Synthesis and Structure of the Decanuclear Gold(I) Cluster Cation $[Au_8(AuCl)_2\{\mu_3\text{-}P(tBu)\}_2\{\mu\text{-}P(tBu){=}C(NMe_2)_2\}_6]^{4+}$ with Bridging Phosphaalkene and Phosphanediide Ligands

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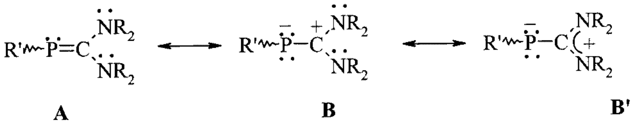
Reaction of the inversely polarized phosphaalkene $HP{=}C(NMe_2)_2$ (**1**) with $[AuCl(PPh_3)]$ (**2a**) in a molar ratio of 2:1 in THF led to the formation of complex $[Au\{HP{=}C(NMe_2)_2\}_2]Cl$ (**3**) as a pale yellow solid. In contrast to this, treatment of **2a** with two molar equivalents of $tBuP{=}C(NMe_2)_2$ (**4**) afforded a mixture of $[Au\{P(tBu){=}C(NMe_2)_2\}_2]^+Cl^-$ (**5**) and $[\{(Me_2N)_2C{=}(tBu)PAu\}_2(\mu\text{-}Cl)]^+Cl^-$ (**6**). In CH_2Cl_2 solution this mixture was slowly converted into the novel decanuclear complex $[Au_8(AuCl)_2\{\mu_3\text{-}P(tBu)\}_2\{\mu\text{-}P(tBu){=}C(NMe_2)_2\}_6]^{4+}(Cl^-)_4$ (**7**) featuring six edge-bridging phosphaalkene ligands and two μ_3-*tert*-butylphosphanediide ligands. In solution the cluster **7** shows a high order $^{31}P\{^1H\}$ NMR spectrum of the $[AB_2C]_2$ type. According to the X-ray structural analysis the Au_{10} framework may be described as a slightly puckered ladder constructed of three quadrangles. The central Au_4 parallelogram is capped on both faces by a pair of $[tBuPAuCl]$ units. (© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

Introduction

The chemistry of multinuclear complexes has been studied by several research groups for academic reasons as well as for potential industrial applications.[1] In contrast to a wide variety of chalcogen-bridged gold complexes,[2] gold clusters with phosphorus-containing ligands in bridging positions are rare. Cluster cations with "naked" phosphorus atoms are $[P(AuL)_4]^+$,[4] $[P(AuL)_5]^{2+}$,[5] $[P(Au_5L_6)]^{2+}$,[6] $[P(AuL)_6]^{3+}$,[7] $[Au\{P(AuL)_4\}_2]^{3+}$.[3] In $[arylP(AuL)_3]^+$ [5a,8] and $[arylP(AuL)_4]^{2+}$ [8] phosphinidene ligands are bridging the Au atoms and the terminal ligands (L) are tertiary phosphanes. The chemistry of gold(I) phosphanides is also poorly developed. Apart from polymeric $[\{Au(\mu\text{-}PR_2)\}_n]$ (R = phenyl, substituted phenyl, ethyl, or *n*-octyl),[9] structurally characterized dinuclear complex anions $[(AuX)_2(\mu\text{-}PPh_2)]^-$ (X = Cl, Br, I)[10,11] are known. Laguna et al. have recently reported the synthesis of dinuclear Au^{III} complexes $[\{Au(C_6F_6)_3\}_2(\mu\text{-}PPh_2)]^-$, $[Au_2(C_6F_5)_4(\mu\text{-}PPh_2)_2)]$[13] as well as the trinuclear $Au^{III}{-}Au^{I}$ phosphanido-bridged derivatives $[\{(C_6F_5)_3Au(\mu\text{-}PPh_2)\}_2Au]^-$,[14] $[\{C_6F_5Au(\mu\text{-}PPh_2)\}_2Au(C_6F_5)_2]^-$,[15] $[\{(Ph_3P)Au(\mu\text{-}PPh_2)\}_2Au(C_6F_5)_2]^+$ [15] and the tetranuclear complex $[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Au\}_2]$.[15] Structurally characterized polynuclear ($n >$ 4) and homometallic μ-phosphanido clusters of gold are without precedent to the best of our knowledge.

C-Amino-substituted phosphaalkenes $R'P{=}C(NR_2)_2$ are zwitterions in which the negatively charged phosphanide unit is stabilized by an adjacent carbenium center[16,17] (Scheme 1).



Scheme 1. Limiting formulae of amino-substituted phosphaalkenes

In the context of the present work, the question as to whether phosphaalkenes with an inverse distribution of π-electron density can function as bridging ligands in polynuclear gold complexes was intriguing.

Results and Discussion

The reaction of the gold complexes $[Au(Cl)L]$ (**2**) (**a**: L = PPh_3, **b**: tetrahydrothiophene (THT), **c**: CO) with two molar equivalents of phosphaalkene **1** in THF at ambient temperature leads to the precipitation of the yellow mononuclear complex **3** (Scheme 2).

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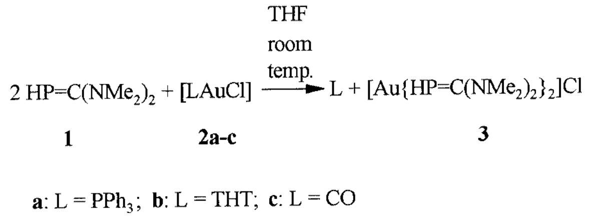
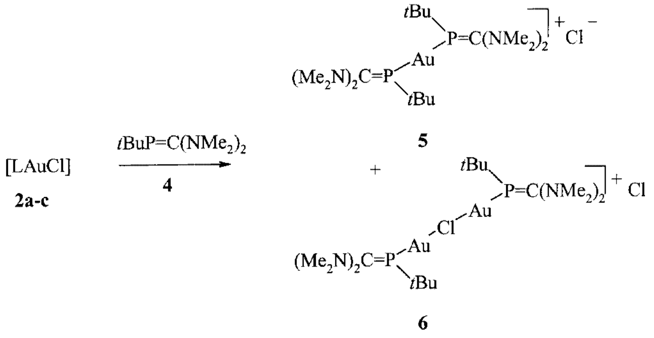


$$2\,HP{=}C(NMe_2)_2 + [LAuCl] \xrightarrow{\text{THF, room temp.}} L + [Au\{HP{=}C(NMe_2)_2\}_2]Cl$$

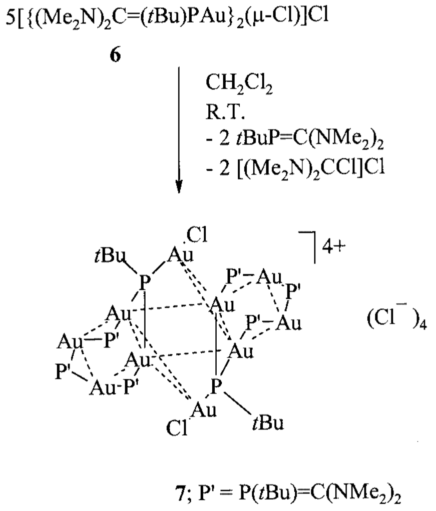
Scheme 2. Reaction of $HP{=}C(NMe_2)_2$ with [LAuCl]

Compound **3** is readily soluble in dichloromethane. The ^{31}P NMR signal in the proton-coupled spectrum of **3** at $\delta = -90$ ppm (d, $^1J_{P,H} = 219$ Hz) is shifted to higher field with respect to the free ligand **1** ($\delta = -73$ ppm, d, $^1J_{P,H} = 156$ Hz). A peak at *m/z* = 461 in the electrospray-ionization mass spectrum (ESI-MS) is assigned to the cation of **3**. The reaction of **2** with the more bulky and more basic phosphaalkene $tBuP{=}C(NMe_2)_2$ (**4**) under analogous conditions produces an amorphous green-yellow precipitate, which according to an ESI mass spectrum contains the complex cations **5** (*m/z* =573) and **6** (*m/z* =805) (Scheme 3).



Scheme 3. Reaction of $tBuP{=}C(NMe_2)_2$ with [LAuCl]

The $^{31}P\{^1H\}$ NMR spectrum of the mixture displays a broad signal at $\delta = 37$ ppm, which again is considerably shielded with respect to the free ligand ($\delta = 81$ ppm). In the ^1H NMR spectrum of the same sample, broad singlets at $\delta = 3.62$ and 1.42 ppm are attributed to the protons of the dimethylamino functions and the *tert*-butyl groups. In free **4** the corresponding resonances are observed at $\delta = 2.83$ and 1.19 ppm. Thus ligand exchange between cations **5** and **6** in solution is obvious. Attempted separation of these salts on a preparative scale was unsuccessful. Also, attempts to separate the components by crystallization from dichloromethane led to the complete transformation of **5** and **6** into the yellow salt **7** with a decanuclear complex cation (Scheme 4). The cation $[(Me_2N)_2CCl]^+$ was formed by an unprecedented nucleophilic cleavage of a P=C double bond by a chloride. This cation was identified from its $^{13}C\{^1H\}$ NMR spectrum, where singlets at $\delta = 44.5$ and 157.9 ppm appeared (ref.:[18] $\delta = 45$ and 159 ppm). The same transformation of **5** and **6** was observed when using acetonitrile as a solvent.



Scheme 4. Formation of **7** from **6** (idealized)

Compound **7** is readily soluble in acetonitrile and water but only moderately soluble in dichloromethane.

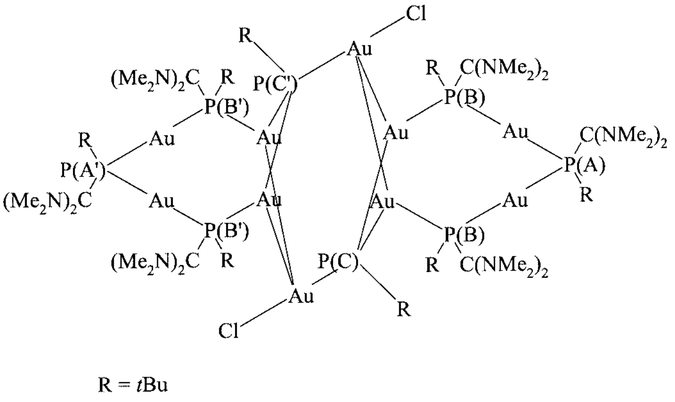
In the $^{31}P\{^1H\}$ NMR spectrum of cluster **7** three groups of signals are observed at $\delta = 42.2$, 34.0, and 20.3 ppm with a relative intensity of 2:1:1 respectively.. The pattern of the signals indicates the presence of an $[AB_2C]_2$ spin system. This is also consistent with the symmetry of the compound as derived from the X-ray diffraction study. The signal at $\delta = 34.0$ ppm shows only four lines and, in a first approximation, may be regarded as the A-part of an AB_2 spectrum, implying that the A nucleus is only coupling with the B nuclei (but not with the B′ nuclei). Thus, the signal at $\delta = 34.0$ ppm is assigned unambiguously to the peripheral phosphorus atoms P_A and $P_{A'}$ in Figure 1.

The signal at $\delta = 42.2$ ppm with the highest intensity is attributed to P_B; consequently, the resonance at $\delta = 20.3$ ppm is caused by P_C. The interaction between both AB_2C parts occurs exclusively through the coupling between the nuclei P_C and $P_{C'}$ and causes the splitting of the higher order signals of P_B and P_C. Within the AB_2C parts $^2J_{PP}$ couplings are observed, whereas between both AB_2C halves of the cation a $^3J_{PP}$ coupling is present, which is also reflected by the different signs of the coupling constants. The relative signs result from the iterative fitting of the spectrum assuming positive values for the two-bond P-P couplings. The relatively large $^2J_{PP}$ coupling constants agree with a trans-arrangement of the coupling P atoms.

The fourfold positive charge of the cation is compensated for by four chloride ions. Accordingly, the ESI mass spectrum features a peak at *m/z* =836.0, indicating a mass of 3344 Dalton for the cation $[C_{62}H_{144}Au_{10}Cl_2N_{12}P_8]^{4+}$; this peak shows the correct isotopic pattern.

X-ray Structural Analysis of $7{\cdot}14CH_2Cl_2$

Bright yellow single crystals of **7** as a solvate with 14 molecules of CH_2Cl_2 were grown over two weeks from a solution of **7** in dichloromethane layered with *n*-hexane at 4 °C. The X-ray structural analysis (Figure 2) shows a cation



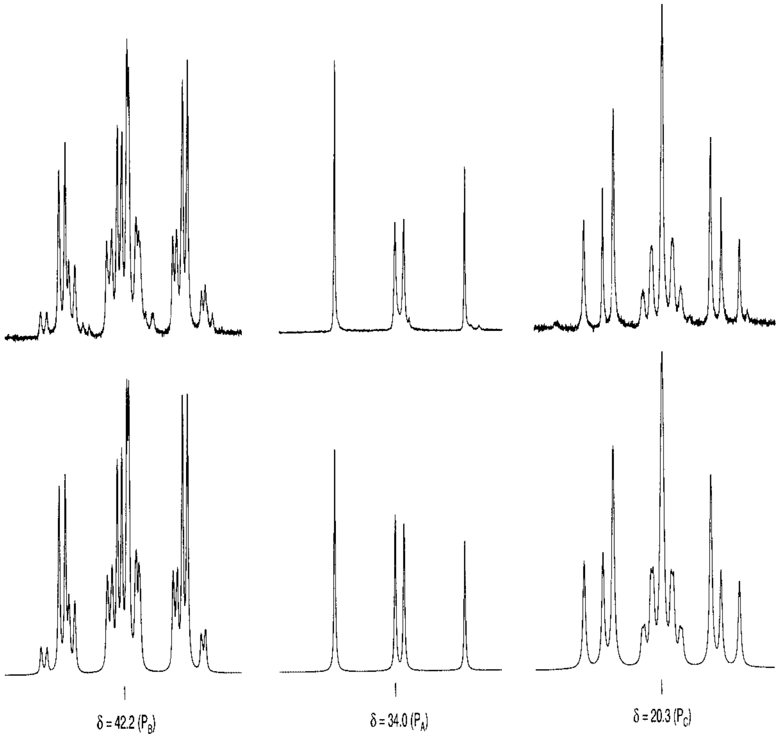


Figure 1. Observed and simulated $^{31}P\{^{1}H\}$ NMR spectrum of **7**

containing ten gold atoms. Eight atoms [Au(1) to Au(4) and Au(1a) to Au(4a)] form a puckered ladder made up of three quadrangles [Au(1)−Au(2)−Au(3) = 158.22(2)°, Au(2)−Au(3)−Au(4) = 159.43(2)°].

The central quadrangle — a parallelogram defined by the atoms Au(2), Au(2a), Au(3), and Au(3a) — is capped on both faces by a [*t*BuPAuCl] entity, which leads to the triangles Au(2),Au(3a),P(2a); Au(2a),Au(3),P(2); Au(2),Au(3a),Au(5a); and Au(2a),Au(3),Au(5). The center of this parallelogram is located on a crystallographic center of inversion. In pairs, the three edges of both peripheral quadrangles Au(1)−Au(4a), Au(1a)−Au(4), Au(1)−Au(2), Au(1a)−Au(2a), Au(3)−Au(4), and Au(3a)−Au(4a) are bridged by six phosphaalkene ligands via their P atoms. The Au−Au distances vary from 3.030(1) Å [Au(2a)−Au(5), Au(2)−Au(5a)] to 3.426(1) Å [Au(1)−Au(4a), Au(1a)−Au(4)] and have to be regarded as weak aurophilic contacts. The Au(5)−P(2a) and Au(5a)−P(2) bond lengths within the [P(*t*Bu)AuCl] units [2.272(4) Å] are similar to the Au−P distances in $[(Ph_3PAu)_6C]^{2+}$ [2.269(1)−2.274(1) Å][19] but they are significantly shorter than the Au−P contacts to the μ-phosphaalkene ligands [2.306(4)−2.324(3) Å]. The Au−P−Au valence angles at the P atoms of the phosphaalkene bridges vary from 90.9(1)° at P(3) to 91.6(1)° at P(1), and to 95.7(1)° at P(4). They are significantly compressed in comparison to the ideal tetrahedral angle. The same holds for the Au(2a)−P(2)−Au(3) angle, which is 92.7(1)°. In contrast to this the Au(3)−P(2)−Au(5a) [119.7(2)°] and Au(2a)−P(2)−Au(5a) [116.4(2)°] angles are significantly widened. The P−Au−P angles at the atoms Au(1) and Au(4) average 170.5° — close to linearity. Similarly the P(2a)−Au(5)−Cl(1) angle is 173.8(1)°. The Au−Cl bond lengths in **7** [2.332(4) Å] exceed those in [tBu$_3$PAuCl] [2.28(6) Å][20] and [Au(CO)Cl] [2.2261(5) Å].[21] The

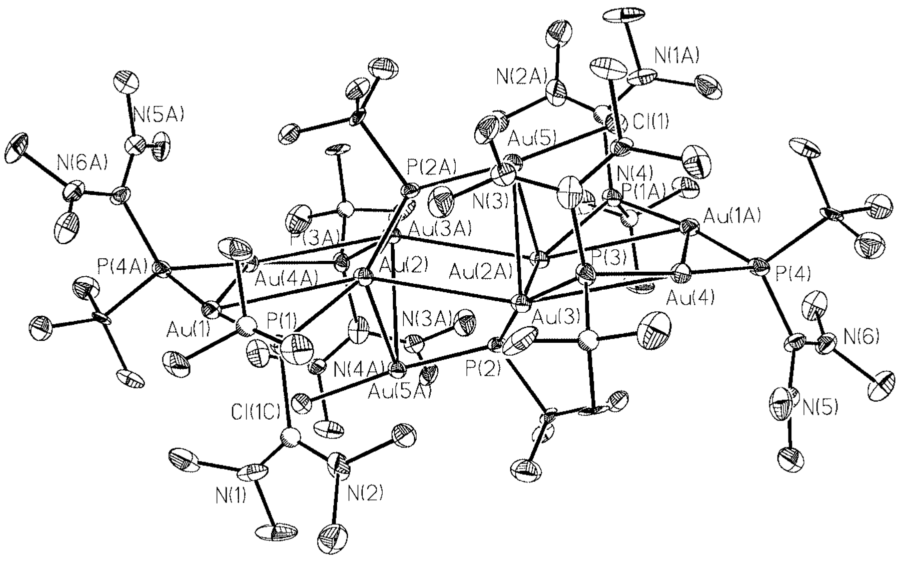


Figure 2. Structure of the cation of **7** in the crystal; selected bond lengths [Å] and angles [°]: Au(1)−Au(2) 3.323(1), Au(2)−Au(3) 3.285(1), Au(3)−Au(4) 3.303(1), Au(4)−Au(1a) 3.426(1), Au(2)−Au(3a) 3.372(1), Au(2)−Au(5a) 3.030(1), Au(3)−Au(5) 3.102(1), Au(1)−P(1) 2.313(4), Au(2)−P(1) 2.322(3), Au(3)−P(3) 2.324(4), Au(4)−P(3) 2.310(4), Au(4)−P(4) 2.316(4), Au(1a)−P(4) 2.306(4), Au(2)−P(2a) 2.332(3), Au(3a)−P(2a) 2.330(3), Au(5)−P(2a) 2.272(4), Au(5)−Cl(1) 2.332(4); Au(4a)−Au(1)−Au(2) 89.31(2), Au(1)−Au(2)−Au(3a) 90.34(2), Au(2)−Au(3a)−Au(4a) 90.59(2), Au(3a)−Au(4a)−Au(1) 89.74(2), Au(2)−Au(3)−Au(2a) 87.51(2), Au(3)−Au(2)−Au(3a) 92.49(2), Au(2a)−Au(5)−Au(3) 66.71(2), Au(5)−Au(3)−Au(2a) 55.62(2), Au(3)−Au(2a)−Au(5) 57.67(2), Au(1)−P(1)−Au(2) 91.60(13), Au(3)−P(3)−Au(4) 90.91(13), Au(1)−P(4a)−Au(4a) 95.67(14), Au(2)−P(2a)−Au(3a) 92.66(12), Au(2)−P(2a)−Au(5) 116.41(16), Au(3a)−P(2a)−Au(5) 119.72(15). P(2a)−Au(5)−Cl(1) 173.77(12), P(4a)−Au(1)−P(1) 170.60(12), P(4)−Au(4)−P(3) 170.41(14)

P=C double bond of precursor **4** {C−P in **1**: 1.740(1) Å[22]} is elongated to single bond length upon incorporation into the cluster cation **7** [1.849(16)−1.877(14) Å]. A similar bond length [1.8751(17) Å] was observed after the ligation of $[Tp^*(CO)_2Mo{\equiv}C{-}P{=}C(NMe_2)_2]$ to two [AuCl] units to give $[Tp^*(CO)_2Mo{\equiv}C{-}P(AuCl)_2C(NMe_2)_2]$ {Tp*= HB(3,5-$Me_2pz)_3$}.[17] The three-coordinate carbon atoms of the phosphaalkenes remain planar. π-Conjugation to the N-atoms of the dimethylamino groups results in short $C(sp^2){-}N(sp^2)$ bonds [1.292(18)−1.358(19) Å] with respect to the standard value for a C−N single bond (1.45 Å).[22] The formation of cluster **7** is remarkable for several reasons:

1) It is the first polynuclear gold compound with bridging phosphaalkene ligands.

2) The degradation of a phosphaalkene to a $tBuP^{2-}$ ligand and a chloroformamidinium ion by chloride ions in the coordination sphere of a metal is without precedent.

3) The structural architecture is new for Au_{10} derivatives.

The metal frameworks in $[Au(AuNCO)(AuPPh_3)_8]Cl$[23] and $[Au(AuCl)(AuPPh_3)_8]^+$ [24] are derived from a square antiprism with a gold atom in the center of the cage. One square-face of the anti-prism is capped by the AuNCO or the AuCl moiety. The cluster $[Au_{10}(C_6F_5)_4(PPh_3)_5]$ is of toroidal geometry,[25] whereas the Au_{10} skeleton of $[PtAu_{10}\{Ph_2P(CH_2)_3PPh_2\}_5](NO_3)_2$ [26] and $[Pt(AuPEt_3)_{10}](BPh_4)_2$ [27] are segments of an icosahedron. In the cation $[Au_{10}Se_4(dppm)_4]^{2+}$ [dppm = $(Ph_2P)_2CH_2$], eight Au atoms form an irregular puckered octagon with two additional Au atoms in the center.[27] The Au_{10} skeleton of $[Au_{10}(AsPh)_4(PhAsSiMe_3)_2(PnPr_3)_6]$ can be described as an edge-shared bioctahedron, the four vertices of which are linked by pairs.[28] The cation $[Au_{10}Se_4(dppf)_4]^{2+}$ (dppf = 1,1′-diphenylphosphanylferrocene) consists of two $[Au\{Se(Au_2dppf)\}]$ subunits, which are combined via aurophilic interactions.[2k] The structure of the cation $[Au_{10}\{\mu\text{-}Ph_2PN(n\text{Pr})PPh_2\}_4(\mu\text{-}S)_4]^{2+}$ is similar to a propeller.[2h]

Experimental Section

General: All manipulations were performed under dry argon. Organic solvents were rigorously dried with an appropriate drying agent and freshly distilled before use. The following compounds were prepared as described in the literature: $[AuCl(PPh_3)]$ (**2a**),[29] [AuCl(THT)],[30] [AuCl(CO)],[31] $HP{=}C(NMe_2)_2$ [32] (**1**), $tBuP{=}C(NMe_2)_2$ [33] (**4**). IR spectra: Bruker FTIR Vector 22, Bruker FTIR IFS66. ^1H, ^{13}C, ^{31}P NMR spectra: Bruker Avance DRX 500 (^1H: 500.13 MHz, ^{13}C: 125.76 MHz, ^{31}P: 202.46 MHz); references: $SiMe_4$ (^1H, ^{13}C), 85% H_3PO_4 (^{31}P). For solution and simulation of the ^{31}P NMR spectrum of **7** the PERCH program package[34] was used. 754 of the 890 allowed transitions were assigned to experimentally observed lines. The simulation converged at an RMS value of 0.95. MS: Esquire 3000/Tune-ESI.MS

$[Au\{HP{=}C(NMe_2)_2\}_2]Cl$ (3): A solution of $[AuCl(PPh_3)]$ (**2a**) (0.30 g, 0.6 mmol) in 10 mL of tetrahydrofuran (THF) was treated at ambient temperature with of $HP{=}C(NMe_2)_2$ (**1**; 0.15 g, 1.15 mmol). After stirring for 2 h the light yellow slurry was filtered, the solid washed with THF (3 × 10 mL), and dried in vacuo to give 0.26 g (85%) of **3**. IR (KBr): $\tilde{\nu}$ = 2949w cm^{-1}, 2328m [ν(PH)], 1558s, 1507w, 1465m, 1410m, 1385s, 1286m, 1173m, 1109m, 919m. ^1H NMR (CD_2Cl_2): δ = 3.27(s, 24 H, NMe_2), 3.71(d, $^1J_{P,H}$=219 Hz, PH) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ =

44.5 (br. s, NCH_3), 197.6 (d, $^1J_{P,C}=56$ Hz, $P=CN_2$) ppm. MS-ESI: m/z = 461.1 $[Au\{HP=C(NMe_2)_2\}]^+$. $C_{10}H_{26}AuClN_4P_2$ (496.71): calcd. C 24.18, H 5.28, N 11.28; found C 24.34, H 5.00, N 10.94.

$[Au_8(AuCl)_2\{\mu_3\text{-}P(tBu)\}_2\{\mu\text{-}P(tBu)=C(NMe_2)_2\}_6]^{4+}(Cl^-)_4$ (7): Neat $tBuP=C(NMe_2)_2$ (**4**) (0.75 g, 3.98 mmol) was added to a solution of $[AuCl(PPh_3)]$ (**2a**) (1.00 g, 2.02 mmol) in THF (50 mL) at 20 °C. The resulting yellow slurry was stirred for 1 h and then filtered. The isolated solid was washed with THF (2 × 5 mL) and dried in vacuo to give 0.95 g of a mixture of **5** and **6**. ^1H NMR (CD_2Cl_2): δ = 1.42 (s, 9n H, *t*Bu), 3.62 (s, 12n H, NMe_2) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 37 (s, br) ppm. MS-ESI: m/z (%) = 805.1 (19) $[Au_2Cl\{tBuP=C(NMe_2)_2\}_2]^+$, 573.2 (100) $[Au\{tBuP=C(NMe_2)_2\}_2]^+$. A sample of this mixture (0.85 g) was dissolved in dichloromethane (40 mL) and then *n*-hexane was added dropwise until a slight cloudiness of the liquid phase persisted. Stirring at 20 °C was continued for three days before the solution was concentrated to about 25% of its volume resulting in the separation of **7** as a yellow powder. The mother liquor was syringed off and the residue was dried to yield 0.58 g (82% yield with respect to **2a**) of **7**. ^1H NMR (CD_3CN): δ = 1.34, 1.37, 1.41 (3s, 72 H, *t*Bu), 3.28 (s, 12 H, NMe_2), 3.66 (br. s, 48 H, NMe_2), 4.29 (s, 12 H, NMe_2) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN): $(AB_2C)_2$-type spectrum: δ(A) = 34.0 (P4, P4a), δ(B) = 42.2 (P1, P1a, P3, P3a), δ(C) = 20.3 (P2, P2a) ppm; $^2J_{AB} = {}^2J_{A'B'} = 221.6$, $^2J_{BC} = {}^2J_{B'C'} = 197.4$, $^3J_{BC'} = {}^3J_{B'C} = -3.6$, $^3J_{CC'} = -94.5$ Hz. MS-ESI: m/z = 836.0 $[Au_8(AuCl)_2(tBuP)_2\{tBuP=C(NMe_2)_2\}_6]^{4+}$. The salt is solvated with varying amounts of dichloromethane. Samples isolated from acetonitrile crystallize with three molecules of CH_3CN as shown by ^1H NMR spectroscopy. $C_{62}H_{144}Au_{10}Cl_6N_{12}P_8\cdot 3CH_3CN$ (3611.26): calcd. C 22.62, H 4.27, N 5.82; found C 22.78, H 4.54, N. 5.81.

X-ray Structural Analysis of $7\cdot 14CH_2Cl_2$: Yellow single crystals of $7\cdot 14CH_2Cl_2$ were grown from a CH_2Cl_2/*n*-hexane solution at +4 °C over 2 weeks; 0.29 × 0.28 × 0.20 mm³, T = 100 K, Nonius Kappa CCD, Mo-K_α (graphite monochromator, λ = 0.71073 Å), empirical formula $[C_{62}H_{144}Au_{10}Cl_2N_{12}P_8]Cl_4\cdot 14CH_2Cl_2$, monoclinic space group $P2_1/n$; unit cell dimensions a = 13.1890(1) Å, b = 16.627(2) Å, c = 33.4040(3) Å, β = 95.2320(5)°; V = 7294.76(12) Å³, d_{calcd} = 2.129 g/cm^{-3}, Z = 2; μ = 10.762 mm^{-1}; range for data collection: 2.9 < θ < 25.0°; index ranges: $-15 \leq h \leq 15$, $-18 \leq k \leq 19$, $-39 \leq l \leq 39$; reflections collected 88813; unique reflections 12561 (R_{int} = 0.098); parameters 661; absorption correction: multi-scan min/max transmission 0.2221/0.1464; Program used: SHELXL-97; structure refinement: full-matrix least-squares on F^2, wR_{F^2} = 0.1405 (all data), R_F = 0.059, wR_F = 0.1314 based on 9916 unique reflections with $I > 2\sigma(I)$. GOOF(F^2) = 1.098; maximum residual electron density 4.099 e·Å^{-3}, 1.01 Å nearby Au(3). Disorder of Cl(4) on two positions (48:52), disorder of Cl(11) on two positions (65:35). CCDC-183582 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2/1EZ, UK; Fax: (internat.)+44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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