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Preparation and Characterization of Novel Os–Diolefin Dimers: New Entry to Os–Cyclooctadiene Complexes

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The complex $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) has been prepared in high yield by treatment of $OsCl_3 \cdot 3H_2O$ (54% Os) with 1,5-cyclooctadiene in ethanol under reflux. Under air, it is unstable and undergoes oxidation by action of O_2 to afford the neutral derivative $\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2$ (**2**). The terminal chlorine ligands of the anion of **1** are activated toward nucleophilic substitution. Thus, reaction of the salt $[NBu_4][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1a**) with NaCp in toluene gives $[NBu_4][\{Os(\eta^1\text{-}C_5H_5)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}]$ (**3**) as a result of the replacement of one of the terminal chlorine atoms by the cyclopentadienyl ligand. The CH_2 group of the latter can be deprotonated by the bridging methoxy ligand of the iridium dimer $[Ir(\mu\text{-OMe})(\eta^4\text{-COD})]_2$. The reaction leads to the trinuclear derivative $[NBu_4][\{(\eta^4\text{-COD})Ir(\eta^5\text{-}C_5H_4\text{-}\eta^1)Os(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}]$ (**4**) containing a bridging C_5H_4 ligand that is η^1-coordinated to an osmium atom of the dimeric unit and η^5-coordinated to the $Ir(\eta^4\text{-COD})$ moiety. Salt **1a** also reacts with $LiC{\equiv}CPh$. In this case, the reaction produces the substitution of both terminal chlorine ligands to afford the bis(alkynyl) derivative $[NBu_4][\{Os(C{\equiv}CPh)(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**5**). Complexes **1**, **2**, **3**, and **4** have been characterized by X-ray diffraction analysis. Although the separations between the osmium atoms are short, between 2.6696(4) and 2.8633(5) Å, theoretical calculations indicate that only in **2** is there direct metal–metal interaction, as the bond order is 0.5.

Introduction

There are complexes that are determinant for development of the chemistry of each particular transition metal. They are obtained in high yield directly from commercially available inorganic salts of the element and the origin of a genealogical tree of compounds families.

Success in the ruthenium chemistry during the past decade has been, in part, due to the ready accessibility of a wide range of this type of starting materials. For instance, the ruthenium polymer $[RuCl_2(COD)]_x$[1] (COD = 1,5-cyclooctadiene) is prepared in 90% yield from $RuCl_3 \cdot 3H_2O$ and 1,5-cyclooctadiene in refluxing ethanol.[2] This complex has proved to be a useful precursor for wide series of derivatives which have promoted development of rich chemistry in both stoichiometric and catalytic transformations.[3]

Osmium is more reducing than ruthenium and prefers coordination saturation and redox isomers with more metal−carbon bonds.[4] As a consequence of these characteristics, the chemistry of osmium is more complex and versatile than that of ruthenium.[5] Thus, one should expect that, in the future, the potentiality of osmium will become greater than that of ruthenium. The current lower development of osmium chemistry is in part a consequence of the lower effort to find

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starting materials from $OsCl_3{\cdot}3H_2O$, or related salts, and optimize the synthetic procedures leading to them.

In 1966, Winkhaus et al. described the preparation of the counterpart osmium polymer $[OsCl_2(COD)]_x$ in 35% yield by reaction of H_2OsCl_6 with 1,5-cyclooctadiene in boiling isoamyl alcohol.[6] In 1974, Schrock and co-workers reported a high-yield procedure for this polymer (90%) which involves heating OsO_4 in a mixture of concentrated HCl and isoamyl alcohol, adding 1,5-cyclooctadiene, and distilling off the solvent to afford the yellow-brown product.[7] However, by this procedure Girolami's group only obtains yields of 15−20%. The difficulty in obtaining $[OsCl_2(COD)]_x$ in high yields has prompted Girolami and co-workers to prepare the bromo analogue $[OsBr_2(COD)]_x$, which has shown to be a useful starting material for any array of osmium complexes.[8] This compound is obtained in 90% yield by reaction of H_2OsBr_6 with excess 1,5-cyclooctadiene in boiling *tert*-butyl alcohol. H_2OsBr_6 is generated by addition of HBr to OsO_4.

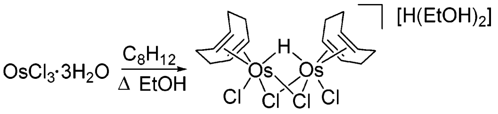
The choice of the solvent is critical for the course of this type of reaction involving metallic salts. A clear example is the synthesis of the triisopropylphosphine complexes $OsHCl(CO)(PiPr_3)_2$[9] and $OsH_2Cl_2(PiPr_3)_2$,[10] which are obtained under the same conditions but using different solvents. While the first one is formed in methanol, the second one precipitates in 2-propanol. In addition, it should be mentioned that OsO_4 is a toxic and dangerous compound which should be avoided in this type of procedure. A recommendable alternative is $OsCl_3{\cdot}3H_2O$.

In the search for a new and original osmium starting material containing the 1,5-cyclooctadiene diolefin, we carried out the reaction of $OsCl_3{\cdot}3H_2O$ with 1,5-cyclooctadiene in ethanol. In this paper we report the discovery, characterization, and first reactions of the novel compound $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ which, in contrast to the polymers $[MCl_2(COD)]_x$ (M = Ru, Os), is dinuclear and anionic.

Results and Discussion

1. Preparation and Characterization of $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$.

Treatment of $OsCl_3{\cdot}3H_2O$ (54% Os) with about 8 equiv of 1,5-cyclooctadiene in ethanol under reflux for 60 h leads to a green solution. After the solvent is replaced by pentane, $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1**) is isolated in 76% yield (eq 1).



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(1)

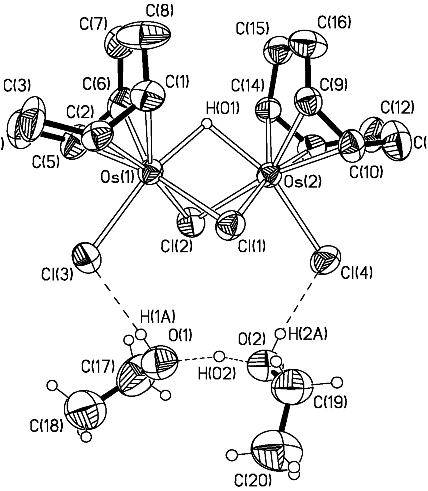

Figure 1. Molecular diagram of complex **1**. Selected bond lengths (Å) and angles (deg): Os(1)−Cl(1) 2.452(2), Os(1)−Cl(2) 2.452(3), Os(1)−Cl(3) 2.408(3), Os(2)−Cl(1) 2.449(2), Os(2)−Cl(2) 2.449(3), Os(2)−Cl(4) 2.417(3), Os(1)−H(01) 1.86(7), Os(2)−H(01) 1.86(7), Os(1)−C(1) 2.144(9), Os(1)−C(2) 2.147(10), Os(1)−C(5) 2.130(11), Os(1)−C(6) 2.152(10), Os(2)−C(9) 2.145(10), Os(2)−C(10) 2.129(10), Os(2)−C(13) 2.151(10), Os(2)−C(14) 2.149(10), C(1)−C(2) 1.397(14), C(5)−C(6) 1.393(15), C(9)−C(10) 1.407(15), C(13)−C(14) 1.422(14), O(1)···H(02) 1.37(12), O(2)···H(02) 1.07(12), O(1)−O(2) 2.400(13), Os(1)···Os(2) 2.8065(6), Cl(3)···H(1A) 2.13, Cl(4)···H(2A) 2.13, Cl(3)−Os(1)−H(01) 161(3), Cl(4)−Os(2)−H(01) 160(3).

Complex **1** was characterized by X-ray diffraction analysis. The structure proves formation of the anion $[\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]^-$ and the bis(ethanol)hydrogen cation $[H(EtOH)_2]^+$, which are connected by Cl···H hydrogen bonds. Figure 1 shows a view of the geometry of both ions.

The anion can be described as a bioctahedral face-shared M_2L_9 dimer with conical $OsCl(\eta^4\text{-COD})$ units, two bridging chlorine atoms (Cl(1) and Cl(2)), and a bridging hydride ligand (H(01)). At 223 K, the latter was located in the difference Fourier maps and refined symmetrically as an isotropic atom together with the remaining of non-hydrogen atoms of the structure, giving Os(1)−H and Os(2)−H distances of 1.86(7) Å. In solution, the presence of the hydride ligand is revealed by the ^1H NMR spectrum, which in benzene-d_6 shows a singlet at −21.10 ppm. In agreement with the dinuclear character of the anion, in the MALDI-TOF MS the highest m/z peak is observed at 741 with the isotope pattern as expected (Figure 2).

The separation between the osmium atoms (2.8065(6) Å) is shorter than those reported for complexes $[\{OsH_2(PiPr_3)_2\}_2(\mu\text{-Cl})_3]^+$ (3.5385(11) Å)[11] or $\{Os(\eta^5\text{-}C_5Me_5)Br\}_2(\mu\text{-Br})_2$ (2.970(1) Å).[12] However, it agrees well with the metal−metal distance in the ruthenium bisoctahedral anion $[\{RuH(PPh_3)_2\}_2(\mu\text{-H})(\mu\text{-Cl})_2]^-$ (2.8251(5) Å) for which a Ru−Ru single bond has been proposed to exist.[13] Both separations are consistent with the osmium−osmium single bond distances found in the triosmium cluster $Os_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}$

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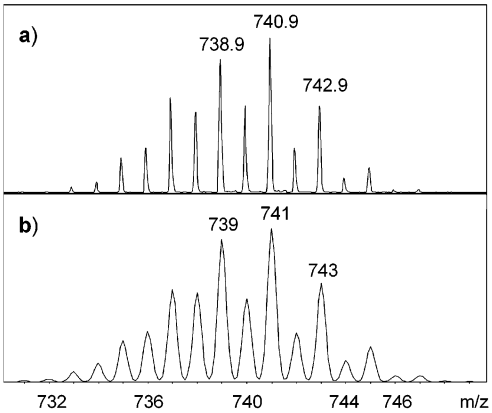

Figure 2. (a) Selected region of the MALDI-TOF MS spectrum showing the isotopic distribution for the anion of **1** (highest peak at *m*/*z* 740.9). (b) Simulated pattern for the molecular formula $C_{16}H_{25}Cl_4Os_2$ corresponding to the anion of **1**.

HapyPh-N,N)$(CO)_9$ (H_2apyPh = 2-amino-6-phenylpyridine; 2.8141(6), 2.7765(6), and 2.7873(6) Å)[14] and only about 0.1 Å shorter than the osmium−osmium bond length reported for $Os_2(\mu\text{-bdt})(CO)_6$ (bdt = benzene-1,2-dithiolate; 2.686(2) Å).[15]

Like **1**, complexes $(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}H)(\mu\text{-}CO)Co(CO)_3$,[16] $[\{IrH(PPh_3)_2\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CR)]^+$ (R = (*R*)-CH(OMe)Ph),[17] and $(P\mathit{i}Pr_3)_2(CO)HRu(\mu\text{-}H)(\mu\text{-}OMe)Ir(\eta^4\text{-}COD)$[18] contain a bridging hydride ligand and the separations between the metal centers are short and consistent with the corresponding metal−metal bonds. However, theoretical calculations suggest that these species do not exhibit any direct metal−metal interaction. To establish whether the short Os(1)−Os(2) separation in **1** is due to some direct interaction between the metal atoms, we performed a topological analysis of the electron density on the basis of Bader's atom-in-molecules (AIM) theory.[19] Both the electron density map and its Laplacian in the Os−H−Os plane are shown in Figure 3.

Analysis of the Laplacian of the electron density and calculations of critical points in the region between Os(1) and Os(2) indicate the absence of any direct metal−metal interaction. Density functional theory (DFT) calculations[20] on **1** help to understand the absence of a bond between Os(1) and Os(2). Figure 4 shows the occupancy for the $S = 0$ associated state of metal-based t_{2g}-derived orbitals, which are split into a pair of orbitals of σ symmetry with regard to the Os(1)−Os(2) axis and a double pair with δ and π character. Because in **1** 12 electrons of 2 d^6 centers occupy all osmium−osmium bonding and antibonding orbitals, a metal−metal bond is precluded.

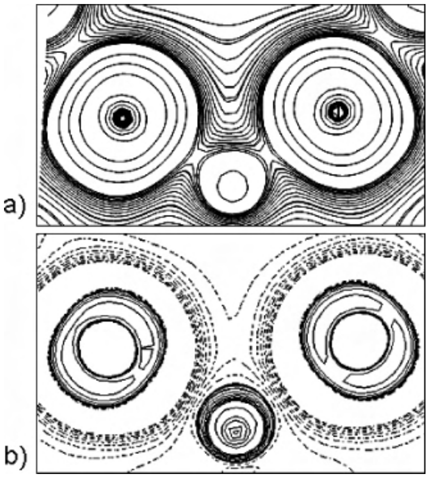

Figure 3. Electron density map (a) and Laplacian (b) for complex **1** in the plane Os−H−Os.

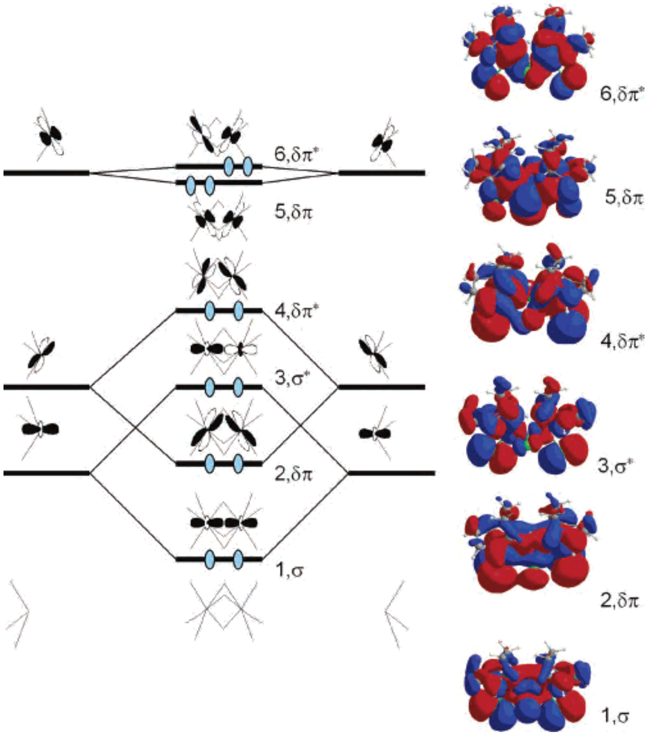

Figure 4. Schematic representation of the metal−metal manifold for the face-shared complex **1**.

The terminal chlorine atoms are pseudo-trans-disposed to the bridging hydride ligand with Cl(3)−Os(1)−H(01) and Cl(4)−Os(2)−H(01) angles of 161(3)° and 160(3)°, respectively. The terminal Os(1)−Cl(3) and Os(2)−Cl(4) bond lengths of 2.408(3) and 2.417(3) Å are statistically identical and about 0.04 Å shorter than the bridging Os−Cl distances, between 2.452(3) and 2.449(3) Å, which are also statistically identical. The 1,5-cyclooctadiene ligand takes its customary "tub" conformation. The olefinic bond distances, between 1.422(14) and 1.393(15) Å, lie within the range reported for

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transition-metal complexes (1.340−1.455 Å).[21] They are also statistically identical and longer than those found in the free 1,5-cyclooctadiene molecule (1.34 Å),[22] in agreement with the usual Chatt, Dewar, and Duncanson metal-bonding scheme. The osmium−diene coordination exhibits Os−C distances between 2.129(10) and 2.152(10) Å, which agree well with those found in other osmium−olefin complexes (2.13−2.28 Å).[23]

The $[H(EtOH)_2]^+$ cation can be regarded as an ethyl-disubstituted $[H_5O_2]^+$ ion.[24] The acid proton lies between the two oxygen atoms, which are separated by 2.400(13) Å. The O(1)−O(2) separation is about 0.2 Å longer than that found in the bis(methanol)hydrogen cation $[H(MeOH)_2]^+$ of the salt $[H(MeOH)_2][NaMn_2(2\text{-}OH\text{-}SALPN)_2(OAc)_4]\cdot 2H_2O$ (2-OH-SALPN = *N*,*N*′-disalicylidene-2-hydroxy-propylenediamine).[25] The terminal OH protons point toward the terminal chlorine ligands of the anion. The separation between them (2.13 Å) is shorter than the sum of the van der Waals radii of hydrogen and chlorine [$r_{vdw}(H) = 1.20$, $r_{vdw}(Cl) = 1.80$ Å],[26] supporting the anion−cation Cl···H−O hydrogen bonds, as a result of the electrostatic interaction of the electronegative chlorine ligands and the electropositive O−H hydrogen atoms. The anion−cation hydrogen bonds are also supported by the IR spectrum of **1** in KBr, which shows two strong ν(OH) bands at 2042 and 1967 cm^{-1}. In agreement with this assignment, they are not observed in the IR spectra of the salts $[NBu_4][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1a**) and $[PPh_3(CH_2Ph)][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (**1b**), which were obtained by stirring **1** with $[NBu_4][PF_6]$ and $[PPh_3(CH_2Ph)]Cl$, respectively, in ethanol. Of great importance in biological and organic chemistry,[27] hydrogen bonding is presently attracting considerable interest in the chemistry of the transition metals.[28]

In benzene-d_6 at room temperature some interaction between the anion and the cation of **1** also exist. This is strongly supported by the chemical shifts of the resonances corresponding to the hydride ligand of the anion in the ^{1}H NMR spectrum of the $[H(EtOH)_2]^+$ and $[NBu_4]^+$ salts, **1** and **1a**, respectively. Because the bridging hydride is trans-disposed to both terminal chlorine ligands, which are the atoms of the anion involved in the anion−cation interaction in **1**, the chemical shifts of the hydride resonance depend on the nature of the cation of the salt. Thus, the resonance due to the hydride of **1a** appears at −19.6 ppm, shifted 1.4 ppm toward lower field with regard to that of **1**. The interaction between the anion and the cation does not hinder any fluxional process, which makes the OH protons of the cation and the 1,5-cyclooctadiene ligands of the anion of **1** equivalent. The bridging and terminal OH protons display only one resonance, which appears at 11.42 ppm as a broad singlet, whereas the olefinic protons of the dienes give rise to two complex signals between 4.64 and 4.54 ppm and between 4.28 and 4.16 ppm. In agreement with the ^{1}H NMR spectrum, the $^{13}C\{^1H\}$ NMR spectrum of **1** contains two resonances at 67.1 and 62.5 ppm for the C(sp^2) atoms of the 1,5-cyclooctadiene ligands. The chemical shift of these resonances is consistent with that previously reported for other osmium 1,5-cyclooctadiene compounds.[8,23a,29]

2. Oxidation of 1: Preparation and Characterization of $\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2$. A noticeable result of the DFT calculations on **1** is that the energy of the HOMO orbital is −2.5 eV. This suggests that one electron of the anion can be easily removed to afford the neutral species $\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2$ (**2**). To confirm this, we carried out an electrochemical study on **1a** in dichloromethane. Figure 5 shows a simple voltammetric profile.

Complex **1a** undergoes reversible ($i_{P,O}/i_{P,O'} \approx 1$) diffusion-controlled ($i_P/V^{1/2}$ is nearly constant for scan rates varying between 50 and 200 mV s^{-1}) one-electron oxidation (ΔE_p

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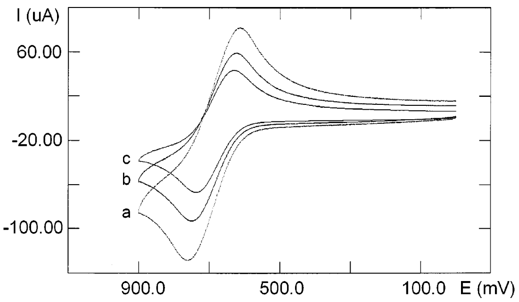


Figure 5. Cyclic voltammogram of a solution 0.5 mM in **1a** and 0.1 M in $[NBu_4]PF_6/CH_2Cl_2$. Scan initiated at 0 V versus SCE in the positive direction. Scan rate (υ): (a) 200, (b) 100, (c) 50 mV/s. $E^{SCE}{}_{1/2} = +0.68$ V.

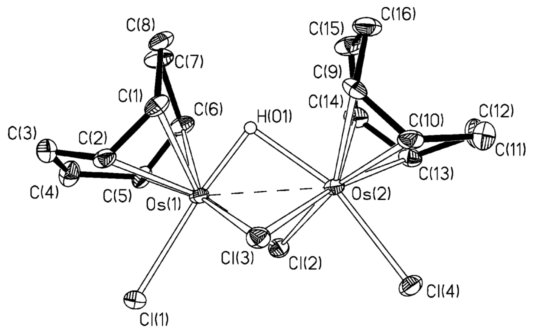
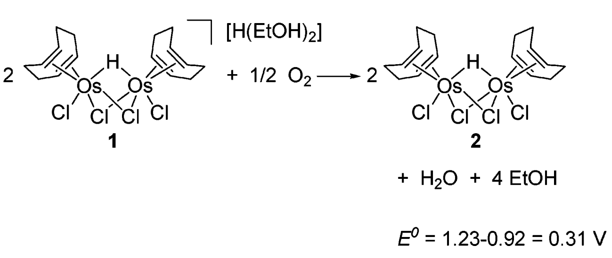


Figure 6. Molecular diagram of complex **2**. Selected bond lengths (Å): Os(1)−Cl(1) 2.3900(14), Os(1)−Cl(2) 2.4380(14), Os(1)−Cl(3) 2.4360(14), Os(2)−Cl(2) 2.4371(14), Os(2)−Cl(3) 2.4279(14), Os(2)−Cl(4) 2.3920(14), Os(1)−H(01) 1.6823, Os(2)−H(01) 2.0031, Os(1)−C(1) 2.196(6), Os(1)−C(2) 2.158(6), Os(1)−C(5) 2.148(6), Os(1)−C(6) 2.187(6), Os(2)−C(9) 2.180(6), Os(2)−C(10) 2.165(6), Os(2)−C(13) 2.165(6), Os(2)−C(14) 2.191(6), C(1)−C(2) 1.395(8), C(5)−C(6) 1.382(8), C(9)−C(10) 1.406(8), C(13)−C(14) 1.407(8), Os(1)···Os(2) 2.6696(4).

= 0.08 V) to give **2** with $E^{SCE}(\mathbf{2},\mathbf{1}) = +0.68$ V. This value corresponds to $E°(\mathbf{2},\mathbf{1}) = +0.92$ V.[30] Since $E°(O_2,H_2O) = 1.23$ V, one should expect the oxidation of **1** to afford **2** by action of atmospheric oxygen, according to eq 2. In fact, when a benzene solution of **1** is left to stand at room temperature for 24 h under air, complex **2** is formed.



(2)

Paramagnetic complex **2** was isolated as dark green needles in 68% yield and characterized by X-ray diffraction analysis. Figure 6 shows a view of the molecular geometry.

The molecule can be described as a bioctahedral face-shared M_2L_9 dimer with $OsCl(\eta^4\text{-COD})$ units, two bridging chlorine atoms, Cl(2) and Cl(3), and a bridging hydride ligand, H(01). At 100 K, the hydride was located in the difference Fourier maps. However, in contrast to that of **1**, it does not refine. The obtained Os−H distances, 1.6823 (Os(1)−H(01)) and 2.0031 (Os(2)−H(01)) Å, are certainly underestimated. In this context, it should be mentioned that DFT calculations on the structure of **2** yield Os−H distances of 1.81 Å, which support a symmetrical bridge and compare well with those of **1**.

The DFT calculations also show that removal of the electron of the HOMO of anion **1** produces a stabilization of the orbital to afford **2** with a half-occupied HOMO at −6.4 eV. Because this orbital has mainly antibonding metal−metal character, oxidation of **1** to give **2** involves an increase of the osmium−osmium bond order from 0 to 0.5. This rise in order results in an approach of the metal centers. Thus, the separation between Os(1) and Os(2) in **2**, 2.6696(4) Å, is about 0.14 Å shorter than that of **1**.

Oxidation of **1** also produces a shortening of the terminal Os−Cl distances. Thus, the Os(1)−Cl(1) and Os(2)−Cl(4) bond lengths, 2.3900(14) and 2.3920(14) Å, respectively, are statistically identical and about 0.014 Å shorter than the terminal Os−Cl distances in **1**. Like in the latter, the terminal Os−Cl distances in **2** are about 0.04 Å shorter than the bridging Os−Cl bond lengths, between 2.4279(14) and 2.4380(14) Å. The distances between the coordinated $C(sp^2)$ atoms of the 1,5-cyclooctadiene ligands, between 1.382(8) and 1.407(8) Å, as well as the $Os-C(sp^2)$ bond lengths, between 2.148(6) and 2.191(6) Å, compare well with those of **1**.

3. Reactions of 1a with Main-Group Organometallic Compounds. Treatment of **1a** with 2.5 equiv of sodium cyclopentadienyl in toluene at room temperature gives rise to replacement of one of the terminal chlorine ligands of the starting compound by a cyclopentadienyl group to afford the η^1-cyclopentadienyl derivative $[NBu_4][\{Os(\eta^1\text{-}C_5H_5)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}]$ (**3**). This complex was isolated as a red solid in 70% yield. The solid is a 3:2 mixture of the two possible isomers resulting from σ coordination of the five-membered ring through a $C(sp^2)$ atom disposed in the α position (a) or alternating in the β position (b) with regard to the $C(sp^3)$ atom (Scheme 1).

Figure 7 shows a view of the structure of the anion of isomer **3a**. The species can be described as an asymmetrical dimer formed by the conical $Os(\eta^1\text{-}C_5H_5)(\eta^4\text{-COD})$ and $OsCl(\eta^4\text{-COD})$ moieties, which are joined by two bridging chlorine atoms and a bridging hydride ligand. The separation between the metal centers, 2.8633(5) Å, agrees well with that of **1**. The cyclopentadienyl group is bonded to one of the osmium atoms with an Os(1)−C(1) bond length of 2.089(7) Å, which compares well with the $Os-C(sp^2)$ single bond distances found in osmium−alkenyl complexes.[23e,31]

The C(1)−C(2) distance of 1.370(9) Å is statistically identical with the C(3)−C(4) bond length, 1.354(11) Å, and both of them agree with the average carbon−carbon distance

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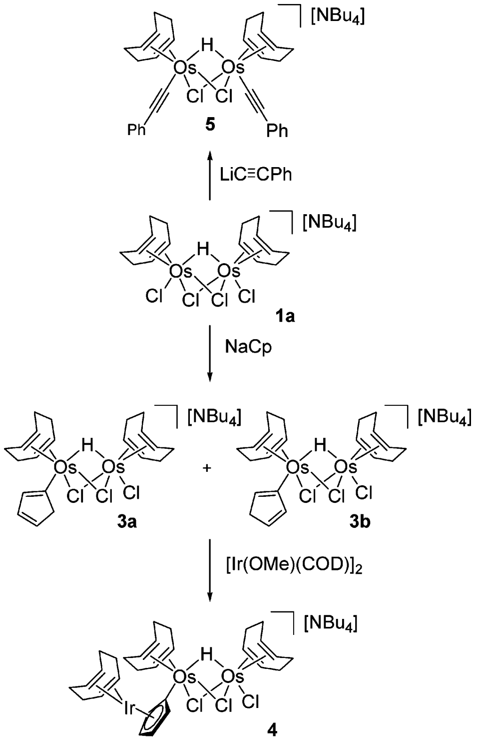
(30) $E° = E^{SCE} + 0.24$.

(31) See, for example: (a) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295. (b) Werner, H.; Weinand, R.; Otto, H. *J. Organomet. Chem.* **1986**, *307*, 49. (c) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (d) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169. (e) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098. (f) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294. (g) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946. (h) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 3965.

Scheme 1



for a C(sp^2)−C(sp^2) double bond (1.32(1) Å).[32] The C(2)−C(3) bond length of 1.472(10) Å also compares well with the distance expected for a C(sp^2)−C(sp^2) single bond (about 1.48 Å). The C(1)−C(5) and C(4)−C(5) distances are 1.506(10) and 1.451(11) Å, respectively.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3a** in dichloromethane-d_2 at room temperature are consistent with the structure shown in Figure 7. The cyclopentadienyl protons display four resonances in the ^{1}H NMR spectrum. Those due to the C(sp^2)−H protons are observed between 6.51 and 6.45 and at 6.39 ppm, while that corresponding to the CH$_2$ group appears at 3.39 ppm. The resonances due to the C(sp^2)H protons of the coordinated dienes are observed between 3.85 and 3.43 ppm. The hydride resonance appears at −13.65 ppm. In the ^{13}C{^{1}H} NMR spectrum the C(sp^2) resonances of the cyclopentadienyl ligands are observed at 145.7 (OsC), 135, 133.5, and 131.7 (CH), while the CH$_2$ resonance appears at 53.6 ppm. The C(sp^2) atoms of the dienes display singlets at 62.1, 61.5, 57.4, and 57.1 ppm. In agreement with coordination of the cyclopentadienyl ligand to the osmium atom by a C$_\alpha$ atom with regard to the CH$_2$ group, the ^{1}H,^{13}C-{^{1}H} HMBC spectrum shows cross-peaks between the CH$_2$ resonance at 3.39 ppm and the C(sp^2) ^{13}C resonances at 145.7 and 133.5 ppm.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3b** are consistent with those of **3a**. In the ^{1}H NMR spectrum the cyclopentadienyl resonances appear at 6.98, 6.26, and 6.19 (CH) and 3.09 (CH$_2$) ppm, while the C(sp^2)H resonances of the dienes are also observed between 3.85 and 3.43 ppm. The hydride ligand gives rise to a singlet at −13.52 ppm. In the ^{13}C{^{1}H} NMR spectrum the cyclopentadienyl resonances appear at 148.4 (CH), 135.4 (OsC), 134.4 and 126.9 (CH), and 42.2 (CH$_2$) ppm, while the C(sp^2) resonances of the dienes are observed at 61.4, 61.3, 57.0, and 56.4 ppm. In this case, in the ^{1}H, ^{13}C{^{1}H}-HMBC spectrum, the CH$_2$ ^{1}H resonance at 3.09 ppm has cross-peaks with the C(sp^2) ^{13}C resonances at 126.9 and 148.4 ppm.

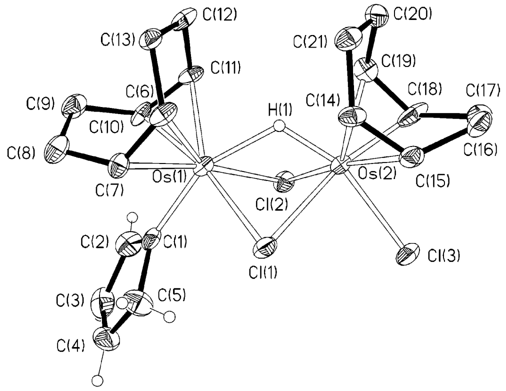


Figure 7. Molecular diagram of the anion of **3a**. Selected bond lengths (Å): Os(1)−Cl(1) 2.4522(17), Os(1)−Cl(2) 2.4585(16), Os(2)−Cl(1) 2.4409(18), Os(2)−Cl(2) 2.4703(15), Os(2)−Cl(3) 2.4292(14), Os(1)−C(1) 2.089(7), Os(1)−C(6) 2.143(6), Os(1)−C(7) 2.113(7), Os(1)−C(10) 2.138(6), Os(1)−C(11) 2.134(6), Os(2)−C(14) 2.139(6), Os(2)−C(15) 2.116(5), Os(2)−C(18) 2.072(8), Os(2)−C(19) 2.135(6), C(1)−C(2) 1.370(9), C(2)−C(3) 1.472(10), C(3)−C(4) 1.354(11), C(4)−C(5) 1.451(11), C(1)−C(5) 1.506(10), C(6)−C(7) 1.410(9), C(10)−C(11) 1.409(9), C(14)−C(15) 1.408(8), C(18)−C(19) 1.407(9), Os(1)···Os(2) 2.8633(5).

The methoxide group of [Ir(μ-OMe)(olefin)]$_2$ complexes has shown to be a very good leaving group in reactions with molecules containing relatively acidic protons.[33] This prompted us to investigate the reaction of **3** with [Ir(μ-OMe)(η^4-COD)]$_2$ since one should expect that the CH$_2$ group of the coordinated cyclopentadienyl ligand was fairly acidic. Treatment of **3** with the iridium dimer in a 2:1 molar ratio, in acetone at room temperature, leads to a red-brown solution from which the trinuclear species [NBu$_4$][{(η^4-COD)Ir(η^5-C$_5$H$_4$-η^1)Os(η^4-COD)}(μ-H)(μ-Cl)$_2${OsCl(η^4-COD)}] (**4**) is isolated as red-brown needles in 54% yield according to Scheme 1.

Complex **4** has been characterized by X-ray diffraction analysis. Figure 8 shows an ORTEP drawing of the anion. The structure proves the formation of **4** containing a bridging five-membered C$_5$H$_4$ ligand which is η^1-coordinated to an osmium atom of the dimeric unit and η^5-coordinated to the Ir(η^4-COD) moiety. Complexes containing this type of ligand are rare.[34] Some examples involving osmium include {μ_2-η^1:η^5-C$_5$(tBu)$_2$H$_2$}$_2$Os$_2$(CO)$_4$[35] and [{Os(η^5-C$_5$H$_5$)}$_2$(μ_2-η^1:η^5-C$_5$H$_4$)$_2$][PF$_6$]$_2$.[36]

Deprotonation of the CH$_2$ group of the C$_5$H$_5$ ligand of **3** and subsequent coordination of the Ir(η^4-COD) unit has no influence on the σ-Os bond. Thus, the Os(1)−C(1) distance,

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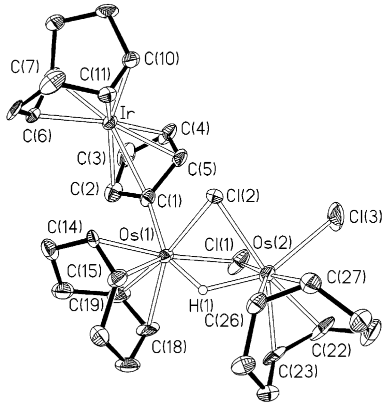

Figure 8. Molecular diagram of the anion of **4**. Selected bond lengths (Å): Os(1)−Cl(1) 2.4343(2), Os(1)−Cl(2) 2.469(2), Os(2)−Cl(1) 2.452(3), Os(2)−Cl(2) 2.468(2), Os(2)−Cl(3) 2.416(3), Os(1)−C(1) 2.117(10), Os(1)−C(14) 2.131(9), Os(1)−C(15) 2.138(10), Os(1)−C(18) 2.124(10), Os(1)−C(19) 2.132(10), Os(2)−C(22) 2.118(10), Os(2)−C(23) 2.153(10), Os(2)−C(26) 2.139(9), Os(2)−C(27) 2.120(11), Ir−C(1) 2.322(9), Ir−C(2) 2.260(10), Ir−C(3) 2.235(10), Ir−C(4) 2.225(10), Ir−C(5) 2.183(9), Ir−C(6) 2.112(9), Ir−C(7) 2.125(9), Ir−C(10) 2.083(10), Ir−C(11) 2.124(8), C(6)−C(7) 1.437(14), C(10)−C(11) 1.439(5), C(14)−C(15) 1.438(14), C(18)−C(19) 1.406(15), C(22)−C(23) 1.452(16), C(26)−C(27) 1.414(14), Os(1)···Os(2) 2.8598(6).

2.117(10) Å, is statistically identical with the Os(1)−C(1) bond length in **3a**. The C_5H_4 ligand coordinates to the iridium atom with Ir−C distances between 2.183(9) and 2.322(9) Å, which agree well with those reported for related half-sandwich iridium compounds.[37]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** in dichloromethane-d_2 at room temperature are consistent with the structure shown in Figure 8. In the ^{1}H NMR spectrum the C_5H_4 ligand gives rise to an AA′BB′ spin system between 5.0 and 5.3 ppm. The hydride resonance is observed at −14.31 ppm. In the ^{13}C{^{1}H} NMR spectrum the resonances due to the C_5H_5 ligands appear at 89.9 (OsC) and 92.9 and 77.5 (CH) ppm, whereas those corresponding to the C(sp^2) atoms of the dienes bonded to osmium are observed at 61.7, 61.6, 57.1, and 56.7 ppm. The C(sp^2) atoms of the diene coordinated to iridium give rise to a singlet at 45.2 ppm. The latter agrees well with those previously reported for Ir(η^5-C_5R_5)(η^4-COD) complexes.[38]

Complex **1a** also reacts with lithium phenylacetylide. The reaction leads to the bis(acetylide) derivative [NBu$_4$][{Os(C≡CPh)(η^4-COD)}$_2$(μ-H)(μ-Cl)$_2$] (**5**) as a result of the replacement of both terminal chlorine atoms of the starting compound by alkynyl ligands. Complex **5** is isolated as dark yellow crystals in 73% yield according to Scheme 1.

The presence of the alkynyl ligands in the complex is mainly supported by the IR and ^{13}C{^{1}H} NMR spectra. In the IR spectrum in KBr, the most noticeable feature is a C≡C band at 2105 cm^{-1}. In the ^{13}C{^{1}H} NMR spectrum the resonances due to the C(sp) atoms of the alkynyl groups appear at 110.3 and 96.1 ppm. In agreement with **1**, the spectrum also shows two olefinic resonances at 58.4 and 55.7 ppm. The ^{1}H NMR spectrum contains the hydride resonance at −8.00 ppm.

Concluding Remarks

This study shows the preparation, characterization, and first reactions of a novel osmium-1,5-cyclooctadiene starting material obtained from a commercially available inorganic salt. In contrast to ruthenium, treatment of $OsCl_3\cdot 3H_2O$ with 1,5-cyclooctadiene in ethanol under reflux leads to the salt [H(EtOH)$_2$][{OsCl(η^4-COD)}$_2$(μ-H)(μ-Cl)$_2$], where the anion can be described as two conical OsCl(η^4-COD) moieties joined by two bridging chlorine atoms and a hydride ligand. Although the separation between the osmium atoms is short, a topological analysis of the electron density in the region between the osmium atoms, on the basis of Bader's atom-in-molecules theory, indicates the absence of a direct metal−metal interaction. In agreement, DFT calculations show that the 12 electrons of the d^6 centers occupy all osmium bonding and antibonding orbitals.

The DFT calculations also indicate that the HOMO of the dimer anion is poorly stabilized. As a consequence, it is easily oxidized to afford the neutral species {OsCl(η^4-COD)}$_2$(μ-H)(μ-Cl)$_2$, with a stabilized half-occupied HOMO orbital and an osmium-osmium bond order of 0.5. The terminal chlorine ligands of the dimer anion are activated toward nucleophilic substitution. Thus, reaction of the [NBu$_4$] salt with LiC≡CPh and NaCp leads to [NBu$_4$][{Os(C≡CPh)(η^4-COD)}$_2$(μ-H)(μ-Cl)$_2$] and [NBu$_4$][{Os(η^1-C_5H_5)(η^4-COD)}(μ-H)(μ-Cl)$_2${OsCl(η^4-COD)}], respectively. The CH_2 group of the cyclopentadienyl ligand of the latter is easily deprotonated by the bridging methoxy ligand of the dimer [Ir(μ-OMe)(η^4-COD)]$_2$ to give the trinuclear derivative [NBu$_4$][{(η^4-COD)Ir(η^5-C_5H_4-η^1)Os(η^4-COD)}(μ-H)(μ-Cl)$_2${OsCl(η^4-COD)}] containing a bridging five-membered C_5H_4 ligand which is η^1-coordinated to an osmium atom of the dimeric unit and η^5-coordinated to the Ir(η^4-COD) moiety.

In conclusion, we report the preparation and full characterization of the dimer [{OsCl(η^4-COD)}$_2$(μ-H)(μ-Cl)$_2$]$^-$, which is directly obtained from $OsCl_3\cdot 3H_2O$, and it is particularly useful for development of the dinuclear chemistry of the Os(η^4-COD) moiety.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. Infrared spectra were recorded on a Spectrum One spectrometer as solids (KBr pellets). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian GEMINI 2000-300 MHz, a Bruker Avance 300, or a Bruker ARX Avance 400 spectrometer. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (85%) (^{31}P{^{1}H}). Coupling constants, *J*, are given in hertz. MALDI-MS measurements were performed on a reflex time-of-flying instrument (Bruker Daltonics Microflex Analyser) equipped with a target micro-SCOUT ion source, operating in the negative reflection mode with pulsed extraction. Ions were formed by a pulsed UV laser beam (nitrogen laser, $\lambda = 337$ nm) and using dithranol (DIT) as a matrix. Cyclic voltammetric studies were performed under argon using an EG&G model 273 potentiostat in

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conjunction with a three-electrode cell. The three-electrode system consists of a platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) separated from the test compartment by a fine-porosity frit. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer. $[Ir(\mu\text{-OMe})(\eta^4\text{-COD})]_2$ was prepared as reported previously.[39]

Preparation of $[H(EtOH)_2][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (1). A solution of $OsCl_3\cdot 3H_2O$ (54%) (1 g, 2.84 mmol) and 1,5-cyclooctadiene (2.8 mL, 22.6 mmol) in ethanol (30 mL) was refluxed for 60 h. After that, the solvent was replaced by pentane to precipitate a dark green solid that was washed twice with pentane and dried in vacuo (900 mg, 1.08 mmol, 76% yield). Anal. Calcd for $C_{20}H_{38}Cl_4O_2Os_2$: C, 28.84; H, 4.60. Found: C, 28.97; H, 4.21. IR (KBr, cm^{-1}): 2042, 1967 [ν_{OH} (H(EtOH)$_2$)]. MS (MALDI-TOF): *m*/*z* 741 (100), [M]$^-$. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 11.42 [br s, 3 H, *H*(EtOH)$_2$], 4.64−4.54 (4 H, C*H*−*C*OD), 4.28−4.16 (4 H, C*H*−*C*OD), 3.51 (q, $^3J_{HH}$ = 6.8 Hz, 4 H, CH_3CH_2OH), 2.88−2.61 (4 H, C*H*$_2$−COD), 2.20−1.90 (12 H, C*H*$_2$−COD), 0.85 (t, $^3J_{HH}$ = 6.8 Hz, 6 H, CH_3CH_2OH), −21.03 (s, 1 H, Os−H). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 293 K): δ 67.1, 62.5 (both s, *C*H−COD), 60.4 (s, CH_3CH_2OH), 35.8, 31.2 (both s, *C*H$_2$−COD), 15.3 (s, CH_3CH_2OH).

Preparation of $[NBu_4][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (1a). A solution of **1** (1.10 g, 1.32 mmol) and $[NBu_4][PF_6]$ (560 mg, 1.45 mmol) in ethanol (40 mL) was stirred overnight at room temperature. The reaction evolves with formation of a green precipitate that was isolated by filtration and washed twice with diethyl ether (973 mg, 0.99 mmol, 75% yield). Anal. Calcd for $C_{32}H_{61}Cl_4NOs_2$: C, 39.13; H, 6.26; N, 1.43. Found: C, 39.23; H, 6.04; N, 1.20. ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 4.70−4.55 (4 H, C*H*−*C*OD), 4.35−4.25 (4 H, C*H*−*C*OD), 3.02−2.90 (4 H, C*H*$_2$−COD), 2.80 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 2.30−2.07 (12 H, C*H*$_2$−COD), 1.30−1.15 [16 H, $N(CH_2CH_2CH_2CH_3)_4$], 0.83 [t, $^3J_{HH}$ = 7.0 Hz, 12 H, $N(CH_2CH_2CH_2CH_3)_4$], −19.6 (s, 1 H, Os−H). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 293 K): δ 66.0, 60.9 (both s, *C*H−COD), 58.5 [s, $N(CH_2CH_2CH_2CH_3)_4$], 36.2, 31.8 (both s, *C*H$_2$−COD), 24.3 [s, $N(CH_2CH_2CH_2CH_3)_4$], 20.1 [s, $N(CH_2CH_2CH_2CH_3)_4$], 14.0 [s, $N(CH_2CH_2CH_2CH_3)_4$].

Preparation of $[PPh_3(CH_2Ph)][\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]$ (1b). A solution of **1** (779 mg, 0.93 mmol) and $[PPh_3(CH_2Ph)]Cl$ (364 mg, 0.93 mmol) in ethanol (30 mL) was stirred overnight at room temperature. The reaction evolves with formation of a green precipitate that was isolated by filtration and washed once with ethanol and twice with diethyl ether (826 mg, 0.75 mmol, 81% yield). Anal. Calcd for $C_{41}H_{47}Cl_4Os_2P$: C, 45.05; H, 4.23. Found: C, 45.06; H, 4.35. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.83 [m, 3 H, $P(C_6H_5)_3$], 7.74−7.44 [12 H, $P(C_6H_5)_3$], 7.30 (m, 1 H, $PCH_2C_6H_5$), 7.20 (m, 2 H, $PCH_2C_6H_5$), 7.01 (m, 2 H, $PCH_2C_6H_5$), 4.88 (d, $^2J_{HP}$ = 14.1 Hz, 2 H, $PCH_2C_6H_5$), 4.05−3.79 (8 H, C*H*−*C*OD), 2.57−2.39 (4 H, C*H*$_2$−COD), 2.36−2.10 (8 H, C*H*$_2$−COD), 2.08−1.93 (4 H, C*H*$_2$−COD), −20.15 (s, 1 H, Os−H). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 293 K): δ 135.9 (d, J_{CP} = 2.5 Hz, arom-*C*H, PCH_2Ph), 135.1 (d, $^3J_{CP}$ = 9.7 Hz, *m*-*C*H, PPh_3), 132.1 (d, $^4J_{CP}$ = 5.5 Hz, *p*-*C*H, PPh_3), 130.9 (d, $^2J_{CP}$ = 12.4 Hz, *o*-*C*H, PPh_3), 129.6 (d, J_{CP} = 3.7 Hz, arom-*C*H, PCH_2Ph), 129.3 (d, J_{CP} = 3.7 Hz, arom-*C*H, PCH_2Ph), 127.7 (d, $^1J_{CP}$ = 8.3 Hz, *ipso*-*C*, $PCH_2C_6H_5$), 117.9 [d, $^1J_{CP}$ = 86.0 Hz, *ipso*-*C*, PPh_3], 65.8, 61.1 (both s, *C*H−COD), 36.1, 31.5 (both s, *C*H$_2$−COD), 32.05 (d, $^1J_{CP}$ = 47.9 Hz, PCH_2Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 25.0.

$\{OsCl(\eta^4\text{-COD})\}_2(\mu\text{-H})(\mu\text{-Cl})_2$ (2). A solution of **1** (50 mg, 0.06 mmol) in a minimum amount of benzene was left to stand at room temperature 24 h in the air. The initially dark green solution turned purple, and dark green crystals were isolated (30 mg, 0.04 mmol, 68%). Anal. Calcd for $C_{16}H_{25}Cl_4Os_2$: C, 25.98; H, 3.41. Found: C, 26.00; H, 3.31. IR (KBr, cm^{-1}): 1616 ($\nu_{C=C}$). MS (MALDI-TOF): *m*/*z* 741 (100), [M]$^-$.

Preparation of $[NBu_4][\{Os(\eta^1\text{-}C_5H_5)(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}]$ (3). To a mixture of complex **1a** (322 mg, 0.33 mmol) and NaCp (72.2 mg, 0.82 mmol) was added toluene (9 mL) at room temperature. The reaction mixture was stirred for 4 h and then filtered to separate salts. The filtrate was dried in vacuo, and the brown-red residue was washed twice with pentane to give a red solid. A 3:2 mixture of isomers **3a**:**3b** was obtained (235 mg, 0.23 mmol, 70%). Anal. Calcd for $C_{37}H_{66}Cl_3NOs_2$: C, 43.92; H, 6.58; N, 1.38. Found: C, 43.84; H, 6.13; N, 1.41. MS (MALDI-TOF): *m*/*z* 771 (100), [M]$^-$. *Major isomer* **3a**. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 6.51−6.45 (2 H, C*H*−*C*$_5$H$_5$), 6.39 (m, 1 H, C*H*−*C*$_5$H$_5$), 3.85−3.78 (2 H, C*H*−*C*OD), 3.60−3.52 (4 H, C*H*−*C*OD), 3.52−3.43 (2 H, C*H*−*C*OD), 3.39 (m, 2 H, C*H*$_2$−C$_5$H$_5$), 3.10 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 2.52−2.32 (6 H, C*H*$_2$−COD), 2.08−1.90 (4 H, C*H*$_2$−COD), 1.80−1.66 (6 H, C*H*$_2$−COD), 1.57 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.40 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.00 [t, $^3J_{HH}$ = 7.2, 12 H, $N(CH_2CH_2CH_2CH_3)_4$], −13.65 (s, 1 H, Os−H). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 293 K): δ 145.7 (s, *C*Os, C$_5$H$_5$), 135.0, 133.5, 131.7 (all s, *C*H, C$_5$H$_5$), 62.1, 61.5, 57.4, 57.1 (all s, *C*H−COD), 59.5 [s, $N(CH_2CH_2CH_2CH_3)_4$], 53.6 (s, *C*H$_2$COs, C$_5$H$_5$), 36.5, 34.7, 33.1, 31.2 (all s, *C*H$_2$−COD), 24.6 [s, $N(CH_2CH_2CH_2CH_3)_4$], 20.6 [s, $N(CH_2CH_2CH_2CH_3)_4$], 14.1 [s, $N(CH_2CH_2CH_2CH_3)_4$]. *Minor isomer* **3b**. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 6.98 (m, 1 H, C*H*−C$_5$H$_5$), 6.26 (m, 1 H, C*H*−*C*$_5$H$_5$), 6.19 (m, 1 H, C*H*−C$_5$H$_5$), 3.85−3.78 (2 H, C*H*−*C*OD), 3.60−3.52 (4 H, C*H*−*C*OD), 3.52−3.43 (2 H, C*H*−*C*OD), 3.09 (m, 2 H, CH$_2$−C$_5$H$_5$, overlapped signal), 3.09 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 2.52−2.32 (6 H, C*H*$_2$−COD), 2.08−1.90 (4 H, C*H*$_2$−COD), 1.80−1.66 (6 H, C*H*$_2$−COD), 1.57 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.39 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.00 [t, $^3J_{HH}$ = 7.2, 12 H, $N(CH_2CH_2CH_2CH_3)_4$], −13.52 (s, 1 H, Os−H). ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 293 K): δ 148.4 (s, *C*HCOs, C$_5$H$_5$), 135.4 (s, *C*Os, C$_5$H$_5$), 134.4 (s, CH*C*HCOs, C$_5$H$_5$), 126.9 (s, CH$_2$*C*HCOs, C$_5$H$_5$), 61.4, 61.3, 57.0, 56.4 (all s, *C*H−COD), 59.5 [s, $N(CH_2CH_2CH_2CH_3)_4$], 42.2 (s, *C*H$_2$CHCOs, C$_5$H$_5$), 36.5, 34.7, 33.1, 31.2 (all s, *C*H$_2$−COD), 24.6 [s, $N(CH_2CH_2CH_2CH_3)_4$], 20.3 [s, $N(CH_2CH_2CH_2CH_3)_4$], 14.1 [s, $N(CH_2CH_2CH_2CH_3)_4$].

Preparation of $[NBu_4][\{(\eta^4\text{-COD})Ir(\eta^5\text{-}C_5H_4\text{-}\eta^1)Os(\eta^4\text{-COD})\}(\mu\text{-H})(\mu\text{-Cl})_2\{OsCl(\eta^4\text{-COD})\}]$ (4). To a mixture of complexes **3** (100 mg, 0.1 mmol) and $[Ir(\mu\text{-OMe})(COD)]_2$ (33 mg, 0.05 mmol) was added 3 mL of acetone, and the reaction was stirred at room temperature for 22 h. The red-brown solution thus obtained was dried in vacuo, and the residue was recrystallized in a mixture CH_2Cl_2/pentane to give red-brown needles (70 mg, 0.05 mmol, 54%). Anal. Calcd for $C_{45}H_{77}Cl_3IrNOs_2$: C, 41.22; H, 5.92; N, 1.07. Found: C, 41.39; H, 5.69; N, 1.09. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 5.30−5.00 (AA′BB′, 4 H, C$_5$H$_4$), 3.78 (m, 2 H, C*H*−*C*OD−Os), 3.68−3.62 (4 H, C*H*−*C*OD−Ir), 3.59 (m, 2 H, C*H*−*C*OD−Os), 3.52 (m, 2 H, C*H*−*C*OD−Os), 3.46 (m, 2 H, C*H*−*C*OD−Os), 3.15 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 2.64−2.58 (2 H, C*H*$_2$−COD−Os), 2.51−2.45 (2 H, C*H*$_2$−COD−Os), 2.42−2.36 (4 H, C*H*$_2$−COD−Os), 2.07−2.00 (2 H, C*H*$_2$−COD−Os), 2.02−1.95 (4 H, C*H*$_2$−COD−Ir), 1.85−1.78 (6 H, C*H*$_2$−COD−Os), 1.72 (m, 4 H, C*H*$_2$−COD−Ir), 1.61 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.52 [m, 8 H, $N(CH_2CH_2CH_2CH_3)_4$], 1.04 [t, $^3J_{HH}$ = 7.2 Hz, 12 H, $N(CH_2CH_2CH_2CH_3)_4$], −14.31 (s, 1 H, Os−H). ^{13}C{^{1}H} NMR

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Table 1. Crystal Data Collection and Refinement for **1**, **2**, **3a**, and **4**

	1	2	3a	4
	crystal data			
formula	$C_{16}H_{25}Cl_4Os_2{\cdot}C_4H_{13}O_2$	$C_{16}H_{25}Cl_4Os_2{\cdot}2C_6H_6$	$C_{37}H_{66}Cl_3NOs_2$	$C_{45}H_{77}Cl_3IrNOs_2$
mol wt	832.70	895.78	1011.66	1311.03
color and habit	irregular block, dark orange	irregular block, orange	orange, prism	orange, prism
size, mm	0.24, 0.24, 0.16	0.26, 0.08, 0.08	0.18, 0.06, 0.04	0.36, 0.10, 0.06
symmetry, space group	monoclinic, *P*2(1)	monoclinic, *P*2(1)/*n*	orthorhombic, *Pna*2(1)	orthorhombic, *Pbcn*
a, Å	9.0837(14)	10.8680(15)	17.941(3)	39.752(4)
b, Å	8.6975(13)	15.263(2)	12.671(2)	11.0636(12)
c, Å	15.876(2)	16.438(2)	16.640(3)	19.758(2)
β, deg	97.064(3)	90.322(2)		
V, Å3	1244.7(3)	2726.7(6)	3782.7(11)	8689.6(16)
Z	2	4	4	8
D_{calcd}, g cm^{-3}	2.222	2.182	1.776	2.004
	data collection and refinement			
diffractometer	Bruker Smart APEX			
λ(Mo-Kα), Å	0.71073			
monochromator	graphite oriented			
scan type	ω scans			
μ, mm^{-1}	10.642	9.720	6.950	9.107
2θ, range deg	4, 58	4, 58	4, 57	4, 58
temp, K	223.0(2)	100.0(2)	100.0(2)	100.0(2)
no. of data collect	15632	33757	32331	104440
no. of unique data	6002 ($R_{\text{int}} = 0.0446$)	6776 ($R_{\text{int}} = 0.0631$)	9174 ($R_{\text{int}} = 0.0584$)	11076 ($R_{\text{int}} = 0.1000$)
no. of params/restrains	266/3	333/0	437/6	487/134
Flack parameter	0.001(12)		0.007(6)	
$R_1{}^a$ [$F^2 > 2\sigma(F^2)$]	0.0394	0.0340	0.0327	0.0539
$wR_2{}^b$ [all data]	0.0848	0.0631	0.0457	0.1241
S^c [all data]	0.961	0.958	0.816	1.024

^{a} $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2(F^2) = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$. ^{c} Goof $= S = \{\sum[F_o{}^2 - F_c{}^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

(100.62 MHz, CD_2Cl_2, 293 K): δ 92.9 (s, *C*HCOs, C_5H_4), 89.9 (s, *C*Os, C_5H_4), 77.5 (s, *C*HCHCOs, C_5H_4), 61.7, 61.6 (both s, *C*H−COD−Os), 59.0 [s, N($CH_2CH_2CH_2CH_3)_4$], 57.1, 56.7 (both s, *C*H−COD−Os), 45.2 (s, *C*H−COD−Ir), 35.9, 34.6 (both s, *C*H_2−COD−Os), 34.3 (s, *C*H_2−COD−Ir), 32.3, 30.7 (both s, *C*H_2−COD−Os), 24.0 [s, N($CH_2CH_2CH_2CH_3)_4$], 19.8 [s, N($CH_2CH_2CH_2CH_3)_4$], 13.5 [s, N($CH_2CH_2CH_2CH_3)_4$].

Preparation of [NBu_4][{Os(C≡CPh)(η^4-COD)}$_2$(μ-H)(μ-Cl)$_2$] (5). To a mixture of complex **1a** (350 mg, 0.36 mmol) and PhC≡CLi (175 mg, 1.62 mmol) was added THF (10 mL) at −60 °C, and the reaction was stirred while the temperature was slowly raising to 0 °C (3 h). Then, the solvent was removed in vacuo, and the product was extracted with CH_2Cl_2 (2 × 3 mL) and recrystallized in CH_2Cl_2/Et_2O mixture to give dark yellow crystals (289 mg, 0.26 mmol, 73%). Anal. Calcd for $C_{48}H_{71}Cl_2NOs_2$: C, 51.78; H, 6.43; N, 1.26. Found: C, 51.67; H, 6.06; N, 1.26. IR (KBr, cm^{-1}): ν 2105 ($\nu_{C\equiv C}$). MS (MALDI-TOF): *m/z* 871 (100), [M]$^-$. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.41 (d, $^3J_{HH} = 7.2$ Hz, 4 H, *o*-C_6H_5), 7.24 (dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 7.2$ Hz, 4 H, *m*-C_6H_5), 7.07 (t, $^3J_{HH} = 7.5$ Hz, 2 H, *p*-C_6H_5), 3.55−3.35 (8 H, C*H*−COD), 3.00 [m, 8 H, N($CH_2CH_2CH_2CH_3)_4$], 2.73−2.65 (4 H, CH_2−COD), 2.62−2.53 (m, 4 H, CH_2−COD), 1.96−1.85 (m, 4 H, CH_2−COD), 1.85−1.76 (4 H, CH_2−COD), 1.53−1.27 [16 H, N($CH_2CH_2CH_2CH_3)_4$], 1.00 [t, $^3J_{HH} = 7.2$ Hz, 12 H, N($CH_2CH_2CH_2CH_3)_4$], −8.00 (s, 1 H, Os−H). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 293 K): δ 131.7 (s, *o*-C_6H_5), 128.4 (s, *m*-C_6H_5), 124.6 (s, *p*-C_6H_5), 110.3 (s, C≡*C*Ph), 96.1 (s, *C*≡CPh), 59.6 [s, N($CH_2CH_2CH_2CH_3)_4$], 58.4, 55.7 (both s, *C*H−COD), 35.2, 32.8 (both s, *C*H_2−COD), 24.5 [s, N($CH_2CH_2CH_2CH_3)_4$], 20.3 [s, N($CH_2CH_2CH_2CH_3)_4$], 14.1 [s, N($CH_2CH_2CH_2CH_3)_4$].

Computational Details. Theoretical calculations were carried out on the model complexes (**1** and **2**) by optimizing the structure at the B3LYP-DFT level with the Gaussian 03 program.[40] The basis sets used were LANL2DZ basis and pseudopotentials for Os, 6-31G(d,p) for hydrogens and 6-31G(d) for the rest of atoms.

Structural Analysis of Complexes 1, 2, 3a, and 4. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 (**1**, **3a**, and **4**) or 40 (**2**) mA. Data were collected over the complete sphere. Each frame exposure time was 10 s (20 s for **3a**) covering 0.3° in ω. Data were corrected for absorption using a multiscan method applied with the SADABS program.[41] The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[42] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms

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were observed in the difference Fourier maps and refined as free isotropic atoms or included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. Hydride ligands were observed, but unfortunately they did not refine properly, and models with fixed positions (**2**, **3a**, and **4**) or restrained geometry (**1**) were used. Crystal data and details of the data collection and refinement are given in Table 1.

For **2**, two molecules of benzene were observed in the asymmetric unit as crystallization solvent. For **4**, the NBu_4 cation was observed disordered. The anion was defined with two moieties, complementary occupancy factors, isotropic atoms, and restrained geometry. The presence of a residual peak very close to the C(11) atom of **4** gives rise to unreasonable anisotropic thermal parameters and bond distances. The poor thermal displacements could be improved by use of the ISOR facility, while the bond distances where restrained to be the same to the other olefinic bonds in the molecule.

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Supporting Information Available: Tables of crystallographic data and bond lengths and angles of complexes **1**, **2**, **3a**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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