(Triphenylphosphane)gold(I) Scrambling in a Hexanuclear Complex of Phenylene-1,2-bis(phosphane)

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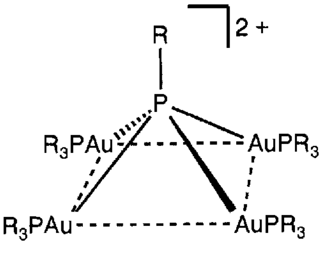
Received August 19, 1996

Keywords: Gold compounds / (Phosphane)gold(I) complexes / Clusters / P Ligands

Phenylene-1,2-bis(phosphane) reacts with two mole-equivalents of tris[(triphenylphosphane)gold(I)]oxonium tetrafluoroborate in dichloromethane at −78°C to give high yields of a hexanuclear complex $\{C_6H_4[P(AuPPh_3)_3]_2\}^{2+} \cdot 2\ BF_4^-$ (**1**). The variable-temperature $^{31}P\{^1H\}$-NMR spectra of the product in CD_2Cl_2 at −80°C are compatible with a static structure featuring three Ph_3PAu units associated with each of the two $C_6H_4P_2$ phosphide functions, as derived from a clear doublet/quartet pattern. At 50°C in $CDCl_3$, however, there is rapid intramolecular scrambling of these Ph_3PAu units, which gives rise to a triplet/septet pattern with the J(P,P) value reduced to exactly one half of the value at the low-temperature limit.

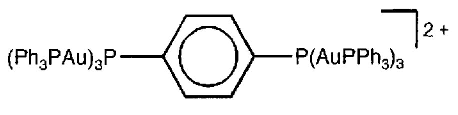
The phosphorus atoms of primary phosphanes can function as nucleation centers for gold atoms to give polynuclear clusters with up to four metal atoms[1,2]. While for the mono-, di- and trinuclear compounds conventional formulae can be drawn (**A**−**C**), the tetranuclear species are electron-deficient hypercoordinate species with a novel type of structure and bonding (**D**). Auration reactions of cations **C** which lead to dications **D** are readily accomplished[3]. This transformation is just one of the many examples of "auriophilicity at work" that have been compiled recently[4]. It also demonstrates an affinity of the trinuclear phosphonium cations for an additional R_3PAu^+ unit. This is a surprising phenomenon, because the process is clearly associated with a build-up of positive charge against Coulomb forces.

$R{-}PH_2$
$R{-}PH_2[Au(PR_3)]^+$ **A**
$\{R{-}PH[Au(PR_3)]_2\}^+$ **B**
$\{R{-}P[Au(PR_3)]_3\}^+$ **C**

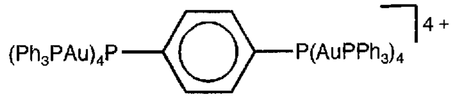


D

The same clustering can also be accomplished at both phosphorus atoms of di-primary phosphanes, as exemplified by the derivatives of phenylene-1,4-diphosphane[5]. This *para*-diphosphane could be converted into a hexa- and even an octanuclear complex, with the long and flat phenylene unit as a spacer between the two nucleation centers preventing steric crowding (**E**, **F**).



E

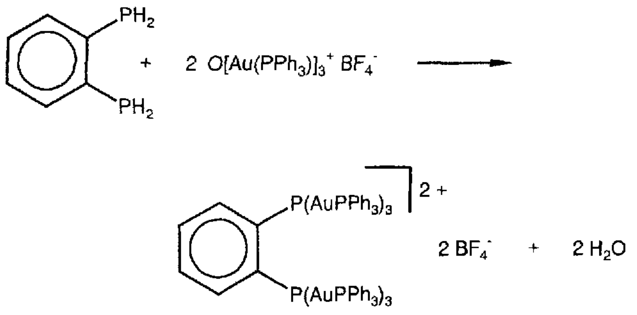


F

An inspection of these formulae suggested that already for a *meta*-, and even more so for an *ortho*-positioning of the phosphane functions, the close proximity of the gold cluster units might lead to interesting structural or dynamic phenomena. The two units could either grow separately to a steric saturation limit, or grow together to one large cluster. Intermediates of this growth should exhibit mobility of the metal components for site-exchange processes. We therefore investigated the auration of $1,2\text{-}C_6H_4(PH_2)_2$ with agents providing $(Ph_3P)Au^+$ units in order to explore the upper limit of the clustering and to investigate the properties of the individual intermediates of this multistep reaction.

Results and Discussion

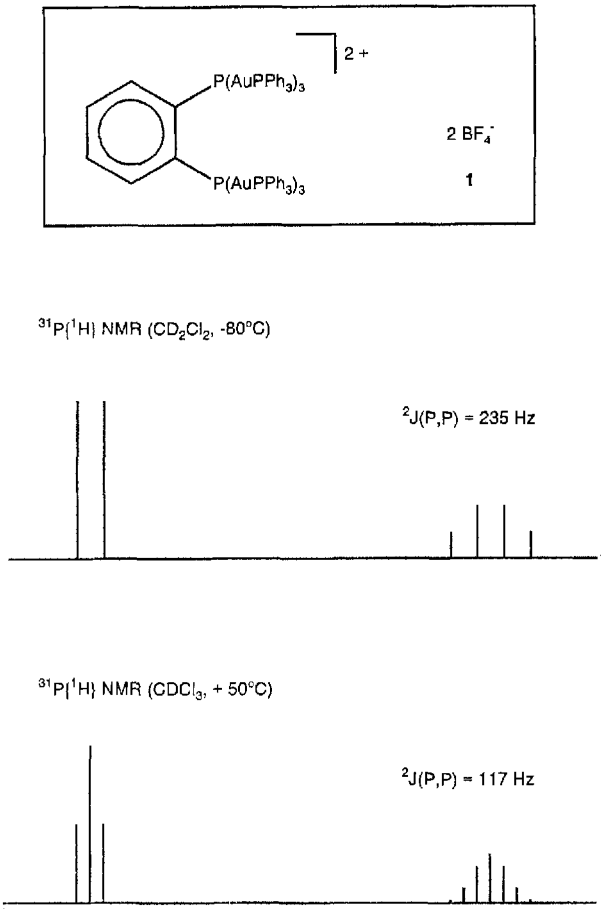
Treatment of phenylene-1,2-bis(phosphane) with two mole-equivalents of tris[(triphenylphosphane)gold(I)]oxonium tetrafluoroborate in dichloromethane at −78 °C gives a crude product which separates from the mixture upon addition of pentane as a red oil, and precipitates as an orange powder after complete removal of the solvents (77% yield, m.p. 130 °C with decomposition). The compound (**1**) is stable in the solid state at ambient temperature, but solutions in di- or trichloromethane decompose slowly upon standing to give black precipitates. Therefore no pure single crystals could be obtained.



1

All attempts to accomplish a higher degree of auration by using more than two mole-equivalents of oxonium salt, or of $[(Ph_3P)Au]^+$ BF_4^-, did not give hepta- or octanuclear compounds. Decomposition was observed instead even under very mild conditions. Compound **1** was identified by its elemental analysis, mass spectrum (Experimental) and variable-temperature solution NMR spectra. The proton NMR spectrum has only a broad multiplet accounting for the phenyl and phenylene groups. The proton-decoupled phosphorus spectrum (in [D$_2$]dichloromethane at −80 °C) shows the expected AX_3 pattern for the two equivalent $P(AuP)_3$ groups with doublet and quartet components of the integral ratio 3:1 and a coupling constant $J(P_A,P_X)$ = 235 Hz. There is some line broadening of the quartet part, indicating some minor unresolved long-range $P_AP_{X'}$ and $P_AP_{A'}$ coupling.

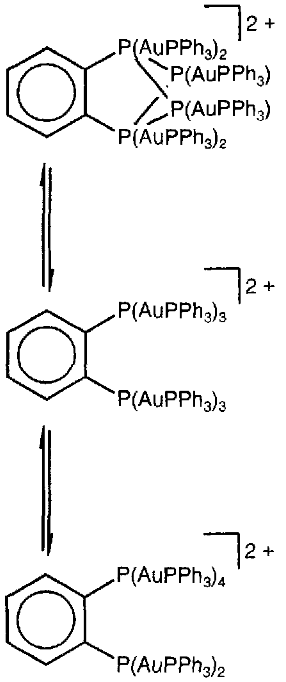
Figure 1. Temperature dependence of the $\{^1H\}^{31}P$-NMR spectrum of compound **1** (in $CDCl_3/CD_2Cl_2$); schematic drawing, not to scale



At room temperature (in CD_2Cl_2 or $CDCl_3$) both multiplets collapse, suggesting intra- or intermolecular exchange processes. At 50 °C (in $CDCl_3$) the pattern is changed to a new A_2X_6 spin system with a sharp 1:2:1 triplet (X) and a 1:6:15:20:15:6:1 septet (A). Only the five central lines of this septet were clearly detectable, but their integral ratio was fully diagnostic. The coupling constant is found to be exactly one half of the low-temperature value: $J(P_AP_X)$ = 117.5 Hz (Figure 1). This result is proof that the exchange process is predominantly *intra*molecular.

The most likely mechanism is a site exchange of the $[(Ph_3P)Au]$ units between the two phosphorus atoms of the phenylene unit that is rapid on the NMR time scale. These two phosphorus atoms (A) thus experience time-averaged coupling to all six triphenylphosphane phosphorus atoms (X), and vice versa. The average coupling constant is therefore the weighted sum of the two-bond coupling constant $J(P_AP_X)$ = 235 Hz and the unresolved five-bond coupling $J(P_AP_{X'}) \approx 0$ Hz.

The transfer of the $[(Ph_3P)Au]$ units may follow an ionic pathway, whereby one of the central phosphorus atoms takes on four gold atoms, leaving the other with only two. The former would then represent a dicationic tetranuclear cation already well established in $\{Ph{-}P[Au(PPh_3)]_4\}^{2+}$ (**D**), while the latter has previously been found in 2,4,6-$tBu_3C_6H_2P[Au(PPh_3)]_2$ (deprotonated **B**). Alternatively, the migrating units may take on bridging positions between the two central phosphorus atoms. Such a situation with gold(I) tricoordinated to three phosphorus donors with an electron



deficit (three-center two-electron count) has not yet been detected in a ground-state species, but may well appear as an intermediate or transition state (Scheme 1). We are not in the position to differentiate experimentally between the two alternatives.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie.* Donation of chemicals by *Degussa AG* and *Heraeus GmbH* is gratefully acknowledged.

Experimental Section

All reactions were carried out in oven-dried glassware using inert gas techniques. The solvents were dried, distilled prior to use, and saturated with nitrogen. Standard commercial laboratory equipment and spectrometers were used throughout. The reagents were prepared following literature procedures: 1,2-$C_6H_4(PH_2)_2$[6], $\{[(Ph_3P)Au]_3O\}^+BF_4^-$[7,8].

Compound **1**: 1.75 g of the oxonium salt (1.18 mmol) was dissolved in CH_2Cl_2 (25 ml) at −78 °C and a solution of the diphosphane (0.08 g, 0.59 mmol) in the same solvent (10 ml) was added. The color of the reaction mixture changed gradually from colorless via yellow to red-orange. After 20 min of stirring, pentane (50 ml) was added. A heavy red oil separated, which was washed with pentane and dried in a vacuum to leave an orange solid (1.40 g, 77% yield, m.p. 130 °C with decomposition). – ^1H NMR (CD_2Cl_2, −90 °C): δ = 6.8–7.6 (m, Ph, C_6H_4). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ = 14.8 (q, *J* = 235 Hz, 1 P); 44.7 (d, *J* = 235 Hz, 3 P). (CD_2Cl_2, 25 °C): δ = 14.8 (br., 1 P); 45.2 (br., 3 P). ($CDCl_3$, 50 °C): δ = 13.2 (sept, *J* = 117.5 Hz, 1 P); 43.6 (t, *J* = 117.5 Hz, 3 P). – MS (FAB) *m/z*: 1667 [M^{2+}, dication of the salt], 2433 [M^{2+} – $AuPPh_3$]. – $C_{114}H_{94}Au_6B_2F_8P_8$ (3067.20): calcd. C 44.64, H 3.09; found C 44.02, H 3.28.

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