

The Dihydride–Osmium(IV) Complex [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]BF₄ as a Precursor for Carbon–Carbon Coupling Reactions

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

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

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The dihydride–osmium(IV) complex [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]BF₄ (**1**) reacts with acetylene (1 atm) at 0 °C to give polyacetylene and the vinyl–carbyne derivative [Os(CH=CH₂)(κ²-O₂CCH₃)(≡CCH₃)(PⁱPr₃)₂]BF₄ (**2**). Both polyacetylene and **2** can also be obtained by reaction of [OsH(κ²-O₂CCH₃)(≡CCH₃)(PⁱPr₃)₂]BF₄ (**3**) with acetylene. Under an acetylene atmosphere, complex **2** yields polyacetylene in a slow but constant manner. Complex **2** reacts with carbon monoxide to give initially the carbene derivative [Os(κ²-O₂CCH₃){C(CH=CH₂)CH₃}(CO)(PⁱPr₃)₂]BF₄ (**4**), by migratory insertion of the carbyne ligand of **2** into the Os–vinyl bond. Under a carbon monoxide atmosphere, complex **2** is unstable and evolves into [Os(κ²-O₂CCH₃)(CO)₂(PⁱPr₃)₂]BF₄ (**5**). Treatment of **2** with KOH in methanol produces the deprotonation of the carbyne ligand and the formation of the vinyl–vinylidene derivative Os(CH=CH₂)(κ²-O₂CCH₃)(=C=CH₂)(PⁱPr₃)₂ (**6**), which reacts with carbon monoxide to give the butadienyl compound Os{C(CH=CH₂)=CH₂}{κ¹-OC(O)CH₃}(CO)₂(PⁱPr₃)₂ (**7**) by migratory insertion of the vinylidene ligand into the Os–vinyl bond. The structure of **7** has been determined by X-ray diffraction analysis. The geometry around the osmium atom can be rationalized as a distorted octahedron with the phosphine ligands occupying opposite positions. The remaining perpendicular plane is formed by the butadienyl ligand, the acetate, and the carbonyl groups mutually *cis* disposed. The Os–butadienyl distance is 2.195(5) Å, whereas the torsion angle in the diene is 50.7(8)°. The butadienyl ligand of **7** acts as a diene in Diels–Alder reactions. Thus, the addition of dimethyl acetylenedicarboxylate and maleic anhydride to benzene solutions of **7** affords the corresponding cycloaddition products Os{C(CH=CH₂)=CH₂}{κ¹-OC(O)CH₃}(CO)₂(PⁱPr₃)₂ (**8**) and Os{C(CH=CH₂)=CH₂}{κ¹-OC(O)CH₃}(CO)₂(PⁱPr₃)₂ (**9**). Treatment of **8** with HBF₄·OEt₂ gives **5** and dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate.

Introduction

The formation of carbon–carbon bonds mediated by transition-metal compounds has emerged in its own right over the past decades as an important step in organic synthesis. These reactions can involve migratory *cis*-ligand insertion, the coupling of adjacent carbon–carbon bonds, or the attack of a reagent to unsaturated organic ligands without metal–reagent bond formation.¹

Among the group of organic molecules most frequently studied in metal-assisted carbon–carbon bond-forming reactions, alkynes play a prominent role, as is evident from their participation in numerous transformations of both fundamental and industrial relevance.^{2,3} In this respect, monohydride,⁴ hydride–dihydrogen,⁵ trihydride,⁶ and dihydride–dihydrogen⁷ derivatives of osmium have shown to be the usual precursors for the stoichiometric and/or catalytic coupling of terminal alkynes. However, the capacity of the dihydride complexes for coupling has not been investigated.

The reactivity of osmium compounds containing two hydrogen atoms bonded to the metallic center toward terminal alkynes is a little-studied field and is difficult to rationalize. The main problem comes from the fact that the four dihydride complexes studied so far lead to four different types of organometallic compounds, all of them different from the usual alkenyl derivatives.

In 1993, we reported that the six-coordinate osmium(IV) complex OsH₂Cl₂(PⁱPr₃)₂ reacted with phen-

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ylacetylene, cyclohexylacetylene, 1-(trimethylsilyl)-1,4-pentadiyne, or (trimethylsilyl)acetylene to give the hydride–carbyne derivatives OsHCl₂(≡CCH₂R)(PⁱPr₃)₂.⁸ Subsequently, we observed that the reaction of the osmium(II) complex OsCl₂(η²-H₂)(CO)(PⁱPr₃)₂, containing an elongated dihydrogen ligand instead of two hydride ligands, with phenylacetylene leads to the carbene compound OsCl₂(=CHCH₂Ph)(CO)(PⁱPr₃)₂.⁹

Recently, as part of our study on the chemical properties of OsH₂Cl₂(PⁱPr₃)₂,¹⁰ we have described the synthesis of the acetate derivatives OsH₂(κ²-O₂CCH₃){κ¹-OC(O)CH₃}(PⁱPr₃)₂¹¹ and [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]₂BF₄.¹² In the presence of alkynes, the behavior of the bis(acetate) complex differs from that previously men-

tioned for OsH₂Cl₂(PⁱPr₃)₂ and OsCl₂(η²-H₂)(CO)(PⁱPr₃)₂. Thus, the reaction of OsH₂(κ²-O₂CCH₃){κ¹-OC(O)CH₃}(PⁱPr₃)₂ with 2-methyl-1-buten-3-yne affords the hydride–vinylidene complex OsH(κ²-O₂CCH₃){=C=CHC(CH₃)=CH₂}(PⁱPr₃)₂.¹¹ The monoacetate neither shows the same reactivity as the bis(acetate) nor follows a behavior similar to that for OsH₂Cl₂(PⁱPr₃)₂ or OsCl₂(η²-H₂)(CO)(PⁱPr₃)₂. The complex [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]₂BF₄ reacts with phenylacetylene and 1,1-diphenyl-2-propyn-1-ol to give the hydride–osmacyclo-

propene derivatives [OsH(κ²-O₂CCH₃){C(R)CH₂}(PⁱPr₃)₂]₂BF₄ (R = Ph, C(OH)Ph₂) and with *tert*-butylacetylene or (trimethylsilyl)acetylene to afford the hydride–carbyne compounds [OsH(κ²-O₂CCH₃)(≡CR)(PⁱPr₃)₂]₂BF₄ (R = CH₂CMe₃, CH₃).¹² whereas the reactions with 2-phenyl-3-butyne-2-ol and 2-methyl-3-butyne-2-ol give mixtures of the corresponding hydride–osmacyclopropene and hydride–carbyne species.¹³

The reactions previously mentioned suggest that the nature of the obtained products depends on both factors related to the electronic nature of the starting complexes and the nature of the substituent of the alkyne.

In the search for new information about the influence of the alkyne in these types of reactions, we have now studied the reactivity of [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]₂BF₄ toward acetylene. In this paper, we report the formation of [Os(CH=CH₂)(κ²-O₂CCH₃)(≡CCH₃)(PⁱPr₃)₂]₂BF₄ and its potential as a precursor of carbon–carbon coupling reactions.

Results and Discussion

1. Reaction of [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]₂BF₄ with Acetylene. At 0 °C, under 1 atm of acetylene, dichloromethane solutions of [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]₂BF₄ (**1**) give a dark blue, intractable, air-sensitive solid and a yellow solution. According to the UV/vis spectrum of the solid, which shows an unstructured absorption at about 700 nm and a weak, very broad band at about 590 nm, the dark material is *trans*-polyacetylene with a minor amount of the *cis* isomer.¹⁴ From the yellow solution, the vinyl–carbyne complex [Os(CH=CH₂)(κ²-O₂CCH₃)(≡CCH₃)(PⁱPr₃)₂]₂BF₄ (**2**) was isolated by addition of diethyl ether, as a yellow solid in 75% yield.

The formed amount of polyacetylene increases by increasing the exposure time of **1** to acetylene, in a slow but constant manner. This suggests that complex **1** is a catalyst precursor for the polymerization of acetylene. The active species should be **2** or a derivative of this compound. In fact, the stirring of dichloromethane solutions of **2** under 1 atm of acetylene affords polyacetylene and a yellow solution, from which complex **2** is recovered in high yield.

The catalytic formation of polyacetylene and the stoichiometric formation of **2** is also observed when dichloromethane solutions of the previously described hydride–carbyne complex [OsH(κ²-O₂CCH₃)(≡CCH₃)(PⁱPr₃)₂]₂BF₄ (**3**) are stirred under 1 atm of acetylene at

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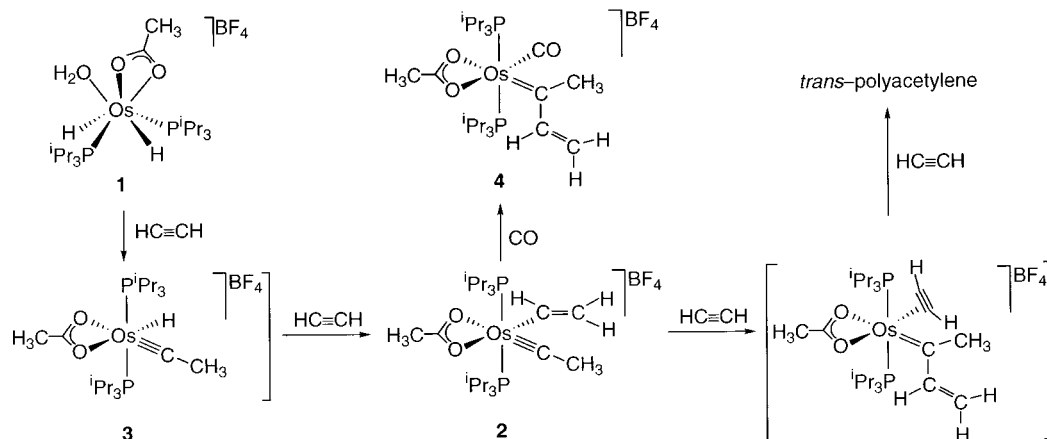
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Scheme 1



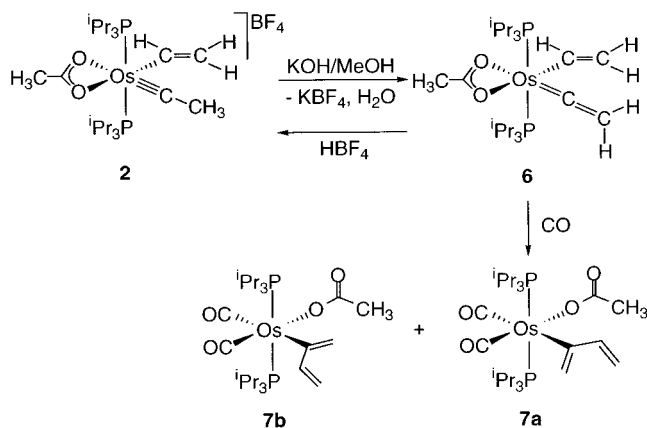
0 °C. This suggests that the reaction of **1** with acetylene to give **2** is a two-step process which involves the initial formation of **3** and subsequent insertion of the alkyne into the Os–H bond of this intermediate (Scheme 1). Once complex **2** has been formed, the migratory insertion of the carbyne ligand into the Os–vinyl bond should afford a carbene derivative, which could be the active species of the catalysis. The polymerization of alkynes in a living manner via alkylidene compounds is a well-known process.¹⁵ In favor of the formation of an alkylidene species from **2** under an acetylene atmosphere, we have observed that, under a carbon monoxide atmosphere, complex **2** evolves into $[\text{Os}(\kappa^2\text{-O}_2\text{CCH}_3)\{\text{C}(\text{CH}=\text{CH}_2)\text{CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (**4**), which is unstable under these conditions and affords, finally, the known compound $[\text{Os}(\kappa^2\text{-O}_2\text{CCH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (**5**).¹¹

Complex **2** was characterized by MS, elemental analysis, and IR and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. In the ^1H NMR spectrum, the most noticeable resonances are a triplet at 1.84 ppm with an H–P coupling constant of 0.9 Hz, due to the methyl group of the carbyne ligand, two doublets at 5.87 and 4.69 ppm with H–H coupling constants of 10.5 and 16.2 Hz, respectively, and a doublet of doublets at 7.55 ppm with the same H–H coupling constants, corresponding to the vinyl ligand. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the $\text{Os}=\text{C}$ resonance appears as a triplet at 289.9 ppm with a C–P coupling constant of 9.0 Hz, whereas the OsCH and $=\text{CH}_2$ resonances are observed at 140.0 and 123.3 ppm, respectively, the first of them as a triplet with a C–P coupling constant of 8.0 Hz and the second one as a singlet. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 22.9 ppm, in agreement with the mutually trans disposition of the phosphine ligands.

In the ^1H NMR spectrum of **4** the CH_3 resonance of the carbene appears at 2.62 ppm, whereas the vinylic resonances are observed as two doublets and a doublet of doublets at 5.91, 6.40, and 8.34 ppm, respectively, with H–H coupling constants of 10.8 and 17.2 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the $\text{Os}=\text{C}$ carbon atom gives rise to a triplet at 288.2 ppm with a C–P coupling constant of 4.0 Hz, while the carbon atoms of the vinyl group display singlets at 149.0 and 114.9 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 28.6 ppm.

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Scheme 2



2. Formation and Characterization of the Butadienyl Complex $\text{Os}\{\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2\}\{\kappa^1\text{-OC}(\text{O})\text{-CH}_3\}(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$. Following the pioneering leads of the Rosenblum¹⁶ and Wojcicki¹⁷ groups, over the last years, several groups have been investigating the organic applications of cycloaddition reactions between transition-metal complexes containing σ bonds to unsaturated ligands and electrophiles.¹⁸ Along this line, we were interested in preparing the title compound, so that its cycloaddition chemistry could be investigated (vide infra).

The synthetic strategy to prepare this butadienyl complex is shown in Scheme 2. Treatment of dichloromethane solutions of **2** with a stoichiometric amount of KOH in methanol produces the deprotonation of the carbyne ligand and formation of the neutral vinyl–

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vinylidene derivative Os(CH=CH₂)(κ²-O₂CCH₃)(=C=CH₂)(PⁱPr₃)₂ (**6**), which under a carbon monoxide atmosphere affords the desired butadienyl compound Os{C(CH=CH₂)=CH₂}[κ¹-OC(O)CH₃](CO)₂(PⁱPr₃)₂ (**7**).

The deprotonation reaction of **2** is reversible. Thus, the addition of a stoichiometric amount of HBF₄·OEt₂ to diethyl ether solutions of **6** regenerates **2**. The C_β atoms of both alkenyl¹⁹ and vinylidene²⁰ ligands have shown to be nucleophilic centers; therefore, the above-mentioned reaction indicates that under, strictly, the same metal–ligand system the C_β of a vinylidene ligand is a stronger nucleophilic center than the C_β atom of an alkenyl group.

The presence of the vinylidene and alkenyl ligands in **6** is strongly supported by the ¹H and ¹³C{¹H} NMR spectra of this compound in benzene-*d*₆. In the ¹H NMR spectrum the =CH₂ protons of the vinylidene display a triplet at 0.64 ppm with an H–P coupling constant of 3 Hz, while the vinylic protons give rise to two doublets of doublets at 6.04 and 4.76 ppm and a doublet of doublets at 8.68 ppm, with H–H coupling constants of 16.5 and 10.5 Hz, respectively, and H–P coupling constants of about 3 Hz. In the ¹³C{¹H} NMR spectrum, the resonances corresponding to the carbon atoms of the vinylidene appear as triplets at 287.2 (Os=C) and 87.7 (=CH₂) ppm with C–P coupling constants of 11.2 and 3.5 Hz, respectively, whereas the resonances due to the carbon atoms of the vinyl ligand are observed at 149.6 (=CH) and 115.7 (=CH₂) ppm. The first of them appears as a triplet with a C–P coupling constant of 8.1 Hz and the second one as a singlet. The ³¹P{¹H} NMR spectrum shows a singlet at 1.1 ppm.

The presence of the butadienyl ligand in **7** has been confirmed by an X-ray investigation on a monocrystal of this complex. A view of the molecular geometry is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying opposite positions (P(1)–Os–P(2) = 177.85(5)°). The perpendicular plane is formed by the mutually *cis*-disposed carbonyl ligands (C(9)–Os–C(10) = 93.3(2)°), the acetate group and the butadienyl ligand also being *cis*-disposed (O(1)–Os–C(1) = 85.55(8)°).

The C(2)–C(1)–C(3)–C(4) torsion angle in the butadienyl ligand is 50.7(8)°. This value is quite similar to those found in related compounds^{18f} and agrees with Wiberg's calculations on rotational barriers in butadiene and heterobutadienes, which predict minimum-energy conformations with typical torsion angles of 25–55°. The bond length Os–C(1) (2.195(5) Å) is as expected for an Os–C(sp²) single bond. It is even longer than those found in the alkenyl–osmium(II) complexes Os{(E)-CH=CHPh}Cl(CO)(PⁱPr₃)₂ (1.99(1) Å),^{4a} [Os{CH=C(Ph)C-

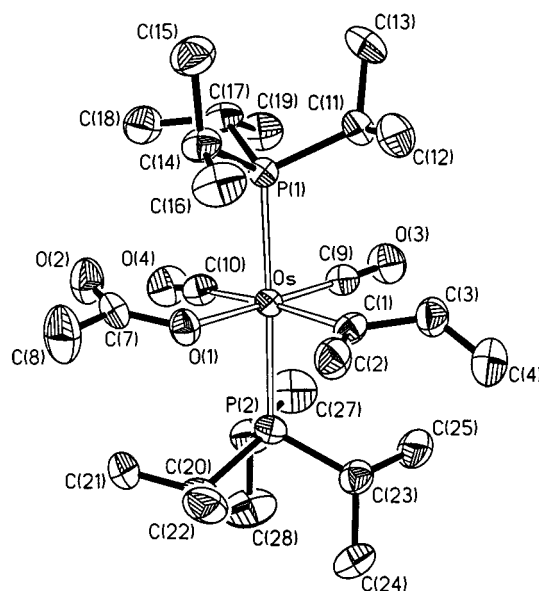


Figure 1. Molecular diagram of the complex Os{C(CH=CH₂)=CH₂}[κ¹-OC(O)CH₃](CO)₂(PⁱPr₃)₂ (**7**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond (Å) and Angles (deg) for the Complex
Os{C(CH=CH₂)=CH₂}[κ¹-OC(O)CH₃](CO)₂(PⁱPr₃)₂ (**7**)

Os–P(1)	2.4592(14)	O(2)–C(7)	1.211(7)
Os–P(2)	2.4609(15)	O(3)–C(9)	1.156(7)
Os–O(1)	2.102(4)	O(4)–C(10)	1.333(7)
Os–C(1)	2.195(5)	C(1)–C(2)	1.317(8)
Os–C(9)	1.838(6)	C(1)–C(3)	1.483(8)
Os–C(10)	1.945(6)	C(3)–C(4)	1.313(9)
O(1)–C(7)	1.285(7)	C(7)–C(8)	1.519(9)
P(1)–Os–P(2)	177.85(5)	C(1)–Os–C(10)	175.1(2)
P(1)–Os–O(1)	89.10(11)	C(9)–Os–C(10)	93.3(2)
P(1)–Os–C(1)	91.38(15)	Os–O(1)–C(7)	126.7(4)
P(1)–Os–C(9)	88.07(18)	O(1)–C(7)–O(2)	127.5(6)
P(1)–Os–C(10)	92.84(18)	O(1)–C(7)–C(8)	113.0(5)
P(2)–Os–O(1)	88.75(12)	O(2)–C(7)–C(8)	119.6(6)
P(2)–Os–C(1)	88.54(15)	Os–C(1)–C(2)	123.6(5)
P(2)–Os–C(9)	94.08(18)	Os–C(1)–C(3)	121.1(4)
P(2)–Os–C(10)	87.15(18)	C(2)–C(1)–C(3)	115.3(5)
O(1)–Os–C(1)	85.55(8)	C(1)–C(3)–C(4)	126.7(7)
O(1)–Os–C(9)	174.1(2)	Os–C(9)–O(3)	177.0(5)
O(1)–Os–C(10)	92.0(2)	Os–C(10)–O(4)	172.2(6)
C(1)–Os–C(9)	89.4(2)		

(OCH₃)=O}{η⁶-C₆H₆}(PⁱPr₃)₂]⁺ (2.02(1) Å),²² Os{CH=CHC(OCH₃)=O}(C₂CO₂CH₃)(CO)(PⁱPr₃)₂ (2.103(4) Å),²³ and [Os{C[C(O)OCH₃]=CH₂}(C=C=CPh₂)(CO)(PⁱPr₃)₂]⁺ (2.146(6) Å).^{5b} The C(1)–C(2) bond lies in the plane containing the carbonyl groups, the osmium atom, and the coordinated oxygen atom of the acetate ligand. Its distance, 1.317(8) Å, is statistically identical with the C(3)–C(4) (1.313(9) Å) bond length and agrees with the average carbon–carbon distance for a C(sp²)–C(sp²) double bond (1.32(1) Å).²⁴ The C(1)–C(3) (1.483(8) Å) bond length also compares well with the distance expected for a C(sp²)–C(sp²) single bond (about 1.48 Å).

(19) See for example: (a) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669. (b) Albéniz, M. J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Oro, L. A.; Sola, E.; Zeier, B. *J. Chem. Soc., Dalton Trans.* **1997**, 181.

(20) See for example: (a) Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636. (b) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657.

(21) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654.

(22) Werner, H.; Weinand, R.; Otto, H. *J. Organomet. Chem.* **1986**, *307*, 49.

(23) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663.

(24) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

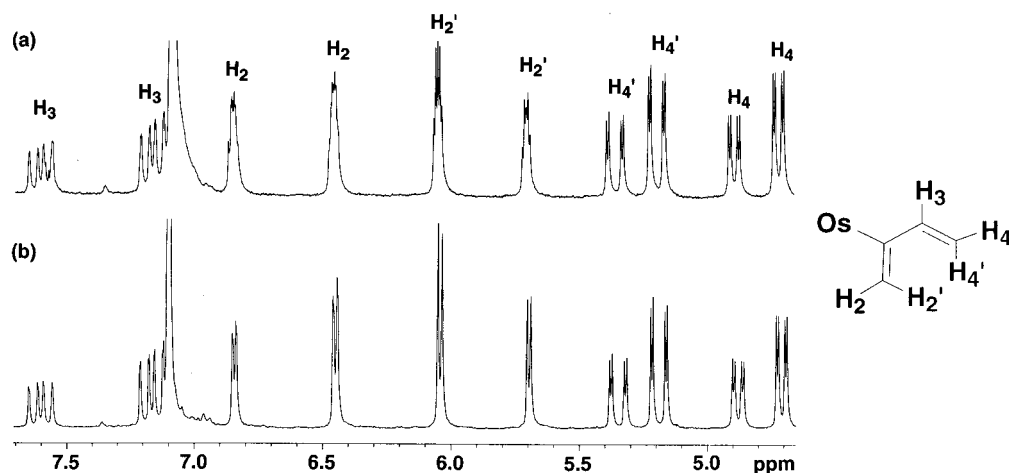


Figure 2. (a) ^1H and (b) $^1\text{H}\{^{31}\text{P}\}$ NMR spectra (benzene- d_6) of the isomeric mixture of $\text{Os}\{\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2\}(\kappa^1\text{-OC}(\text{O})\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$ (**7**) in the vinylic proton region.

In accordance with the sp^2 hybridization at C(1), the angles around this atom are in the range $115.2(5)$ – $123.6(5)^\circ$.

In solution, complex **7** exists as a mixture of the isomers **7a** and **7b** shown in Scheme 2. We assume that the major isomer is **7b** (60%), which is the one found in the solid state. The existence of these isomers can be explained by hindered rotation around the Os–C(1) axis. Because the Os–C(1) bond length does not suggest any degree of double-bond character, the reason for the existence of **7a** and **7b** appears to be steric in origin, probably due to the high steric demand of the isopropyl groups of the phosphine ligands.

Figure 2 shows the ^1H NMR spectrum of the isomeric mixture in the vinylic region. Each isomer gives rise to five resonances. Those corresponding to the $\text{Os}(\text{C}=\text{CH}_2)$ unit (H_2 and H_2') are observed between 5.5 and 7.0 ppm and show spin coupling with the phosphorus atoms bonded to the metallic center (about 3 Hz). The resonances corresponding to the H_2 protons, those disposed *trans* to the $\text{CH}=\text{CH}_2$ unit, appear as a doublet of doublets by spin coupling with H_3 (about 1 Hz) and H_2' (about 4 Hz), whereas H_2' is observed as a doublet by spin coupling with H_2 . The geminal H_4 and H_4' protons of the $\text{CH}=\text{CH}_2$ unit appear as two doublets of doublets between 4.7 and 5.4 ppm, as a result of the geminal spin coupling (about 3 Hz) and the *cis* H_3 – H_4 (about 10 Hz) or *trans* H_3 – H_4' (about 17 Hz) spin couplings. The resonances due to the $=\text{CH}$ protons (H_3) are observed between 7.0 and 7.7 ppm, as the expected doublet of doublets.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the isomers **7a** and **7b**, the resonances of the Os–C carbon atoms are observed as triplets at 157.1 (**7a**) and 153.6 (**7b**) ppm with C–P coupling constants of about 11 Hz, whereas the resonances due to the $\text{CH}=\text{CH}_2$, $\text{OsC}=\text{CH}_2$ and $\text{CH}=\text{CH}_2$ carbon atoms are observed as singlets at 150.4, 123.4, and 106.3 (**7a**) ppm and at 154.9, 120.2, and 107.4 (**7b**) ppm, respectively.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the isomeric mixture shows two singlets at 6.2 (**7a**) and 4.1 (**7b**) ppm, indicating that although the rotation of the butadienyl ligand around the Os–C bond is hindered, the rotation of the $\text{CH}=\text{CH}_2$ moiety around the $\text{OsC}=\text{CH}_2$ bond of the dienyl is free.

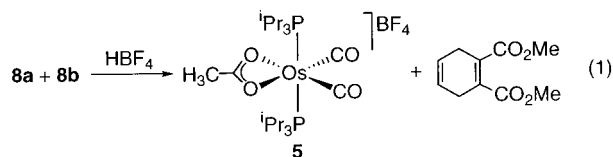
3. Diels–Alder Reactions on the Butadienyl Complex $\text{Os}\{\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2\}(\kappa^1\text{-OC}(\text{O})\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$

At 45°C , a benzene solution of **7** reacts with dimethyl acetylenedicarboxylate to give the cyclohexenyl derivative $\text{Os}\{\text{C}=\text{CHCH}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{CH}_2\}(\kappa^1\text{-OC}(\text{O})\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$ (**8**), as a result of a Diels–Alder reaction between the butadienyl ligand of **7** and the activated alkyne. The cycloaddition was carried out using 2 equiv of alkyne, and after 33 h, the product was obtained in quantitative yield, according to the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture.

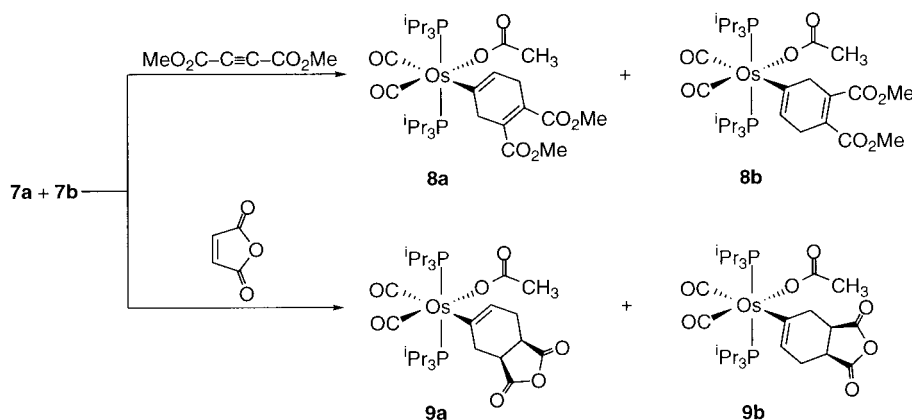
In solution complex **8** also exists as a mixture of the isomers **8a** and **8b** shown in Scheme 3. During the reaction the molar ratio between them (4:6) is constant and is the same as that between the starting isomers. This suggests that both **7a** and **7b** are active dienes and that the rates of formation of **8a** and **8b** are similar.

In the ^1H NMR spectrum of the isomeric mixture of **8a** and **8b**, the most noticeable resonances are those corresponding to the $=\text{CH}$ protons of the cyclohexadienyl ligands, which appear as broad signals at about 6.5 ppm. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the OsC and $\text{CH}=\text{CH}_2$ resonances of the cyclohexadienyl groups are observed as triplets at 140.3 and 130.0 (**8a**) ppm and at 132.8 and 124.6 (**8b**) ppm, with C–P coupling constants of about 12 and 3 Hz, respectively, whereas the $\text{C}(\text{CO}_2\text{Me})$ and CH_2 carbon atoms display singlets between 140 and 129 ppm and between 44 and 29 ppm, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains two singlets at 4.7 (**8a**) and 3.1 (**8b**) ppm, indicating that the phosphine ligands are equivalent. This suggests that the carbon–carbon double bonds of the cyclohexadienyl ligand of **8** lie in the plane containing the osmium atom, the carbonyl groups, and the oxygen atom of the acetate ligand.

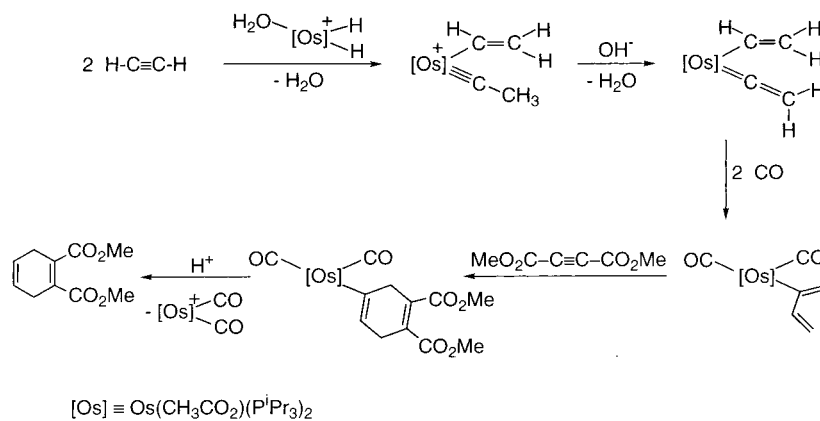
The isomeric mixture of **8a** and **8b** in chloroform- d reacts with 1 equiv of $\text{HBF}_4\cdot\text{OEt}_2$ to give the acetate–dicarbonyl complex **5** and dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate in quantitative yield, according to eq 1.



Scheme 3



Scheme 4



Dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate has been previously synthesized by three methods: (i) dimethyl 3-vinyl-1,2-dichlorocyclobutane-1,2-dicarboxylate undergoes a ring expansion, with concomitant loss of the chlorines to give the cyclohexadiene in 52% yield, upon treatment with Ni(CO)₄ in refluxing benzene-dimethylformamide;²⁵ (ii) butadiene sulfone and dimethyl acetylenedicarboxylate have been allowed to reflux in xylene for 150 min, and (iii) butadiene and dimethyl acetylenedicarboxylate have been mixed in dioxane in a sealed tube and allowed to stand at room temperature for 5 days.²⁶ For methods ii and iii, the yields of the reaction were not given.

The reactions shown in Scheme 4, which summarize some of the processes described in this paper, constitute a novel method to prepare dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate. The method starts from 2 equiv of acetylene and 1 equiv of dimethyl acetylenedicarboxylate and uses the Os(CH₃CO₂)(PⁱPr₃)₂ unit as a template.

Complex **7** also reacts with maleic anhydride. In this case the cycloaddition reaction leads to Os{C=CHCH₂-CH[C(O)OC(O)]CHCH₂}{κ¹-OC(O)CH₃}(CO)₂(PⁱPr₃)₂ (**9**) in quantitative yield after 1 week. The reaction was carried out in benzene as solvent, at room temperature, using 2 equiv of maleic anhydride. Under reflux, the reagents give rise to an *ill-defined straw-colored solid*.

In solution, as is the case for **7** and **8**, complex **9** also exists as a mixture of the isomers **9a** and **9b** shown in Scheme 3. During the reaction, the rate of disappearance of **7b** is higher than that of **7a**. As a consequence, the molar ratio between **9a** and **9b** (25:75) is lower than that between **7a** and **7b**, when the reaction is finished. Attempts to separate the bicycle from the metallic fragment by reaction of the isomeric mixture with H₂ or I₂ were unsuccessful.

In the ¹H NMR spectrum of the isomeric mixture of **9a** and **9b**, the most noticeable feature is the presence of two broad resonances at 6.60 (**9a**) and 6.27 (**9b**) ppm, due to the vinylic CH= hydrogen atom of the bicyclic ligands. In the ¹³C{¹H} NMR spectrum the OsC and CH= resonances of the bicycles are observed as triplets at 138.5 and 126.0 (**9a**) ppm and at 148.2 and 132.6 (**9b**) ppm with C-P coupling constants of about 11 and 4 Hz, respectively, while the CH and CH₂ resonances appear as singlets at about 40 ppm and between 38 and 26 ppm, respectively. The ³¹P{¹H} NMR spectrum shows an AB spin system for each isomer, indicating that the phosphine ligands are not equivalent, in agreement with the structure proposed for these isomers in Scheme 3.

Concluding Remarks

This study has revealed that the dihydride-osmium(IV) complex [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂][BF₄] is a useful precursor for stoichiometric and catalytic carbon-carbon coupling reactions, including the formation of novel organometallic derivatives such as carbene, butadienyl, cyclohexadienyl, and dioxohexahydroisobenz-

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(26) DiFrancesco, D.; Pinhas, A. R. *J. Org. Chem.* **1986**, *51*, 2098.

furanyl compounds, the polymerization of acetylene, and the synthesis of dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate.

In contrast to the previously observed reactions between alkynes and osmium compounds containing two hydrogen atoms bonded to the metallic center, two molecules of alkyne are activated when the dihydride–osmium(IV) complex $[\text{OsH}_2(\kappa^2\text{-O}_2\text{CCH}_3)(\text{H}_2\text{O})(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ is exposed under 1 atm of acetylene. The resulting product, $[\text{Os}(\text{CH}=\text{CH}_2)(\kappa^2\text{-O}_2\text{CCH}_3)(\equiv\text{CCH}_3)(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$, is the key to the carbon–carbon bond-forming processes.

The carbyne ligand of this vinyl–carbyne complex has a tendency to undergo a migratory insertion into the Os–vinyl bond to give a carbene species, which can be detected under carbon monoxide atmosphere and is responsible for the acetylene polymerization.

In basic medium, the carbyne ligand of the vinyl–carbyne complex undergoes deprotonation to give the vinyl–vinylidene derivative $\text{Os}(\text{CH}=\text{CH}_2)(\kappa^2\text{-O}_2\text{CCH}_3)(=\text{C}=\text{CH}_2)(\text{P}^i\text{Pr}_3)_2$. Under a carbon monoxide atmosphere, this complex also evolves by migration insertion, in this case of the vinylidene into the osmium–vinyl bond, to afford the butadienyl compound $\text{Os}\{\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2\}(\kappa^1\text{-OC}(\text{O})\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$. The butadienyl ligand of this complex acts as a diene in Diels–Alder reactions with activated dienophiles such as dimethyl acetylenedicarboxylate and maleic anhydride. The protonation of the cyclohexadienyl derivative $\text{Os}\{\text{C}=\text{CHCH}_2\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{CH}_2\}(\kappa^1\text{-OC}(\text{O})\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$, resulting from the reaction of the butadienyl complex with dimethyl acetylenedicarboxylate, yields dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate.

The previously mentioned sequence of reactions constitutes a novel method to prepare dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate, starting from acetylene and dimethyl acetylenedicarboxylate and using the $\text{Os}(\text{CH}_3\text{CO}_2)(\text{P}^i\text{Pr}_3)_2$ unit as a template.

Experimental Section

All reactions were carried out with rigorous exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. $[\text{OsH}_2(\kappa^2\text{-O}_2\text{CCH}_3)(\text{H}_2\text{O})(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (**1**) and $[\text{OsH}(\kappa^2\text{-O}_2\text{CCH}_3)(\equiv\text{CCH}_3)(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (**3**) were prepared as previously reported.¹² $\text{MeOCC}\equiv\text{CCO}_2\text{Me}$ (Fluka) was distilled prior to use, while maleic anhydride (Fluka) was used as received. Infrared spectra were recorded either on a Nicolet 550 or on a Perkin-Elmer 883 spectrometer as solids (KBr pellet or Nujol mull) or in solution (CH_2Cl_2). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{31}P NMR spectra were recorded either on a Varian Gemini 2000 or a Bruker AXR 300 instrument. Chemical shifts are referenced to residual solvent peaks (^1H , $^{13}\text{C}\{^1\text{H}\}$) or external H_3PO_4 (^{31}P). Coupling constants, J and N ($N = J_{\text{P-H}} + J_{\text{P'-H}}$ for ^1H ; $N = J_{\text{P-C}} + J_{\text{P'-C}}$ for $^{13}\text{C}\{^1\text{H}\}$) are given in hertz. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Auto Spec instrument.

Preparation of $[\text{Os}(\text{CH}=\text{CH}_2)(\kappa^2\text{-O}_2\text{CCH}_3)(\equiv\text{CCH}_3)(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (2**).** This compound was prepared by starting from **1** or from **3**, using the same procedure. Only the synthesis from **1** is described. A solution of **1** (116 mg, 0.17 mmol) in dichloromethane (10 mL) was cooled to 0 °C. The argon atmosphere was replaced by an acetylene atmosphere, and the reaction mixture was stirred for 6 h at 0 °C, during which time the formation of a dark blue precipitate (polyacetylene) was

observed. The polyacetylene was then removed by filtration to obtain a yellow solution. This yellow solution was concentrated to ca. 0.5 mL and diethyl ether added to afford a pale yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 90.5 mg (75%). Anal. Calcd for $\text{C}_{24}\text{H}_{51}\text{BF}_4\text{O}_2\text{OsP}_2$: C, 40.57; H, 7.23. Found: C, 40.75; H, 7.20. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{C})$ 1625, $\nu_{\text{asym}}(\text{OCO})$ 1572, $\nu_{\text{sym}}(\text{OCO})$ 1470, $\nu(\text{BF}_4)$ 1000–1100. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 7.55 (dd, $J_{\text{H-H}} = 16.2$, $J_{\text{H-H}} = 10.5$, 1 H, $\text{CH}=\text{CH}_2$), 5.87 (d, $J_{\text{H-H}} = 10.5$, 1 H, $\text{CH}=\text{CH}_2$), 4.69 (d, $J_{\text{H-H}} = 16.2$, 1 H, $\text{CH}=\text{CH}_2$), 2.80–2.60 (m, 6 H, $\text{PCH}(\text{CH}_3)_2$), 1.84 (t, $J_{\text{P-H}} = 0.9$, 3 H, $\equiv\text{CCH}_3$), 1.66 (s, 3 H, OCOCH_3), 1.38 (dvt, $N = 14.4$, $J_{\text{H-H}} = 7.2$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 1.35 (dvt, $N = 15.0$, $J_{\text{H-H}} = 7.2$, 18 H, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CDCl_3 , 25 °C): δ 22.9 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CD_2Cl_2 , –30 °C, plus APT): δ 289.9 (t, $J_{\text{P-C}} = 9.0$, $\text{Os}=\text{CCH}_3$), 186.5 (s, OCOCH_3), 140.0 (t, $J_{\text{P-C}} = 8.0$, $\text{Os}-\text{CH}=\text{CH}_2$), 123.3 (s, $\text{Os}-\text{CH}=\text{CH}_2$), 41.4 (s, $\text{Os}=\text{CCH}_3$), 25.5 (s, OCOCH_3), 24.7 (vt, $N = 26.6$, $\text{PCH}(\text{CH}_3)_2$), 19.2 and 19.1 (both s, $\text{PCH}(\text{CH}_3)_2$). MS (FAB⁺): m/z 625 (100) (M^+), 465 (25) ($\text{M}^+ - \text{P}^i\text{Pr}_3$).

Reaction of $[\text{Os}(\text{CH}=\text{CH}_2)(\kappa^2\text{-O}_2\text{CCH}_3)(\equiv\text{CCH}_3)(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ with Carbon Monoxide. Formation of $[\text{Os}(\kappa^2\text{-O}_2\text{CCH}_3)(=\text{C}(\text{CH}=\text{CH}_2)\text{CH}_3)(\text{CO})(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (4**) and $[\text{Os}(\kappa^2\text{-O}_2\text{CCH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ (**5**).** A solution of **2** (120 mg, 0.17 mmol) in dichloromethane (10 mL) was stirred overnight under a carbon monoxide atmosphere. The resulting solution was concentrated to ca. 0.5 mL and diethyl ether added to afford a pale yellow solid. Yield: 97.2 mg. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy show a 70:30 mixture of compounds **4** and **5**. All attempts to separate the two products either by column chromatography or by fractional crystallization failed. The spectroscopic data of **5** agree with those reported previously.¹¹

Spectroscopic data for **4** are as follows. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 1946 (s), $\nu(\text{OCO})$ 1626 (m), 1389 (m), $\nu(\text{BF}_4)$ 1100–1000 (s). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 8.34 (dd, $J_{\text{H-H}} = 10.8$, $J_{\text{H-H}} = 17.2$, 1 H, $-\text{CH}=\text{CH}_2$), 6.40 (d, $J_{\text{H-H}} = 17.2$, 1 H, $=\text{CH}_2$), 5.91 (d, $J_{\text{H-H}} = 10.8$, 1 H, $=\text{CH}_2$), 2.62 (s, 3 H, $\text{Os}=\text{C}(\text{CH}_3)$), 2.47 (m, 6 H, $\text{PCH}(\text{CH}_3)_2$), 2.04 (t, $J_{\text{P-H}} = 1.2$, 3 H, OCOCH_3), 1.33 (dvt, $N = 15$, $J_{\text{H-H}} = 7.5$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 1.27 (dvt, $N = 14.1$, $J_{\text{H-H}} = 6.9$, 18 H, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CDCl_3 , 25 °C): δ 28.6 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3 , 25 °C): δ 288.2 (t, $J_{\text{P-C}} = 4.0$, $\text{Os}=\text{C}$), 187.5 (s, OCOCH_3), 180.3 (t, $J_{\text{P-C}} = 8.6$, $\text{Os}-\text{CO}$), 149.0 (s, $-\text{CH}=\text{CH}_2$), 114.9 (s, $=\text{CH}_2$), 45.1 (s, $-\text{CH}_3$), 26.9 (vt, $N = 25.6$, $\text{PCH}(\text{CH}_3)_2$), 24.9 (s, OCOCH_3), 19.6 and 19.4 (both s, $\text{PCH}(\text{CH}_3)_2$). MS (FAB⁺): m/z 653 (M^+).

Preparation of $[\text{Os}(\text{CH}=\text{CH}_2)(\kappa^2\text{-O}_2\text{CCH}_3)(=\text{C}=\text{CH}_2)(\text{P}^i\text{Pr}_3)_2]$ (6**).** A solution of **2** (100 mg, 0.14 mmol) in CH_2Cl_2 (10 mL) was treated with a stoichiometric amount of KOH in methanol (0.75 mL, 0.14 mmol, 0.187 N). After it was stirred for 20 min at room temperature, the solution was evaporated to dryness. Toluene (10 mL) was added, and the resulting suspension was filtered through Celite. The filtrate was dried in vacuo, and an oil was obtained. All attempts to get a solid from this oil failed. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 8.68 (dd, $J_{\text{H-H}} = 16.5$, $J_{\text{H-H}} = 10.5$, 1 H, $\text{Os}-\text{CH}=\text{CH}_2$), 6.04 (ddt, $J_{\text{H-H}} = 10.5$, $J_{\text{P-H}} = 2.4$, $J_{\text{H-H}} = 2.1$, 1 H, $\text{Os}-\text{CH}=\text{CH}_2$), 4.76 (ddt, $J_{\text{H-H}} = 16.5$, $J_{\text{P-H}} = 2.7$, $J_{\text{H-H}} = 2.1$, 1 H, $\text{Os}-\text{CH}=\text{CH}_2$), 2.91 (m, 6 H, $\text{PCH}(\text{CH}_3)_2$), 1.65 (s, 3 H, OCOCH_3), 1.34 (dvt, $N = 12.9$, $J_{\text{H-H}} = 7.2$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 1.27 (dvt, $N = 12.6$, $J_{\text{H-H}} = 6.9$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 0.64 (t, $J_{\text{P-H}} = 3$, 1 H, $\text{Os}=\text{C}=\text{CH}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, C_6D_6 , 25 °C): δ 1.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 20 °C): δ 287.2 (t, $J_{\text{P-C}} = 11.2$, $\text{Os}=\text{C}=\text{CH}_2$), 181.6 (s, OCOCH_3), 149.6 (t, $J_{\text{P-C}} = 8.1$, $\text{Os}-\text{CH}=\text{CH}_2$), 115.7 (s, $\text{Os}-\text{CH}=\text{CH}_2$), 87.7 (t, $J_{\text{P-C}} = 3.5$, $\text{Os}=\text{C}=\text{CH}_2$), 25.5 (s, OCOCH_3), 23.2 (vt, $N = 22.8$, $\text{PCH}(\text{CH}_3)_2$), 19.8 and 19.6 (both s, $\text{PCH}(\text{CH}_3)_2$).

Preparation of $\text{Os}\{\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2\}(\kappa^1\text{-OC}(\text{O})\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$ (7**).** A solution of **6** (200 mg, 0.16 mmol) in toluene (10 mL) was stirred overnight under a carbon monoxide atmosphere. The resulting solution was concentrated to

dryness, and pentane was added to afford a pale yellow solid, which was washed several times with pentane and dried in vacuo. Yield: 124 mg (57%). Anal. Calcd for C₂₆H₅₀O₄OsP₂: C, 46.00; H, 7.42. Found: C, 45.63; H, 7.15. IR (Nujol, cm⁻¹): ν(CO) 2002, 1919 ν_{asym}(OCO) 1630. The ¹H and ³¹P{¹H} NMR spectra show the presence of two isomers (ratio 40:60).

NMR data of the minor isomer (40%) are as follows. ¹H NMR (300 MHz, C₆D₆, 25 °C, plus COSY): δ 7.67 (ddd, J_{H-H} = 17.1, J_{H-H} = 10.5, J_{H-H} = 0.9, 1 H, Os-C(CH=CH₂)=CH₂), 6.91 (ddt, J_{H-H} = 4.0, J_{H-H} = 0.9, J_{P-H} = 2.7, 1 H, Os-C(CH=CH₂)=CH₂), 5.77 (dt, J_{H-H} = 4.0, J_{P-H} = 2.4, 1 H, Os-C(CH=CH₂)=CH₂), 5.42 (dd, J_{H-H} = 17.2, J_{H-H} = 3, 1 H, Os-C(CH=CH₂)=CH₂), 4.95 (dd, J_{H-H} = 10.5, J_{H-H} = 3, 1 H, Os-C(CH=CH₂)=CH₂), 2.52 (m, 6 H, PCH(CH₃)₂), 2.20 (s, 3 H, OCOCH₃), 1.15 (dvt, J_{H-H} = 7.2, N = 13.5, 36 H, PCH(CH₃)₂). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 25 °C): δ 6.2 (s). ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 20 °C, plus DEPT): δ 185.9 (t, J_{P-C} = 7.3, Os-CO), 185.0 (t, J_{P-C} = 6.9, Os-CO), 176.6 (s, OCOCH₃), 157.1 (t, J_{P-C} = 11.5, Os-C), 150.4 (s, Os-C(CH=CH₂)=CH₂), 123.4 (br s, Os-C(CH=CH₂)=CH₂), 106.3 (s, Os-C(CH=CH₂)=CH₂), 25.9 (vt, N = 24.9, PCH(CH₃)₂), 24.4 (s, OCOCH₃), 19.8 (s, PCH(CH₃)₂).

NMR data of the major isomer (60%) are as follows. ¹H NMR (300 MHz, C₆D₆, 25 °C, plus COSY): δ 7.23 (ddd, J_{H-H} = 16.6, J_{H-H} = 10.2, J_{H-H} = 1, 1 H, Os-C(CH=CH₂)=CH₂), 6.52 (ddt, J_{H-H} = 4.7, J_{H-H} = 1, J_{P-H} = 2.7, 1 H, Os-C(CH=CH₂)=CH₂), 6.11 (dt, J_{H-H} = 4.7, J_{P-H} = 2.4, 1 H, Os-C(CH=CH₂)=CH₂), 5.26 (dd, J_{H-H} = 16.6, J_{H-H} = 2.7, 1 H, Os-C(CH=CH₂)=CH₂), 4.78 (dd, J_{H-H} = 10.2, J_{H-H} = 2.7, 1 H, Os-C(CH=CH₂)=CH₂), 2.52 (m, 6 H, PCH(CH₃)₂), 2.23 (s, 3 H, OCOCH₃), 1.21 (dvt, J_{H-H} = 7.2, N = 12.9, 18 H, PCH(CH₃)₂), 1.19 (dvt, J_{H-H} = 7.2, N = 12.9, 18 H, PCH(CH₃)₂). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 25 °C): δ 4.1 (s). ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 20 °C, plus DEPT): δ 185.1 (t, J_{P-C} = 7.3, Os-CO), 184.6 (t, J_{P-C} = 8.3, Os-CO), 176.4 (s, OCOCH₃), 154.9 (s, Os-C(CH=CH₂)=CH₂), 153.6 (t, J_{P-C} = 11.4, Os-C), 120.2 (br s, Os-C(CH=CH₂)=CH₂), 107.4 (s, Os-C(CH=CH₂)=CH₂), 26.2 (vt, N = 24.7, PCH(CH₃)₂), 24.4 (s, OCOCH₃), 19.8 (s, PCH(CH₃)₂), 19.5 (s, PCH(CH₃)₂).

Reaction of 7 with MeO₂CC≡CCO₂Me: Preparation of

Os{C=CHCH₂C(CO₂Me)=C(CO₂Me)CH₂{κ¹-OC(O)CH₃}-CO₂(PⁱPr₃)₂ (8). To a solution of 7 (196 mg, 0.29 mmol) in benzene (15 mL) was added MeO₂CC≡CCO₂Me (71 μL, 0.58 mmol) with a syringe. The resulting solution was heated at 45 °C for 33 h. After this time the solution was filtered through Celite and was then dried to ca. 0.5 mL. Addition of pentane (5 mL) gave an oily residue. After the mixture was stirred for 5 min, the pentane was removed with a cannula, and more pentane was added. After this mixture was stirred for 3 h, a beige solid was obtained, which was washed with pentane and dried in vacuo. Yield: 84 mg (35.6%). The reaction was found to be quantitative (¹H and ³¹P{¹H} NMR spectroscopy); the low isolated yield is due to the high solubility in pentane. Anal. Calcd for C₃₂H₅₆O₈OsP₂: C, 46.18; H, 7.50. Found: C, 46.62; H, 6.88. IR (Nujol, cm⁻¹): ν(CO) 2001, 1922; ν(C=O) 1733, 1722; ν_{asym}(OCO) 1630. The ¹H and ³¹P{¹H} NMR spectra show the presence of two isomers (ratio 40:60).

NMR data of the minor isomer (40%) are as follows. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 6.43 (br, 1 H, =CH), 3.78 (t, J_{H-H} = 7.8, 2 H, -CH₂-), 3.54 (s, 3 H, CO₂Me), 3.41 (s, 3 H, CO₂-Me), 3.20 (m, 2 H, -CH₂-), 2.44 (m, 6 H, PCH(CH₃)₂), 2.20 (s, 3 H, OCOCH₃), 1.15 (m, 36 H, PCH(CH₃)₂). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 25 °C): δ 4.7 (s). ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 20 °C, plus DEPT): δ 185.6 (t, J_{P-C} = 7.1, Os-CO), 184.8 (t, J_{P-C} = 7.8, Os-CO), 176.2 (s, OCOCH₃), 170.1 (s, CO₂CH₃), 167.8 (s, CO₂CH₃), 140.3 (t, J_{P-C} = 11.5, Os-C), 139.8 (s, C-CO₂CH₃), 130.2 (s, C-CO₂CH₃), 130.0 (t, J_{P-C} = 3, =CH), 51.4 (s, CO₂CH₃), 51.3 (s, CO₂CH₃), 36.3 (s, -CH₂-), 32.5 (s, -CH₂-), 26.4 (vt, N = 24.7, PCH(CH₃)₂), 24.2 (s, OCOCH₃), 19.7 (s, PCH(CH₃)₂), 19.5 (s, PCH(CH₃)₂).

NMR data of the major isomer (60%) are as follows. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 6.70 (br, 1 H, =CH), 3.88 (t, J_{H-H} = 7.8, 2 H, -CH₂-), 3.56 (s, 3 H, CO₂Me), 3.35 (s, 3 H, CO₂-Me), 3.27 (m, 2 H, -CH₂-), 2.44 (m, 6 H, PCH(CH₃)₂), 2.18 (s, 3 H, OCOCH₃), 1.15 (m, 36 H, PCH(CH₃)₂). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 25 °C): δ 3.1 (s). ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 20 °C, plus DEPT): δ 185.1 (t, J_{P-C} = 7.6, Os-CO), 184.4 (t, J_{P-C} = 8.3, Os-CO), 176.3 (s, OCOCH₃), 170.2 (s, CO₂CH₃), 167.8 (s, CO₂CH₃), 139.6 (s, C-CO₂CH₃), 132.8 (t, J_{P-C} = 11.9, Os-C), 129.7 (s, C-CO₂CH₃), 124.6 (t, J_{P-C} = 3, =CH), 51.6 (s, CO₂CH₃), 51.2 (s, CO₂CH₃), 43.7 (s, -CH₂-), 29.3 (s, -CH₂-), 26.2 (vt, N = 24.9, PCH(CH₃)₂), 24.3 (s, OCOCH₃), 19.5 (s, PCH(CH₃)₂), 19.3 (s, PCH(CH₃)₂).

Reaction of 7 with Maleic Anhydride: Preparation of

Os{C=CHCH₂CH[C(O)OC(O)]CHCH₂}{κ¹-OC(O)CH₃}(CO)₂-(PⁱPr₃)₂ (9). A solution of 7 (200 mg, 0.29 mmol) in benzene (15 mL) was treated with maleic anhydride (58 mg, 0.59 mmol). The resulting solution was stirred at room temperature for 1 week. After this time the solution was filtered through Celite and evaporated to ca. 0.5 mL. Addition of pentane (0.5 mL) gave an oily residue. After the mixture was stirred for 5 min, the pentane was removed with a cannula and more pentane was added. After this mixture was stirred for 3 h, a beige solid was obtained, which was washed with pentane and dried in vacuo. Yield: 105 mg (46%). The reaction was found to be quantitative (¹H and ³¹P{¹H} NMR spectroscopy); the low isolated yield is due to the high solubility in pentane. Anal. Calcd for C₃₀H₅₂O₇OsP₂: C, 46.38; H, 6.75. Found: C, 45.99; H, 6.54. IR (Nujol, cm⁻¹): ν(CO) 2001 (s), 1922 (m), 1955 (s), 1920 (m); ν(C=O) 1852 (m), 1776 (s); ν(C-O-C) 914 (s). The ¹H and ³¹P{¹H} NMR spectra show the presence of two isomers (ratio 75:25).

NMR data of the major isomer (75%) are as follows. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 6.27 (br, 1 H, =CH), 3.53 (dd, J_{H-H} = 7.8, J_{H-H} = 16, 1 H, -CH₂-), 2.52 (m, 1 H, -CH), 2.39 (m, 1 H, -CH), 2.26 (m, 9 H, PCH(CH₃)₂, -CH₂-), 2.16 (s, 3 H, OCOCH₃), 1.14–0.98 (m, 36 H, PCH(CH₃)₂). Most of the aliphatic protons of the bicycle are overlapping with the PCH(CH₃)₂ multiplet. ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 25 °C): two lines (AB pattern) at 6.76 and 6.74 ppm. ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 20 °C, plus DEPT): δ 185.3 (t, J_{P-C} = 7.5, Os-CO), 184.8 (t, J_{P-C} = 8.7, Os-CO), 176.4 (s, OCOCH₃), 174.9 (s, C=O), 174.7 (s, C=O), 148.2 (t, J_{P-C} = 11.7, Os-C), 132.6 (t, J_{P-C} = 4, =CH), 40.7 (s, CH), 40.2 (s, CH), 30.2 (s, -CH₂-), 27.8 (s, -CH₂-), 26.2 (vt, N = 24.5, PCH(CH₃)₂), 24.4 (s, OCOCH₃), 19.4 (s, PCH(CH₃)₂), 19.3 (s, PCH(CH₃)₂).

NMR data of the minor isomer (25%) are as follows. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 6.60 (br, 1 H, =CH), 2.89 (m, 1 H), 2.52 (m, 1 H), 2.26 (m, 10 H, PCH(CH₃)₂ plus 4 H of the bicycle), 2.11 (s, 3 H, OCOCH₃), 1.14–0.98 (m, 36 H, PCH(CH₃)₂). Most of the aliphatic protons of the bicycle are overlapping with the PCH(CH₃)₂ multiplet. ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 25 °C): two lines (AB pattern) at 3.73 and 3.71 ppm. ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 20 °C, plus DEPT): δ 184.6 (t, J_{P-C} = 7.5, Os-CO), 184.3 (t, J_{P-C} = 8.4, Os-CO), 176.3 (s, OCOCH₃), 174.6 (t, J_{P-C} = 4, =CH), 174.5 (s, C=O), 138.5 (t, J_{P-C} = 11, Os-C), 126.0 (t, J_{P-C} = 4, =CH), 40.9 (s, CH), 39.1 (s, CH), 37.4 (s, -CH₂-), 26.7 (vt, N = 24, PCH(CH₃)₂), 26.5 (s, -CH₂-), 24.4 (s, OCOCH₃), 19.7 (s, PCH(CH₃)₂), 19.6 (s, PCH(CH₃)₂).

Reaction of 8 with HBF₄·OEt₂: Formation of [Os(κ²-O₂CCH₃)(CO)₂(PⁱPr₃)₂]BF₄ (5) and Dimethyl 1,4-Cyclohexadiene-1,2-dicarboxylate. A solution (0.5 mL) of 8 (18.5 mg, 0.02 mmol) in CDCl₃ was placed in a 5 mm NMR tube, and a stoichiometric amount (3 μL, 0.02 mmol) of HBF₄·OEt₂ was added from a syringe. The ¹H and ³¹P{¹H} NMR spectra recorded after 3 min show quantitative formation of 5¹¹ and dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 5.69 (s, 2 H, =CH), 3.76 (s, 6 H, CO₂-

Table 2. Crystal Data and Data Collection and Refinement for $\text{Os}\{\text{C}(\text{CH}=\text{CH}_2)=\text{CH}_2\}(\kappa^1\text{-OC}(\text{O})\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$ (7)

Crystal Data	
formula	$\text{C}_{26}\text{H}_{50}\text{O}_4\text{OsP}_2$
mol wt	678.8
color and habit	colorless, prismatic block
symmetry, space group	monoclinic, $P2_1/c$
a , Å	17.198(3)
b , Å	10.774(2)
c , Å	17.028(3)
β , deg	107.93(2)
V , Å ³	3001.9, 4
Z	4
D_{calcd} , g cm ⁻³	1.502
Data Collection and Refinement	
diffractometer	Bruker-Siemens STOE-AED2
λ (Mo K α), Å	0.71073
monochromator	graphite oriented
μ , mm ⁻¹	4.38
scan type	$\omega/2\theta$
2θ range, deg	$3 \leq 2\theta \leq 50$
temp, K	298.0(2)
no. of data collected	6610 (h , -2 to +20; k , -12 to 0; l , -20 to +20)
no. of unique data	5260 (merging R factor 0.046)
no. of params refined	311
$R1^a$ ($F^2 > 2\sigma(F^2)$)	0.0339
$wR2^b$ (all data)	0.09
S^c (all data)	0.971

^a $R1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2(F^2) = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$. ^c $\text{GOF} = S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

CH_3), 2.97 (s, 4 H, $-\text{CH}_2-$), 2.64 (m, 6 H, $\text{PCH}(\text{CH}_3)_2$), 1.38 (dvt, $J_{\text{H-H}} = 6.9$, $N = 14.1$, 36 H, $\text{PCH}(\text{CH}_3)_2$). $^3\text{P}\{^1\text{H}\}$ NMR (121.42 MHz, CDCl_3 , 25 °C): δ 30.0 (s). The peaks corresponding to dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate agree well

with those reported previously.²⁶ MS (EI): m/z 163 ($\text{C}_{10}\text{H}_{12}\text{O}_4 - \text{OMe} - 2 \text{ H}$), 149 ($\text{C}_{10}\text{H}_{12}\text{O}_4 - \text{OMe} - \text{Me} - \text{H}$), 134 ($\text{C}_{10}\text{H}_{12}\text{O}_4 - 2\text{OMe}$), 106 ($\text{C}_{10}\text{H}_{12}\text{O}_4 - \text{OMe} - \text{CO}_2\text{Me}$).

Crystal Data for 7. Crystals suitable for the X-ray diffraction study were obtained by cooling an acetone solution of **7** at -30 °C. A summary of crystal data and refinement parameters is reported in Table 2. The colorless crystal was mounted onto a glass fiber and transferred to an Bruker-Siemens STOE AED-2 ($T = 298.0(2)$ K) automatic diffractometer (Mo K α radiation, graphite monochromator, $\lambda = 0.71073$ Å). Accurate unit cell parameters were determined by least-squares fitting from the settings of 60 high-angle reflections. Data were collected by the $\omega/2\theta$ scan method. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standards throughout data collection. Corrections for decay and absorption (semiempirical ψ -scan method) were also applied.

The structure was solved by Patterson methods and refined by full-matrix least-squares methods on F^2 .²⁷ Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were observed or included at idealized positions.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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