Ylide-Stabilized Phosphenium Cations: Impact of the Substitution Pattern on the Coordination Chemistry

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On the occasion of the 60th birthday of Prof. Holger Braunschweig.

Abstract: Although N-heterocyclic phosphonium (NHP) cations have received considerable research interest due to their application in organocatalysis, including asymmetric synthesis, phosphenium cations with other substitution patterns have hardly been explored. Herein, the preparation of a series of ylide-substituted cations of type [YPR]" (with Y = Ph, PC(Ph), R = Ph, Cy or Y) and their structural and coordination properties are reported. Although the diylide-substituted cation forms spontaneous from the chlorophosphine precursor, the monoylidylphosphenium ions required the addition of a halide-abstraction reagent. The molecular structures of the cations reflected the different degrees of electron donation from the ylide to the phosphorus center depending on the second substituent. Molecular orbital analysis confirmed the stronger donor properties of the ylide systems compared to NHPs with the mono-ylide substituted cations featuring a more pronounced electrophilicity. This was mirrored by the reaction of the cations towards gold chloride, in which only the diylide-substituted cation [Y,P]" formed the expected LAuCl" complex, while the monoylid-substituted compounds reacted to the chlorophosphine ligands by transfer of the chloride from gold to the phosphorus center. These results demonstrate the tunability of ylide-functionalized phosphorus cations, which should allow for further applications in coordination chemistry in the future.

Introduction

Phosphenium cations are compounds of type R_P" and hence valence isoelectronic to carbenes.[1] However, owing to their positive charge phosphonium ions usually exhibit a weaker σ-donor strength but increased π-acceptor abilities.[2] These electronic properties make phosphenium cations attractive ligands for metal complexation which might be used complementarily to stable singlet carbenes, such as N-heterocyclic carbenes (NHCS), which are in general strong donor ligands. Despite many advances made in the past years in phosphonium cation chemistry, their properties and coordination chemistry are far less explored than those of their carbon analogues. The limitation is mostly due to the higher reactivity connected with their cationic nature. Thus, only few phosphenium cations have been isolated and thoroughly explored. The most extensively studied systems are – analogous to carbenes[3] – N-heterocyclic phosphonium cations (NHPs). Since the first reports on NHPs in 1970s[4] various derivatives[5] and metal complexes have been reported[6,7] and more recently also applied in catalysis including asymmetric organocatalysis.[8]

Apart from amino groups also other π-donor substituents have been employed to stabilize these carbene-like species. In the 1990s Schmidpeter pioneered the use of ylide groups in phosphonium cation chemistry. He realized that depending on the second substituent R, ylide-substituted chlorophosphines of type YRPCI (Y = ylide) can spontaneously dissociate into the phosphonium cations.[9,10] Diylide-substituted cations are particularly stable due to the strong π-donation from both ylide groups resulting in an efficient charge delocalization in the C–P–C linkage. In case of the cyclic cation A this delocalization even results in a partial phosphide character at the central P atom (A1, Figure 1).1[1] Nonetheless, these systems exhibit phosphonium cation reactivity and for example react with nucleophiles such as organolithium compounds at the central

Figure 1. Diylidephosphenium cation reported by Schmidpeter and its different mesomeric structures.
generate the first diylide-substituted boron cations

In the course of our research program on ylidic compounds we became interested in the stabilization of reactive main group compounds. With the isolation of metalated ylides as versatile reagents for ylide-functionalization we were able to generate the first diylide-substituted boron cations and heavier tetrylenes. Furthermore, the introduction of ylide substituents in phosphines led to a remarkable increase of their donor capacity and hence to excellent performance in gold and palladium catalysis. This led us to re-investigate the chemistry of ylide-substituted phosphonium cations to evaluate their potential as ligands in transition metal chemistry.

Results and Discussion

Synthesis of the phosphonium cations

We began our studies with the synthesis of the diylidyphosphonium cation 2a reported by Schmidpeter. To further explore the impact of the substitution pattern also the isolation of the monoylide cations 4 was targeted. With only one π-donating ylide substituent, we expected these phosphonium cations to be more reactive and stronger acceptor ligands. All three ligands were prepared via a chlorosilane elimination protocol by reaction of the silyl-substituted ylide with PCl₃. In case of the diylide-substituted compound chloride elimination, the monoylidyl compounds formed stable chlorophosphines 3a and 3b. In case of the diylide-substituted compound chloride exchange to the BF₄⁻ salt was conducted to exclude any weak interaction of the counter-anion with the phosphorus cation. The chlorophosphines 3 were isolated as colorless solids in 85% yield and are characterized by two doublets in the 31P H NMR spectrum appearing at approx. 24 ppm for the PPh₃ group and at 132 ppm (for 3a) and at 160 ppm (for 3b), respectively. In the molecular structures (Figure 2), both chlorophosphines feature remarkably different P–Cl bond lengths. As a consequence of the stronger donor properties of the cyclohexyl substituent, 3b (2.256(1) Å) shows a 55 pm longer P–Cl bond than 3a (2.191(1) Å). Such varying P–X distances have been discussed in the past as snapshots of the pending dissociation.

With the chlorophosphines in hand, we next addressed their conversion into the corresponding phosphonium cations. Chloride abstraction from 3 was accomplished with AlCl₃, thus delivering the cations 4 as colorless solids in good yields (72 for 4a, 73 for 4b). The cations 2 and 4 were characterized by multi-nuclear NMR spectroscopy, elemental and single-crystal X-ray diffraction analysis. The 31P [1H] NMR spectrum shows that the cyclohexyl-substituted cation 4b features the most deshielded signal (Figure 3, Table 1), which resonates at 403.1 ppm and hence is considerably downfield shifted compared to 4a, 2, NHPs and acyclic aminophosphonium cations.

This suggests that 4b exhibits the smallest HOMO-LUMO gap in this series of compounds (see below for discussion) and presumably is the most nucleophilic species with the strongest acceptor properties. Interestingly, the 1JPP coupling constants

![Scheme 1. Synthesis of the phosphonium cations 2 and 4 from the silyl-substituted ylide 1.](image)

![Figure 2. Molecular structure of 3a and 3b. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): 3a: P1–C1 1.7426(19), C1–P2 1.7424(19), P2–C1 2.1914(6), P1–C1–C2 119.91(14), P1–C2–P2 114.00(8), C2–C1–P2 111.73(10), C1–P2–C1 107.13(7), C1–P2–C2 97.79(6), C1–P1–C2 106.60(9), 3b: P1–C1 1.7359(14), C1–P2 1.7382(14), P2–C1 2.2560(5), P1–C1–C2 117.54(10), P1–C2–P2 114.00(8), C2–C1–P2 126.93(10), C1–P2–C1 108.57(5), C1–C2–P2 94.18(5), C1–C2–P2 104.20(7).](image)

![Figure 3. 31P NMR shifts of the ylide-substituted phosphonium cations.](image)
increase from 4b to 4a and 2 and become significantly smaller compared to the chlorophosphine precursors. Overall, the mono-ylidylyphosphonium cations exhibited are considerably higher reactivities and more readily decomposed in solution. However, in the solid state they could be stored for weeks at –20 °C.

Single crystals for 2b, 4a and 4b with BF₄⁻ or AlCl₄⁻ as counter-ions were obtained by layering DCM solutions of the cations with cyclohexane. All structures are depicted in Figure 4, important structure parameters are listed in Table 1. The molecular structures clearly reflect the different stabilizing abilities of the second substituent at P2 and its impact on the π-interaction from the ylide substituent. Due to the competing π-interaction by both ylide groups in 2b, the diylide cation features the longest C1–P2 distance of approx. 1.72 Å. The P2–C1 bonds in the monoylide phosphonium cations are considerably shorter, with the phenyl compound featuring the shortest distance of 1.673(5) Å. The reverse trend is found for the P1–C1 distances to the phosphonium group. With increasing π-bonding between the ylide and the phosphonium center, the electrostatic attraction to the phosphonium group decreases. Consistent with the C1–P2 bonds, this results in the shortest C1–P1 bond for 2 and the longest in the phenyl-substituted compound, suggesting that the strongest ylide-P bond is found in cation 4a. It is noteworthy that the phenyl substituent in 4a is not or only little involved in π-interaction with the central phosphorus atom. The same is true for the phenyl groups in the ylide-backbone. While the two ylide groups in 2b form a fully delocalized π-system over the planar P–C–P–C–P linkage, the phenyl group in 4a is oriented out of the P1–C1–P2 plane with dihedral angles of approx. 20°. Consequently, no changes in the C–C bond lengths are observed within the phenyl groups of 4a compared to that in 3a, which contrasts for example the quinoidal structure reported for the borinium cation MesB⁺.$^{22}$ It is also noteworthy, that in contrast to some ylide-substituted phosphines only one conformational isomer of 2 and 4 are observed in the solid-state and in solution.$^{12b}$ In these isomers, the lone pair at phosphorus is perpendicularly arranged to the lone pair at the ylidy carbon atom in order to minimize electronic repulsion and enable π-stabilisation of the empty p orbital at P2. Due to additional steric effects an anti/zigzag arrangement is favored, which in case of 2 leads to the conformer with the smaller phenyl groups facing each other.

To shed light on the electronic structure and the observed spectroscopic properties of the synthesized cations we per-

![Image](image-url)

**Figure 4.** Molecular structure of (left) [YPB(Cy)·AuCl](4b), (middle) [YPPh]AlCl(4a) and (right) [YPCy]AlCl(4b). Hydrogen atoms, counter anions and solvent molecules are omitted for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): 2b: P1–C1 1.7523(14), P2–P1 1.7216(14), C26–P2 1.7141(14), C26–P3 1.7566(14), P1–C1–P2 113.34(8), P1–C1–C2 116.15(10), C2–C1–P2 130.51(10), C2–P1–C2 111.91(7), P3–C26–P2 112.36(8), P3–C26–C27 116.70(10), C27–C26–P2 130.93(10), 4a: P1–C1 1.807(5), C1–P2 1.673(5), C2–C1–P1 116.13(3), C2–C1–P2 128.4(4), P2–C1–P1 115.4(3), C1–P2–C6 108.4(3), 4c: P1–C1 1.797(2), C1–P2 1.668(2), C2–C1–P1 118.22(14), C2–C1–P2 125.79(14), P2–C1–P1 115.93(11), C1–P2–C6 104.58(9).
formed computational studies on the PW6B95D3/def2tzvpp level of theory (see the Supporting Information for details). Calculations of the molecular orbitals show that the ylide-substituted phosphonium cations feature energetically high-lying LUMOs (LUMO = lowest occupied molecular orbital) and hence are less electrophilic/weaker acceptors than NHPs (Figure 5). This agrees well with the stronger \( \pi \)-donor ability of the ylide compared to the amino substituent. Accordingly, the diylidyl cation \( 2^+ \) is the by far weakest acceptor in this series of compounds. While the LUMO in all cations represents the empty \( \pi \) orbital at P2 and thus is always predominantly localized at the phosphonium center, the HOMO (except for \( 4b \)) displays a \( \pi \)-symmetric orbital delocalized over the substituents with a strong contribution by the ylidelic carbon centers. In general, the energy of the molecular orbitals representing the lone pair at the phosphorus center in \( 2 \) already indicated by the NMR spectroscopic data. Upon treatment of \( 2 \) with one equivalent of (tht)AuCl, the signal of the central phosphorus atom experienced a distinct high field shift by more than 250 ppm in the \( ^3\text{P}(\text{H}) \) NMR spectrum for \( 2 \) from 290.4 ppm in \( 2b \) to 229.2 ppm in \( 2b \). This bond length is comparable to other phosphido-gold complexes\(^\text{25,13a} \). However, in contrast to previously reported complexes, the central phosphorus atom adopts a completely planar geometry with a sum of angles of 360°. This was confirmed by XRD analysis of the complex formed with \( 2a \), suggesting considerable changes in the ligand structure. This was supported by the chlorophosphine ligand \( \text{tht} \). This structure matches well with the NMR spectroscopic observations.

Interestingly, the monoylide-substituted phosphonium cations \( 4 \) showed a different coordination behavior towards gold chloride as suggested by the different orbital energies. This was already indicated by the NMR spectroscopic data. Upon treatment of \( 4a \) and \( 4b \), respectively, with one equivalent (tht)AuCl, the central phosphorus atom experienced a distinct high field shift by more than 250 ppm in the \( ^3\text{P}(\text{H}) \) NMR spectrum, giving rise to a signal at 93.3 ppm for \( 4a \) and 73.2 ppm for \( 4b \), respectively. This shift is much more pronounced than in case of \( 2b \), suggesting considerable changes in the ligand structure. This was confirmed by XRD analysis of the complex formed with \( 4a \), which revealed the formation of complex \( 6a \) (Scheme 3), in which a cationic gold center is coordinated by the chlorophosphine ligand \( \text{tht} \) and \( \text{Au} \). This structure matches well with the NMR spectroscopic observations.

\( 6a \) is presumably formed from the expected AuCl complex by chloride shift from gold to phosphorus. Thus, this gold complex should also be accessible from a simple AuCl complex of the chlorophosphines precursors \( 3 \). Indeed, treatment of \( 3a \) and \( 3b \), respectively, with one equivalent (tht)AuCl delivered the corresponding gold chloride complexes \( 7 \), which could both be isolated in moderate yields of approx. 40% and unambiguously characterized, including XRD analysis (Figure 6 and the Supporting Information). Treatment of the gold chloride complexes with aluminium trichloride finally yielded the cationic complexes as judged by \( ^3\text{P} \) NMR spectroscopy (Scheme 3). Using an excess of AlCl\(_3\) or NaBAr\(_4\)) did not lead to the abstraction of the chloride at the phosphorus center in \( 6 \) to form the corresponding dication. The same holds true for the cationic gold complex \( 5b \).
Figure 6. Molecular structures of \([Y \cdot \text{AuCl} \cdot \text{BF}_4]^- \), \([\text{YP} \cdot \text{Ph} \cdot \text{Au} \cdot \text{tht}) \cdot \text{AlCl}_3\) and \([\text{YP} \cdot \text{Cl} \cdot \text{Au} \cdot \text{Cl}^-\) in the gold species. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): \([Y \cdot \text{AuCl} \cdot \text{BF}_4]^-\); \(P1 - C1 1.768(3), P3 - C26 1.758(3), P2 - C1 1.692(3), P2 - C26 1.691(3), Au1 - P2 2.212(7), Au1 - C11 2.2777(7), C2 - C1 - P2 127.98(19), C2 - C1 - P1 113.18(15), P2 - C1 - P1 118.81(15), C27 - C26 - P3 116.51(18), P2 - C26 - P3 119.87(15), C1 - P2 - Au1 121.58(9), C26 - P2 - Au1 120.8(9), P2 - Au1 - C11 178.78(2), \([\text{YP} \cdot \text{Au} \cdot \text{tht}) \cdot \text{AlCl}_3\]; P1 - C1 1.734(7), C26 1.691(3), Au1 1.713(5), Cl1 1.728(4), P2 2.2273(11), Au1 - P2 2.2273(11), Au1 - C11 2.2873(11), C2 - C1 - P1 117.9(3), P2 - C1 - P1 120.13(3), P2 - Au1 - C12 176.72(4).

Table 2. Bond length of the shortest Au-arene interaction in the discussed gold complexes.

|       | 5b         | 6a         | 7a         | 7b         |
|-------|------------|------------|------------|------------|
| Au-C$_{\text{ipso}}$ | 3.132 Å    | 3.160 Å    | 3.220 Å    | 3.371 Å    |

Single crystals for 6a could be obtained by slow vapor diffusion of pentane into a saturated dichloromethane solution. In the crystal (Figure 6), the gold center adopts a linear geometry between the phosphine and tetrahydrothiophene ligand with an Au–P distance of 2.260(2) Å. This bond length is slightly longer than the one found in 5b and also longer than the one in the AuCl precursor 7a. The P2–C1 bond shortens in the compound series 3a > 7a > 6a from 1.742(2) to 1.700(7) Å, thus accounting for an increasing shift of electron density from the ylidic carbon atom to the phosphorus (and metal) center. The C1-P1 distance increases in the same sequence of compounds.

An interesting combining structural feature of all gold complexes shown in Figure 6 are short distances between the gold center and one phenyl group of the phosphonium moiety. A survey (Table 2) of all structures revealed that the Au-C$_{\text{ipso}}$ distance is shorter in the cationic gold complex 6a (3.160 Å) than in the neutral AuCl complexes 7 which exhibits an Au-C$_{\text{ipso}}$ distance of 3.220 Å. Also, the cationic Au complex 5b with the diylidylphosphonium ligand shows a short distance of 3.132 Å. Such short distances have been attributed to attractive arene gold interactions and have often been discussed in the context of gold catalysis and their importance for stabilizing catalytically active cationic gold species. Prominent examples are the Echavarren’s catalysts with Buchwald’s biarylphosphine JohnPhos. Here, an arene Au distance of 3.04 Å was reported in the gold cation which is slightly shorter than the one in 6a thus indicating a weak attractive interaction. It is important to note that such interactions have also been suggested for gold complexes of ylide-substituted phosphines (YPhos) and thought to be one reason for their high catalytic efficiency. However, no cationic Au-YPhos complex has been isolated until today. Thus, 6a constitutes the first complex of its kind.

Unfortunately, all attempts to apply the cationic gold complexes as catalysts in hydroaminations or enyne cyclization reactions remained unsuccessful. This can probably be attributed to the partial phosphide character and the resulting lower electrophilicity compared with other cationic gold species as well as the sensitivity of the complexes. To further investigate the coordination properties of the monoylide-substituted phosphonium cations 4 and the chloride transfer from other transition metals we probed...
their reaction towards a series of late transition metal complexes. Although, the isolation of any reaction product revealed to be difficult due to the formation of further side products or the sensitivity of the formed complexes, NMR spectroscopic analyses of the reaction mixtures with [Pd-(cod)Cl]2 clearly indicated the formation of the corresponding chlorophosphines 3, for example with two doublets at δ = 78.4 and 17.4 ppm with a coupling constant of 9.2 Hz for 3a. In the case of [RhcodCl]2, however, the formation of a phosphonium complex was observed as evidenced by a considerably downfield-shifted signal in the 31P{1H} NMR spectrum for the P(III) center (δ = 371.5 ppm, 1JPP = 163.5 Hz and 2JPP = 52.5 Hz for 4b). Although all attempts to isolate these complexes failed, single crystals were obtained from the crude reaction mixture of 4b in CD2Cl2, which confirmed the still intact Rh–Cl bond (Figure 7). The Rh–P bond amounts to 2.217(4) Å and is thus longer compared with the rhodium phosphorus bond of 2.089(2) Å reported for an NHP-RhCl(PPh3)2 complex with a bis(alkylamido)naphthalene framework,[24] and in the range of Rh–P bonds in phosphine complexes.[23] Overall, the marked difference between the coordination chemistry of [Y2P]+ and the monoylide cations clearly shows that a certain stabilization of the cation is required for selective applications in transition metal chemistry. One ylide moiety as sole ν-donating substituent seems to be insufficient so that future research endeavors should focus on the diylidyl or monoylide systems with a further ν-donor substituent.

**Conclusion**

The synthesis of three phosphorus cations stabilized by two or one ylide moiety is reported. Due to the strong electron-donating ability of the ylide group, these formal phosphonium cations are considerably more electron-rich than N-heterocyclic phosphonium cations but can be tuned by variation of the second substituent bound to the phosphorus center. Thus, the bis(ylidy)phosphonium cation Y2P+ forms spontaneously from the corresponding chlorophosphine in solution, whereas the mono(ylidy)phosphonium ions are only accessible by halide abstraction. The stronger electrophilic nature of the monoylide substituted compounds was also confirmed by computational studies and led to a different coordination chemistry compared to [Y2P]+. Although the bis(ylidy) cation formed the expected cationic LAgCl complex, the monoylide systems reacted with (THT)AuCl by chloride transfer from gold to phosphorus, thus resulting in the formation of a cationic chlorophosphine gold complex. Crystallographic studies on the phosphonium cations and their metal complexes reflected the electron donation from the ylide to the phosphorus center. As such, the P–C distances in the ligand backbone changed depending on the second substituent at phosphorus and the presence of a metal center.

Overall, these studies clearly demonstrate that ylide groups efficiently stabilize cationic phosphorus species and allow a tuning of their properties by changing the molecular design. Although systematic studies on the impact of the substituents in the ylide backbone on the stability and reactivity of phosphonium cations are missing, it can be assumed that a further control of reactivity should be possible.

**Crystallographic Details**

Deposition Number(s) 2121597 (for HYSiMe2), 2121588 (for 1), 2121592 (for 2[BF4]), 2121599 (for 3a), 2121593 (for 3b), 2121594 (for 4a), 2121596 (for 4b), 2121589 (for 5a), 2121600 (for 5b), 2121598 (for 7a), 2121595 (for 7b), 2121590 (for 6a), 2121591 (for 4bRh(cod)Cl)AlCl3) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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