Heterometallic "butterfly" cluster $[Fe_3(CO)_9(\mu_3\text{-}OBu^t)Au(PPh_3)]$

S. P. Gubin,* L. A. Polyakova, A. V. Churakov, and L. G. Kuz'mina

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117907 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: gubin@ionchran.rinet.ru

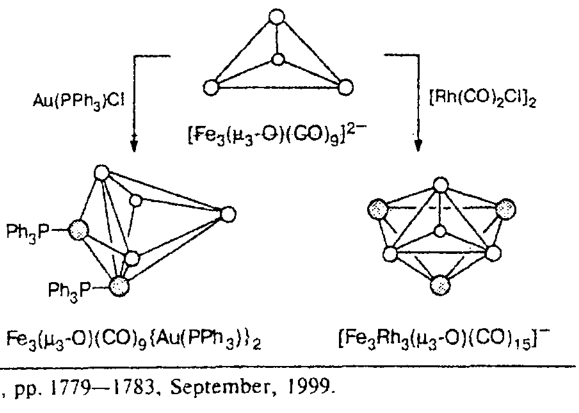
Alkylation of the $[Fe_3(\mu_3\text{-}O)(CO)_9]^{2-}$ dianion with *tert*-butyl iodide afforded the $[Fe_3(\mu_3\text{-}OBu^t)(CO)_9]^-$ monoanion. The reaction of the latter with $Au(PPh_3)Cl$ in the presence of $TlBF_4$ yielded the new heterometallic "butterfly" cluster $[Fe_3(CO)_9(\mu_3\text{-}OBu^t)Au(PPh_3)]$. According to the X-ray data, both clusters synthesized contain the unchanged $Fe_3(\mu_3\text{-}O)$ fragment of the initial dianion. The addition of the $Au(PPh_3)$ fragment to the monoanion occurred in such a way as to minimize steric changes. As a result, a "turned inside out" heterometallic "butterfly," which contains the μ_3-O ligand on the outside rather than on the inside, was obtained. The dihedral angle characterizing the "butterfly" is 151°.

Key words: iron, gold, μ_3-O ligand, carbonyl clusters, heterometallic "butterfly" cluster.

Presently, the known "butterfly" clusters are classified into two groups: (1) clusters whose wings are tied up with a particular ligand; (2) clusters in which two triangles linked *via* a shared edge do not contain tightening ligands.[1] Clusters belonging to the second group are few in number. However, the mere fact that these structures exist casts doubt on the "tightening" role of ligands, which are bound simultaneously to all four metal atoms of the "butterfly." Generally, ligands of a special type, *viz.*, the least sterically demanding monoatomic ligands, act as "tightening" ligands. In this series, boron,[2,3] carbon,[4–8] nitrogen,[9–11] and sulfur,[12] for which a wide variety of bond types, large coordination numbers, and unusual reactivity are known, have received the most study. Oxygen[12] is less well studied as a monoatomic ligand.

Presently, monooxygen is structurally characterized as a ligand in a small number of coordination modes. Actually, only a few examples of each mode are available in the literature, which is far less than the abundance of clusters containing monoatomic B, C, N, and S ligands. Thus, it was established that in carbonyl clusters, elemental oxygen can act as a bridge between two metal atoms, as in the cases of $Mo_2Ru_4(\mu_6\text{-}C)(\mu\text{-}O)(CO)_{12}Cp_2$ [13] and $Os_3(CO)_9W(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)Cp$,[14] or can be located at the center of the triangular face, as in the case of $Os_6(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_{18}$.[15] In addition, oxygen can act as a μ_4-ligand and link wings of the heterometallic "butterfly" in the $[PPN][Fe_3M(CO)_{12}(\mu_4\text{-}O)]$ clusters (M = Mn or Re; PPN = $(Ph_3P)_2N$)[12] or can center the tetragonal face of the tetragonal pyramid in $[PPN]_2[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]$. [16] In carbonyl-free clusters, oxygen can act also as a terminal ligand.[17] Unlike the carbide and nitride analogs, organometallic clusters with an inner oxo ligand are as yet unknown, although many examples of these oxo ligands are available for polyoxometallates[18] and ligand-free metallic oxo clusters.[19]

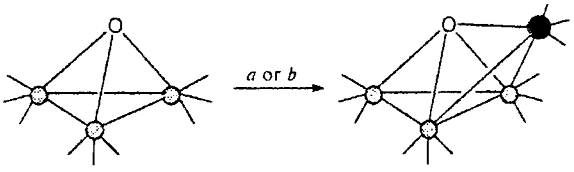
Previously, we have demonstrated[20] that the metal core of the $[Fe_3(\mu_3\text{-}O)(CO)_9]^{2-}$ dianion (**1**)[21] is triangle formed by the iron atoms with three terminal CO ligands at each Fe atom. The bridging oxygen atom is located at equal distances from the iron atoms. This dianion can serve as a good source for the construction of the desired cluster molecules (the so-called cluster design). The reaction of dianion **1** with an excess of $[Rh(CO)_2Cl]_2$ afforded the heterometallic cluster of composition $[Fe_3Rh_3(\mu_3\text{-}O)(CO)_{15}]^-$, which contains 86 cluster valence electrons (CVE).[20] X-ray analysis demonstrated that the resulting cluster is the first example of a heterometallic octahedron containing the μ_3-O ligand. In the same study,[20] the trigonal-bipyramidal cluster $Fe_3(\mu_3\text{-}O)(CO)_9\{Au(PPh_3)\}_2$, containing the μ_3-O ligand and possessing 72 CVE, was prepared for the first time by the reaction of dianion **1** with $Au(PPh_3)Cl$ in CH_2Cl_2 in the presence of $TlBF_4$ and the resulting cluster was structurally characterized. X-ray analysis demonstrated that the Fe_3O fragment remains virtually unchanged in both structures of these complicated clusters.



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1779—1783, September, 1999.

1066-5285/99/4809-1757 $22.00

An alternative direction of the reaction of dianion **1** is also known. This dianion can react with metal-containing (Mn or Re) groups to form heterometallic "butterflies," the coordination number being increased from three to four.[12]



$[Fe_3(\mu_3\text{-}O)(CO)_9]^{2-}$ $[Fe_3M(\mu_4\text{-}O)(CO)_{12}]^-$

M = Mn, Re

Reagents: *a*. $[Mn(CO)_3(MeCN)_3]^+$. *b*. $Re(CO)_5(OSO_2CF_3)$.

It is believed that the driving force for this reaction are interactions of the metal atom with the lone electron pair of the μ_3-O ligand in dianion **1** and the 2− charge, which lead to coordination of the former at the edge instead of coordination on the opposite side, *viz*., at the "free" plane of the Fe_3 ring to form the heterometallic tetrahedron. To preclude this possibility, we decided to fix the lone pair of the μ_3-O ligand. For this purpose, we alkylated dianion **1**. It was demonstrated that the alkyl group readily added to the μ_3-O ligand to form $[Fe_3(\mu_3\text{-}OR)(CO)_9]^-$ monoanions (**2a**,**b**, where R = $\mathrm{Bu^t}$ (**a**) or R = Me (**b**)) under the action of RI (R = Me or $\mathrm{Bu^t}$) in acetone at room temperature. Although the syntheses of analogous compounds with R = H, Me, and $CH_2CH{=}CH_2$ have been mentioned in the brief communication,[21] data on the properties and structures of these clusters are lacking in the literature. Cluster **2a** was prepared for the first time by us. The structure of **2a** is shown in Fig. 1. The selected bond lengths and bond angles are given in Table 1. Compound **2a** contains the cluster $[Fe_3(\mu_3\text{-}OBu^t)(CO)_9]^-$ anion possessing 48 CVE, and the $[(Ph_3P)_2N]^+$ cation (PPN^+). The metal core of the anion is a virtually regular triangle formed by the iron atoms (the average Fe—Fe distance is 2.481 Å). This triangle is symmetrically bound to the $\mu_3\text{-}OBu^t$ ligand (with approximate molecular symmetry C_{3v}). Analysis of the data available in the Cambridge Structural Database (CSD, November 1998)[22] demonstrated that complex **2a** is the first example of a structure in which the alkoxide ligand is bound to three Fe atoms in tridentate fashion. The average Fe—O distance (1.940 Å) is larger than those in the related oxo complexes containing the $(\mu_3\text{-}O)Fe_3$ fragment, *viz*., in $[Fe_3(\mu_3\text{-}O)(CO)_9]^{2-}$ (1.892 Å),[21] $[Fe_3(\mu_3\text{-}O)(CO)_9\{Au(PPh_3)\}_2]$ (1.876 Å),[20] and $[Fe_3Rh_3(\mu_3\text{-}O)(CO)_{15}]^-$ (1.90 Å).[20] The O(1)—C(1) bond in the *tert*-butoxy group is virtually perpendicular to the planes through the three Fe atoms (the deviation is 0.7°), the Me groups being in a pseudo-hindered orientation with respect to the Fe atoms.

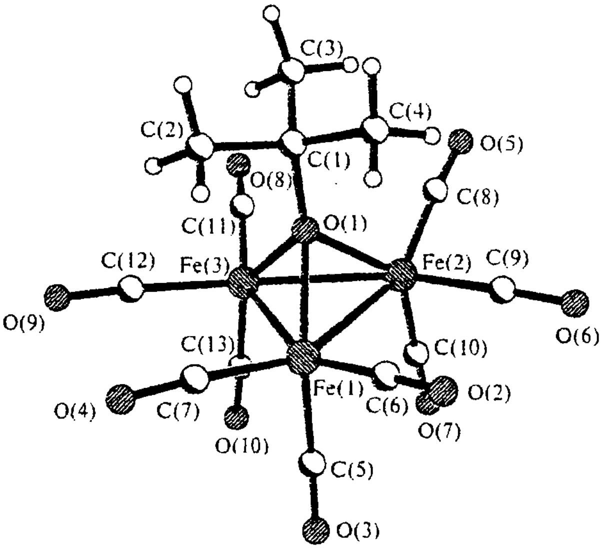


Fig. 1. Molecular structure of cluster **2a**.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecule **2a**

Bond	*d*/Å	Angle	ω/deg
Fe(1)—O(1)	1.941(3)	Fe(3)—Fe(1)—Fe(2)	59.79(3)
Fe(2)—O(1)	1.938(3)	Fe(3)—Fe(2)—Fe(1)	59.80(3)
Fe(3)—O(1)	1.942(3)	Fe(2)—Fe(3)—Fe(1)	60.42(3)
Fe(1)—Fe(2)	2.492(1)	C(1)—O(1)—Fe(2)	133.0(3)
Fe(1)—Fe(3)	2.477(1)	C(1)—O(1)—Fe(1)	131.7(3)
Fe(2)—Fe(3)	2.4764(9)	C(1)—O(1)—Fe(3)	132.6(3)
O(1)—C(1)	1.474(5)	Fe(2)—O(1)—Fe(1)	79.9(1)
P(1)—N(1)	1.571(3)	Fe(2)—O(1)—Fe(3)	79.3(1)
P(2)—N(1)	1.578(3)	Fe(1)—O(1)—Fe(3)	79.3(1)
		P(1)—N(1)—P(2)	143.2(2)

As can be seen from Fig. 1, the Fe atoms are each bound to three terminal carbonyl groups. Six of these carbonyl groups lie virtually in the plane through the three Fe atoms and the remaining three groups are virtually perpendicular to this plane (the corresponding angles are 75.8°, 77.8°, and 80.1°). The average Fe—C and C—O distances are 1.768 and 1.146 Å, respectively.

The P—N bond lengths (1.571 and 1.578 Å) and the P—N—P angle (143.2°) in the PPN^+ cation differ only slightly from those determined previously. Thus, according to the CSD data (725 fragments), the corresponding average values are 1.576 Å and 143.1°. The parameters of the structure of **2a** agree well with the corresponding values in the molecule of the S-containing analog. Thus, the average values of the Fe—O—C bond angles in **2a** and of the Fe—S—C bond angles in $[Fe_3(\mu_3\text{-}SPr^i)(CO)_9]^-$ [23] are 132.4° and 133.9°, respectively.

From Fig. 1 it can be also seen that the "outer side" of the Fe_3 ring as well as the the μ_3-O ligand are positively shielded by the $\mathrm{Bu^t}$ group. There were reasons to believe that the attack of the metal-containing reagent should occur preferentially on the "open" underside of the Fe_3 triangle. Actually, in the reaction of $Au(PPh_3)Cl$ with anion **2a**, the $Au(PPh_3)^+$ group readily added to form the uncharged cluster $[Fe_3(CO)_9(\mu_3\text{-}OBu^t)Au(PPh_3)]$ (**3**) in good yield. The number of CVE in this cluster (60) corresponds to the magic number of CVE for the tetrahedron. However, X-ray analysis demonstrated that compound **3** (Fig. 2) is a tetranuclear heterometallic "butterfly" cluster containing the Fe_3Au core (60 CVE), which is a product of addition of the $Au(PPh_3)^+$ cation to anion **2a** at the edge of the Fe_3 triangle, as in the cases of Mn- and Re-containing groups.[12] Interestingly, the interaction of the gold-containing fragment with the Fe—Fe bond leaves the geometry of the initial core of $[Fe_3(\mu_3\text{-}OBu^t)(CO)_9]$ virtually unchanged. Thus, the addition of the Au atom at the Fe(1)—Fe(2) bond results in a slight elongation of the latter (2.585 Å) compared to that in the structure of **2a** and the average Fe—O distance increases to 1.954 Å (Table 2). The angle between the wings of the Fe_3Au "butterfly" in cluster **3** is 151.0°, which is substantially larger than those in the related clusters. The Au—Fe bond lengths (2.680 and 2.721 Å, see Table 2) are in the range typical of the closely related structures containing the $[(R_3P)(\mu_2\text{-}Au)\{Fe(CO)_3\}_2]$ fragment (2.622—2.760 Å; CSD data for 15 fragments).

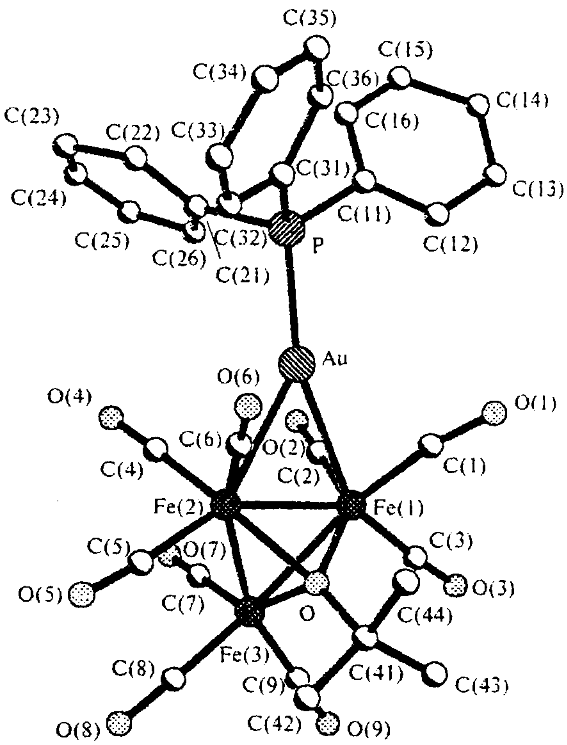


Fig. 2. Molecular structure of cluster **3**.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in molecule **3**

Bond	*d*/Å	Angle	ω/deg
Au—P	2.280(3)	P—Au—Fe(1)	155.44(1)
Au—Fe(1)	2.680(2)	P—Au—Fe(2)	146.8(1)
Au—Fe(2)	2.721(2)	Fe(1)—Au—Fe(2)	57.18(6)
Fe(1)—Fe(3)	2.490(3)	Fe(3)—Fe(1)—Fe(2)	58.87(7)
Fe(1)—Fe(2)	2.585(3)	Fe(3)—Fe(2)—Fe(1)	58.68(8)
Fe(2)—Fe(3)	2.495(3)	Fe(1)—Fe(3)—Fe(2)	62.46(8)
Fe(1)—O	1.952(8)	C(41)—O—Fe(2)	133.4(8)
Fe(2)—O	1.958(8)	C(41)—O—Fe(3)	130.7(8)
Fe(3)—O	1.952(9)	C(41)—O—Fe(1)	131.1(8)
O—C(41)	1.50(2)	Fe(2)—O—Fe(1)	82.8(3)
		Fe(3)—O—Fe(1)	79.3(3)
		Fe(2)—O—Fe(3)	79.3(3)

Previously,[24] the correlation between the dihedral angles in tetranuclear "butterfly" clusters and the number of cluster valence electrons was established. Thus 62-electron clusters are characterized by dihedral angles of 90—117°, while 64-electron clusters can be in essence described as a distorted rhombus rather than as a "butterfly" and the angles in these clusters are in the range of 140—180°. The angles between the "butterfly" wings for a series of analogous clusters containing the AuM_3 core are given in Table 3, from which it follows that the angles between the triangles have the largest values in the first two clusters, which contain the $AuRu_3$ and $AuFe_3$ cores and in which the bulky $\mathrm{Bu^t}$ group is bound to the μ_3 ligand.

The structure of the metal core of cluster **3** is shown in Fig. 3. It can be seen that the "butterfly" in cluster **3** is "turned" away from the μ_3-OR ligand. The Au atom is located so that it causes the minimum steric "disturbance" of the initial monoanion **2a**. The Au—C distances to the nearest CO groups are in the range of 2.627—2.753 Å. Hence, the $Au(PPh_3)^+$ fragment adds to the initial monoanion in such a way as to minimize the structural changes. As a result, the heterometallic "butterfly," which is turned inside out with respect to the bridging ligand, is formed. This butterfly contains the μ_3-O ligand on the outside rather than on the inside.

Table 3. Dihedral angles (φ) in the tetranuclear heterometallic "butterfly" clusters with the M_3Au core

Cluster	φ/deg	Reference
$AuFe_3(\mu_3\text{-}OBu^t)(CO)_9(PPh_3)$	151	*
$AuRu_3(\mu_3\text{-}SBu)(CO)_9(PPh_3)$	147.5	25
$AuRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$	129.3	26
$AuFe_3(\mu_3\text{-}SPr^i)(CO)_9(PPh_3)$	123.9	23
$AuRu_3(\mu\text{-}H)(\mu_3\text{-}PPh_3)(CO)_9(PMe_2Ph)$	106.2	27, 28
$AuRu_3(\mu_3\text{-}COMe)(CO)_{10}(PPh_3)$	117	29—31
$AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)$	111.8	29—31
$AuRu_3(\mu\text{-}Cl)(CO)_{10}(PPh_3)$	117.2	32

* The data of the present work.

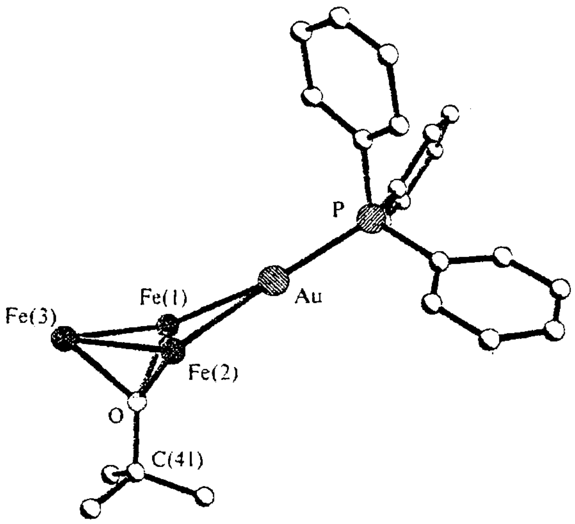


Fig. 3. Overall view of the heterometallic core of cluster **3** (CO ligands are omitted).

Experimental

The initial cluster $[Fe_3(\mu_3\text{-}O)(CO)_9]^{2-}$ (**1**) and $Au(PPh_3)Cl$ were prepared according to known procedures.[12,33] All experiments were carried out under an argon atmosphere using freshly distilled solvents. The elemental analysis of the resulting compounds was performed on a CHN-3 analyzer. The IR spectra were recorded on a Specord M-80 spectrophotometer. The IR spectrum of cluster **2a** is identical to that of dianion **1**, but the bands are shifted by 30 cm^{-1} to the high-frequency region. The IR spectrum of compound **3** does not have bands typical of bridging carbonyl groups and is shifted to the higher-frequency region.

[μ-Nitridobis(triphenylphosphine)(1+)]nanocarbonyl-μ$_3$-butoxytriferrate(1−), $[PPN][Fe_3(\mu_3\text{-}OBu^t)(CO)_9]$ (2a). A mixture of $[PPN]_2[Fe_3(\mu_3\text{-}O)(CO)_9]$ (**1a**) (0.453 g, 0.3 mmol) and Bu^tI (0.15 mL) in acetone (10 mL) was vigorously stirred under an argon atmosphere at −20 °C for 40 min. The solution was filtered and concentrated on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (10 mL) and the solution was filtered. Then hexane (20 mL) was added, the solution was partially evaporated, and brown crystals that precipitated were filtered off, washed with hexane, and dried *in vacuo*. Cluster **2a** was obtained in a yield of 0.295 g (95%). Found (%): C, 56.95; H, 3.69; N, 1.26. $C_{49}H_{39}Fe_3NO_{10}P_2$. Calculated (%): C, 57.07; H, 3.81; N, 1.36. IR (CH_2Cl_2), νCO/cm^{-1}: 2030 br, 1969 s, 1935 s, 1910 sh.

Tetraethylammoniumnanocarbonyl-μ$_3$-butoxytriferrate(1−), $[Et_4N][Fe_3(\mu_3\text{-}OMe)(CO)_9]$ (2b). A mixture of $[Et_4N]_2[Fe_3(\mu_3\text{-}O)(CO)_9]$ (0.696 g, 0.01 mmol) (**1a**) and MeI (0.3 mL) in acetone (10 mL) was vigorously stirred under an argon atmosphere at −20 °C for 40 min. Then the solution was treated as described above. Cluster **2b** was obtained in a yield of 0.546 g (94%). Found (%): C, 37.10; H, 3.85; N, 2.50. $C_{18}H_{23}Fe_3NO_{10}$. Calculated (%): C, 37.22; H, 3.99; N, 2.41. IR (CH_2Cl_2), νCO/cm^{-1}: 2030 br, 1969 s, 1935 s, 1910 sh.

Nanocarbonyl-μ$_3$-butoxy-μ$_2$-triphenylphosphinegoldtriiron, $[Fe_3(CO)_9(\mu_3\text{-}OBu^t)Au(PPh_3)]$ (3). A mixture of cluster **2a** (0.0502 g, 0.05 mmol), $Au(PPh_3)Cl$ (0.0247 g, 0.05 mmol), and $TlBF_4$ (0.0145 g, 0.05 mmol) in acetone (10 mL) was stirred under an argon atmosphere for 3 min. Then CH_2Cl_2 (10 mL) was added to the solution and the mixture was vigorously stirred for 30 min and filtered. The solvent was evaporated on a rotary evaporator. The residue was chromatographed on a column with silica gel using a 1 : 2 CH_2Cl_2—hexane mixture as the eluent. The brown fraction was separated and concentrated. Cluster **3** was obtained in a yield of 0.02 g (42%). Found (%): C, 39.00; H, 2.44. $C_{31}H_{24}AuFe_3O_{10}P$. Calculated (%): C, 39.11; H, 2.54. IR (hexane), νCO/cm^{-1}: 2047 m, 2000 vs, 1990 s, 1970 m, 1947 m, 1930 sh.

Table 4. Crystallographic data and details of X-ray diffraction study and structure refinement for compounds **2a** and **3**

Parameter	**2a**	**3**
Molecular formula	$C_{49}H_{39}Fe_3N_1O_{10}P_2$	$C_{31}H_{24}Au_1Fe_3O_{10}P_1$
Molecular weight	1031.30	951.99
System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	14.695(3)	13.173(3)
b/Å	18.838(4)	16.179(4)
c/Å	17.591(4)	16.518(3)
β/deg	93.63(3)	106.33(2)
V/Å^3	4860(2)	3378(1)
Z	4	4
d_{calc}/g cm^{-3}	1.410	1.872
F(000)	2112	1848
μ(Mo-Kα)/mm^{-1}	1.006	5.692
Crystal dimensions/mm	0.5×0.3×0.3	0.3×0.3×0.05
θ scanning mode /(range/deg)	ω/(2.06—25.96)	ω/(2.04—23.97)
Ranges of reflection indices	$-18 \le h \le 17$, $0 \le k \le 22$, $0 \le l \le 20$	$-15 \le h \le 14$, $-4 \le k \le 18$ $0 \le l \le 18$
Number of measured reflections	7720	5004
Number of independent reflections (R_{int})	7466 (0.0235)	4259 (0.0686)
Number of reflections with $I > 2\sigma(I)$	5250	2593
Number of refinable parameters	590	388
R factors:		
using reflections with $I > 2\sigma(I)$	$R_1 = 0.0426$, $wR_2 = 0.1310$	$R_1 = 0.0487$, $wR_2 = 0.1125$
using all reflections	$R_1 = 0.0728$, $wR_2 = 0.1576$	$R_1 = 0.1069$, $wR_2 = 0.1783$
Goodness of fit based on F^2	1.107	0.986
Residual electron density (min/max)/e · Å^{-3}	−0.365/0.396	−0.807/1.505*

* About the Au atom.

X-ray analysis of clusters 2a and 3. Crystals of **2a** were prepared by slow diffusion of hexane into a solution of this compound in CH_2Cl_2. Crystals of **3** were prepared by recrystallization from hexane. X-ray diffraction data sets were collected on an automated Enraf-Nonius CAD-4 diffractometer at −20 °C (Mo-Kα radiation, 0.71069 Å, graphite monochromator). Both structures were solved by direct methods[34] and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-93).[35] All hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. The crystallographic data and details of X-ray analysis and structure refinement for compounds **2a** and **3** are given in Table 4.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-32976a and 98-03-33142a).

References

1. E. Sappa, A. Tiripicchio, A. J. Carty, and G. E. Toogood, in *Progress in Inorganic Chemistry*, Ed. S. J. Lippard, Wiley, New York, 1987, **35**, 437.
2. K. S. Wong, W. R. Scheidt, and T. P. Fehlner, *J. Am. Chem. Soc.*, 1982, **104**, 1111.
3. C. E. Housecroft and A. L. Rheingold, *Organometallics*, 1987, **6**, 1332.
4. J. A. Hriljac, P. N. Swepston, and D. F. Shriver, *Organometallics*, 1985, **4**, 158.
5. J. A. Hriljac, E. M. Holt, and D. F. Shriver, *Inorg. Chem.*, 1987, **26**, 2943.
6. S. P. Gubin, T. V. Galuzina, I. F. Golovaneva, A. P. Klyagina, L. A. Poliakova, O. A. Belyakova, Ya. V. Zubavichus, and Yu. L. Slovokhotov, *J. Organomet. Chem.*, 1997, **549**, 55.
7. M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 4541.
8. E. M. Holt, K. H. Whitmire, and D. F. Shriver, *J. Organomet. Chem.*, 1981, **213**, 125.
9. D. E. Fjare and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1984, **106**, 4799.
10. M. Tachikawa, J. Stein, E. L. Muetterties, R. G. Teller, M. A. Beno, E. Gebert, and J. M. Williams, *J. Am. Chem. Soc.*, 1980, **102**, 6648.
11. D. E. Fjare and W. L. Gladfelter, *Inorg. Chem.*, 1981, **20**, 3533.
12. C. K. Schauer, S. Harris, M. Sabat, E. J. Voss, and D. F. Shriver, *Inorg. Chem.*, 1995, **34**, 5017.
13. S. H. Adams, L. J. Gill, and M. J. Morris, *Organometallics*, 1996, **5**, 464.
14. J. R. Shapley, J. R. Park, J. T. Churchill, M. R. Ziller, and L. R. Beanan, *J. Am. Chem. Soc.*, 1984, **106**, 1144.
15. P. R. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby, and K. H. Whitmire, *J. Chem. Soc., Chem. Comm.*, 1983, 246.
16. C. K. Schauer, E. J. Voss, M. Sabat, and D. F. Shriver, *J. Am. Chem. Soc.*, 1989, **111**, 7662.
17. C.-J. Su, P.-C. Su, Y. Chi, S.-M. Peng, and G.-H. Lee, *J. Am. Chem. Soc.*, 1996, **118**, 3289.
18. M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983, 344.
19. F. Bottomley and L. Sutin, in *Advances in Organometallic Chemistry*, Eds. F. G. A. Stone and R. West, Academic Press, New York, 1988, **28**, 339.
20. L. A. Poliakova, S. P. Gubin, O. A. Belyakova, Ya. V. Zubavichus, and Yu. L. Slovokhotov, *Organometallics*, 1997, **16**, 4527.
21. A. Ceriotti, L. Resconi, F. Demartin, G. Longoni, M. Manassero, and M. Sansoni, *J. Organomet. Chem.*, 1983, **249**, C35.
22. F. H. Allen and O. Kennard, *Chemical Design Automation News*, 1993, **8**, 1.
23. E. Delgado, E. Hernandez, O. Rossell, M. Seco, and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1993, 2191.
24. A. J. Carty, S. A. MacLaughlin, J. Van Wagner, and N. J. Taylor, *Organometallics*, 1982, **1**, 1013.
25. M. I. Bruce and O. B. Shawkataly, *J. Organomet. Chem.*, 1985, **286**, 427.
26. P. Braunstein, G. Predieri, A. Tiripicchio, and E. Sappa, *Inorg. Chim. Acta*, 1982, **63**, 113.
27. M. J. Mays, P. R. Raithby, P. L. Taylor, and K. Henrick, *J. Organomet. Chem.*, 1982, **224**, C45.
28. M. J. Mays, P. R. Raithby, P. L. Taylor, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 959.
29. L. W. Bateman, M. Green, J. A. K. Howard, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Comm.*, 1982, 773.
30. L. W. Bateman, M. Green, J. A. K. Howard, K. A. Mead, R. M. Mills, I. D. Salter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2599.
31. J. A. K. Howard, I. D. Salter, and F. G. A. Stone, *Polyhedron*, 1984, **3**, 567.
32. G. Lavigne, R. Papageorgiou, and J.-J. Bonnet, *Inorg. Chem.*, 1984, **23**, 609.
33. M. I. Bruce, B. K. Nicholson, and O. B. Shawkataly, in *Inorganic Synthesis*, Ed. H. D. Kaesz, Wiley, New York, 1989, **26**, 324.
34. G. M. Sheldrick, *Acta Crystallogr., A*, 1990, **A46**, 467.
35. G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1993.

Received March 19, 1999