Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

DOI: 10.1002/zaac.201700209

ARTICLE

N-Heterocyclic Phosphenium Dihalido-Aurates: On the Borderline between Classical Coordination Compounds and Ion Pairs

Jan Nickolaus,[a] Simon H. Schlindwein,[a] Martin Nieger,[b] and Dietrich Gudat*[a]

Dedicated to Professor Dr. Thomas Schleid on the Occasion of his 60th Birthday

Abstract. 2-Bromo- and 2-chloro-1,3,2-diazaphospholenes react with (tht)AuCl to afford isolable N-heterocyclic phosphenium (NHP) dihalido-aurates, which were characterized by analytical and spectroscopic data and in one case by a single-crystal X-ray diffraction study. The T-shaped metal coordination sphere found in the crystal consists of a pseudo-linear AuX_2 unit that is perturbed by a weakly bound NHP unit. DFT studies indicate that the subunits interact mainly through electrostatic and dispersion forces, with negligible covalent contributions, and that the phosphenium dibromido-aurate is slightly more stable than an isomeric complex with an intact bromophosphane ligand. NMR studies reveal that the NHP-AuX_2 pairs persist in solution but are kinetically labile and readily undergo halide scrambling. The hydride/fluoride exchange reaction between a secondary phosphane-AuCl complex and [Ph_3C][BF_4] implies that a gold complex with an intact 2-halogeno-1,3,2-diazaphospholene ligand may be more stable than its phosphenium dihalido-aurate isomer when covalent P–X bonding contributions are strengthened.

Introduction

2-Halogeno-1,3,2-diazaphospholenes **I** (Figure 1) were first reported in the 1980s.[1] Their molecular structure resembles closely that of the 1,3,2-diazaphospholidines **II**, but an increased electronic interaction between the exocyclic P–X σ-bonding electron pair and delocalized π-type orbitals in the heterocycle yields enhanced ionic P–X bond polarization[2] and facilitates halide cleavage [3] to yield the exceedingly stable diazaphospholenium cations **III**.[4]

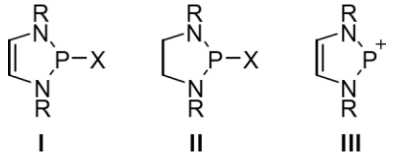


Figure 1. Molecular structures of 2-halogeno-1,3,2-diazaphospholenes **I**, 2-halogeno-1,3,2-diazaphospholidines **II**, and 1,3,2-diazaphospholenium cations **III** (R = alkyl, aryl; X = halogen).

The N-heterocyclic phosphenium (NHP) cations **III** are considered [5] isoelectronic analogues of N-heterocyclic carbenes (NHCs) and have as these found broad application as ligands in coordination chemistry.[6] Despite the isoelectronic relationship, the bonding properties of NHCs and NHPs are complementary rather than similar: while NHCs are strong σ-donors and weak π-acceptors, the cationic NHPs exhibit strong π-acceptor but only weak σ-donor character [6] and are thus ideally suited to support electron rich metal fragments.

Quite remarkably, the stabilizing effect of the cationic ligands can be exerted through two structurally very different bonding modes which are characterized by a combination of planar coordination arrangement at the phosphorus atom and a short P–M distance (type A), or pyramidal coordination at the phosphorus atom and an elongated P–M distance (type B), respectively. The metal–ligand interaction in type A complexes is commonly portrayed as a formal double bond arising from superposition of a weak dative $M \rightarrow P$ σ bond and a stronger retro-dative $M \leftarrow P$ π bond (Figure 2, A), and these species were considered [7] analogues of Fischer-type carbene complexes. The bonding in type B complexes was pictured in two alternative ways by invoking either the interaction of an electrophilic phosphenium ion ("Z-type ligand"[8]) with a nucleophilic metal fragment via an "inverse" dative $M \rightarrow P$ σ bond (Figure 2, B1),[9] or the binding of an anionic ("X-type") phosphido ligand to a formally oxidized central metal atom

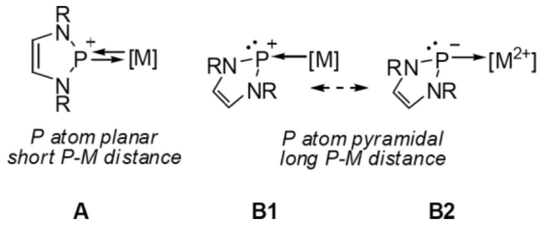


Figure 2. Bonding descriptions in phosphenium complexes featuring either planar (type **A**) or pyramidal (type **B**) coordination arrangement at phosphorus.

---

* Prof. Dr. Dr. h. c. D. Gudat
E-Mail: gudat@iac.uni-stuttgart.de
[a] Institut für Anorganische Chemie
Universität Stuttgart
Pfaffenwaldring 55
70550 Stuttgart, Germany
[b] Department of Chemistry,
University of Helsinki
P.O. Box 55
00014 Helsinki, Finland

Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201700209** or from the author.

(Figure 2, B2).[10] It has been noted that the dualism between the A and B2 notations allows one to draw parallels to the "non-innocent" behavior of metal nitrosyls.[10] A similar dichotomy between planar and pyramidal phosphorus coordination was also discussed for phosphenium carbene[11] and silylene[12] adducts, respectively.

We have recently described a platinum complex **1** (Figure 3), which exhibits a NHP unit with a pyramidal phosphorus atom and was according to the results of computational and reaction studies assigned as a B1 type species containing a cationic phosphenium ligand and a zerovalent metal atom.[13]

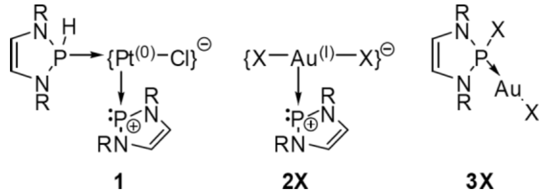


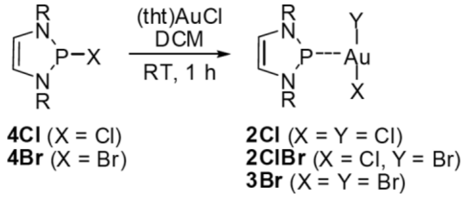
Figure 3. Molecular structures of a complex phosphenium-platinum(0)chloride **1** (*R* = Dipp), an isovalent phosphenium dihaloaurate **2X** and an isomeric halogenophosphane-gold halide **3X** (*X* = halide).

Having noticed that the metal bonding situation in the anionic {(phosphane)PtCl}-fragment of **1** is similar to that in [AuCl$_2$]$^-$, we anticipated that corresponding phosphenium dihalido-aurates **2X** might likewise accessible. Herein, we report on synthesis and characterization of isolable derivatives of this type (with *R* = *t*Bu) and demonstrate that the metal-phosphenium interaction represents an intermediate case between the strong and kinetically inert bonding in complex **1** and the entirely ionic constitution of previously known[14] NHP trichlorido-germanates and -stannates, respectively. In addition, we make some comments regarding the relative stability of the isomeric structures **2X** and **3X**, respectively.

Results and Discussion

Reaction of 2-halogeno-1,3,2-diazaphospholenes **4Cl** and **4Br** with an equimolar amount of (tht)AuCl (tht = tetrahydrothiophene) in dichloromethane (DCM) gave after work-up yellow colored, highly moisture sensitive solids. The ^{1}H NMR spectra displayed exclusively signals of NHP units, and the ^{31}P NMR spectra showed singlets at δ = 181.5 ppm and 186.8 ppm which appear at higher chemical shifts compared to the starting materials, indicating that the expected complex formation has occurred. Elemental analyses are in accord with the presence of 1:1 complexes of composition **4Cl**·AuCl or **4Br**·AuCl, respectively.

Since the spectroscopic data do not allow to distinguish between the isomeric constitutions of **2X** and **3X** (Figure 3), respectively, we attempted to deduce the molecular structures from crystallographic data. While attempts to obtain crystalline samples of the product of the reaction of AuCl with **4Cl** remained unsuccessful, recrystallization of the product obtained with **4Br** from THF produced, gratifyingly, a small crop of crystals that were suitable for a single-crystal X-ray diffraction study. The solid phase consists of molecular N-heterocyclic phosphenium dihalido-aurate units **2X** (Scheme 1) in which Cl- and Br-atoms are disordered over the two possible positions (Figure 4). Analysis of the occupancy factors indicates a Br/Cl ratio of 1.33. The deviation from the original 1:1 composition is presumably attributable to different crystallization properties of Cl- and Br-containing species.



Scheme 1. Reaction of 2-halogeno-diazaphospholenes **4Cl**, **4Br** with (tht)AuCl (*R* = *t*Bu, tht = tetrahydrothiophene).

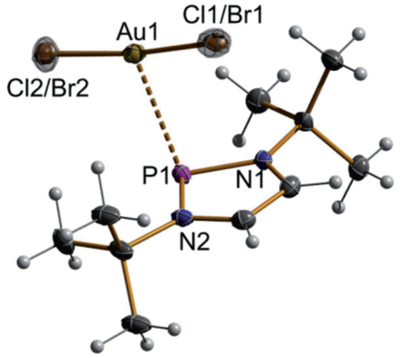


Figure 4. Molecular structure of **2ClBr** in the crystal. Thermal ellipsoids are drawn at the 50 % probability level. Selected distances /Å and angles /°: Br(1)–Au(1) 2.371(2), Cl(1)–Au(1) 2.319(6), Br(2)–Au(1) 2.356(2), Cl(2)–Au(1) 2.317(7), Au(1)–P(1) 2.9093(5), P(1)–N(2) 1.664(2), P(1)–N(1) 1.664(2), Cl(2)–Au(1)–Cl(1) 172.2(3), Br(2)–Au(1)–Br(1) 172.5(1), Cl(2)–Au(1)–P(1) 87.5(2), Cl(1)–Au(1)–P(1) 99.9(2), Br(2)–Au(1)–P(1) 87.3(1), Br(1)–Au(1)–P(1) 100.1(1), N(2)–P(1)–N(1) 90.4(1), N(2)–P(1)–Au(1) 92.9(1), N(1)–P(1)–Au(1) 98.1(1).

Intermolecular contacts between the P1 and Cl2/Br2 atoms of neighboring molecules [3.462(8)/3.489(2) Å] below the sum of the van der Waals radii (3.55/3.65 Å) connect individual units to linear arrays that extend parallel to the crystallographic *c* axis (Figure 5). A qualitative similar arrangement of anionic and cationic constituents had been observed for the 2-iodo-

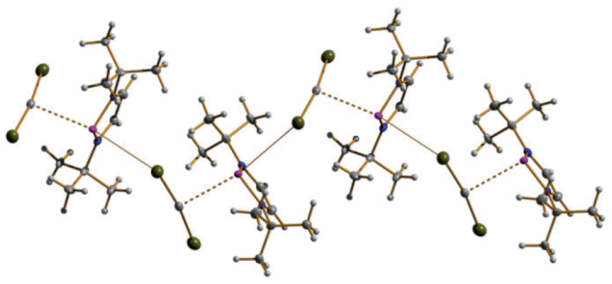


Figure 5. Representation of the one-dimensional molecular stacks in crystalline **2ClBr**. For clarity, only the positions of Br atoms in Au(Cl,Br)$_2$-moieties are displayed.

1,3,2-diazaphospholene ^{tBu}NHP-I (we use ^{R}NHP as a shortcut for a NHP unit with *R* substituents in 1,3-position).[15]

The gold atom exhibits a roughly T-shaped coordination arrangement that is characterized by a nearly linear X_2Au unit [Br(1)–Au(1)–Br(2) 172.5(1)°, Cl(1)–Au(1)–Cl(2) 172.2(3)°] and an elongated Au–P distance [2.909(1) Å] compared to a standard value of 2.262 Å[16] in Au^{I}-phosphane complexes. The Au–Br [2.356(1)–2.371(1) Å] and Au–Cl distances [2.317(7)–2.319(6) Å] are reasonably close to typical Au–*X* distances in $[AuX_2]^-$ anions (median 2.377 for *X* = Br and 2.262 Å for *X* = Cl in reference[16]) but the disorder precludes a detailed discussion of metrical parameters. Even so it is notable that the intermolecular Br(2)/Cl(2)···P contact to the phosphorus atom of an adjacent molecule seems to incite no significant lengthening of the Br(2)/Cl(2)–Au bonds [which are similar or even slightly shorter than the Br(1)/Cl(1)–Au bonds], suggesting that the interaction should not be associated with a bridging coordination of the halide ion. In total, the structural features of **2ClBr** support a partitioning of the metal coordination environment into a pseudo-linear primary unit that is perturbed by a weakly bound secondary ligand. A qualitatively similar description had been given for the recently reported platinum complex **1**,[13] but the difference between the primary and secondary ligands is in the present case even more pronounced.

The phosphorus atom adopts a pyramidal coordination mode (sum of bond angles at P1 281.4(2)°], and the heterocycle is nearly planar. The P–N distances of 1.664(2) Å are similar as in other 2-halogeno-1,3,2-diazaphospholenes (1.65–1.68 Å[17]) and 1,3,2-diazaphospholenium ions (1.66–1.69 Å[17]), respectively.

In view of the composition of **2ClBr**, it cannot be ruled out that its solutions do not contain a single complex with two different halide ligands but a (presumably statistic) mixture of all possible dihalido complexes which undergo rapid dynamic exchange on the NMR time scale. The feasibility of halide exchange is proven by the observations that reaction of the isolated complex with excess Me_3SiBr yields a product with a still larger ^{31}P NMR chemical shift of 191.8 ppm which we address as dibromido-aurate **2Br** (see Scheme 1), and that the ^{31}P NMR spectrum of a mixture of the homoleptic complexes **2Br**, **2Cl** contains again a single resonance rather than separate signals for individual components. We have currently no indication for a signal decoalescence at low temperature. Similar observations had been made in case of Lewis adducts between NHP ions and the corresponding chloro-phosphanes[18] and imply that the exchange is either very fast, or that **2ClBr** is indeed present as the dominant component.

The dependence of the ^{31}P NMR chemical shifts of the phosphenium dihalido-aurates **2X** on the Cl/Br-ratio confirms that – even if the complexes are kinetically labile – the metal-phosphenium interaction persists in solution. In order to cast light on the nature of the bonding and assess the stability of the phosphenium dihalido-aurate relative to the isomeric halogeno-phosphane complex form, we carried out a DFT study on the bromido complexes **2Br** and **3Br**. The calculations were done at the B3LYP/def2-tzvp level both with and without the inclusion of dispersion effects and a solvation model using a PCM-approach, respectively (see Experimental Section for more details). Energy optimized molecular structures of **2Br** and **3Br** at the PCM-B3LYP-D3BJ/def2-tzvp level are displayed in Figure 6, and relative free energies $\Delta G^{298}{}_{\mathrm{rel}}$ as well as selected metrical parameters obtained at all computational levels studied are listed in Table 1.

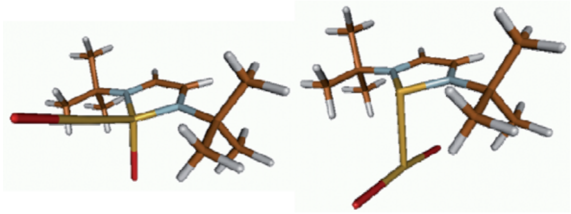


Figure 6. Wireframe representation of the energy optimized molecular structures of **2Br** (right) and **3Br** (left) calculated at the PCM-B3LYP-D3BJ/def2-tzvp level.

The computed gas phase molecular structure of **2Br** is, apart from an underestimation of the Au–P distance by 11 pm and a slight but not significant overestimation of all other bond lengths, in close agreement with the observed constitution of a single phosphenium dibromido-aurate unit in the crystal. Consideration of dispersion effects and a solvation model has no significant effect on the bond lengths in the phosphenium and the $AuBr_2$ subunits but exerts a tremendous effect on the P···Au distance: inclusion of an empirical dispersion correction shortens this distance by some 11 pm while simulation of the effect of a polar dielectric solvent increases the distance to a value beyond the sum of the van der Waals radii, resulting in effective dissociation into an ion pair. When both the dispersion correction and the solvation model are included, the oppo-

Table 1. Calculated (B3LYP/def2-tzvp) relative free energies $\Delta G^{298}{}_{\mathrm{rel.}}$ /kcal·mol^{-1} and selected intramolecular distances /Å for **2Br** and **3Br**.

	Model a)	$\Delta G^{298}{}_{\mathrm{rel}}$	Au–Br b)	P–Au	P–N c)	P–Br
2Br	---	0.0	2.452	2.798	1.688	–
3Br	---	2.9	2.419	2.266	1.681	2.428
2Br	Disp	0.0	2.450	2.671	1.687	–
3Br	Disp	3.4	2.416	2.249	1.676	2.403
2Br	Solv	0.0	2.450	3.932	1.679	–
3Br	Solv	11.9	2.450	2.269	1.671	2.555
2Br	Disp+solv	0.0	2.461	2.827	1.682	–
3Br	Disp+solv	6.4	2.447	2.252	1.667	2.495

a) --- = gas phase calculation, Disp = inclusion of dispersion effects using Grimme's D3BJ formalism,[24] Solv = inclusion of solvation effects using a PCM model (solvent = CH_3CN). b) Average of both distances for 2Br. c) Average of both distances.

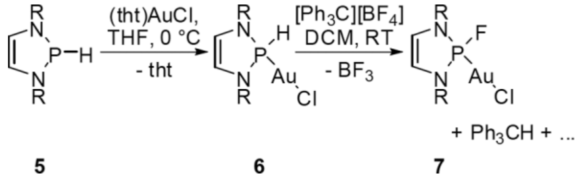
site effects cancel out to produce a minor elongation of the P···Au distance by 3 pm.

The observed trends are qualitatively reproduced by calculations performed with the BP86 instead of the B3LYP functional, although the absolute distances differ substantially and variations induced by the neglect or inclusion of solvation and dispersion effects are in this case less pronounced (see Supporting Information for details). A very similar bond length variation depending on intermolecular interactions like solvation or dipolar polarization by neighboring molecules in a crystal was established experimentally and computationally for the P–Cl bonds in 2-chloro-1,3,2-diazaphospholenes and related to an exceptionally low degree of covalent character of the bond.[3b,15,18] This is in case of **2Br** confirmed by an NBO analysis[19] of the PCM-B3LYP-D3BJ/def2-tzvp density which discloses that the leading resonance structure features no covalent Au–P bond and the Au–P Wiberg Bond Index (WBI) adopts a very low value of 0.24. A partial charge on the NHP moiety of +0.94 indicates that – regardless of some net charge transfer from the metal fragment – the ligand retains more or less unperturbed phosphenium character. Calculated interaction energies between $AuBr_2$ and NHP fragments (in the same arrangement as in the gas phase structure of **2Br**) of –72.1 and –86.6 $kcal{\cdot}mol^{-1}$ at the B3LYP/ def2-tzvp and B3LYP-GD3BJ/ def2-tzvp level, respectively, reflect that dispersion forces have also a sizeable effect on the Au–P bond energy. However, considering that the structural implications of dispersion effects vary greatly with the functional used, the size of the computed energy correction of –14.5 $kcal{\cdot}mol^{-1}$ (or 20 % of the total interaction) can provide at best a qualitative estimate of this influence.

In total, these results indicate that the gold-phosphenium interaction in **2Br** arises mainly from electrostatic and dispersive interactions. "Inverse dative" $M \rightarrow L$ charge transfer contributions play at best a minor role, and covalent bonding contributions remain insignificant. Complex **2Br** should thus not be considered a classical coordination compound but rather a contact ion pair that is mainly held together by non-covalent interactions. This situation is in stark contrast to the situation in **1** where the analysis of fragment charges and orbital interactions provided evidence for significant covalent bonding contributions.[13] In this sense, **2Br** may be considered an intermediate case between a classical coordination compound like **1** and phosphenium salts like $[^{tBu}NHP][ECl_3]$ (E = Ge, Sn),[14] which lack any specific anion–cation interactions and exist both in the crystalline state and in solution as separated ion pairs. It should be noted that the calculated charge distribution also rules out a description of **2Br** as a phosphide complex.

The molecular structure calculated for a phosphane complex **3Br** displays the expected linear and tetrahedral coordination arrangement at the gold and phosphorus atoms, respectively. The Au–P distance is shorter than in **2Br** and close to the standard distance of 2.262 Å[16] for Au^I-phosphane complexes. The Au–Br and P–Br distances show some compliance to solvent effects, which parallels the behavior of P–X bonds in free 2-halogenodiazaphospholenes[2] and is also attributable to hyperconjugation induced bond polarization. Energetically, phosphane complex **3Br** is slightly less stable than **2Br**, but the difference in free energies $\Delta G^{298}{}_{rel}$ increases from some 3 $kcal{\cdot}mol^{-1}$ in the gas phase to 6–12 $kcal{\cdot}mol^{-1}$ (depending on whether dispersion effects are also included or not) when a solvation model is applied. The obvious increase in the relative stability of **3Br** with growing separation of the phosphenium and dibromide-aurate units (cf. Table 1) implies that the decline in interaction energy between the fragments is offset by the gain in solvation energy accompanying increasing charge separation.

It is tempting to interpret the lengthening of the P–Br bond of **3Br** upon immersion in a polar solvent as the first step towards bond dissociation, which facilitates eventual rearrangement of **3Br** to **2Br**. If this is true, it might be possible to stabilize a phosphane complex structure **3X** by reacting a gold(I) precursor with a diazaphospholene featuring a less polarizable exocyclic P–X bond. In accord with this hypothesis, we found that reaction of secondary diazaphospholene **5**[14] with (tht)AuCl yields a phosphane complex **6** (Scheme 2), which was unambiguously identified by spectroscopic data. Diagnostically significant are the observation of the signals of a P–H spin pair with a large mutual spin coupling ($^1J_{PH}$ = 395 Hz) that is a characteristic for diazaphospholene complexes,[13] and the detection of a pseudo molecular ion with an appropriate nominal mass [m/z = 663.19, (**6** + Na)$^+$] and isotope pattern in the (+)-ESI-MS.



Scheme 2. Reaction of the secondary diazaphospholene **5** with (tht)AuCl and $[Ph_3C][BF_4]$ (R = Dipp).

In contrast to platinum complexes with secondary diazaphospholenes,[13] **6** undergoes no reactions involving oxidative metal atom insertion into the P–H bond or proton abstraction. However, treatment with one equivalent of $[Ph_3C][BF_4]$ proceeds readily to yield triphenylmethane and a species identified as fluorophosphane complex **7** besides minor amounts of unidentified side products. Even if **7** could neither be isolated in analytically pure or crystalline form, its constitution was unequivocally established from spectroscopic data. The presence of a gold complex follows from the appearance of the appropriate pseudo molecular ion in the (+)-ESI-MS [m/z = 681.19, (**7** + Na)$^+$], and the attachment of the fluorine atom to phosphorus rather than gold is evidenced by the characteristic large doublet splitting ($^1J^{PF}$ = 1267 Hz) of both the ^{31}P and ^{19}F NMR signals.

The formation of **7** can be envisaged to proceed via hydride abstraction from the starting complex **6** by the trityl cation to give an elusive cationic phosphenium complex $[(^{Dipp}NHP)AuCl]^+$ which then abstracts a fluoride from the $[BF_4]^-$ counterion. The preference to form a fluoro-phosphane-AuCl complex rather than a phosphenium dihalido-aurate in the last step is attributable to the high P–F bond strength –

which had also been identified [3b] as decisive for the decrease of hyperconjugation induced polarization in 2-fluoro- compared to 2-chloro-diazaphospholenes – and the low fluorophilicity of Au^I.

Conclusions

2-Halogeno-1,3,2-diazaphospholenes react with (tht)AuCl under activation of the P–*X* bond (*X* = Cl, Br) to yield isolable phosphenium dihalido-aurates [(NHP)Au(X_2)]. The T-shaped metal coordination arrangement established by a crystallographic study on one such complex can be described in terms of a pseudo-linear primary $[AX_2]^-$ unit, which is perturbed by a weakly interacting cationic phosphenium unit. DFT studies indicate that the phosphorus-metal bonding arises mainly from electrostatic and dispersion interactions and suggest that the product should not be regarded as a classical coordination compound but rather as a strongly interacting contact ion pair. A reduced covalent *M*–P bonding contribution compared to the structurally similar platinum phosphenium complex **1** owes presumably to the lower back-donation capability of Au^I compared to Pt^0 and definitely rules out a description of the product as a phosphido complex with a redox-“non-innocent” R_2P moiety. The formation of a complex with an intact 2-fluoro-1,3,2-diazaphospholene ligand instead of a phosphenium dihalido-aurate upon hydride / fluoride exchange between a secondary diazaphospholene-AuCl complex and $[Ph_3C][BF_4]$ suggests that the relative stabilities of both isomeric forms may be switched when covalent P–*X* bonding contributions are strengthened.

Experimental Section

All reactions were performed in an atmosphere of dry argon, using standard vacuum line or glove box techniques. All solvents used were dried by established procedures. NMR spectra were recorded with a Bruker Avance 250 NMR spectrometer (^{1}H: 250.1 MHz, ^{13}C: 62.9 MHz, ^{19}F: 235.3 MHz, ^{31}P: 101.2 MHz) at ambient temperature. Chemical shifts were referenced to external TMS (^{1}H, Ξ = 100.000000 MHz) using H_3PO_4 (^{31}P, Ξ = 40.480742 MHz) and $CFCl_3$ (^{19}F, Ξ = 94.094011 MHz) as secondary references. Coupling constants are given as absolute values. (+)-ESI-mass spectra were obtained from methanolic solutions with a Bruker Daltronics Micro TOF Q instrument. Elemental analyses were determined with a Thermo Micro Cube CHN/S analyzer. Analytical and spectroscopic characterization of the phosphenium complexes was severely obstructed by their extreme sensitivity towards hydrolysis.

Synthesis of 2ClBr: Solid (tht)AuCl (0.11 g, 0.36 mmol) was added to a solution of **4Br** (0.10 g, 0.36 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for 1 h at room temperature before the solvent was removed under reduced pressure and the remaining solid washed 4 times with Et_2O (2 mL each). The product was obtained as brownish, highly moisture sensitive solid (yield 0.11 g, 62 %). Further purification of the bulk sample was not successful, but recrystallization from THF afforded a small crop of crystals one of which was selected for a single-crystal XRD study. **^{1}H NMR** ($CDCl_3$): δ = 7.44 (s, 2 H, NC*H*), 1.70 (d, 18 H, $^4J_{PH}$ = 1.7 Hz, CH_3). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 186.8 (broad). $C_{10}H_{20}AuBrClN_2P$ (511.6 g·mol^{-1}): calcd. C 23.48 H 3.94, N 5.48 %; found C 25.25 H 5.08 N 5.66 %.

Synthesis of 2Cl: The synthesis of **2Cl** was performed by analogy to the synthesis of **2ClBr** from **4Cl** (0.10 g, 0.43 mmol) and (tht)AuCl (0.14 g, 0.36 mmol) in CH_2Cl_2 (2 mL) at room temperature of the corresponding chloro-diazaphospholene. The product was obtained as yellow solid (yield 0.10 g, 51 %). **^{1}H NMR** ($CDCl_3$): δ = 7.39 (s, 2 H, NC*H*), 1.66 (d, 18 H, $^4J_{PH}$ = 1.6 Hz, CH_3). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 181.5. $C_{10}H_{20}AuCl_2N_2P$: calcd. C 25.71, H 4.32, N 6.00 %; found: C 25.29 H 4.64, N 5.97 %.

Reaction of 2BrCl with Me_3SiBr: Me_3SiBr (0.17 g, 1.1 mmol) was added to a solution of **2Cl** (0.12 g, 0.26 mmol) in CH_2Cl_2 (2 mL) at room temperature. The resulting mixture was stirred for 1 h. The solvent was evaporated under reduced pressure, the remaining solid washed with Et_2O (3 × 3 mL), and dried under vacuum. Attempts to further purification of the crude, spectroscopically impure product remained unsuccessful (yield: 0.12 g, 84 %). **^{1}H NMR** ($CDCl_3$): δ = 7.76 (s, 2 H, NC*H*), 1.76 (d, 18 H, $^3J_{PH}$ = 2.0 Hz, CH_3). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 191.8 (broad).

Synthesis of 6: (Tht)AuCl (0.12 g, 0.37 mmol, 1 equiv.) was added in two portions to a stirred solution of **5** (0.15 g, 0.37 mmol) in THF (3 mL) at 0 °C. The reaction was stirred for 2 h while being allowed to warm to room temperature. The solvent was removed under reduced pressure and the solid residue washed with *n*-hexane (5 × 3 mL) to afford 0.20 g of **6** (0.32 mmol, 88 % yield) in the form of a yellow, microcrystalline solid. **^{1}H NMR** ($CDCl_3$): δ = 8.70 (d, 1 H, $^1J_{PH}$ = 396 Hz, P*H*), 7.31 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, *para*-H), 7.19 (m, 4 H, *meta*-H); 6.00 (d, 2 H, $^3J_{PH}$ = 13.0 Hz, NC*H*), 3.36 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$), 3.07 (sept, 2 H, $^3J_{HH}$ = 7.0 Hz, C*H*CH$_3$), 1.37 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$), 1.23 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$), 1.19 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$), 1.14 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 74.3 (s). **^{31}P NMR** ($CDCl_3$): δ = 74.3 (d, $^1J_{PH}$ = 396 Hz). **^{13}C NMR** ($CDCl_3$): δ = 149.1 (d, 2 C, $^3J_{PC}$ = 2.3 Hz, *ortho*-C); 148.5 (d, 2 C, $^3J_{PC}$ = 3.0 Hz, *ortho*-C), 133.2 (d, 2 C, $^2J_{PC}$ = 6.1 Hz, *ipso*-C), 129.5 (d, 2 C, $^5J_{PC}$ = 2.1 Hz, *para*-C), 125.1 (d, 2 C, $^4J_{PC}$ = 1.1 Hz, *meta*-C), 124.2 (d, 2 C, $^4J_{PC}$ = 1.4 Hz, *meta*-C), 121.3 (d, 2 C, $^2J_{PC}$ = 4.6 Hz, NCH), 29.5 (s, 2 C, *C*HCH$_3$), 29.3 (s, 2 C, *C*HCH$_3$), 25.5 (s, 2 C, *C*H$_3$), 24.9 (s, 2 C, *C*H$_3$), 24.0 (s, 2 C, *C*H$_3$), 23.8 (s, 2 C, *C*H$_3$). (+)-**ESI-MS**: *m*/*z*: 663.19 ([M + Na]$^+$). $C_{26}H_{37}AuClN_2P$ (640.99 g·mol^{-1}): calcd. C 48.72 H 5.82 N 4.37 %; found C 46.79 H 5.78 N 4.11 % (the low carbon value is presumably due to carbide formation).

Reaction of 6 with Trityl Tetrafluoroborate: Triphenylmethyl tetrafluoroborate (41 mg, 0.12 mmol) was added to a stirred solution of **6** (80 mg, 0.12 mmol) in CH_2Cl_2 (2 mL). Stirring was continued for 12 h at room temperature before the solvent was removed under reduced pressure. The resulting crude product was washed with hexane (5 × 3 mL) and dried under vacuum. NMR spectroscopic analysis allowed identifying the light yellow solid as a mixture of complex **7** (no yield determined), triphenylmethane, and further unidentified side products. Separation of **7** was unfeasible due to similar solubility of the individual components. **^{1}H NMR** ($CDCl_3$): δ = 7.38 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, *para*-H), 7.05 (m, 4 H, *meta*-H); 6.17 (d, 2 H, $^3J_{PH}$ = 12.4 Hz, NC*H*), 3.24 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$), 3.03 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$), 1.38 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$), 1.21 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$), 1.10 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 108.2 (d, $^1J_{PF}$ = 1267 Hz). **^{31}P NMR** ($CDCl_3$): δ = 108.2 (dd, $^1J_{PF}$ = 1267, $^3J_{PH}$ = 12.4 Hz). **^{19}F NMR** ($CDCl_3$): δ = –6.50 (d, $^1J_{PF}$ = 1267 Hz). (+)-**ESI-MS**: *m*/*z*: 681.19 ([M + Na]$^+$).

Crystallographic Studies: Single crystal X-ray diffraction data of **2ClBr** were measured with a Bruker AXS Nanostar C diffractometer equipped with a Kappa APEX II Duo CCD-detector and a KRYOFLEX cooling device at 100(2) K using Mo-K_α radiation (λ = 0.71073 Å). A crystal was selected under Fomblin Y perfluoro-oil, mounted on a nylon loop, and immediately placed in a cold stream of nitrogen. The structure was solved by direct methods (SHELXS-2014[20]) and refined with a full-matrix least-squares scheme on F^2 (SHELXL-2014[20]). A semi-empirical absorption correction from equivalents was applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms with a riding model. The occupancy factors of the disordered halogen atoms were determined as 0.538(2)/0.462(2) for Br(1)/Cl(1) and 0.604(2)/0.396(2) for Br(2)/Cl(2), respectively. Listings of crystallographic data and details on the structure solution are given in the Supporting Information.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1558044 for **2ClBr** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Computational Studies: DFT calculations were carried out with the Gaussian09 suite[21] using the B3LYP functional[22] and a def2-tzvp basis set[23] by *Weigend* and *Ahlrichs*. Grimme's D3BJ formalism[24] was used to include dispersion effects. Numerical integrations were performed on an ultrafine grid and solvent effects were modeled by using a PCM model as implemented in the Gaussian package (SCRF = acetonitrile; this choice was made in order to emphasize the effects arising from the dielectric properties of the solvent). Molecular structures were energy optimized without symmetry constraints and identified as local minima on the energy hypersurface by harmonic vibrational frequency calculations. Natural bond analysis[19] was performed with the NBO3.1 program as implemented in Gaussian09, and MOLDEN[25] was used for visualization.

Supporting Information (see footnote on the first page of this article): Crystallographic data for **2ClBr**, details on the computational studies, calculated atomic coordinates and relative energies for **2Br**, **3Br** at different computational levels, reproductions of selected NMR spectra

Acknowledgements

The computational studies were supported by the bwHPC initiative and the bwHPC-C5 project provided through the associated compute services of the JUSTUS HPC facility at the University of Ulm. bwHPC and bwHPC-C5 (http://www.bwhpc-c5.de) are funded by the state of Baden-Württemberg and the DFG (grant no. INST 40/467–1 FUGG). We further thank B. Förtsch for elemental analyses, and J. Trinkner and Dr. W. Frey (both from Institute of Organic Chemistry, University of Stuttgart) for the measurement of mass spectra and the collection of X-ray data sets, respectively.

Keywords: N-heterocyclic phosphenium ions; P ligands; Gold; Coordination modes; Ion pairs

References

[1] A. M. Kibardin, Yu. B. Mikhailov, T. V. Gryaznova, A. N. Pudovik, *Izv. Akad. Nauk SSSR Ser. Khim.* **1986**, 960–960.
[2] Review: D. Gudat, *Dalton Trans.* **2016**, *45*, 5896–5907.
[3] a) M. K. Denk, S. Gupta, R. Ramachandran, *Tetrahedron Lett.* **1996**, *37*, 9025–9028; b) D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, *Chem. Eur. J.* **2000**, *6*, 3414–3425.
[4] a) I. A. Litvinov, V. A. Naumov, T. V. Gryaznova, A. N. Pudovik, A. M. Kibardin, *Dokl. Akad. Nauk SSSR* **1990**, *312*, 623–625; b) M. K. Denk, S. Gupta, A. J. Lough, *Eur. J. Inorg. Chem.* **1999**, 41–49.
[5] a) D. Gudat, *Eur. J. Inorg. Chem.* **1998**, 1087–1097; b) H. M. Tuononen, R. Roesler, J. L. Dutton, P. J. Ragogna, *Inorg. Chem.* **2007**, *46*, 10693–10706.
[6] Recent reviews: a) D. Gudat, *Coord. Chem. Rev.* **1997**, *163*, 71–106; b) H. Nakazawa, *Adv. Organomet. Chem.* **2004**, *50*, 107–143; c) L. Rosenberg, *Coord. Chem. Rev.* **2012**, *256*, 606–626.
[7] C. A. Caputo, M. C. Jennings, H. M. Tuononen, N. D. Jones, *Organometallics* **2009**, *28*, 990–1000.
[8] M. L. H. Green, *J. Organomet. Chem.* **1995**, *485-505*, 127–148.
[9] L. Hutchins, E. Duesler, R. Paine, *Organometallics* **1982**, *1*, 1254–1256.
[10] B. Pan, Z. Xu, M. W. Bezpalko, B. M. Foxman, C. M. Thomas, *Inorg. Chem.* **2012**, *51*, 4170–4179.
[11] N. J. Hardman, M. B. Abrams, M. A. Pribisko, T. M. Gilbert, R. L. Martin, G. J. Kubas, R. T. Baker, *Angew. Chem.* **2004**, *116*, 1989 –1992.
[12] R. Pietschnig, *Chem. Commun.* **2004**, 546–547.
[13] J. Nickolaus, D. A. Imbrich, S. H. Schlindwein, A. H. Geyer, M. Nieger, D. Gudat, *Inorg. Chem.* **2017**, *56*, 3071–3080.
[14] S. Burck, D. Gudat, M. Nieger, W. W. Du Mont, *J. Am. Chem. Soc.* **2006**, *128*, 3946–3955.
[15] S. Burck, D. Gudat, M. Nieger, Z. Benkö, L. Nyulászi, D. Szieberth, *Z. Anorg. Allg. Chem.* **2009**, *635*, 245–255.
[16] Median values as obtained from queries for structures containing Au^{I}-phosphane and dihalido-aurate fragments, respectively, in the CSD database.
[17] D. Gudat, *Top. Heterocycl. Chem.* **2010**, *21*, 63–102.
[18] S. Burck, D. Gudat, *Inorg. Chem.* **2008**, *47*, 315–321.
[19] A. E. Reed, R. B. Weinstock, F. Weinhold, Natural population analysis, *J. Chem. Phys.* **1985**, *83*, 735–746.
[20] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[21] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.
[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[23] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[24] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
[25] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.

Received: July 4, 2017

J. Nickolaus, S. H. Schlindwein, M. Nieger,
*D. Gudat** **1–7**

N-Heterocyclic Phosphenium Dihalido-Aurates: On the Borderline between Classical Coordination Compounds and Ion Pairs