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Cluster synthesis by photolysis of R_3PAuN_3. Crystal structure of $[(Ph_3PAu)_7Mo(CO)_3]OH$ and $[(Ph_3PAu)_6AuCo_2(CO)_6]NO_3$

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Abstract

Photolysis of R_3PAuN_3 (**1**) results in a reductive elimination of the azide group yielding R_3PAu^0 moieties which then combine to form Au clusters. In the presence of metal carbonyls heterometallic clusters are obtained. In the case of $Mo(CO)_6$ the cationic cluster $[(Ph_3PAu)_7Mo(CO)_3]^+$ (**2**) is formed. It crystallizes as $\mathbf{2} \cdot OH^-$ in the monoclinic space group $P2_1/n$ with *a* 1446.0(4), *b* 3016.6(5), *c* 3007.3(8) pm, β 91.63(2)°, $Z = 4$. In **2** seven Au atoms form an icosahedral fragment $(Ph_3PAu)_7{}^+$ which acts as a six electron donor for the $Mo(CO)_3$ group. The Mo–Au bond lengths are in the range 277.1 to 286.0 pm. The Au–Au distances lie between 283.8 and 303.1 pm. $\nu(CO)$ are observed at 1835 and 1895 cm^{-1}. Photolysis of **1** with $Co_2(CO)_8$ results in the formation of $[(Ph_3PAu)_6AuCo_2(CO)_6]^+$ (**3**). It crystallizes as $\mathbf{3} \cdot NO_3{}^- \cdot 2$ EtOH in the monoclinic space group $C2/c$ with *a* 3402.3(8), *b* 1568.3(6), *c* 2436.1(8) pm, β 117.62(3)°, $Z = 4$. **3** has the symmetry C_2. It consists of two Au_4Co trigonal bipyramids sharing one axial Au atom. The $Co(CO)_3$ groups are at a basal position of each trigonal bipyramid having four Au neighbours at 257.8 to 265.5 pm. The Au–Au distances are 278.2 to 291.9 pm. The CO vibrations lie at 1920 and 1970 cm^{-1}. Whereas $Mo(CO)_6$ does not react with **1** in the dark, $Co_2(CO)_8$ and **1** yield $Ph_3PAuCo(CO)_4$ (**4**) which upon irradiation with an excess of **1** forms $\mathbf{3} \cdot NCO^-$.

Introduction

Transition metal azido complexes usually decompose upon controlled thermolysis by cleavage of the N_α–N_β bond forming nitrido or nitrene complexes [1,2]. Reaction with phosphanes PR_3 yields phosphorane iminato complexes $L_nM{=}N{=}PR_3$ again by cleavage of the N_α–N_β bond of the azide group [3]. Nitrene complexes $L_nM{\equiv}NR$ are also obtained by the reaction of organic azides RN_3 with metal complexes [4,5]. With regard to these findings we have now investigated the behaviour of R_3PAuN_3.

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The controlled thermolysis however only yields gold metal. Reaction with phosphanes leads to the coordination at the Au atom leaving the azide group unchanged [6]. With metal chlorides Ph_3PAuN_3 undergoes a substitution reaction yielding metal azide chlorides and Ph_3PAuCl, rather than forming complexes $Cl_nM{\equiv}N{-}AuPPh_3$ with a nitrido bridge, as might be expected from consideration of the RN_3 reaction [4,5]. However, by irradiation of Ph_3PAuN_3 a reductive elimination of the complete azide group is observed yielding Ph_3PAu^0 moieties, which then combine to form Au clusters. By photolysis in the presence of transition metal carbonyls heterometallic clusters are obtained. We report here the synthesis and structure of $[(Ph_3PAu)_7Mo(CO)_3]^+$ and $[(Ph_3PAu)_6AuCo_2(CO)_6]^+$. The former has been briefly discussed in a preliminary communication [7].

Experimental

Synthesis of Ph_3PAuN_3 (1)

1 precipitates as a white crystalline solid when a stoichiometric amount of NaN_3 dissolved in methanol is added to a solution of Ph_3PAuNO_3 [8] in methanol/acetonitrile. The yield is almost quantitative. (Anal. Found: C, 43.47; H, 3.05; N, 8.32. $C_{18}H_{15}N_3PAu$ calcd.: C, 43.13; H, 3.02; N, 8.38%).

Synthesis of $Ph_3PAuCo(CO)_4$ (4)

Dissolution of 2.01 g (4 mmol) of **1** and 1.03 g (3 mmol) of $Co_2(CO)_8$ in 70 ml tetrahydrofuran resulted in vigorous effervescence and a brownish suspension, which was then stirred for 30 min at room temperature. After evaporation to dryness the product was extracted with diethyl ether, again evaporated, and recrystallized from methanol. 2.14 g (85% yield). (Anal. Found: C, 42.03; H, 2.39. $C_{22}H_{15}O_4PAuCo$ calcd.: C, 41.93; H, 2.40%).

Synthesis of $[(Ph_3PAu)_6AuCo_2(CO)_6]^+$ (3)

790 mg (1.25 mmol) of **4** dissolved in 70 ml tetrahydrofuran was irradiated (Heraeus Original Hanau TQ 150 high pressure mercury vapor immersion lamp) for 2 h, yielding a dark, brownish red solution. After addition of 630 mg (1.26 mmol) of **1** to this solution irradiation was continued for a further 60 min. The solution was then evaporated to dryness and again dissolved in dichloromethane for separation on an Al_2O_3 column. Elution with dichloromethane afforded a brownish band (180 mg, ν(CO) 2050(m), 1990(s), 1940(sh), 1910(br,vs), 1875(sh) cm^{-1}). Further elution with dichloromethane/ethanol (3/1) afforded an orange band, from which $\mathbf{3} \cdot NCO^-$ (ν(NCO) 2190 cm^{-1}) was obtained in 30% yield. A brown orange material was retained at the top of the column. The counterion of **3** can easily be exchanged by reaction with KPF_6 or $LiNO_3$ in THF. Suitable crystals for the structure determination have been obtained with $\mathbf{3} \cdot NO_3^-$ from CH_2Cl_2/EtOH. (Anal. Found: C, 41.32; H, 2.91; N, 0.54. $C_{114}H_{90}P_6O_6Au_7Co_2 \cdot NO_3$ calcd.: C, 41.49; H, 2.75; N, 0.42%); IR: $\nu_{as}(NO_3)$ 1390 cm^{-1}; ν(CO) 1920, 1970 cm^{-1}).

Crystal structure determination of $3 \cdot NO_3^- \cdot 2EtOH$

The crystals of $\mathbf{3} \cdot NO_3^- \cdot 2$ EtOH visibly undergo degradation when removed from the mother liquor. As a consequence, samples for the X-ray work were sealed in capillaries containing a minimal amount of mother liquor. One crystal with the dimensions 0.3 × 0.2 × 0.5 mm was chosen for all diffraction experiments. The

Table 1

Lattice constants and parameter of the structure determination of **2**·OH^- and **3**·NO_3^-·2EtOH.

		2·OH^-	**3**·NO_3^-·2EtOH
formula		$C_{129}H_{106}Au_7MoO_4P_7$	$C_{118}H_{102}Au_7Co_2NO_{11}P_6$
formula weight		3411.79	3392.59
lattice constants	a	1446.0(4) pm	3402.3(8) pm
	b	3016.6(5) pm	1568.3(6) pm
	c	3007.3(8)	2436.1(8) pm
	β	91.63(2)°	117.62(3)°
volume [pm^3]	V	13112.1×10^6	11516.9×10^6
formula units	Z	4	4
crystal system		monoclinic	monoclinic
space group		$P2_1/n$	$C2/c$
density [$g\ cm^{-3}$]	ρ_x	1.813	1.956
radiation		Cu-K_α	Mo-K_α
absorption coefficient [cm^{-1}]	μ	169.48	92.83
temperature of data collection		18°C	18°C
scan type		ω-scan	ω/θ-scan
scan range	ν	5–55°	3–30°
crystal dimension [mm]		$0.6 \times 0.1 \times 0.25$	$0.3 \times 0.2 \times 0.5$
No. of reflections measured		12992	14395
No. of independent observed reflections with $I > 3\sigma(I)$		7772	4736
No. of parameters		669	367
R-values	R	0.047	0.051
	R_ω	0.052	0.056

crystal symmetry and the approximate lattice constants were determined with Buerger precession photographs. The latter were refined on the automated single crystal diffractometer [9] using 25 reflections of high θ values. The intensity of 14395 reflections was measured in the range of $3 \leq \theta \leq 30°$ with Mo-K_α radiation and ω/θ-scans. After an empirical absorption correction [10] and merging, 4736 intensity values with $I > 3\sigma(I)$ were obtained. The position of the Au atoms was derived from direct methods [11]. Subsequent Fourier synthesis then gave the position of all atoms of **3** and of the slightly disordered solvent molecules. The R value at this point was 0.065. The introduction of anisotropic temperature factors for the Au, Co and P atoms improved R to 0.052. A difference Fourier synthesis then showed the NO_3^- group, which was disordered over two equivalent positions. As the position of the NO_3^- groups could not be refined satisfactorily, the relevant atoms have been used only in the structure factor calculation with fixed coordinates. The final R value was 0.051 with the H atoms not being taken into account. The lattice constants and parameters of the structure determination are given in Table 1. Atomic coordinates and equivalent isotropic temperature parameters are in Table 3 *.

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* Further details of the structure determination have been deposited as Supplementary Publication no. CSD 53435. Copies may be obtained through the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen.

Table 2

Atomic coordinates and isotropic equivalent thermal parameters B_{eq} ($\mathrm{pm}^2 \times 10^4$) for **2**$\cdot\mathrm{OH}^-$ with esd's in parentheses. ($B_{\mathrm{eq}} = 4/3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta)$)

Atom	x	y	z	B_{eq}
Au1	0.61069(5)	0.29969(3)	0.19625(3)	2.88(2)
Au2	0.56580(6)	0.29444(3)	0.28800(3)	3.30(2)
Au3	0.60426(6)	0.38026(3)	0.24694(3)	3.63(2)
Au4	0.52964(6)	0.37720(3)	0.15739(3)	3.76(2)
Au5	0.44878(6)	0.29034(3)	0.13887(3)	3.56(2)
Au6	0.46087(6)	0.23910(3)	0.21924(3)	3.51(2)
Au7	0.37317(6)	0.27867(3)	0.29451(3)	4.02(2)
Mo	0.4421(1)	0.33086(5)	0.22469(5)	2.93(4)
P1	0.7498(3)	0.2674(2)	0.1776(2)	3.2(1)
P2	0.6551(4)	0.2826(2)	0.3524(2)	3.8(1)
P3	0.6661(4)	0.4454(2)	0.2773(2)	4.4(1)
P4	0.5560(4)	0.4303(2)	0.1045(2)	4.4(1)
P5	0.3930(4)	0.2670(2)	0.0688(2)	4.1(1)
P6	0.4213(4)	0.1657(2)	0.2058(2)	4.5(2)
P7	0.2722(4)	0.2559(2)	0.3470(2)	4.4(1)
O1	0.236(1)	0.3003(6)	0.2065(6)	6.3(4)
O2	0.406(1)	0.3911(6)	0.3078(6)	5.7(4)
O3	0.334(1)	0.4127(7)	0.1857(7)	8.2(5)
O4	0.566(2)	0.066(1)	0.484(1)	11.6(7)
C1	0.314(2)	0.3095(9)	0.2159(9)	5.5(6)
C2	0.421(1)	0.3670(7)	0.2770(7)	3.5(4)
C3	0.384(2)	0.3830(9)	0.1987(9)	5.9(6)
C111	0.767(1)	0.2129(7)	0.2017(7)	3.9(4)
C112	0.822(2)	0.1805(9)	0.1793(9)	5.9(6)
C113	0.835(2)	0.140(1)	0.202(1)	6.5(6)
C114	0.795(2)	0.1313(9)	0.2419(9)	5.5(6)
C115	0.742(2)	0.162(1)	0.263(1)	6.7(6)
C116	0.728(1)	0.2031(8)	0.2414(8)	4.9(5)
C121	0.857(1)	0.2969(7)	0.1929(7)	3.8(4)
C122	0.860(2)	0.3403(9)	0.1808(9)	5.4(5)
C123	0.946(2)	0.3639(9)	0.1897(9)	6.1(6)
C124	1.026(2)	0.340(1)	0.206(1)	6.8(7)
C125	1.018(2)	0.2966(9)	0.2170(8)	5.4(5)
C126	0.934(1)	0.2732(8)	0.2132(8)	4.9(5)
C131	0.765(1)	0.2601(7)	0.1182(7)	3.5(4)
C132	0.857(1)	0.2571(8)	0.0996(8)	4.9(5)
C133	0.868(2)	0.2495(9)	0.055(1)	6.3(6)
C134	0.787(2)	0.2430(9)	0.0269(9)	6.2(6)
C135	0.700(2)	0.2473(9)	0.0454(9)	5.9(6)
C136	0.689(1)	0.2536(8)	0.0897(9)	5.2(5)
C211	0.764(1)	0.3118(7)	0.3533(7)	4.0(5)
C212	0.806(2)	0.3227(9)	0.3144(9)	5.7(6)
C213	0.891(2)	0.345(1)	0.314(1)	7.0(7)
C214	0.939(2)	0.351(1)	0.354(1)	6.9(7)
C215	0.900(2)	0.342(1)	0.392(1)	7.4(7)
C216	0.809(2)	0.3230(9)	0.3934(9)	5.7(6)
C221	0.595(1)	0.3016(8)	0.4012(7)	4.3(5)
C222	0.526(1)	0.3343(8)	0.3953(8)	5.0(5)
C223	0.479(2)	0.351(1)	0.432(1)	7.9(7)
C224	0.502(2)	0.334(1)	0.473(1)	8.5(8)
C225	0.567(2)	0.2991(9)	0.4802(9)	6.1(6)
C226	0.615(2)	0.2851(9)	0.4436(9)	5.5(5)
C231	0.686(1)	0.2261(7)	0.3661(7)	4.1(5)

Table 2 (continued)

Atom	x	y	z	B_{eq}
C232	0.777(2)	0.213(1)	0.375(1)	7.0(7)
C233	0.799(2)	0.169(1)	0.389(1)	6.9(7)
C234	0.730(2)	0.1372(9)	0.3895(9)	6.2(6)
C235	0.635(2)	0.151(1)	0.381(1)	7.3(7)
C236	0.618(2)	0.196(1)	0.3688(9)	6.4(6)
C311	0.710(1)	0.4425(8)	0.3351(8)	5.2(5)
C312	0.645(2)	0.433(1)	0.365(1)	9.4(9)
C313	0.672(2)	0.430(1)	0.413(1)	11(1)
C314	0.761(2)	0.442(1)	0.422(1)	8.8(8)
C315	0.825(2)	0.454(1)	0.393(1)	8.0(8)
C316	0.802(2)	0.454(1)	0.347(1)	6.8(7)
C321	0.755(2)	0.4734(9)	0.2450(9)	5.5(5)
C322	0.782(2)	0.452(1)	0.208(1)	7.5(7)
C323	0.848(2)	0.474(1)	0.179(1)	9.2(9)
C324	0.884(2)	0.513(1)	0.191(1)	8.7(8)
C325	0.855(2)	0.535(1)	0.229(1)	7.2(7)
C326	0.785(2)	0.5164(9)	0.2565(9)	5.7(6)
C331	0.572(1)	0.4851(7)	0.2777(7)	4.1(5)
C332	0.574(2)	0.518(1)	0.311(1)	6.4(6)
C333	0.495(2)	0.549(1)	0.312(1)	6.7(6)
C334	0.427(2)	0.546(1)	0.281(1)	8.4(8)
C335	0.428(2)	0.515(1)	0.247(1)	8.2(8)
C336	0.502(2)	0.483(1)	0.246(1)	7.0(7)
C411	0.546(1)	0.4891(8)	0.1230(8)	5.1(5)
C412	0.461(2)	0.510(1)	0.117(1)	7.5(7)
C413	0.446(2)	0.553(1)	0.134(1)	8.9(8)
C414	0.517(2)	0.574(1)	0.151(1)	8.0(8)
C415	0.602(2)	0.556(1)	0.156(1)	8.4(8)
C416	0.616(2)	0.511(1)	0.143(1)	7.5(7)
C421	0.468(2)	0.4268(9)	0.0567(9)	5.8(6)
C422	0.385(2)	0.411(1)	0.069(1)	6.5(6)
C423	0.312(2)	0.411(1)	0.032(1)	9.4(9)
C424	0.341(2)	0.424(1)	−0.009(1)	9.0(9)
C425	0.426(2)	0.437(1)	−0.018(1)	8.1(8)
C426	0.499(2)	0.441(1)	0.015(1)	8.2(8)
C431	0.669(1)	0.4271(8)	0.0825(8)	5.1(5)
C432	0.712(2)	0.463(1)	0.060(1)	7.9(8)
C433	0.804(2)	0.455(1)	0.042(1)	11(1)
C434	0.848(2)	0.418(1)	0.048(1)	8.6(8)
C435	0.801(2)	0.381(1)	0.066(1)	8.8(8)
C436	0.714(2)	0.3876(9)	0.0844(9)	6.2(6)
C511	0.457(1)	0.2854(8)	0.0212(7)	4.2(5)
C512	0.442(1)	0.2661(8)	−0.0201(8)	4.5(5)
C513	0.494(2)	0.2840(9)	−0.0567(9)	6.1(6)
C514	0.553(2)	0.320(1)	−0.050(1)	7.0(7)
C515	0.567(2)	0.337(1)	−0.009(1)	6.7(7)
C516	0.516(2)	0.3217(8)	0.0278(8)	5.2(5)
C521	0.276(1)	0.2877(8)	0.0607(7)	4.2(5)
C522	0.242(1)	0.3048(8)	0.0203(8)	4.9(5)
C523	0.150(2)	0.322(1)	0.015(1)	7.1(7)
C524	0.097(2)	0.318(1)	0.049(1)	7.9(8)
C525	0.123(2)	0.304(1)	0.092(1)	9.2(9)
C526	0.218(2)	0.286(1)	0.097(1)	8.1(8)
C531	0.384(2)	0.2092(9)	0.0547(9)	5.6(6)
C532	0.299(2)	0.189(1)	0.036(1)	6.8(7)

Table 2 (continued)

Atom	x	y	z	B_{eq}
C533	0.306(2)	0.145(1)	0.020(1)	8.9(9)
C534	0.384(2)	0.121(1)	0.023(1)	8.8(8)
C535	0.463(2)	0.140(1)	0.042(1)	7.6(7)
C536	0.463(2)	0.1831(9)	0.0594(9)	5.5(6)
C611	0.506(1)	0.1314(8)	0.1773(8)	5.0(5)
C612	0.571(2)	0.1532(9)	0.1550(9)	5.7(6)
C613	0.639(2)	0.130(1)	0.132(1)	6.6(6)
C614	0.637(2)	0.084(1)	0.132(1)	6.9(7)
C615	0.567(2)	0.061(1)	0.154(1)	7.6(7)
C616	0.497(2)	0.088(1)	0.177(1)	7.8(7)
C621	0.311(1)	0.1628(8)	0.1726(8)	4.7(5)
C622	0.297(2)	0.132(1)	0.141(1)	6.4(6)
C623	0.201(2)	0.129(1)	0.121(1)	8.7(8)
C624	0.136(2)	0.157(1)	0.133(1)	8.3(8)
C625	0.151(2)	0.188(1)	0.164(1)	10(1)
C626	0.245(2)	0.192(1)	0.182(1)	8.9(8)
C631	0.396(1)	0.1331(7)	0.2537(7)	3.8(4)
C632	0.439(2)	0.141(1)	0.293(1)	6.6(6)
C633	0.418(2)	0.118(1)	0.332(1)	9.4(9)
C634	0.361(2)	0.082(1)	0.330(1)	9.5(9)
C635	0.308(2)	0.076(1)	0.292(1)	8.6(8)
C636	0.323(2)	0.101(1)	0.252(1)	8.1(8)
C711	0.171(2)	0.2295(9)	0.3249(9)	5.6(6)
C712	0.180(2)	0.192(1)	0.301(1)	7.5(7)
C713	0.105(2)	0.166(1)	0.279(1)	11(1)
C714	0.018(2)	0.187(1)	0.287(1)	6.8(7)
C715	0.007(2)	0.222(1)	0.309(1)	7.3(7)
C716	0.082(2)	0.2473(9)	0.3316(9)	5.7(6)
C721	0.228(1)	0.3013(7)	0.3809(7)	4.0(4)
C722	0.238(2)	0.344(1)	0.365(1)	7.8(7)
C723	0.202(2)	0.381(1)	0.390(1)	8.4(8)
C724	0.155(2)	0.370(1)	0.429(1)	7.8(7)
C725	0.148(2)	0.329(1)	0.444(1)	7.7(7)
C726	0.184(2)	0.2916(9)	0.4193(9)	6.1(6)
C731	0.315(1)	0.2176(8)	0.3891(8)	4.6(5)
C732	0.395(2)	0.228(1)	0.412(1)	6.6(6)
C733	0.437(2)	0.199(1)	0.445(1)	7.3(7)
C734	0.390(2)	0.160(1)	0.455(1)	7.6(7)
C735	0.310(2)	0.148(1)	0.431(1)	10(1)
C736	0.273(2)	0.177(1)	0.398(1)	7.5(7)

Synthesis and crystal structure determination of 2 · OH^-

The synthesis and crystal structure determination of **2** · OH^- has been previously described [7]. Lattice constants and parameters of the structure determination are given in Table 1. Atomic coordinates and equivalent isotropic temperature parameters are in Table 2.

Results and discussion

Synthesis and properties of $[(Ph_3PAu)_7Mo(CO)_3]^+$ *(2) and* $[(Ph_3PAu)_6AuCo_2(CO)_6]^+$ *(3)*

On irradiation of Ph_3PAuN_3 (**1**) with UV-light in THF the azide group is reductively eliminated with formation of Ph_3PAu radicals, which subsequently unite to form homonuclear gold clusters. In the presence of excess transition metal carbonyls heteronuclear metal clusters are obtained (eq. 1 and 2).

$$7Ph_3PAuN_3 + Mo(CO)_6 \rightarrow [(Ph_3PAu)_7Mo(CO)_3]^+ NCO^- + 2CO + 10N_2 \qquad (1)$$

$$7Ph_3PAuN_3 + Co_2(CO)_8 \rightarrow [(Ph_3PAu)_6AuCo_2(CO)_6]^+ NCO^- + CO + 10N_2 + PPh_3 \qquad (2)$$

An excess of the carbonyl is necessary as otherwise mainly pure gold clusters are formed. The cationic heterometal clusters $[(Ph_3PAu)_7Mo(CO)_3]^+$ (**2**) and $[(Ph_3PAu)_6AuCo_2(CO)_6]^+$ (**3**) are obtained only in small yield. A separation from the by-products by column chromatography must therefore be performed. After that procedure **2** $\cdot OH^-$ and **3** $\cdot NCO^-$ crystallize from the CH_2Cl_2 solution in the form of air stable, red crystals. The IR spectrum of the Au_7Mo cluster proves that the initially formed isocyanate ion is now substituted by an OH^- ion. $Co_2(CO)_8$ also reacts with **1** in the dark to yield almost quantitatively the previously known $Ph_3PAuCo(CO)_4$ [12]:

$$4Ph_3PAuN_3 + 3Co_2(CO)_8 \rightarrow 4Ph_3PAuCo(CO)_4 + 2Co(N_3)_2 + 8CO \qquad (3)$$

Irradiation of $Ph_3PAuCo(CO)_4$ dissolved in THF produces a reactive, brownish solution that forms **3** after addition of **1**. $Mo(CO)_6$ in contrast does not react with **1** in the dark. On heating mainly gold metal and decomposition products of the carbonyl are obtained. In agreement with the local C_{3v} symmetry of the $M(CO)_3$ groups in **2** and **3**, two CO stretching vibrations are observed in each case. The low frequencies of 1835 and 1895 cm^{-1} for **2** point to a pronounced donor behaviour of the $(Ph_3PAu)_7$ residue, while for **3** higher values of 1920 and 1970 cm^{-1} are found.

Crystal structures

The structures of the cationic heterometal clusters $[(Ph_3PAu)_7Mo(CO)_3]^+$ (**2**) and $[(Ph_3PAu)_6AuCo_2(CO)_6]^+$ (**3**) are shown in Fig. 1 and 2. Important bond distances and bond angles are given in Tables 4 and 5.

In the structure of **2** the $(Ph_3PAu)_7{}^+$ moiety forms an icosahedral fragment which coordinates a $Mo(CO)_3$ group with similar Mo–Au distances of 277.1 to 286.0 pm (Table 4) to all seven Au atoms. **2** can be regarded as a half sandwich complex of Mo^0 in which the arene ligand is replaced by the $(Ph_3PAu)_7{}^+$ icosahedral fragment acting as a six electron donor. With these six electrons the Mo atom achieves a stable 18-electron configuration. In an alternative view the Au_7Mo cluster can be described as a monocapped pentagonal bipyramid with Au7 as the cap and the Mo atom in an axial position. Since according to a general principle [13] a capping atom does not change the number of skeletal electrons there remain six electrons for the Au_7Mo pentagonal bipyramid. The same number is calculated for the homonuclear Au_7 cluster $(Ph_3PAu)_7{}^+$ [14] which also has pentagonal bipyramidal geometry.

Table 3

Atomic coordinates and isotropic equivalent thermal parameters B_{eq} ($pm^2 \times 10^4$) for **3**$\cdot NO_3^- \cdot 2EtOH$ with esd's in parentheses ($B_{eq} = 4/3(B_{11}s^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)$)

Atom	x	y	z	B_{eq}
Au1	0.14853(2)	0.32584(7)	0.32724(4)	3.38(2)
Au2	0.06946(3)	0.23635(6)	0.25377(4)	2.93(2)
Au3	0.07197(3)	0.42227(6)	0.25082(4)	2.97(2)
Au4	0.000	0.33410(9)	0.250	2.57(2)
Co1	0.08039(7)	0.3345(2)	0.3466(1)	2.63(6)
P1	0.2201(2)	0.3258(5)	0.3441(2)	3.1(1)
P2	0.0717(2)	0.1165(4)	0.2008(3)	3.2(1)
P3	0.0778(2)	0.5337(4)	0.1947(3)	3.6(1)
O1	0.0131(5)	0.310(2)	0.3868(6)	6.9(6)
O2	0.1341(7)	0.200(1)	0.4303(8)	7.5(6)
O3	0.1202(6)	0.494(1)	0.4084(8)	6.2(5)
C1	0.0353(6)	0.324(2)	0.3635(9)	4.2(5)
C2	0.1126(8)	0.250(2)	0.392(1)	5.5(7)
C3	0.1044(8)	0.433(2)	0.382(1)	5.3(7)
C111	0.2274(7)	0.347(2)	0.275(1)	4.4(5)
C112	0.1959(7)	0.328(2)	0.221(1)	4.7(5)
C113	0.2026(9)	0.346(2)	0.167(1)	6.9(8)
C114	0.2382(9)	0.383(2)	0.171(1)	6.1(7)
C115	0.274(1)	0.400(2)	0.230(1)	7.4(8)
C116	0.2676(8)	0.382(2)	0.284(1)	5.1(6)
C121	0.2508(6)	0.409(1)	0.3993(8)	2.6(4)
C122	0.2935(7)	0.396(2)	0.446(1)	4.0(5)
C123	0.3142(8)	0.466(2)	0.488(1)	4.8(6)
C124	0.2943(9)	0.539(2)	0.484(1)	5.7(7)
C125	0.2514(8)	0.551(2)	0.439(1)	5.1(6)
C126	0.2287(8)	0.485(2)	0.395(1)	5.3(6)
C131	0.2493(7)	0.230(2)	0.380(1)	4.1(5)
C132	0.2450(7)	0.199(2)	0.430(1)	4.0(5)
C133	0.2671(8)	0.126(2)	0.460(1)	4.9(6)
C134	0.298(1)	0.087(2)	0.446(1)	7.0(8)
C135	0.301(1)	0.115(2)	0.393(1)	7.8(9)
C136	0.2784(9)	0.194(2)	0.362(1)	6.6(8)
C211	0.1028(7)	0.034(2)	0.257(1)	4.1(5)
C212	0.0861(9)	−0.050(2)	0.251(1)	6.2(7)
C213	0.1119(9)	−0.111(2)	0.298(1)	6.4(7)
C214	0.1526(8)	−0.086(2)	0.346(1)	5.5(6)
C215	0.1663(8)	−0.007(2)	0.350(1)	5.0(6)
C216	0.1420(7)	0.057(2)	0.308(1)	4.4(5)
C221	0.1004(7)	0.131(2)	0.154(1)	4.0(5)
C222	0.1338(8)	0.078(2)	0.158(1)	5.5(6)
C223	0.155(1)	0.090(2)	0.119(1)	7.5(9)
C224	0.1381(9)	0.153(2)	0.075(1)	6.9(8)
C225	0.103(1)	0.203(2)	0.067(1)	8.1(9)
C226	0.0826(9)	0.195(2)	0.107(1)	6.6(8)
C231	0.0182(7)	0.069(2)	0.1473(9)	3.6(5)
C232	0.0159(7)	0.013(2)	0.099(1)	4.6(5)
C233	−0.0245(8)	−0.029(2)	0.065(1)	5.2(6)
C234	−0.0608(9)	−0.021(2)	0.077(1)	5.8(7)
C235	−0.0578(7)	0.034(2)	0.125(1)	4.4(5)
C236	−0.0165(8)	0.077(2)	0.162(1)	4.6(5)
C311	0.1322(8)	0.586(2)	0.237(1)	4.9(6)
C312	0.1665(8)	0.559(2)	0.225(1)	5.5(6)

Table 3 (continued)

Atom	x	y	z	B_{eq}
C313	0.210(1)	0.594(3)	0.261(2)	9(1)
C314	0.2142(9)	0.661(2)	0.293(1)	7.0(7)
C315	0.181(1)	0.686(2)	0.316(1)	7.8(9)
C316	0.1367(9)	0.645(2)	0.282(1)	6.8(8)
C321	0.0727(7)	0.510(2)	0.118(1)	4.2(5)
C322	0.081(1)	0.566(3)	0.083(2)	9(1)
C323	0.075(1)	0.545(3)	0.020(2)	9(1)
C324	0.062(1)	0.466(3)	0.002(2)	9(1)
C325	0.048(1)	0.407(3)	0.028(2)	12(1)
C326	0.057(1)	0.428(3)	0.092(2)	8(1)
C331	0.0345(8)	0.615(2)	0.176(1)	4.9(6)
C332	−0.0051(9)	0.592(2)	0.171(1)	5.6(7)
C333	−0.039(1)	0.652(3)	0.157(1)	8.1(9)
C334	−0.033(1)	0.736(3)	0.145(2)	9(1)
C335	0.006(1)	0.759(3)	0.147(2)	9(1)
C336	0.043(1)	0.700(2)	0.164(1)	8(1)
C4	0.404(1)	0.335(4)	0.434(2)	15(2)
C5	0.383(1)	0.345(3)	0.376(1)	10(1)
O4	0.449(2)	0.302(2)	0.486(1)	21(2)
N11	0.7160	0.2161	0.5176	10
O11	0.6690	0.1809	0.4930	10
O22	0.7749	0.2280	0.5379	10

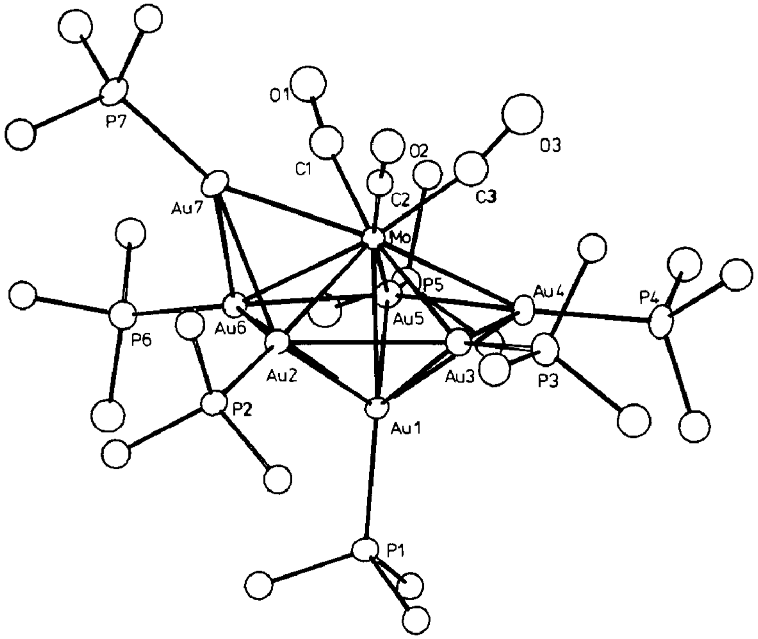

Fig. 1. Structure of the cationic cluster **2** with the atom numbering scheme. From the phenyl groups of the phosphane ligands only the head atoms are drawn.

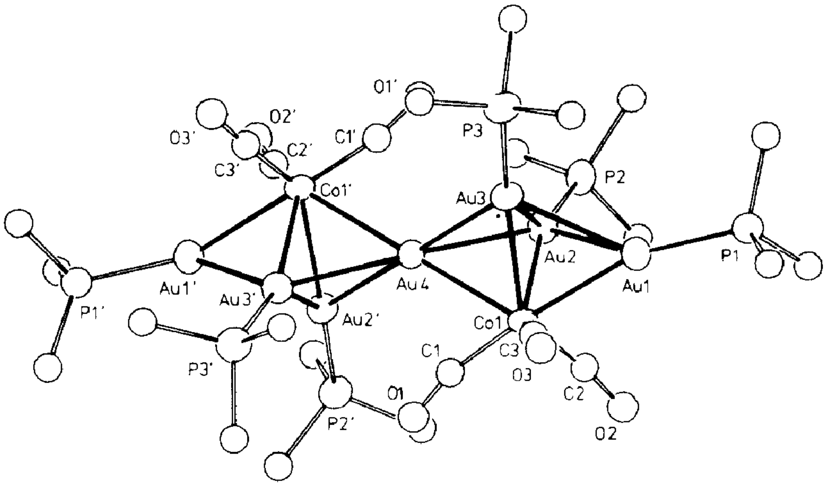

Fig. 2. Structure of the cationic cluster **3** with the atom numbering scheme. From the phenyl groups of the phosphane ligands only the head atoms are drawn.

The central unit of **3** consists of two Au_4Co trigonal bipyramids sharing one axial Au atom. The $Co(CO)_3$ units are at a basal position of each trigonal bipyramid having four Au neighbours at distances ranging from 257.8 to 265.5 pm (Table 5). As the central atom Au(4) occupies a twofold axis the entire cluster has the point symmetry C_2. The $[(Ph_3PAu)_6Au]^+$ unit itself has the form of two Au_4 butterflies

Table 4

Selected bond lengths (pm) and angles (deg) for **2**·OH^-

Bond lengths			
Au1–Au2	285.69(1)	Mo–Au1	277.11(1)
Au1–Au3	287.20(2)	Mo–Au2	279.98(1)
Au1–Au4	285.11(1)	Mo–Au3	284.22(1)
Au1–Au5	288.23(1)	Mo–Au4	279.24(1)
Au1–Au6	293.19(1)	Mo–Au5	285.97(2)
Au2–Au3	292.82(2)	Mo–Au6	278.66(1)
Au2–Au6	303.09(2)	Mo–Au7	282.83(1)
Au2–Au7	283.80(1)	Mo–C1	197.4(2)
Au3–Au4	287.40(2)	Mo–C2	194.6(2)
Au4–Au5	291.64(2)	Mo–C3	193.8(2)
Au5–Au6	286.99(2)	C1–O1	119.1(2)
Au6–Au7	288.45(1)	C2–O2	120.1(2)
Au1–P1	231.77(5)	C3–O3	121.2(2)
Au2–P2	232.43(4)		
Au3–P3	233.50(4)		
Au4–P4	229.77(5)		
Au5–P5	234.21(4)		
Au6–P6	232.09(5)		
Au7–P7	228.65(4)		
Bond angles			
Mo–C1–O1	171.8(2)		
Mo–C2–O2	176.3(1)		
Mo–C3–O3	168.5(2)		

Table 5

Selected bond lengths (pm) and angles (deg.) in **3**·NO_3^-·2EtOH

Bond lengths			
Au1–Au2	281.89(3)	Co1–C1	177.1(5)
Au1–Au3	283.57(3)	Co1–C2	175.0(8)
Au2–Au3	291.90(3)	Co1–C3	177.5(7)
Au2–Au4	278.24(3)	C1–O1	115.7(9)
Au3–Au4	280.41(3)	C2–O2	118.2(9)
Au1–P1	227.3(1)	C3–O3	114.0(9)
Au2–P2	230.2(1)		
Au3–P3	228.4(1)		
Co1–Au1	257.57(6)		
Co1–Au2	261.63(7)		
Co1–Au3	260.91(6)		
Co1–Au4	265.57(6)		
Bond angles			
Au1–Co1–Au2	65.76(2)	Co1–C1–O1	164.7(5)
Au1–Co1–Au3	66.32(2)	Co1–C2–O2	168.9(6)
Au1–Co1–Au4	118.81(3)	Co1–C3–O3	176.1(6)
Au2–Co1–Au3	67.92(1)		
Au2–Co1–Au4	63.71(1)		
Au3–Co1–Au4	64.36(1)		
Au2–Au1–Au3	62.156(7)		
Au1–Au2–Au3	59.205(9)		
Au1–Au2–Au4	107.01(2)		
Au3–Au2–Au4	58.863(9)		
Au1–Au3–Au2	58.639(9)		
Au1–Au3–Au4	105.96(1)		
Au2–Au3–Au4	58.14(1)		

with one common corner. Each Au_4 fragment coordinates one $Co(CO)_3$ group. The $[(Ph_3PAu)_6Au]^+$ unit holds six electrons and therefore can donate three electrons to each $Co(CO)_3$ group so that a sum of 18 electrons is attained for the Co atoms. Homonuclear gold clusters with seven to thirteen gold atoms are characterized by a central Au atom [15]. A remarkable feature is that the bonds between the peripheral Au atoms are always 10 to 20 pm longer than the distances to the central Au atom. In **2** the Au–Au distances range from 283.8 to 303.1 pm and in **3** from 278.2 to 291.9 pm as typical for distances between peripheral Au atoms in homonuclear gold clusters. The strongest bonds in **2** and **3** are, like in the homonuclear gold clusters or in bimetallic gold-transition metal clusters [16], between the central Mo or Co atom and the peripheral Au atoms as indicated by the short distances (Tables 4 and 5). The distances in the $M(CO)_3$ groups are in agreement with previous examples. A slight deviation from the ideal linear M–C–O arrangement is presumably due to steric reasons.

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