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Synthesis, crystal and molecular structure of η^3-allylundecacarbonylosmium tetrafluoroborate

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Abstract

The η^3-allylundecacarbonylosmium tetrafluoroborate has been synthesized in high yield by treatment of $Os_3(CO)_{11}MeCN$ with allyl alcohol and subsequent protonation. It has been studied by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group $Pna2_1$ (no. 33) with a 17.933(2), b 11.440(2), c 11.797(2)Å and D_c 2.76 g cm^{-3} for $Z = 4$. A final R value of 0.046 ($R_w = 0.083$) based on 2067 reflections was obtained. The presence of the positively charged allyl ligand in the triosmium cluster lengthens the Os1–Os2 and Os2–Os3 bonds (0.057Å) and 0.074 Å, respectively) relative to the Os–Os bonds in $Os_3(CO)_{12}$.

Introduction

We recently reported a preparation of the first cationic π-allyltriosmium cluster I. The synthesis involves treatment of $Os_3(CO)_{12}$ with trimethylamine oxide in the presence of allyl alcohol and subsequent addition of $HBF_4 \cdot Et_2O$ [1]. The yield of I was not more than 30%. The purpose of the present study was to investigate the possibility of preparing this cationic cluster in higher yield, and to determine its structure by an X-ray diffraction study.

Results and discussion

(a) Synthesis

We tried to use the labile monoacetonitrile derivative of osmium dodecacarbonyl [2], as a starting compound in the reaction with allyl alcohol and a strong protonic acid. We found that treatment of $Os_3(CO)_{11}MeCN$ in CH_2Cl_2 solution with allyl

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alcohol in the presence of $HBF_4 \cdot Et_2O$, gave two cationic clusters, the allyl derivative I and the protonated starting compound II being formed with a 1/2 ratio as indicated by the ^{1}H NMR spectrum of the mixture.

$$Os_3(CO)_{11}MeCN + CH_2 = CHCH_2OH + HBF_4 \cdot EtO_2 \rightarrow$$

$$\underset{(I)}{[Os_3(CO)_{11}(\eta\text{-}C_3H_5)]^+BF_4^-} + \underset{(II)}{[Os_3(CO)_{11}(MeCN)H]^+BF_4^-}$$

The salt of the protonated cation with PF_6 as anion was prepared previously [3]. Since the separation of the products I and II is difficult and the yield of I is not very high we decided to carry out the reaction in two steps. In the first step only allyl alcohol was added to the CH_2Cl_2 solution of the initial compound and when the replacement of the MeCN by the olefin ligand was complete the acid was added to the mixture. This procedure gave I in high yield (78%) and practically pure. When substituted allyl alcohols RCH=CHCH$_2$OH (R = Me, Ph) were used, the displace-

Table 1

Fractional coordinates and equivalent isotropic temperature factors for I ($B_{eq} = \frac{1}{3} \cdot [a^3 \cdot B_{1,1} + b^2 \cdot B_{2,2} + c^2 \cdot B_{3,3} + ab(\cos\gamma) \cdot B_{1,2} + ac(\cos\beta) \cdot B_{1,3} + bc(\cos\alpha) \cdot B_{2,3}]$)

atom	x	y	z	B_{eq}(Å^2) [a]
OS1	0.23226(5)	0.21022(6)	0.126	2.55(1)
OS2	0.30250(4)	−0.01116(7)	0.1277(2)	2.72(1)
OS3	0.13809(4)	0.00028(6)	0.1270(2)	2.52(1)
O11	0.218(1)	0.211(2)	0.394(2)	5.4(6) *
O12	0.245(1)	0.219(2)	−0.129(2)	2.9(3) *
O13	0.119(1)	0.411(1)	0.151(2)	4.2(4) *
O14	0.369(1)	0.367(2)	0.147(3)	7.1(6) *
O21	0.311(1)	−0.010(2)	0.400(2)	3.4(3) *
O22	0.286(2)	−0.012(3)	−0.128(3)	6.9(8) *
O23	0.456(1)	0.099(2)	0.167(2)	5.7(5) *
O24	0.355(1)	−0.269(2)	0.152(2)	4.3(4) *
O31	0.132(1)	0.023(2)	0.390(2)	5.2(5) *
O32	0.152(2)	−0.018(3)	−0.134(3)	7.0(7) *
O33	0.172(1)	−0.264(2)	0.109(2)	4.1(4) *
C11	0.224(1)	0.208(2)	0.293(2)	2.3(4) *
C12	0.245(1)	0.215(2)	−0.040(3)	2.8(4) *
C13	0.163(1)	0.332(2)	0.144(3)	2.7(3) *
C14	0.316(2)	0.309(2)	0.131(7)	4.5(5) *
C21	0.309(1)	−0.010(2)	0.301(2)	2.3(4) *
C22	0.292(2)	−0.011(3)	−0.026(4)	4.7(7) *
C23	0.400(1)	0.051(2)	0.154(2)	3.6(5) *
C24	0.335(1)	−0.170(2)	0.142(3)	3.2(4) *
C31	0.137(2)	0.019(3)	0.291(3)	3.6(5) *
C32	0.141(2)	−0.015(2)	−0.040(3)	3.6(5) *
C33	0.164(1)	−0.161(2)	0.116(3)	3.5(4) *
C34	0.044(1)	0.141(2)	0.140(4)	4.1(5) *
C35	0.017(1)	0.038(2)	0.082(2)	4.1(6) *
C36	0.016(1)	−0.077(2)	0.104(2)	4.2(6) *
B1	−0.002(5)	0.290(7)	0.413(8)	5.0(fix) *
B2	0.493(5)	0.199(7)	0.849(9)	5.0(fix) *

[a] Starred atoms were refined isotropically; multiplicity of the *B*-atoms is 0.5.

Table 2

Relevant bond distances (Å) and angles (°) for I with e.s.d.'s in parentheses

Os(1)–Os(2)	2.829(1)		
Os(1)–Os(3)	2.936(1)		
Os(2)–Os(3)	2.951(1)		
Os(1)–C(11)	1.98(3)	C(11)–O(11)	1.19(4)
Os(1)–C(12)	1.97(3)	C(12)–O(12)	1.06(4)
Os(1)–C(13)	1.88(2)	C(13)–O(13)	1.20(3)
Os(1)–C(14)	1.89(3)	C(14)–O(14)	1.17(4)
Os(2)–C(21)	2.05(3)	C(21)–O(21)	1.17(3)
Os(2)–C(22)	1.82(4)	C(22)–O(22)	1.21(5)
Os(2)–C(23)	1.91(3)	C(23)–O(23)	1.15(4)
Os(2)–C(24)	1.92(2)	C(24)–O(24)	1.19(3)
Os(3)–C(31)	1.95(3)	C(31)–O(31)	1.17(4)
Os(3)–C(32)	1.98(3)	C(32)–O(32)	1.13(5)
Os(3)–C(33)	1.91(2)	C(33)–O(33)	1.19(3)
Os(3)–C(34)	2.34(2)	C(34)–C(35)	1.45(4)
Os(3)–C(35)	2.28(2)	C(35)–C(36)	1.34(3)
Os(3)–C(36)	2.38(2)		
Os(1)–Os(3)–Os(2)	57.43(3)		
Os(2)–Os(1)–Os(3)	61.56(3)	Os(2)–C(22)–O(22)	179(3)
Os(1)–Os(2)–Os(3)	61.01(3)	Os(2)–C(21)–O(21)	179(2)
Os(1)–C(11)–O(11)	177(2)	Os(2)–C(24)–O(24)	180(3)
Os(1)–C(12)–O(12)	173(2)	Os(3)–C(31)–O(31)	174(3)
Os(1)–C(13)–O(13)	177(3)	Os(3)–C(32)–O(32)	170(3)
Os(1)–C(14)–O(14)	173(6)	Os(3)–C(33)–O(33)	173(2)
Os(2)–C(23)–O(23)	174(2)	C(34–C(35)–C(36)	136(2)

ment of MeCN in the initial compound was much slower, especially in the case of the phenyl substituted olefin. All attempts to prepare pure cationic complexes of type I were unsuccessful.

The IR and NMR spectra of the compounds I and II were in a good agreement with the data that we obtained previously [1]. The structure of I was determined by X-ray diffraction.

(b) Crystal structure of I

Fractional coordinates and equivalent isotropic temperatures are listed in Table 1. The bond distances and angles are listed in Table 2. The X-ray data shows that I (Fig. 1) is an η^3-bonded π-allyl complex with allyl ligand bonded to one of the osmium atoms (Os(3)) of the triosmium cluster in an equatorial position. (It is noteworthy that the MeCN ligand in the starting compound was in axial position [4].) The presence of the positively charged allyl ligand an Os(3) causes lengthening of the bond distances between the carbonyl-substituted osmium atoms and allyl substituted osmium from the value of 2.877(3) Å in symmetric $Os_3(CO)_{12}$ [5] to values of 2.936(1) Å (Os(1)–Os(3)) and 2.9151(1) Å (Os(2)–Os(3)). Correspondingly the bond distance between the carbonyl substituted osmium atoms (Os(1)–Os(2)) shortens to 2.829(1) Å. A similar variation in bond distances was found in $(Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2)(Os(CO)_3Cl)$ [3], where the bond distances are: 3.002(2) (bonded to hydrido ligand), 2.886(2) and 2.882(2) Å for the osmium atoms. The equatorially bonded allyl ligand has nearly symmetrical bond distances between the

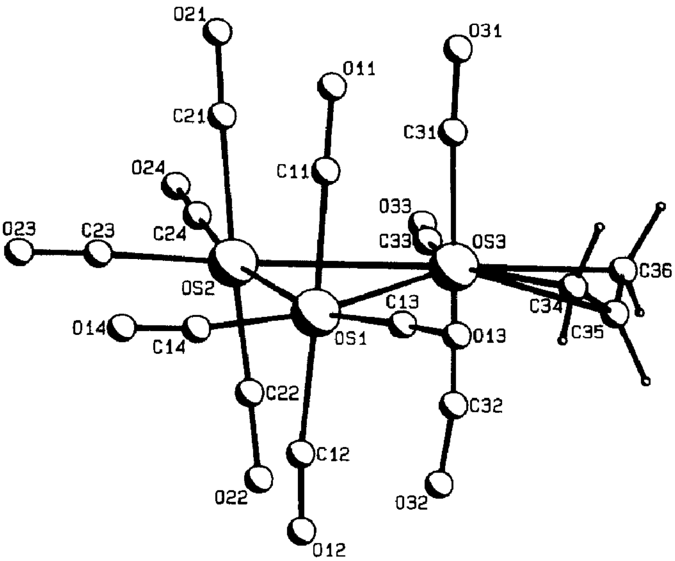

Fig. 1. X-ray picture of I.

carbon atoms, C(34)–C(35) 1.45 and C(35)–C(36) 1.34 Å and the angle C(34)–C(35)–C(36) is 136(2); and this can be regarded as a normal conformation for η^3-bonded allyl ligand. The conformation of the allyl ligand differs slightly from that in osmium cluster compounds in which the allyl ligand also acts as a bridging ligand (μ-η^3-allylosmium clusters) [6,7]. The bond distances between the allyl ligand and the osmium atoms, 2.34(2) (Os(3)–C(34)), 2.28(2) (Os(3)–C(35)) and 2.38(2)Å (Os(3)–C(36)) are slightly longer than those in bridging allyl osmium clusters [6,7] in accord with the positive charge in the allyl ligand. All the other bond distances and angles are comparable to those in other osmium carbonyl clusters [2–7]. The packing is maintained by ionic forces between the cationic cluster and BF_4 anion with no unusually short intermolecular contacts.

Experimental

The synthesis and isolation of the complexes were performed under argon and anhydrous solvents were used. The IR spectra were recorded with a Perkin–Elmer 283 infrared spectrometer and the PMR spectra with a JEOL GSX spectrometer (270 MHz). The crystals (orthorhombic) were grown from CH_2Cl_2/$MeNO_2$ (1/1) as a solvent.

Interaction of $Os_3(CO)_{11}MeCN$ with allyl alcohol and $HBF_4 \cdot Et_2O$

(a) One step reaction. Allyl alcohol (0.6 ml) and $HBF_4 \cdot Et_2O$ (0.15 ml) were added to a solution of $Os_3(CO)_{11}MeCN$ (0.0935 g, 0.1 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 1.5 h and evaporated to dryness. The residue was washed with ether (3 × 3 ml) and reprecipitated from nitromethane by addition of ether. The yellow precipitate was filtered off and dried. The combined yield of I and II was 0.0778 g [1].

(b) Two step reaction. Allyl alcohol (0.6 ml) was added to a solution of $Os_3(CO)_{11}MeCN$ (0.0935 g, 0.1 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred

for 1.5 h and $HBF_4 \cdot Et_2O$ (0.15 ml) was added dropwise with vigorous stirring. After 15 minutes the solution was evaporated, the residue was washed with ether, and reprecipitated from nitromethane solution by addition of ether. The precipitate was dried in vacuo. The yield of I was 0.0787 g (78). IR ($MeNO_2$): 2148w, 2100s, 2097, 2059vs, 2046s, 2020s, 2001m cm^{-1}. ^1H NMR (δ, ppm), (CF_3COOH/CD_2Cl_2): 2.86dd(2H, J_1 11.0 Hz, H_{anti}), 4,47ddd (2H, J_1 7.0 Hz, J_2 3.7 Hz, J_3 1.0 Hz, H_{syn}), 4.86(tt)(1H, $H_{centr.}$)

Crystal structure

Crystal data: $C_{14}H_5Os_3O_{11}BF_4$, orthorhombic, $Pna2_1$ (no.33), a 17.933(2), b 11.440(2), c 11.797(2) Å, V 2420.1(11) $Å^3$, D_c 2.76 g cm^{-3}, $M = 1006.6$, $F(000) = 1784$, μ 15.81 mm^{-1}, $Z = 4$. Unit cell parameters were determined from a least-squares fit of 25 reflections with $7 < \theta < 15°$. An orange crystal of I was mounted on a Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation (λ 0.71073 Å). 3946 reflections were measured up to θ 30° with bisecting geometry and $W/2\theta$ scan mode. 2067 reflections were considered as observed on the criterion $I > 2\sigma(I)$.

The data were corrected for Lorenz, polarization, and absorption [8] factors. The structure was solved by MULTAN11/82 [7], which gave the positions of the Os atoms, and refined by full matrix least-squares. The BF_4 anion was found to be highly disordered, there were two discrete BF_4 anions with population parameter = 0.50 for the B atoms, and the F atoms were even more disordered, and eight F positions with populations of 0.25 bonded to each atom were used. Owing to the disorder only the Os atoms could be refined anisotropically, the O and C atoms being refined isotropically.

From the difference Fourier map (with Os, O and C atoms) the B and F atoms were located, but refinement with normal isotropic temperature factors was unsuccessful so the BF_4 anion was optimized to tetrahedral geometry and ideal bond distances. From the coordinates found from the difference Fourier map the fluorine atoms were placed in ideal positions and used as riding atoms with fixed bond distance (B–F 1.45 Å) and fixed isotropic temperature factor (B_{eq} 5.0 $Å^2$). The isotropic temperature factor for the boron atom was also held fixed (B_{eq} 5.0 $Å^2$). The allylic hydrogens positions were calculated and these atoms treated as riding atoms at a fixed bond distance (C–H 1.00 Å) and with a fixed isotropic temperature factor (B_{eq} 5.0 $Å^2$) in the final refinement. The final refinement with the above conditions converged to $R = 0.046$ ($R_w = 0.083$) for 133 variables with $(\Delta/\sigma)_{max} = 0.12$. The weight was defined as $w = 1/((\sigma F)^2 + 0.15F)^2$, σF from counting statistics. The maximal residual electron density 1.03 $eÅ^3$ was close to one of the disordered BF_4 anion, and seemed to have chemical significance. The scattering factors were taken from International Tables for X-ray Crystallography [10]. Calculations were performed with the Enraf–Nonius program package [11] and the plot drawn with PLUTO [12] on a μ-VAX II computer. A list of observed and calculated structure factors is available from the authors.

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