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Synthesis and Structure of $(OC)_4(\mathrm{Bu^t}NC)OsOs(CO)_3(CNBu^t)W(CO)_5$, a Second Example of a Compound with Dative Metal–Metal Bonds in Tandem

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We have recently described the synthesis and structure of $(OC)_3[MeC(CH_2O)_3P]_2OsOs(CO)_4W(CO)_5$, believed to be the first example of a structurally-characterized compound with two dative metal–metal bonds in tandem (i.e., $Os\rightarrow Os\rightarrow W$).[1] An isomer of this compound was observed as a byproduct in the preparation of $[MeC(CH_2O)_3P](OC)_4OsW(CO)_5$, which has a single unbridged Os–W dative bond. This was in contrast to the preparation of other derivatives of the type $(R_3P)(OC)_4OsW(CO)_5$, where the cluster compounds $(OC)_5W[Os(CO)_3(PR_3)]_2$ were the observed byproducts.[2]

The other phosphorus-donor ligands employed in this study had larger cone angles than the $P(OCH_2)_3CMe$ ligand. It therefore appeared that a requirement for the formation of the complex with the chain of dative metal–metal bonds was that the phosphorus ligand be small so that it could occupy a position cis to the first dative metal–metal bond without causing too much repulsion with the neighboring carbonyl ligands. Another donor ligand that meets this steric requirement is $\mathrm{Bu^t}NC$. This prompted a reinvestigation of the reaction of $Os(CO)_4(CNBu^t)$ with $W(CO)_5(THF)$, which we have previously demonstrated yields, as the major product, $(OC)_4(\mathrm{Bu^t}NC)OsW(CO)_5$ (i.e., with the non-carbonyl ligand cis to the dative metal–metal bond).[3]

In this note we report the isolation of isomers of formula $WOs_2(CO)_{12}(CNBu^t)_2$ (**1**) from this reaction. The X-ray crystal structure of one of these isomers shows that it has two unbridged, metal–metal bonds in a linear arrangement. An electron count for each metal atom indicates that these bonds should also be regarded as dative bonds.

Experimental Section

Manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Hexane, tetrahydrofuran (THF), and dichloromethane were distilled under nitrogen from potassium, potassium benzophenone ketyl, and P_2O_5, respectively. The precursor compounds $W(CO)_5(THF)$ and $Os(CO)_4(CNBu^t)$ were prepared according to literature methods.[2,3]

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies of gaseous CO. NMR spectra were recorded on either a Bruker WM400 spectrometer (operating frequencies: 400 MHz for ^1H and 100.6 MHz for ^{13}C) or a Bruker SY-100 spectrometer. The ^{13}C NMR spectra were obtained on samples enriched with ^{13}CO (~30%) which, in turn, were prepared from ^{13}CO-enriched $W(CO)_5(THF)$.[2] The microanalyses were obtained by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $(OC)_4(\mathrm{Bu^t}NC)OsOs(CO)_3(CNBu^t)W(CO)_5$ (1a) and $(OC)_3(\mathrm{Bu^t}NC)_2OsOs(CO)_4W(CO)_5$ (1b). A solution of $W(CO)_5(THF)$ was prepared from $W(CO)_6$ (120 mg, 0.341 mmol) and THF (30 mL). The solution was reduced in volume to ~2 mL and immediately cooled to −196 °C. A solution of $Os(CO)_4(CNBu^t)$ (40 mg, 0.10 mmol) in hexane (10 mL) was added to the frozen $W(CO)_5(THF)$/THF solution and the resulting mixture allowed to warm with stirring to room temperature. The stirring was continued for a further 20 min at this temperature. The solvent was then removed on the vacuum line, and the remaining solid was chromatographed on a silica gel column (15 × 1 cm). Elution with hexane removed $W(CO)_6$; elution with hexane/CH_2Cl_2 (5/1) afforded the dinuclear species $(OC)_4(\mathrm{Bu^t}NC)OsW(CO)_5$. The desired products eluted as a yellow band with hexane/CH_2Cl_2 (1/1). Collection of this fraction and removal of the solvent gave $(OC)_7(\mathrm{Bu^t}NC)_2Os_2W(CO)_5$ (11 mg, 20%) as a mixture of the isomers **1a** and **1b** plus a trace of a third compound (**1c**) also believed to be an isomer of $(OC)_7(\mathrm{Bu^t}NC)_2Os_2W(CO)_5$. The **1a**/**1b** ratio appeared somewhat variable, as ascertained by IR spectroscopy, but was determined in one preparation as 1.1 by ^1H NMR spectroscopy.

Attempts to separate the isomers by chromatography were unsuccessful. Partial separation was, however, achieved by fractional recrystallization: Crystals from four such preparations described above were combined and recrystallized from hexane/CH_2Cl_2. The first batch of crystals obtained by this recrystallization consisted essentially of **1b**. A further recrystallization of these crystals from hexane/CH_2Cl_2 gave **1b** that was pure by ^{13}C NMR spectroscopy. The supernatant solution from the first recrystallization was evaporated to dryness, and the residue was recrystallized from a minimum of hexane/CH_2Cl_2. This afforded a yellow sample that by ^{13}C NMR spectroscopy consisted of mainly isomer **1a** but also contained **1b** (<10%) and traces of **1c**.

Compound **1a**: IR (CH_2Cl_2) $\nu(CN)$ 2216 (w), 2170 (w) cm^{-1}, $\nu(CO)$ 2102 (m), 2047 (s), 2031 (s), 1954 (s), 1899 (s), 1847 (m, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (s), 1.46 (s); ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, 4/1, CO region, 0 °C) δ 207.4 (C(35), J_{WC} = 177 Hz), 204.9 (C(31)–C(34), J_{WC} = 125 Hz), 197.5 (C(21), C(23)), 192.2 (C(22)), 180.9 (C(11), C(13)), 177.0 (C(12)), 162.5 (C(14)); see Figure 1 for the assignment of the resonances. Anal. Calcd for $C_{22}H_{18}N_2O_{12}Os_2W$: C, 24.77; H, 1.70; N, 2.63. Found: C, 25.03; H, 1.85; N, 2.40. Compound **1b**: IR (CH_2Cl_2) $\nu(CN)$ 2216 (w), 2195 (w) cm^{-1}, $\nu(CO)$ 2089 (s), 2056 (s), 2031 (s), 2016 (s), 1968 (vs), 1900 (s), 1856 (m, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (s); ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, 4/1, CO region, 0 °C) δ 206.9 (1 C, J_{WC} = 179 Hz), 204.4 (4 C, J_{WC} = 124 Hz), 196.3 (4 C), 179.2 (2 C), 162.9 (1 C). Anal. Calcd for $C_{22}H_{18}N_2O_{12}Os_2W$: C, 24.77; H, 1.70; N, 2.63. Found: C, 24.90; H, 1.66; N, 2.50. Compound **1c**: ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, 4/1, CO region, 0 °C) δ 204.1 (4 C), 195.8 (4 C), 183.0 (2 C), 163.8 (1 C); the expected signal of intensity 1 due to the axial carbonyl on tungsten was not observed. An attempt to obtain an EI mass spectrum of **1a** was unsuccessful.

X-ray Analysis of 1a. The single crystal of **1a** was obtained by recrystallization from hexane/C_6H_5Cl/CH_2Cl_2. It was mounted on an Enraf-Nonius CAD-4F diffractometer and a unique set of intensity data collected at ambient temperature with the use of graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The unit cell was determined from 25 well-centered reflections ($28° \leq 2\theta \leq 36°$). Two intensity standards, measured every 1.33 h of acquisition time, decreased systematically in intensity by 25%. An analytical absorption correction[4] (checked against ψ-scan measurements) was applied to the measured intensity data. Data reduction included corrections for intensity scale variation and Lorentz and polarization effects.

The positions of the Os and W atoms were determined from the Patterson map. Subsequent electron density difference synthesis revealed the remaining non-hydrogen atoms. The final full-matrix least-squares refinement of 172 parameters for 2122 observed data ($I \geq 2.5\sigma(I)$) included coordinates for all non-hydrogen atoms, anisotropic thermal parameters for the osmium and tungsten atoms, and isotropic temperature factors for carbon, nitrogen, and oxygen atoms. Hydrogen atoms were included in calculated positions with assigned isotropic thermal parameters. These positions were recalculated prior to the final cycles of refinement. A weighting scheme, based on counting statistics, was applied for which $\langle w(|F_o| - |F_c|)^2\rangle$ was nearly constant as a function of both $|F_o|$ and $((\sin\theta)/\lambda)^2$. The highest peak in the final electron density difference map was 1.2 (2) e $Å^{-3}$, occuring 1.07 Å from the tungsten atom.

Complex scattering factors for neutral atoms[5] were used in the calculation of structure factors. The programs used were from the NRCVAX

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(1) Batchelor, R. J.; Davis, H. B.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 2036.

(2) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. *Organometallics* **1989**, *8*, 1030.

(3) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620.

(4) DeMeulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

(5) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England (present distributor Kluwer Academic: Dordrecht, The Netherlands), 1975; Vol. IV, p 99.

0020-1669/92/1331-3155$03.00/0

Table I. Crystal Data for **1a**

a, Å[a]	11.750 (3)	formula	$C_{22}H_{18}O_{12}Os_2N_2W$
b, Å	14.039 (4)	cryst syst	monoclinic
c, Å	18.615 (4)	space group	$P2_1/n$
β, deg	91.89 (2)	λ, Å	0.710 69
V, Å^3	3069	Z	4
R[b]	0.046	observed data	2122 ($I \geq 2.5\sigma(I)$)
R_w[c]	0.048	2θ range, deg	4–45
GOF[d]	1.38	parameters	172

[a] The unit cell was determined from 25 reflections, 28° < 2θ <36°. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = [\sigma^2(F_o) = 0.0004F_o^2]^{-1}$. [d] GOF = $(\sum w(|F_o| - |F_c|)^2/\text{degrees of freedom})^{-1/2}$.

Table II. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of **1a**

	x/a	y/b	z/c	B_{iso} (B_{eq})
Os(1)	0.10972 (8)	0.20280 (7)	0.28479 (5)	4.15[a]
Os(2)	0.34179 (8)	0.19590 (7)	0.23558 (5)	3.94[a]
W	0.58679 (8)	0.17043 (7)	0.19277 (5)	4.85[a]
O(11)	0.0818 (14)	0.0115 (11)	0.2048 (9)	6.7 (4)
O(12)	0.0587 (14)	0.3028 (11)	0.1418 (9)	6.5 (4)
O(13)	0.1991 (16)	0.3840 (14)	0.3536 (10)	8.8 (5)
O(14)	−0.1313 (20)	0.2156 (15)	0.3357 (11)	10.3 (6)
O(21)	0.3711 (14)	0.3879 (12)	0.1624 (9)	6.9 (4)
O(22)	0.4429 (16)	0.2683 (13)	0.3773 (10)	8.2 (5)
O(23)	0.3776 (14)	−0.0091 (12)	0.2853 (8)	6.4 (4)
O(31)	0.5391 (21)	−0.0392 (19)	0.1489 (13)	12.7 (7)
O(32)	0.5180 (19)	0.2460 (16)	0.0374 (12)	11.4 (6)
O(33)	0.6452 (19)	0.3785 (17)	0.2398 (12)	11.3 (6)
O(34)	0.6412 (19)	0.0885 (15)	0.3479 (13)	11.0 (6)
O(35)	0.8411 (18)	0.1471 (13)	0.1569 (10)	9.1 (5)
N(1)	0.2068 (15)	0.1004 (12)	0.4247 (9)	4.7 (4)
N(2)	0.2579 (16)	0.1264 (13)	0.0835 (11)	5.9 (5)
C(11)	0.0921 (18)	0.0841 (16)	0.2377 (11)	4.7 (5)
C(12)	0.0780 (19)	0.2656 (15)	0.1967 (13)	5.4 (5)
C(13)	0.1671 (23)	0.3137 (18)	0.3253 (13)	6.7 (6)
C(14)	−0.0347 (29)	0.2135 (21)	0.3198 (16)	8.8 (8)
C(21)	0.3543 (18)	0.3164 (15)	0.1951 (11)	4.5 (5)
C(22)	0.4027 (22)	0.2418 (18)	0.3211 (14)	6.8 (6)
C(23)	0.3630 (17)	0.0718 (14)	0.2660 (11)	4.1 (5)
C(31)	0.5581 (24)	0.0447 (21)	0.1645 (14)	7.5 (7)
C(32)	0.5427 (26)	0.2139 (21)	0.0938 (16)	8.3 (7)
C(33)	0.6228 (22)	0.2951 (20)	0.2250 (13)	6.7 (6)
C(34)	0.6246 (23)	0.1209 (19)	0.2916 (15)	7.3 (7)
C(35)	0.7418 (24)	0.1548 (19)	0.1697 (13)	7.2 (6)
C(1)	0.1708 (19)	0.1347 (15)	0.3740 (12)	5.2 (5)
C(100)	0.2546 (22)	0.0551 (17)	0.4915 (13)	5.9 (6)
C(101)	0.3394 (26)	−0.0147 (21)	0.4718 (15)	8.8 (8)
C(102)	0.1600 (25)	0.0099 (20)	0.5297 (15)	8.4 (7)
C(103)	0.3085 (24)	0.1345 (20)	0.5330 (15)	8.4 (8)
C(2)	0.2878 (16)	0.1488 (14)	0.1414 (11)	3.9 (4)
C(200)	0.2158 (25)	0.1022 (22)	0.0089 (16)	8.0 (7)
C(201)	0.0884 (39)	0.1065 (31)	0.0134 (23)	16.1 (14)
C(202)	0.2457 (37)	0.1800 (28)	−0.0424 (22)	14.4 (13)
C(203)	0.2456 (44)	0.0067 (38)	−0.0050 (26)	18.7 (17)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

crystal structure system.[6] All computations were carried out on a MicroVAX-II computer. Crystallographic data are summarized in Table I, the final positional and isotropic or equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table II, and selected distances and angles are listed in Table III. Additional experimental details, the coordinates and temperature factors for the hydrogen atoms, anisotropic temperature factors, bond torsion angles, and observed and calculated structure factors are deposited as supplementary material.

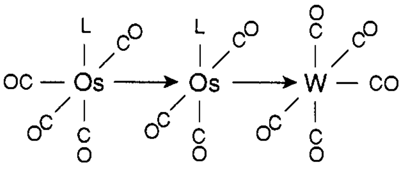
Results and Discussion

Addition of $Os(CO)_4(CNBu^t)$ to $W(CO)_5(THF)$ in hexane/THF affords as the major product $(OC)_4(Bu^tNC)OsW(CO)_5$ (**2**).[3] The compounds of interest here, $(OC)_4(Bu^tNC)OsOs(CO)_3(CNBu^t)W(CO)_5$ (**1a**) and $(OC)_3(Bu^tNC)_2OsOs(CO)_4W(CO)_5$ (**1b**), were isolated as minor products (combined yield of 20%) from the same reaction (eq 1). The **1a**/**1b** ratio of the complexes

$$\begin{aligned} &Os(CO)_4(CNBu^t) + W(CO)_5(THF) \rightarrow \\ &\quad \underset{\mathbf{2}}{(OC)_4(Bu^tNC)OsW(CO)_5} + \\ &\quad \underset{\mathbf{1a}}{(OC)_4(Bu^tNC)OsOs(CO)_3(CNBu^t)W(CO)_5} + \\ &\quad \underset{\mathbf{1b}}{(OC)_3(Bu^tNC)_2OsOs(CO)_4W(CO)_5} \qquad (1) \end{aligned}$$

produced by this method was estimated as 1.1 by ^1H NMR spectroscopy. Compounds **1a** and **1b** were separated from **2** by chromatography; they were separated from each other by fractional crystallization (**1b** is much less soluble in hexane/CH_2Cl_2 than **1a**). In this way, samples of **1b** could be obtained that were pure by ^{13}C NMR spectroscopy. The best samples of **1a**, however, contained **1b** (<10%) and traces of a third compound, **1c**, believed to also be an isomer of $WOs_2(CO)_{12}(CNBu^t)_2$ (this is discussed below).

The structure of **1a** was determined by X-ray crystallography. A view of the molecule is shown in Figure 1; bond length and angle data are given in Table III. An electron count for each metal atom in **1a** indicates that both metal–metal bonds should be regarded as dative bonds in order for each metal atom to achieve an 18-electron configuration, i.e.



L = BuᵗNC

Two dative metal–metal bonds in tandem are believed to be present in $(OC)_3[MeC(CH_2O)_3P]_2OsOs(CO)_4W(CO)_5$ (**3**).[1] Compound **1a** represents the second example where this type of bonding has been supported by an X-ray crystal structure.

We previously pointed out that the dative metal–metal bonds in **3** and complexes such as $(Me_3P)(OC)_4OsW(CO)_5$ are somewhat longer than comparable (nondative) bonds in compounds where the atoms are part of a closed polyhedron of metal atoms.[1] They are, however, similar in length to nondative metal–metal bonds between the same elements in compounds with a linear arrangement of metal atoms. This is also true of the metal–metal lengths in **1a**. The Os–Os bond length in **1a** of 2.9066 (15) Å is, for example, somewhat longer than the average Os–Os bond length in $Os_3(CO)_{12}$ (2.877 Å)[7] but slightly shorter than the Os–Os distances in $Os_3(CO)_{12}(SiCl_3)_2$ (2.912 (1) Å)[8] and $Os_3(CO)_{12}(I)_2$ (2.935 (2) Å).[9] The Os–W length in **1a** (3.0335 (16) Å) may be compared to that in **3** (3.039 (1) Å)[1] and that in $(Me_3P)(OC)_4OsW(CO)_5$ (3.0756 (5) Å).[2] That the Os–Os distance in **1a** is shorter than that in **3** (2.940 (1) Å) may indicate that there are less repulsive interactions between the radial ligands in **1a** than in **3**.

As found for dinuclear compounds with unbridged, dative metal–metal bonds,[2,3] there is an inward leaning of the radial carbonyls on the donor metal atom toward the acceptor metal atom in **1a** (the appropriate Os(2)–Os(1)–C angles are in the range 79.8 (8)–85.1 (6)°; the W–Os(2)–C angles are in the range 81.3 (6)–85.6 (8)°). On the other hand, the corresponding angles for the radial carbonyls on the terminal acceptor metal atom are

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(6) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L. NRCVAX—An Interactive Program System for Structure Analysis. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(7) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(8) Willis, A. C.; van Buuren, G. N.; Pomeroy, R. K.; Einstein, F. W. B. *Inorg. Chem.* **1983**, *22*, 1162.

(9) Cook, N.; Smart, L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1744.

Table III. Bond Lengths (Å) and Selected Angles (deg) for **1a**

Bond Distances			
Os(1)–Os(2)	2.9066 (15)	Os(2)–W	3.0335 (16)
Os(1)–C(1)	2.027 (22)	Os(2)–C(2)	1.958 (20)
N(1)–C(1)	1.13 (3)	N(2)–C(2)	1.17 (3)
N(1)–C(100)	1.49 (3)	N(2)–C(200)	1.50 (4)
⟨Os–C(O)⟩	1.86 (range 1.84 (3)–1.89 (3))		
⟨W–C⟩	1.93 (range 1.87 (3)–2.00 (3))		
⟨C–O⟩	1.19 (range 1.15 (3)–1.23 (3))		
⟨C–C⟩	1.47 (range 1.41 (6)–1.50 (6))		
Bond Angles			
Os(1)–Os(2)–W	174.27 (4)	C(11)–Os(1)–C(12)	89.6 (9)
Os(2)–Os(1)–C(11)	85.1 (6)	C(11)–Os(1)–C(13)	164.7 (10)
Os(2)–Os(1)–C(12)	84.4 (7)	C(11)–Os(1)–C(14)	98.5 (11)
Os(2)–Os(1)–C(13)	79.8 (8)	C(11)–Os(1)–C(1)	89.7 (9)
Os(2)–Os(1)–C(14)	176.4 (9)	C(12)–Os(1)–C(13)	91.1 (10)
Os(2)–Os(1)–C(1)	86.1 (6)	C(12)–Os(1)–C(14)	96.4 (11)
Os(1)–Os(2)–C(21)	100.6 (7)	C(12)–Os(1)–C(1)	170.5 (9)
Os(1)–Os(2)–C(22)	93.3 (8)	C(13)–Os(1)–C(14)	96.6 (12)
Os(1)–Os(2)–C(23)	93.1 (6)	C(13)–Os(1)–C(1)	87.0 (10)
Os(1)–Os(2)–C(2)	90.8 (6)	C(14)–Os(1)–C(1)	93.1 (11)
W–Os(2)–C(21)	85.0 (7)	C(21)–Os(2)–C(22)	89.9 (10)
W–Os(2)–C(22)	85.6 (8)	C(21)–Os(2)–C(23)	166.2 (9)
W–Os(2)–C(23)	81.3 (6)	C(21)–Os(2)–C(2)	88.4 (8)
W–Os(2)–C(2)	90.4 (6)	C(22)–Os(2)–C(23)	91.1 (10)
Os(2)–W–C(31)	91.2 (8)	C(22)–Os(2)–C(2)	175.8 (10)
Os(2)–W–C(32)	89.2 (9)	C(23)–Os(2)–C(2)	89.6 (8)
Os(2)–W–C(33)	90.7 (8)	C(31)–W–C(32)	89.4 (11)
Os(2)–W–C(34)	89.0 (8)	C(31)–W–C(33)	176.6 (11)
Os(2)–W–C(35)	177.9 (7)	C(31)–W–C(34)	87.9 (11)
C(32)–W–C(35)	92.8 (11)	C(31)–W–C(35)	89.6 (12)
C(33)–W–C(34)	89.4 (11)	C(32)–W–C(33)	93.4 (11)
C(33)–W–C(35)	88.4 (11)	C(32)–W–C(34)	176.8 (11)
C(34)–W–C(35)	89.0 (11)	C(1)–N(1)–C(100)	179.0 (5)
Os(1)–C(1)–N(1)	177.1 (19)	C(2)–N(2)–C(200)	177.0 (22)
Os(2)–C(2)–N(2)	175.6 (18)		
⟨M[a]–C–O⟩	176 (range 171 (2)–179 (2))		
⟨N–C–C⟩	107 (range 103 (3)–110 (3))		
⟨C–C–C⟩	111 (range 105 (3)–120 (3))		

[a] M = Os or W.

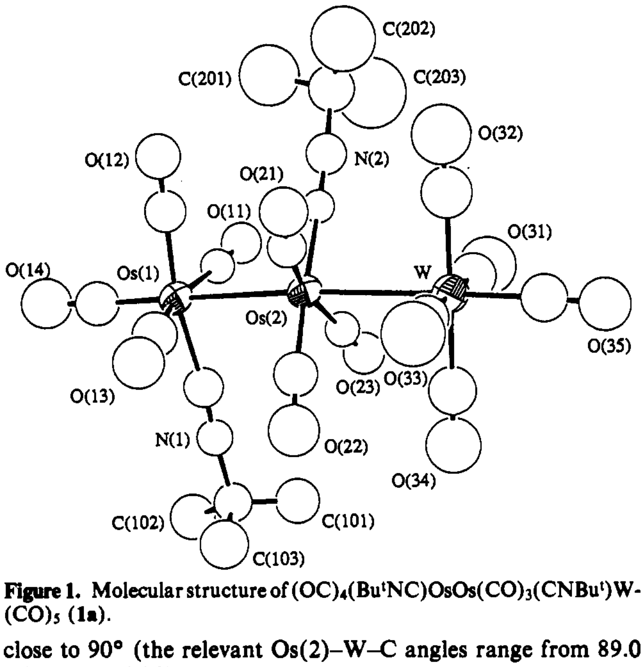
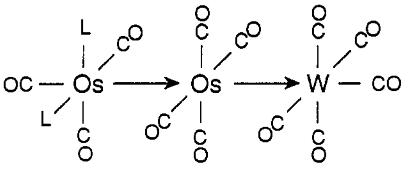


Figure 1. Molecular structure of $(OC)_4(Bu^tNC)OsOs(CO)_3(CNBu^t)W(CO)_5$ (**1a**).

close to 90° (the relevant Os(2)–W–C angles range from 89.0 (8) to 91.2 (8)°).

The ^{13}C NMR spectrum of **1a** in CH_2Cl_2/CD_2Cl_2 exhibits a 1/4/2/1/2/1/1 pattern of signals in the CO region, consistent with the view that the structure found for the molecule in the solid state is also adopted in solution. The assignment of the resonances given in the Experimental Section readily follows from intensity considerations, satellites due to coupling to ^{183}W, and comparison of the spectrum with the ^{13}C NMR spectra of **1b**, **2**,[2] and **3**,[1] where the assignment is unambiguous. As we have noted previously, the ^{13}C NMR resonances of carbonyls trans to dative metal–metal bonds appear at unusually high fields.[2,3,10] In **1a** this resonance occurs at δ 162.5.

Compound **1b** is assigned a structure similar to that of **1a**, but with both isocyanide ligands on the terminal osmium atom in a cis arrangement:



L = BuᵗNC

The assignment is based on the 1/4/4/2/1 pattern of peaks in the carbonyl region of the ^{13}C NMR spectrum of the compound in CH_2Cl_2/CD_2Cl_2 and the fact that there are two CN stretches in the infrared spectrum, consistent with a cis arrangement of the Bu^tNC ligands. That **1b** is the isomer with an isocyanide ligand trans to the Os–Os bond is thought unlikely. Such an isomer would not be expected to exhibit a ^{13}C resonance in the δ 160–170 region. This, as mentioned above, appears characteristic of a carbonyl that is trans to a dative metal–metal bond.

There was evidence in the ^{13}C NMR spectrum of **1a** for a third compound (**1c**). The pattern of the signals, with the exception that one signal of intensity 1 was not observed, was consistent with **1c** having a structure similar to that proposed for **1b**, but with the isocyanide ligands in a trans arrangement. This type of isomerization was observed for $(OC)_3(Bu^tNC)_2OsM(CO)_5$ (M = Cr, Mo, W), but whereas the two isomers of the dinuclear complexes were in dynamic equilibrium in solution at room temperature, this was not the case for **1b** and **1c**: A sample of pure **1b** was unchanged (by ^{13}C NMR spectroscopy) after it had been stirred in CH_2Cl_2 at room temperature for 7 d.

The possible isomerization of **1a** in solution was also studied by ^{13}C NMR spectroscopy: A sample containing approximately equal amounts of **1a** and **1b** (each ^{13}CO-enriched) was stirred in CH_2Cl_2 at room temperature for 9 d. The intensities of the ^{13}C NMR resonances of the sample before and after this treatment were compared to those of an internal standard of ^{13}CO-enriched $Os_3(CO)_{12}$. From this comparison, it was judged that **1a** had almost completely decomposed during this period but the concentration of **1b** (and **1c**) was unchanged.

These results indicate that the formation of **1b** from $Os(CO)_4(CNBu^t)$ and $W(CO)_5(THF)$ (i.e., as in eq 1) does not involve the initial formation of **1a** followed by its isomerization to **1b**. This has parallels to observations regarding the synthesis of **3** in that $(L')(OC)_4OsOs(CO)_3(L')W(CO)_5$ (L′ = $P(OCH_2)_3CMe$) did not isomerize to **3** under the same conditions used to prepare **3** from $Os(CO)_4(L')$ and $(L')(OC)_4OsW(CO)_5$.[1] It is perhaps more surprising in the present case, since Bu^tNC is known to act, in some cases, as a bridging ligand whereas $P(OCH_2)_3CMe$ is not known to bond in this fashion.

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Supplementary Material Available: Tables of additional crystal data and data collection parameters (Table SI), fractional hydrogen atom coordinates (Table SII), anisotropic temperature factors (Table SIII), and selected bond torsion angles for **1a** (Table SIV) (3 pages); a listing of calculated and observed structure factors (Table SV) (12 pages). Ordering information is given on any current masthead page.

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(10) (a) Fleming, M. M.; Pomeroy, R. K.; Rushman, P. *J. Organomet. Chem.* **1984**, *273*, C33. (b) Einstein, F. W. B.; Johnston, V. J.; Ma, A. K.; Pomeroy, R. K. *Organometallics* **1990**, *9*, 52.