Cluster Synthesis by Photolysis of R_3PAuN_3. VI. Synthesis and Structure of $[(Ph_3PAu)_6V(CO)_4]^+$

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Photolysis of the $Ph_3PAuV(CO)_6/Ph_3PAuNCO/Ph_3PAuN_3$ system in a tetrahydrofuran solution, followed by chromatography on aluminia, gave $(Ph_3PAu)_3V(CO)_5$, $[(Ph_3PAu)_6V(CO)_4]NCO$ (**1**·NCO) and homometallic gold clusters in about equal proportions. Upon addition of KPF_6, the heterometallic cluster cation **1** crystallizes as $[(Ph_3PAu)_6V(CO)_4]_2(PF_6)[(OH)_x,F_y]\cdot 2EtOH$, $x+y = 1$, in the form of brownish-red prisms, space group $C2/c$ and $a = 2687.3(7)$, $b = 2725.4(9)$, $c = 3301(1)$ pm, $\beta = 92.47(8)°$, $Z = 4$. The central Au_6V cluster unit exhibits the structure of a bicapped trigonal bipyramid with the vanadium atom in an equatorial position. The V–Au distances are in the range 273–284 pm, while the Au–Au distances range from 275 to 296 pm. Compound **1** represents the first crystallographically established seven-membered system of the series of heterometallic gold–metal carbonyl cluster compounds of the general formula $[(Ph_3PAu)_xM(CO)_y]^{z+}$; as in the other clusters of the same series, the Au_6 species can be regarded as a fragment of an icosahedron. The frontier orbitals of $V(CO)_4$ and of the six Ph_3PAu units form two occupied bonding cluster molecular orbitals.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Some of us have recently shown[1-6] that photolysis of Ph_3PAuN_3 is a convenient method of generating the Ph_3PAu fragment, as an alternative to the treatment of mononuclear gold(I)–PR_3 complexes with BH_4^-,[7,8] B_2H_6,[9] $Ti(\eta\text{-}C_6H_5CH_3)_2$[10] or CO.[11] When the photolysis is carried out in the presence of metal carbonyl derivatives, heterometallic clusters may result with the general formula $[(Ph_3PAu)_xM(CO)_y]^{z+}$. Thus, several combinations with the one-electron donor $AuPPh_3$ may be anticipated, the composition of these metal clusters being determined by the electronic demand of the transition metal M with the electronic configuration d^n, which, being a system with a low oxidation state, requires a closed-shell configuration, i.e. $x + 2y + n - z = 18$. For vanadium, uncharged ($z = 0$) members of this series are represented by the complexes $Ph_3PAuV(CO)_6$[12] and $(Ph_3PAu)_3V(CO)_5$.[13]

In the 1+ charged terms of the series obtained earlier[1-6] by the photolytic method, the Au_xM skeleton forms a structure in which the transition metal M was found at bonding distances from all gold atoms. Each Au_x species consists of triangular faces of an icosahedron fragment. This arrangement produces the closest packing and allows the maximum interaction among the Au atoms. In earlier papers, examples of Au_4M, Au_5M and Au_7M clusters were reported. The Au_6M term was represented by $[(Ph_3PAu)_6Mn(CO)_3]PF_6$.[1,5] However, the crystals of this compound were not suitable for an X-ray investigation. We therefore reckoned that the stable isoelectronic vanadium compound $[(Ph_3PAu)_6V(CO)_4]^+$ should also exist, and that useful structural information could be obtained with this system. We report here the synthesis and the crystal structure of the $[(Ph_3PAu)_6V(CO)_4]^+$ cation.

Experimental

Ph_3PAuN_3 was synthesized from Ph_3PAuNO_3[14] and NaN_3 in MeOH/MeCN (2/1). $Ph_3PAuNCO$ was obtained from Ph_3PAuNO_3 and KOCN in MeOH/MeCN (2/1). $Ph_3PAuV(CO)_6$[15] was prepared from the reaction of $NaV(CO)_6$[16] with Ph_3PAuCl in THF at room temperature.

Synthesis of $(Ph_3PAu)_3V(CO)_5$ and $[(Ph_3PAu)_6V(CO)_4]^+$ (**1**). A mixture of 407 mg (0.6 mmol) $Ph_3PAuV(CO)_6$, 300 mg (0.6 mmol) $Ph_3PAuNCO$ and 200 mg (0.4 mmol) Ph_3PAuN_3 in 70 ml THF was kept under an atmosphere of N_2 and irradiated at room temperature for 15 min with a high-pressure mercury vapour immersion lamp. Then the brownish-red reaction mixture was evaporated to dryness, dissolved in CH_2Cl_2 and chromatographed on an Al_2O_3 column. Elution with CH_2Cl_2/EtOH (4/1) yielded a first fraction ($R_f \approx 0.8$) of an orange–red solution containing $(Ph_3PAu)_3V(CO)_5$[13] in about 30% yield. IR (CH_2Cl_2):

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Table 1. Crystal data and details of the data collection and structure refinement of $[(Ph_3PAu)_6V(CO)_4]_2(PF_6)[(OH)_x,F_y]\cdot 2EtOH$, $x+y = 1$.

Molecular formula		$C_{228}H_{192+x}Au_{12}F_{6+y}O_{10+x}P_{13}V_2$
Space group		*C2/c*
Temperature of data collection/°C		−70
Cell parameters at −70 °C	*a*/pm	2688.0(7)
	b/pm	2726.2(9)
	c/pm	3304.7(12)
	β/°	92.47(8)
Volume	*V*/nm³	24.1940
Formula units	*Z*	4
Density	ϱ_x/g cm^{-3}	1.672
Linear absorption coefficient	μ(Mo K_α)/cm^{-1}	74.419
Crystal size/mm³		0.4 × 0.2 × 0.15
Absorption correction, minimum, maximum factors		DIFABS,[18] 0.552–1.729
Instrument		CAD4
Scan type		ω
Θ range/°		4–24
Radiation		Mo K_α (λ = 71.073 pm)
No. of reflections measured		11992
No. of observed reflections with $I>3\sigma(I)$		4071
No. of variables refined		582
Weighting scheme	ω	$1/\sigma_F^2$
Agreement factors	*R*	0.090
	R_ω	0.109

ν(CO) 1955 (vs), 1880 (m), 1835 (vs) cm^{-1}, in satisfactory agreement with the reported[13] spectrum [CH_2Cl_2, ν(CO) 1954 (vs), 1879 (sh), 1825 (s) cm^{-1}]. Anal. Found: C 45.0; H 2.8. Calc. for $C_{59}H_{45}Au_3O_5P_3V$: C 45.2; H 2.9.

The second fraction ($R_f \approx 0.6$) contained the brownish-red $[(Ph_3PAu)_6V(CO)_4]NCO$ (**1**·NCO) in ca. 35% yield. IR (CH_2Cl_2): ν(NCO) 2205 (s); ν(CO) 1900 (s), 1840 (m), 1820 (s) cm^{-1}.

With CH_2Cl_2/EtOH (1/3) a third fraction was isolated which consisted of homoatomic gold clusters (ca. 30% yield).

To obtain single crystals, the anion in **1**·NCO was exchanged by adding KPF_6 in CH_2Cl_2/MeCN. After evaporating to a small volume, dissolving in CH_2Cl_2 and careful covering with a layer of diisopropyl ether, $[(Ph_3PAu)_6V(CO)_4]_2(PF_6)[(OH)_x,F_y]\cdot 2EtOH$, $y+y = 1$, crystallized as brownish-red prisms.

Crystal structure determination. Single-crystal X-ray investigations were carried out with an Enraf–Nonius CAD4 diffractometer using Mo K_α radiation and a single crystal with a composition of $\mathbf{1}\cdot(PF_6)_{0.5}(OH)_{0.5}\cdot EtOH$, or, alternatively, $\mathbf{1}\cdot(PF_6)_{0.5}F_{0.5}\cdot EtOH$, or any possible OH^-/F^- substitutive combination. The crystal data and experimental details of the structure determination are presented in Table 1. The lattice parameters were calculated by least-squares refinement on the basis of the accurate position of 25 reflections. Of the possible space groups, *C2/c* was established in the course of the structure solution.

As the quality of the crystals was low in consequence of a partial loss of solvent molecules, several crystals were tested prior to data collection. Finally one with the approximate dimensions 0.4 × 0.2 × 0.15 mm was used for the data collection in the range of Θ = 4–24°. It resulted in 11992 reflections of which only 4168 had an intensity $I>3\sigma(I)$. Merging reduced the number of reflections to 4071, which were used for the structure determination. The position of the six gold atoms could be derived with direct methods.[17] Subsequent difference Fourier syntheses then showed the $V(CO)_4$ group and the PPh_3 units as well as one half of a PF_6^- anion per cluster cation on a twofold axis.

After an empirical absorption correction with the program DIFABS[18] and refinement with anisotropic temperature parameters for the metal atoms, an additional difference Fourier synthesis revealed the position of an EtOH molecule in a general position. The additional anion required by the charge balance could, however, not be assigned with certainty, although weak electron densities were observed at the twofold axis at (0.0, 0.401, 0.25) and (0.0, 0.722, 0.25), which may originate from F^- or OH^- ions. We assigned them to OH^-, as the scattering powers of OH^- and F^- are about equal. They have been included in the refinement with an occupancy factor of 0.5, to match the formula $[(Ph_3PAu)_6V(CO)_4]_2(PF_6)(OH)\cdot 2EtOH$. Because of the insufficient number of observations, further refinement with anisotropic thermal parameters for the P, C and O atoms was not performed. The final *R*-value was 0.090. the atomic coordinates and the equivalent isotropic temperature parameters are given in Table 2.†

† Supplementary material can be obtained referring to the CSD file No. CSD55111, and by full citation of the present article at: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany.

Table 2. Atomic positional parameters and equivalent isotropic temperature factors, B_{eq}.[a]

Atom	*x*	*y*	*z*	B_{eq}	Atom	*x*	*y*	*z*	B_{eq}
Au1	0.2949(1)	0.5287(1)	0.49005(9)	3.11(7)	C233	0.311(4)	0.360(3)	0.393(3)	7(3)*
Au2	0.2260(1)	0.4567(1)	0.50430(9)	2.85(6)	C234	0.291(4)	0.313(3)	0.375(3)	7(3)*
Au3	0.2461(1)	0.5213(1)	0.56851(9)	3.36(7)	C235	0.252(4)	0.291(4)	0.401(3)	8(3)*
Au4	0.2269(1)	0.5092(1)	0.42687(9)	3.27(7)	C236	0.246(4)	0.306(4)	0.454(3)	8(3)*
Au5	0.2540(1)	0.6063(1)	0.4436(1)	3.53(7)	C311	0.229(2)	0.569(2)	0.659(2)	3(1)*
Au6	0.1489(1)	0.4906(1)	0.5514(1)	3.48(7)	C312	0.207(3)	0.606(3)	0.643(2)	5(2)*
V	0.1976(4)	0.5528(4)	0.4992(4)	3.1(3)	C313	0.177(3)	0.642(3)	0.652(2)	5(2)*
O1	0.247(1)	0.634(1)	0.540(1)	1.8(9)*	C314	0.167(4)	0.631(4)	0.699(4)	11(4)*
O2	0.113(2)	0.497(2)	0.454(1)	4(1)*	C315	0.191(4)	0.603(4)	0.719(3)	9(3)*
O3	0.126(1)	0.601(1)	0.556(1)	2.2(9)*	C316	0.232(3)	0.571(3)	0.706(3)	7(2)*
O4	0.137(2)	0.626(2)	0.442(2)	6(1)*	C321	0.323(3)	0.570(3)	0.637(3)	5(2)*
C1	0.232(2)	0.596(2)	0.535(2)	1(1)*	C322	0.358(2)	0.585(2)	0.605(2)	2(1)*
C2	0.146(2)	0.516(2)	0.470(2)	3(1)*	C323	0.401(3)	0.612(3)	0.613(3)	5(2)*
C3	0.153(2)	0.584(2)	0.534(2)	0(1)*	C324	0.419(3)	0.628(3)	0.648(3)	5(2)*
C4	0.167(2)	0.603(2)	0.456(2)	3(1)*	C325	0.391(3)	0.616(3)	0.680(3)	5(2)*
P1	0.3793(7)	0.5165(7)	0.4932(6)	2.6(4)*	C326	0.345(3)	0.589(3)	0.678(3)	6(2)*
P2	0.2376(7)	0.3740(7)	0.5022(7)	3.3(4)*	C331	0.279(3)	0.478(3)	0.661(2)	5(2)*
P3	0.2760(8)	0.5354(8)	0.6329(7)	4.3(5)*	C332	0.239(2)	0.449(2)	0.671(2)	3(2)*
P4	0.2138(7)	0.4855(8)	0.3608(6)	3.8(5)*	C333	0.246(3)	0.409(3)	0.695(3)	5(2)*
P5	0.2862(9)	0.6724(9)	0.4101(8)	4.9(6)*	C334	0.294(3)	0.398(3)	0.715(3)	6(2)*
P6	0.0845(7)	0.4563(7)	0.5849(6)	2.9(4)*	C335	0.325(3)	0.430(3)	0.708(2)	5(2)*
P7	0.500	0.468(2)	0.750	10(1)*	C336	0.323(3)	0.467(3)	0.684(3)	6(2)*
F1	0.515(3)	0.469(3)	0.703(2)	12(2)*	C411	0.272(3)	0.475(3)	0.332(2)	4(2)*
F2	0.442(4)	0.471(4)	0.733(3)	21(4)*	C412	0.279(2)	0.427(2)	0.312(2)	2(1)*
F3	0.500	0.529(6)	0.750	23(6)*	C413	0.321(2)	0.427(2)	0.291(2)	3(1)*
F4	0.500	0.415(5)	0.750	20(5)*	C414	0.351(3)	0.464(3)	0.289(2)	5(2)*
O10	0.039(3)	0.238(3)	0.347(2)	11(2)*	C415	0.342(3)	0.510(3)	0.305(2)	4(2)*
C11	−0.002(4)	0.248(4)	0.377(4)	9(3)*	C416	0.302(3)	0.517(3)	0.327(2)	5(2)*
C12	0.019(2)	0.275(2)	0.411(2)	2(1)*	C421	0.175(3)	0.430(3)	0.349(2)	4(2)*
O11	0.000	0.722(9)	0.250	14(8)*	C422	0.172(2)	0.394(2)	0.385(2)	2(1)*
O22	0.000	0.401(9)	0.250	13(7)*	C423	0.143(2)	0.353(2)	0.376(2)	2(1)*
C111	0.401(2)	0.498(2)	0.538(2)	0(1)*	C424	0.113(3)	0.348(3)	0.336(2)	5(2)*
C112	0.370(3)	0.466(3)	0.564(3)	6(2)*	C425	0.116(3)	0.382(3)	0.306(3)	6(2)*
C113	0.390(3)	0.443(2)	0.598(2)	3(2)*	C426	0.147(2)	0.424(2)	0.316(2)	3(2)*
C114	0.433(3)	0.464(3)	0.618(2)	4(2)*	C431	0.166(4)	0.533(4)	0.345(3)	8(3)*
C115	0.462(3)	0.500(3)	0.601(3)	6(2)*	C432	0.140(3)	0.552(3)	0.360(3)	6(2)*
C116	0.446(3)	0.516(3)	0.563(2)	4(2)*	C433	0.115(4)	0.586(4)	0.337(4)	10(3)*
C121	0.414(2)	0.571(2)	0.489(2)	3(2)*	C434	0.112(5)	0.600(5)	0.301(4)	11(4)*
C122	0.399(2)	0.617(2)	0.500(2)	3(2)*	C435	0.148(3)	0.590(3)	0.281(3)	6(2)*
C123	0.424(3)	0.660(3)	0.492(3)	7(2)*	C436	0.177(3)	0.546(3)	0.297(3)	5(2)*
C124	0.469(3)	0.661(3)	0.473(3)	5(2)*	C511	0.327(3)	0.659(3)	0.369(3)	5(2)*
C125	0.485(3)	0.616(3)	0.455(2)	5(2)*	C512	0.327(3)	0.680(3)	0.333(3)	6(2)*
C126	0.462(3)	0.568(3)	0.461(2)	4(2)*	C513	0.366(3)	0.665(3)	0.306(2)	4(2)*
C131	0.400(2)	0.474(2)	0.457(2)	3(1)*	C514	0.399(3)	0.632(3)	0.314(2)	4(2)*
C132	0.389(2)	0.482(2)	0.417(2)	3(1)*	C515	0.405(3)	0.613(3)	0.350(3)	6(2)*
C133	0.409(2)	0.452(2)	0.388(2)	2(1)*	C516	0.369(2)	0.620(2)	0.386(2)	3(2)*
C134	0.435(3)	0.410(3)	0.402(3)	6(2)*	C521	0.323(3)	0.716(2)	0.439(2)	3(2)*
C135	0.451(3)	0.399(3)	0.446(3)	6(2)*	C522	0.353(3)	0.744(3)	0.419(2)	4(2)*
C136	0.427(3)	0.437(2)	0.466(2)	3(2)*	C523	0.379(3)	0.778(3)	0.451(2)	4(2)*
C211	0.284(2)	0.348(2)	0.537(2)	2(1)*	C524	0.367(2)	0.784(2)	0.490(2)	1(1)*
C212	0.267(2)	0.362(2)	0.585(2)	3(1)*	C525	0.328(3)	0.752(3)	0.512(3)	5(2)*
C213	0.302(3)	0.337(3)	0.609(3)	7(2)*	C526	0.304(3)	0.719(3)	0.479(3)	6(2)*
C214	0.340(3)	0.306(3)	0.597(3)	5(2)*	C531	0.236(3)	0.712(3)	0.387(3)	7(2)*
C215	0.352(4)	0.295(4)	0.559(3)	8(3)*	C532	0.240(4)	0.761(4)	0.392(3)	8(2)*
C216	0.316(3)	0.315(3)	0.531(2)	4(2)*	C533	0.198(3)	0.787(3)	0.368(2)	4(2)*
C221	0.177(3)	0.340(3)	0.508(2)	4(2)*	C534	0.165(5)	0.759(5)	0.344(4)	13(4)*
C222	0.182(4)	0.295(4)	0.535(3)	8(3)*	C535	0.161(4)	0.706(4)	0.339(4)	10(3)*
C223	0.131(2)	0.270(2)	0.534(2)	1(1)*	C536	0.207(4)	0.684(4)	0.365(3)	8(3)*
C224	0.090(3)	0.286(3)	0.515(2)	4(2)*	C611	0.100(3)	0.408(3)	0.626(2)	4(2)*
C225	0.092(3)	0.333(3)	0.491(2)	4(2)*	C612	0.132(2)	0.372(2)	0.614(2)	2(1)*
C226	0.133(2)	0.357(2)	0.491(2)	1(1)*	C613	0.150(4)	0.334(3)	0.635(3)	7(3)*
C231	0.268(2)	0.351(2)	0.460(2)	0(1)*	C614	0.119(3)	0.332(3)	0.675(2)	5(2)*
C232	0.293(2)	0.383(2)	0.439(2)	2(1)*	C615	0.089(3)	0.372(3)	0.687(3)	6(2)*

cont.

Table 2. Cont.

Atom	x	y	z	B_{eq}
C616	0.076(3)	0.409(3)	0.662(2)	4(2)*
C621	0.037(4)	0.425(4)	0.555(3)	8(3)*
C622	0.032(3)	0.441(3)	0.518(2)	4(2)*
C623	0.000(3)	0.425(3)	0.492(2)	4(2)*
C624	−0.030(3)	0.376(3)	0.506(3)	5(2)*
C625	−0.023(3)	0.364(3)	0.541(3)	6(2)*
C626	0.009(3)	0.387(3)	0.566(2)	5(2)*
C631	0.049(2)	0.504(2)	0.610(2)	2(1)*
C632	−0.005(2)	0.503(2)	0.609(2)	3(2)*
C633	−0.028(3)	0.545(3)	0.629(3)	7(3)*
C634	−0.003(3)	0.582(3)	0.650(3)	6(2)*
C635	0.048(3)	0.579(3)	0.640(3)	6(2)*
C636	0.075(3)	0.541(3)	0.630(3)	5(2)*

$^aB_{eq} = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ac(\cos\beta)B_{13}]$ (10^4 pm^2). Starred atoms were refined with isotropic temperature parameters.

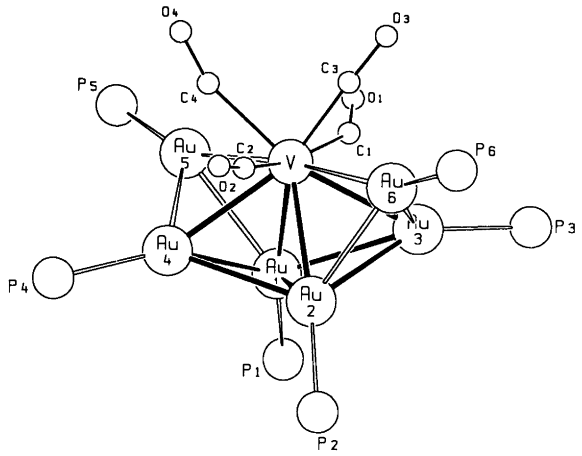

Fig. 1. Structure[25] of the central unit $[(PAu)_6V(CO)_4]^+$ in $[(Ph_3PAu)_6V(CO)_4]_2(PF_6)[(OH)_x,F_y]\cdot 2EtOH$, $x+y = 1$. The central Au_4V trigonal bypiramid is emphasized by bold bonds.

Results and discussion

Synthesis. Our first attempts to synthesize **1** from $Ph_3PAuV(CO)_6$ and Ph_3PAuN_3 as previously described[6] for the preparation of the cluster cation $[(Ph_3PAu)_4Co(CO)_3]^+$ were not successful, as only homoatomic gold clusters with $V(CO)_6^-$ as counterion could be obtained. The main product was $[(Ph_3PAu)_8(AuCl)_2Au][V(CO)_6]$ after treatment of the reaction mixture with CH_2Cl_2 and chromatographic separation. Presumably an excess of azido groups reduced $Ph_3PAuV(CO)_6$ to the stable carbonyl vanadate $V(CO)_6^-$.

The synthesis of **1** was therefore carried out substituting Ph_3PAuN_3 partly by $Ph_3PAuNCO$ to avoid an excess of azide groups and to provide an appropriate counterion to stabilize **1**. The best results were obtained with a 3:2 molar mixture of $Ph_3PAuNCO/Ph_3PAuN_3$, giving a ca. 35 % yield of **1**. Under these conditions, yields of 30 % homoatomic gold clusters and 30 % $(Ph_3PAu)_3V(CO)_5$ resulted as by-products.

After chromatography on alumina, a fraction containing **1**·NCO was isolated. This compound had the characteristic absorption of the NCO^- anion at 2205 cm^{-1} and, moreover, showed CO stretching vibrations (dichloromethane) at 1990, 1840 and 1820 cm^{-1}, i.e. at lower wavenumbers than reported[13] for the neutral four-membered cluster $(Ph_3PAu)_3V(CO)_5$, thus suggesting a higher nuclearity of the new cluster, in consideration of the donor properties of the Ph_3PAu species. **1**·NCO was treated in CH_2Cl_2/MeCN with KPF_6 to achieve better crystallization. Air-stable, brownish-red crystals of composition $[(Ph_3PAu)_6V(CO)_4]_2(PF_6)[(OH)_x,F_y]\cdot 2EtOH$, $x+y = 1$ were thus isolated.

Structure of **1**. The structure of the central unit $[(PAu)_6V(CO)_4]^+$ of **1** is shown in Fig. 1. Selected bond distances and angles are given in Table 3.

The Au_6V core exhibits the structure of a bicapped trigonal bipyramid with the atoms V, Au1 and Au2 in equatorial and Au3 and Au4 in axial positions. Au5 and Au6 each cap one Au_2V triangular face. This arrangement allows the distances of the V atom to all Au atoms to be in the narrow range 273–284 pm.

Similar structures are found for $[(Ph_3PAu)_6Pt(CC\text{-}But)(PPh_3)]^+[Au(CC\text{-}But)_2]^-$ (Ref. 19) and $[(Ph_3PAu)_6Pt(CO)(PPh_3)]^{2+}(NO_3)_2$.[20] Puddephatt *et al.*[19] describe the central Au_6Pt core of $[(Ph_3PAu)_6Pt(CC\text{-}But)(PPh_3)]^+$ as comprising two $PtAu_4$ square-based pyramids with the Pt atom at the apical position, fused about a common $PtAu_2$ triangular face. Small deformations transfer this cluster geometry into

Table 3. Selected bond distances (in pm) and bond angles (in °) with estimated standard deviations in parentheses for $[(Ph_3PAu)_6V(CO)_4]_2(PF_6)[(OH)_x,F_y]\cdot 2EtOH$, $x+y = 1$.

Au1–Au2	275.3(5)	Au1–P1	230(2)
Au1–Au3	296.2(4)	Au2–P2	228(2)
Au1–Au4	276.7(4)	Au3–P3	227(2)
Au1–Au5	281.0(4)	Au4–P4	229(2)
Au2–Au3	279.1(4)	Au5–P5	230(2)
Au2–Au4	293.2(4)	Au6–P6	230(2)
Au2–Au6	280.2(4)	V–C1	188(6)
Au3–Au6	278.0(4)	V–C2	193(6)
Au4–Au5	279.4(4)	V–C3	190(5)
V–Au1	273(1)	V–C4	212(6)
V–Au2	273(1)	C1–O1	113(6)
V–Au3	273(1)	C2–O2	116(8)
V–Au4	281(1)	C3–O3	114(7)
V–Au5	284(1)	C4–O4	112(8)
V–Au6	279(1)		
V–Au1–P1	169.4(6)	V–C3–O3	178(5)
V–Au2–P2	170.3(6)	V–C4–O4	154(6)
V–Au3–P3	150.4(6)	C1–V–C2	164(3)
V–Au4–P4	153.2(6)	C1–V–C3	96(2)
V–Au5–P5	159.4(7)	C1–V–C4	101(2)
V–Au6–P6	158.7(5)	C2–V–C3	94(2)
V–C1–O1	146(5)	C2–V–C4	75(2)
V–C2–O2	174(6)	C3–V–C4	83(2)

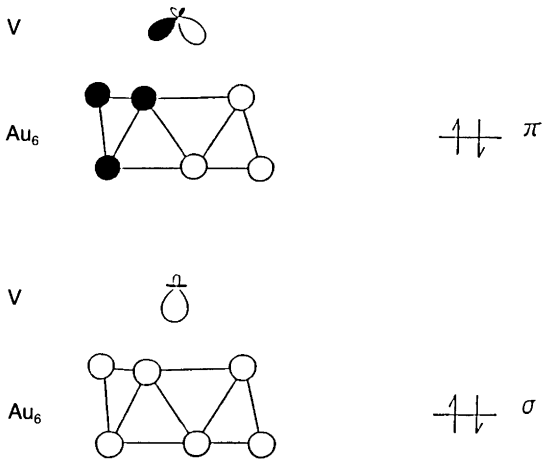

Fig. 2. Proposed cluster MOs for **1**. The drawning shows the radial and tangential frontier orbital of the $V(CO)_4$ group, which overlap with the also radially oriented sp-orbitals of the six Ph_3PAu species.

the structures of $[(Ph_3PAu)_6Pt(CO)(PPh_3)]^+$ and **1**, which are more closely related.

The Au–Au distances in **1** are 275–296 pm (Table 3) and lie in the range usually found in gold cluster compounds between peripheral gold atoms.[21] They can be assigned to weak gold–gold interactions. The distances V–Au = 273–284 pm indicate strong radial bonds from the central vanadium to the peripheral Au atoms. The Au–P distances are in the expected range from 227 to 230 pm.

Within the cluster a strong steric repulsion is detectable. It is caused by the bulky phosphine ligands and by the interaction between the $V(CO)_4$ group and the Au_6 fragment, and results in short distances between the Au and the carbonyl C atoms as well as in a bending of these groups (Table 3 and Fig. 1). The shortest distances C1–Au3 = 232 pm and C4–Au5 = 236 pm correspond to CO groups being arranged above a V–Au edge and are comparable to a semi-bridging behaviour. These groups exhibit, in agreement with this observation, the smallest bond angles of V–C1–O1 = 146° and V–C4–O4 = 154°. The atoms of the PF_6^- anion exhibit large temperature factors and P–F distances between 140 and 170 pm, with high standard deviations.

The $V(CO)_4$ part of **1** can use two frontier orbitals for bonding. They can be characterized according to Wade[22] and Owen[23] as radial and tangential. The radial orbital is pointing towards the centre of the polyhedron, whereas the second frontier orbital is oriented tangentially with respect to the pseudospherical surface of the cluster. Both combine with the sp hybrid orbitals of the six Ph_3PAu units, which are also tangentially oriented, to form one MO with σ symmetry and one with π symmetry (Fig. 2). The observed elliptical geometry of the Au_6V cluster facilitates a good overlap, especially in the case of the π-MO.

The Au_6 species forms, as in the other known cluster cations $[(Ph_3PAu)_xM(CO)_y]^+$, a fragment of an icosahedron, the centre of which is occupied by the transition metal M (Fig. 3). This method of description allows one to clarify the geometrical relationship between the different cluster cations. Starting from Au_4M the cluster Au_7M is gradually generated, adding each time an additional corner to the incomplete icosahedron. Further completion of the icosahedron to an Au_8M core is realized by the cluster cation $[Au_8Cl_2(PPh_3)_6Rh(CNC_8H_9)_2]^+$.[24]

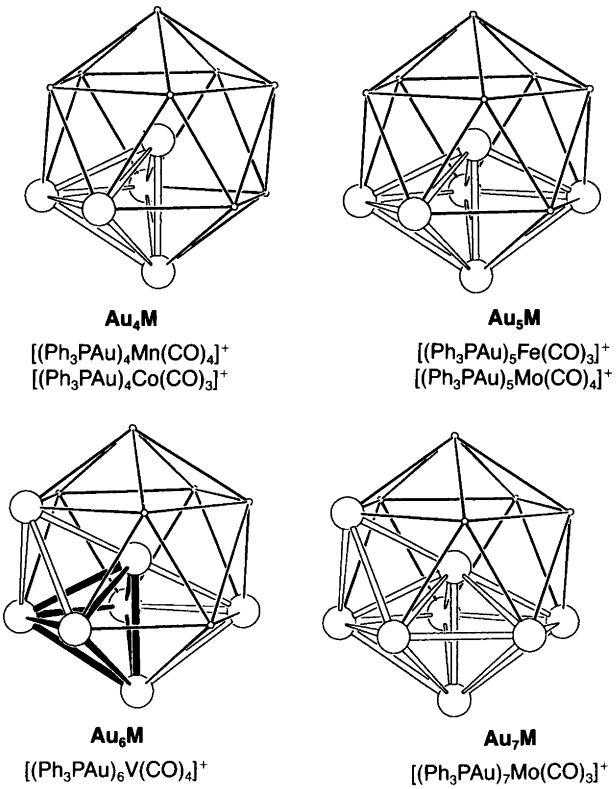

Fig. 3. Representation of the clusters Au_xM (x = 4–7) as fragments of an icosahedron. The transition metal M occupies the centre of the incomplete icosahedron.

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