3260 *Organometallics* **2000,** *19,* 3260−3262

Reaction of a Cationic Osmium(IV) Dihydride with Ethylene: Formation and Structure of the Novel Tetraethylene Dimer Complex $[\{(P^iPr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$

Miguel A. Esteruelas,* Cristina García-Yebra, Montserrat Oliván, and Enrique Oñate

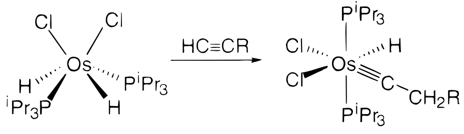
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Received March 6, 2000

Summary: The seven-coordinate osmium(IV) dihydride cation $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ reacts with ethylene to give the tetraethylene dimer complex $[\{(P^iPr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$, which has been characterized by X-ray diffraction analysis. Two ethylene molecules are disposed trans to the hydroxo bridges, and the other two lie trans to the oxygen atoms of the acetate group.

Reactions between transition-metal hydride complexes and unsaturated organic molecules, in particular alkynes and olefins, are fundamental steps in many catalytic processes.[1] In general, when the starting transition-metal compound contains only one hydride ligand, the reactions with alkynes afford alkenyl derivatives, whereas the reactions with olefins yield alkyl species. Both types of compounds are the result of the insertion of the unsaturated carbon−carbon bond into the M−H bond.[2]

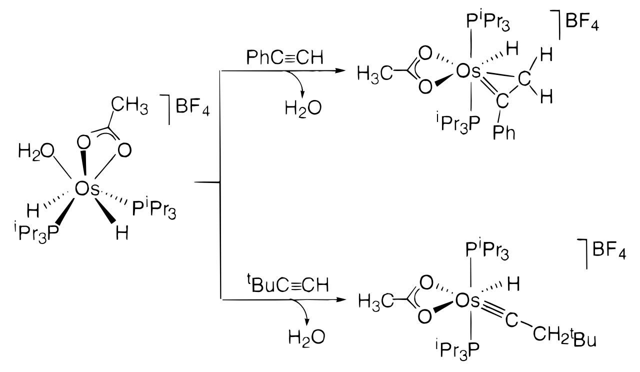
The reactivity of osmium dihydride complexes toward alkynes, HC≡CR, is less clear. It appears that the nature of the obtained products depends on factors related to the electronic nature of the starting complex and also on the nature of the substituent (R) of the alkyne. Thus, in 1993, we reported that the six-coordinate osmium(IV) dihydride $OsH_2Cl_2(P^iPr_3)_2$ reacted with phenylacetylene, cyclohexylacetylene, 1-(trimethylsilyl)-1,4-pentadiyne, and (trimethylsilyl)acetylene to give the hydride−carbyne derivatives $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ (eq 1).[3] However, recently, we have observed that the reaction of the related seven-coordinate osmium(IV) dihydride cation $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]^+$ with phenylacetylene affords the metallacyclopropene derivative $[OsH(\kappa^2\text{-}O_2CCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]^+$, while carbyne compounds, related to the ones shown in eq 1, are obtained with *tert*-butylacetylene and (trimethylsilyl)acetylene (Scheme 1).[4]



(1)

R = Ph, Cy, $CH_2C\equiv C(SiMe_3)$, H

Scheme 1



The reactions of osmium dihydride complexes with olefins start to point out a situation similar to that found with alkynes. Recently, Caulton and co-workers have reported that the complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with propene and styrene to give equimolecular amounts of $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ (R = CH_3, Ph) and of the hydrogenated olefin.[5] Now, we report that the related complex $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ reacts with ethylene to afford the tetraethylene dimer compound $[\{(P^iPr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$ and ethane, according to eq 2, while styrene is inert.

The formation of the tetraethylene complex is remarkable, and as far as we know, dimeric compounds containing two ethylene molecules coordinated to each metallic center are unknown in osmium chemistry. The reaction, like those previously reported by Caulton's group, involves the hydrogenation of 1 equiv of olefin/

---

[1] (a) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (b) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980. (c) Master, C. *Homogeneous Transition-Metal Catalysis-A Gentle Art*; Chapman and Hall: New York, 1981. (d) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.

[2] Collman, J. P.; Hegedus, L. S. *Principes and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988. (c) Elschenbroich, C. H.; Salzer, A. *Organometallics*; VCH: Weinheim, Germany, 1989.

[3] Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683.

[4] Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949.

[5] Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999.

10.1021/om000214p CCC: \$19.00

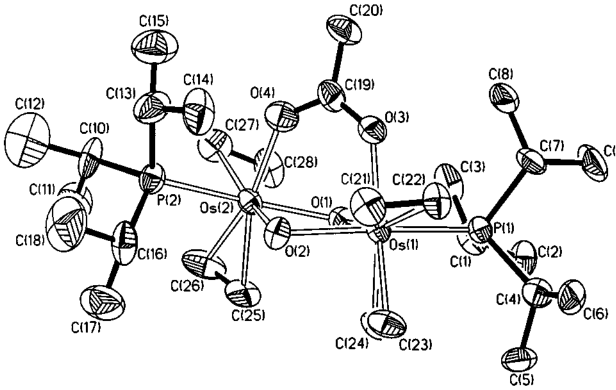
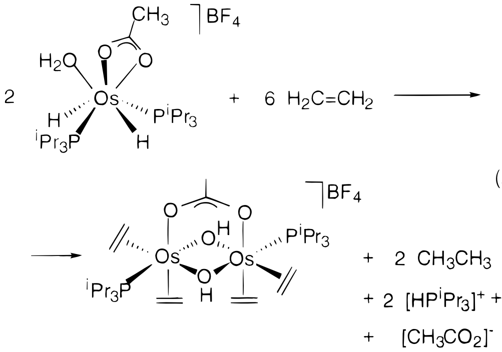


Figure 1. Molecular diagram of $[\{(P^iPr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]^+$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

equiv of dihydride. Furthermore, in this case, a deep transformation in the skeleton of the starting complex is observed. The most noticeable feature is the deprotonation of the water molecule by one of the coordinated phosphine ligands.



(2)

Figure 1 shows a view of the cation of $[\{(P^iPr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$. Selected bond distances and angles are listed in Table 1. The cation consists of two $Os(\eta^2\text{-}C_2H_4)_2(P^iPr_3)$ fragments connected though an acetate and two hydroxo bridges. Although crystallographically the two fragments are not related, they can be considered equivalent from a chemical point of view, due to the presence of a pseudo-C_2 axis, which contains the C(19)−C(20) bond of the acetate group. In agreement with this, the $^{31}P\{^1H\}$ NMR spectrum shows only one singlet at −18.3 ppm.

The coordination geometry around the osmium atoms, Os(1) and Os(2), can be rationalized as being derived from highly distorted octahedrons with the ethylene molecules C(21)−C(22) and C(27)−C(28) disposed trans to the hydroxo bridges O(1)−H and O(2)−H, respectively, and the ethylene molecules C(23)−C(24) and C(25)−C(26) disposed trans to the oxygen atoms O(3) and O(4) of the acetate group, respectively.

The olefinic ligands C(21)−C(22) and C(23)−C(24) coordinated to the Os(1) atom are mutually orthogonal, with an angle between the respective vectors of 88.0(7)°. The ethylene C(21)−C(22) eclipses the O(2)−P(1) vector, whereas the ethylene C(23)−C(24) lies parallel to the vector defined by O(1) and the midpoint of the C(21)−C(22) bond (M1). The angles between the vectors are 4(6) and 8(1)°, respectively. The orthogonal disposition of the ethylene ligands has been also observed in the mononuclear bis(ethylene) complex $[OsH(\eta^2\text{-}C_2H_4)_2(PMe_2Ph)_3]^+$. Such orthogonality avoids competition of the two olefin π^* orbitals for back-bonding from the same filled d_π orbital.[6]

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $[\{(P^iPr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$[a]

Os(1)−P(1)	2.394(3)	Os(2)−P(2)	2.404(3)
Os(1)−O(1)	2.083(7)	Os(2)−O(1)	2.133(8)
Os(1)−O(2)	2.166(7)	Os(2)−O(2)	2.103(7)
Os(1)−O(3)	2.132(8)	Os(2)−O(4)	2.095(8)
Os(1)−C(21)	2.168(11)	Os(2)−C(25)	2.138(12)
Os(1)−C(22)	2.211(10)	Os(2)−C(26)	2.160(12)
Os(1)−C(23)	2.148(13)	Os(2)−C(27)	2.234(12)
Os(1)−C(24)	2.158(11)	Os(2)−C(28)	2.153(12)
C(21)−C(22)	1.435(16)	C(25)−C(26)	1.32(2)
C(23)−C(24)	1.456(15)	C(27)−C(28)	1.42(2)
O(4)−C(19)	1.286(14)	O(3)−C(19)	1.268(14)
P(1)−Os(1)−O(1)	92.7(2)	P(2)−Os(2)−O(1)	158.1(2)
P(1)−Os(1)−O(2)	165.15(18)	P(2)−Os(2)−O(2)	86.2(2)
P(1)−Os(1)−O(3)	92.6(2)	P(2)−Os(2)−O(4)	89.3(3)
P(1)−Os(1)−M(1)	96.7(1)	P(2)−Os(2)−M(3)	95.0(4)
P(1)−Os(1)−M(2)	90.6(3)	P(2)−Os(2)−M(4)	99.8(4)
O(1)−Os(1)−O(2)	73.0(3)	O(1)−Os(2)−O(2)	73.3(3)
O(1)−Os(1)−O(3)	80.6(3)	O(1)−Os(2)−O(4)	82.2(3)
O(1)−Os(1)−M(1)	158.1(4)	O(1)−Os(2)−M(3)	95.8(5)
O(1)−Os(1)−M(2)	100.6(4)	O(1)−Os(2)−M(4)	98.3(4)
O(2)−Os(1)−O(3)	88.9(3)	O(2)−Os(2)−O(4)	86.4(3)
O(2)−Os(1)−M(1)	98.1(4)	O(2)−Os(2)−M(3)	99.8(4)
O(2)−Os(1)−M(2)	88.4(4)	O(2)−Os(2)−M(4)	164.1(4)
O(3)−Os(1)−M(1)	79.3(4)	O(4)−Os(2)−M(3)	172.7(4)
O(3)−Os(1)−M(2)	176.5(4)	O(4)−Os(2)−M(4)	79.0(5)
M(1)−Os(1)−M(2)	99.0(4)	M(3)−Os(2)−M(4)	94.4(6)

[a] M(1), M(2), M(3), and M(4) are the midpoints of the C(21)−C(22), C(23)−C(24), C(25)−C(26), and C(27)−C(28) double bonds, respectively.

In contrast with the ethylenes coordinated to Os(1), the vectors of the ethylenes coordinated to Os(2) (C(25)−C(26) and C(27)−C(28)) are not orthogonal, the angle between them being 50(1)°. The vector C(27)−C(28) is parallel to the vector P(2)−O(1). The angle between these is 9.3(8)°. However, the vector C(25)−C(26) and that defined by O(2) and the midpoint of the C(27)−C(28) bond (M4) form an angle of 34.7(9)°.

The ethylenes disposed trans to the acetate bridge (C(23)−C(24) and C(25)−C(26)) coordinate to the respective osmium atoms in a symmetrical fashion, with Os−C distances between 2.138(12) and 2.160(12) Å. However, the coordination of the ethylenes disposed trans to the hydroxo bridges (C(21)−C(22) and C(27)−C(28)) is asymmetrical. The Os(1)−C(21) (2.168(10) Å) and Os(2)−C(28) (2.153(12) Å) bond distances agree well the separations found between the osmium atoms and the carbon atoms of the olefins disposed trans to the acetate group, while the Os(1)−C(22) (2.211(10) Å) and Os(2)−C(27) (2.234(12) Å) bond lengths are between 0.05 and 0.09 Å longer than the latter. In the complex $OsH(OH)(CO)\{\eta^2\text{-}CH_2{=}CHCO_2CH_3\}(P^iPr_3)_2$, an asymmetrical coordination of methyl acrylate has been also found.[7] The olefinic bond distances (between 1.32(2) and 1.456(15) Å) are within the range reported for other osmium ethylene complexes.[8]

The different coordination manner of the ethylenes is reflected in the $^{13}C\{^1H\}$ and ^1H NMR spectra of the

---

(6) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966.

(7) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828.

complex at room temperature. The $^{13}C\{^{1}H\}$ NMR spectrum shows three olefinic resonances at 51.1, 50.2, and 47.3 ppm, whereas the ^{1}H NMR spectrum contains two complex olefinic resonances between 3.24 and 3.00, and 2.66 and 2.54 ppm, with a 3:1 intensity ratio. In addition, we should mention the resonance corresponding to the protons of the hydroxo groups, which appears at 1.47 ppm as the AA′ part of an AA′XX′ spin system. Variable-temperature ^{1}H NMR spectra are poorly informative, since peaks corresponding to the $P^{i}Pr_3$ ligands are overlapping with some of the ethylene peaks.

The osmium atoms and the hydroxo bridges form a four-membered M_2L_2 core, which has a slightly bent configuration. The dihedral angle between the O(1)−Os(1)−O(2) and O(1)−Os(2)−O(2) planes is 162.8(2)°. The Os−OH bonds disposed trans to the ethylene ligands (d(Os(1)−O(1)) = 2.083(7) Å and d(Os(2)−O(2)) = 2.103(7) Å) are shorter than those disposed trans to the phosphines (d(Os(1)−O(2)) = 2.166(7) Å and d(Os(2)−O(1)) = 2.133(8) Å), which is probably due to the different trans influence of the olefin and phosphine ligands. The separation between the osmium atoms (3.3696(9) Å) indicates that there is no bond between them, in agreement with the saturated character of both osmiums.

In conclusion, ethylene reacts with the seven-coordinate osmium(IV) dihydride cation $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^{i}Pr_3)_2]^+$ to afford the novel tetraethylene dimer complex $[\{(P^{i}Pr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]^+$, whereas styrene is inert.

The marked difference in behavior between these olefins and the marked difference in behavior between the cationic dihydride and $OsH_2Cl_2(P^{i}Pr_3)_2$ indicate that the prediction of the products resulting from reactions between osmium compounds containing two hydrogen atoms bonded to the metal and olefins presents limitations similar to those previously mentioned for the reactions of this type of species with terminal alkynes.[4]

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^{i}Pr_3)_2]BF_4$ was prepared by the published method.[4]

Preparation of $[\{(P^{i}Pr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$. A solution of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^{i}Pr_3)_2]BF_4$ (138 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was stirred for 5 h at 0 °C under an ethylene atmosphere. The resulting solution was concentrated to dryness to afford a yellow residue (the $^{31}P\{^{1}H\}$ NMR spectrum of this residue shows that the reaction is almost quantitative). The yellow residue was dissolved in ca. 0.5 mL of CH_2Cl_2, and diethyl ether was added to afford a pale yellow solid. NMR data (^{1}H and $^{31}P\{^{1}H\}$) of this solid show a mixture (10:6) of phosphonium salt and the title complex. Succesive crystallizations in mixtures of CH_2Cl_2/diethyl ether allowed us to separate yellow crystals of $[\{(P^{i}Pr_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$ from the phosphonium salt. Yield: 15 mg (15%). IR (Nujol, cm^{-1}): ν(OH) 3570 and 3541, ν_{asym}(OCO) 1580, ν(B−F) 1056. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 3.24−3.00 (m, 12H, $CH_2{=}CH_2$), 2.66−2.54 (m, 4H, $CH_2{=}CH_2$), 2.54−2.46 (m, 6H, PCH), 1.88 (s, 3H, $MeCO_2$), 1.47 (m, AA′ part of an AA′XX′ spin system, 2H, OH), 1.19 (dd, 18H, ^{3}J(PH) = 12.3 Hz, ^{3}J(HH) = 6.9 Hz, $PCHCH_3$). $^{31}P\{^{1}H\}$ NMR (121.42 MHz, $CDCl_3$, 298 K): δ −18.3 (s). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K, plus APT): δ 179.9 (s, $MeCO_2$), 51.1 (s, $CH_2{=}CH_2$), 50.2 (s, $CH_2{=}CH_2$), 47.3 (s, $CH_2{=}CH_2$), 25.7 (s, $MeCO_2$), 24.6 (d, ^{1}J(PC) = 26.3 Hz, PCH), 19.9 and 19.5 (both s, $PCHCH_3$). Anal. Calcd for $C_{28}H_{63}BF_4O_4Os_2P_2$: C, 33.87; H, 6.40. Found: C, 34.04; H, 6.46. MS (FAB+): m/z 907 (30) (M^+), 879 (35) (M^+ − ($CH_2{=}CH_2$)), 851(50) (M^+ − 2($CH_2{=}CH_2$)), 803(100) (M^+ − ($CH_2{=}CH_2$)−(OH)−($CH_2{=}CH_2$)).

X-ray Structure Analysis of $[\{(P^{i}Pr_3)_2(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)]BF_4$. A crystal suitable for X-ray diffraction analysis (0.28 × 0.22 × 0.04 mm) was mounted onto a glass fiber and transferred to a Siemens-P4 automatic diffractometer (T = 200.0(2) K, Mo Kα radiation, graphite monocromator, λ = 0.710 73 Å). Accurate unit cell parameters and an orientation matrix were determined by least-squares fitting from the settings of 60 high-angle reflections (monoclinic, space group $P2_1/n$, a = 15.371(3) Å, b = 11.934(3) Å, c = 19.360(5) Å, β = 90.00(1), V = 3551.4 Å^3, Z = 4). Data were collected by the $\omega/2\theta$ scan method over a θ range of 1.5−25°. Corrections for decay and absorption (semiempirical method) were applied. The structure was solved by Patterson (Os atom) and conventional Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL97).[9] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms (except those corresponding to hydroxy and olefinic groups) were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. Atomic scattering factors, corrected for anomalous dispersion, were implemented by the program. The refinement converges to R1(F) = 0.0488 ($F^2 > 2\sigma(F^2)$), and wR2(F^2) = 0.1162 (all data), with weighting parameters x = 0.0505 and y = 0.

Acknowledgment. We thank the DGES (Project PB98-1591, Programa de Promoción General del Conocimiento). C. García-Yebra thanks the CSIC-(Repsol-YPF) for a postdoctoral grant.

Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000214P

---

(8) (a) Kiel, G.-Y.; Takats, J.; Grevels, F.-W. *J. Am. Chem. Soc.* **1987**, *109*, 2227. (b) Gallop, M. A.; Jonhson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1809. (c) Chen, Y.-J.; Knobler, C. B.; Kaesz, H. D. *Polyhedron* **1988**, *7*, 1891. (d) Gallop, M. A.; Gómez-Sal, M. P.; Housecroft, C. E.; Johnson, B. F. G.; Lewis, J.; Owen, S. M.; Raithby, P. R.; Wright, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 2502. (e) Bender, B. R.; Norton, J. R.; Melter, M. M.: Anderson, O. P.; Rappe, A. K. *Organometallics* **1992**, *11*, 3427. (f) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 2545.

(9) Sheldrick, G. SHELX-97 package, University of Göttingen, Göttingen, Germany, 1997.