The Os(CO)(P^iPr_3)$_2$ Unit as a Support for the Transformation of Two Alkyne Molecules into New Organometallic Ligands

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Received April 9, 1997[⊗]

In 2-propanol, the C−C triple bond of one of the two alkynyl ligands of the complex Os(C$_2$Ph)$_2$(CO)(P^iPr_3)$_2$ (**1**) can be broken by water to give Os(CH$_2$Ph)(C$_2$Ph)(CO)$_2$(P^iPr_3)$_2$ (**2**). The reaction involves a metal-promoted, hydration−disproportionation of the transformed alkynyl ligand catalyzed by the solvent. Thus, the treatment of **1** with $H_2{}^{18}O$ yields Os(CH$_2$Ph)(C$_2$Ph)(C^{18}O)(CO)(P^iPr_3)$_2$ (**2-^{18}*O***), and the reaction of **1** with water in the presence of deuterated 2-propanol (^{i}PrOD-d_8) affords Os(CD$_2$Ph)(C$_2$Ph)(CO)$_2$(P^iPr_3)$_2$ (**2-*d*$_2$**). In methanol and in the presence of trifluoroacetic acid, complex **2** isomerizes into the osmaindene derivative Os{C(CH$_2$Ph)=CHC$_6$H$_4$}(CO)$_2$(P^iPr_3)$_2$ (**3**). The structure of **3** has been determined by X-ray diffraction. The geometry around the osmium atom can be described as a distorted octahedron with the two triisopropylphosphine ligands occupying two relative *trans* positions. The remaining perpendicular plane is formed by the carbonyl ligands mutually *cis* disposed and the metallacycle, which forms a planar five-membered ring with the osmium atom. In methanol-d_4, complex **2** reacts with CF_3COOD to give Os{C(CH$_2$Ph)=CDC$_6$H$_4$}(CO)$_2$(P^iPr_3)$_2$ (**3-*d*$_1$**) and **3** in a 2.5:1 molar ratio. Complex **2** also reacts with HBF_4. The reaction leads to a mixture of **3** and the π-allyl complex [Os{η^3-CH(Ph)CHCHPh}(CO)$_2$(P^iPr_3)$_2$]BF_4 (**4**), which is a result from the addition of the proton from the acid and the carbon−carbon coupling of the benzyl and alkynyl ligands of **2**. Similar to **2**, complex **2-*d*$_2$** reacts with HBF_4 to give a mixture of Os{C(CD$_2$Ph)=CHC$_6$H$_4$}(CO)$_2$(P^iPr_3)$_2$ (**3-*d*$_2$**) and [Os{η^3-CD(Ph)CDCHPh}(CO)$_2$(P^iPr_3)$_2$] BF_4 (**4-*d*$_2$**). On the basis of the isotope labeling experiments, the mechanisms of the above-mentioned transformations are discussed.

Introduction

Owing to the increasing demand for the products of organic syntheses, the developement of highly efficient and selective synthetic methods is one of the most urgent tasks for chemical science. In this respect, the formation of carbon−carbon bonds mediated by transiton metal compounds is significant and of general interest.[1]

Among the group of organic molecules most frequently studied in metal-assisted C−C bond-forming reactions, alkynes play a prominent role, as is evident from their participation in numerous transformations of both fundamental and industrial relevance.[2] In this area, we have observed that if the nature (dihydrido or dihydrogen) and the number of hydrido ligands (1, 2, 3, or 4) of the precursors are appropiately selected, the reactions of hydrido−osmium compounds with terminal alkynes allow the preparation of specific organometallic complexes (Scheme 1),[3] which should promote reactions of C−C bond formation.

In an effort to develop new models for homogeneous systems effective in the synthesis of functionalized

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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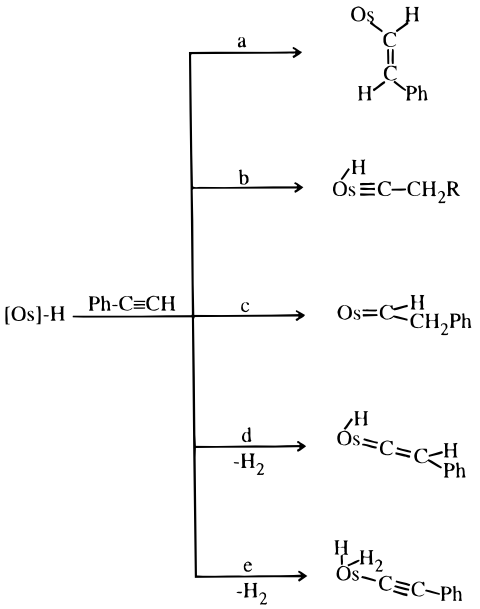
S0276-7333(97)00301-4 CCC: $14.00

Scheme 1[a]

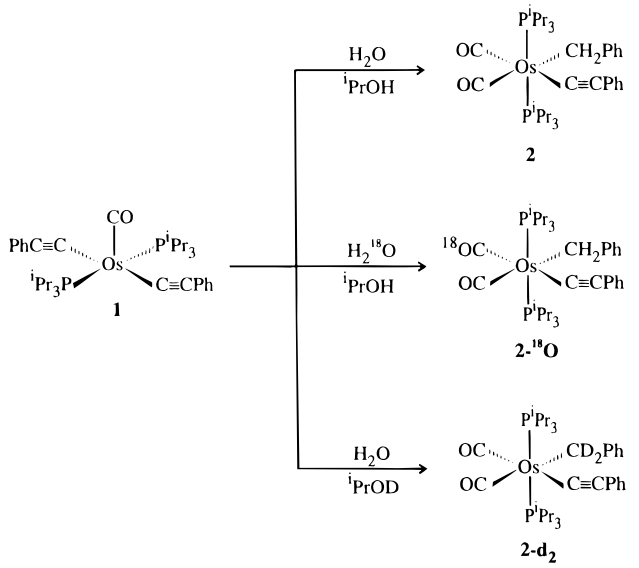


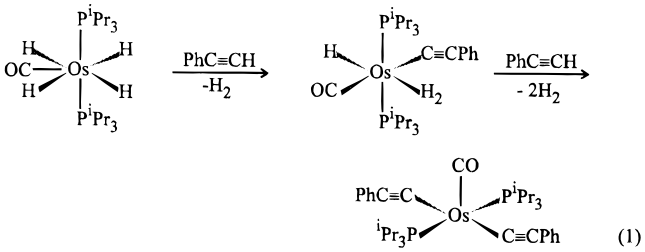
[a] [Os]−H ≡ $OsHCl(CO)P^iPr_3)_2$ (a), $OsH_2Cl_2(P^iPr_3)_2$ (b), $OsCl_2(\eta_2\text{-}H_2)(CO)(P^iPr_3)_2$, (c), $OsH_3(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (d), and $OsH_4(CO)(P^iPr_3)_2$ (e).

organic molecules from basic hydrocarbon units, we have recently initiated a research program centered around the transformation of these complexes affording new C−C bonds. Thus, in order to combine C−C coupling reactions together with C−H activation processes, we have previously reported the reactions of the complexes Os{(*E*)-CH=CHR′}Cl(CO)(P^iPr_3)$_2$ (R′ = H, Ph) with RLi and RMgBr.[4] Treatment of the alkenyl complexes with main group organometallic compounds leads to osmium(0) species containing olefin ligands. These transformations involve the replacement of the Cl^- anion by the organic fragments R′ and the subsequent reductive carbon−carbon coupling of the η^1-carbon ligands. For butadiene and phenylbutadiene, the osmium(0) species are stable and they do not undergo a subsequent transformation.[4a] However, for *trans*-stylbene and *trans*-methylstyrene, the metallic center is capable of activating a C−H bond of the substituents of the coordinated olefin to afford hydrido−osmium(II) derivatives. The C−H activation products depend upon the substituents present at the alkene ligand and can be rationalized in light of the thermodynamic and kinetic considerations. When the alkene ligand is *trans*-methylstyrene, the activation of an *ortho* position of the phenyl ring to give $\overline{OsH(C_6H_4CH{=}CH\text{-}CH_3)}(CO)(P^iPr_3)_2$ is kinetically favored. $\overline{OsH(C_6H_4\text{-}CH{=}CHCH_3)}(CO)(P^iPr_3)_2$ evolves to the most favored thermodynamic species, the allyl derivative $OsH(\eta^3\text{-}CH_2CHCHPh)(CO)(P^iPr_3)_2$, resulting of the C−H activation of the methyl group.[4b]

Our most recent interest has been centered in the transformation of two alkyne molecules into new organic fragments by the carbon−carbon triple bond cleavage of one of them and subsequent carbon−carbon coupling between the resulting fragments and the other alkyne molecule. In agreement with Scheme 1, the bis(alkynyl) complex $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ can be prepared according to eq 1. As a result of the new studies in the carbon−carbon coupling field, we report the transformation of the above-mentioned bis(alkynyl) complex into the derivatives $\overline{Os\{C(CH_2Ph){=}CHC_6H_4\}}(CO)_2(P^iPr_3)_2$ and $[Os\{\eta^3\text{-}CH(Ph)CHCHPh\}(CO)_2(P^iPr_3)_2]BF_4$ via the compound $Os(CH_2Ph)(C_2Ph)(CO)_2(P^iPr_3)_2$.

Scheme 2





Results and Discussion

C−C Triple Bond Cleavage of One of the Two Alkynyl Ligands of $Os(C_2Ph)_2(CO)(P^iPr_3)_2$. Treatment of a refluxing suspension of $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ (**1**) in 2-propanol with water in a ca. 1:25 molar ratio for 1 h gives a colorless solution, from which the benzyl−dicarbonyl complex $Os(CH_2Ph)(C_2Ph)(CO)_2(P^iPr_3)_2$ (**2**) was isolated as a white solid in 65% yield (Scheme 2).

The spectroscopic data obtained for complex **2** support the proposed structure. The *cis* relative position of the carbonyl ligands was inferred from the IR spectrum, which shows, together with a $\nu_{C\equiv C}$ band at 2105 cm^{-1}, two strong ν_{CO} absorptions at 1988 and 1925 cm^{-1}, a typical pattern for mononuclear *cis*-dicarbonyl complexes. The $^{13}C\{^1H\}$ NMR spectrum also supports this proposal, showing two triplets at 188.01 (J_{C-P} = 7.2 Hz) and 180.09 ppm (J_{C-P} = 8.3 Hz) attributable to the carbonyl ligands. This spectrum also contains the expected resonances for the alkynyl and benzyl ligands. The C_β, C_α, and CH_2− carbon atoms appear at 113.41, 103.30, and 4.56 ppm as triplets with C−P coupling constants of 2.5, 17.9, and 6.7 Hz, respectively. The CH groups of the phosphine ligands give a virtual triplet

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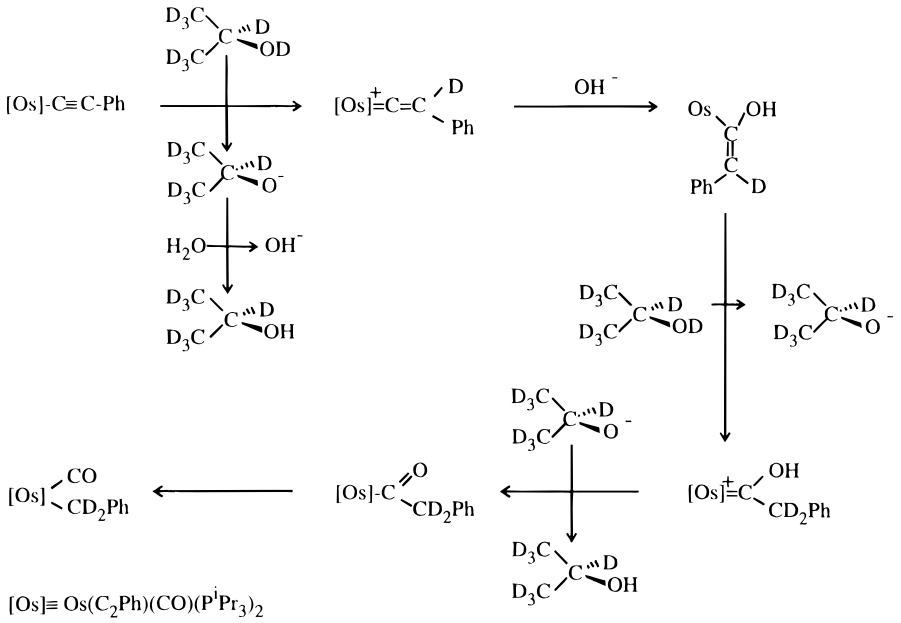
Scheme 3



at 25.52 ppm (N = 25.4 Hz), which is characteristic of two equivalent phosphine ligands in a *trans* relative position. This is in agreement with the singlet at −0.78 ppm found in the $^{31}P\{^1H\}$ NMR spectrum. In the ^1H NMR spectrum, the most noticiable resonance is a triplet at 2.95 ppm (J_{H-P} = 7.3 Hz) assigned to the CH_2− protons of the benzyl group.

With $H_2{}^{18}O$, the reaction product was found to be Os(CH_2Ph)(C_2Ph)($C^{18}O$)(CO) (P^{i}Pr$_3$)$_2$ (**2-^{18}*O***) (Scheme 2) by the shift of ν_{CO} from **2** (1988 and 1925 cm^{-1}) to **2-^{18}*O*** (1963 and 1890 cm^{-1}), as a result of the change in the reduced mass. So, the reactions shown in Scheme 2 involve a metal-promoted hydration−disproportionation of one of the two alkynyl ligands of **1**. Some related processes have been previously described. Thus, it has been reported that the reaction of [OsI(η^6-C_6H_6)(=C=CHR)(PMe^{t}Bu$_2$)]PF_6 (R = H, Me) with water gives the carbonyl−osmium compound [OsI(η^6-C_6H_6)(CO)(PMe-^{t}Bu$_2$)]PF_6.[5] The reaction is quite general for cationic vinylidene complexes, which afford alkyl−carbonyl derivatives in the presence of water,[6] and for octahedral complexes of ruthenium(II) and osmium(II) with one labile halide ligand, such as *cis*-$RuCl_2$(bpy)$_2$ (bpy = 2,2′-bipyridine), *cis*-[RuCl(trpy)(bpy)]PF_6 (trpy = 2,2′,2″-terpyridine), and *cis*-$OsCl_2$(phen)[1,2-bis(diphenylphosphino)benzene] (phen = 1,10-phenanthroline), which react with terminal alkynes and water to give the corresponding monocarbonyl derivatives and alkane.[7] Recently, Bianchini and co-workers have also observed that the hydration of phenylacetylene in the presence of *mer,trans*-$RuCl_2$(PNP)(PPh_3) leads to the cleavage of the C−C triple bond with formation of the carbonyl complex *fac,cis*-$RuCl_2$(CO)(PNP) (PNP = CH_3CH_2-$CH_2N(CH_2CH_2PPh_2)$) and toluene. As a result of an elegant mechanistic study, they propose that the most relevant steps of the mechanism are 1-alkyne to vinylidene tautomerism, conversion of the vinylidene ligand to hydroxycarbene by intramolecular attack of water, deprotonation of the hydroxycarbene to σ-acyl, deinsertion of CO from the acyl ligand, and hydrocarbon elimination by protonation of the metal−alkyl moiety.[8]

Bianchini's reaction was carried out in tetrahydrofuran at 60 °C. However, under the same conditions, the formation of **2** does not take place. The transformation of **1** into **2** was not observed in either toluene or acetone. This suggests that during the hydration of the alkynyl ligand of **1**, the 2-propanol solvent plays a main role. In fact, the reaction of **1** with water in 2-propanol-d_8 under reflux leads to Os(CD_2Ph)(C_2Ph)$(CO)_2$(P^{i}Pr$_3$)$_2$ (**2-*d*$_2$** in Scheme 2) in 70% yield. The presence of a CD_2-Ph group in **2-*d*$_2$** was inferred from its ^2H NMR spectrum in benzene, which shows only one broad singlet at 2.86 Hz. In agreement with this, the ^1H NMR spectrum does not contain any resonance at 2.95 ppm. A plausible mechanism for the formation of **2** which allows one to rationalize the deuteration of the benzyl group and agrees with the Bianchini's proposal is shown in Scheme 3. In general, the coordination of an acetylide anion to a transition metal center transfers the nucleophilicity from the C_α to C_β carbon atom.[9] Thus, the formation of **2** could initially involve the electrophilic attack of the −OH proton from the alcohol to the C_β carbon atom of **1**. In this context, it should be noted that the addition of electrophiles to the electron-rich C_β of metal alkynyls has been described on many ocassions and is the best entry to the synthesis of vinylidene complexes.[10] The alkoxide anion formed should regenerate 2-propanol by water deprotonation. At this stage, the OH^- anion could attack to the vinylidene ligand to give an α-hydroxyalkenyl group. This is in agreement with previous studies on vinylidene complexes, which have identified the electron deficiency of the vinylidenes at the α-carbon atom.[11] The reaction of the α-hydroxy-

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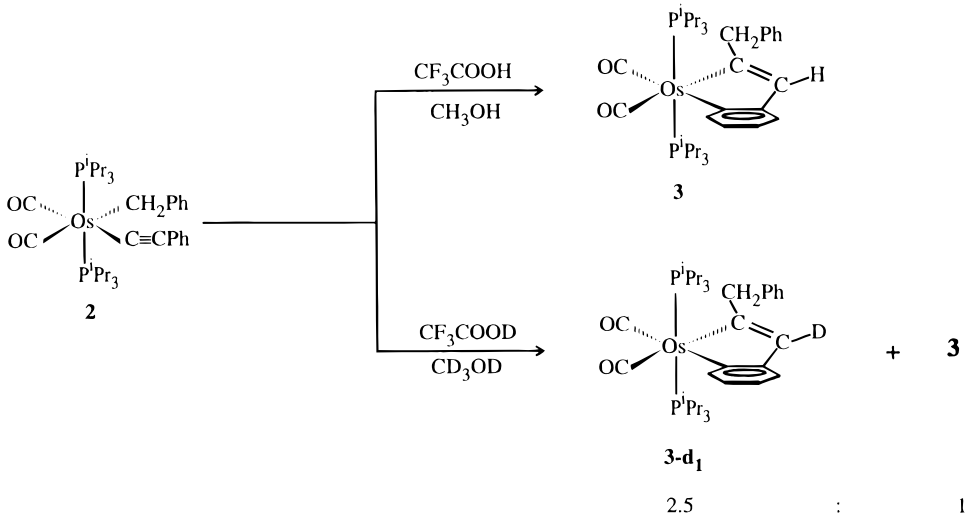
Scheme 4



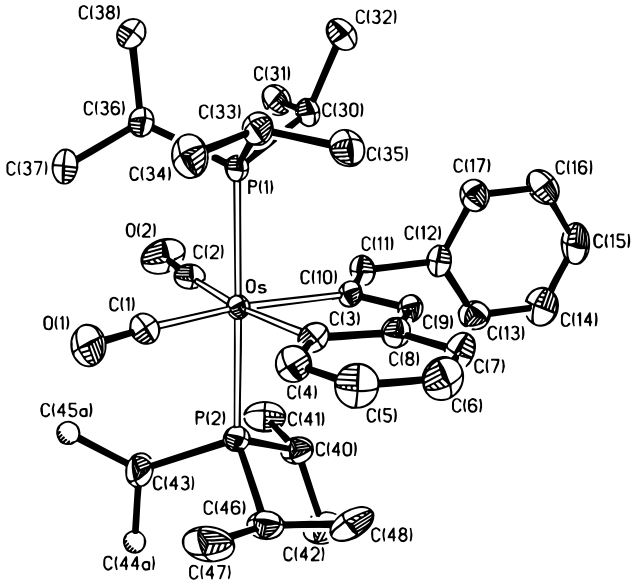


Figure 1. Molecular diagram of Os[C(CH$_2$Ph)=CC$_6$H$_4$](CO)$_2$(P^{i}Pr$_3$)$_2$ (**3**).

alkenyl species with a second 2-propanol molecule could yield a hydroxycarbene intermediate. The deprotonation of the hydroxycarbene group by the alkoxide anion formed in the last step should afford an acyl complex. Finally, the CO deinsertion could give **2** (and **2-*d*$_2$**).

Alkenyl−Benzyl Coupling in the Presence of CF$_3$COOH. In methanol under reflux and in the presence of catalytic amounts of trifluoroacetic acid, the alkynyl benzyl complex **2** isomerizes into the osmaindene derivative **3** (Scheme 4), which is a result from the C−C coupling between the benzyl and alkynyl fragments of **2**.

Complex **3** was isolated as a white solid in 50% yield and characterized by elemental analysis, IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopies, and X-ray diffraction. A view of the molecular geometry of **3** is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The coordination geometry around the osmium center can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying opposite positions (P(1)−Os−P(2) = 176.99(4)°). An ideal equatorial plane is formed by the atoms C(3) and C(10) of the chelating organic ligand coordinating with the osmium atom to form a five-membered ring (C(3)−Os−C(10) = 77.5(2)°) and the two carbonyl ligands mutually *cis* disposed (C(1)−Os−C(2)=

Table 1. Selected Bond Distances (Å) and Angles (deg) for Os[C(CH$_2$Ph)=CC$_6$H$_4$](CO)$_2$(P^{i}Pr$_3$)$_2$ (3)

Os−P(1)	2.455(1)	C(3)−C(4)	1.417(6)
Os−P(2)	2.456(1)	C(3)−C(8)	1.429(6)
Os−C(1)	1.932(4)	C(4)−C(5)	1.411(7)
Os−C(2)	1.926(5)	C(5)−C(6)	1.388(7)
Os−C(3)	2.168(4)	C(6)−C(7)	1.417(7)
Os−C(10)	2.180(4)	C(7)−C(8)	1.408(6)
O(1)−C(1)	1.163(5)	C(8)−C(9)	1.482(6)
O(2)−C(2)	1.160(6)	C(9)−C(10)	1.356(6)
		C(11)−C(12)	1.530(5)
P(1)−Os−P(2)	176.99(4)	Os−C(1)−O(1)	175.7(4)
P(1)−Os−C(1)	91.8(2)	Os−C(2)−O(2)	177.3(4)
P(1)−Os−C(2)	85.6(1)	Os−C(3)−C(8)	114.4(3)
P(1)−Os−C(3)	92.3(1)	C(3)−C(8)−C(9)	115.1(4)
P(1)−Os−C(10)	90.1(1)	C(8)−C(9)−C(10)	117.8(4)
P(2)−Os−C(1)	88.6(2)	Os−C(10)−C(9)	115.3(3)
P(2)−Os−C(2)	91.4(1)	Os−C(10)−C(11)	124.4(3)
P(2)−Os−C(3)	90.8(1)	C(9)−C(10)−C(11)	120.3(4)
P(2)−Os−C(10)	90.2(1)	C(10)−C(11)−C(12)	116.8(3)
C(1)−Os−C(2)	98.8(2)	C(2)−Os−C(3)	171.8(2)
C(1)−Os−C(3)	89.2(2)	C(2)−Os−C(10)	94.6(2)
C(1)−Os−C(10)	166.6(2)	C(3)−Os−C(10)	77.5(2)

Table 2. Crystallographic Data for Complex Os[C(CH$_2$Ph)=CC$_6$H$_4$](CO)$_2$(P^{i}Pr$_3$)$_2$ (3)

formula	$C_{35}H_{54}O_2OsP_2$	scan method	ω
mol wt	758.92	θ (min−max), deg	1.2−25
a, Å	34.980(4)	no. of measd reflns	6227
b, Å	12.560(1)	no. of indep reflns	6114 (R_{int} = 0.0269)
c, Å	16.439(2)	no. of params	372
β, deg	104.171(9)	no. of restraints	4
V, Å^3	7003(1)	GOOF	1.042
cryst syst	monoclinic	λ, Å	0.710 73
space group	$C2/c$	ρ_{calcd}, g cm^{-3}	1.440
Z	8	μ, mm^{-1}	3.761
temp, °C	−100	R_1[a]	0.0280
		R_2[a]	0.0737

[a] SHELXL-93: $R_1 = (\sum||F_o| - |F_c||/\sum|F_o|)$ calculated using 5057 observed reflections [$F_o > 4\sigma(F_o)$]. $R_2 = (\{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2})$, $w = (1/[\sigma^2(F_o^2) + (0.0340P)^2 + 14.7276P])$, $P = ([F_o^2 + 2F_c^2/3])$ calculated using all reflections.

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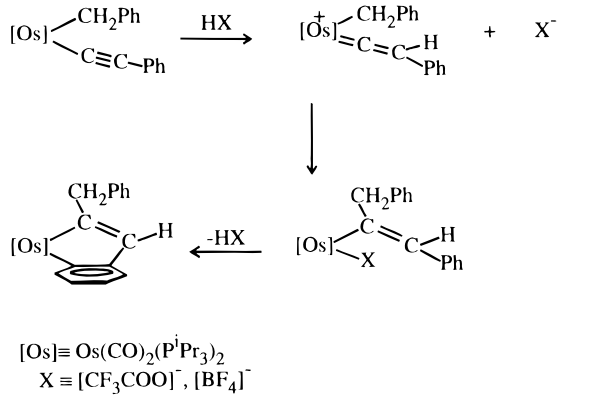
98.8(2)°). The five-membered metallacycle is almost planar. The deviations from the best plane are −0.0025(1) (Os), 0.005(5) (C(3)), −0.006 (5) (C(8)), 0.003(4) (C(9)), and −0.001(5) (C(10)) Å. A similar situation has been observed for the metallacycle of the complex Os(C_2CO_2Me){CH=CHC(=O)OMe}(CO)(P^{i}Pr$_3$)$_2$.[3c] In contrast to the OsC_4 ring of **3**, the RhC_4 rings of the compounds Rh(η^5-C_5H_5){C(Ph)=CHC_6H_4}(P^{i}Pr$_3$)[12] and Rh(η^5-C_5H_5)-{$C_4(C_6F_5)_4$}(PPh_3)[13] show an envelope conformation with the rhodium atoms displaced by 0.228 and 0.239 Å, respectively, from the plane defined by the carbon atoms. The planarity of the OsC_4 ring in **3** most probably is a consequence of the steric hindrance imposed by the triisopropylphosphine ligands. The Os−C(10) distance (2.180(4) Å) is slightly longer than the Os−C distances found in the alkenyl−osmium(II) complexes Os{(*E*)-CH=CHPh}Cl(CO)(P^{i}Pr$_3$)$_2$ (1.99(1) Å),[3a] [Os{CH=C(I)C(=O)OMe}(η^6-C_6H_6)(P^{i}Pr$_3$)]$^+$ (2.02(1) Å),[14] and Os(C_2CO_2Me){CH=CHC(=O)OMe}(CO)(P^{i}Pr$_3$)$_2$ (2.103(4) Å).[3c] The distances C(9)−C(10) (1.356(6) Å), C(8)−C(9) (1.482(6) Å), and C(3)−C(8) (1.429(6) Å) are comparable to those found for the same structural disposition of the organic ligand in Werner's complex Rh(η^5-C_5H_5){C(Ph)=CHC_6H_4}(P^{i}Pr$_3$) (1.34(1), 1.440(8), and 1.41(1) Å, respectively).[12] The Os−C(3) distance (2.168(4) Å) is statistically identical with the Os−C bond length found in the aryl complex OsH{C_6H_4CH=CHPh}-(CO)(P^{i}Pr$_3$)$_2$ (2.136(7) Å)[4b] and agrees well with the values previously reported for Os−C(aryl) distances (mean 2.09(3) Å).[15] The Os−P and Os−CO distances are clearly in the range expected and deserve no further comments.

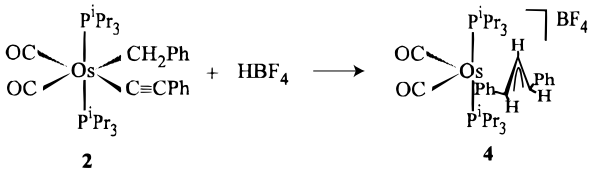
The spectroscopy data obtained for **3** are in agreement with the structure shown in Figure 1. According to the mutally *cis* disposition of the carbonyl ligands, the IR spectrum contains two strong ν_{CO} bands at 1970 and 1905 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum shows two triplets at 189.76 (J_{C-P} = 8.1 Hz) and 188.41 (J_{C-P} = 8.7 Hz) ppm. Furthermore, this spectrum exhibits a triplet at 166.44 ppm, with a C−P coupling constant of 10.4 Hz, corresponding to the aromatic carbon atom bonded to the osmium. The rest of the carbon atoms of the phenyl rings give singlets between 145.34 and 120.84 ppm. A singlet at 164.35 ppm and a triplet at 153.49 ppm (J_{C-P} = 11.1 Hz) were assigned, respectively, to the C_β and C_α atoms of the alkenyl moiety. The −CH_2Ph carbon atom appears as a singlet at 52.45 ppm. In the ^1H NMR spectrum, the most noticiable signals are a triplet at 6.33 ppm (J_{H-P} = 2.1 Hz) due to the −C*H*= proton and a broad singlet at 4.15 ppm (J_{H-P} < 1 Hz) assigned to the −CH_2Ph protons. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −2.89 ppm, in agreement with the mutually *trans* disposition of the triisopropylphosphine ligands.

Scheme 5



In methanol-d_4 and in the presence of CF_3COOD, complex **2** affords Os{C(CH_2Ph=CDC_6H_4}(CO)$_2$(P^{i}Pr$_3$)$_2$ (**3-*d*$_1$** in Scheme 4) and **3** in a 2.5:1 molar ratio. The presence of a deuterium atom at the C_β carbon atom of the alkenyl unit of **3-*d*$_1$** is supported by the ^2H NMR spectrum of this compound, which contains only one singlet at 6.39. The position of the deuterium atom in **3-*d*$_1$** suggests that the reaction of the formation of **3** initially proceeds by electrophilic attack of H^+ at the C_β carbon atom of the alkynyl ligand of **2** followed by migratory insertion of the resulting vinylidine ligand into the benzyl group (Scheme 5). The C−H activation of the *ortho*-CH bond of the phenyl group located at the C_β carbon atom of the resulting alkenyl ligand most probably involves an Os{C(CH_2Ph)=CHPh}{η^1-OC(O)-CF_3}(CO)$_2$(P^{i}Pr$_3$)$_2$ intermediate, which eliminates CF_3-COOH. There are precedents for this reaction. Werner has previously reported that the alkenyl−trifluoroacetato complex Os(CH=CHPh){η^1-OC(O)CF_3}(η^6-C_6H_6)-(P^{i}Pr$_3$) is relatively labile and reacts readily at room temperarure (also in methanol) to form the related metallacycle compound Os(CH=CHC_6H_4)(η^6-C_6H_6)-(P^{i}Pr$_3$).[16] The complexes M{C(Ph)=CHC_6H_4}(η^5-C_5H_5)-(P^{i}Pr$_3$) have been similarly prepared from the alkenyl derivatives M{C(Ph)=CHPh}{η^1-OC(O)CF_3}(η^5-C_5H_5)-(P^{i}Pr$_3$) (M = Rh, Ir) by CF_3COOH elimination.[12,17]

Alkenyl-Benzyl Coupling in the Presence of HBF_4. Complex **2** also isomerizes into **3** in the presence of ca. 1 equivalent of HBF_4. However, the yield of the isomerization is lower than that in the presence of CF_3-COOH. Thus, treatment of **2** with HBF_4 leads to a



(2)

mixture of **3** (30%) and the π-allyl complex [Os{η^3-CH(Ph)CHCHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF_4 (**4**), which is formed by addition of H^+ and C−C coupling of the alkenyl and benzyl fragments of **2** according to eq 2.

Complex **4** was isolated as a white solid in 55% yield and characterized by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies. As expected for a *cis*-dicarbonyl compound, the IR spectrum in Nujol

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

(16) Werner, H.; Weinand, R.; Knaup, W.; Peters, K.; von Schnering, H. G. *Organometallics* **1991**, *10*, 3967.

(17) Werner, H.; Höhn, A. *J. Organomet. Chem.* **1984**, *272*, 105.

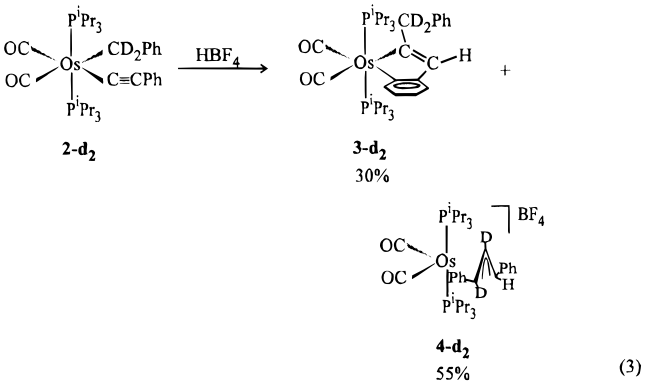
contains two ν(CO) bands at 2020 and 1964 cm^{-1}. Furthermore, the spectrum shows the absorption due to the $[BF_4]^-$ anion with T_d symmetry at about 1100 cm^{-1}. The ^1H NMR spectrum exhibits the resonances due to the phosphine ligands and the phenyl groups, along with a triplet (J_{H-H} = 11.1 Hz) of doublets (J_{H-P} = 7.5 Hz) at 6.14 ppm and a doublet (J_{H-H} = 11.1 Hz) of doublets (J_{H-P} = 11.1 Hz) of doublets (J_{H-P} = 2.1 Hz) at 5.11 ppm, corresponding to the *meso*-CH and −C*H*Ph protons of the allyl ligand, respectively. According to the value of the H-H coupling constant, there is no doubt that the *meso*-CH and −C*H*Ph protons are mutually *trans* disposed. The *syn* disposition of both phenyl rings appears to be sterically more favored, being the usual form adopted for this type of ligands in other compounds.[4b,18] In addition, it should be mentioned that the chemical shift of the *anti*-C*H*Ph protons is displaced toward lower field with regard to that expected for *anti*-CH allyl protons.[19] In this context, it should be noted that according to the structure proposed in eq 2, the *anti*-CH allyl protons of **4** are in the region of a negative shielding contribution produced by the ring current effect of the phenyl ring. Also in agreement with the structure proposed for **4** in eq 2, the $^{31}P\{^1H\}$ NMR spectrum shows an AB system (δ_A = 5.94 and δ_B = 4.54) with a P-P coupling constant of 185.3 Hz, which requires a *trans* disposition of the phosphine ligands. The π-coordination of the allyl ligand agrees well with the $^{13}C\{^1H\}$ NMR spectrum, which shows two singlets at 92.72 and 56.13 ppm for the central and terminal carbon atoms, respectively.

We have previously mentioned that during the reaction of **2** with HBF_4 to give **4**, significant amounts of **3** are also formed. Accordingly, at first glance one could think that complex **4** is a result of the isomerization from **2** into **3** and the subsequent protonation of the latter. However, this must be ruled out because **3** is stable in the presence of 1 equiv of HBF_4.

Previously, Werner[20] has reported that the but-2-yne compound Rh(η^5-C_5H_5)(η^2-C_2Me_2)(P^iPr_3) reacts with Brønsted acids to form the 1-methylallylrhodium cation [Rh(η^5-C_5H_5)(η^3-$CH_2CHCHMe$)(P^iPr_3)]$^+$. The conversion of the alkyne to the 1-methylallyl unit occurs via the alkenyl cation [Rh(η^5-C_5H_5){(*E*)-C(CH_3)=$CHCH_3$}(P^iPr_3)]$^+$, which rearranges to give the isomeric allene−hydrido intermediate [Rh(η^5-C_5H_5)H(η^2-CH_2=C=CHMe)(P^iPr_3)]$^+$. The migration of the hydrido ligand to the central carbon atom of the allene yields, finally, the allyl complex. In agreement with Werner's proposal, Schwartz et al.[21] have observed that the iridium complex *trans*-Ir{(*Z*)-C(CH_3)=$CHCH_3$}(CO)(PPh_3)$_2$ reacts on warming in benzene-d_6 in a sealed tube to give the allyl isomer Ir(η^3-$CH_2CHCHMe$)(CO)(PPh_3)$_2$ and in the reaction of Mo(η^5-C_5H_5)(η^2-C_2Me_2)LL′]BF_4 (L = L′ = $P(OMe)_3$; L = CO, L′ = PEt_3) with hydrido donors an alkenyl intermediate is also formed, which rearranges to the corresponding η^3-1-methylallylmolybdenum compound.[22]

The key for the above-mentioned processes is the presence of a coordination site at the metallic center of the alkenyl complexes, which allows the abstraction of a hydrogen atom from the alkyl substituent, situated at the C_α carbon atom of the alkenyl group, and the subsequent migration of the resulting hydrido ligand to the central carbon atom of the allene. In other words, the alkenyl−π-allyl isomerization involves a 1,2-hydrogen shift inside the alkenyl group.

According to Scheme 5, the isomerization of **2** to **3** in the presence of HBF_4 involves the alkenyl intermediate Os{C(CH_2Ph)=CHPh}(FBF_3)(CO)$_2$(P^iPr_3)$_2$, which is formed by direct attack of the proton from the acid to the C_β carbon atom of the alkenyl ligand of **2** and subsequent migratory insertion of the resulting vinylidene into the metal−benzyl bond. The $[BF_4]^-$ anion is a very weak Lewis base.[23] So, it is reasonable to assume that in solution, Os{C(CH_2Ph)=CHPh}(FBF_3)(CO)$_2$(P^iPr_3)$_2$ is in equilibrium with the unsaturated cation [Os{C(CH_2Ph)=CHPh}(CO)$_2$(P^iPr_3)$_2$]$^+$, which could afford by a 1,2-hydrogen shift the π-allyl complex **4**. If our assumption is correct, the addition of HBF_4 to solutions of the deuterated complex **2-*d*$_2$** should afford a mixture of Os{C(CD_2Ph)=CHC_6H_4}(CO)$_2$(P^iPr_3)$_2$ (**3-*d*$_2$**) and [Os{η^3-CD(Ph)CDCHPh}(CO)$_2$(P^iPr_3)$_2$]BF_4 (**4-*d*$_2$**). In fact, the treatment of dichloromethane solutions of **2-*d*$_2$** with ca. 1 equiv of HBF_4 leads to a mixture of **3-*d*$_2$** and **4-*d*$_2$** (eq 3) in a molar ratio similar to the **3**:**4** molar ratio obtained from the treatment of **2** with HBF_4.



(3)

The positions of the deuterium atoms in **3-*d*$_2$** and **4-*d*$_2$** are supported by the corresponding ^2H NMR spectra. The ^2H NMR spectrum of **3-*d*$_2$** shows only one singlet at 4.31 ppm, whereas the ^2H NMR spectrum of **4-*d*$_2$** contains two broad singlets at 6.16 and 5.17 ppm. A possible mechanism for the formation of **3-*d*$_2$** and **4-*d*$_2$** which accounts for the deuterium distribution in these compounds is shown in Scheme 6. The lower coordination power of the $[BF_4]^-$ anion compared to that of the $[CF_3COO]^-$ can explain why HBF_4 produces not only the isomerization of **2** into **3** but also the formation of **4**.

Concluding Remarks

This study has revealed that in 2-propanol, the C−C triple bond of one of the two alkynyl ligands of complex

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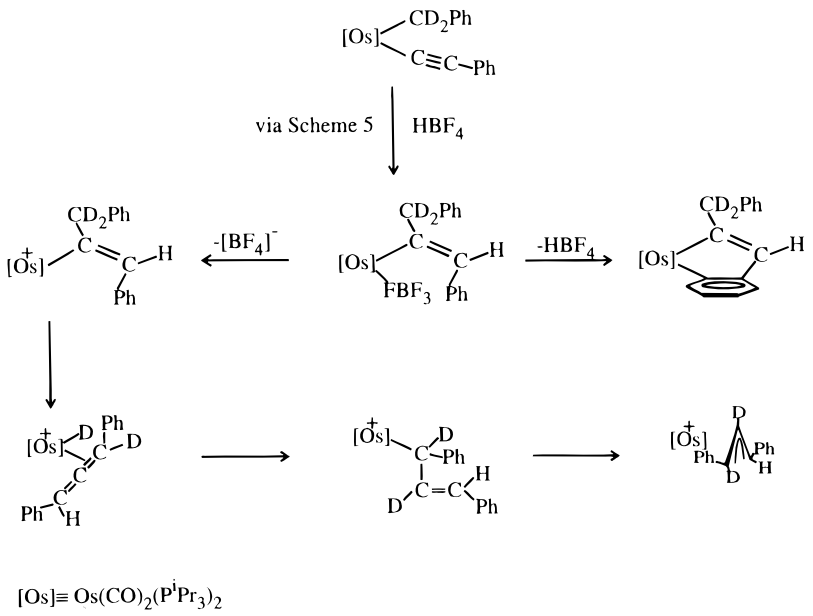
(22) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1983**, 927.

(23) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

Scheme 6



$Os(C_2Ph)_2(CO)(P^iPr_3)_2$ (**1**) can be selectively broken by reaction with water to afford $Os(C_2Ph)(CH_2Ph)(CO)_2(P^iPr_3)_2$ (**2**). The reaction involves a metal-promoted hydration-disproportionation of the transformed alkynyl ligand catalyzed by the solvent.

In methanol, the trifluoroacetic acid catalyzes the isomerization of complex **2** into $Os\{C(CH_2Ph)=CHC_6H_4\}(CO)_2(P^iPr_3)_2$ (**3**), which contains an *ortho*-metalated phenyl group. According to the results from isotope labeling experiments, the isomerization involves the initial attack of the proton from the acid to the C_β carbon atom of the alkynyl ligand of the starting compound. The subsequent migratory insertion of the resulting vinylidene into the metal−benzyl bond gives an alkenyl intermediate containing a coordinated trifluoroacetato anion, which evolves into **3** by trifluroacetic acid elimination. In the presence of tetrafluoroboric acid, complex **2** also isomerizes into **3** but, furthermore, it produces the π-allyl derivative $[Os\{\eta^3\text{-}CH(Ph)CHCHPh\}(CO)_2(P^iPr_3)_2]BF_4$ (**4**), which is a result from the addition of the proton from the acid and the carbon−carbon coupling of the benzyl and alkynyl fragments of **2**. In this case the isotope labeling experiments suggest that the formation of **4** involves the unsaturated alkenyl intermediate $[Os\{C(CH_2Ph)=CHPh\}(CO)_2(P^iPr_3)_2]^+$, which by a 1,2-hydrogen shift evolves into **4**. The different behavior of **2** toward trifluoroacetic acid and tetrafluoroboric acid can be rationalized in terms of different coordination powers of the corresponding anions. The trifluoroacetato, which has a stronger coordination power than the tetrafluoroborato, prevents the formation of the unsaturated alkenyl intermediate $[Os\{C(CH_2Ph)=CHPh\}(CO)_2(P^iPr_3)_2]^+$, which is the key for the formation **4**. Thus, complex **3** is the only species formed from **2**, in the presence of this acid.

In conclusion, we prove that the $Os(CO)(P^iPr_3)_2$ unit permits not only the introduction, in a sequential manner, of two alkyne molecules into the metallic center (eq 1), but also the selective transformation of one of them (Scheme 2) and the C−C coupling of the η^1-carbon ligands of the resulting complex to afford new organic fragments (Scheme 4, eq 2).

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere by using Schlenk techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complex $Os(C_2Ph)_2(CO)(P^iPr3)2$ (**1**) was prepared by a published method.[24]

Physical Measurements. NMR spectra were recorded on a Varian Unity 300 or on a Bruker ARX 300 spectrometer at room temperature unless stated. Chemical shifts are expresed in parts per million, upfield from $Si(CH_3)_4$ (^{1}H, ^{13}C{^{1}H}) and 85% H_3PO_4 (^{31}P{^{1}H}). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^{1}H and $N = J(CP) + J(CP')$ for ^{13}C) are given in Hertz. Infrared spectra were recorded on a Nicolet 550 spectrometer using Nujol mulls on polyethylene sheets. C and H analyses were carried out on a Perkin Elmer 240C microanalyzer.

Reaction of $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ (1) with H_2O: preparation of $Os(C_2Ph)(CH_2Ph)(CO)_2(P^iPr_3)_2$ (2). A stirred suspension of $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ (**1**) (165 mg, 0.22 mmol) in 6 mL of 2-propanol was treated with water (10 μL, 0.55 mmol). The mixture was stirred for 60 min at reflux temperature. The resulting yellow solution was cooled, and a white solid precipitated. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 110 mg (65%). Anal. Calcd For $C_{35}H_{54}O_2OsP_2$: C, 55.39; H, 7.17. Found: C, 55.12; H, 7.03.

IR (Nujol, cm^{-1}): ν(C≡C) 2105 (s); ν(CO) 1988, 1925(s); $\nu(C_6H_5)$ 1596 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 7.53 (d, 2H, $J_{H-H} = 7.8$ Hz), 7.51 (d, 2H, $J_{H-H} = 7.8$ Hz), 7.26 (t, 2H, $J_{H-H} = J_{H-H'} = 7.8$ Hz), 7.19 (t, 2H, $J_{H-H} = J_{H-H'} = 7.8$ Hz), 6.99 (m, 2H) [C_6H_5 and C−C_6H_5], 2.95 (t, 2H, $J_{H-P} = 7.3$ Hz, −CH_2); 2.60 (m, 6H, PC*H*), 1.37 and 1.09 (both dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 13.8$ Hz, PCCH_3). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ −0.78 (s). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 188.01 (t, $J_{C-P} = 7.2$ Hz, *C*O), 180.09 (t, $J_{C-P} = 8.3$ Hz, *C*O), 155.19 (t, $J_{C-P} = 1.2$ Hz, C_{ipso}), 129.67 (t, $J_{C-P} = 1.8$ Hz, C_{ipso}), 130.76 (t, $J_{C-P} = 1.4$ Hz), 129.98 (s), 128.42 (s), 125.2 (s), 122.56 (s), [C_6H_5 and C−C_6H_5), 113.41 (t, $J_{C-P} = 2.5$ Hz, ≡C_β), 103.30 (t, $J_{C-P} = 17.9$ Hz, C_o≡), 25.52(vt, $N = 25.4$ Hz, PC*H*), 20.37 (s, PC*C*H$_3$), 19.28 (s, PC*C*H$_3$), 4.56 (t, $J_{C-P} = 6.7$ Hz, *C*H$_2$).

Reaction of $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ (1) with $H_2{}^{18}O$ Preparation of $Os(C_2Ph)(CH_2Ph)(C^{18}O)(CO)(P^iPr_3)_2$ (2-^{18}*O*). A stirred suspension of $Os(C_2Ph)_2(CO)(P^iPr_3)_2$ (**1**) (344 mg, 0.46

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mmol) in 6 mL of 2-propanol was treated with $H_2{}^{18}O$ (55 μL, 3.05 mmol). The mixture was stirred for 2 h at reflux temperature. The resulting yellow solution was cooled, and a white solid precipitated. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 228 mg (65%).

IR (Nujol, cm^{-1}): ν(C≡C) 2105 (s); ν(CO) 1963, 1890 (s); $\nu(C_6H_5)$ 1596 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.53 (d, 2H, J_{H-H} = 7.8 Hz), 7.51 (d, 2H, J_{H-H} = 7.8 Hz), 7.26 (t, 2H, J_{H-H} = $J_{H-H'}$ = 7.8 Hz), 7.19 (t, 2H, J_{H-H} = $J_{H-H'}$ = 7.8 Hz), 6.99 (m, 2H) [C_6H_5 and C−C_6H_5], 2.95 (t, J_{H-P} = 7.3 Hz, 2H, Os−CH_2), 2.60 (m, 6H, PC*H*), 1.37 and 1.09 (both dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.8 Hz, PCCH_3). $^{31}P\{^1H\}$NMR (121.4 MHz, C_6D_6): δ −0.78 (s).

Reaction of Os(C_2Ph)$_2$(CO)(P^{i}Pr$_3$)$_2$ (1) with H_2O in 2-Propanol-d_8: Preparation of Os(C_2Ph)(CD_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (2-d_2). A stirred suspension of Os(C_2Ph)$_2$(CO)(P^{i}Pr$_3$)$_2$ (**1**) (260 mg, 0.35 mmol) in 2 mL of 2-propanol-d_8 was treated with H_2O (16 μL, 0.87 mmol). The mixture was stirred for 60 min at reflux temperature. The resulting yellow solution was cooled, and a white solid precipitated. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 186 mg (70%).

IR (Nujol, cm^{-1}): ν(C≡C) 2105(s); ν(CO) 1988, 1925(s); $\nu(C_6H_5)$ 1596. ^1H NMR (300 MHz, C_6D_6): δ 7.53 (d, 2H, J_{H-H} = 7.8 Hz), 7.51 (d, 2H, J_{H-H} = 7.8 Hz), 7.26 (t, 2H, J_{H-H} = $J_{H-H'}$ = 7.8 Hz), 7.19 (t, 2H, J_{H-H} = $J_{H-H'}$ = 7.8 Hz), 6.99 (m, 2H) [C_6H_5 and C−C_6H_5]; 2.60 (m, 6H, PC*H*), 1.37 and 1.09 (both dvt, 18H, J_{H-H} = 6.9 Hz, N= 13.8 Hz, PCCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ −0.78 (s). ^2H NMR (C_6H_6): δ 2.86 (br, −CD_2).

Isomerization of Os(C_2Ph)(CH_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (2) in the Presence of CF_3COOH: Preparation of Os{C(CH_2Ph)=CHC_6H_4}(CO)$_2$(P^{i}Pr$_3$)$_2$ (3). To a stirred suspension of Os(C_2Ph)(CH_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (**2**) (200 mg, 0.26 mmol) in 5 mL of methanol was added CF_3COOH (5 μL, 0.06 mmol). The mixture was stirred for 16 h at reflux temperature. A white solid was formed. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 100 mg (50%). Anal. Calcd for $C_{35}H_{54}O_2OsP_2$: C, 55.38; H, 7.17. Found: C, 54.81; H, 7.11.

IR (Nujol, cm^{-1}): ν(CO) 1970, 1905(s). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.82 (d, 1H, J_{H-H} = 6.9 Hz, C_6H_4), 7.34−7.09 (m, 5H, Ph), 6.75−6.5 (m, 3H, C_6H_4), 6.33 (t, 1H, J_{H-H} = 2.1 Hz, =C*H*), 4.15 (br, 2H, CH_2Ph), 2.53 (m, 6H, PC*H*); 1.25 and 1.05 (both dvt, 18H, J_{H-H} = 7.5 Hz, N = 13.5 Hz, PCCH_3). $^{31}P\{^1H\}$NMR (121.4 MHz, CD_2Cl_2): δ −2.89 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, CD_2Cl_2): δ 189.76 (t, J_{C-P} = 8.1 Hz, *C*O), 188.41 (t, J_{C-P} = 8.7 Hz, *C*O), 166.44 (t, J_{C-P} = 10.4 Hz, Os*C*), 164.35 (s, =*C*), 153.49 (t, J_{C-P} =11.1 Hz, Os*C*=); 145.34, 143.99, 143.80, 129.98, 128.40, 125.54, 123.07, 121.90, 120.84 (all s, C_6H_4 and *Ph*), 52.45 (s, *C*H_2), 26.59 (vt, N = 23.6 Hz, P*C*H), 20.19 (s, PC*C*H_3), 19.28 (s, PC*C*H_3).

Isomerization of Os(C_2Ph)(CH_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (2) in the Presence of CF_3COOD: Preparation of Os{C(CH_2Ph)=CDC_6H_4}(CO)$_2$(P^{i}Pr$_3$)$_2$ (3-d_1). To a stirred suspension of Os(C_2Ph)(CH_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (**2**) (150 mg, 0.198 mmol) in 5 mL of methanol-d_4 was added CF_3COOD (8 μL, 0.1 mmol). The mixture was stirred for 24 h at reflux temperature. A white solid was formed. The solution was decanted, and the white solid was washed with methanol-d_4 and dried in vacuo. Yield: 75 mg (50%). The solid was indentified by ^1H NMR spectroscopy as a mixture of **3-d_1** and **3** in a 2.5:1 molar ratio. Spectroscopy data for **3-d_1**: ^1H NMR (300 MHz, CD_2Cl_2) δ 7.82 (d, 1H, J_{H-H} = 6.9 Hz, C_6H_4), 7.34−7.09 (m, 5H, Ph), 6.75−6.5 (m, 3H, C_6H_4), 4.15 (br, 2H, CH_2Ph), 2.53 (m, 6H, PC*H*), 1.25 and 1.05 (both dvt, 18H, J_{H-H} = 7.5 Hz, N = 13.5 Hz, PCCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ −2.89 (s). ^2H NMR (CH_2Cl_2): δ 6.39 (br, =C*D*).

Reaction of Os(C_2Ph)(CH_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (2) with HBF_4: Preparation of [Os{η^3-CH(Ph)CHCHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF_4 (4). A solution of Os(C_2Ph)(CH_2Ph)(CO)$_2$ (P^{i}Pr$_3$)$_2$ (**2**) (237 mg, 0.31 mmol) in 6 mL of dicloromethane was treated with HBF_4 (43 μL, 0.31 mmol). Immediately a yellow solution was observed. The mixture was stirred for 20 min. The solution was concentrated to ca. 0.5 mL, and after the addition of diethyl ether, a white solid and a yellow solution were obtained. The solution was decanted, and the white solid was washed with diethyl ether and dried in vacuo. The white solid was characterized as [Os(η^3-CH(Ph)CHCHPh)(CO)$_2$(P^{i}Pr$_3$)$_2$]-BF_4 (**4**). Yield: 145 mg (55%). The yellow solution was concentrated to dryness, and the residue was treated with 4 mL of methanol to yield a white solid which was washed with methanol and dried in vacuo. The product was characterized as **3** by ^1H and $^{31}P\{^1H\}$ NMR. Yield: 71 mg (30%).

Data for **4**: Anal. Calcd for $C_{35}H_{55}BF_4O_2OsP_2$: C, 49.64; H, 6.55. Found: C, 50.18; H, 6.65. IR (Nujol, cm^{-1}): ν(CO) 2020, 1964(s). ^1H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, 4H, J_{H-H} = 6.9 Hz, *o*-C_6H_5), 7.39 (t, 4H, J_{H-H} = 7.2 Hz, *m*-C_6H_5), 7.32 (d, 2H, J_{H-H} = 7.2 Hz, *p*-C_6H_5), 6.14 (td, 1H, J_{H-H} = 11.1 Hz, J_{H-P} = 7.5 Hz, allyl-C*H meso*), 5.11 (ddd, 2H, J_{H-H} = J_{H-P} = 11.1 Hz, J_{H-P} = 2.1 Hz, allyl-C*H*Ph), 2.84 (m, 3H, PC*H*), 2.13 (m, 3H, PC*H*), 1.55 (dd, 18 H, J_{H-H} = 6.9 Hz, J_{H-P} = 13.5 Hz, PCCH_3), 0.81 (dd, 18H, J_{H-H} = 7.2 Hz, J_{H-P} = 14.4 Hz, PCCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): AB system δ_A= 5.94, δ_B= 4.54, J_{AB}= 185.3 Hz. $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 183.33 (t, J_{C-P} = 9.8 Hz, *C*O), 137.27 (s, *Cipso*−Ph), 130.29 (s, *CHortho*-Ph), 129.18 (s, *CHmeta*−Ph), 128.36 (s, *CHpara*−Ph), 96.72 (s, allyl−*CH meso*), 56.13 (s, allyl−*C*HPh), 26.97 (d, J_{C-P} = 24.1 Hz, P*C*H), 26.63 (d, J_{C-P} = 20.7 Hz, P*C*H), 19.96 (s, PC*C*H_3), 19.00 (s, PC*C*H_3).

Reaction of Os(C_2Ph)(CD_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (2-d_2) with HBF_4: Preparation of [Os{η^3-CD(Ph)CDCHPh}(CO)$_2$(P^{i}Pr$_3$)$_2$]BF_4 (4-d_2) and Os{C(CD_2Ph)=CHC_6H_4} (CO)$_2$(P^{i}Pr$_3$)$_2$ (3-d_2). A solution of Os(C_2Ph)(CD_2Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (**2-d_2**) (190 mg, 0.25 mmol) in 6 mL of dicloromethane was treated with HBF_4 (34 μL, 0.25 mmol). Inmediately a yellow solution was observed. The mixture was stirred for 40 min. The solution was concentrated to ca. 0.5 mL, and after the addition of diethyl ether, a white solid and a yellow solution were obtained. The solution was decanted, and the white solid was washed with diethyl ether and dried in vacuo. The white solid was characterized as [Os{η^3-CD(Ph)CDCHPh}(CO)$_2$-(P^{i}Pr$_3$)$_2$]BF_4 (**4-d_2**). Yield: 116mg (55%). The yellow solution was concentrated to dryness, and the residue was treated with 4 mL of methanol to yield a white solid which was washed with methanol, and dried in vacuo. The solid was characterized as Os{C(CD_2Ph)=CHC_6H_4}(CO)$_2$(P^{i}Pr$_3$)$_2$ (**3-d_2**). Yield: 71 mg (30%).

Spectroscopy data for **4-d_2**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, 4H, J_{H-H} = 6.9 Hz, *o*-C_6H_5), 7.39 (t, 4H, J_{H-H} = 7.2 Hz, *m*-C_6H_5), 7.32 (d, 2H, J_{H-H} = 7.2 Hz, *p*-C_6H_5), 5.11 (dd, 1H, J_{H-P} = 11.1 Hz, J_{H-P} = 2.1 Hz, allyl−C*H*Ph), 2.85 (m, 3H, PC*H*), 2.14 (m, 3H, PC*H*), 1.55 (dd, 18H, J_{H-H} = 6.9 Hz, J_{H-P} = 13.5 Hz, PCCH_3), 0.81 (dd, 18H, J_{H-H} = 7.2 Hz, J_{H-P} = 14.4 Hz, PCCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): AB system δ_A = 5.94, δ_B = 4.54, J_{AB} = 185.3 Hz. ^2H NMR (CH_2Cl_2): δ 6.16 (br, allyl−C*D meso*), 5.17 (br, allyl−C*D*Ph).

Spectroscopy data for **3-d_2**: ^1H NMR (300 MHz, CD_2Cl_2) δ 7.82 (d, 1H, J_{H-H} = 6.9 Hz, C_6H_4), 7.34−7.09 (m, 5H, Ph), 6.75−6.5 (m, 3H, C_6H_4), 6.33 (t, 1H, J_{H-H} = 2.1 Hz, =C*H*), 2.53 (m, 6H, PC*H*), 1.25 and 1.05 (both dvt, 18H, J_{H-H} = 7.5 Hz, N = 13.5 Hz, PCCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ −2.89 (s). ^2H NMR (CH_2Cl_2): δ 4.31 (br, C*D*$_2$Ph).

Crystal Data for Os[C(CH_2Ph)C=CHC_6H_4](CO)$_2$(P^{i}Pr$_3$)$_2$ (3). Crystals suitable for the X-ray diffraction study were obtained from a saturated solution of **3** in acetone at −20 °C. A yellow crystalline prism of approximate dimensions 0.64 × 0.30 × 0.28 mm was glued onto the tip of a glass fiber. A set of randomly searched reflections were indexed to monoclinic

symmetry and accurate unit cell dimensions determined by least-squares refinement of 25 carefully centred reflections ($25 \leq 2\theta \leq 30°$). Data were collected on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation by the ω scan method. Three orientation and intensity standards were monitored every 100 reflections throughout data collection; no significant variation was observed. Data were corrected for absorption using a numerical method (Face-Indexed). The structure was solved by Patterson and conventional Fourier techniques and refined by full-matrix by least-squares on F^2 (SHELXL-93).[25] The two methyl groups of an isopropyl substituent were observed disordered (atoms C44a, C45a, C44b, and C45b). These groups were refined with two moieties with complementary occupancy factors (0.41(2) a-labeled and 0.59(2) b-labeled atoms) and restrained geometry. All non-hydrogen atoms were refined anisotropic, and all hydrogens, except those of the disordered group, were fixed in idealized positions. The largest peak and hole in the final difference map were 1.25 and -0.78 e Å^{-3}.

(25) Sheldrick, G. M. *SHELXTL*, version 5. Siemens Analytical Automation, Inc., Analytical Instrumentation: WI, 1994.

Acknowledgment. We thank the DGICYT (Project No. PB95-0806, *Programa de Promoción General del Conocimiento*) for financial support. E.O. thanks the DGA (Diputación General de Aragón) for a grant.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray study, bond distances and angles, and interatomic distances (15 pages). Ordering information is given on any current masthead page.

OM970301Q