Synthesis of 7-Alkyl/aryl-1,3,5-triaza-7-phosphonia-adamantane Cations and Their Reductive Cleavage to Novel *N*-Methyl-*P*-alkyl/aryl[3.3.1]bicyclononane Ligands

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Two reaction pathways for the synthesis of 1,3,5-triaza-7-phosphoniaadamantane salts, $RP[(CH_2)_6N_3]^+X^-$ (**1**), were followed. Route 1 starts with commercial tetrakis(hydroxymethyl)phosphonium chloride, which is converted into $P(CH_2OH)_3$ by treatment with a base. Subsequent quaternization with alkyl halides RX and cyclization with formaldehyde and ammonia afford $[R\text{-}TPA]^+X^-$. This process is only applicable for R = Me (**1a**) and Et (**1b**), however. Route 2 is more general and starts with primary phosphanes RPH_2, which are converted into organotris(hydroxymethyl)phosphonium salts with formaldehyde and hydrochloric acid followed by ring closure with CH_2O/NH_3 to give compounds **1c**–**1f** (R = *t*-Bu, *c*-Hex, Bz, and Ph, respectively, and X = Cl, I, PF_6, or BPh_4). Reductive cleavage of compounds **1** by sodium in liquid ammonia proceeds with either external (P–R) or internal (P–CH_2) bond rupture. P–R cleavage affords the 1,3,5-triaza-7-phosphaadamantane (TPA), while cage cleavage leads to new bowl- or helmet-shaped ligand systems with peripheral amine and phosphane functions (**2**). Yields of the cage-opening reaction are highest for R = Ph (**2f**), moderate for R = Me and Et (**2a**, **2b**), and poor with the remaining R groups (**2c**–**2e**). A radical mechanism is proposed for this reaction, the leaving group properties of R determining the direction of the cleavage. The crystal and molecular structures of compounds **2a** and **2f** were determined by X-ray diffraction studies. *Exo* positions were found for the N–Me and P–R groups. The isomers with the R group in the *endo* position are also present in solution in small amounts, as detected by NMR spectroscopy. Isomer interconversion by P inversion is slow on the NMR time scale. Compounds **2a**, **2b** and **2f** were oxidized with elemental sulfur and selenium to give the monosulfides and selenides, respectively (**2aS**, **2aSe**, **2bS**, **2bSe**, **2fS**, **2fSe**). Oxidation with H_2O_2 led to degradation. Compound **2a** was quaternized at the P atom by treatment with MeI to give the corresponding phosphonium salt. Treatment with equimolar quantities of $(Me_2S)AuCl$ led to the 1:1 complexes **2aAuCl**, **2bAuCl** and **2fAuCl**, with the AuCl units solely P-bonded, as determined by X-ray diffraction of **2aAuCl** and **2fAuCl**. Compound **2a** forms an ionic 2:1 complex with AuCl, composed of the ions $[(\mathbf{2a})_2Au]^+$ Cl^- (with unidentate ligands), while its reaction with $[Me_2AuCl]_2$ leads to $[Me_2Au(\mathbf{2a})]^+$ $[Me_2AuCl_2]^-$ (with a chelating **2a** ligand), as again confirmed by crystal structure analysis in both cases. Ligands **2a**, **2b** and **2f** also act as chelating ligands in their tetracarbonylmolybdenum complexes obtained in the reactions with $(C_7H_8)Mo(CO)_4$.

Tertiary phosphanes R_3P are versatile ligands in coordination chemistry. Indroduction of functional groups in their organic substituents R can be used as a method to modify the properties of the ligands and of the complexes derived therefrom. The phosphanes can, for example, become (P,N)-ambi- or polydentate in nature, as tertiary amine functions become part of the organic framework[1]. Owing to the hydrophilic nature of these amine functions, such ligands and their complexes will become soluble in water and other polar solvents.

An example in case is 1,3,5-triaza-7-phospha-adamantane (TPA)[2], which is known to be a suitable "soft" P-donor for low-valent transition metals[3] with a small cone angle at the phosphorus atom, but also a "hard" ligand for metals in higher oxidation states[4]. It can be integrated into hydrogen-bonding networks based on its three tertiary amine functions, and it is easily solvated. The molecule is a strong nucleophile and forms both phosphonium and ammonium cations if treated with acids or alkyl halides[5].

We therefore studied the ligand properties of TPA for the coinage and platinum group metals, where its coordination chemistry has been investigated so far only in a few cases[6]. Following a preliminary communication on our initial results[7] and a paper on the synthesis and luminescence properties of gold(I) complexes[8], we now present new data on two improved methods for the preparation of TPA-based phosphonium salts, on the reductive cleavage of these cage-type phosphonium salts with sodium in liquid ammonia, which leads to novel bowl- or helmet-shaped ambidentate ligand systems, and on a few typical metal complexes of these ligands. The mechanism of the reductive TPA-cage opening reaction is discussed in terms of an electron-transfer process.

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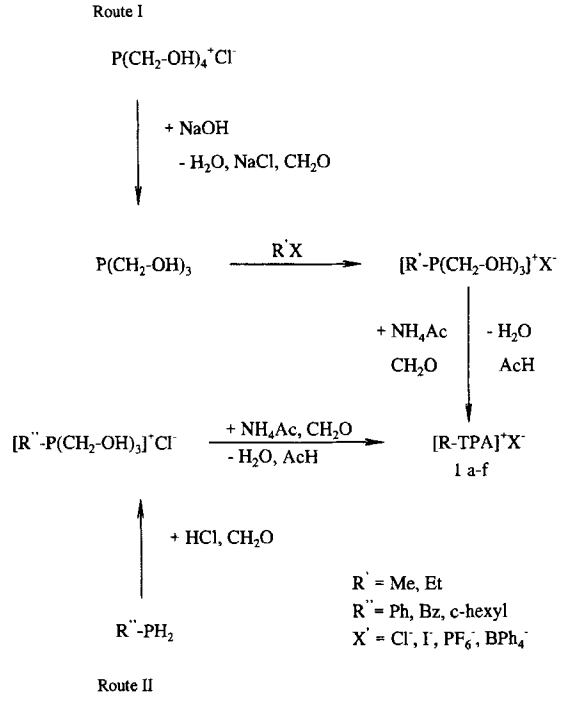
Synthesis of 7-Aryl/alkyl-1,3,5-triazaphosphonia-adamantane Salts

All attempts to quaternize TPA with alkyl halides led to N-alkylated *ammonium* salts. It therefore appears that onium salts based on cations alkylated at the *phosphorus* atom have to be prepared via alternative routes. Two pathways are suggested by the literature, but only one of these has been actually used for the preparation of the required phosphonium salts. This procedure (Route I in Scheme 1) starts with the commercially available tetrakis(hydroxymethyl)-phosphonium chloride (prepared from phosphane and formaldehyde)[9], which is transformed into tris(hydroxymethyl)phosphane by treatment with a base. This phosphane can be quaternized with alkyl halides to give alkyltris(hydroxymethyl)phosphonium salts, which are cyclized to the cage-type cations by reactions with ammonia (introduced as ammonium acetate) and formaldehyde. This process was first used by Fluck et al. for the preparation of the methyl derivative (R = Me)[10]. It was found, however, that it is not generally applicable, and that groups larger than R = Et cannot be introduced through simple quaternization of $P(CH_2OH)_3$. The same of course holds for arylated products (R = Ph, etc.).

Scheme 1



In Route II (Scheme 1) the synthesis therefore starts with the appropriate primary phosphanes already bearing the required substituents R at phosphorus. These can be converted into the organo-tris(hydroxymethyl)phosphonium cations by using again formaldehyde and hydrochloric acid. This process was used once in the literature for the preparation of the cyclohexylphosphorus derivative[11]. The subsequent cage closure was effected according to the method already delineated in Route I.

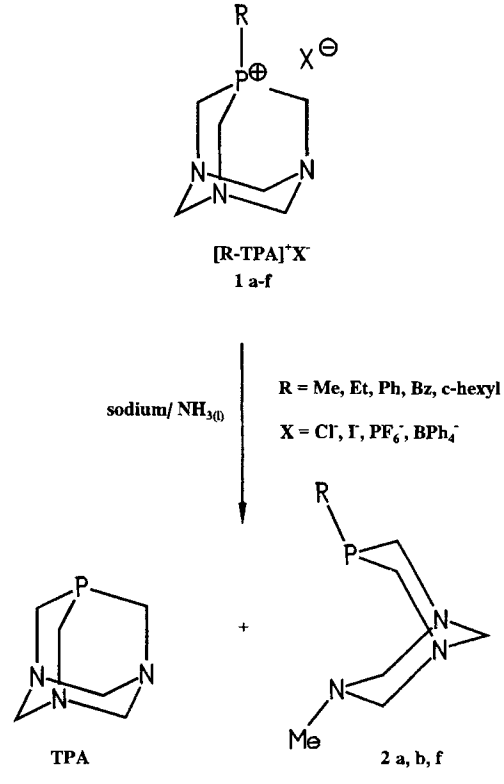
Route I was applied to cations **1a** and **1b** (R = Me, Et), while Route II provided cations **1c**–**1f** (R = *t*-Bu, *c*-Hex, Bz, Ph). It should be noted that there is a choice of counterions X in all cases, depending on the route and on the salts employed for conversion of chlorides, which often exist as oily products, into crystalline materials. The anions Cl, I, PF_6, and BPh_4 were used in this work, and this is indicated in the following where appropriate.

Compounds $\mathbf{1^+X^-}$ were characterized by their analytical and spectroscopic data (see Experimental). Assignments are unambiguous in most cases.

Reductive Cleavage of 1,3,5-Triaza-7-organophosphonia-adamantane Cations

Salts containing the title cations were initially treated with a strong base, including sodium in liquid ammonia, in attempts to deprotonate these cations and to convert them into the corresponding ylides. None of these reactions produced the expected ylide, and it was observed that reductive dealkylation of phosphorus was the predominant reaction, leading primarily to dealkylation of the cation to produce TPA, i.e. the product of external dealkylation (cleavage of the P–C bond between the phosphorus atom and the side group R, Scheme 2). It was with the Na/NH_3 (liq) system, that cage cleavage was observed as one of the major reaction pathways (up to 30%), and therefore this procedure was elaborated up further and optimized to give the novel bowl- (or helmet-) shaped cage-opened products as the main products (**2**).

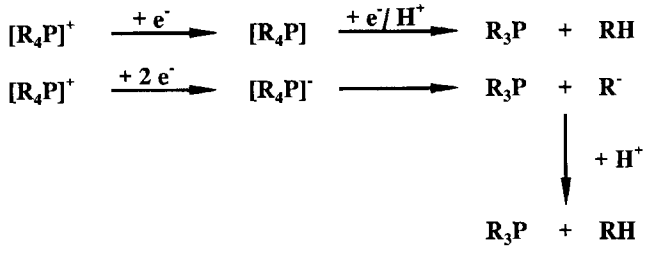
Scheme 2



The general procedure given in the experimental section was found to be most efficient for cage cleavage. Its success is dependent on the nature of R, however, and good leaving group properties of R lead to reduced yields of cage cleavage products. The yields are highest for R = Ph (45% of **2f**), moderate for R = Me and Et (ca. 25% for **2a** and **2b**), but very poor or zero for R = *t*-Bu, *c*-Hex, and Bz. This is in agreement with the classification of Ph and Bz as very poor and very efficient leaving groups, respectively, in both polar and radical reactions.

As a mechanism of the well-established reductive cleavage of phosphonium cations $[R_4P]^+$ a single-electron transfer from sodium (in liquid ammonia: ammonia-solvated electrons and sodium cations) to the LUMO of the cation has been proposed. The resulting radicals $[PR_4]^\bullet$ can lose a radical $R^\bullet$, which is trapped by another solvated electron and by a proton to give a hydrocarbon RH. A phosphane R_3P is produced in this process. As an alternative mechanism, a two electron-reduction can be invisaged, which leads to $[R_4P]^-$ anions[12]. These species can lose a carbanion R^-, which is trapped by a proton to give again the hydrocarbon RH and a phosphane R_3P (Scheme 3). For different substituents R at phosphorus, the leaving group properties of the individual R groups are determining the course of the cleavage.

Scheme 3

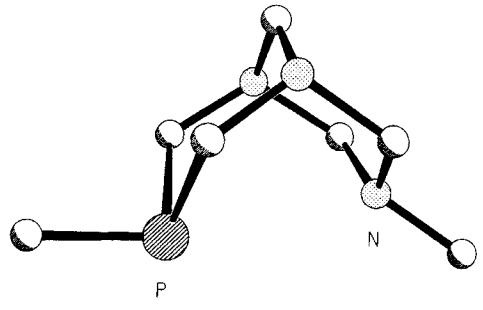


For the P–C cleavage in TPA-based phosphonium cations (**1**) there is a choice between the exo group R and one of three cage P–CH_2 bonds. Suitable radical leaving groups like benzyl or *t*-butyl and cyclohexyl are cleaved preferentially, while methyl, ethyl and phenyl are largely retained, although some TPA is also liberated as a by-product. This result is in agreement with rules established for the reduction of open-chain phosphonium salts[12].

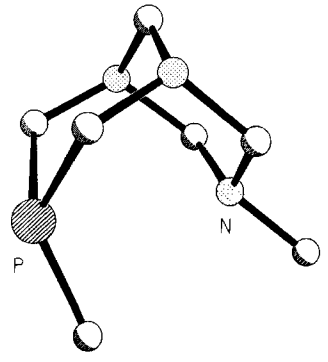
Structure, Isomerism and Properties of Compounds 2a, 2b, and 2f

Compounds **2a** and **2f** were isolated as colorless, crystalline solids, which could be sublimed in a vacuum. Compound **2b** is a colorless, distillable liquid. The phosphanes are soluble in all common organic solvents (from water to benzene). They are monomers in solution and in the gas phase as demonstrated by mass spectrometry (CI, and EI techniques). Their composition was confirmed by elemental analyses. Both gas chromatography and NMR studies demonstrate, however, that compounds of type **2** can exist in at least two different isomers, arising from the absolute and relative orientation of the *N*-methyl and P–R groups at the opening of the bowl (helmet) (Scheme 4). Both groups can have exo and endo orientations, the combination of which can lead to four isomers, all with mirror symmetry (point group C_s). Isomerism arising from the various relative conformations of the two six-membered rings are not considered here, since there was no evidence of the existence of other than chair conformations.

Scheme 4a



Scheme 4b



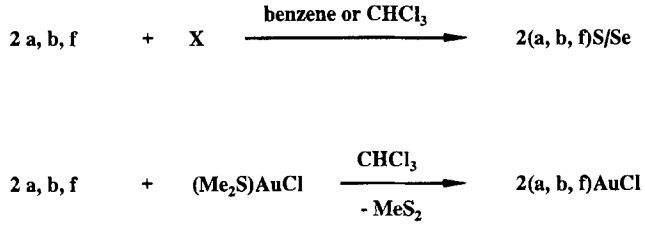
For **2a** two isomers were detected by GC/MS and NMR spectroscopy. The major isomer (after both crystallization and sublimation) was shown to have the *exo*/*exo* constitution by single crystal X-ray diffraction (**2a'**, Figure 1). In the crystal this structure was found to be disordered regarding the positions of N-Me and P-Me groups, but this does not affect the assignment of both groups to have the exo orientation. [It should be noted that the three complexes of ligand **2a** also possess an *exo*/*exo* structure (below), but this can only be taken as indirect evidence for the structure of the ligand, since P/N inversion can take place upon complexation.]

The second isomer (**2a''**) is tentatively assigned the P–Me *endo*/N–Me *exo* structure based on the similarity of the N–Me NMR characteristics. Interconversion of the two isomers appears to be slow in solution on the NMR time scale at ambient temperature. It is assumed that it is the slow inversion at phosphorus, which allows the separation (analytically on GLC columns) and identification (by NMR spectroscopy) of the isomers **2a'**/**2a''**, while the inversion at the nitrogen atom appears to be rapid in solution, thus ruling out the detection of the remainder isomers.

The single crystal structure analysis of compound **2f** gave only preliminary results due to crystal quality problems. The data are sufficient, however, to prove that the major

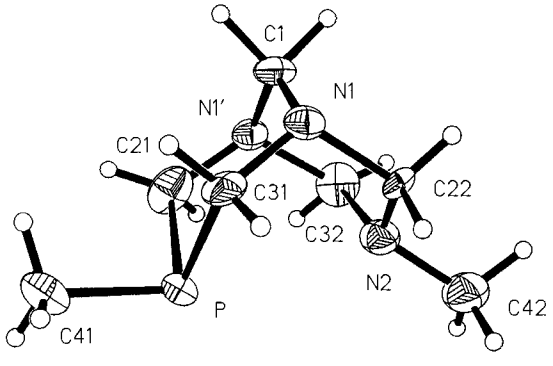
isomer is again the *exo/exo* compound. The structure of the AuCl complex (below) is in agreement with this tentative result.

Scheme 5



Compounds of type **2** are not sensitive to oxidation and hyrolysis, but all materials are hygroscopic owing to the hydrogen-bond acceptor properties of the tertiary amine functions. Oxidation of **2a** with aqueous hydrogen peroxide did not give the monooxide (P=O), but more extensive degradation occurred. Treatment of **2a**, **2b** and **2f** with sulfur or selenium led to almost quantitative yields of the monosulfides or monoselenides, respectively, which could be obtained as stable crystalline solids (**2aS**, **2aSe**, **2bS**, **2bSe**, **2fS**, **2fSe**, Scheme 5). The analytical and spectral data of these compounds indicate that all species occur as one isomer, most likely the P–R *exo*/N–Me *exo* form, as proposed by the formula in Scheme 2.

Figure 1. Molecular structure of the phosphane $C_7H_{16}N_3P$, **2a** (ORTEP, 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: P–C41 1.78(3), P–C31 1.87(3), P–C21 1.99(3), N2–C22 1.36(2), N2–C32 1.47(3), N2–C42 1.49(4). C41–P–C31 96(1), C41–P–C21 98(1), C31–P–C21 93(1), C22–N2–C32 116(1), C22–N2–C42 111(2), C32–N2–C42 113(2)



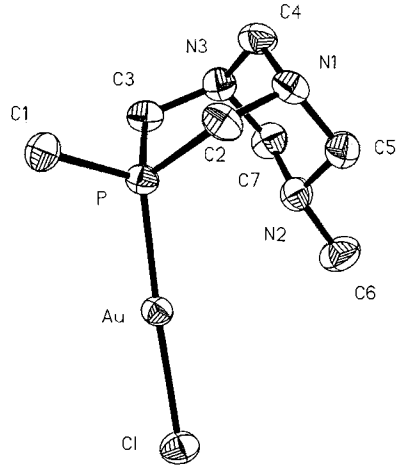
Compound **2a** was quaternized with methyl iodide to give the dimethyl*phosphonium* salt **2aMe$^+$I$^-$** in almost quantitative yield. There is no evidence for a competing quaternization at the nitrogen atoms in **2a** by MeI.

Ligand Properties of Compounds 2a, 2b, and 2f in Gold(I) and Gold(III) Complexes

The current interest in the optical properties of (phosphane)gold(I) complexes, mainly the strong luminescence of compounds with cage-type ligands[8], led us to investigate the gold(I) coordination chemistry of the novel ligand systems of type **2**.

Treatment of **2a**, **2b**, and **2f** with chloro(dimethyl sulfide)-gold(I) in the molar ratio of 1:1 in chloroform or dichloromethane gave high yields of colorless crystalline products **2aAuCl**, **2bAuCl**, and **2fAuCl** (Scheme 5). The structures of compounds **2aAuCl**[7] and **2fAuCl** were determined by X-ray diffraction studies. The results of these studies are presented in Figures 2 and 3. As expected, the gold atoms are attached to the phosporus donor centers in both cases, with a linear configuration of the P–Au–Cl units. The P–Me/P–Ph and N–Me moities exhibit the *exo* configuration already present in the major isomer of the free ligands. No other isomers of these complexes and of **2bAuCl** were dedected by standard analytical and spectroscopic methods.

Figure 2. Molecular structure of $C_7H_{16}AuClN_3P$, **2aAuCl** · $CHCl_3$ (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–P 2.218(2), Au–Cl 2.294(2). Cl–Au–P 173.2(1)



The reaction of ligand **2a** with $(Me_2S)AuCl$ in the molar ratio of 2:1 afforded a 2:1 complex as a stable crystalline solid in virtually quantitative yield. A single crystal X-ray structure determination revealed an ionic structure **[(2a)$_2$Au]$^+$Cl$^-$** (Figure 4). In the cations there is a linear P–Au–P bridge between the two *P*-bonded ligands. The configuration of the two ligands, which are related by symmetry, is the same as in the 1:1 complex.

In order to demonstrate the *P,N*-chelating properties of ligands **2**, compound **2a** was also treated with the chlorodimethylgold(III) dimer $[Me_2AuCl]_2$ in halogenated hydrocarbon solution. From a mixture of products a crystalline material in a 1:1 ratio of the components could be isolated, which was shown by X-ray crystallography to be again an ionic compound of the formula **[Me$_2$Au(2a)]$^+$ [Me$_2$AuCl$_2$]$^-$** (Figure 5). In the crystal, the ligand of the cation, **2a**, is again disordered (P/N), but the structure could be accounted for by a satisfactory split level model. Details of this structure will be considered together with the data on related platinum and palladium complexes in a forthcoming publication. The luminescence properties of the gold compounds will also be presented in a different context.

Figure 3. Molecular structure of $C_{12}H_{18}AuClN_3P$, **2fAuCl** (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–P 2.226(2), Au–Cl 2.293(2). Cl–Au–P 177.4(1)

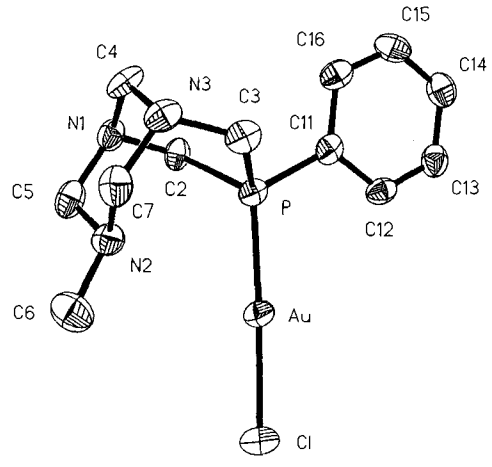
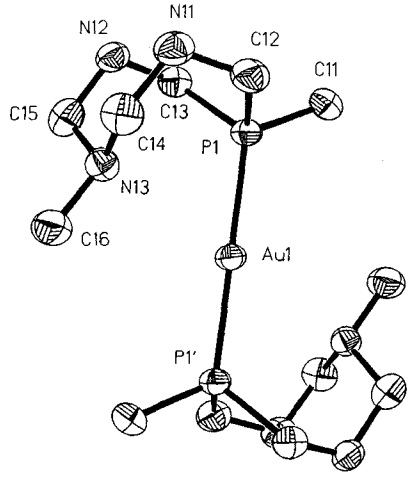


Figure 4. Molecular structure of the cation $[(C_7H_{16}N_3P)_2Au]^+$ in the chloride salt **[(2a)$_2$Au]$^+$ Cl$^-$** $CHCl_3$ (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). The phosphane ligands **2a** are related to each other by a center of inversion placed at the gold atom. Selected bond lengths [Å] and angles [°]: Au1–P1 2.307(2), P1′–Au–P1 180°



Tetracarbonylmolybdenum Complexes of Ligands 2a, 2b and 2f

The above complexes of gold(I) and gold(III) are examples of mono- and bidentate ligand functionality of compounds **2** at two- and four-coordinate centers. In order to provide also representative examples of coordination at a six-coordinate metal center, $(C_7H_8)Mo(CO)_4$ was treated with the ligands **2a**, **2b** and **2f** (Scheme 6). The expected products (**2a**, **2b**, **2f**) **Mo(CO)$_4$** were isolated in yields of approximately 85% as yellow solids, which could be readily identified by their analytical and spectroscopic data.

Unfortunately, all crystalline samples of **(2b)Mo(CO)$_4$** were twinned or disordered, and the structural details could not be derived with sufficient accuracy. All data support a standard octahedral structure with a *P,N*-chelating ligand of overall mirror symmetry (point group C_s). As in the case

Scheme 6

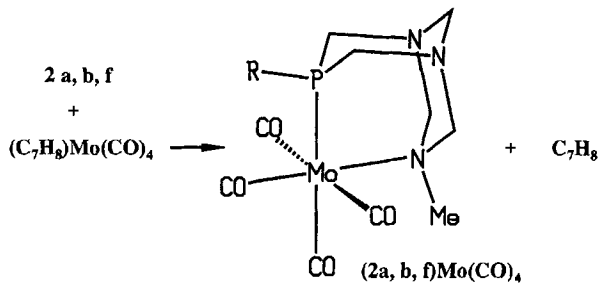
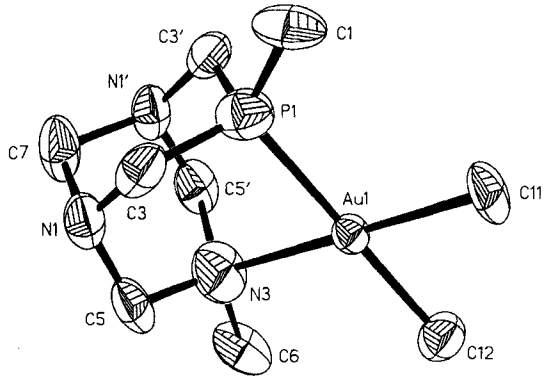
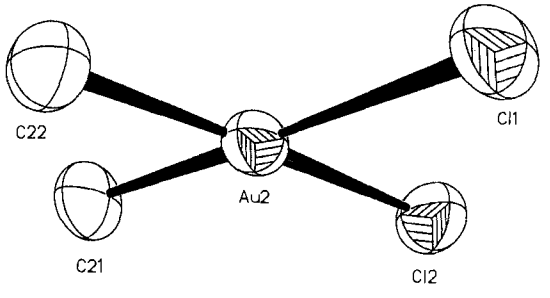


Figure 5. Molecular structure of $C_{11}H_{28}Au_2Cl_2N_3P$, **[2aAuMe$_2$]$^+$-[Me$_2$AuCl$_2$]$^-$** (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). (a) Selected bond lengths [Å] and angles [°] for the cation: Au1–P1 2.181(9), Au1–N3 2.22(1), Au1–C11 2.04(1), Au1–C12 2.03(2). P1–Au1–N3 82.7(5), P1–Au1–C11 96.7(7), N3–Au1–C12 97.0(8), C11–Au1–C12 83.7(9)



(b) Selected bond lengths [Å] and angles [°] for the anion: Au2–C21 2.02(2), Au2–C22 2.07(2), Au2–Cl1 2.397(4), Au2–Cl2 2.355(6). C21–Au2–C22 84.8(9), C21–Au2–Cl2 91.1(7), C22–Au2–Au2–Cl1 92.1(6), Cl1–Au2–Cl2 92.0(2)



of **[Me$_2$Au(2a)]$^+$ [Me$_2$AuCl$_2$]$^-$** (above), coordination of one nitrogen atom to the metal center can be concluded from the observation of large ^3J(P–C) coupling via the metal atom.

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Experimental

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieves under nitrogen. – NMR: TMS as internal standard for ^1H and $^{13}C\{H\}$,

external H_3PO_4 (85% in H_2O) for $^{31}P\{^1H\}$, and external nitromethane for ^{15}N; r.t. = room temperature; Jeol GX 270, Jeol GX 400. – MS: Finnigan MAT90 (CI, isobutane; FAB; FD) and Varian MAT311A (EI, 70 eV).

7-Methyl-1,3,5-triaza-7-phosphoniaadamantane Iodide (**1a**): see ref.[5]

7-Ethyl-1,3,5-triaza-7-phosphoniaadamantane Iodide (**1b**): 37.2 g (0.3 mol) of tris(hydroxymethyl)phosphane[13] in 150 ml of methanol is treated dropwise with 46.8 g (0.3 mol) of ethyl iodide under nitrogen whereby the temperature is kept at 10°C. In a slightly exothermic reaction ethyltris(hydroxymethyl)phosphonium iodide is formed. The mixture is diluted with 200 ml of methanol, and 69.4 g (0.9 mol) of NH_4Ac and 27 g (0.9 mol) of paraformaldehyde are added. Upon heating to reflux all solids are completely dissolved. Cooling to −30°C yields 41.8 g (44.5% based on $P(CH_2OH)_3$) of colorless crystals (dec. temp. 215°C). – ^1H NMR (D_2O, r.t.): δ = 1.05 [dt, (CH_3), ^3J(HH) = 7.8 Hz, ^3J(PH) = 21.5 Hz]; 2.14 [dq, (CH_2), ^3J(HH) = 7.8 Hz, ^3J(PH) = 15 Hz]; 4.33 [s, (N−CH_2−N)]; 4.38 [s, (N−CH_2−N)]; 4.4 [d, (P−CH_2−N) ^2J(PH) = 6.1 Hz]. – $^{31}C\{^1H\}$ NMR (D_2O, r.t.): δ = 4.08 [d, (CH_3), ^2J(CP) = 6.1 Hz]; 12.58 [d, (CH_2), ^1J(CP) = 28.1 Hz]; 45.67 [d, (P−CH_2−N), ^1J(CP) = 34.7 Hz]; 70.92 [d, (N−CH_2−N), ^3J(CP) = 9.4 Hz). – $^{31}P\{^1H\}$ NMR (D_2O, r.t.): δ = −35.52 [s]. – $[(C_8H_{17}N_3P)^+I^-]$ (313.12): calcd. C 30.69, H 5.47, N 13.42; found C 30.37, H 5.40, N 13.56. – MS (FAB), *m/z*: 186 [M^+].

7-tert-Butyl-1,3,5-triaza-7-phosphoniaadamantane Hexafluorophosphate (**1c**): To a stirred solution of freshly distilled *t*-Bu−PH_2[14] (10.5 g, 0.12 mol) in 75 ml of THF is added rapidly 25 ml of 37% aqueous HCl. After addition of 14.4 g (0.48 mol) of solid paraformaldehyde the suspension is stirred until all solid has dissolved (4 h). Removal of all volatile components in vacuo leaves oily $[t\text{-Bu}-P(CH_2-OH)_3]^+Cl^-$. The residue is dissolved in 75 ml of methanol and a mixture of 30.8 g (0.4 mol) of NH_4Ac and 12 g (0.4 mol) of paraformaldehyde is added slowly and in portions. The suspension is heated at reflux until all solids have dissolved. After stirring overnight $[t\text{-Bu}-TPA]^+PF_6^-$ is precipitated by adding 9.8 g (0.06 mol) of NH_4PF_6. The resulting white solid is collected on a glass frit, washed with cold methanol, and recrystallized from acetone/methanol to yield 15.3 g (0.04 mol, 33.3% based on *t*-Bu−PH_2) of colorless crystals (decomp. temp. 230°C). – ^1H NMR ([D_6]DMSO, r.t.): δ = 1.18 [d, (CH_3), ^3J(PH) = 17.7 Hz]; 4.42 [s, (N−CH_2−N)]; 4.53 [d, (P−CH_2−N), ^2J(PH) = 5.5 Hz]. – $^{13}C\{^1H\}$ NMR (DMSO, r.t.): δ = 22.66 [s, (CH_3)]; 28.32 [d, (C), ^1J(CP) = 23.0 Hz]; 43.56 [d, (P−CH_2−N), ^1J(CP) = 26.7 Hz]; 70.42 [d, (N−CH_2−N), ^3J(CP) = 9.2 Hz]. – $^{31}P\{^1H\}$ NMR (DMSO, r.t.): δ = −34.21 [s]; −143.9 [sept, (PF_6^-), ^1J(PF) = 708.6 Hz]. – $[(C_{10}H_{21}N_3P)^+PF_6^-]$ (359.23): calcd. C 37.61, H 5.52, N 10.96; found C 36.80, H 5.46, N 11.23. – MS (FAB), *m/z*: 214 [M^+].

7-Cyclohexyl-1,3,5-triaza-7-phosphoniaadamantane Hexafluorophosphate (**1d**): Compound **1d** is prepared as described for **1c** using 15.0 g (0.13 mol) of *c*-hexyl−PH_2[15], 100 ml of THF, 40 ml of 37% aqueous HCl, and 13.0 g (0.43 mol) of CH_2O. For ring closure 26.4 g (0.34 mol) of NH_4Ac and 10.3 g (0.34 mol) of paraformaldehyde are used. Addition of 9.0 g (0.055 mol) of NH_4PF_6 to the methanol solution of $[c\text{-hexyl}-TPA]^+Cl^-$ gives 16.6 g (0.043 mol, 33.2% yield based on *c*-hexyl−PH_2) of a white crystalline product (decomp. 205°C). – ^1H NMR ([D_6]acetone, r.t.): δ = 1.26 [m, (CH_2)]; 1.65 [broad, (CH_2)]; 1.76 [broad, (CH)]; 4.37 [d, (N−CH_2−N), ^2J(HH) = 13.4 Hz]; 4.44 [d, (N−CH_2−N), ^2J(HH) = 13.4 Hz]; 4.51 [d, (P−CH_2−N), ^2J(PH) = 5.8 Hz]. – $^{13}C\{^1H\}$ NMR ([D_6]-acetone, r.t.): δ = 23.34 [d, (CH_2), ^3J(CP) = 2.8 Hz]; 24.63 [s, (CH_2)]; 25.09 [d, (CH_2), ^2J(CP) = 13.8 Hz]; 29.03 [d, (CH), ^1J(CP) = 24.8 Hz]; 44.58 [d, (P−CH_2−N), ^1J(CP) = 29.4 Hz]; 70.74 [d, (N−CH_2−N), ^3J(CP) = 9.2 Hz]. – $^{31}P\{^1H\}$ NMR ([D_6]acetone, r.t.): δ = −41.49 [s]; −142.9 [sept, (PF_6^-), ^1J(PF) = 712.8 Hz]. – $[(C_{12}H_{23}N_3P)^+PF_6^-]$ (385.27): calcd. C 37.41, H 6.02, N 10.91; found C 36.11, H 6.30, N 10.63. – MS (FAB), *m/z*: 240 [M^+].

7-Benzyl-1,3,5-triaza-7-phosphoniaadamantane Hexafluorophosphate (**1e**): Compound **1e** is prepared analogously to **1c** by using 13.3 g (0.11 mol) of Ph−CH_2−PH_2[16], 80 ml of THF, 25 ml of 37% aqueous HCl and 10.0 g (0.33 mol) of CH_2O. $[Ph-CH_2-P(CH_2-OH)_3]^+Cl^-$ is converted into **1e** by using 12.9 g (0.43 mol) of CH_2O, 33.4 g (0.43 mol) of NH_4Ac, and 12.0 g (0.074 mol) of NH_4PF_6. Yield: 17.0 g (0.043 mol), 39.3% based on Ph−CH_2−PH_2 (decomp. 215°C). – ^1H NMR ([D_6]acetone, r.t.): δ = 3.83 [d, (Ar−CH_2−P), ^2J(HP) = 16.2 Hz]; 4.46 [d, (N−CH_2−N), ^2J(HH) = 13.7 Hz]; 4.58 [d, (N−CH_2−N), ^2J(HH) = 13.7]; 4.64 [d, (P−CH_2−N), ^2J(HP) = 5.9 Hz]; 7.29−7.45 [m, (aryl-C)]. – $^{13}C\{^1H\}$ NMR ([D_6]acetone, r.t.): δ = 26.85 [d, (Ar−CH_2−P), ^1J(CP) = 21.6]; 47.65 [d, (P−CH_2−N), ^1J(CP) = 30.8 Hz]; 72.31 [d, (N−CH_2−N), ^3J(CP) = 9.2 Hz]; 126.98 [d, (aryl−C), ^2J(CP) = 9.7 Hz]; 129.42 [d, (aryl-C), ^5J(CP) = 3.7 Hz]; 130.47 [d, (aryl-C), ^3J(CP) = 8.3 Hz]; 130.52 [d, (aryl−C), ^4J(CP) = 6.0 Hz]. – $^{31}P\{^1H\}$ NMR ([D_6]acetone, r.t.): δ = −44.84 [s]; −143.8 [sept, (PF_6^-), ^1J(PF) = 711 Hz]. – $[(C_{13}H_{19}N_3P)^+PF_6^-]$ (393.25): calcd. C 39.71, H 4.87, N 10.69; found C 39.24, H 5.01, N 10.32. – MS (FAB), *m/z*: 248 [M^+].

7-Phenyl-1,3,5-triaza-7-phosphoniaadamantane Hexafluorophosphate (**1f**): Compound **1f** is prepared analogously to **1c** by using 20.0 g (0.18 mol) of PH−PH_2[17], 150 ml of THF, 50 ml of 37% aqueous HCl, and 22 g (0.73 mol) of CH_2O. $[Ph-P(CH_2-OH)_3]^+Cl^-$ is converted into **1f** by using 18.0 g (0.6 mol) of CH_2O, 46.2 g (0.6 mol) of NH_4Ac, and 16.3 g (0.1 mol) of NH_4PF_6. Yield: 31 g (0.08 mol) 45.4% based on from Ph−PH_2 (decomp. 210°C). – ^1H NMR ([D_6]acetone, r.t.): δ = 4.49 [d, (N−CH_2−N), ^2J(HH) = 13.2 Hz]; 4.56 [d, (N−CH_2−N), ^2J(HH) = 13.2 Hz]; 4.93 [d, (P−CH_2−N), ^2J(PH) = 7.3 Hz]; 7.66−7.91 [m, (aryl−C)]. – $^{13}C\{^1H\}$ NMR ([D_6]acetone, r.t.): δ = 47.28 [d, (P−CH_2N), ^1J(CP) = 32.2 Hz]; 70.68 [d, (N−CH_2−N), ^3J(CP) = 10.2 Hz]; 118.39 [d, (aryl−C), ^1J(CP) = 60.9 Hz]; 129.64 [d, (aryl−C), ^2J(CP) = 12.7 Hz]; 132.24 [d, (aryl−C), ^3J(CP) = 10.5 Hz]; 134.83 [d, (aryl−C), ^4J(CP) = 3.6 Hz]. – $^{31}P\{^1H\}$ NMR ([D_6]acetone, r.t.): δ = −53.53 [s]; −142.9 [sept, (PF_6^-), ^1J(PF) = 712.8 Hz]. – $(C_{12}H_{17}N_3P)^+PF_6^-$ (379.23): calcd. C 38.01, H 4.52, N 11.08; found C 38.19, H 5.03, N 10.35. – MS (FAB), *m/z*: 234 [M^+].

3,7-Dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane (**2a**): To 100 ml of condensed liquid ammonia is added 12.3 g (41.3 mmol) of $[Me-TPA]^+I^-$ (**1a**). To the stirred suspension is added at −60°C sodium metal (1.2 g, 52.2 mmol) until the color turned to dark blue. Upon gently heating of the solution to room temp., the ammonia is slowly evaporated. The light yellow residue is transferred to a sublimation apparatus. At 0.05 Torr/80°C white crystals (2.5 g, 35% yield) of **2a** are obtained (m.p. 82°C). – ^1H NMR (C_6D_6, r.t.): δ = 0.77 [d, (P−CH_3), ^2J(PH) = 5.5 Hz]; 1.82 [s, (N−CH_3)]; 3.25 [dd, (P−CH_2−N), ^2J(HH) = 14.3 Hz, ^2J(HP) = 8.2 Hz]; 3.39 [d, (N−CH_2−N), ^2J(HH) = 10.1 Hz]; 3.64 [dd, (P−CH_2−N), ^2J(HH) = 14.3 Hz, ^3J(HP) = 25.9 Hz]; 3.72 [d, (N−CH_2−N), ^2J(HH) = 10.1 Hz]; 3.75 [d, (N−CH_2−N), bridge, ^2J(HH) = 13.1 Hz]; 3.89 [d, (N−CH_2−N, bridge), ^2J(HH) = 13.1 Hz]. – $^{13}C\{^1H\}$ NMR (C_6D_6, r.t.): δ = 10.21 [d, (P−CH_3), ^1J(CP) = 21.1 Hz]; 38.16 [s, (N−CH_3)]; 56.93 [d, (P−CH_2−N),

^1J(CP) = 26.2 Hz]; 71.26 [d, (N−CH_2−N), ^3J(CP) = 8.9 Hz]; 77.26 [d, (N−CH_2−N), ^3J(CP) = 2.8 Hz]. − $^{31}P\{^1H\}$ NMR (C_6D_6, r.t.): δ = −91.8 [s]. − $^{15}N\{^1H\}$ NMR (C_6D_6, r.t.): δ = −326.7 [d, ^4J(NP) = 4.8 Hz]; − 329.14 [d, ^2J(NP) = 8.9 Hz]. − $C_7H_{16}N_3P$ (173.20): calcd. C 48.54, H 9.31, N 24.26; found C 48.21, H 9.16, N 24.40. − MS (EI), *m/z*: 173 [M^+], 158 [M^+ − Me].

3-Ethyl-7-methyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane (**2b**): Compound **2b** is prepared as described for **2a** by using 16 g (51.1 mmol) of **1b** and 2.1 g (91.3 mmol) of sodium metal. At 0.05 Torr/50 °C, 2.1 g (11.2 mmol, 22% yield) of a colorless liquid is obtained. − ^1H NMR ($CDCl_3$, r.t.): δ = 0.9 [dt, (CH_3), ^3J(HH) = 7.3 Hz, ^3J(PH) = 15.1 Hz]; 1.45 [q, (CH_2), ^3J(HH) = 7.3 Hz]; 2.02 [s, (N−CH_3)]; 3.26 [dd, (P−CH_2−N), ^2J(HH) = 13.5 Hz, ^2J(HP) = 8.3 Hz]; 3.42 [d, (N−CH_2−N), ^2J(HH) = 11.0 Hz]; 3.51 [dd, (P−CH_2−N), ^2J(HH) = 13.5 Hz, ^3J(HP) = 24.0 Hz]; 3.72 [d, (N−CH_2−N, bridge), ^2J(HH) = 13.0 Hz]; 3.75 [d, (N−CH_2−N), ^2J(HH) = 11.0 Hz]; 3.82 [d, (N−CH_2−N, bridge), ^2J(HH) = 13.0 Hz]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 9.19 [d, (CH_3), ^2J(CP) = 16.5 Hz]; 25.71 [d, (CH_2), ^1J(CP) = 17.0 Hz]; 37.83 [s, (N−CH_3)]; 53.64 [d, (P−CH_2−N), ^1J(CP) = 24.8 Hz]; 70.26 [d, (N−CH_2−N, bridge), ^3J(CP) = 8.3 Hz]; 76.52 [s, (N−CH_2−N)]. − ^{31}P NMR ($CDCl_3$, r.t.): δ = −75.13 [qtt, ^3J(PH) = 15.1 Hz, ^2J(PH) = 24.0 Hz, ^2J(PH) = 8.3 Hz]. − $^{15}N\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = −350.57 [d, ^4J(NP) = 4.1 Hz]; −351.48 [d, ^2J(NP) = 8.7 Hz]. − $C_8H_{18}PN_3$ (187.22): calcd. C 51.32, H 9.69, N 22.44; found C 50.17, H 9.64, N 23.32. − MS (EI), *m/z*: 187 [M^+], 158 [M^+ − Et].

7-Methyl-3-phenyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane (**2f**): Compound **2f** is prepared as described for **2a** by using 22.0 g (58.0 mmol) of **1f** and 2.4 g (104.4 mmol) of sodium metal. At 0.05 Torr/120 °C, 6.1 g (0.26 mol, 45% yield) of white crystals are obtained. − ^1H NMR ($CDCl_3$, r.t.): δ = 2.16 [s, (N−CH_3)]; 3.58 [d, (N−CH_2−N), ^2J(HH) = 11.0 Hz]; 3.77 [dd, (P−CH_2−N), ^2J(HH) = 13.7 Hz, ^3J(PH) = 25.0 Hz]; 3.87 [d, (N−CH_2−N, bridge), ^2J(HH) = 14.7 Hz]; 3.91 [dd, (P−CH_2−N), ^2J(HH) = 13.7 Hz, ^3J(PH) = 8.5 Hz]; 3.94 [d, (N−CH_2−N9, ^2J(HH) = 11.0 Hz]; 4.01 [d, (N−CH_2−N, bridge), ^2J(HH) = 14.7 Hz]; 7.28 [t, (aryl−C), ^3J(HH) = 7.3 Hz]; 7.35 [t, (aryl-C), ^3J(HH) = 7.3 Hz]; 7.48 [dt, (aryl-C), ^3J(HH) = 7.3 Hz, ^3J(HP) = 6.4 Hz]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 38.26 [s, (N−CH_3)]; 53.96 [d, (P−CH_2−N), ^1J(CP) = 25.7 Hz]; 70.70 [d, (N−CH_2−N, bridge), ^3J(CP) = 9.2 Hz]; 76.99 [s, (N−CH_2−N)]; 128.23 [d, (aryl−C), ^2J(CP) = 26.7 Hz]; 128.42 [s, (aryl−C)]; 131.42 [d, (aryl−C), ^3J(CP) = 18.4 Hz]; 144.38 [d, (aryl−C), ^1J(CP) = 28.7 Hz]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = −77.06 [s]. − $^{15}N\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = −349.68 [d, ^4J(NP) = 4.4 Hz]; −350.53 [d, ^2J(NP) = 9.6 Hz]. − $C_{12}H_{18}N_3P$ (235.27): calcd. C 61.26, H 7.71, N 17.86; found C 60.88, H 7.55, N 18.13. − MS (CI), *m/z*: 235 [M^+], 158 [M^+ − Ph].

3,7-Dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane 3-Sulfide (**2aS**): To a suspension of 25 mg (0.78 mmol) of sulfur in 10 ml of benzene is added a solution of 131.6 mg (0.76 mmol) of **2a** in 10 ml of benzene. The solution is stirred for several minutes. Filtration followed by evaporation leaves 151 mg (0.74 mmol, 97% yield) of white **2aS** (m.p. 80 °C). − ^1H NMR (C_6D_6, r.t.): δ = 1.10 [d, (P−CH_3), (^2J(HP) = 11.2 Hz)]; 2.14 [s, (N−CH_3)]; 2.8−3.6 [m, (−CH_2−)]. − $^{13}C\{^1H\}$ NMR (C_6D_6, r.t.): δ = 40.35 [s, (N−CH_3)]; 61.56 [d, (P−CH_2−N), ^1J(CP) = 37.5 Hz]; 67.84 [d, (N−CH_2−N, bridge), ^3J(CP) = 18.2 Hz]; 77.3 [d, (N−CH_2−N), ^3J(CP) = 41.9]. − $^{31}P\{^1H\}$ NMR (C_6D_6, r.t.): δ = −8.6 [s]. − $C_7H_{16}N_3PS$ (205.26): calcd. C 40.98, H 7.80, N 20.49; found C 39.37, H 7.60, N 19.86. − MS (CI), *m/z*: 205 [M^+], 190 [M^+ − Me].

3,7-Dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane 3-Selenide (**2aSe**): To a suspension of 37.0 mg (0.47 mmol) of black selenium in 15 ml of chloroform is added a solution of 81.2 mg (0.47 mmol) of **2a** in $CHCl_3$ (5 ml). After stirring and refluxing for 1 h the solution is filtered and the solvent is removed from the filtrate; **2aSe** remains as a white solid (112.5 mg, 95% yield, m.p. 118 °C). − ^1H NMR ([D_6]DMSO, r.t.): δ = 1.82 [d, (P−CH_3), (^2J(HP) = 11.2 Hz)]; 2.14 [s, (N−CH_3)]; 3.48−4.43 [m, (−CH_2−)]. − $^{13}C\{^1H\}$ NMR (DMSO, r.t.): δ = 38.52 [s, (N−CH_3)]; 60.42 [d, (P−CH_2−N), ^1J(CP) = 27.8 Hz]; 67.90 [d, (N−CH_2−N, bridge), ^3J(CP) = 17.4 Hz]; 76.92 [s, (N−CH_2−N)]. − $^{31}P\{^1H\}$ NMR (DMSO, r.t.): δ = −25.75 [s], −24.6 [d, ^1J(PSe) = 720 Hz)]. − $C_7H_{16}N_3PSe$ (252.16): calcd. C 33.34, H 6.46, N 16.66; found C 32.90, H 6.23, N 17.24. − MS (CI), *m/z*: 253 [M^+].

3-Ethyl-7-methyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane 3-Sulfide (**2bS**): Compound **2bS** is prepared as described for **2aS** by using 101.5 mg (0.54 mmol) of **2b** and 17.4 mg (0.54 mmol) of sulfur. Yield: 113.6 mg (96%); m.p. 95 °C. − ^1H NMR ($CDCl_3$, r.t.): δ = 1.19 [dt, (CH_3), ^3J(HP) = 17.4 Hz, ^3J(HH) = 7.3 Hz]; 1.77 [dq, (CH_2), ^3J(HH) = 7.3 Hz, ^2J(HP) = 9.8 Hz]; 2.09 [s, (N−CH_3)]; 3.45−4.01 [m, (−CH_2)]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 6.71 [d, (CH_3), ^2J(CP) = 4.6 Hz]; 30.86 [d, (CH_2), ^1J(CP) = 47.3 Hz]; 38.06 [s, (N−CH_3)]; 59.58 [d, (P−CH_2−N), ^1J(CP) = 36.3 Hz]; 67.79 [d, (N−CH_2−N), ^3J(CP) = 17.9 Hz]; 76.96 [s, (N−CH_3)]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 0.7 [s]. − $C_8H_{18}N_3PS$ (219.28): calcd. C 43.82, H 8.27, N 19.16; found C 42.24, H 8.07, N 18.62. − MS (CI): 220 [M^+], 191 [M^+ − Et].

3-Ethyl-7-methyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane 3-Selenide (**2bSe**): Compound **2bSe** is prepared as described for **2aSe** by using 93.5 mg (0.5 mmol) of **2b** and 39.6 mg (0.5 mmol) of black selenium powder. Yield: 130 mg (98%); m.p. 128 °C. − ^1H NMR ($CDCl_3$, r.t.): δ = 1.19 [dt, (CH_3), ^3J(HP) = 17.8 Hz, ^3J(HH) = 7.6 Hz]; 1.90 [dq, (CH_2), ^2J(HP) = 9.8 Hz, ^3J(HH) = 7.6 Hz]; 2.09 [s, (N−CH_3)]; 3.57 [d, (N−CH_2−N), ^2J(HH) = 10.5 Hz]; 3.66 [ddd, (P−CH_2−N), ^2J(HH) = 15.8 Hz, ^2J(HP) = 9.8 Hz, ^4J(HH) = 1.7 Hz]; 3.76 [d, (N−CH_2−N), ^2J(HH) = 10.5 Hz]; 3.79 [dq, (N−CH_2−N, bridge), ^2J(HH) = 13.7 Hz, ^4J(HH) = 1.7 Hz]; 3.96 [dq, (N−CH_2−N, bridge), ^2J(HH) = 13.7 Hz, ^4J(HH) = 1.7 Hz]; 4.18 [dd, (P−CH_2−N), ^2J(HH) = 15.8 Hz, ^2J(HP) = 5.5 Hz]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 7.58 [d, (CH_3), ^2J(CP) = 4.4 Hz]; 31.50 [d, (CH_2), ^1J(CP) = 39.1 Hz]; 37.72 [s, (N−CH_3); 59.25 [d, (P−CH_2−N), ^1J(CP) = 28.1 Hz]; 67.70 [d, (N−CH_2−N, bridge), ^3J(CP) = 17.6 Hz]; 76.78 [s, (N−CH_2−N)]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = −16.72 [s]; −17.76 [d, ^1J(PSe) = 390.2 Hz]. − $C_8H_{18}N_3PSe$ (266.18): calcd. C 35.95, H 6.79, N 15.73; found C 36.07, H 6.93, N 15.50. − MS (CI), *m/z*: 267 [M^+].

7-Methyl-3-phenyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane 3-Sulfide (**2fS**): Compound **2fS** is prepared as described for **2aS** by using 150 mg (0.64 mmol) of **2f** and 20.4 mg (0.64 mmol) of sulfur. Yield: 164 mg (96%); m.p. 160 °C. − ^1H NMR ($CDCl_3$, r.t.): δ = 2.16 [s, (N−CH_3)]; 3.5−4.5 [m, (−CH_2−)]; 7.4−8.2 [m, (aryl−C)]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 38.03 [s, (N−CH_3)]; 63.02 [d, (P−CH_2−N), ^1J(CP) = 36.25 Hz]; 74.77 [s, (N−CH_2−N, bridge)]; 76.78 [s, (N−CH_2−N)]; 128.39 [d, (aryl−C), ^2J(CP) = 10.1 Hz]; 130.79 [d, (aryl−C), ^4J(CP) = 2.75 Hz]; 131.7 [d, (aryl−C), ^3J(CP) = 8.27 Hz]; 135.93 [d, (aryl−C), ^2J(CP) = 63.43 Hz]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = −4.23 (s). − $C_{12}H_{18}N_3PS$ (267.33): calcd. C 53.92, H 6.79, N 15.72; found C 54.54, H 6.85, N 16.38. − MS (CI), *m/z*: 267 [M^+].

7-Methyl-3-phenyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane 3-Selenide (**2fSe**): Compound **2fSe** is prepared as described for **2aSe** by using 69 mg (0.29 mmol) of **2f** and 25 mg (0.32 mmol) of black selenium. Yield: 85 mg (93%); m.p. 172 °C. − ^1H NMR ($CDCl_3$, r.t.): δ = 2.14 [s, (N−CH_3)]; 3.66−4.7 [m, (−CH_2−)]; 7.45−8.15

[m, (aryl–C)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 37.70 [s, (N–CH_3)]; 62.78 [d, (P–CH_2–N), ^1J(CP) = 29.4 Hz]; 68.17 [d, (N–CH_2–N, bridge), ^3J(CP) = 18.39 Hz]; 76.68 [s, (N–CH_2–N)]; 128.4 [d, (aryl–C), ^2J(CP) = 10.1 Hz]; 130.83 [d, (aryl–C), ^4J(CP) = 2.8 Hz]; 132.28 [d, (aryl–C), ^3J(CP) = 8.3 Hz]; 135.30 [d, (aryl–C), ^2J(CP) = 54.2 Hz]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = –20.15 [s]; –20.16 [d, ^1J(PSe) = 752 Hz]. – $C_{12}H_{18}N_3PSe$ (314.23): calcd. C 45.87, H 5.77, N 13.37; found C 44.80, H 5.56, N 12.68. – MS (CI), *m/z*: 314 [M^+].

3,3,7-Trimethyl-1,5,7-triaza-3-phosphoniabicyclo[3.3.1]nonane Iodide (**2aMe$^+$I$^-$**): To a stirred solution of 504 mg (2.9 mmol) of **2a** in 20 ml of $CHCl_3$ is added at room temp. dropwise and slowly 413 mg (0.18 ml, 2.9 mmol) of methyl iodide. After stirring for 30 min the solvent is removed and **2aMe$^+$I$^-$** is obtained as a white powder (882 mg, 96% yield, decomp. 230°C). – ^1H NMR (D_2O, r.t.): δ = 1.82 [d, (P–CH_3), ^2J(PH) = 13.4 Hz]; 2.2 [d, (P–CH_3), ^2J(PH) = 14.7 Hz]; 2.2 [s, (N–CH_3)]; 3.7–4.3 [m, (–CH_2–)]. – $^{13}C\{^1H\}$ NMR (D_2O, r.t.): δ = 11.80 [d, (P–CH_3), ^1J(CP) = 50.1 Hz]; 12.62 [d, (P–CH_3), ^1J(CP) = 54.4 Hz]; 38.16 [s, (N–CH_3)]; 49.11 [d, (P–CH_2–N), ^1J(CP) = 40.7 Hz]; 71.26 [d, (N–CH_2–N, bridge), ^3J(CP) = 18.2 Hz]; 75.88 [s, (N–CH_2–N)]. – ^{31}P NMR (D_2O, r.t.): δ = –20.6 [ttqq, ^2J(PH) = 10.1 Hz, ^2J(PH) = 10.4 Hz, ^2J(PH) = 13.4 Hz, ^2J(PH) = 13.4 Hz]. – $[(C_8H_{19}N_3P)^+I^-]$ (315.15): calcd. C 30.49, H 6.08, N 13.33; found C 30.01, H 6.21, N 13.89. – MS (FAB), *m/z*: 188 [M^+].

(3,7-Dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane)-gold(I) Chloride (**2aAuCl**): To a solution of 192 mg (0.65 mmol) of $(Me_2S)AuCl$[18] in 10 ml of $CHCl_3$ is added slowly a solution of 113 mg (0.65 mmol) of **2a** in 10 ml of $CHCl_3$. After stirring for 2 h the light yellow solution is filtered and the solvent is removed from the filtrate under reduced pressure. Recrystallization of the white residue from $CHCl_3$/hexane gives colorless crystals (210 mg, 80% yield, decomp. 150°C). – ^1H NMR ($CDCl_3$, r.t.): δ = 1.46 [d, (P–CH_3), ^2J(HP) = 9.2 Hz]; 2.13 [s, (N–CH_3)]; 3.6–4.60 [m, (–CH_2–)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 17.15 [d, (P–CH_3), ^1J(CP) = 23.9 Hz]; 38.03 [s, (N–CH_3)]; 54.91 [d, (P–CH_2–N), ^1J(CP) = 24.8 Hz]; 69.81 [d, (N–CH_2–N, bridge), ^3J(CP) = 16.8 Hz]; 76.27 [s, (N–CH_2–N)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = –39.14 [s]. – $C_7H_{16}AuClN_3P$ (405.62): calcd. C 20.73, H 3.98, N 10.36; found C 20.61, H 4.10, N 10.06. – MS (FD), *m/z*: 405 [M^+], 390 [M^+ – Me].

(3-Ethyl-7-methyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane)-gold(I) Chloride (**2bAuCl**): Compound **2bAuCl** is prepared as described for **2aAuCl** by using 178 mg (0.6 mmol) of $(Me_2S)AuCl$ and 113.2 mg (0.6 mmol) of **2b**. The temperature of the solution is maintained at 0°C. Removal of the solvent leaves 239 mg (0.57 mmol, 95% yield) of **2bAuCl** (decomp. 70°C). – ^1H NMR ($CDCl_3$, r.t.): δ = 1.14 [dt, (CH_3), ^3J(HH) = 7.8 Hz, ^3J(HP) = 18.6 Hz]; 1.67 [dq, (CH_2), ^3J(HH) = 7.8 Hz, ^2J(HP) = 1.5 Hz]; 2.13 [s, (N–CH_3)]; 3.5–4.0 [m, (–CH_2)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 8.81 [d, (CH_3), ^2J(CP) = 1.7 Hz]; 24.78 [d, (CH_2), ^1J(CP) = 25.3 Hz]; 37.99 [s, (N–CH_3)]; 53.11 [d, (P–CH_2–N), ^1J(CP) = 23.7 Hz]; 69.69 [d, (N–CH_2–N, bridge), ^3J(CP) = 13.8 Hz]; 76.44 [s, (N–CH_2–N)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = –24.85 (s). – $C_8H_{18}AuClN_3P$ (419.64): calcd. C 22.90, H 4.32, N 10.01; found C 22.61, H 4.30, N 10.06. – MS (FD), *m/z*: 419 [M^+].

(3-Methyl-7-phenyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane)gold(I) Chloride (**2fAuCl**): Compound **2fAuCl** is prepared as described for **2aAuCl** by using 106.8 mg (0.36 mmol) of (Me_2S)AuCl and 85.3 mg (0.36 mmol) **2b**. On recrystallization from pentane colorless crystals (155 mg, 0.33 mmol, 92% yield) of **2fAuCl** are obtained (decomp. 180°C). – ^1H NMR ($CDCl_3$, r.t.): δ = 2.21 [s, (N–CH_3)]; 3.65–4.36 [m, (–CH_2–)]; 7.23–7.92 (m, (aryl–C)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 38.18 [s, (N–CH_3)]; 55.37 [d, (P–CH_2–N), ^1J(CP) = 22.9 Hz]; 69.87 [d, (N–CH_2–N, bridge), ^3J(CP) = 14.6 Hz]; 76.44 [d, (N–CH_2–N), ^3J(CP) = 0.8 Hz]; 129.31 [d, (aryl–C), ^3J(CP) = 10.5 Hz]; 131.99 [d, (aryl–C), ^4J(CP) = 2.5 Hz]; 132.71 [d, (aryl–C), ^1J(CP) = 38.29 Hz]; 133.40 [d, (aryl–C), ^2J(CP) = 13.5 Hz]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = –25.03 [s]. – $C_{12}H_{18}AuClN_3P$ (467.69). calcd. C 30.82, H 3.88, N 8.98; found C 30.53, H 4.27, N 9.35. – MS (CI), *m/z*: 468 [M^+].

Bis(3,7-dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]-nonane)gold(I) Chloride (**[(2a)$_2$Au]$^+$Cl$^-$**): To a solution of 240 mg (0.82 mmol) of $(Me_2S)AuCl$ in 15 ml of chloroform is added slowly a solution of 282 mg (1.64 mmol) of **2a** in 10 ml of $CHCl_3$. After stirring for 2 h the solution is filtered and the solvent is evaporated. Recrystallization of the white residue from $CHCl_3$/pentane gives colorless crystals (446 mg, 0.77 mmol, 94% yield). – ^1H NMR ($CDCl_3$, r.t.): δ = 1.45 [s, (P–CH_3)]; 2.13 [s, (N–CH_3)]; 3.5–4.3 [m, (–CH_2–)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 16.60 [s, (P–CH_3); 39.08 [s, (N–CH_3)]; 54.67 [s, (P–CH_2–N)]; 67.74 [s, (N–CH_2–N, bridge)]; 76.32 [s, (N–CH_2–N)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = –30.7 [s]. – $[(C_{14}H_{32}AuN_6P_2)^+Cl^-]$ (578.82): calcd. C 29.05, H 5.57, N 14.52; found C 26.93, H 5.82, N 12.87. – MS (FAB) *m/z*: 544 [M^+].

(3,7-Dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]nonane-N,P)-cis-dimethyl-gold(III) cis-Dichloro-dimethylaurate(III) (**[(2a)AuMe$_2$]$^+$[Me$_2$AuCl$_2$]$^-$**): To 33.6 mg (0.19 mmol) of **2a** in 10 ml of $CHCl_3$ kept at –10°C is added 102 mg (0.19 mmol) of $[Me_2AuCl]_2$[19] in 10 ml of pentane. After stirring of the solution for 2 h, 100 ml of cold pentane is added to yield 40 mg (0.06 mmol, 32%) of white crystals of **[(2a)AuMe$_2$]$^+$[Me$_2$AuCl$_2$]** (decomp. 120°C). – ^1H NMR (D_2O, r.t.): δ = 0.70 [d, (Au–CH_3), ^2J(HP) = 7.8 Hz]; 1.01 [s, (Au–CH_3, aurate)]; 1.21 [d, (Au–CH_3), ^2J(HP) = 8.3 Hz]; 1.52 [d, (P–CH_3), ^2J(HP) = 12.2 Hz]; 2.54 [s, (N–CH_3)]; 3.8–4.6 [m, (–CH_2–)]. – $^{13}C\{^1H\}$ NMR (D_2O, r.t.): δ = 0.96 [d, (P–CH_3), ^1J(CP) = 19.83 Hz]; 3.05 [d, (Au–CH_3, *cis*), ^3J(CP) = 3.31 Hz]; 19.23 [d, (Au–CH_3, *trans*), ^3J(CP) = 109.6 Hz]; 46.31 [s, (N–CH_3)]; 48.12 [d, (P–CH_2–N), ^1J(CP) = 19.3 Hz]; 68.55 [d, (N–CH_2–N, bridge), ^3J(CP) = 9.9 Hz]; 77.06 [d, (N–CH_2–N), ^3J(CP) = 3.9 Hz]. – $^{31}P\{^1H\}$ NMR (D_2O, r.t.): δ = –42.39 [s]. – $[C_9H_{22}AuPN_3]^+$ $[C_2H_6AuCl_2]^-$ (689.18): calcd. C 18.92, H 4.04, N 6.02; found C 18.21, H 3.82, N 6.53. – MS (FAB), *m/z*: 400 [M^+], 370 [M^+ – 2 Me].

Tetracarbonyl(3,7-dimethyl-1,5,7-triaza-3-phosphabicyclo[3.3.1]-nonane-N,P)molybdenum (**(2a)Mo(CO)$_4$**): To 272 mg (0.91 mmol) of $(C_7H_8)Mo(CO)_4$[20] in 10 ml of pentane kept at 0°C is added dropwise 157 mg (0.91 mmol) of **2a** in 10 ml of pentane. The lemon-yellow precipitate immediately formed is filtered and washed with cold pentane. Yield: 250 mg (0.67 mmol) 85%; decomp. 165°C. – ^1H NMR ($CDCl_3$, r.t.): δ = 1.43 [d, (P–CH_3), (^2J(HP) = 7.3 Hz]; 2.60 [d, (N–CH_3), ^4J(HP) = 2.1 Hz]; 3.65–4.43 [m, (CH_2)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 12.08 [d, (P–CH_3), ^1J(CP) = 12.4 Hz]; 54.82 [d, (N–CH_3), ^3J(CP) = 4.8 Hz]; 56.08 [d, (P–CH_2–N), ^1J(CP) = 11.3 Hz]; 71.90 [d, (N–CH_2–N, bridge), ^3J(CP) = 7.8 Hz]; 83.85 [d, (N–CH_2–N), ^3J(CP) = 2.3 Hz]; 208.34 [d, (CO), J(CP_{cis}) = 9.9 Hz]; 213.85 [d, (CO) J(CP_{trans}) = 33.1 Hz]; 221.80 [d, (CO), ^2J(CP_{cis}) = 9.0 Hz]. – $^{31}P\{H\}$ NMR: δ = –45.6 (s). – $C_{11}H_{16}MoN_3O_4P$ (381.18): calcd. C 34.47, H 4.21, N 10.97; found C 35.03, H 4.18, N 10.89. – MS (CI), *m/z*: 383 [M^+], 354 [M^+ – CO], 173 [M^+ – $Mo(CO)_4$], 158 [M^+ – $Mo(CO)_4$ – Me].

Tetracarbonyl(3-ethyl-7-methyl-1,5,7-triaza-3-phosphabicyclo-[3.3.1]nonane-N,P)molybdenum (**(2b)Mo(CO)$_4$**): Compound **(2b)Mo(CO)$_4$** is prepared similarly as described for **(2a)Mo(CO)$_4$**

Table 1. Crystal and structure solution and refinement data for compounds **2a**, **[(2a)$_2$Au]$^+$Cl$^-$**, **2fAuCl**, **[2aAuMe$_2$]$^+$[Me$_2$AuCl$_2$]$^-$**

	2a	**[(2a)$_2$Au]$^+$ Cl$^-$**	**2fAuCl**	**[2aAuMe$_2$]$^+$ [Me$_2$AuCl$_2$]$^-$**
formula	$C_7H_{16}N_3P$	$C_{17}H_{35}AuCl_{10}N_6P_2$	$C_{12}H_{18}AuClN_3P$	$C_{11}H_{18}Au_2Cl_2N_3P$
M_r	173.20	936.92	467.68	698.17
crystal syst.	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	Pbcn	Pbcn	Pbca	$P2_1/n$
a [Å]	7.414 (1)	9.473 (1)	7.086 (1)	8.660 (1)
b [Å]	17.146 (1)	18.823 (2)	21.328 (1)	7.232 (1)
c [Å]	7.383 (1)	38.551 (2)	19.142 (1)	14.854 (1)
ß [°]	90	90	90	101.15 (1)
V [Å^3]	938.6 (1)	6874.0 (3)	2879.3 (7)	912.7 (2)
ρ_{calc} [gcm^{-1}]	1.23	1.81	2.17	2.54
Z	4	8	8	2
F(000) [e]	376	3664	1776	644
μ [cm^{-1}]	2.4	51.7	105.0	164.3
T [°C]	-70	-68	-62	20
hkl-range	±9, +21, +9	+12, +24, +49	+9, +27, +24	+11, ±9, ±18
Abs. cor.	None	empirical	empirical	empirical
T_{min}/T_{max}	-	76.67/99.88	25.87/99.86	56.74/99.80
scan mode	ω	ω	θ-θ	θ-2θ
scan range [°]	$3 < \theta < 27$	$3 < \theta < 27$	$3 < \theta < 27$	$3 < \theta < 27$
measured data	1424	7704	3800	4206
unique data	856	6651	2964	2127
observed data	597	5423	2291	1557
No.of parameters	89	312	163	110
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$
R	0.0583[a]	0.0413[a]	0.0437[a]	0.0393[c]
R_w	0.0638[b]	0.0453[b]	0.0434[b]	0.1017[c]
k[b]	0.001199	0.001138	0.000909	-
$\Delta\rho_{max/min}$ [eÅ^{-3}]	2.08/-2.03[d]	0.93/-1.23[d]	1.53/-2.41[d]	1.74/1.91[d]

[a] $R = \sum(\|F_o\| - \|F_c\|)/\sum|F_c|$. - [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w = [\sigma^2(F_o) + k F_o^2]^{-1}$. - [c] $R = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$; $w = q/\sigma^2(F_o^2) + (ap)^2 + bp$, $p = \max(f_o,0) + 2F_c^2/3$, a = 0.0728, b = 0.0181.-[d] Residual electron densities located at Au atoms.

by using 365 mg (1.22 mmol) of $(C_7H_8)Mo(CO)_4$ and 228 mg (1.22 mmol) of **2b**. By recrystallization from $CHCl_3$ at −30°C yellow needles (439 mg, 1.11 mmol, 91% yield) are obtained (decomp. 170°C). – ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.19 [dt, (CH_3), ^3J(HH) = 7.6 Hz, J(HP) = 18.1 Hz]; 1.74 [dq, (CH_2), ^3J(HH) = 7.6 Hz, ^2J(HP) = 7.6 Hz]; 2.61 [d, (N−CH_3), ^4J(HP) = 2.0 Hz]; 3.64−4.41 [m, (−CH_2−)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 7.61 [d, (CH_3), ^2J(CP) = 2.8 Hz]; 20.61 [d, (CH_2), ^1J(CP) = 13.5 Hz]; 54.36 [d, (P−CH_2−N), ^1J(CP) = 9.6 Hz]; 54.85 [d, (N−CH_3), ^3J(CP) = 4.7 Hz]; 71.86 [d, (N−CH_2−N), ^3J(CP) = 7.7 Hz]; 83.90 [d, (N−CH_2−N, bridge), ^3J(CP) = 2.2 Hz]; 208.38 [d, (CO), $^2J(CP_{cis}) \doteq$ 9.6 Hz]; 213.84 [d, (CO), $^2J(CP_{trans})$ = 32.8 Hz]; 222.08 [d, (CO), $^2J(CP_{cis})$ = 8.5 Hz]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = −33.3 [s]. – $C_{12}H_{18}MoN_3O_4P$ (395.21): calcd. C 36.47, H 4.59, N 10.63; found C 36.27, H 4.78, N 10.69. – MS (CI) *m/z*: 397 [M$^+$], 369 [M$^+$ − CO], 187 [M$^+$ − $Mo(CO)_4$], 185 [M$^+$ − $Mo(CO)_4$ − Et].

Tetracarbonyl(7-methyl-3-phenyl-1,5,7-triaza-3-phosphabicyclo-[3.3.1]nonane-N,P)molybdenum (**(2f)Mo(CO)$_4$**): Compound **(2f)Mo(CO)$_4$** is prepared as described for **(2a)Mo(CO)$_4$** by using 300 mg (1.0 mmol) of $(C_7H_8)Mo(CO)_4$ and 235.3 mg (1.0 mmol) of **2f**. Yield: 385 mg (0.87 mmol), 87%; decomp. 165°C. – ^{1}H NMR ($CDCl_3$, r.t.): δ = 2.70 [d, (N−CH_3), ^4J(HP) = 1.7 Hz]; 3.94−4.19 [m, (−CH_2−)]; 7.71−7.78 [m, (aryl−C)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 54.98 [d, (N−CH_3), ^3J(CP) = 4.4 Hz]; 55.56 [d, (P−CH_2−N), ^1J(CP) = 9.9 Hz]; 71.70 [d, (N−CH_2−N, bridge), ^3J(CP) = 8.5 Hz]; 83.91 [d, (N−CH_2−N), ^3J(CP) = 1.7 Hz]; 129.12 [d, (aryl−C), ^2J(CP) = 9.4 Hz]; 131.13 [d, (aryl−C), ^4J(CP) = 2.5 Hz]; 131.41 [d, (aryl−C), ^1J(CP) = 24.2 Hz]; 131.98 [d, (aryl−C), ^3J(CP) = 13.2 Hz]; 208.04 [d, (CO), $^2J(CP_{cis})$ = 9.7 Hz]; 213.91 [d, (CO), $^2J(CP_{trans})$ = 33.3 Hz]; 222.15 [d, (CO), $^2J(CP_{cis})$ = 8.8 Hz]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = −40.19 [s]. – $C_{16}H_{18}MoN_3O_4P$ (443.25): calcd. C 43.36, H 4.09, N 9.48; found C 42.08, H 4.24, N 9.51. – MS (CI) *m/z*: 445 [M$^+$], 417 [M$^+$ − CO].

X-ray Structure Determinations: All samples were mounted in glass capillaries. Graphite-monochromated Mo-K_α radiation was used. The structures were solved by direct methods (programs: SHELXTL-PC and SHELXL-93)[21,22]. With the exception of one phosphane ligand **2a** in the structure of **[(2a)$_2$Au]$^+$ Cl$^-$**, hydrogen atoms were included in idealized, fixed positions. The structures of **2a**, **[(2a)$_2$Au]$^+$ Cl$^-$** and **[2aAuMe$_2$]$^+$[Me$_2$AuCl$_2$]$^-$** were complicated

by disorder of one complete phosphane ligand **2a** in each case. These distributions were taken into account by using split models with SOF = 0.5/0.5. The final cell parameters and specific data collection parameters are summarized in Table 1. Details of the X-ray structure determinations have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the depository number CSD-59018.

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