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ARTICLE

P-P σ -Bond Activation by Gold(I) Coordination

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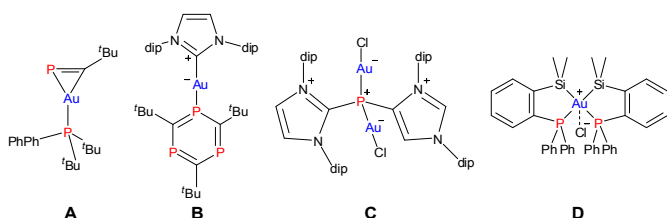
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Bond activation by gold is of immanent interest with respect to catalytic activity. By coordination of an AuCl fragment onto the P–P σ -bond of an azadiphosphiridine, the P–P bond is cleaved to give a PNP type of ligand in the gold(I) complex. Another equivalent of the gold precursor selectively binds on a P lone pair. The bonding situation was further studied by means of computation, indicating the existence of a 3-center-2-electron bond.

Introduction

In recent research, gold complexes have been mainly targeted for their catalytic activity and their potential anti-tumor effects. However, complex chemistry of gold recently has put forth astonishing examples like Bertrand's cAAC-stabilized gold(0) and gold(I) complexes and trinuclear clusters.^{1–3} The coordination of phosphalkynes to gold(I) was investigated by Russell et al. (Scheme 1), who observed side-on coordination of the P–C unit as the preferred bonding mode (**A**)⁴ and the σ -coordination of (PC^tBu)₃ to a Au–NHC complex (**B**).⁵ Furthermore, Weigand et al. were able to elegantly demonstrate the coordination of a phosphanide to up to two AuCl moieties (**C**).⁶ Bourissou et al. recently studied the oxidative addition of a Si–Si σ -bond to gold(I) species, resulting in the formation of a square planar gold(III) complex (**D**), which is an important example of spontaneous oxidative addition of a Si–Si σ -bond at a gold complex.⁷



Scheme 1 Selected examples for Au complexes coordinated to P species.

Azadiphosphiridines feature a bent σ -bond between the two P atoms. $\lambda^3\lambda^3$ - and $\lambda^3\lambda^5$ -azadiphosphiridines have been intensively studied 1981 by Niecke et al.^{8–14} Also their coordination behaviour has been explored, covering imido-complexes that feature an azadiphosphiridine backbone^{15,16} and a spirocyclic $\lambda^3\lambda^5$ -azadiphosphiridine molybdenum complex reported by Gudat et al.¹⁷ In this contribution we report on the cleavage of a P–P σ -bond by coordination of gold(I) which retains its oxidation state.

Results

The reactivity of [P(μ -NTer)]₂ (**1**) (Ter = 2,6-dimesityl-phenyl) has been utilized widely to activate small molecules such as alkenes and alkynes leading to bicycles and cages compounds.^{18–20} Here we want to report on the activation of a phosphalkyne, P \equiv C^tBu,^{21–24} its rearrangement reaction to a [2.1.1]heterobicycles (**2**, Scheme 2) and its application in gold(I) complexation reactions (Scheme 3).

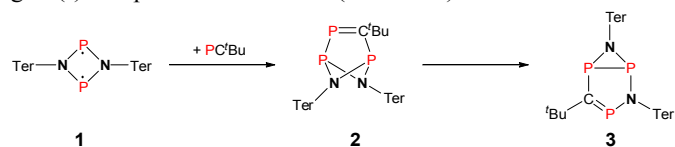
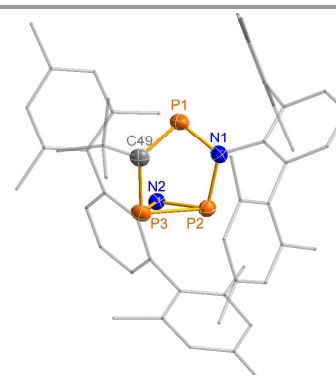
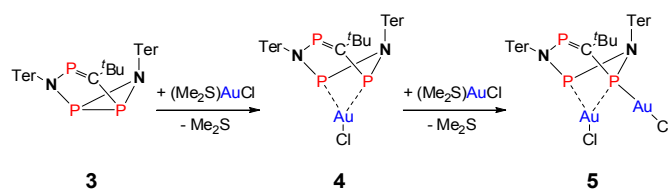
Scheme 2 Preparation of **3** (Ter = 2,6-dimesityl-phenyl).

Figure 1 Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å]: P1–C49 1.681(2), P1–N1 1.718(2), P2–N2 1.701(1), P2–N1 1.732(2), P2–P3 2.2166(7), P3–N2 1.758(1), P3–C49 1.802(2). Sum of inner angles in the five-membered ring: 538.58°.

As shown in Scheme 2, the facile addition of phosphalkyne P \equiv C^tBu onto the singlet biradicaloid **1** is complete within minutes and cage compound **2** is formed in quantitative yield. The structure of **2** can be derived from ¹H and ³¹P NMR data

(AMX spin system, Table 1 and see supporting information), which are consistent with the formation of a [2.1.1]bicyclic featuring a bridging P=C moiety. Also the rearrangement reaction from **2** to the azadiphosphiridine **3** proceeds very fast compared to the alkyne analogue (see supporting information, 1st order kinetics, $\tau_{1/2}$ of **2** ~150 min, completion after 16 hours; cf. completion after 7 weeks for C₂H₂). This rearrangement reaction can be nicely monitored by ³¹P NMR spectroscopy (Figure S2). The singlet resonance at 276.4 ppm for **1** disappears to give rise to an AMX pattern of **2**, that then vanishes to be replaced by an AMX pattern of **3** (cf. Table 1). After completion of the reaction, **3** can be isolated in almost quantitative yield (>90%). As depicted in Figure 2 the three-membered ring is almost perpendicular to the planar five-membered ring and the transannular P–P bond lengths with 2.2166(7) Å is in the expected range for a covalent P–P single bond (cf. $\Sigma r_{\text{cov}}(\text{P}-\text{P}) = 2.22$ Å), which, according to NBO and ELF computation, can be referred to as banana bond (Figure S4).



Scheme 3 Preparation of **4** and **5**.

Table 1 ³¹P NMR data for the compounds **2** - **5** (*J* in Hz, δ in ppm).

	2	3	4	5
$\delta(\text{PA})$	358.4	316.2	328.8	334.4
$\delta(\text{PM})$	259.7	-23.6	-9.6	11.2
$\delta(\text{PX})$	218.4	-62.1	-21.1	-7.8
$ J_{\text{AM}} $	190.1	26.2	5.6	20.8
$ J_{\text{MX}} $	23.2	125.6	20.6	10.4
$ J_{\text{AX}} $	18.5	13.2	26.0	20.8

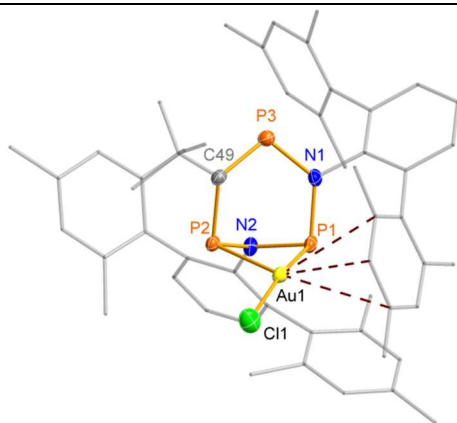


Figure 2 Molecular structure of **4**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: P1–P2 2.661(1), Au1–P1 2.3533(8), Au1–P2 2.3657(8), Au1–Cl1 2.3608(8), Au1–C17 3.002(4), Au1–C18 2.759(4), Au1–C19 3.142(4), P1–N1 1.739(2), P1–N2 1.723(2), P2–N2 1.722(2), P2–C49 1.784(3), P3–C49 1.689(3), P3–N1 1.697(2), P1–Au1–Cl1 171.30(3), P1–Au1–P2 68.66(3), Cl1–Au1–P2 111.07(3).

The intriguing transannular P–P “banana” bond situation in **3** prompted us to carry out reactions with metal complexes to

explore if this P–P bond can be cleaved and/or the PNP moiety be utilized as ligand. We decided to use less bulky species such as AuCl rather than carbonyl complexes e.g. Mo(CO)₆ or Fe(CO)₅, for which sterical problems were anticipated. In **3** there are three different phosphorus atoms with lone pairs available for metal coordination. However, due to steric congestion, we considered only P2 accessible (Figure 1). Upon addition of one equivalent of (Me₂S)AuCl, three new low field shifted (compared to **3**, Table 1) ³¹P NMR resonances appeared, which could be assigned to AuCl adduct species **4**, but surprisingly, they no longer displayed a strong P–P coupling (>90 Hz) expected for ¹J_{PP} (obsd.: $J_{\text{P1-P3}} = 5.6$ Hz, $J_{\text{P2-P3}} = 20.6$ Hz, $J_{\text{P1-P2}} = 26.0$ Hz). These observations led to the assumption that Au was inserted into the P–P bond, which was unequivocally confirmed by X-ray single crystal diffraction and computation (Figures 2 and 3, see below). Yet, the initially assumed accessible lone pair of P2 was still vacant, so another equivalent of (Me₂S)AuCl was added, which led to the predicted coordination via P2 and the formation of diadduct **5** (Figure 4). Employing an even larger excess of gold(I)-chloride does not lead to further complexation. **5** exhibits ³¹P NMR resonances at even lower field than **4**, as is expected from further deshielding by donation of electron density onto the metal (328.7, 11.2, -11.6 ppm, Table 1). The P–P coupling constants are in the same range as they were observed for **4** (<30 Hz; $J_{\text{P1-P3}} = 20.8$, $J_{\text{P1-P2}} = 10.4$, $J_{\text{P2-P3}} = 20.8$ Hz) also indicating no transannular strong covalent P–P interaction.

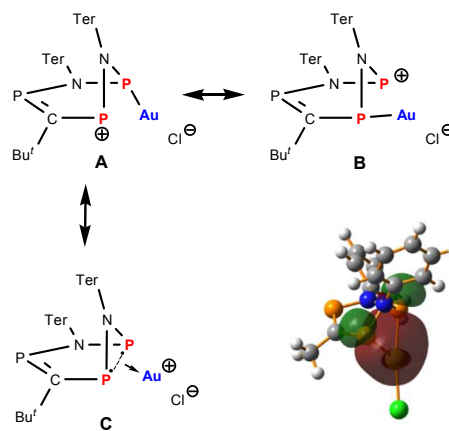


Figure 3 Two-electron-three-center P–Au–P bond according to NBO analysis

Comparison of the structural data clearly reveal the P–P bond cleavage in **4** and **5** as can be deduced from the determined P–P interatomic distances of **3**, **4**, and **5** (cf. 2.2166(7) Å vs. 2.655(3) and 2.632(1) Å). While P–P distances of 2.1 - 2.3 Å span the range for a P–P single bond, values larger than 2.6 Å are significantly larger than the sum of covalent radii for a single bond ($\Sigma r_{\text{cov}}(\text{P}-\text{P}) = 2.22$ Å) and thus bond breaking can be assumed. Beyond the P–P distance change, addition of AuCl has only a minor effect on the bond lengths within the heterocycle (cf. **3** → **4**: P1–N1 1.732(1) → 1.739(2), N1–P3 1.718(1) → 1.697(3), P3–C49 1.681(2) → 1.689(3), C49–P2 1.801(2) → 1.784(3) Å). The Au–P distances for the bridging Au atom are similar (**4**: 2.3533(8) / 2.3657(8), **5**: 2.3470(9) / 2.3533(8) Å) and in the typical range for gold(I) with two

phosphane ligands.²⁶ In contrast, the terminal Au2–P2 distance in **5** (Figure 4) is considerably smaller and amounts to 2.2158(8) Å in accord with values known from terphenyl-phosphane complexes auf Au–Cl.²⁷ Interestingly, the Au–Cl unit is localized asymmetrically between the two P atoms with an almost linear P1–Au1–Cl1 moiety (**4**: 171.30(3)°, **5**: 172.36(4)) leading to a “T-shaped” P1–Au–P2–Cl fragment with a rare pseudo-square planar coordination geometry. This rather awkward arrangement in AuCl adducts **4** and **5** is stabilized by η^3 coordination (Au \cdots C 2.65 – 3.2 Å, cf. $\sum r_{\text{vdw}}(\text{Au}\cdots\text{C}) = 3.21$ Å) of one aryl ring of the terphenyl substituent to the Lewis acidic gold(I) center (Figures 2 and 4). Taking this η^3 coordination into account, the coordination at the gold atom might also be understood as square-planar coordination which is suspicious with respect to a formal oxidation state of +III for gold. In this case, the P–P bond cleavage can be understood as oxidative addition. To shed light into this bonding problem (two-electron-three-center bond with Au^(I) versus oxidative addition with Au^(III) center), we carried out computations at the DFT level and CAS(2,2) calculations. CAS(2,2) calculations revealed open shell singlet biradical character mainly localized along the P–P unit for species **4** (Figure 3, structure C) in accord with the idea of a 3c-2e bond and Au^(I) rather than Au^(III). The P–P bond cleavage was also manifested by MO, NBO and ELF (electron localization function) computations. The ELF of **4** and **5** display no disynaptic basin between the two P atoms, while NBO analysis revealed the presence of a two-electron-three-center P–Au–P bond as depicted in Figure 3. A closer look at the NBO data clearly identifies the AuCl fragment as electron acceptor and species **3** as donor. For an oxidative process it should be the other way around. The overall charge transfer amounts to $-0.14 e$ in **4** which mainly arises from the P atoms. Interestingly, the partial charges at the gold center do not change considerably upon coordination (AuCl: 0.49, **4**: 0.48, **5**: 0.52 e), however, the charge is mainly accepted by the Cl atom leading to a more ionic Au–Cl bond. The overall charge transfer in **5** amounts to 0.24 e . It should be noted that beside the Au partial charge as well as the occupations numbers of the five d orbitals are almost the same in AuCl, **4** and **5** (between 9.6–9.9 e). In case of an oxidative addition, displaying a formal Au^(III) center, small but significant differences should be observed, that is an Au partial charge $> +1 e$ and a smaller d orbital occupation ($< 9.3 e$).²⁸

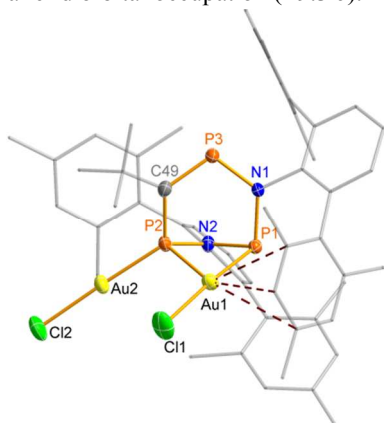


Figure 4 Molecular structure of **5**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: Au1–P2 2.3470(9), Au1–P1 2.3533(8), Au1–Cl1 2.363(1), Au1–C8 2.918(4), Au1–C9 2.652(3), Au1–C10 3.111(4), Au2–P2 2.2158(8), Au2–Cl2 2.2778(9), P1–P2 2.6324(11), P2–Au1–P1 68.12(3), P2–Au1–Cl1 110.36(3), P1–Au1–Cl1 172.36(4), P2–Au1–C9 157.20(8), P1–Au1–C9 98.26(8), P2–Au2–Cl2 178.14(4).

Conclusions

In summary, we successfully demonstrated the activation of a P–P σ -bond by coordination of a gold(I) complex resulting in the formation of a two-electron-three-center-bond. This finding is supported by the breakdown of the J_{PP} coupling, the large increase of the transannular P–P distance and by NBO and ELF computations.

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Notes and references

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