Inorg. Chem. **1992**, *31*, 4075–4080

New Transition Metal-Gold Clusters: Synthesis and Characterization of the Tungsten-Gold Clusters $[W(CO)_4(AuPPh_3)_5](PF_6)$, $[W(CO)_3(AuPPh_3)_7](PF_6)$, and $[W(CO)_4(AuPPh_3)_6](NO_3)_2$. Crystal Structures of $[W(CO)_4(AuPPh_3)_5](PF_6){\cdot}CH_2Cl_2$ and $[W(CO)_3(AuPPh_3)_7](PF_6)$

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Received March 25, 1992

Three new tungsten-centered gold cluster compounds are reported: $[W(CO)_4(AuPPh_3)_5]^+$ (**1**), $[W(CO)_3(AuPPh_3)_7]^+$ (**2**), and $[W(CO)_4(AuPPh_3)_6]^{2+}$ (**3**). The cluster compounds **1** and **2** are formed by reactions of $[Au(PPh_3)(AuPPh_3)_7]^{2+}$ with $W(CO)_3(C_2H_5CN)_3$ or $W(CO)_6$. **3** is formed by the electrophilic addition of $AuPPh_3^+$ to **1**; this reaction can be reversed by the addition of PPh_3 to **3** yielding the starting cluster **1** and $Au(PPh_3)_2^+$. **1** was characterized by elemental analysis, ICP analysis and by IR, ^{13}C NMR, and ^{31}P NMR spectroscopy. The crystal and molecular structure of $[W(CO)_4(AuPPh_3)_5](PF_6){\cdot}CH_2Cl_2$ has been determined by a single-crystal X-ray analysis. The compound crystallizes as the PF_6^- salt in the monoclinic space group $P2_1$, with $Z = 2$, $a = 13.603$ (2) Å, $b = 25.381$ (2) Å, $c = 14.256$ (8) Å, $\beta = 103.52$ (9)°, and $V = 4785$ (3) Å^3. Mo Kα radiation was used. The residuals are $R = 0.047$ and $R_w = 0.069$ for 9156 observed reflections and 368 variables. The symmetry of the metal cluster is nearly C_s. The central tungsten atom of **1** is bound to five gold atoms and four CO ligands, leading to a total connectivity of nine for the central tungsten atom. A triphenylphosphine is attached to each of the gold atoms. **2** was characterized by elemental analysis, ICP analysis and by IR, and ^{31}P NMR spectroscopy; its solid state structure was determined by a single-crystal X-ray analysis. This compound crystallizes as the PF_6^- salt in the monoclinic space group $P2_1/n$, with $Z = 4$, $a = 14.452$ (4) Å, $b = 30.151$ (7) Å, $c = 30.07$ (1) Å, $\beta = 91.6$ (1)°, $V = 13099$ (7) Å^3. Mo Kα radiation was used. The residuals are $R = 0.065$ and $R_w = 0.076$ for 4870 observed reflections and 458 variables. The symmetry of the cluster is nearly C_s. The central tungsten atom of **2**, which has a total connectivity of 10, is bound to three CO ligands and seven gold atoms; each of these gold atoms is attached to a triphenylphosphine ligand. **3** was characterized by IR and ^{31}P NMR spectroscopy and by its chemical behavior.

Introduction

A large number of mixed metal–gold clusters is known, in which 1–12 gold atoms are attached to a central metal atom. The variety of the center metal in these clusters is extensive, ranging from the early transition metals like vanadium[1] to the platinum group[2] and coinage metals.[3]

From gold cluster chemistry it is known that $[Au(PPh_3)(AuPPh_3)_7]^{2+}$, in which gold is also in the center of the metal frame, is reactive in fragmentation and recombination reactions.[3,4] It can be used in the synthesis of mixed metal–gold cluster compounds. For instance the reaction of $Pt(COD)(NO_3)_2$ with $[Au(PPh_3)(AuPPh_3)_7]^{2+}$ and $NaBH_4$ in ethanol yields the mixed platinum–gold clusters $[Pt(AuPPh_3)_8]^{2+}$ and $[Pt(PPh_3)(AuPPh_3)_6]^{2+}$.[5] At the moment it is not clear whether Pt is incorporated in the $[Au(PPh_3)(AuPPh_3)_7]^{2+}$ cluster to form $[Pt(AuPPh_3)_8]^{2+}$ or whether the latter is formed by a fragmentation–recombination reaction. To further investigate this kind of reaction, other metal complexes were reacted with $[Au(PPh_3)(AuPPh_3)_7]^{2+}$. During these investigations some new tungsten-centered gold clusters were found. $[W(CO)_4(AuPPh_3)_5]^+$ (**1**) and $[W(CO)_3(AuPPh_3)_7]^+$ (**2**) are formed by reaction of $W(CO)_3(C_2H_5CN)_3$ with $[Au(PPh_3)(AuPPh_3)_7]^{2+}$. They are the tungsten analogues of the clusters $[Mo(CO)_4(AuPPh_3)_5]^+$ and $[Mo(CO)_3(AuPPh_3)_7]^+$, formed by the photolysis of PPh_3AuN_3 in the presence of $Mo(CO)_6$.[6,7]

A large number of compounds containing tungsten–gold bonds are known from literature,[8] but they differ significantly from the mixed tungsten–gold clusters described in this article. Most of the literature-known tungsten–gold compounds contain only one or two tungsten–gold bonds, whereas compounds **1** and **2** contain five and seven tungsten–gold bonds, respectively, and a large number of gold–gold interactions; furthermore, the tungsten and gold atoms in the literature-known compounds are often connected by bridging ligands, whereas all the ligands in **1** and **2** are terminally bonded to the metal atoms. Compounds **1** and **2** can be seen as tungsten-centered gold clusters.

The electrophilic addition of Au(I) species to centered gold clusters is demonstrated by the reaction[9]

$$[Au(AuPPh_3)_7]^{2+} + AuPPh_3^+ \rightarrow [Au(AuPPh_3)_8]^{3+} \qquad (1)$$

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0020-1669/92/1331-4075$03.00/0

Other electrophilic additions of coinage metals to mixed metal–gold clusters are also known, e.g.[10]

$$[\mathrm{Pt(CO)(AuPPh_3)_8}]^{2+} + \mathrm{Ag}^+ \rightarrow [\mathrm{Pt(CO)(Ag)(AuPPh_3)_8}]^{3+} \quad (2)$$

In this paper we report the synthesis and characterization of the clusters $[\mathrm{W(CO)_4(AuPPh_3)_5}]^+$ **1** and $[\mathrm{W(CO)_3(AuPPh_3)_7}]^+$ **2**. We also report the electrophilic addition of $\mathrm{AuPPh_3}^+$ to **1**, which leads to the formation of a third tungsten–gold cluster $[\mathrm{W(CO)_4(AuPPh_3)_6}]^{2+}$ **3**. It will be shown that this reaction can be reversed by addition of $\mathrm{PPh_3}$ as a $\mathrm{AuPPh_3}^+$ scavenger to yield the parent cluster **1**.

Experimental Section

Measurements. Elemental analyses were carried out at the microanalytical department of the University of Nijmegen. ICP analyses giving Au:P ratios were carried out on a Plasma 200 ICP-AE spectrometer in DMSO solutions with $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{PF_6})_2$ as the reference. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of $\mathrm{CH_2Cl_2}$ solutions were recorded on a Bruker WM-200 spectrometer operating at 81.015 MHz and on a Bruker CXP-300 spectrometer operating at 121.442 MHz with trimethyl phosphate (TMP) in $\mathrm{CD_2Cl_2}$ as external reference. The variable-temperature $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of **3** in $\mathrm{CD_2Cl_2}$ were recorded on a Bruker AM-500 spectrometer operating at 202.462 MHz with TMP as internal reference. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of $\mathrm{CD_2Cl_2}$ solutions were also recorded on a Bruker AM-500 spectrometer operating at 125.759 MHz with tetramethylsilane (TMS) being the reference. The infrared (IR) spectra were measured in CsI pellets on a Perkin-Elmer 1720-X Fourier transform infrared spectrometer.

Preparation. $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{PF_6})_2$ and $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{NO_3})_2$ were prepared according to literature methods.[3,11] This is also the case for $\mathrm{W(CO)_3(C_2H_5CN)_3}$.[12] All solvents were of reagent grade and were used without further purification.

$[\mathrm{W(CO)_4(AuPPh_3)_5}](\mathrm{PF_6})$ [(1)$\mathrm{PF_6}$]. A mixture of 107 mg (0.0270 mmol) of $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{PF_6})_2$ and 25 mg (0.0578 mmol) of $\mathrm{W(CO)_3(C_2H_5CN)_3}$ was refluxed in 40 mL tetrahydrofuran under a nitrogen atmosphere. After 10 h the color of the mixture had changed from red to black. This black mixture was filtered and the black residue washed with 50 mL tetrahydrofuran. The yellow filtrate was evaporated to dryness under reduced pressure. After this yellow residue was redissolved in dichloromethane, yellow-orange crystals of $[\mathrm{W(CO)_4(AuPPh_3)_5}](\mathrm{PF_6})\cdot\mathrm{CH_2Cl_2}$ were obtained within 24 *h* after addition of *n*-hexane (yield: 52 mg, 0.0190 mmol; 45%, calculated for Au).

Anal. Calcd for $\mathrm{WAu_5P_6C_{94}H_{75}O_4F_6}$ (mol wt 2737.15): C, 41.25; H, 2.76. Found: C, 40.86; H, 2.79. IR: characteristic absorption at 840 $\mathrm{cm^{-1}}$ originating from $\mathrm{PF_6}^-$; several absorption bands characteristic for the $\mathrm{PPh_3}$ ligands; ν(CO) at 1878, 1888, 1910, and 1972 $\mathrm{cm^{-1}}$. ^{31}P NMR: $\delta = 56.71$ ppm with $^2J(\mathrm{P}{-}^{183}\mathrm{W})$ (doublet) = 27.8 Hz. ^{13}C NMR: $\delta(^{13}\mathrm{CO}) = 213.7$ ppm (no $^1J(\mathrm{C}{-}^{183}\mathrm{W})$ visible because of a low S/N ratio).

The nitrate salt of **1** was prepared in the same way using $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{NO_3})_2$ instead of $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{PF_6})_2$.

Anal. Calcd for $\mathrm{WAu_5P_5C_{94}H_{75}O_7N}$ (mol wt 2654.18): C, 42.54; H, 2.85; N, 0.53. Found: C, 41.98; H, 2.88; N, 0.50. ICP: Au:P = 1:1.05.

$[\mathrm{W(CO)_3(AuPPh_3)_7}](\mathrm{PF_6})$ [(2)$\mathrm{PF_6}$]. A 99-mg (0.0250-mmol) sample of $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{PF_6})_2$ was dissolved in 30 mL of dichloromethane under a nitrogen atmosphere and 11.1 mg (0.0257 mmol) of $\mathrm{W(CO)_3(C_2H_5CN)_3}$ was added. This mixture was refluxed for 3 h, while the color changed from red to black. The mixture was then filtered. The orange-red filtrate was evaporated to dryness under reduced pressure. After this orange-red residue was redissolved in dichloromethane, orange-red crystals of $[\mathrm{W(CO)_3(AuPPh_3)_7}](\mathrm{PF_6})$ were obtained by addition of *n*-hexane (yield: 11 mg, 0.00303 mmol; 11%, calculated for Au).

Anal. Calcd for $\mathrm{WAu_7P_8C_{129}H_{105}O_3F_6}$ (mol wt 3627.65): C, 42.71; H, 2.92. Found: C, 42.67; H, 2.93. IR: characteristic absorption at 840 $\mathrm{cm^{-1}}$ due to $\mathrm{PF_6}^-$; several absorption bands characteristic for the $\mathrm{PPh_3}$ ligands; ν(CO) at 1828, 1886, and 1966 $\mathrm{cm^{-1}}$. ^{31}P NMR: $\delta = 54.21$ ppm with $^2J(\mathrm{P}{-}^{183}\mathrm{W})$ (doublet) = 29.0 Hz.

Table I. Crystal Data for $[\mathrm{W(CO)_4(AuP(C_6H_5)_3)_5}]\mathrm{PF_6}\cdot\mathrm{CH_2Cl_2}$ and $[\mathrm{W(CO)_3(AuP(C_6H_5)_3)_7}]\mathrm{PF_6}$

chem formula	$\mathrm{Au_5C_{95}Cl_2F_6H_{77}O_4P_6W}$	$\mathrm{Au_7C_{129}F_6H_{105}O_3P_8W}$
fw	2822	3628
a/Å	13.603 (2)	14.452 (4)
b/Å	25.381 (2)	30.151 (7)
c/Å	14.256 (8)	30.07 (1)
β/deg	103.52 (9)	91.6 (1)
V/Å^3	4785 (3)	13099 (7)
Z	2	4
space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
T/°C	20	20
λ/Å	0.710 73	0.710 73
$\rho_{\mathrm{calc}}/\mathrm{g\cdot cm^{-3}}$	1.959	1.839
$\mu(\mathrm{Mo}\ K\alpha)/\mathrm{cm^{-1}}$	90.50	88.29
R^a	0.047	0.065
$R_w{}^b$	0.069	0.076

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{0.5}$.

The nitrate salt of **2** was prepared in the same way using $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{NO_3})_2$ instead of $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{PF_6})_2$.

Anal. Calcd for $\mathrm{WAu_7P_7C_{129}H_{105}O_6N}$ (mol wt 3544.69): C, 43.71; H, 2.99; N, 0.40. Found: C, 43.09; H, 3.03; N, 0.45. ICP: Au:P = 1:1.08.

$[\mathrm{W(CO)_4(AuPPh_3)_6}](\mathrm{NO_3})_2$ [(3)$(\mathrm{NO_3})_2$]. A concentrated solution of the nitrate salt of **1** in dichloromethane or tetrahydrofuran was reacted with an equimolar amount of $\mathrm{AuPPh_3NO_3}$. After 10 min of stirring *n*-hexane was added to precipitate the orange product (**3**)$(\mathrm{NO_3})_2$. The yield was nearly 100%.

Compound **3** has not yet been analyzed by elemental analysis because the product could not be obtained as pure material, but the chemical behavior of **3** indicates it to be $[\mathrm{W(CO)_4(AuPPh_3)_6}]^{2+}$ (see Results and Discussion). IR: several absorption bands characteristic for the $\mathrm{PPh_3}$ ligands; ν(CO) at 1900, 1924, 1966, and 1981 $\mathrm{cm^{-1}}$. ^{31}P NMR: $\delta = 56.12$ ppm with $^2J(\mathrm{P}{-}^{183}\mathrm{W})$ (doublet) = 21.9 Hz.

Clusters **1** and **2** could also be obtained by refluxing a mixture of 369 mg (1.049 mmol) of $\mathrm{W(CO)_6}$ and 431 mg (0.109 mmol) of $[\mathrm{Au(PPh_3)(AuPPh_3)_7}](\mathrm{PF_6})_2$ in 40 mL of tetrahydrofuran. The first tungsten–gold cluster to be formed in this reaction was **1** (after 30 min); **2** was observed after refluxing for 5 h. This route, however, had substantial drawbacks compared with the syntheses for **1** and **2** as described above: the number of side products is larger, so the yields of **1** and **2** are considerably less.

Structure Determination of $[\mathrm{W(CO)_4(AuPPh_3)_5}](\mathrm{PF_6})\cdot\mathrm{CH_2Cl_2}$ [(1)$\mathrm{PF_6}\cdot\mathrm{CH_2Cl_2}$] and $[\mathrm{W(CO)_3(AuPPh_3)_7}](\mathrm{PF_6})$ [(2)$\mathrm{PF_6}$]. Collection and Reduction of Crystallographic Data. Since single crystals decomposed very quickly upon removal from the solvent, crystals of **1** and **2** were mounted in a capillary together with a mixture of dichloromethane and *n*-hexane. X-ray data were measured on an Enraf-Nonius CAD4 diffractometer. Standard experimental details are given elsewhere;[13] the crystal data for **1** and **2** are listed in Table I.

Solution and Refinement of the Structures. $[\mathrm{W(CO)_4(AuPPh_3)_5}](\mathrm{PF_6})\cdot\mathrm{CH_2Cl_2}$ [(1)$\mathrm{PF_6}\cdot\mathrm{CH_2Cl_2}$]. The positions of the metal atoms were found from an automatic orientation and translation search (ORIENT, TRACOR[14]) with a $\mathrm{Au_6}$ fragment (from $[(\mathrm{AuP(C_6H_5)_3})_7\mathrm{Mo(CO)_3}]\mathrm{OH}$[7]) as search model followed by a phase refinement procedure to expand the fragment (DIRDIF[14]). The remaining non-hydrogen atoms were positioned from successive difference Fourier maps. The phenyl rings were converted into regular hexagons and their hydrogen atoms were placed at ideal positions (C–H = 1.00 Å). A difference Fourier map showed the presence of one $\mathrm{PF_6}$ ion and two partially occupied solvent molecules. The positional parameters and the occupation factors of the atoms of these solvent molecules were refined with a constrained ideal geometry. The total occupation factor leads to one solvent molecule for one cluster. To determine the absolute structure the Bijvoet coefficient was calculated and found to be negative ($B = -0.945$ on 200 Bijvoet pairs, using a new version of the program Bijvoet[15]); consequently the structure was inverted. Least-squares refinement using SHELX[14] was performed in two blocks. During the final stage of refinement, the anisotropic parameters of the gold, tungsten, and phosphorus atoms were refined. Final convergence was reached at $R = 0.047$; the function minimized was $\sum w(F_o - F_c)^2$ with

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Table II. Selected Fractional Positional and Thermal Parameters (Å^2) for [W(CO)$_4$(AuP(C$_6$H$_5$)$_3$)$_5$]PF$_6$·CH$_2$Cl$_2$[a]

atom	x	y	z	$100U_{eq}$[b]
W	0.94360 (8)	0.9739 (2)	1.00074 (7)	2.56 (4)
Au(2)	1.15639 (8)	0.9759 (2)	1.07052 (8)	3.45 (4)
Au(3)	1.04796 (8)	1.0682 (2)	1.06799 (8)	3.22 (4)
Au(4)	0.87289 (8)	1.0686 (2)	0.90751 (7)	2.96 (4)
Au(5)	1.05603 (8)	1.0203 (2)	0.88591 (8)	3.02 (4)
Au(6)	0.85522 (9)	0.9775 (2)	0.79889 (8)	3.76 (4)
P(2)	1.3203 (6)	0.9514 (3)	1.1347 (6)	3.4 (3)
P(3)	1.1009 (6)	1.1429 (3)	1.1644 (6)	3.1 (3)
P(4)	0.7930 (6)	1.1499 (3)	0.8632 (5)	3.2 (3)
P(5)	1.1513 (6)	1.0335 (3)	0.7722 (5)	3.6 (3)
P(6)	0.7789 (7)	0.9478 (4)	0.6479 (6)	4.3 (3)
C(1)	0.985 (3)	0.941 (1)	1.132 (3)	5 (1)
O(1)	1.002 (2)	0.922 (1)	1.206 (2)	6 (1)
C(2)	1.009 (2)	0.918 (1)	0.941 (2)	3 (1)
O(2)	1.035 (2)	0.878 (1)	0.910 (2)	8 (1)
C(3)	0.874 (3)	1.016 (2)	1.073 (3)	6 (1)
O(3)	0.821 (3)	1.036 (2)	1.125 (3)	11 (1)
C(4)	0.817 (3)	0.937 (2)	0.969 (3)	6 (1)
O(4)	0.747 (2)	0.905 (1)	0.944 (2)	9 (1)

[a] The numbering scheme for the gold and phosphorus atoms starts with number 2; this oddity originates from the fragment search using a Au$_6$ fragment (see Experimental Section). [b] $U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for [W(CO)$_4$(AuP(C$_6$H$_5$)$_3$)$_5$]PF$_6$·CH$_2$Cl$_2$

W–Au(2)	2.833 (2)	Au(5)–Au(6)	2.932 (3)
W–Au(3)	2.832 (5)	Au(2)–P(2)	2.289 (8)
W–Au(4)	2.806 (5)	Au(3)–P(3)	2.355 (8)
W–Au(5)	2.752 (3)	Au(4)–P(4)	2.349 (9)
W–Au(6)	2.849 (3)	Au(5)–P(5)	2.325 (9)
Au(2)–Au(3)	2.763 (5)	Au(6)–P(6)	2.288 (9)
Au(2)–Au(5)	2.895 (3)	W–C(1)	2.01 (3)
Au(3)–Au(4)	2.891 (3)	W–C(2)	1.96 (3)
Au(3)–Au(5)	2.892 (3)	W–C(3)	1.89 (4)
Au(4)–Au(5)	2.858 (3)	W–C(4)	1.93 (4)
Au(4)–Au(6)	2.763 (5)		

Au(2)–W–Au(3)	58.4 (2)	C(2)–W–C(3)	168 (1)
Au(2)–W–Au(4)	111.1 (2)	C(2)–W–C(4)	91 (1)
Au(2)–W–Au(5)	62.4 (1)	C(3)–W–C(4)	82 (2)
Au(2)–W–Au(6)	120.6 (2)	W–Au(2)–P(2)	162.8 (3)
Au(3)–W–Au(4)	61.7 (1)	W–Au(3)–P(3)	159.9 (3)
Au(3)–W–Au(5)	62.4 (1)	W–Au(4)–P(4)	165.0 (3)
Au(3)–W–Au(6)	112.0 (1)	W–Au(5)–P(5)	162.7 (3)
Au(4)–W–Au(5)	61.7 (1)	W–Au(6)–P(6)	158.6 (3)
Au(4)–W–Au(6)	58.5 (1)	W–C(1)–O(1)	176 (3)
Au(5)–W–Au(6)	63.1 (1)	W–C(2)–O(2)	167 (3)
C(1)–W–C(2)	93 (1)	W–C(3)–O(3)	169 (3)
C(1)–W–C(3)	78 (2)	W–C(4)–O(4)	167 (3)
C(1)–W–C(4)	93 (2)		

$w = 1.0/[\sigma^2(F_o) + 0.0036F_o^2]$. A maximum residual density of 3.1 e/Å^3 was found near the W and Au atoms, further residual density being below 0.8 e/Å^3.

Positional and thermal parameters of selected atoms are given in Table II, and selected bond distances and angles, in Table III. The molecular structure of **1** is given in Figure 1.[16]

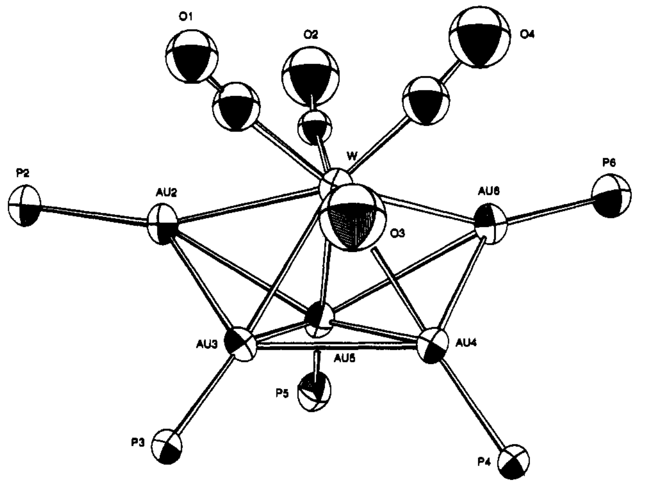

Figure 1. X-ray structure of [W(CO)$_4$(AuP(C$_6$H$_5$)$_3$)$_5$]PF$_6$·CH$_2$Cl$_2$ with atom labeling for Au, P, and carbonyl C. Phenyl rings and the PF$_6^-$ ion have been omitted for the sake of clarity. Thermal ellipsoids are at 50% probability.

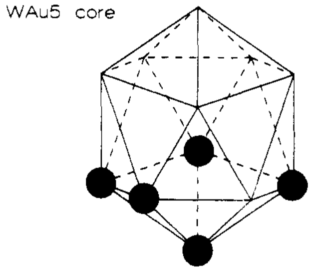

Figure 2. Schematic representation of the metal core of **1**. The tungsten atom, which occupies the center of the incomplete icosahedron, has been omitted for the sake of clarity.

Table IV. Selected Fractional Positional and Thermal Parameters (Å^2) for [W(CO)$_3$(AuP(C$_6$H$_5$)$_3$)$_7$]PF$_6$

atom	x	y	z	$100U_{eq}$[a]
W	0.0629 (2)	0.16599 (8)	0.27397 (8)	3.0 (1)
Au(1)	−0.1033 (1)	0.19856 (8)	0.30317 (7)	2.9 (1)
Au(2)	0.0478 (2)	0.25756 (8)	0.27912 (8)	3.8 (1)
Au(3)	0.0606 (2)	0.20669 (9)	0.35970 (7)	3.8 (1)
Au(4)	−0.0230 (2)	0.12074 (8)	0.34250 (7)	4.1 (1)
Au(5)	−0.1007 (2)	0.11709 (8)	0.25367 (8)	3.8 (1)
Au(6)	−0.0603 (1)	0.20246 (8)	0.21109 (7)	3.5 (1)
Au(7)	0.1344 (2)	0.21671 (9)	0.20411 (7)	4.4 (1)
P(1)	−0.2429 (9)	0.2309 (5)	0.3224 (5)	3.3 (6)
P(2)	0.0903 (11)	0.3301 (6)	0.2919 (5)	4.5 (7)
P(3)	0.1178 (10)	0.2306 (5)	0.4296 (5)	3.8 (6)
P(4)	−0.0465 (12)	0.0688 (6)	0.3970 (5)	5.0 (7)
P(5)	−0.1634 (11)	0.0529 (5)	0.2241 (6)	4.6 (7)
P(6)	−0.1516 (9)	0.2148 (6)	0.1477 (5)	4.4 (6)
P(7)	0.2337 (11)	0.2385 (6)	0.1510 (5)	5.6 (7)
C(1)	0.195 (4)	0.182 (2)	0.287 (2)	12 (2)
O(1)	0.274 (3)	0.193 (1)	0.293 (1)	7 (1)
C(2)	0.123 (4)	0.114 (2)	0.299 (2)	5 (2)
O(2)	0.167 (3)	0.083 (2)	0.311 (1)	9 (1)
C(3)	0.083 (4)	0.126 (2)	0.220 (2)	4 (2)
O(3)	0.094 (3)	0.104 (1)	0.191 (1)	7 (1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$.

[W(CO)$_3$(AuPPh$_3$)$_7$](PF$_6$) [(2)PF$_6$]. The positions of the metal atoms were found from an automatic orientation and translation search (ORIENT, TRACOR[14]) with an ideal WAu fragment (from [(AuP(C$_6$H$_5$)$_3$)$_7$Mo(CO)$_3$]OH[7]) as search model followed by a phase refinement procedure to expand the fragment (DIRDIF[14]). The remaining non-hydrogen atoms were positioned from successive difference Fourier maps. The phenyl rings were converted into regular hexagons, and their hydrogen atoms were placed at ideal positions (C–H = 1.00 Å). A difference Fourier map showed the presence of one PF$_6$ ion on an inversion center and one partially occupied PF$_6$ ion. The positional parameters and the occupation factors of the atoms of the latter PF$_6$ ion were refined. The occupation factors were in the range 0.4–0.6. On chemical evidence the occupation factor is fixed on 0.5. The total occupation factor leads to one PF$_6$ ion for one cluster. During the final stage of the least-squares refinement using SHELX,[14] the anisotropic parameters of the gold, tungsten, and phosphorus atoms were refined. Final convergence was reached at $R = 0.065$; the function minimized was $\sum w(F_o - F_c)^2$ with $w = 1.0/[\sigma^2(F_o) + 0.0008F_o^2]$. A maximum residual density of 1.9 e/Å^3 was found near the W and Au atoms, further residual density being below 0.9 e/Å^3.

Positional and thermal parameters of selected atoms are given in Table IV, and selected bond distances and angles, in Table V. The molecular structure of **2** is given in Figure 3.[16]

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(16) Johnson, C. K. *A Thermal-ellipsoid Plot Program for Crystal Structures Illustrations*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

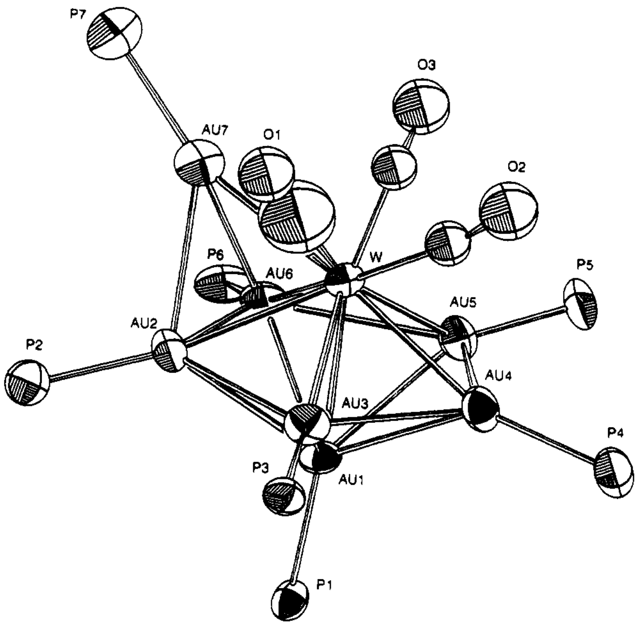

Figure 3. X-ray structure of $[W(CO)_3(AuP(C_6H_5)_3)_7]PF_6$ with atom labelling for Au, P, and carbonyl C Phenyl rings and the PF_6^- ion have been omitted for the sake of clarity. Thermal ellipsoids are at 50% probability.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for $[W(CO)_3(AuP(C_6H_5)_3)_7]PF_6$

W–Au(1)	2.760 (4)	Au(3)–Au(4)	2.900 (4)
W–Au(2)	2.774 (4)	Au(4)–Au(5)	2.871 (4)
W–Au(3)	2.856 (3)	Au(5)–Au(6)	2.941 (4)
W–Au(4)	2.791 (4)	Au(6)–Au(7)	2.860 (3)
W–Au(5)	2.838 (3)	Au(1)–P(1)	2.33 (2)
W–Au(6)	2.787 (4)	Au(2)–P(2)	2.30 (2)
W–Au(7)	2.818 (4)	Au(3)–P(3)	2.35 (2)
Au(1)–Au(2)	2.922 (3)	Au(4)–P(4)	2.30 (2)
Au(1)–Au(3)	2.887 (4)	Au(5)–P(5)	2.30 (2)
Au(1)–Au(4)	2.859 (4)	Au(6)–P(6)	2.32 (2)
Au(1)–Au(5)	2.873 (3)	Au(7)–P(7)	2.27 (2)
Au(1)–Au(6)	2.857 (3)	W–C(1)	1.99 (5)
Au(2)–Au(3)	2.870 (3)	W–C(2)	1.93 (6)
Au(2)–Au(6)	3.035 (4)	W–C(3)	2.05 (6)
Au(2)–Au(7)	2.886 (4)		

Au(1)–W–Au(2)	63.8 (2)	Au(4)–W–Au(7)	174.6 (2)
Au(1)–W–Au(3)	61.8 (2)	Au(5)–W–Au(6)	63.0 (1)
Au(1)–W–Au(4)	62.0 (1)	Au(5)–W–Au(7)	116.3 (2)
Au(1)–W–Au(5)	61.7 (2)	Au(6)–W–Au(7)	61.4 (2)
Au(1)–W–Au(6)	62.0 (1)	C(1)–W–C(2)	73. (2)
Au(1)–W–Au(7)	112.6 (2)	C(1)–W–C(3)	98. (2)
Au(2)–W–Au(3)	61.3 (1)	C(2)–W–C(3)	76. (2)
Au(2)–W–Au(4)	114.1 (1)	W–Au(1)–P(1)	174.6 (4)
Au(2)–W–Au(5)	117.6 (2)	W–Au(2)–P(2)	159.1 (5)
Au(2)–W–Au(6)	66.1 (1)	W–Au(3)–P(3)	157.9 (5)
Au(2)–W–Au(7)	62.1 (1)	W–Au(4)–P(4)	159.5 (5)
Au(3)–W–Au(4)	61.8 (1)	W–Au(5)–P(5)	146.7 (5)
Au(3)–W–Au(5)	112.8 (2)	W–Au(6)–P(6)	163.6 (4)
Au(3)–W–Au(6)	114.8 (1)	W–Au(7)–P(7)	158.8 (5)
Au(3)–W–Au(7)	117.0 (1)	W–C(1)–O(1)	177 (4)
Au(4)–W–Au(5)	61.3 (1)	W–C(2)–O(2)	172 (5)
Au(4)–W–Au(6)	113.9 (2)	W–C(3)–O(3)	179 (5)

Results and Discussion

Synthesis, Characterization, and Crystal Structure of $[W(CO)_4(AuPPh_3)_5](PF_6)$ [(1)PF$_6$]. The cluster compound $[W(CO)_4(AuPPh_3)_5](PF_6)$ [(1)PF$_6$] is obtained by refluxing a mixture of $W(CO)_3(C_2H_5CN)_3$ and $[Au(PPh_3)(AuPPh_3)_7](PF_6)_2$ in tetrahydrofuran. An unknown reorganization process must occur to provide the fourth CO in the $[W(CO)_4(AuPPh_3)_5]^+$ ion. **1** can also be prepared from $W(CO)_6$ and $[Au(PPh_3)(AuPPh_3)_7](PF_6)_2$, although the yield of this route is low. **1** was characterized by elemental analysis, ICP analysis, and IR, ^{13}C NMR, and ^{31}P NMR spectroscopy. Its solid-state structure was determined by means of a single-crystal X-ray analysis.

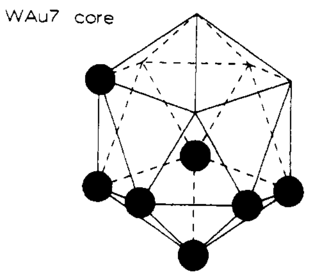

Figure 4. Schematic representation of the metal core of **2**. The tungsten atom, which occupies the center of the incomplete icosahedron, has been omitted for the sake of clarity.

The ^{31}P NMR spectrum of **1** consists of a singlet at $\delta = 56.71$ ppm with $^2J(P-^{183}W) = 27.8$ Hz. This singlet reflects the fast fluxional behavior of the phosphine sites at room temperature, which is commonly observed for this type of cluster compounds.[17] The NMR appearance clearly shows that the tungsten must be in the central position of the cluster framework, surrounded by $AuPPh_3$ units. This observation is confirmed by X-ray analysis (vide infra). The relative intensity of the ^{183}W satellites is in good agreement with the natural abundance of 14.4% for this nucleus. The magnitude of the $J(P-^{183}W)$ is in the range expected for a ^2J coupling via a gold nucleus, which is normally a factor 5–10 less than the corresponding ^1J coupling.

The IR spectrum shows CO stretching vibrations at 1878, 1888, 1910, and 1972 cm^{-1}. These relative low values indicate the electron donor behavior of the five $AuPPh_3$ groups. The X-ray structure analysis of the solid shows that the cluster ion has a central tungsten and five peripheral gold atoms, each of these gold atoms bonded to a phosphine; furthermore the central tungsten is connected to four carbonyls, leading to a total connectivity of nine for the central tungsten atom (Figure 1). There is no direct W–P bond as confirmed by the absence of $^1J(P-^{183}W)$ in the NMR spectrum. The carbonyls and the $AuPPh_3$-groups surround the tungsten in a (quasi-)spheroidal symmetry, which is in accordance with the $(S^\sigma)^2(P^\sigma)^6$ electron configuration (18 electrons) of the cluster. The topological parameters S and P,[18] which correlate with the cluster electron count, are 0.92 and 1.00, respectively, and therefore justify the classification of the cluster geometry as being spheroidal.

The Au_5 atoms of this cluster are positioned at five adjacent vertices of an icosahedron in such a way that the maximum number of seven close Au–Au contacts is obtained (Figure 2). The tungsten atom is situated in the center of the fictitiously completed icosahedron. This is evidenced by the observation that all Au–W–Au bond angles are close to 63.45°, the theoretical value for a perfect icosahedron.

The W-Au distances range from 2.752 to 2.849 Å. These distances are comparable with the sum of the atomic radii of tungsten and gold and are all in the range normally found for W–Au distances.[8] The W–Au–P bond angles, ranging from 158.6 to 165.0°, substantially deviate from linearity. These deviations are directed toward the CO region of the molecule, alluding to the sterical nature of these deflections.

The W–C(CO) distances, ranging from 1.89 to 2.01 Å, are also in the range normally observed for tungsten carbonyls. The W–C–O bond angles vary from 167 to 176°. The deviations from linearity of these bond angles are presumably caused by steric factors. The C–O bond lengths (varying from 1.13 to 1.25 Å) are in the normal range found for tungsten carbonyls.

Synthesis, Characterization, and Crystal Structure of $[W(CO)_3(AuPPh_3)_7](PF_6)$ [(2)PF$_6$]. $[W(CO)_3(AuPPh_3)_7](PF_6)$ [(2)PF$_6$]

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(17) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J.; Steggerda, J. J.; Maas, W. E. J. R.; Janssen, R. *Inorg. Chem.* **1991**, *30*, 1709.

(18) Kanters, R. P. F.; Steggerda, J. J. *J. Cluster Sci.* **1990**, *1*, 229.

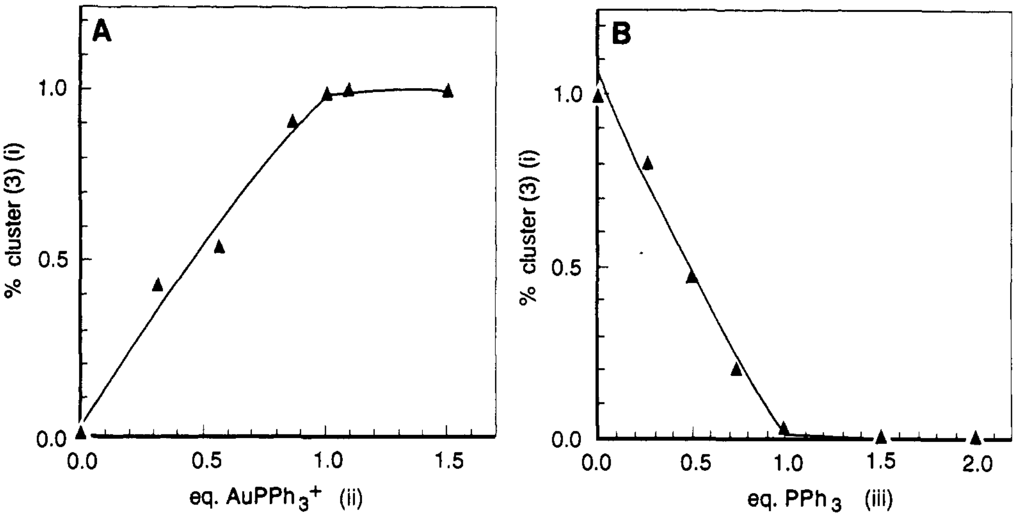


Figure 5. Course of reaction 3 in CH_2Cl_2 as followed by ^{31}P NMR: (A) results of the forward reaction with different amounts of $AuPPh_3^+$ to **1**; (B) results of the backward reaction caused by the addition of different amounts of PPh_3 to **3**. These curves clearly show that both reactions proceed in 100% yield by the addition of 1 equiv of $AuPPh_3^+$ or PPh_3 respectively. Conditions: (i) % cluster **3** is expressed as the amount of cluster **3** divided by the total amount of clusters **1** and **3** as estimated from ^{31}P NMR spectra; (ii) the equivalents of $AuPPh_3^+$ were calculated for the starting amount of cluster **1**; (iii) the equivalents of PPh_3 were calculated for the starting amount of cluster **3**.

can be prepared by refluxing $[Au(PPh_3)(AuPPh_3)_7](PF_6)_2$ with either $W(CO)_3(C_2H_5CN)_3$ in dichloromethane or $W(CO)_6$ in tetrahydrofuran. **2** was characterized by elemental analysis, ICP analysis, and IR and ^{31}P NMR spectroscopy. Its solid-state structure was determined by a single-crystal X-ray analysis.

The ^{31}P NMR spectrum of **2** consists of a singlet at $\delta = 54.21$ ppm with ^{183}W satellites at 29.0 Hz. The singlet nature is a result of the fluxional behavior of the phosphine sites in solution; the relative intensity of the satellites corresponds to the 14.4% natural abundance of ^{183}W. The magnitude of the $J(P\text{–}^{183}W)$ shows it to be a ^2J coupling. The NMR appearance clearly indicates that **2** has a central tungsten atom, surrounded by $AuPPh_3$ units.

The IR spectrum shows CO stretching vibrations at 1828, 1886, and 1966 cm^{-1}. These low frequencies for **2** point to a strong donor behavior of the seven $AuPPh_3$ groups, causing a substantial π-back-donation to the carbonyls.

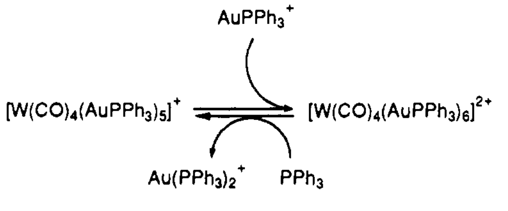
The solid-state structure of cluster ion **2** (Figure 3) shows a central tungsten atom surrounded by three carbonyls and seven gold atoms, each of the gold atoms connected to a phosphine ligand. This coordination geometry leads to a connectivity of 10 for the central tungsten atom. There is no direct W–P bond in this cluster ion, as confirmed by the absence of $^1J(P\text{–}^{183}W)$ in the NMR spectrum.

The metal core of **2** is derived from an icosahedral geometry: the seven gold atoms are positioned at seven adjacent vertices of an icosahedron (Figure 4) whereas the tungsten atom is situated in the center. The number of close Au–Au contacts for this geometry is 12. The carbonyls, bonded to the tungsten atom, are placed at the top of this metal core on the side opposite to the Au_7 atoms. The carbonyls and the $AuPPh_3$ groups surround the central tungsten in a (quasi-)spheroidal symmetry, as indicated by the topological parameters S and P,[18] which are 0.91 and 0.94, respectively, in accordance with the $(S^\sigma)^2(P^\sigma)^6$ electron configuration (18 electrons) of **2**.

The W–Au distances, ranging from 2.760 to 2.856 Å, are about the same as those for **1**. The Au–P bond distances are in the range normally found for (mixed metal–) gold clusters. The W–Au–P bond angles range from 146.7 to 174.6°. Except for the W–Au(1)–P(1) bond angle (174.6°), the deviations from linearity are considerable; as for **1** these deviations are directed toward the CO region, which further supports the indication that these deviations are caused by steric factors. The W–C(CO) distances range from 1.93 to 2.05 Å and are comparable to those for **1** and other tungsten carbonyls.

The C–O bond lengths (1.12, 1.19, and 1.20 Å) are in the range normally observed for tungsten carbonyls; the W–C–O bond angles vary from 172 to 179°. The deviations from linearity of the bond angles are less than those for cluster ion **1**. This must be related to two cooperative factors: the tungsten atom in **2** is somewhat more tilted above the five-membered ring (Au(2)–Au(3)–Au(4)–Au(5)–Au(6)) than the tungsten atom in **1** is above the partially filled five-membered ring (Au(2)–Au(3)–Au(4)–Au(6)). This leaves more room for the carbonyls of **2** to be placed on the tungsten at the other side of this five-membered ring. On the other hand there are only three carbonyls to be placed in **2**, whereas four are to be placed in **1**, and the hindrance of Au(7) in **2** is of significantly less importance compared to that of the fourth carbonyl in **1** because of the larger W–Au bond length compared to W–C.

Electrophilic Addition of $AuPPh_3^+$ to $[W(CO)_4(AuPPh_3)_5]^+$. The reaction of $[W(CO)_4(AuPPh_3)_5]^+$ with $AuPPh_3^+$ in dichloromethane or tetrahydrofuran yields a third tungsten–gold cluster which is to be formulated as $[W(CO)_4(AuPPh_3)_6]^{2+}$ on the basis of chemical and spectroscopic considerations (vide infra). The yield of this reaction is nearly 100%, indicating this electrophilic addition must be straightforward. Furthermore this new product reacts with PPh_3 to yield the parent cluster $[W(CO)_4(AuPPh_3)_5]^+$ and $Au(PPh_3)_2^+$, the PPh_3 thereby acting as a $AuPPh_3^+$ scavenger.[3] Reaction 3 in CH_2Cl_2 at room temperature, with



(3)

different amounts of $AuPPh_3^+$ or PPh_3 respectively, was followed by ^{31}P NMR; the results are shown in Figure 5A,B. Both reactions proceed in 100% yield by the addition of 1 equiv $AuPPh_3^+$ or PPh_3, respectively, and no side products other than $Au(PPh_3)_2^+$ are formed during the cycle.

The ^{31}P NMR spectrum of **3** consists of a singlet at $\delta = 56.12$ ppm with ^{183}W satellites at 21.9 Hz. The size of this coupling shows it to be $^2J(P\text{–}^{183}W)$, thereby indicating that the central tungsten atom is surrounded by $AuPPh_3$ units.

$^2J(P\text{–}^{183}W)$ decreases from 27.8 Hz in the parent compound **1** to 21.9 Hz in **3**. This must be related to the lowering of the

W–Au bond order upon addition of a AuPPh$_3^+$ unit to the central tungsten atom since with the same number of bonding electrons an additional bond has to be made.

The IR spectrum shows CO stretching vibrations at 1900, 1924, 1966, and 1981 cm^{-1}. The increase of these frequencies compared with those of **1** is consistent with the view that the extra W–Au bond that has to be maintained after the addition of AuPPh$_3^+$ to **1** decreases the electron density at the tungsten atom. This results in a decrease of π-back-donation to the carbonyls and therefore in an increase in ν(CO).

Single crystals of **3** suitable for X-ray analysis have not yet been obtained, so no X-ray structure is available at this moment. Nevertheless we feel quite sure about its structure. The tungsten atom of **3** is connected to four carbonyls and six AuPPh$_3$ groups, leading to a total connectivity of 10 for the tungsten. The carbonyls and the AuPPh$_3$ groups must surround the central tungsten in a (quasi-)spheroidal geometry according to the $(S^\sigma)^2(P^\sigma)^6$ electron configuration (18 electrons) of **3**. The four carbonyls will probably be situated on one side of the tungsten and the gold atoms will be placed on the other side. There are three possible ways for these six gold atoms to be placed in an icosahedral derived geometry (Figure 6). The geometry of Figure 6A is found for the Au$_6$ atoms in [Mn(CO)$_3$(AuPPh$_3$)$_6$](PF$_6$)[19] and in [Au(PPh$_3$)(AuPPh$_3$)$_6$](OH);[11] the geometry of Figure 6B is observed for the [V(CO)$_4$(AuPPh$_3$)$_6$]$^+$ ion[20] and for the [Pt(PPh$_3$)(CO)(AuPPh$_3$)$_6$]$^{2+}$ ion[21] while the geometry of Figure 6C is not known yet for any cluster compound. The geometry of Figure 6A has the maximum number of 10 close Au–Au contacts for an assembly of six gold atoms arranged in an icosahedral derived geometry, whereas the geometries of Figure 6B,6C both have nine such contacts.

The geometry of Figure 6A can be ruled out for **3** because at 205–173 K the single ^{31}P NMR line that is present at higher temperatures begins to split into three lines, which indicates that the compound has at least three different phosphine sites. This observation leaves the geometries of Figure 6B,C for **3**, which are in accordance with the electronic arguments given for the [V(CO)$_4$(AuPPh$_3$)$_6$]$^+$ cluster.[20]

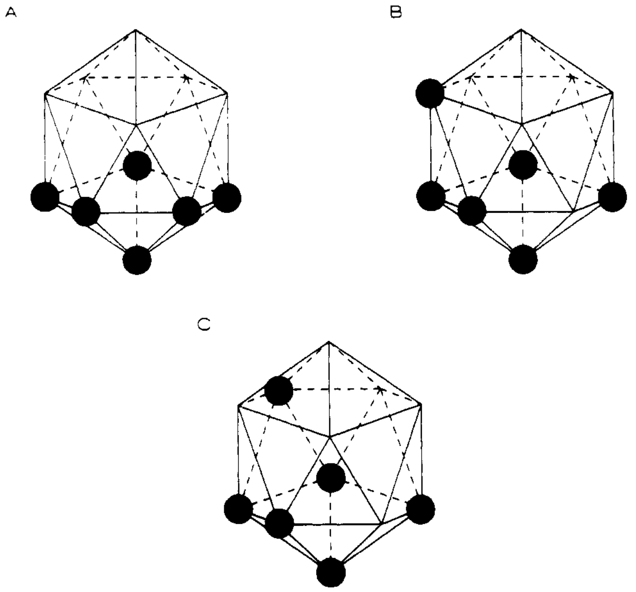


Figure 6. (A, B, C) Schematic representations of the possible geometries for the metal core of **3**. The tungsten atoms, which occupy the centers of the incomplete icosahedra, have been omitted for the sake of clarity.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with fundamental support from the Netherlands Organization for the Advancement of Pure Research (NWO).

Supplementary Material Available: Tables of crystallographic details and additional fractional positional parameters, anisotropic thermal parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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