$Os_3(CO)_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Fc)\}$, the second example of a cluster with the "face" coordination of the metallacyclopentadiene fragment and its conversion to the $Os_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}\eta^1\text{-}C(SiMe_3)C(Me)C(H)C(C_5H_3FeC_5H_5)\}$ complex with the *ortho*-metallated ferrocene moiety

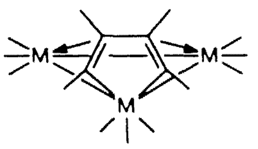
A. A. Koridze,[*] A. M. Sheloumov, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov,[†] and P. V. Petrovskii

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: koridz@ineos.ac.ru

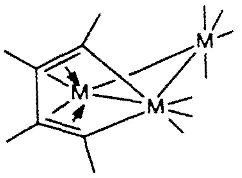
$Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ alkyne complexes react with ferrocenylacetylene in hot benzene to form $Os_3(CO)_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Fc)\}$ and a small amount of the isomeric $Os_3(CO)_9\{\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}C(SiMe_3)C(Me)C(Fc)C(H)\}$ complex. The structure of the major isomer was confirmed by X-ray structural analysis of the single crystal. Thermolysis of this complex in refluxing benzene affords the $Os_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}\eta^1\text{-}C(SiMe_3)C(Me)C(H)C(C_5H_3FeC_5H_5)\}$ complex with the *ortho*-metallated ferrocene moiety. The spectral characteristics of clusters with the $\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2$ and $\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4$ coordinations of the metallacyclopentadiene fragment have been established, which made it possible to choose between the alternative modes of bonding of diene with the trimetallic core.

Key words: osmium clusters, alkynes, dimerization of alkynes, osmacyclopentadienes, ferrocenylacetylene, silylacetylenes, X-ray structural study.

Recently,[1,2] it was reported that the $Os_3(CO)_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Ph)\}$ cluster (**2a**), in which the metallacyclopentadiene fragment is symmetrically located with respect to the metal triangle, was obtained for the first time. Although the possibility of formation of clusters with this "face" coordination of the diene unit (the type **I** structure) in reactions of cluster metal carbonyls with acetylenes has been discussed for more than 20 years,[3,4] all osmium, ruthenium, and iron clusters with the metallacyclopentadiene fragment have the "side" $\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4$ coordination[3,5—10] (the type **II** structure).



I



II

In this work, the second example of the triosmium cluster of type **I**, $Os_3(CO)_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Fc)\}$, is described, and the results of X-ray structural analysis are given. Thermolysis of this cluster was carried out to form the $Os_3(\mu\text{-}H)(CO)_8\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}\eta^1\text{-}C(SiMe_3)C(Me)C(H)\text{—}C(C_5H_3FeC_5H_5)\}$ complex with the *ortho*-metallated ferrocene unit; the spectral characteristics of complexes of types **I** and **II** have been established, which makes it possible to choose between these alternative structures.

Results and Discussion

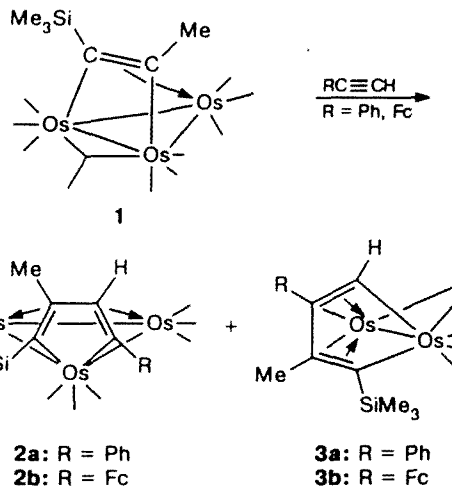
The $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}Me_3SiC_2Me)$ alkyne cluster (**1**)[11] reacts with ferrocenylacetylene FcC≡CH in hot benzene to give isomeric clusters $Os_3(CO)_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Fc)\}$ (**2b**) and $Os_3(CO)_9\{\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}C(SiMe_3)C(Me)C(Fc)C(H)\}$ (**3b**), which are ferrocene analogs of the $Os_3(CO)_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}C(SiMe_3)C(Me)C(H)C(Ph)\}$ (**2a**) and $Os_3(CO)_9\{\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}C(SiMe_3)C(Me)C(Ph)C(H)\}$ clusters (**3a**), respectively (Scheme 1), characterized recently.[1,2]

The major product of the reaction, cluster **2b**, was isolated from the reaction mixture chromatographically on a column packed with silica gel and was characterized by elemental analysis, spectroscopy (IR and ^1H NMR), and by X-ray structural study of the single crystal (see below).

[†] Deceased.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 741—747, March, 1996.

Scheme 1



As demonstrated recently,[1,2] thermolysis of cluster **2a** affords $Os_3(\mu$-$H)(CO)_8\{\mu$-η^1-η^1-η^4-η^1-$C(SiMe_3)C(Me)C(H)C(C_6H_4)\}$ hydride (**4a**) with the *ortho*-metallated benzene ring. Previously, formation of analogous products was observed upon thermolysis of clusters of type **II** containing the aryl substituents in the α position of the metallacyclopentadiene rings.[3,6,10] Now we establish that thermolysis of cluster **2b** in refluxing benzene proceeds with *ortho*-metallation of the ferrocenyl group to give $Os_3(\mu$-$H)(CO)_8\{\mu_3$-η^1-η^1-η^4-η^1-$C(SiMe_3)C(Me)C(H)C(C_5H_3FeC_5H_5)\}$ hydride (**4b**) (Scheme 2).

Scheme 2

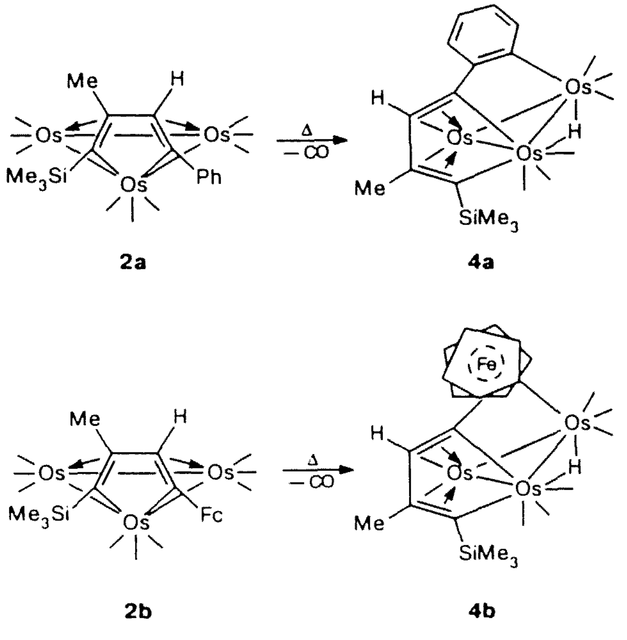


Table 1. Spectroscopic data for complexes **2a,b—4a,b**[a]

Complex	^{1}H NMR[b], δ, *J*/Hz	IR, ν(CO)[c]/cm^{-1}
2a	7.06—7.40 (m, 5 H), 5.69 (s, 1 H), 2.14 (s, 3 H), 0.34 (s, 9 H)	2085 m, 2049 v.s, 2026 v.w, 2011 s, 1996 w, 1984 m
2b	6.24 (s, 1 H), 4.27 (m, 1 H), 4.20 (m, 1 H), 4.17 (s, 5 H), 4.15 (m, 1 H), 4.12 (m, 1 H), 2.23 (s, 3 H), 0.47 (s, 9 H)	2089 s, 2050 v.s, 2013 v.s, 2000 (sh), 1993 (sh), 1988 s
3a	7.93 (s, 1 H), 7.06—7.20 (m, 5 H), 2.30 (s, 3 H), 0.50 (s, 9 H)	2108 m, 2053 v.s, 2035 m, 2030 s, 2011 v.s, 1994 m, 1982 m, 1936 m.
3b	8.41 (s, 1 H), 4.3—4.1 (m, 4 H), 4.18 (s, 5 H), 2.49 (s, 3 H), 0.50 (s, 9 H)	
4a	6.9—8.0 (m, 4 H), 6.11 (s, 1 H), 2.29 (s, 3 H), 0.34 (s, 9 H), −14.76 (s, 1 H, $^1J_{OsH}$ = 32.3, 60.5)	2095 s, 2055 s, 2029 v.s, 2017 s, 2012 m, 1995 m, 1985 s, 1972 m
4b	6.57 (s, 1 H), 4.48 (m, 1 H), 4.39 (m, 1 H), 4.01 (s, 5 H), 3.93 (m, 1 H), 2.45 (s, 3 H), 0.33 (s, 9 H), −13.91 (s, 1 H, $^1J_{OsH}$ = 32.6, 61.0)	2095 s, 2056 s, 2030 v.s, 2017 s, 2012 s, 1997 m, 1985 m, 1970 m

[a] At room temperature.
[b] In a C_6D_6 solution.
[c] In a hexane solution.

Therefore, thermolysis of clusters **2a** and **2b** with type **I** structures with the μ_3-η^1-η^1-η^2-η^2 coordinated diene fragment affords hydride complexes **4a** and **4b**, respectively; in these complexes, the diene carbon atoms are μ-η^1-η^1-η^4 coordinated by the metal core. Because products with analogous structures are also formed from $Os_3(CO)_9(\mu$-η^1-η^1-η^4-$C_4Ph_4)$[1] and related complexes,[10] which have structures **II**, it remains unclear whether the **2a,b**→**4a,b** conversion involves initial decarbonylation of complexes **2a,b** and subsequent rearrangement of the diene ligand from the face position to the side position accompanied by *ortho*-metallation of the aromatic ring, or whether isomerization of **2a,b** to unstable intermediates, which have structures **II**, the $Os_3(CO)_9\{\mu$-η^1-η^1-η^4-$C(SiMe_3)C(Me)C(H)C(R)\}$ clusters (R = Ph or Fc), occurs.

Table 1 gives spectral characteristics of clusters **2a—4a** and **2b—4b** containing the phenyl and ferrocenyl groups as substituents at the five-membered heterocycle.

The preliminary conclusion about the structure of cluster **2b** was based on spectroscopic data. The IR spectrum of cluster **2b** is similar to that of cluster **2a**, whose structure was unambiguously established by X-ray structural analysis[2] and clearly differs from the spectra of complex **3a** and related compounds of type **II**. The

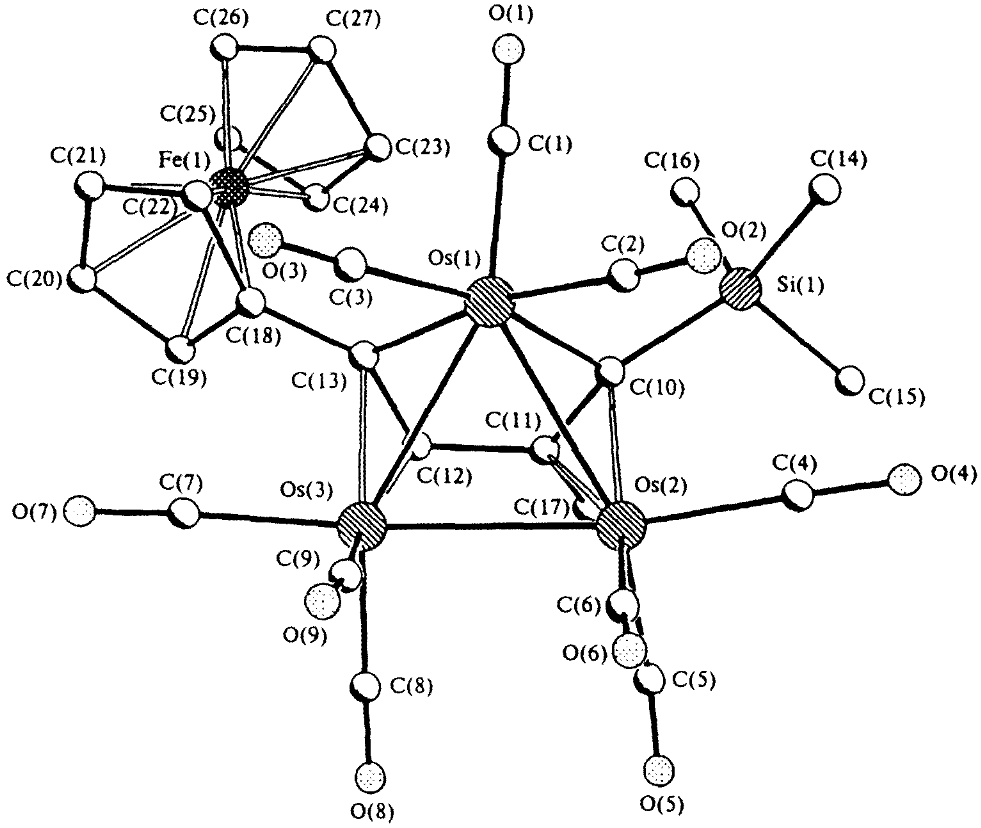


Fig. 1. Structure of molecule **2b**.

occurrence of the medium intensity absorption band in the region 2100 cm^{-1}, which (*cf.* the spectra of complexes **2a** and **3a**) is not observed in the spectra of complexes **2a** and **2b**, is typical of complex **3a** and related compounds.

When examining the ^{1}H NMR spectra of the pairs of complexes **2a** and **2b**, **3a** and **3b**, **4a** and **4b**, the systematic deshielding of the signal of the single hydrogen atom of the diene ligand by ~0.5 p.p.m. in going from the phenyl to the ferrocenyl derivative attracted our attention. Because ferrocenyl is not an electron-withdrawing substituent compared to phenyl (in uncharged compounds, the electronic effect of the ferrocenyl is similar to those of alkyl groups[12]), the spectral regularity mentioned should be the result of magnetic anisotropy of aromatic rings of the corresponding groups, which have different orientations with respect to the H atom because of the difference in the volumes of the phenyl and ferrocenyl groups.

The conclusion about the structure of cluster **2b**, which was made based on the spectral data, was confirmed by X-ray structural study of the single crystal.

The crystal structure of **2b** contains two independent molecules (A and B), which are characterized by virtually identical geometric parameters. The structure of one molecule is shown in the figure; the bond lengths and the selected bond angles are given in Tables 2 and 3, respectively.

The replacement of the Ph substituent at one of the α carbon atoms of the osmacyclopentadienyl fragment in **2a** by ferrocenyl in **2b** has essentially no noticeable effect on the geometry of the coordination unit of the complex. As in the case of **2a**, in both molecules of **2b**, the osmacyclopentadiene cycle adopts an envelope conformation; the folding angle along the C(10)...C(13) line is 27.5° and 26.0° and the Os(1) atom deviates from the C(10)C(11)C(12)C(13) plane by 0.769 and 0.731 Å in molecules A and B, respectively (the corresponding values in **2a** are 28.8° and 0.794 Å). The most remarkable geometric feature (asymmetry of the π-bonds of the Os(2) and Os(3) atoms with the corresponding olefin fragments of metallacyclopentadiene) observed in the structure of **2b** is retained in the structure of **2a**. Actually, as in **2a**, one osmium atom in **2b** (the Os(3) atom) is located at equal distances from the C atoms of the olefin bond coordinated to the above-mentioned Os atom (Os(3)—C(12) 2.26(1) and 2.27(1), Os(3)—C(13) 2.25(1) and 2.25(1) Å in A and B, respectively), whereas the second osmium atom (Os(2)) forms substantially unequal bonds with the C atoms of the second olefin fragment of the osmacyclopentadiene ring (Os(2)—C(10) 2.17(1) and 2.17(1), Os(2)—C(11) 2.43(1) and

Table 2. Bond lengths in the structure of **2b**

Bond	d/Å A	d/Å B	Bond	d/Å A	d/Å B	Bond	d/Å A	d/Å B
Os(1)—C(1)	1.88 (1)	1.89 (1)	Fe(1)—C(23)	2.01 (2)	2.00 (2)	O(6)—C(6)	1.10 (2)	1.13 (2)
Os(1)—C(2)	1.93 (2)	1.95 (2)	Fe(1)—C(18)	2.03 (1)	2.07 (1)	O(7)—C(7)	1.12 (2)	1.12 (2)
Os(1)—C(3)	1.94 (1)	1.91 (1)	Fe(1)—C(19)	2.03 (1)	2.02 (1)	O(8)—C(8)	1.13 (2)	1.12 (2)
Os(1)—C(13)	2.15 (1)	2.15 (1)	Fe(1)—C(24)	2.02 (2)	2.03 (2)	O(9)—C(9)	1.13 (2)	1.14 (2)
Os(1)—C(10)	2.19 (1)	2.18 (1)	Fe(1)—C(27)	2.04 (2)	2.04 (2)	C(10)—C(11)	1.39 (2)	1.41 (2)
Os(1)—Os(3)	2.818 (1)	2.825 (1)	Fe(1)—C(25)	2.03 (2)	2.03 (2)	C(11)—C(12)	1.49 (2)	1.47 (2)
Os(1)—Os(2)	2.819 (1)	2.831 (1)	Fe(1)—C(21)	2.04 (1)	2.04 (2)	C(11)—C(17)	1.52 (2)	1.52 (2)
Os(2)—C(5)	1.89 (1)	1.85 (2)	Fe(1)—C(22)	2.04 (1)	2.05 (1)	C(12)—C(13)	1.41 (2)	1.41 (2)
Os(2)—C(4)	1.92 (2)	1.94 (2)	Fe(1)—C(26)	2.04 (2)	2.03 (2)	C(13)—C(18)	1.49 (2)	1.47 (2)
Os(2)—C(6)	1.93 (2)	1.91 (2)	Fe(1)—C(20)	2.04 (2)	2.03 (2)	C(18)—C(19)	1.41 (2)	1.43 (2)
Os(2)—C(10)	2.17 (1)	2.17 (1)	Si(1)—C(16)	1.85 (2)	1.89 (2)	C(18)—C(22)	1.41 (2)	1.44 (2)
Os(2)—C(11)	2.43 (1)	2.48 (1)	Si(1)—C(14)	1.86 (2)	1.82 (2)	C(19)—C(20)	1.40 (2)	1.36 (2)
Os(2)—Os(3)	2.804 (1)	2.815 (1)	Si(1)—C(15)	1.87 (2)	1.87 (1)	C(20)—C(21)	1.40 (2)	1.41 (3)
Os(3)—C(8)	1.90 (1)	1.90 (2)	Si(1)—C(10)	1.91 (1)	1.91 (1)	C(21)—C(22)	1.40 (2)	1.42 (2)
Os(3)—C(9)	1.92 (2)	1.90 (2)	O(1)—C(1)	1.13 (2)	1.16 (2)	C(23)—C(24)	1.37 (3)	1.42 (3)
Os(3)—C(7)	1.94 (2)	1.93 (2)	O(2)—C(2)	1.15 (2)	1.14 (2)	C(23)—C(27)	1.40 (3)	1.35 (3)
Os(3)—C(13)	2.25 (1)	2.25 (1)	O(3)—C(3)	1.13 (2)	1.16 (2)	C(24)—C(25)	1.35 (3)	1.39 (3)
Os(3)—C(12)	2.26 (1)	2.27 (1)	O(4)—C(4)	1.13 (2)	1.11 (2)	C(25)—C(26)	1.39 (3)	1.39 (3)
			O(5)—C(5)	1.12 (2)	1.15 (2)	C(26)—C(27)	1.38 (3)	1.35 (3)

2.48(1) Å). The asymmetry, which is less pronounced but clearly observed, in the osmacyclopentadiene ligand in all three cases (in the structure of **2a** and two independent molecules **2b**) is associated with the difference in endocyclic σ-bonds with the participation of the Os(1) atom; in all three cases, the distance to the C(10) atom that bears the trimethylsilyl substituent (2.19(1) and 2.18(1) Å in molecules A and B, respectively) appears to be slightly longer than the Os(1)—C(13) bond (2.15(1) and 2.14(1) Å in A and B, respectively).

The causes of the geometric features of molecules **2a** and **2b** noted are not entirely known. It can be proposed that the repulsion between the C(17)H$_3$ methyl group and the C(5)O(5) carbonyl (the C(17)...C(5) distance is 3.27(2) and 3.24(2) Å in A and B, respectively) plays a particular role in the asymmetry of π-coordination, whereas elongation of the Os(1)—C(10) distance is favorable for relieving unfavorable contacts between the trimethylsilyl group and the carbonyls at the Os(1) atom (Si(1)...C(4) 3.23(1) and 3.31(1) Å in molecules A and B, respectively). It is also not improbable that some geometric distortions are caused by a strong positive inductive effect of the trimethylsilyl group. Unfortunately, it is impossible to test this proposal because the described structures are, as far as we know, the first examples of π-complexes in which the olefin fragment with the trimethylsilyl and methyl substituents is involved in π-coordination of the transition metal.

Experimental

All reactions were carried out under an argon atmosphere. The obtained compounds are air-stable, and their chromatographic separation was carried out by column or thin-layer chromatography on silica gel. The solvents were purified by distillation under an inert atmosphere over drying agents. IR spectra were recorded on a Bruker IFS-113v spectrometer; ^{1}H NMR spectra were obtained on a Bruker WP-200SY spectrometer.

Reaction of $Os_3(\mu-CO)(CO)_9(\mu_3-Me_3SiC_2Me)$ with ferrocenylacetylene. A solution of $Os_3(\mu-CO)(CO)_9(\mu_3-Me_3SiC_2Me)$ (155 mg, 0.161 mmol) and ferrocenylacetylene (44 mg, 0.209 mmol) in 30 mL of benzene was stirred at 50—55 °C for 5 h. The color of the solution changed from yellow to violet. Then the solvent was removed *in vacuo*, and the residue was separated chromatographically on a column with hexane as eluent. Unreacted FcC≡CH (yellow band), $Os_3(CO)_9\{\{\mu_3-C(SiMe_3)C(Me)C(H)C(Fc)\}$ (**2b**) (87 mg, 47 %, dark-violet band), and $Os_3(CO)_9\{\{\mu-C(SiMe_3)C(Me)C(Fc)-C(H)\}$ (**3b**) (8 mg, 4 %, red band) were washed off successively. Analysis of compound **2b**. Found (%): C, 28.54; H, 2.06; Fe, 4.43; Os, 49.58; Si, 2.94. $C_{27}H_{12}FeO_{10}Os_3Si$. Calculated (%): C, 28.31; H, 1.92; Fe 4.87; Os, 49.85; Si, 2.45.

Thermolysis of complex 2b. A solution of complex **2b** (87 mg, 0.077 mmol) in 40 mL of benzene was refluxed for 6 h. The color of the solution gradually changed from dark violet to dark brown. After evaporation of benzene *in vacuo*, the residue was chromatographed on silica gel plates; hexane was used as an eluent. The $Os_3(\mu-H)(CO)_8(\{\mu_3-C(SiMe_3)C(Me)C(H)C(C_5H_3FeC_5H_5)\}$ complex (**4b**) was obtained in a yield of 55 mg (65 %). We failed to isolate this complex in analytically pure form; its spectral characteristics are given in Table 1.

X-ray structural study of 2b. Crystals of compound **2b** suitable for X-ray structural analysis were grown from a hexane solution at −5 °C. Crystals of **2b** are triclinic, at 20 °C a = 10.057 (4), b = 15.401 (6), c = 20.076 (7) Å, α = 95.24 (3), β = 97.68 (3), g = 98.84 (3), V = 3025 (2) Å^3, d_{calc} = 2.514 g cm^{-3}, Z = 4, space group $P\bar{1}$. The unit cell parameters and intensities of 12014 independent reflections were measured on a four-circle automated Siemens P3/PC

Table 3. Selected bond angles in the structure of **2b**

Angle	φ/deg	
	A	B
C(1)—Os(1)—C(2)	94.7 (7)	94.0 (6)
C(1)—Os(1)—C(3)	96.6 (6)	93.9 (6)
C(2)—Os(1)—C(3)	93.1 (6)	91.0 (7)
C(1)—Os(1)—C(13)	92.9 (5)	93.0 (5)
C(2)—Os(1)—C(13)	171.3 (6)	171.0 (5)
C(3)—Os(1)—C(13)	90.2 (5)	94.1 (6)
C(1)—Os(1)—C(10)	91.4 (5)	95.9 (5)
C(2)—Os(1)—C(10)	96.0 (5)	94.9 (6)
C(3)—Os(1)—C(10)	167.3 (5)	168.1 (6)
C(13)—Os(1)—C(10)	79.6 (5)	78.7 (5)
C(1)—Os(1)—Os(3)	144.5 (4)	143.7 (4)
C(2)—Os(1)—Os(3)	120.8 (5)	122.0 (5)
C(3)—Os(1)—Os(3)	81.1 (4)	82.6 (5)
C(13)—Os(1)—Os(3)	51.8 (3)	51.6 (3)
C(10)—Os(1)—Os(3)	86.7 (3)	85.5 (3)
C(1)—Os(1)—Os(2)	138.0 (4)	142.1 (4)
C(2)—Os(1)—Os(2)	78.2 (4)	77.4 (5)
C(3)—Os(1)—Os(2)	124.8 (4)	122.8 (5)
C(13)—Os(1)—Os(2)	93.3 (3)	93.6 (3)
C(10)—Os(1)—Os(2)	49.3 (3)	49.2 (3)
Os(3)—Os(1)—Os(2)	59.67 (2)	59.69 (3)
C(5)—Os(2)—C(4)	92.4 (7)	91.8 (6)
C(5)—Os(2)—C(6)	90.2 (7)	90.3 (7)
C(4)—Os(2)—C(6)	88.6 (9)	89.8 (7)
C(5)—Os(2)—Os(10)	118.8 (6)	117.0 (6)
C(4)—Os(2)—C(10)	88.5 (6)	91.2 (6)
C(6)—Os(2)—C(10)	150.9 (7)	152.6 (6)
C(5)—Os(2)—C(11)	91.4 (6)	90.4 (5)
C(4)—Os(2)—C(11)	112.0 (7)	115.3 (5)
C(6)—Os(2)—C(11)	159.3 (7)	154.9 (6)
C(10)—Os(2)—C(11)	34.8 (4)	34.6 (4)
C(5)—Os(2)—Os(3)	99.7 (5)	101.5 (4)
C(4)—Os(2)—Os(3)	167.7 (5)	166.2 (4)
C(6)—Os(2)—Os(3)	89.1 (6)	86.7 (5)
C(10)—Os(2)—Os(3)	87.6 (3)	85.9 (3)
C(11)—Os(2)—Os(3)	70.3 (3)	68.6 (3)
C(5)—Os(2)—Os(1)	154.5 (5)	154.8 (4)
C(4)—Os(2)—Os(1)	108.8 (5)	108.2 (5)
C(6)—Os(2)—Os(1)	104.0 (5)	104.5 (4)
C(10)—Os(2)—Os(1)	50.2 (3)	49.5 (3)
C(11)—Os(2)—Os(1)	67.9 (3)	67.5 (3)
Os(3)—Os(2)—Os(1)	60.15 (3)	60.06 (2)
C(8)—Os(3)—C(9)	96.7 (6)	97.2 (6)
C(8)—Os(3)—C(7)	93.7 (6)	93.1 (6)
C(9)—Os(3)—C(7)	89.3 (7)	88.2 (6)
C(8)—Os(3)—C(13)	127.6 (5)	129.6 (6)
C(9)—Os(3)—C(13)	135.6 (5)	132.9 (5)
C(7)—Os(3)—C(13)	84.7 (6)	85.3 (5)
C(8)—Os(3)—C(12)	94.0 (5)	95.3 (5)
C(9)—Os(3)—C(12)	164.6 (6)	165.2 (6)
C(7)—Os(3)—C(12)	101.0 (6)	99.0 (5)
C(13)—Os(3)—C(12)	36.3 (4)	36.3 (4)
C(8)—Os(3)—Os(2)	90.6 (5)	88.9 (4)
C(9)—Os(3)—Os(2)	91.7 (5)	93.6 (4)
C(7)—Os(3)—Os(2)	175.4 (4)	177.1 (4)
C(13)—Os(3)—Os(2)	91.5 (3)	91.8 (3)
C(12)—Os(3)—Os(2)	77.2 (3)	78.7 (3)
C(8)—Os(3)—Os(1)	148.1 (5)	147.1 (5)
C(9)—Os(3)—Os(1)	96.7 (4)	95.9 (5)
C(7)—Os(3)—Os(1)	115.3 (4)	117.3 (4)
C(13)—Os(3)—Os(1)	48.6 (3)	48.4 (3)
C(12)—Os(3)—Os(1)	68.7 (3)	69.3 (3)
Os(2)—Os(3)—Os(1)	60.18 (2)	60.25 (2)
C(16)—Si(1)—C(14)	106.6 (9)	107.6 (8)
C(16)—Si(1)—C(15)	105.9 (9)	106.6 (8)
C(14)—Si(1)—C(15)	107.6 (9)	107.9 (7)
C(16)—Si(1)—C(10)	108.1 (7)	106.5 (7)
C(14)—Si(1)—C(10)	112.7 (7)	111.9 (7)
C(15)—Si(1)—C(10)	115.5 (7)	116.0 (7)
O(1)—C(1)—Os(1)	178.1 (12)	177.2 (13)
O(2)—C(2)—Os(1)	177.1 (14)	176.0 (2)
O(3)—C(3)—Os(1)	178.1 (14)	178.0 (2)
O(4)—C(4)—Os(2)	175.0 (2)	174.0 (2)
O(5)—C(5)—Os(2)	175.7 (14)	177.1 (13)
O(6)—C(6)—Os(2)	175.0 (2)	176.7 (13)
O(7)—C(7)—Os(3)	175.0 (2)	178.3 (13)
O(8)—C(8)—Os(3)	176.0 (13)	178.0 (2)
O(9)—C(9)—Os(3)	174.0 (2)	176.7 (14)
C(11)—C(10)—Si(1)	122.9 (9)	120.3 (9)
C(11)—C(10)—Os(2)	82.9 (8)	84.9 (7)
Si(1)—C(10)—Os(2)	124.6 (6)	123.5 (6)
C(11)—C(10)—Os(1)	108.3 (8)	109.4 (8)
Si(1)—C(10)—Os(1)	123.7 (6)	124.8 (6)
Os(2)—C(10)—Os(1)	80.5 (4)	81.3 (4)
C(10)—C(11)—C(12)	116.8 (10)	116.5 (11)
C(10)—C(11)—C(17)	126.5 (13)	126.4 (12)
C(12)—C(11)—C(17)	114.1 (12)	114.8 (12)
C(10)—C(11)—Os(2)	62.3 (7)	60.6 (7)
C(12)—C(11)—Os(2)	106.6 (8)	108.0 (8)
C(17)—C(11)—Os(2)	116.7 (10)	115.4 (8)
C(13)—C(12)—C(11)	118.2 (11)	117.0 (11)
C(13)—C(12)—Os(3)	71.4 (7)	71.0 (7)
C(11)—C(12)—Os(3)	105.7 (9)	104.3 (8)
C(12)—C(13)—C(18)	122.4 (11)	120.1 (11)
C(12)—C(13)—Os(1)	107.6 (9)	109.6 (8)
C(18)—C(13)—Os(1)	129.6 (8)	130.1 (9)
C(12)—C(13)—Os(3)	72.3 (7)	72.8 (7)
C(18)—C(13)—Os(3)	119.1 (9)	117.4 (9)
Os(1)—C(13)—Os(3)	79.6 (4)	80.0 (4)
C(19)—C(18)—C(22)	108.7 (12)	105.0 (12)
C(19)—C(18)—C(13)	124.9 (11)	127.3 (12)
C(22)—C(18)—C(13)	126.4 (12)	127.7 (12)
C(20)—C(19)—C(18)	107.9 (12)	111.0 (2)
C(21)—C(20)—C(19)	107.0 (14)	108.8 (14)
C(20)—C(21)—C(22)	110.3 (13)	107.4 (14)
C(21)—C(22)—C(18)	106.1 (13)	108.0 (2)
C(24)—C(23)—C(27)	106.0 (2)	110.0 (2)
C(25)—C(24)—C(23)	109.0 (2)	105.0 (2)
C(24)—C(25)—C(26)	110.0 (2)	108.0 (2)
C(27)—C(26)—C(25)	105.0 (2)	109.0 (2)
C(26)—C(27)—C(23)	110.0 (2)	108.0 (2)

diffractometer (20 °C, Mo-*K*α-radiation, graphite monochromator, θ/2θ scanning technique, θ < 25).

The structure was solved by the direct method. The atomic coordinates of the Os atom were located from the E-synthesis;

Table 4. Atomic coordinates (×10⁴) and isotropic equivalent temperature factors (×10³/ Å) in the structure of **2b**

Atom	Molecule A				Molecule B			
	x	*y*	*z*	U_{eq}	*x*	*y*	*z*	U_{eq}
Os(1)	3605 (1)	1128 (1)	4324 (1)	30 (1)	2491 (1)	−7720 (1)	−1653 (1)	29 (1)
Os(2)	1682 (1)	1176 (1)	3176 (1)	37 (1)	4337 (1)	−7967 (1)	−520 (1)	33 (1)
Os(3)	1643 (1)	2247 (1)	4378 (1)	34 (1)	5040 (1)	−6598 (1)	−1312 (1)	31 (1)
Fe(1)	6582 (2)	3693 (1)	5448 (1)	41 (1)	842 (2)	−5087 (1)	−2041 (1)	40 (1)
Si(1)	5063 (1)	1140 (3)	2772 (2)	42 (1)	909 (4)	−8095 (3)	−161 (2)	40 (1)
O(1)	6592 (11)	1057 (8)	4654 (6)	56 (3)	−534 (12)	−7791 (9)	−2120 (7)	80 (4)
O(2)	2748 (15)	−854 (7)	3831 (6)	76 (4)	2137 (15)	−9761 (7)	−1772 (6)	72 (4)
O(3)	2892 (13)	833 (8)	5736 (5)	63 (3)	3211 (14)	−7752 (9)	−3092 (6)	76 (4)
O(4)	1908 (15)	−289 (11)	2088 (8)	97 (5)	−3313 (14)	−9708 (9)	4 (7)	83 (4)
O(5)	−52 (13)	2100 (10)	2227 (6)	77 (4)	6298 (13)	−7337 (9)	756 (6)	73 (4)
O(6)	−810 (15)	−48 (13)	3430 (8)	114 (6)	6448 (15)	−8907 (9)	−1096 (7)	81 (4)
O(7)	1719 (12)	3338 (10)	5740 (6)	74 (4)	5683 (11)	−5099 (8)	−2177 (6)	60 (3)
O(8)	−190 (10)	3322 (8)	3607 (6)	60 (3)	7398 (11)	−5855 (8)	−210 (6)	61 (3)
O(9)	−520 (13)	920 (9)	4844 (8)	82 (4)	6518 (12)	−7697 (8)	−2208 (7)	67 (3)
C(1)	5467 (13)	1071 (9)	4524 (6)	34 (3)	623 (14)	−7742 (9)	−1947 (7)	40 (3)
C(2)	3073 (20)	−111 (12)	3998 (7)	60 (5)	2317 (17)	−9006 (12)	−1712 (8)	53 (4)
C(3)	3163 (16)	957 (10)	5221 (6)	42 (3)	2956 (16)	−7727 (11)	−2544 (7)	47 (4)
C(4)	1876 (18)	281 (12)	2482 (9)	59 (4)	3625 (17)	−9060 (12)	−180 (8)	54 (4)
C(5)	612 (15)	1740 (11)	2560 (7)	45 (4)	5548 (15)	−7601 (9)	267 (8)	44 (3)
C(6)	65 (20)	426 (15)	3339 (8)	76 (6)	5658 (15)	−8543 (10)	−898 (8)	48 (4)
C(7)	1748 (16)	2959 (11)	5241 (7)	48 (4)	5426 (15)	−5653 (11)	−1863 (7)	45 (4)
C(8)	458 (14)	2909 (10)	3907 (8)	44 (4)	6539 (15)	−6120 (9)	−628 (7)	43 (3)
C(9)	250 (16)	1399 (12)	4635 (8)	53 (4)	5988 (15)	−7289 (11)	−1855 (8)	46 (4)
C(10)	3873 (12)	1574 (8)	3336 (6)	28 (3)	2372 (12)	−7541 (9)	−576 (6)	30 (3)
C(11)	3539 (14)	2420 (10)	3329 (7)	39 (3)	3128 (13)	−6711 (9)	−289 (6)	32 (3)
C(12)	3515 (13)	2918 (9)	3996 (7)	35 (3)	3455 (12)	−6062 (8)	−762 (6)	29 (3)
C(13)	3934 (13)	2537 (8)	4584 (7)	32 (3)	2906 (13)	−6305 (7)	−1447 (6)	30 (3)
C(14)	5213 (18)	−33 (11)	2856 (8)	59 (4)	122 (17)	−9167 (10)	−615 (7)	54 (4)
C(15)	4632 (20)	1242 (15)	1850 (8)	74 (6)	1338 (18)	−8246 (13)	754 (7)	61 (5)
C(16)	6784 (16)	1791 (14)	3041 (9)	69 (5)	−420 (17)	−7350 (13)	−210 (9)	67 (5)
C(17)	3609 (17)	2991 (11)	2754 (7)	54 (4)	3306 (16)	−6327 (10)	447 (7)	48 (4)
C(18)	4616 (12)	3079 (9)	5224 (6)	32 (3)	2609 (13)	−5625 (9)	−1885 (6)	35 (3)
C(19)	4683 (12)	4000 (9)	5360 (7)	39 (3)	2847 (14)	−4689 (9)	−1704 (8)	46 (4)
C(20)	5352 (15)	4261 (11)	6024 (8)	52 (4)	2482 (17)	−4268 (12)	−2250 (10)	62 (5)
C(21)	5678 (17)	3500 (11)	6287 (7)	52 (4)	1957 (17)	−4909 (13)	−2810 (9)	60 (5)
C(22)	5259 (14)	2764 (10)	5800 (7)	44 (3)	2025 (15)	−5753 (10)	−2589 (7)	43 (3)
C(23)	7547 (21)	3362 (15)	4671 (11)	76 (6)	−221 (23)	−4836 (15)	−1291 (11)	82 (6)
C(24)	7604 (22)	4261 (16)	4753 (12)	84 (7)	−504 (22)	−4294 (15)	−1812 (13)	84 (7)
C(25)	8256 (20)	4586 (15)	5379 (13)	86 (7)	−1072 (20)	−4883 (16)	−2378 (14)	87 (8)
C(26)	8646 (19)	3906 (17)	5730 (12)	83 (6)	−1109 (18)	−5740 (16)	−2201 (12)	81 (6)
C(27)	8249 (19)	3155 (16)	5272 (15)	95 (8)	−604 (18)	−5696 (15)	−1538 (10)	70 (6)

the remaining nonhydrogen atoms were located by subsequent electron density syntheses. The structure was refined first isotropically and then anisotropically. Hydrogen atoms were calculated geometrically and refined using the riding model (with temperature factors 20 % higher than the equivalent isotropic temperature factors of the corresponding C atoms). The final values of the *R* factors are as follows: $R_1 = 0.0573$ (based on *F* for 8506 observed reflections with $I > 2\sigma(I)$), $wR_2 = 0.1968$ (based on F^2 for all 11915 independent reflections used in the refinement). All calculations were performed on an IBM PC using the SHELXTL PLUS 5 program (gamma version). Atomic coordinates are given in Table 4.

This work was supported by the Russian Foundation for Basic Research (Project Nos. 94-03-08167 and 94-03-08338) and the International Science Foundation (Grants J8M100 and M04300).

References

1. A. A. Koridze, N. M. Astakhova, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, and P. V. Petrovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 766 [*Russ. Chem. Bull.*, 1994, **43**, 718 (Engl. Transl.)].
2. A. A. Koridze, N. M. Astakhova, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, and P. V. Petrovskii, *Organometallics*, 1995, **14**, 2167.
3. O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organomet. Chem.*, 1971, **30**, 381.
4. R. Giordano and E. Sappa, *J. Organomet. Chem.*, 1993, **448**, 157.
5. G. Ferrarris and G. Gervasio, *J. Chem. Soc., Dalton Trans.*, 1974, 1813.
6. O. Gambino, R. P. Ferrari, M. Chinone, and G. A. Vaglio, *Inorg. Chim. Acta*, 1975, **12**, 155.

7. R. P. Ferrari, G. A. Vaglio, O. Gambino, M. Valle, and G. Cetini, *J. Chem. Soc., Dalton Trans.*, 1972, 1998.
8. A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1616.
9. M. Tachikawa, J. R. Shapley, and C. G. Pierpont, *J. Am. Chem. Soc.*, 1975, **97**, 7172.
10. B. F. G. Johnson, R. Khattar, F. J. Lahoz, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, 1987, **319**, c51.
11. A. A. Koridze, N. M. Astakhova, P. V. Petrovskii, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1994, **481**, 247.
12. S. P. Gubin, A. A. Koridze, N. A. Ogorodnikova, A. A. Bezrukova, and B. A. Kvasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1170 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 929 (Engl. Transl.)].

Received July 20, 1995;
in revised form January 11, 1996