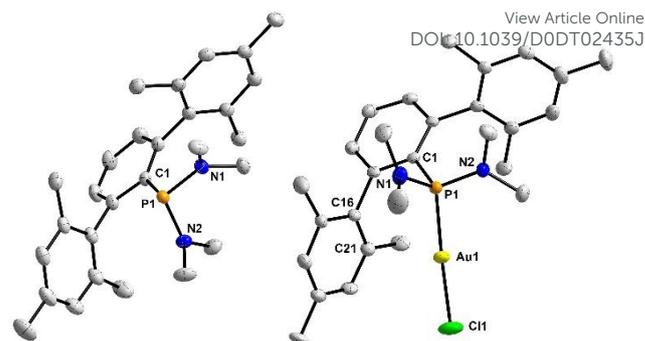
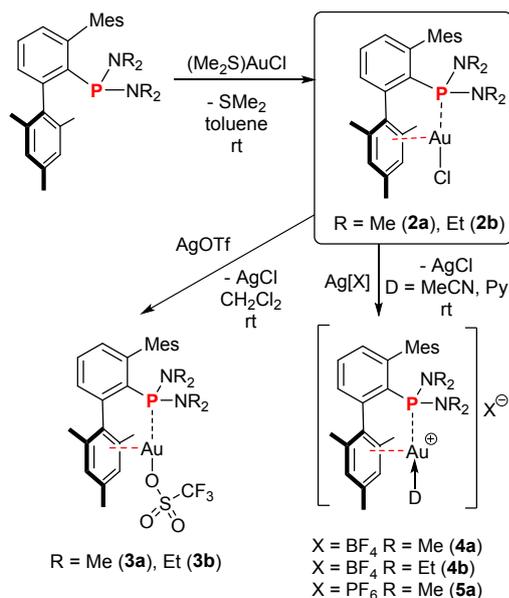


Figure 2. POV-Ray depiction of the molecular structure of **1a** (left) and **2a** (right). Ellipsoids are drawn at 50% probability, 150(2) K. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) of **1a** (left): C1–P1 1.8591(14), P1–N1 1.6827(12), P1–N2 1.6850(13), P1–C1 1.8591(14); N2–P1–N1 107.79(6), N1–P1–C1 108.37(6), N2–P1–C1 97.87(6), C25–N1–C26 112.90(13), C25–N1–P1 126.32(11), C26–N1–P1 118.37(11), C27–N2–C28 112.66(13), C27–N2–P1 117.47(10), C28–N2–P1 126.48(10). **2a** (right): P1–N2 1.657(4), P1–N1 1.659(4), P1–C1 1.846(4), P1–Au1 2.2366(11), C1–Au1 2.3017(14), C16–Au1 3.2839(33), C21–Au1 3.1008(43); N2–P1–N1 108.5(2), N2–P1–C1 113.3(2), N1–P1–C1 99.33(19); C25–N1–C26 112.1(4), C25–N1–P1 118.2(3), C26–N1–P1 124.0(3), C27–N2–C28 112.5(4), C27–N2–P1 123.4(3), C28–N2–P1 123.5(3); Au1–P1–C1–C2 -128.2(3).

respective ClP(NR₂)₂ precursors. In the ¹H NMR spectrum of **1a** and **1b** two signals for the ortho and para CH₃-groups of the mesityl groups in a 2:1 ratio are observed. In **1a** a doublet corresponding to the two NMe₂ groups is detected, indicating C₂ symmetry in solution. In **1b** a complex multiplet is observed for the methylene protons in the Et-groups of the NEt₂-moiety, and a triplet for the Me-groups. X-ray quality crystals of **1a** and **1b** were grown from saturated *n*-hexane solutions at 5 °C over a period of 24 h. The phosphorus atoms show a coordination environment deviating significantly from an ideal trigonal pyramid [Σ(<P) (**1a**) 314.03°, (**1b**) 317.26°, cf. TerPMe₂³¹ 309.0°, TerPCl₂³² 305.58°], which is further supported by NBO analysis [wB97XD/6-31g(d,p) level of theory] showing a 50/50 contribution of 3s and 3p orbitals for the lone pair (LP) on phosphorus.³³ The P–C_{Ter} bond lengths are [(**1a**) 1.8591(14), (**1b**) 1.813(11) Å] indicative of P–C single bonds [Σr_{cov}(P–C) = 1.85 Å].³⁴ The P–N distances [(**1a**) P1–N1 1.6981(11), P1–N2 1.6942(12) Å; (**1b**) P1–N1 1.6981(11), P1–N2 1.6942(12); cf. (Me₃Si)₂NPCl₂ P–N 1.6468(8) Å]³⁵ are contracted [Σr_{cov}(P–N) = 1.82 Å],³⁴ hinting at partial double bond character through interaction of the N-LPs with the other σ*(P–N) orbitals as shown through 2nd order perturbation analysis using NBO with stabilization energies for **1a** of 14.5 and 10.2 and for **1b** of 18.1 and 9.5 kcal/mol, respectively. The sum of angles at the N in **1b** deviate from the expected trigonal planar coordination environment, and minimal pyramidalization is observed [Σ(<N1) = 352.78°].

With the structural analysis of **1a** and **1b** in hand, the structural resemblance with Buchwald's dialkylbiarylphosphines became evident. These are regarded as privileged ligands in various Pd- and Au-catalyzed reactions. In analogy to the Buchwald systems the 2,6-substitution pattern on the central aryl moiety of the terphenyl-framework, affords a binding pocket about the phosphorus that would allow for arene interactions of a



Scheme 2. Synthesis of gold complexes **2** and transformation into **3** and donor-stabilized complexes **4** and **5a**.

coordinated metal with one of the flanking mesityl groups. Similar systems based on redox-responsive terphenyl-substituted phosphonites have been recently described by Breher and co-workers.³⁶ Jones et al. pushed this concept further by introducing bisbiphenyl phosphines providing enhanced stability for cationic gold centers.³⁷ In addition, the steric and electronic properties of related Ar₂C₆H₃-PR₂ systems have been studied in detail.^{38, 39} Combination of **1a** or **1b** with one equivalent of AuCl(SMe₂) in CH₂Cl₂ under the exclusion of light at room temperature for 1 h, subsequent concentration and layering with *n*-hexane afforded **2a** (67%) and **2b** (91%) in good to excellent isolated yields as colorless X-ray quality crystals (Scheme 2). Upon coordination the P atom is minimally shielded as shown by a ³¹P NMR shift of 96.7 ppm (**2a**) and 93.3 ppm (**2b**), respectively. This trend is also reflected in the theoretic NMR shifts obtained from GIAO calculations on the wB97XD/6-31g(d,p)/ECP60MWD level of theory.³³ In the ¹H NMR spectrum both complexes show only two signals for the Me-groups of the terphenyl-moiety, indicating free rotation about the P-C_{Ter} axis on the NMR timescale at room temperature. SXRD experiments revealed the expected arene-interactions between the Au(I)-center and one of the ortho-mesityl groups of the terphenyl moiety. Upon coordination to AuCl the sum of angles at phosphorus increases [Σ(<P) (**2a**) 321.13°, (**2b**) 323.55°, cf. (TerPMe₂)AuCl 318.33°]²⁹ and the P-N bonds are contracted by ca. 2% [(**2a**) P1-N1 1.659(4) Å, P1-N2 1.657(4) Å; (**2b**) P1-N1 1.6665(17) Å, P1-N2 1.6604(17) Å] when compared with the free ligands **1a** and **1b**. The complexes show a nearly linear P-Au-Cl arrangement with P-Au distances [(**2a**) P1-Au1 2.2366(11); (**2b**) 2.2445(5) Å; cf. (TerPMe₂)AuCl 2.2964(10) Å]²⁹ in the expected range for phosphine gold complexes.

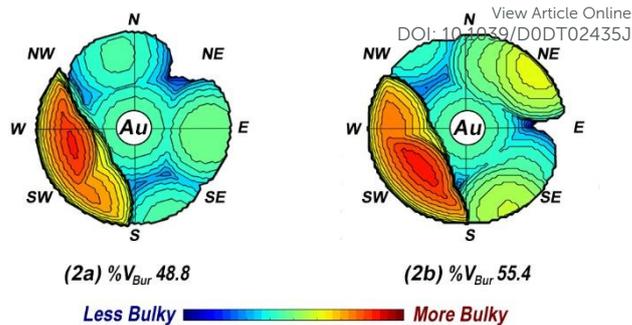


Figure 3. Steric maps of gold complexes **2a** (left) and **2b** (right).

In **2a** and **2b** there are close contacts between Au1 and one of the flanking terphenyl groups [(**2a**) C21-Au1 3.1008(43); (**2b**) C17-Au1 2.9707(20) Å], which is in contrast to the known complex (TerPMe₂)AuCl.²⁹ This stabilizing arene-interaction was further authenticated through an analysis of the electron density of an optimized structure at the wB97XD/6-31g(d,p) level of theory, using the AIM (Atoms in Molecules) approach.⁴⁰ This showed a line critical point between Au and C21 (**2a**) and C17 (**2b**), respectively (see ESI for details),⁴¹ and supports the notion that the mesityl group provide meaningful stabilization. Using the SambVca 2.1 online application the steric properties of ligands **1a** and **1b** were analysed (based on the molecular structures of complexes **2**).⁴² This showed percent buried volumes (%V_{Bur}) of 48.8% (**1Me**) and 55.4% (**1Et**), respectively. The %V_{Bur} describes how much volume of a sphere centered on the metal (*r*_{sphere} = 3.5 Å; *d*_{M-L} = **2a** 2.2366(11); **2b** 2.2445(5) Å) is occupied by the ligand. From the steric maps it is evident that the flanking mesityl group takes up major space in the SW-quadrant of the xy-plane perpendicular to the P-Au-axis (Figure 3), while the NMe₂ groups occupy less space than the NEt₂-groups, which is clearly reflected in the NE, E and SE quadrants of the steric maps. This is in the range of JohnPhos (50.9%), however, exceeds the value of simple phosphines (PPh₃ 34.5%, P^tBu₃ 42.4%).⁴³

In a next series of experiments, we investigated the formation of cationic gold complexes. As an entry **2a** and **2b** were treated with AgOTf in benzene and ³¹P NMR spectroscopy of the reaction mixtures showed the formation of new species with singlet resonance at 86.5 ppm and 78.9 ppm, respectively. Interestingly, the ¹⁹F NMR spectrum showed a singlet at -76.6 ppm, which is in agreement with a covalently bound triflate group (c.f. Ter[Me₂(OTf)Si]N-Sb(Cl)Me δ(¹⁹F) = -76.95 ppm).³⁵ After removal of AgCl by filtration, concentration to incipient crystallization, and layering with *n*-hexane [TerP(NMe₂)₂]AuOTf (**3a**) and [TerP(NEt₂)₂]AuOTf (**3b**) were afforded as colourless solids in 64% and 49% isolated yield, respectively. X-Ray quality crystals of **3b** were obtained from a saturated CH₂Cl₂ solution layered with *n*-hexane after standing at 5 °C for 24 h (Figure 4, left). The Au-P distance is shorter than in **2a** and **2b** [(**3b**) P1-Au1 2.2187(4) Å], hinting at a more positive Au-center. This increase is further supported by two close contacts between gold and one of the flanking mesityl groups [C7-Au1 3.0506(14), C8-Au1 2.9955(13) Å]. Overall, the metrical parameters are close to complexes **2a** and **2b**.

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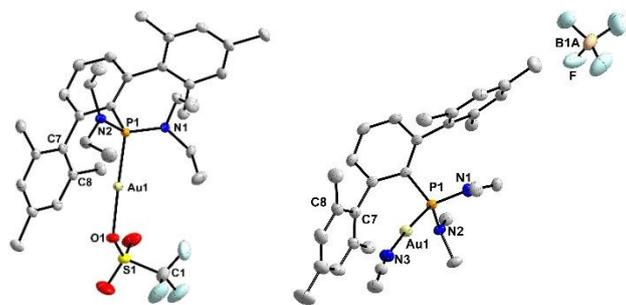
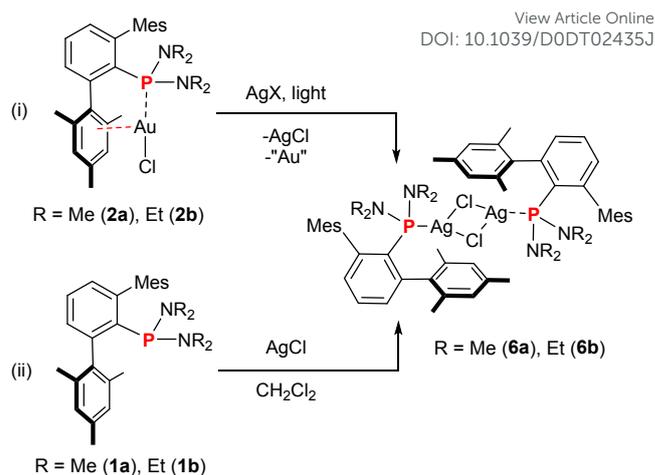


Figure 4. POV-Ray depiction of the molecular structure of **3b** (left) and **4a** (right). Ellipsoids are drawn at 50% probability, 150(2) K. All hydrogen atoms in **4a** have been omitted for clarity. Selected bond lengths (Å) and angles (°) of **3b** (left): C1–P1 1.8632(14), P1–N1 1.6528(13), P1–N2 1.6580(13), P1–Au1 2.2187(4), P1–O1 2.0948(11), C7–Au1 3.0506(14), C8–Au1 2.9955(13); N2–P1–N1 109.44(7), N1–P1–C1 115.66(6), N2–P1–C1 100.83(6), C25–N1–C26 115.42(13), C27–N1–P1 123.76(11), C25–N1–P1 120.55(11), C29–N2–C31 115.62(12), C29–N2–P1 124.48(10), C31–N2–P1 119.79(10), O1–Au1–P1 174.42(4). **4a** (right): P1–N2 1.6559(18), P1–N1 1.6588(19), P1–C1 1.837(2), P1–Au1 2.2376(5), Au1–N3 2.0431(18), C7–Au1 3.1364(23), C8–Au1 3.0504(24); N2–P1–N1 108.69(10), N2–P1–C1 101.34(9), N1–P1–C1 113.57(10); C25–N1–C26 112.75(18), C25–N1–P1 122.20(15), C26–N1–P1 123.72(15), C27–N2–C28 112.48(18), C27–N2–P1 117.44(15), C28–N2–P1 125.49(15), N3–Au1–P1 174.33(6), C29–N3–Au1 169.5(2); Au1–P1–C1–C2 47.17(16).

To obtain an active catalyst for the hydroamination of alkynes with anilines, **2a** and **2b** were treated with AgBF_4 in CH_3CN and after filtration, an aliquot was taken for NMR analysis. In the ^{31}P NMR spectrum new signals highfield-shifted at 89.7 (**4a**) and 84.4 ppm (**4b**), respectively, compared to the starting material were detected. Broad resonances in the ^1H NMR spectrum at 0.98 and 1.46 ppm, respectively, indicate a coordinated CH_3CN molecule, which is further supported by a ^{19}F NMR shift for both complexes of -150.2 ppm, showing a non-interacting $[\text{BF}_4]^-$ anion. Colourless X-ray quality crystals of **4a** were obtained from a saturated C_6D_6 solution and revealed the expected ion-separated structure with a threefold disordered $[\text{BF}_4]^-$ anion (Figure 4, right). Additionally, we treated **2a** with AgPF_6 in CH_2Cl_2 , added an excess of pyridine and the mixture was stirred overnight. Upon removal of the solvent and excess pyridine, X-Ray quality crystals were obtained from a saturated CH_2Cl_2 solution layered with *n*-hexane. In analogy to complex **4a** the base adduct, pyridine in this case, of the cationic gold complex was obtained with a non-coordinating $[\text{PF}_6]^-$ anion in $[\text{TerP}(\text{NMe}_2)_2\text{Au}(\text{py})][\text{PF}_6]$ (**5a**). In **4a** and **5a** the Au–P distances are similar to complexes **2** [P1–Au1 (**4a**) 2.2376(5); (**5a**) 2.247(3) Å; cf. $(\text{TerPMe}_2)\text{AuCl}$ 2.2964(10) Å] and two contacts with the flanking mesityl group below 3.1 Å are detected in the base-stabilized cations. Overall, the structural parameters clearly show that the terphenyl structural motif gives rise to stabilizing Au–arene interactions, which should prove beneficial in catalytic trials, as was shown by Xu and co-workers in terms of complex stability in intermolecular hydroamination reactions.¹⁵

Preparing complexes **3–5**, sometimes the formation of a new species characterized by a doublet of doublets in the ^{31}P NMR spectrum was noted. This species was only observed if AgCl was not completely removed during filtration and when the solution was kept in daylight. In one instance we obtained X-ray quality



Scheme 3. Serendipitous decomposition of cationic gold complexes into $[(1\text{AgCl})_2]$ dimeric complexes **6** (i) and their rational synthesis from **L** and AgCl (ii).

crystals that were identified as the neutral silver chloride complex $[(1\text{AgCl})_2]$ (**6a**). We therefore conclude that it is of the utmost importance to carefully remove any traces of silver chloride and work in the dark, when preparing cationic gold complexes, as the formation of the respective ligand silver chloride complexes might proceed unnoticed and influence catalytic tests.⁴⁴ **6a** and the related complex $[(1\text{bAgCl})_2]$ (**6b**) were independently synthesized by combining **1** with AgCl in a 1:1 stoichiometry in CH_2Cl_2 and continued stirring for 16 h under the exclusion of light afforded **6a** and **6b** as colourless air and moisture stable crystalline solids (Scheme 3). In the ^{31}P NMR spectra **6a** and **6b** show two doublets due to coupling with the two spin $\frac{1}{2}$ silver isotopes (^{107}Ag and ^{109}Ag) at 99.3 ($^1J_{109\text{Ag,P}} = 862.3$ Hz, $^1J_{107\text{Ag,P}} = 746.4$ Hz) and 94.3 ppm ($^1J_{109\text{Ag,P}} = 864.0$ Hz, $^1J_{107\text{Ag,P}} = 748.9$ Hz), respectively. X-ray quality crystals were grown from saturated acetone solutions in air and **6a** and **6b** (Figure 5) crystallize as centrosymmetric dimers.³³

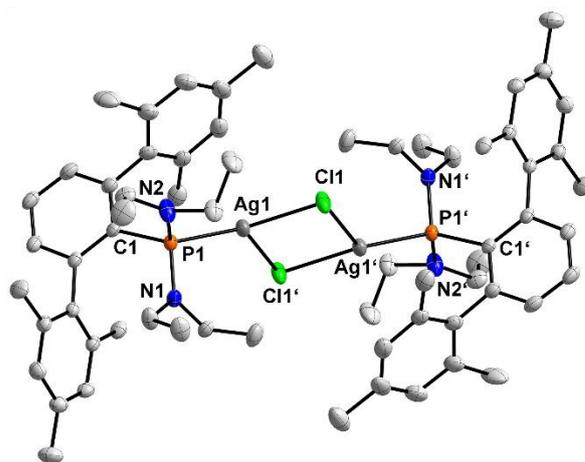


Figure 5. POV-Ray depiction of the molecular structure of **6b**. Ellipsoids are drawn at 30% probability, 150(2) K. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–P1 1.8652(18), P1–N1 1.6701(17), P1–N2 1.6700(17), P1–Ag1 2.4038(6), Ag1–Cl1 2.5060(6), Ag1–Cl1' 2.6120(6), Ag1–Ag1' 3.6518(7) Å; P1–Ag1–Cl1 135.850(19), Ag1–Cl1–Ag1' 91.017(18).

The molecular structures show a μ -Cl bridged dimer with a deltoid Ag_2Cl_2 core coordinated by two ligands **1a** or **1b**, respectively. The solid structures of **6a** and **6b** are closely related to that of $[\text{XPhosAg}(\mu\text{-Cl})_2]$.⁴⁵ Complexes with a $(\text{Ag}-\mu\text{-Cl})_2$ core comprising a single phosphine ligand on Ag are rare and restricted to bulky monodentate phosphine ligands, such as $\text{P}(\text{NC}_4\text{H}_8\text{NMe})_3$,⁴⁶ $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{Cl}$,⁴⁷ and the simple $\text{P}(\text{Cy})_3$.⁴⁸

To further characterize the electronic character of terphenyl(bisamino)phosphine ligands DFT calculations were carried out to determine the theoretical TEP-value ($\text{TEP}_{\text{Ni,theo}}$) of terphenyl(bisamino)phosphines **1**. Therefore, the complexes $[(\mathbf{1a})\text{-Ni}(\text{CO})_3]$ and $[(\mathbf{1b})\text{-Ni}(\text{CO})_3]$ were constructed *in silico* and their gas-phase structures were optimized at the BP86/def2SVP level of theory and confirmed as minima by frequency analyses.³³

Of the resulting unscaled frequencies, the A_1 symmetrical CO stretching mode was chosen for the evaluation of the donor parameters. To fit the theoretical frequencies to experimental values the $\nu_{\text{theor.}}(\text{CO})$ for eleven different complexes $[\text{LNi}(\text{CO})_3]$ were calculated and a linear dependency with respect to their

experimental TEP values was noted (Figure 6).³³ Complexes were chosen to span from extremely electron-rich phosphazanyl phosphines to electron-poor phosphines such as PCl_3 and PF_3 giving a range of experimental TEPs from 2017.3 to 2110.8 cm^{-1} .^{7, 8, 17, 18, 32, 49, 50} A linear regression allowed to derive the TEP_{Ni} values for ligands **1a** and **1b** of 2059.6 cm^{-1} and 2053.0 cm^{-1} , respectively. This is more electron rich than classical PPh_3 and approaches the donor strength of IMes, while the more electron rich IAPs and phosphazanyl phosphines are not surpassed. Especially **1b** is a stronger donor (based on TEP_{Ni}) than P^tBu_3 and falls in the range of newly developed YPhos ligands.⁵¹ 2019 Carmona, Nicasio and co-workers described a series of nickel carbonyl complexes of dialkylterphenyl phosphines, and the A_1 mode for $[(\text{TerPMe}_2)\text{Ni}(\text{CO})_3]$ was detected at 2063 cm^{-1} .³⁹ This illustrates the influence of the amino groups on phosphorus to render ligands **1a** and **1b** more electron rich and thus as a class with superior donor properties for the gold-catalyzed hydroamination of alkynes.

In order to evaluate the catalytic activity of complexes **4a** and **4b** in the hydroamination of aryl alkynes with anilines we first did a screening of the general reaction conditions, such as catalyst loading, solvent, temperature and reaction time using the phenylacetylene, p-toluidine pairing. Monitoring of the hydroamination between phenylacetylene and p-toluidine with 2 mol% of **4a** or **4b** in MeCN at $60\text{ }^\circ\text{C}$ via NMR spectroscopy ($1,3,5\text{-}(\text{OMe})_3\text{-C}_6\text{H}_3$ as internal standard) showed that conversion plateaued after ca. 6 h, we therefore decided to run catalytic reactions overnight (ca. 16 h) to take into account different sterics of the substrates to be used. Variation of the catalyst loading revealed that no significant drop of conversion occurs going from 2 mol% to 1 mol% and minimally worse results were obtained with 0.5 mol%. Catalytic activity ceases when only 0.1 mol% of **4a** or **4b** were used as catalyst. Considering that in many gold-catalyzed transformations catalyst loadings in excess of 5 mol% are present,⁹⁻¹¹ this catalyst system is competitive with known systems. To further underline this, complex **4b** was compared with $[(\text{JohnPhos})\text{Au}(\text{CNMe})]\text{BF}_4$ using the p-toluidine phenylacetylene pairing in MeCN at $80\text{ }^\circ\text{C}$ and after 2 h GC yields (vs. biphenyl as internal standard) in excess of 89 % and 84 %, respectively, were recorded. In contrast, $[(\text{Ph}_3\text{P})\text{Au}(\text{NCMe})]\text{BF}_4$ only gave 12 % of the respective imine after 5 h under the same conditions.³³ In a next series of experiments, we changed the solvent from MeCN to benzene and a minimal drop in conversion was noted. We therefore chose MeCN for our substrate scope. Lowering the temperature at optimized conditions from $60\text{ }^\circ\text{C}$ to $40\text{ }^\circ\text{C}$ resulted in a consistent drop of the isolated yield from 78% to 65%. We thus chose $60\text{ }^\circ\text{C}$ to evaluate the substrate scope.

With the optimized parameters in hand we tested both, different anilines and acetylenes (Scheme 4). To investigate the influence of the steric bulk of the aniline, p-toluidine, Mes-NH₂ (Mes = 2,4,6-Me₃-C₆H₂) and Dip-NH₂ (Dip = 2,6-diisopropylphenyl) were tested. Overall, 12 different derivatives could be synthesized using different aryl-substituted alkynes. It should be noted that the electron-rich alkynes 4-MeO- and

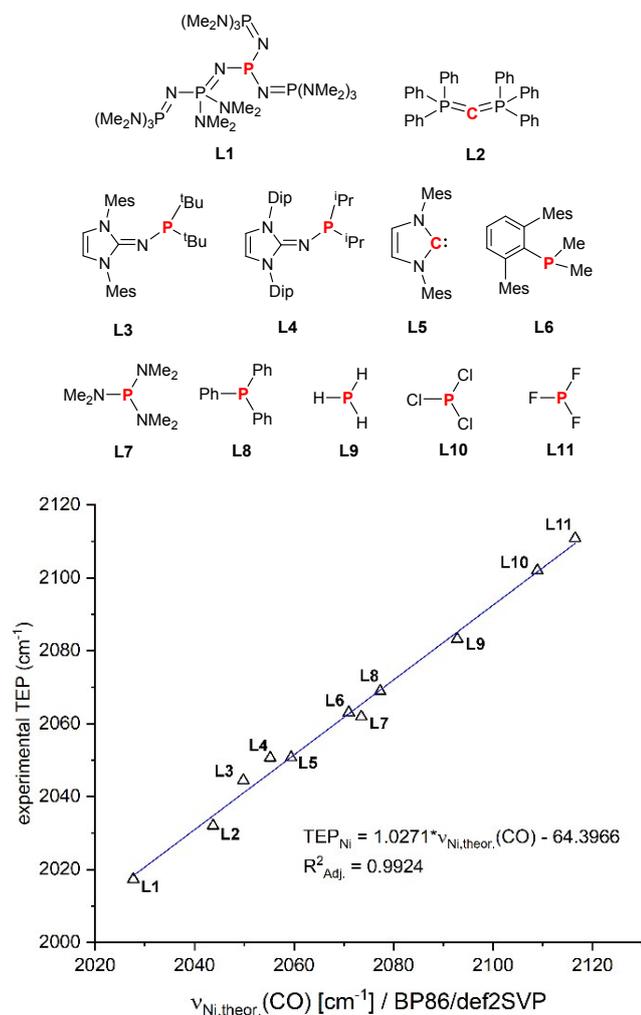
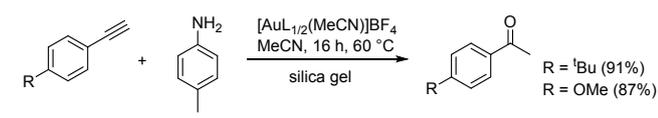
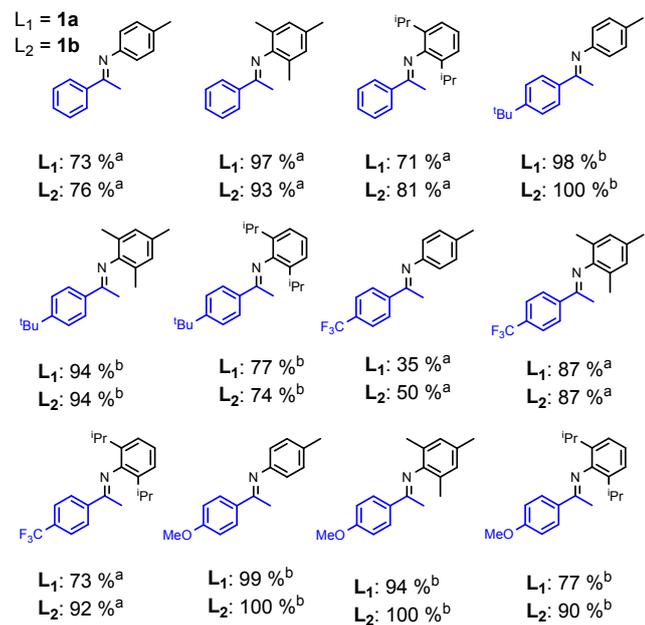
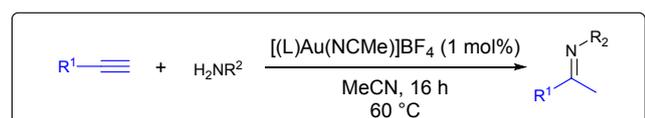


Figure 6. Diagram showing the correlation between experimental TEP_{Ni} -values of selected complexes $[\text{LNi}(\text{CO})_3]$ and their corresponding theoretical $A_1(\text{CO})$ values obtained at the BP86/def2SVP level of theory.

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Scheme 4. Substrate scope of the gold-catalysed hydroamination of various aryl alkynes with anilines of varying bulk. (^adenotes isolated yields; ^bdenotes NMR yields, (MeO)₃C₆H₃ as internal standard)

4-^tBu-phenylacetylene could be converted into the respective imines quantitatively as determined by ¹H NMR spectroscopy, using 1,3,5-(OMe)₃-C₆H₃ as an internal standard. However, attempts to isolate these electron-rich imines after column chromatography on silica with *n*-Hex/EtOAc (4:1) as the eluent, resulted in the isolation of the corresponding benzophenone derivatives in good isolated yields (Scheme 4, bottom). The isolated yields for the hydroamination of phenylacetylene are generally good, with up to 97% yield for the reaction with Mes-NH₂. Interestingly, for F₃C-C₆H₄-CCH with the yield increases with the steric demand of the respective aniline and up to 92% of the respective Dip-substituted imine were isolated. In general, we observed that the isolated yields are usually over 70% and nearly independent of whether **1a** or **1b** were used as a ligand. In summary, ligands of the type **1** represent a potent class of electron-rich Buchwald-type phosphines, which have proven to be efficient in stabilizing gold(I) complexes for the intramolecular hydroamination of alkynes. It is known that in the presence of amines the corresponding amine complexes [LAu(H₂N-R)]X form and inhibit coordination of the alkyne to the metal. In the presence of a strongly donating ligand, amine dissociation should be more favourable.⁵² We therefore independently synthesized [(**1a**)Au(NH₂-*p*-Tol)]BF₄ (**7a**) by

addition of *p*-toluidine to **4a**. **7a** was characterized by multinuclear NMR spectroscopy, showing a sharp NMR signal at 93.8 ppm and a broad signal for the *p*-toluidine-NH₂ at 4.5 ppm in the ¹H NMR spectrum. Using 1mol% of **7a** as a catalyst for the hydroamination of *p*-toluidine with phenylacetylene at 80 °C, showed a yield of the desired imine of 72% (GC). This clearly shows that electron rich ligands favour amine dissociation and therefore enhance turnover even at low catalyst loadings.

Conclusions

Overall, we report the isolation, spectroscopic and structural characterization of bulky terphenyl(bisamino)phosphines **1**. These Buchwald-type ligands with flanking mesityl groups have been shown to possess attractive interactions between the gold center and one of the flanking mesityl groups, as was ascertained by determination of the molecular structures of a series of gold complexes **2**, **3**, **4** and **5**. The percent buried volume of **1b** amounts to ca. 55% and a linear fit of known TEP-values with their respective gas phase structures (obtained by DFT studies) revealed that particularly **1b** can be classified as an electron-rich phosphine and their application in the intermolecular hydroamination of alkynes was tested. Preparing catalyst solutions by chloride ion abstraction from **2** with AgX salts, sometimes the formation of the respective dimeric Ag-complexes [(L)Ag-μ-Cl]₂ **6a** and **6b** was noted, which were independently synthesized. This is another example that AgCl contamination can result in erroneous catalyst screening results. Screening of the catalytic reaction conditions showed efficient hydroamination to take place at 60°C in MeCN with a catalyst loading of **4** of 1 mol% and moderate to excellent yields were achieved for bulky anilines such as Dip-NH₂ and different phenyl acetylene derivatives. No obvious difference in performance between ligands **1a** and **1b** was noted. In summary, terphenylbisaminophosphines meet the criteria of efficient ligands for intermolecular gold-catalyzed hydroamination reactions, as they combine strong donor properties with the 2-biphenyl structural motif, which is needed to enhance complex stability and dissociation of additives during catalysis.

Experimental

General methods

All reactions were performed under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk techniques or an inert atmosphere glovebox (MBraun LABstar ECO). Acetonitrile, diethylether, toluene, *n*-hexane and dichloromethane were purified with the Grubbs-type column system "Pure Solve MD-5" and dispensed into thick-walled Schlenk bombs equipped with Young-type Teflon valve stopcocks and stored under an atmosphere of argon prior to use. Benzene was refluxed over Na/benzophenone and freshly distilled prior to use. Dichloromethane was additionally refluxed over CaH₂ and freshly distilled prior to use. Acetonitrile was additionally stored over molecular sieves (4 Å, 4-8 mesh)

prior to use. C₆D₆ was refluxed over Na and freshly distilled prior to use. CDCl₃ was refluxed over P₄O₁₀ and distilled prior to use. CD₂Cl₂ was refluxed over P₄O₁₀ and distilled onto CaH₂ and was refluxed again and then distilled prior to use.

2,6-Mes₂-C₆H₃-I (Ter-I),⁵³ 2,6-Mes₂-C₆H₃-Li (Ter-Li),²⁴ and CIP(NEt₂)₂⁵⁴ have been reported previously and were prepared according to modified literature procedures. *n*-BuLi (2.5 M in *n*-hexane, ACROS), CIP(NMe₂)₂ (99%, Alfa Aesar), AuCl(SMe₂) (>97%, TCI), AgPF₆ (98%, TCI), AgSO₃CF₃ (≥99%, Sigma Aldrich), AgCl (99%, Sigma Aldrich), JohnPhos (97%, Sigma Aldrich), PPh₃ (95%, Sigma Aldrich) and AgBF₄ (98%, Sigma Aldrich) were stored under an argon atmosphere and used as received. DippNH₂ (ABCR, 90%) and MesNH₂ (98% Alfa Aesar) were distilled prior to use. Acetylenes PhCCH (98%, Sigma Aldrich), 4-OMe-C₆H₄-CCH (97%, Sigma Aldrich), 4-CF₃-C₆H₄-CCH (97% Sigma Aldrich) and 4-^tBu-C₆H₄-CCH (96%, Acros Organics) were recondensed, degassed three times and stored over sieves (4 Å) prior to use. Pyridine (99.8%, Sigma Aldrich) was refluxed over KOH, distilled and stored over molecular sieves (3 Å) prior to use.

¹H, ¹³C{¹H}of, ¹¹B, ¹⁹F{¹H} and ³¹P{¹H} NMR spectra were recorded on BRUKER AV300, AV400 or Fourier300 spectrometers. All ¹H NMR and ¹³C NMR spectra are referenced using the chemical shifts of residual proton solvent resonances (benzene-d₆: δ_H 7.16, δ_C 128.06; chloroform-d: δ_H 7.26, δ_C 77.16; dichloromethane-d₂: δ_H 5.32, δ_C 53.84). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane. The ³¹P{¹H} NMR spectra were referenced to external 85% H₃PO₄ and the ¹⁹F NMR spectra to CFCl₃ as external standard. IR spectra were recorded in ATR mode on a Bruker Alpha II IR spectrometer under an atmosphere of argon. Elemental analysis was done using a Leco Tru Spec elemental analyzer. Melting points were determined on a Mettler-Toledo MP 70 apparatus. Melting points are uncorrected and were measured in sealed capillaries under an Ar atmosphere. Mass spectra were recorded on a MAT 95XP Thermo Fisher mass spectrometer in electrospray ionization mode.

Synthesis of TerP(NMe₂)₂ (1a)

From Ter-Li: Terphenyllithium (0.994 g, 3.106 mmol) was suspended in toluene (80 mL) and the yellowish suspension was cooled to -78 °C. CIP(NMe₂)₂ (0.479 g, 3.106 mmol) in toluene (5 mL) was added dropwise over a period of 5 min. The cooling bath was removed, and the mixture was allowed to warm to ambient temperature over a period of 1 h. The resulting white suspension was filtered using a celite-padded frit. The filtrate was then concentrated to incipient crystallization (ca. 5 mL) and placed in the fridge (ca. 5 °C) for 72 h. This resulted in clear colorless blocks of TerP(NMe₂)₂ (**1a**, 0.898 g, 2.078 mmol, 67%). X-Ray quality crystals were obtained from a saturated *n*-hexane solution at 5 °C after 24 h.

From Ter-I: Ter-I (2.500g, 5.677 mmol) was suspended in Et₂O and cooled to -78 °C and *n*-BuLi (2.49 mL, 2.5 M, 1.1 eq.) was added dropwise over a period of 5 min. The yellowish solution was allowed to warm to ambient temperatures over a period of 1 h and was then stirred for an additional 30 min. Subsequently,

CIP(NMe₂)₂ (0.930 g, 6.016 mmol, 1.05 eq.) in Et₂O (10 mL) was added dropwise at -78 °C. The reaction mixture was slowly warmed to ambient temperature and stirred overnight. Afterwards, the solvent was removed under reduced pressure and the remaining white powder was extracted with toluene (65 mL) and filtered using a G4 frit, packed with celite. The volume of the clear filtrate was reduced to ca. 4 mL and the flask was placed in the freezer (-30 °C) for 48 h. This resulted in clear colorless blocks of TerP(NMe₂)₂ (**1a**, 1.940 g, 4.485 mmol, 79%). ¹H NMR (300 MHz, C₆D₆): δ = 7.12 (td, ³J_{HH} = 7.2 Hz, ⁵J_{HH} = 0.7 Hz, 1H, *p*-C₆H₃), 6.90 (dd, ³J_{HH} = 7.2 Hz, ⁴J_{PH} = 2.7 Hz, 2H, *m*-C₆H₃), 6.89 (s (br), 4H, *m*-CH-Mes), 2.24 (s, 6H, Ar-CH₃), 2.22 (s, 12H, Ar-CH₃), 2.21 (d, ³J_{PH} = 8.6 Hz, 12H, NCH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 144.1, 140.5, 140.4, 135.6 (d, ²J_{CP} = 27.7 Hz), 130.5, 127.8, 127.7, 42.4 (d, ²J_{CP} = 19.5 Hz), 21.4 (d, ⁵J_{PC} = 5.0 Hz), 21.2. ³¹P{¹H} NMR (122 MHz, C₆D₆): δ = 103.42. IR (ATR, 32 scans, cm⁻¹): ν = 2967 (w), 2915 (w), 2855 (m), 2827 (m), 2785 (m), 1608 (w), 1558 (w), 1478 (w), 1443 (m), 1375 (w), 1267 (m), 1197(m), 1059 (w), 979 (m), 964 (s), 848 (s), 809 (m), 773 (m), 755(m), 719 (w), 672 (s), 646 (m), 576 (m), 561 (m), 550 (m), 534 (w), 452 (m), 409 (m). MS (ESI-TOF): expected m/z = 433.2773, found: m/z = 433.2767. EA: calc.: C 77.74, H 8.62, N6.48, found: C 77.39, H 8.54, N 6.08%.

Synthesis of TerP(NEt₂)₂ (1b)

From Ter-Li: Terphenyllithium (0.465 g, 1.428 mmol) was suspended in toluene (15 mL) and the yellowish suspension was cooled to -78 °C. To this suspension CIP(NEt₂)₂ (0.360 g, 1.571 mmol) in toluene (5 mL) was added dropwise over a period of 5 min. The cooling bath was removed, and the mixture was allowed to warm to ambient temperature over a period of 1 h. Subsequently, toluene was removed using an external solvent trap, resulting in a yellowish pasty material, which was then extracted with *n*-hexane (20 mL) and filtered using a celite-padded frit (G4). The filtrate was then concentrated to incipient crystallization (ca. 2 mL) and placed in the fridge (ca. 5 °C) for 72 h. This resulted in colorless, X-ray quality blocks of TerP(NEt₂)₂ (**1b**, 0.273 g, 0.568 mmol, 40%).

From Ter-I: Ter-I (2.500 g, 5.677 mmol) was suspended in Et₂O and cooled to -78 °C and *n*-BuLi (2.49 mL, 2.5 M, 1.1 eq.) is added dropwise. The yellowish solution is allowed to warm to ambient temperatures over a period of 1 h and stirred for an additional 30 minutes. Then CIP(NEt₂)₂ (1.311 g, 6.245 mmol, 1.1 eq.) in Et₂O (10 mL) was added dropwise at -78 °C. The reaction mixture was slowly warmed to ambient temperature and was further stirred overnight. Afterwards the volatiles were evaporated, *n*-hexane (70 mL) was added to the solid yellow residue and the mixture was then filtered using a G4 frit packed with celite. The volume of the clear filtrate was reduced to ca. 4 mL and the flask was placed in the freezer (-30 °C) for 48 h. This resulted in the deposition of colorless, crystalline blocks, which were washed with 5 mL of cold *n*-hexane (-30 °C). TerP(NEt₂)₂ (**1b**, 2.472 g, 5.150 mmol, 89%).

¹H NMR (300 MHz, C₆D₆): δ = 7.10 (td, ³J_{HH} = 7.1 Hz, ⁵J_{HP} = 0.6 Hz, 1H, *p*-C₆H₃), 6.89 (d, ⁴J_{HH} = 0.7 Hz, 4H, *m*-Mes), 6.84 (dd, ³J_{HH} = 7.1 Hz, ⁴J_{PH} = 2.6 Hz, 2H, *m*-C₆H₃), 2.83-2.46 (m, 8H, NCH₂),

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2.26 (s, 12H, Ar-CH₃), 2.24 (s, 6H, Ar-CH₃), 0.84 (t, ³J_{HH} = 7.1 Hz, 12H, NCH₂CH₃). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 144.7 (d, J_{CP} = 18.38 Hz), 142.1 (d, J_{CP} = 34.7 Hz), 141.2 (d, J_{CP} = 3.41 Hz), 136.2 (d, J_{CP} = 1.33 Hz), 135.7, 130.9, 128.6, 127.98, 45.8 (d, ²J_{CP} = 20.4 Hz), 22.0 (d, ⁵J_{CP} = 5.5 Hz), 21.2, 15.6 (d, ³J_{CP} = 4.1 Hz). ³¹P{¹H} NMR (122 MHz, C₆D₆): δ = 100.24. IR (ATR, 32 scans, cm⁻¹): ν = 2963 (m), 2913 (m), 2864 (m), 2835 (w), 2726 (w), 1610 (w), 1559 (w), 1443 (m), 1371 (m), 1327 (w), 1293 (w), 1277 (w), 1189 (m), 1180 (s), 1117 (w), 1074 (w), 1026 (m), 1014 (s), 907 (m), 850 (s), 804 (m), 787 (m), 750 (m), 718 (w), 664 (m), 636 (m), 577 (w), 559 (w), 551 (w), 535 (w), 491 (w), 473 (m), 437 (m). MS (ESI-TOF): expected m/z = 489.3398, found: m/z = 489.3394, EA: calc.: C 78.65, H 9.28, N 5.73, found: C 78.49, H 9.10, N 5.51%.

Synthesis of TerP(NMe₂)₂AuCl (2a)

TerP(NMe₂)₂ (0.130 g, 0.30 mmol) and ClAu(SMe₂) (0.110 g, 0.30 mmol) were dissolved in dichloromethane (5 mL) under the exclusion of light (wrap flask with tin foil) and stirred at ambient temperature for 1 h. Subsequently, the volume of the reaction mixture was reduced to ca. 1 mL, layered with *n*-hexane (3-5 mL) and placed in the fridge (ca. 5 °C) for 72 h. This resulted in the deposition of colorless, X-ray quality crystals of [TerP(NMe₂)₂AuCl] (**2a**, 0.130 g, 0.20 mmol, 66%).

¹H NMR (300 MHz, CDCl₃): δ = 7.51 (td, ³J_{HH} = 7.1 Hz, ⁵J_{HP} = 1.6 Hz, 1H, *p*-C₆H₃), 7.04 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{PH} = 4.0 Hz, 2H, *m*-C₆H₃), 6.89 (d, ⁶J_{PH} = 0.7 Hz, 4H, *m*-Mes), 2.34 (s, 12H, Ar-CH₃), 2.31 (s, 6H, Ar-CH₃), 2.06 (s, 12H, NCH₃). ¹³C NMR (75 MHz, CDCl₃): δ = 145.8 (d, J_{CP} = 12.1 Hz), 138.5 (d, J_{CP} = 5.3 Hz), 137.2, 135.6, 132.0 (d, ³J_{CP} = 8.4 Hz), 131.4 (d, ⁴J_{CP} = 2.0 Hz), 129.0, 41.2 (d, ²J_{CP} = 9.1 Hz), 21.9, 21.2. ³¹P{¹H} NMR (122 MHz, CDCl₃): δ = 96.94. MS (ESI-TOF): expected m/z = 629.2360, found: m/z = 629.2368. EA: calc.: C 50.57, H 5.61, N 4.21, found: C 50.67, H 5.61, N 4.24%.

Synthesis of TerP(NEt₂)₂AuCl (2b)

TerP(NEt₂)₂ (0.960 g, 2.000 mmol) and ClAu(SMe₂) (0.600 g, 2.000 mmol) were dissolved in dichloromethane (20 mL) under the exclusion of light (wrap flask with tin foil) and stirred at ambient temperature for 1 h. The solvent was removed in vacuo, resulting in an off-white solid of TerP(NEt₂)₂AuCl (**2b**, 1.313 g, 1.821 mmol, 91%). X-ray quality crystals were obtained from layering a saturated CH₂Cl₂ solution with *n*-hexane (5 °C for 72 h).

¹H NMR (300 MHz, C₆D₆): δ = 6.99 (t (br), ³J_{HH} = 7.5, 1H, *p*-C₆H₃), 6.95 (m, 4H, *m*-Mes), 6.66 (dd, ³J_{HH} = 7.5, ⁴J_{PH} = 3.9 Hz, 2H, *m*-C₆H₃), 2.59 (q, ³J_{HH} = 7.1 Hz, 4H, NCH₂), 2.56 (q, ³J_{HH} = 7.1 Hz, 4H, NCH₂), 2.30 (s, 6H, Ar-CH₃), 2.09 (s, 12H, Ar-CH₃), 0.77 (t, ³J_{HH} = 7.1 Hz, 12H, NCH₂CH₃). ¹³C{¹H} NMR (101 MHz, C₆D₆): δ = 146.1 (d, J_{CP} = 12.1 Hz), 139.6 (d, J_{CP} = 5.2 Hz), 137.4, 135.7, 134.3, 132.4 (d, J_{CP} = 8.0 Hz), 130.9 (d, J_{CP} = 2.1 Hz), 129.7, 44.7 (d, ³J_{CP} = 10.0 Hz), 22.4, 21.3, 15.3 (d, ⁴J_{CP} = 1.9 Hz). ³¹P{¹H} NMR (122 MHz, C₆D₆): δ = 93.26. MS (ESI-TOF): expected m/z = 743.2571, found: m/z = 743.2574. EA: calc.: C 53.30, H 6.29, N 3.88, found: C 53.26, H 6.25, N 3.64. MP (°C): dec. >160 °C.

Synthesis of TerP(NMe₂)₂AuOTf (3a)

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DOI: 10.1039/D0DT02435J

In a round-bottomed flask TerP(NMe₂)₂AuCl (66.5 mg, 0.100 mmol) and AgOTf (25.7 mg, 0.100 mmol) are suspended in 5 mL benzene under the exclusion of light. The solution was stirred at room temperature for 2 h and subsequently filtered using a filter canula. The volume of the filtrate was reduced to ca. 1 mL, layered with *n*-hexane (4 mL) and placed in the fridge (5 °C, 72 h). This resulted in the deposition of TerP(NMe₂)₂AuOTf (50.1 mg, 0.064 mmol, 64%) as an amorphous powder.

¹H NMR (300 MHz, C₆D₆): δ = 6.95 (td, ³J_{HH} = 7.6 Hz, ⁵J_{PH} = 1.7 Hz, 1H, *p*-C₆H₃), 6.91 – 6.82 (m, 4H, *m*-Mes), 6.62 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{PH} = 4.3 Hz, 2H, *m*-C₆H₃), 2.28 (s, 6H, Ar-CH₃), 1.89 (s, 12H, Ar-CH₃), 1.84 (d, ³J_{PH} = 11.3 Hz, 12H, NCH₃). ¹⁹F{¹H} NMR (282 MHz, C₆D₆): –76.8. ³¹P{¹H} NMR (122 MHz, C₆D₆): δ = 86.5.

X-Ray quality crystals of this compound could not be grown. CHN and MS were not obtained for this compound.

Synthesis of TerP(NEt₂)₂AuOTf (3b)

In a round-bottomed flask TerP(NEt₂)₂AuCl (0.100 g, 0.140 mmol) and AgOTf (0.036 mg, 0.140 mmol) are suspended in CH₂Cl₂ (5 mL) and the mixture stirred under the exclusion of light at room temperature for 1 h. Afterwards the mixture is filtered using a filter canula. The volume of the filtrate is reduced to ca. 1 mL, layered with *n*-hexane (4 mL) and placed in the fridge (5 °C, 72 h). This resulted in the deposition of colorless, X-ray quality crystals of TerP(NEt₂)₂AuOTf (0.054 g, 0.069 mmol, 49%).

¹H NMR (300 MHz, C₆D₆): δ = 7.02-6.94 (m, 1H, *p*-C₆H₃), 6.92 (s, 4H, *m*-Mes), 6.62 (dd, 2H, *m*-C₆H₃), 2.63-2.44 (m, 8H, NCH₂), 2.31 (s, 6H, Ar-CH₃), 2.02 (s, 12H, Ar-CH₃), 0.76 (t, ³J_{PH} = 7.1 Hz, 12H, NCH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 146.28 (d, J_{CP} = 12.4 Hz), 139.18 (d, J_{CP} = 5.8 Hz), 138.13, 136.23, 133.12 (d, J_{CP} = 8.6 Hz), 132.25 (d, J_{CP} = 2.4 Hz), 129.5, 128.7, 44.5 (d, J = 9.6 Hz), 22.3, 21.3, 15.1. ¹⁹F{¹H} NMR (376 MHz, CD₂Cl₂): δ = –76.62 ppm. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ = 78.89 ppm. MS (ESI-TOF): expected m/z = 834.2506, found: m/z = TerP(NEt₂)₂Au 685.2980, AuOTf 345.1763. EA: calc.: C 47.48, H 5.43, N 3.36, S 3.84, found: C 47.02, H 5.69, N 3.38, S 3.89%.

Synthesis of [TerP(NMe₂)₂Au-MeCN]BF₄ (4a)

Complex **2a** (0.030 g, 0.045 mmol) and AgBF₄ (0.009 g, 0.045 mmol) combined in a round-bottomed flask, dissolved in acetonitrile (2.5 mL) and stirred under exclusion of light for 30 min at room temperature. The solution was then filtered using a canula fitted with a glass microfiber filter. This mixture was then dried and extracted with benzene-d₆ and filtered into an NMR-tube equipped with a J-young-type screw cap. X-ray quality crystals of [TerP(NMe₂)₂Au-MeCN]BF₄ (**4a**) were obtained upon standing at room temperature for 48 h.

¹H NMR (300 MHz, C₆D₆) δ = 6.97 (td, ³J_{HH} = 7.6 Hz, ⁵J_{PH} = 1.7 Hz, 1H, *p*-C₆H₃), 6.88 (s, 4H, *m*-Mes), 6.62 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{PH} = 4.2 Hz, 2H, *m*-C₆H₃), 2.27 (s, 6H, Ar-CH₃), 2.12 (d, ³J_{PH} = 11.3 Hz, 12H, NMe₂), 1.93 (s, 12H, Ar-CH₃), 0.98 (s, 3H, CH₃CN).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, C_6D_6): $\delta = -150.24$ ppm. **$^{31}\text{P}\{^1\text{H}\}$ NMR** (122 MHz, C_6D_6): $\delta = 89.7$ ppm.

^{13}C NMR, CHN and MS were not obtained for this compound.

Synthesis of [TerP(NEt₂)₂Au-MeCN]BF₄ (**4b**)

Complex **2b** (0.032 g, 0.045 mmol) and AgBF₄ (0.009 g, 0.045 mmol) combined in a round-bottomed flask, dissolved in acetonitrile (2.5 mL) and stirred under exclusion of light for 30 min at room temperature. The solution was then filtered using a canula fitted with a glass microfiber filter. This mixture was then dried and extracted with benzene-d₆ and filtered into an NMR-tube equipped with a J-young-type screw cap.

^1H NMR (300 MHz, C_6D_6) $\delta = 6.99$ (td, $^3J_{\text{HH}} = 7.6$ Hz, $^5J_{\text{PH}} = 1.7$ Hz, 1H, *p*-C₆H₃), 6.94 (s, 4H, *m*-Mes), 6.60 (dd, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{PH}} = 4.0$ Hz, 2H, *m*-C₆H₃), 2.67-2.52 (m, 8H, NCH₂CH₃), 2.41 (s, 6H, Ar-CH₃), 2.01 (s, 12H, Ar-CH₃), 1.46 (s, 3H, CH₃CN), 0.80 (t, $^3J_{\text{HH}} = 7.1$ Hz, 12H, NCH₂CH₃). **$^{19}\text{F}\{^1\text{H}\}$ NMR** (282 MHz, C_6D_6): $\delta = -150.22$ ppm. **$^{31}\text{P}\{^1\text{H}\}$ NMR** (122 MHz, C_6D_6): $\delta = 84.4$ ppm.

Single crystal X-ray analysis, ^{13}C NMR, CHN and MS were not obtained for this compound.

Synthesis of [TerP(NMe₂)₂Au-py]PF₆ (**5a**)

TerP(NMe₂)₂AuCl (0.066 g, 0.1 mmol) and AgPF₆ (0.025 g, 0.1 mmol) were dissolved in 5 mL dichloromethane. 10 μL pyridine was added to the solution and stirred overnight. After canula filtration the clear solution is reduced to 1 mL, layered with 5 mL *n*-hexane and placed in the freezer (-70 °C) for 4 h. The solvent was removed and the resulting colorless crystals of [TerP(NMe₂)₂Au-py]PF₆ (0.062 g, 0.088 mmol, 88%) were dried in vacuo.

^1H NMR (300 MHz, CD₂Cl₂) $\delta = 8.15$ -8.10 (m, 3H, *p,m*-CH-py), 7.73-7.68 (m, 2H, *o*-CH-py), 7.67-7.58 (m, 1H, *p*-CH-Ph), 7.09 (dd, $^1J_{\text{HH}} = 7.6$ Hz, $^1J_{\text{HP}} = 4.2$ Hz, 2H, *m*-CH-Ph), 6.88 (s, 4H, *m*-CH-Ph), 2.40 (s, 6H, NCH₃), 2.36 (s, 6H, NCH₃), 2.14 (s, 6H, Ar-CH₃), 2.07 (s, 6H, Ar-CH₃). **^{13}C NMR** (75 MHz, CD₂Cl₂): $\delta = 150.95$, 146.30, 146.13, 142.04, 138.97 (d, $^2J_{\text{CP}} = 5.8$ Hz), 137.78, 136.82, 132.76 (d, $J_{\text{CP}} = 8.8$ Hz), 129.26, 127.10, 40.81 (d, $J_{\text{CP}} = 8.7$ Hz), 22.00, 21.15. **^{19}F NMR** (282 MHz, CD₂Cl₂): $\delta = -73.38$ (d, $J = 707.6$ Hz). **^{31}P NMR** (122 MHz, CD₂Cl₂): $\delta = 91.49$, -144.45 (septet, $^1J_{\text{P-F}} = 707.6$ Hz).

Sufficient CHN analyses for this compound were not obtained, despite crystals showing no impurities on the basis of ^1H NMR spectroscopy.³³

Synthesis of [TerP(NMe₂)₂AgCl]₂ (**6a**)

AgCl (0.019 g, 0.129 mmol) and TerP(NMe₂)₂ (0.056 g, 0.129 mmol) were dissolved in 5 mL of dichloromethane under the exclusion of light (wrap flask with tin foil) and the reaction mixture was stirred for 16 h at room temperature, which was accompanied by precipitation of slight amounts of solid material. After canula filtration all volatile components were removed under vacuum, the residue was washed with small amounts of *n*-hexane (2 \times 2 mL) and dried under vacuum to yield **6a** 0.046 g (0.040 mmol; 62%) as a colorless solid.

Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution of **6a** in acetone.

^1H NMR (300 MHz, CDCl₃, 298 K): $\delta = 2.04$ (s, 24H, *o*-CH₃C₆H₃), 2.25 (s, 12H, N(CH₃)₂), 2.28 (s, 12H, N(CH₃)₂), 2.34 (s, 12H, *p*-CH₃C₆H₃), 6.99-7.00 (m, 8H, CH_{Mes}), 7.00-7.03 (m, 4H, *m*-CH_{ArYl}P), 7.47-7.51 (m, 2H, *p*-CH_{ArYl}P) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (75 MHz, CDCl₃, 298 K): $\delta = 21.2$ (*p*-CH₃C₆H₃), 21.55 (*o*-CH₃C₆H₃), 21.57 (*o*-CH₃C₆H₃), 41.78 (d, $^2J_{\text{P,C}} = 13.5$ Hz, N(CH₃)₂), 41.80 (d, $^2J_{\text{P,C}} = 13.7$ Hz, N(CH₃)₂), 129.2 (CH_{Mes}), 130.9 (*p*-CH_{ArYl}P), 131.4 (d, $^3J_{\text{P,C}} = 5.8$ Hz, *m*-CH_{ArYl}P), 133.7 (m, C_{q,ArYl}P), 135.2 (*o*-C_{q,Mes}C₆H₃), 137.4 (*p*-C_{q,Mes}C₆H₃), 138.0 (d, $^3J_{\text{P,C}} = 6.1$ Hz, C_{q,Mes}), 144.5 (d, $^2J_{\text{C,P}} = 15.3$ Hz, *o*-C_{q,ArYl}P) ppm. **$^{31}\text{P}\{^1\text{H}\}$ NMR** (122 MHz, CDCl₃, 298 K): $\delta = 99.3$ (dd, $^1J_{\text{Ag,P}} = 862.3$ Hz, $^1J_{\text{Ag,P}} = 746.4$ Hz) ppm. **MS** (ESI-TOF): expected: $m/z = 1113.3184$ [M-Cl]⁺; found: $m/z = 1113.3202$. **EA**: calculated: C 58.40, H 6.48, N 4.86; found: C 58.56, H 6.96, N 4.34%.

Synthesis of [TerP(NEt₂)₂AgCl]₂ (**6b**)

AgCl (0.147 g, 1.023 mmol) and TerP(NEt₂)₂ (0.500 g, 1.023 mmol) were dissolved in 15 mL of dichloromethane under the exclusion of light (wrap flask with tin foil) and the reaction mixture was stirred for 16 h at room temperature which was accompanied by precipitation of slight amounts of solid material. After canula filtration all volatile components were removed under vacuum, the residue was washed with *n*-hexane (2 \times 5 mL) and dried under vacuum to yield **6b** 0.546 g (0.422 mmol; 83%) as a colorless solid. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution of **6b** in acetone.

^1H NMR (300 MHz, CDCl₃, 298 K): $\delta = 0.91$ (t, $^3J_{\text{H,H}} = 7.1$ Hz, 24H, NCH₂CH₃), 2.10 (s, 24H, *o*-CH₃C₆H₃), 2.36 (s, 12H, *p*-CH₃C₆H₃), 2.54-2.79 (m, 16H, NCH₂CH₃), 6.94-6.97 (m, 4H, *m*-CH_{ArYl}P), 7.00-7.01 (m, 8H, CH_{Mes}), 7.44-7.48 (m, 2H, *p*-CH_{ArYl}P) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (75 MHz, CDCl₃, 298 K): $\delta = 15.1$ (d, $^3J_{\text{P,C}} = 2.7$ Hz, NCH₂CH₃), 21.3 (*p*-CH₃C₆H₃), 21.83 (*o*-CH₃C₆H₃), 21.84 (*o*-CH₃C₆H₃), 45.0 (d, $^2J_{\text{P,C}} = 17.0$ Hz, NCH₂CH₃), 129.6 (CH_{Mes}), 130.6 (*p*-CH_{ArYl}P), 131.8 (d, $^3J_{\text{P,C}} = 5.5$ Hz, *m*-CH_{ArYl}P), 133.9 (m, C_{q,ArYl}P), 135.2 (*o*-C_{q,Mes}C₆H₃), 137.7 (*p*-C_{q,Mes}C₆H₃), 138.8 (d, $^3J_{\text{P,C}} = 6.3$ Hz, C_{q,Mes}), 144.5 (m, *o*-C_{q,ArYl}P) ppm. **$^{31}\text{P}\{^1\text{H}\}$ NMR** (122 MHz, CDCl₃, 298 K): $\delta = 94.3$ (dd, $^1J_{\text{Ag,P}} = 864.0$ Hz, $^1J_{\text{Ag,P}} = 748.9$ Hz) ppm. **MS** (ESI-TOF): expected: $m/z = 1227.4428$ [M-Cl]⁺; found: $m/z = 1227.4449$. **EA**: calculated: C 60.81, H 7.18, N 4.43; found: C 60.83, H 7.74, N 4.28 %.

Synthesis of [TerP(NMe₂)₂Au(H₂N-*p*-Me-C₆H₄)₂] (**7a**)

Complex **2a** (0.100 g, 0.150 mmol) and AgBF₄ (0.031 g, 0.159 mmol) were combined in a round-bottomed flask, dissolved in acetonitrile (5 mL) and stirred under exclusion of light for 30 min at room temperature. The solution was then filtered using a canula fitted with a glass microfiber filter. To the filtrate *p*-toluidene (0.020 g, 0.186 mmol) was added, resulting in the formation of a white precipitate. The supernatant solution was removed by canula filtration and the residual off-white solid triturated with *n*-pentane and dried in vacuo. This afforded

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[TerP(NMe₂)₂Au(H₂N-*p*-Me-C₆H₄)] (7a, 0.095 g, 0.113 mmol, 75%) as a greyish powder.

¹H NMR (300 MHz, CCl₃) δ = 7.55 (td, ³J_{HH} = 7.6 Hz, ⁵J_{PH} = 1.7 Hz, 1H, *p*-C₆H₃), 7.09-7.00 (m, 4H, *m*-C₆H₃, *p*-Tol), 6.88 (d, br ³J_{HH} = 8.4 Hz, 2H, *p*-Tol), 4.50 (br, 2H, *p*-Tol-NH₂), 2.32 (s, 6H, Ar-CH₃), 2.28 (s, 3H, *p*-Tol-*p*-CH₃), 2.27 (d, ³J_{PH} = 11.2 Hz, 12H, NCH₃), 2.02 (s, 12H, Ar-CH₃). ¹⁹F{¹H} NMR (282 MHz, C₆D₆): -151.15 ppm. ³¹P{¹H} NMR (122 MHz, C₆D₆): δ = 93.77 ppm.

Catalytic hydroamination of acetylenes.

The complex [Au(L)Cl] (0.045 mmol, 1 equiv; L = 1a, 1b) and AgBF₄ (0.045 mmol, 1 equiv) were dissolved in MeCN (2.5 mL) and stirred under exclusion of light for 30 min at room temperature and the solution was then filtered using a filter canula fitted with a glass microfiber filter. This 0.018 M solution was used as a stock solution. Acetylenes (0.455 mmol) and aryl amines (0.503 mmol) were weighed in a glovebox and were dissolved in 1.75 mL MeCN in a vial fitted with a septum screw cap. Afterwards 0.25 mL of the respective catalyst standard solutions of was added and stirred for 16 h at 60 °C. The NMR yields were determined by ¹H NMR spectroscopy as an average of two runs using 1,3,5-MeO-C₆H₃ as an internal standard. The characteristic singlet of the CH³ group of the imines that appears around 2.3 ppm was used for the integration. For the isolated yields, the products were purified by column chromatography on silica gel. Spectroscopic data is provided in the ESI.³³

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

C. H.-J. thanks Prof. M. Beller for his support, the European Union for funding (H2020-MSCA-IF-2017 792177), the Max Buchner-Foundation for a Scientific Fellowship and support by an Exploration Grant of the Boehringer Ingelheim Foundation (BIS) is acknowledged. We thank our technical and analytical staff for assistance, especially Dr. Anke Spannenberg for her support regarding X-ray analysis. Dr. Alexander Villinger is acknowledged for assistance with the X-ray analysis of **4a**. Dr. Jonas Bresien is kindly acknowledged for help with vibrational spectroscopy and fruitful discussions on DFT calculations.

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Synopsis

Simple terphenyl(bisamino)phosphines are strong donors and can be utilized as ligands in Au(I)-catalyzed intramolecular hydroamination of alkyne.

View Article Online
DOI: 10.1039/D0DT02435J

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