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Reactivity of $OsH_4(CO)(P\mathit{i}Pr_3)_2$ toward Terminal Alkynes: Synthesis and Reactions of the Alkynyl–Dihydrogen Complexes $OsH(C_2R)(\eta^2\text{-}H_2)(CO)(P\mathit{i}Pr_3)_2$ (R = Ph, $SiMe_3$)

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The tetrahydrido $OsH_4(CO)(P\mathit{i}Pr_3)_2$ (**1**) reacts with the stoichiometric amount of phenylacetylene under hydrogen atmosphere to give $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P\mathit{i}Pr_3)_2$ (**2**). After several hours, under hydrogen atmosphere, **2** is converted into $OsH_2(\eta^2\text{-}H_2C{=}CHPh)(CO)(P\mathit{i}Pr_3)_2$ (**4**), which subsequent evolves to **1** and styrene. **4** and acetone are produced from the reaction of **2** with 2-propanol. The dihydrogen ligand of **2** is easily displaced by neutral ligands such as CO, $P(OMe)_3$, and Hpz to give the complexes $OsH(C_2Ph)(CO)L(P\mathit{i}Pr_3)_2$ (**5**–**7**). The reaction of **2** with phenylacetylene affords $Os(C_2Ph)_2(CO)(P\mathit{i}Pr_3)_2$ (**8**), which reacts with hydrogen to give **2** and styrene. The reaction of **8** with pyrazole gives rise to $Os(C_2Ph)_2(CO)(Hpz)(P\mathit{i}Pr_3)_2$ (**9**). The complexes $OsH(C_2SiMe_3)(\eta^2\text{-}H_2)(CO)(P\mathit{i}Pr_3)_2$ (**10**), $OsH(C_2SiMe_3)(CO)L(P\mathit{i}Pr_3)_2$ (L = $P(OMe)_3$ (**11**), Hpz (**12**)), $Os(C_2SiMe_3)_2(CO)(P\mathit{i}Pr_3)_2$ (**13**), and $Os(C_2SiMe_3)_2(CO)L(P\mathit{i}Pr_3)_2$ (L = $P(OMe)_3$ (**14**), Hpz (**15**)) were prepared similarly to the related **2**–**9** starting from **1** and (trimethylsilyl)acetylene. The reaction of **1** with methylpropiolate gives $Os(C_2CO_2Me)(CH{=}C(H)C(OMe){=}O)(CO)(P\mathit{i}Pr_3)_2$ (**16**). The molecular structure of complex **16** has been determined. Crystals of **16** are orthorhombic, space group $Pna2_1$, with unit cell dimensions $a = 14.9009$ (6) Å, $b = 14.6152$ (5) Å, and $c = 14.0339$ (6) Å. The structure was solved and refined to the following R and Rw values: 0.022 and 0.022 on 4589 observed ($F \geq 5.0s(F)$) data. The molecular structure determination has confirmed the σ-alkynyl coordination of a $\sigma\text{-}C{\equiv}CCO_2Me$ ligand, together with the reduction of a second alkyne molecule to give the corresponding vinylic ligand, which is bonded as a chelate group through the terminal vinylic carbon and the ketonic oxygen, generating a five-membered metallacycle ring. Two triisopropylphosphine molecules coordinated in relative trans positions and a carbonyl ligand, trans to the vinylic carbon, complete the osmium coordination sphere.

Introduction

We have recently reported that the five-coordinated hydrido–osmium compound $OsHCl(CO)(P\mathit{i}Pr_3)_2$ reacts with $NaBH_4$ in benzene/methanol to give the octahedral complex $OsH(\eta^2\text{-}H_2BH_2)(CO)(P\mathit{i}Pr_3)_2$.[1] Under reflux in 2-propanol it decomposes to the tetrahydrido $OsH_4(CO)(P\mathit{i}Pr_3)_2$,[2] which affords $OsH_2(CO)(P\mathit{i}Pr_3)_2$[3] that acts as a catalyst for the hydrogen-transfer reactions from 2-propanol to cyclohexanone, acetophenone,[4] benzylideneacetone, benzylideneacetophenone,[5] and phenylacetylene.[6]

A detailed study of the rate of the reaction for the reduction of phenylacetylene by hydrogen transfer from 2-propanol has shown that, initially, the solution which contains $OsH_4(CO)(P\mathit{i}Pr_3)_2$ rapidly reduces the substrate to styrene. However, the reaction rate falls, progressively, as the colorless solution of $OsH_4(CO)(P\mathit{i}Pr_3)_2$ is transformed into a dark red solution of $Os(C_2Ph)_2(CO)(P\mathit{i}Pr_3)_2$.[4,6] Continuing with our work in this field, and as a part of a general study on the catalytic properties of iron,[7] ruthenium,[8] and osmium[9] systems, we have in detail investigated the reaction of $OsH_4(CO)(P\mathit{i}Pr_3)_2$ with phenylacetylene. As a result, we have found that the alkynyl–dihydrogen complex $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P\mathit{i}Pr_3)_2$ is an intermediate in the formation of $Os(C_2Ph)_2(CO)(P\mathit{i}Pr_3)_2$.

Since the first report by Kubas et al. on the coordination of molecular hydrogen to a transition metal,[10] the synthesis, spectroscopic and structural characterization,[11] and some theoretical[12] aspects on the nature and stability of the $M(\eta^2\text{-}H_2)$ bond of such compounds have been intensively studied. However, the catalytic properties of these type of complexes has received relatively little attention.

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Previous applications of $M(\eta^2\text{-}H_2)$ compounds in homogeneous catalysis include hydrogenation of alkynes and alkenes,[7,13] hydrogenation of ketones and arenes,[13f,14] hydrosilylation of alkynes,[9c] hydrogen production from alcoholic substrates,[15] and dimerization of alkynes.[16] In addition, we prove in this paper that compounds of the type $OsH(C_2R)(\eta^2\text{-}H_2)(CO)(P\textit{i}Pr_3)_2$ can play a main role in the reduction of terminal alkynes by hydrogen-transfer reactions from alcohols.

Results and Discussion

Reactions of $OsH_4(CO)(P\textit{i}Pr_3)_2$ with PhC_2H. Treatment of a solution of $OsH_4(CO)(P\textit{i}Pr_3)_2$ (1) with phenylacetylene in a 1:1 molar ratio, in methanol, gives a green-brown solid. The ^1H NMR spectrum of this solid in benzene-d_6 contains, in the hydride region, a broad resonance at −4.18 ppm (T_1 = 13.9 ms), characteristic of a η^2-bonded H_2 ligand, and two triplets at −8.03 and −8.70 ppm with P–H coupling constants of 22.5 and 24.4 Hz, respectively. Furthermore, the spectrum shows a complex phosphine signal about 1.2 ppm and a group of signals between 7.0 and 7.6 ppm, assigned to the phenyl group of the alkyne. Bubbling H_2 through the solution contained in the NMR tube causes the spectrum simplification. The hydride region of the new spectrum contains the broad resonance and the triplet at −8.03 ppm in an intensity ratio of 2:1. The phosphine methyl signals also undergo significant changes; the above mentioned complex signal at 1.2 ppm is converted into a simple doublet of virtual triplets (N = 13.4 Hz, J(HH) = 7.0 Hz). When the hydrogen atmosphere of the NMR tube was evacuated and the tube refilled with argon, the broad signal at −4.18 ppm and the triplet at −8.03 ppm disappeared and the triplet at −8.70 ppm appeared. In addition, the doublet of virtual triplets was transformed into a broad resonance. These reactions can be rationalized in terms of eq 1.

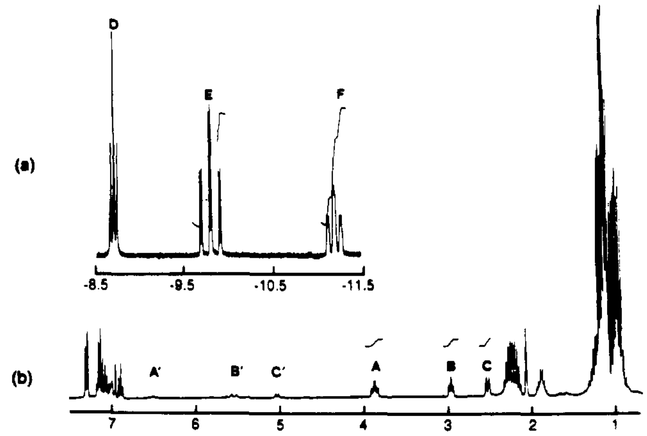
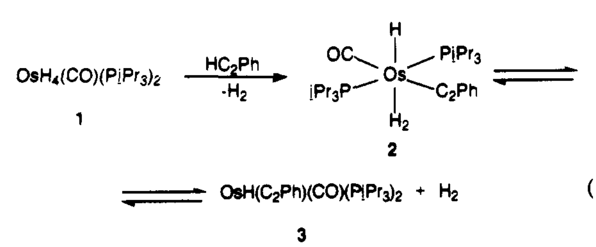


Figure 1. ^1H NMR spectra of $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P\textit{i}Pr_3)_2$ (2) in toluene-d_8 after 16 h under hydrogen atmosphere: (a) upfield from −8.5 to −11.5 ppm; (b) downfield from 1 to 7 ppm.



(1)

The tetrahydride 1 reacts with the stoichiometric amount of phenylacetylene to give molecular hydrogen and the alkynyl–dihydrogen compound 2, spectroscopically characterized by the broad resonance at −4.18 ppm and the triplet at −8.03 ppm. Complex 2 can be obtained as a white solid in quantitative yield when it is isolated under hydrogen atmosphere. Upon removal of the hydrogen atmosphere, 2 is slowly transformed to the 5-coordinate hydride–alkynyl complex 3, characterized by the triplet at −8.70 ppm. This reaction is very fast under vacuo.

After several hours, under hydrogen atmosphere, 2 is converted into $OsH_2(CO)(\eta^2\text{-}H_2C{=}CHPh)(P\textit{i}Pr_3)_2$ (4), which subsequently evolves to 1 and styrene (eq 2).

Figure 1 shows the spectrum recorded after 16 h. The signals A, B, and C were assigned to the styrene ligand coordinated to the osmium atom, while the signals A′, B′, and C′ were assigned to the free olefin. In the hydride region, the triplet at −8.71 ppm (J(HP) = 10.7 Hz), signal D, was assigned to the four hydride ligands of 1 by comparison of this spectrum with a pure sample. The other two doublets of triplets were assigned to the hydride

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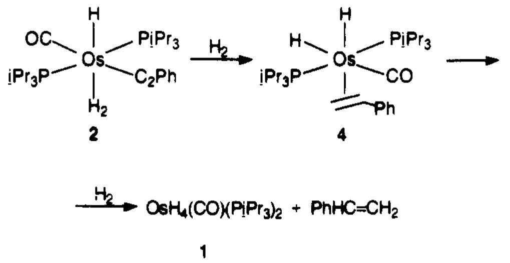


(2)

ligands of 4, E to the hydride trans to the CO group and F to the hydride trans to the olefin. The structure proposed for 4 in eq 2 led to a situation where the two phosphine ligands are not equivalent. In keeping with this proposal, the $^{31}P\{^1H\}$ NMR spectrum of 4 in benzene-d_6 shows a typical AB splitting pattern.

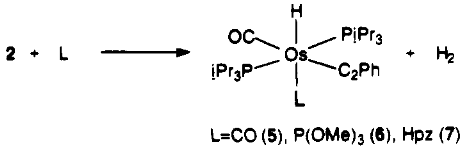
4 can also be formed from 2 under argon atmosphere. The stirring of a solution of 2 in 2-propanol led to 4 and acetone in quantitative yield after 15 h (eq 3).

$$2 + (CH_3)_2CHOH \rightarrow 4 + (CH_3)_2C{=}O \qquad (3)$$

The chemical transformations collected in eqs 1–3 are elegantly accommodated by the cycles shown in Scheme I. A recent kinetic study has suggested that the activation of 1 involves the loss of one hydrogen molecule per molecule of tetrahydride, to yield $OsH_2(CO)(PiPr_3)_2$.[3] Cycle A summarizes the stoichiometric reduction of phenylacetylene with molecular hydrogen in the presence of 1. Cycle B contains the stoichiometric steps that could summarize the process of hydrogen transfer from 2-propanol to phenylacetylene.

The reaction of alkynes with transition-metal hydride complexes usually results in the formation of vinyl derivatives by an insertion reaction of the alkyne into the M–H bond. Scheme I illustrates a new reaction pattern which involves the formal oxidative addition of a terminal alkyne to a dihydride complex of 16 electrons and subsequent intramolecular reduction. Because HC≡CPh is fairly acidic and the $OsH_2(CO)(PiPr_3)_2$ fragment probably rich in electrons, the formation of 2 could involve the protonation of $OsH_2(CO)(PiPr_3)_2$ to give the cationic intermediate $[OsH(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]^+$, recently isolated in our laboratory,[17] which reacts rapidly with $[C{\equiv}CPh]^-$ to give 2. In a few instances, it has been reported that the reaction of terminal alkynes and metal hydrides gives rise to σ-alkynyl complexes. However, in these cases, the initial formation of vinyl complexes, which react with a second molecule of alkyne to give the σ-alkynyl compound and an olefin, has been demonstrated.[18]

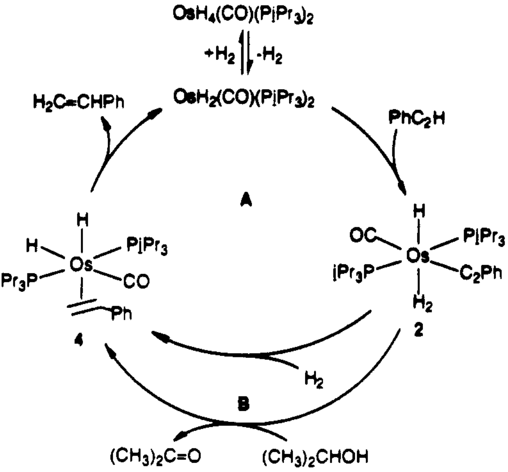
Reactions of 2. The above mentioned spectroscopic data for 2 suggest that $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ is not only isoelectronic with $OsHCl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$[9a] but also isostructural, showing a similar reactivity pattern toward Lewis bases as CO, $P(OMe)_3$, and pyrazole (Hpz). The reactions of 2 with these ligands led to the corresponding hydride–alkynyl complexes and molecular hydrogen (eq 4).



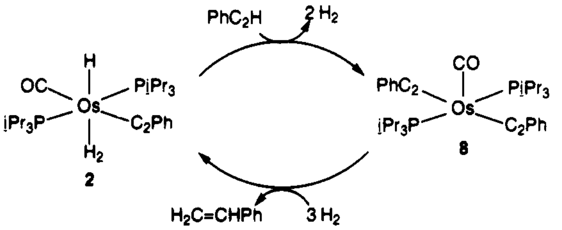
(4)

L=CO (5), P(OMe)$_3$ (6), Hpz (7)

Scheme I



Scheme II



Complex 5, which can be also obtained by starting from 3, has been previously reported.[19]

There is, however, a marked difference in reactivity between $OsHCl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ and 2 toward phenylacetylene. Whereas the hydride–chloride compound reacts with phenylacetylene to give the vinyl complex $Os((E)\text{-}CH{=}CHPh)Cl(CO)(PiPr_3)_2$,[9b] the alkynyl analogue on treatment with equimolecular amount of phenylacetylene gives the bis(alkynyl) derivative $Os(C_2Ph)_2(CO)(PiPr_3)_2$ (8) and molecular hydrogen. This bis(alkynyl) complex reacts with molecular hydrogen under atmospheric pressure in an NMR tube to give, initially, 2 and styrene. Subsequently, 2 evolves to 4 and 1, as it has been previously mentioned.

The reactions of 2 with phenylacetylene and 8 with molecular hydrogen can be accommodated by the cycle shown in Scheme II, which illustrates a stoichiometric hydrogenation of phenylacetylene to styrene where, visibly, vinyl intermediates are not involved.

The coordination number 6 for 8 can be achieved by addition of Hpz (eq 5). As the IR spectrum of 9 shows only one C≡C stretching frequency at 2070 cm^{-1} and the $^{13}C\{^1H\}$ NMR contains only one Os–C≡ absorption at 112 ppm (t, $J(CP) = 12.0$ Hz), we assume that the two alkynyl ligands are symmetrically coordinated, and thus, the structure shown in eq 5 has been assigned.

Reactions of $OsH_4(CO)(PiPr_3)_2$ with Other Terminal Alkynes. It has been previously observed that the reactivity of some transition-metals hydrides toward terminal alkynes depends critically on the electronic and

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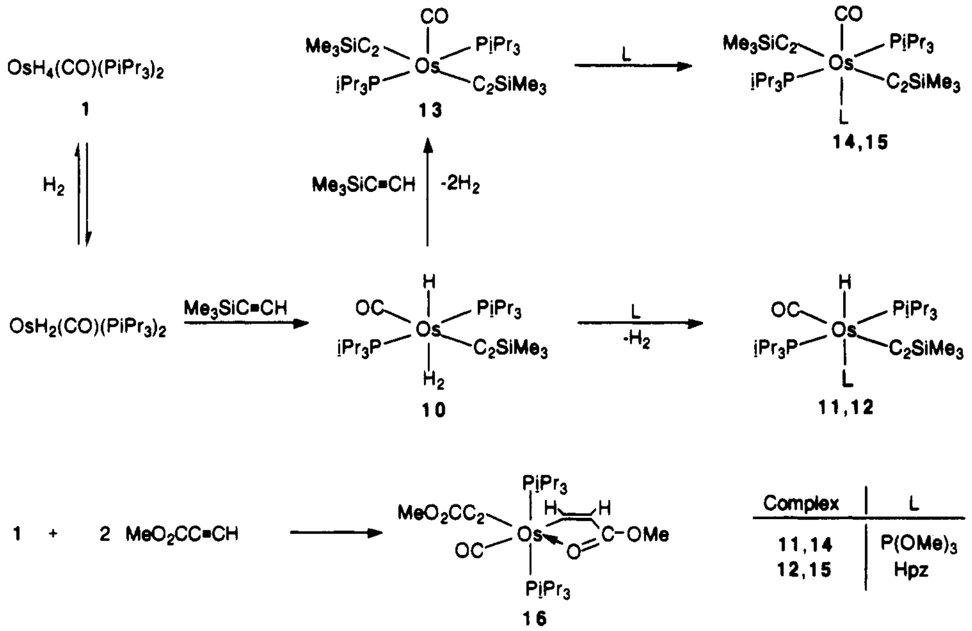
[19] Complex 5 has been previously prepared by reaction of the hydride–methyl compound $OsH(CH_3)(CO)_2(PiPr_3)_2$ with phenylacetylene.[2]

Scheme III

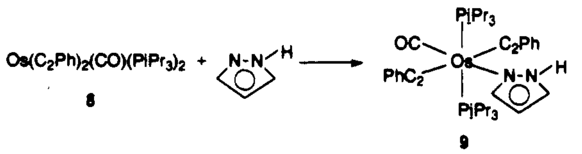


Complex	L
11,14	P(OMe)3
12,15	Hpz

Table I. ¹H NMR[a] Data for 2, 3, 6, 7, and 9–15

	δ(Hpz)[b]				δ(P(OMe)$_3$) [J(HP)]	δ(PCH)	δ(PCCH$_3$) [N, J(HH)]	δ(SiMe$_3$)	δ(OsH) [J(HP)]; δ(OsH$_2$)
	NH	H^3	H^5	H^4					
2[c]						2.5 (m)	1.20 (dvt) [13.4, 7.0]		–8.03 (t) [22.5]; –4.18 (br)[d]
3[c]						2.6 (m)	1.20 (br)		–8.70 (t) [24.4]
6[c]					3.50 (d) [10.4]	2.8 (m)	1.40 (dvt) [13.0, 7.0]		–9.40 (dt) [133.0, 24.0][e]
7[c]	12.92	7.84	7.38	6.25		2.6 (m)	1.30 (dvt), 1.05 (dvt) [13.0, 7.0]		–16.40 (t) [19.5]
9[c]	13.26	8.82	6.31	5.70		2.6 (m)	1.36 (dvt) [11.0, 6.4], 1.30 (dvt) [13.0, 6.8]		
10						2.5 (m)	1.22 (dvt) [13.7, 7.1]	0.19 (s)	–8.10 (t) [19.5]; –4.44 (br)[f]
11					3.57 (d) [10.3]	2.8 (m)	1.40 (dvt) [13.0, 6.3]	0.26 (s)	–9.53 (dt) [121.2, 23.6][e]
12a	14.0	7.25	6.45	5.60		1.9 (m)	1.30 (dvt) [13.0, 6.9]	0.41 (s)	–8.16 (t) [19.0]
12b	13.8	8.90	6.50	5.75		2.4 (m)	1.30–1.20[g]	0.34 (s)	–14.43 (t) [21.0]
12c	13.53	7.73	6.70	5.80		2.7 (m)	1.28 (dvt), 1.02 (dvt) [12.6, 6.9]	0.29 (s)	–16.32 (t) [19.2]
13						3.03 (m)	1.30 (dvt) [13.6, 7.1]	0.29 (s)	
14					3.37 (d) [9.0]	2.86 (m)	1.56 (br)	0.37 (s)	
15	13.87	8.98	6.62	5.80		2.7 (m)	1.30 (dvt) [13.4, 6.2]	0.42 (s)	

[a] δ in ppm. Me$_4$Si internal standard. J and N in Hz. Abbreviations used: s = singlet, d = doublet, t = triplet, m = multiplet, vt = virtual triplet, br = broad, and ms = milisecond. ¹H in C$_6$D$_6$. [b] Singlet for NH protons of *H*pz and broad signals for H^3, H^5, and H^4 of H*pz*. [c] Multiplet for C$_6$H$_5$ protons between 7.0 and 7.6. [d] T_1 = 13.9 ms. [e] [(J(HP$_1$), J(HP$_2$)]; P$_1$ = P(OMe)$_3$, P$_2$ = P*i*Pr$_3$. [f] T_1 = 13 ms. [g] The signal of PCCH$_3$ protons is partially masked by PCCH$_3$ resonance of **12a** and **12c**.



(5)

steric properties of the R substituent.[9b,18a,b,d] In order to obtain information about the generality of the results previously described with phenylacetylene, we have also studied the reactivity of 1 toward Me$_3$SiC≡CH and MeO$_2$CC≡CH. The investigations aimed to elucidate this point are summarized in Scheme III. Whereas 1 reacts with Me$_3$SiC≡CH in the same way as with PhC≡CH, the reaction between 1 and MeO$_2$CC≡CH leads to the alkynyl–vinyl complex 16. The use of a 1:1 molar ratio of MeO$_2$CC≡CH to osmium compound gives the same product along with unreacted tetrahydride.

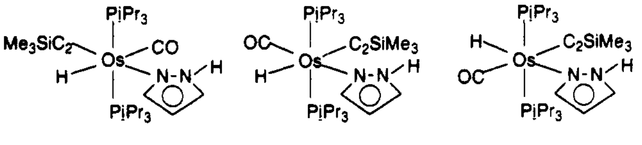
The structures proposed for 10–12 in Scheme III are in good agreement with the spectroscopic data collected in Tables I and II. The ¹H NMR spectrum of 10 in benzene-d_6 contains in the hydride region a broad signal at –4.44 ppm (T_1 = 13 ms) characteristic of the dihydrogen ligand and a triplet at –8.10 ppm (J(HP) = 19.5 Hz). In the same region, the spectrum of 11 shows a doublet of triplets at –9.53 ppm with P–H coupling constants of 121.2 and 23.6 Hz. The hydride ligand of 12 appears as a triplet at –16.32 ppm with a P–H coupling constant of 19.2 Hz. Over the course of 5 days at room temperature, the intensity of this hydride resonance decreases and a new triplet at –8.16 ppm (J(HP) = 19.0 Hz) is observed. The relative amounts of the two hydride products are 1:1. After 28 days, an apparent equilibrium has been reached between the two hydride species at –8.16 ppm (74%) and –16.32 ppm (16%) and a new compound characterized by a triplet at –14.43 ppm (J(HP) = 21 Hz) (10%). The three hydride resonances at –8.16, –14.43, and –16.32 ppm were assigned to the isomers 12a, 12b, and 12c (Figure 2), respectively, by comparison of the spectra with those observed for the analogue chloro complexes.[17]

Compounds 14 and 15 are other members of the M(C$_2$R)$_2$(CO)L(P*i*Pr$_3$)$_2$ (M = Ru, Os) series.[6] As the IR spectra of 13–15 show only one C≡C stretching frequency around 2010 cm^{-1}, we assume that the two alkynyl ligands are symmetrically coordinated, and thus, the structures shown in Scheme III have been assigned. The same structures have been proposed for the analogue complexes containing the phenylacetylide ligand[6] and for compounds

Table II. IR and $^{31}P\{^1H\}$ NMR Data for 2–4, 6, 7, and 9–16

	IR[a]					$\delta(^{31}P\{^1H\})$[b]		
complex	ν(NH) (w)	ν(C≡C) (m)	ν(OsH) (w)	ν(C≡O) (s)	others	P*i*Pr₃	P(OMe)₃	*J*(PP)
2[c]		2090	2060	1912.5	1590[d]	34.9 (s)		
3[c]		2090	2060	1912	1590[d]	27.0 (s)		
4[c]			2075	1955	1590[d]	31.7, 29.3[e]		127
6		2090	2060	1925	1590,[d] 1040[f]	18.3 (d)	100.8 (t)	16
7	3230	2150	2070	1900	1600[d]	34.9 (s)		
9	3230	2070		1910	1600[d]	1.2 (s)		
10[c]		2030	2010	1910		34.3 (s)		
11		2050	2030	1935	1035[f]	18.3 (d)	102.3 (t)	17
12a						24.1 (s)		
12b						21.4 (s)		
12c	3200	2110	2000	1875	1520[d]	20.7 (s)		
13[c]		2000		1880		30.6 (s)		
14		2010		1885	1040[f]	−13.6 (d)	91.6 (t)	20
15	3180	2020		1915	1520[d]	0.9 (s)		
16		2060		1920	1660,[g] 1570[h]	9.0 (s)		

[a] IR: ν in cm^{-1}. Mull in Nujol. Abbreviations used: m = medium, s = strong, w = weak. [b] δ in ppm. ^{31}P: 85% H_3PO_4 external standard. *J* in Hz. Abbreviations used: s = singlet, d = doublet, t = triplet. ^{31}P NMR in C_6D_6. [c] IR in benzene. [d] ν(C═C) (m). [e] AB system. [f] ν(PO) (s). [g] $\nu(C{=}O)_{free}$ (m). [h] $\nu(C{=}O)_{coord}$ (m).



12a **12b** **12c**

Figure 2. Proposed structures for the isomers **12a**, **12b**, and **12c**.

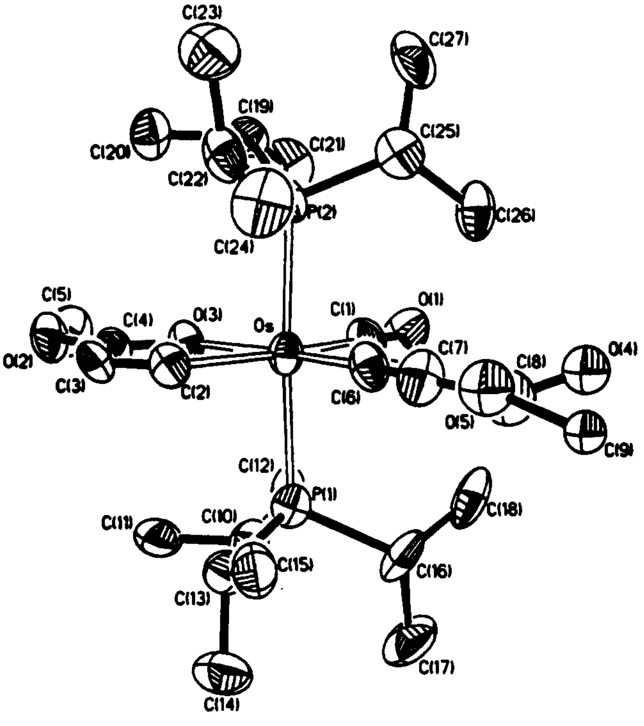


Figure 3. Crystal structure of complex **16**. Hydrogen atoms were omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) for the Complex[a]

$\overline{\text{Os}}(C_2CO_2Me)(CH{=}C(H)C(OMe){=}\overline{\text{O}})(CO)(PiPr_3)_2$

Os–P(1)	2.400 (4)	C(1)–O(1)	1.155 (5)
Os–P(2)	2.403 (4)	C(2)–C(3)	1.351 (6)
Os–O(3)	2.188 (2)	C(3)–C(4)	1.435 (6)
Os–C(1)	1.897 (4)	C(4)–O(3)	1.244 (5)
Os–C(2)	2.103 (4)	C(4)–O(2)	1.344 (5)
Os–C(6)	1.977 (4)	C(5)–O(2)	1.441 (6)
C(6)–C(7)	1.212 (6)		
C(7)–C(8a)	1.422 (9)	C(7)–C(8b)	1.517 (24)
C(8a)–O(4a)	1.229 (11)	C(8b)–O(4b)	1.218 (31)
C(8a)–O(5a)	1.341 (10)	C(8b)–O(5b)	1.304 (31)
C(9a)–O(5a)	1.474 (10)	C(9b)–O(5b)	1.627 (21)
P(1)–C(10)	1.825 (14)	P(2)–C(19)	1.877 (13)
P(1)–C(13)	1.860 (15)	P(2)–C(22)	1.878 (14)
P(1)–C(16)	1.899 (13)	P(2)–C(25)	1.839 (13)
P(1)–Os–P(2)	174.8 (1)	P(2)–Os–C(6)	86.7 (2)
P(1)–Os–O(3)	92.3 (1)	O(3)–Os–C(1)	91.0 (1)
P(1)–Os–C(1)	91.0 (2)	O(3)–Os–C(2)	75.4 (1)
P(1)–Os–C(2)	90.2 (2)	O(3)–Os–C(6)	171.2 (1)
P(1)–Os–C(6)	88.1 (2)	C(1)–Os–C(2)	166.3 (2)
P(2)–Os–O(3)	92.9 (1)	C(1)–Os–C(6)	97.9 (2)
P(2)–Os–C(1)	89.6 (2)	C(2)–Os–C(6)	95.8 (2)
P(2)–Os–C(2)	90.5 (2)		
Os–C(1)–O(1)	171.1 (4)	C(3)–C(4)–O(2)	118.0 (3)
Os–C(2)–C(3)	116.5 (3)	O(2)–C(4)–O(3)	120.6 (3)
C(2)–C(3)–C(4)	113.3 (4)	C(4)–O(2)–C(5)	117.1 (3)
C(3)–C(4)–O(3)	121.5 (4)	Os–O(3)–C(4)	113.3 (2)
Os–C(6)–C(7)	176.9 (4)		
C(6)–C(7)–C(8a)	165.8 (6)	C(6)–C(7)–C(8b)	163.4 (10)
C(7)–C(8a)–O(4a)	127.0 (7)	C(7)–C(8b)–O(4b)	124.3 (20)
C(7)–C(8a)–O(5a)	113.4 (7)	C(7)–C(8b)–O(5b)	106.4 (17)
O(4a)–C(8a)–O(5a)	119.4 (8)	O(4b)–C(8b)–O(5b)	115.7 (22)
C(8a)–O(5a)–C(9a)	117.0 (7)	C(8b)–O(5b)–C(9b)	103.8 (16)

[a] Atoms O(4), O(5), C(8), and C(9) were observed disordered in two positions. The relative occupancy factor assigned was 0.65 for *a*-labeled atoms and 0.35 for the *b*-labeled ones.

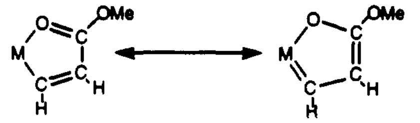
of the type $Fe(C_2R)_2(L_2)_2$ (L_2 = diphosphine) characterized by X-ray diffraction analysis.[18c]

The structure of **16** was deduced from an X-ray diffraction experiment. A view of the molecular geometry of this compound is shown in Figure 3. Selected bond distances and angles are listed in Table III.

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) = 174.8 (1)°). An ideal equatorial plane is formed by the atoms C(2) and O(3) of the chelating vinylic ligand—defining with the osmium atom a five-membered ring (O(3)–Os–C(2) = 75.4 (1)°)—the atom C(6) of the alkynyl group disposed trans to O(3) (O(3)–Os–C(6) = 171.2 (1)°), and the CO ligand located trans to C(2) (C(1)–Os–C(2) = 166.3 (2)°).

The five-membered metalacycle is almost planar (maximum deviation 0.0178 (1) Å). The Os–C(2) distance is 2.103 (4) Å, shorter than the Os–C distances found in the osmium(II) complexes $Os((CH_2)_2SiMe_2)(PMe_3)_4$ (2.24 (1) Å)[20] and $OsH(CH_3)(CO)_2(PiPr_3)_2$ (2.198 (17) Å)[2] but analogous to those observed in the vinyl compounds

Scheme IV



Os((*E*)-CH=CHPh)Cl(CO)(P*i*Pr$_3$)$_2$ (1.99 (1) Å)[21] and [Os(CH=C(I)C(OMe)=O)(η^6-C$_6$H$_6$)(P*i*Pr$_3$)]$^+$ (2.02 (1) Å).[22] The distances C(2)–C(3) (1.351 (6) Å), C(3)–C(4) (1.435 (6) Å), C(4)–O(3) (1.244 (5) Å), and O(3)–Os (2.188 (2) Å) are quite comparable to those found for the same structural disposition of the vinyl ligand in the cation [Os(CH=C(I)C(OMe)=O)(η^6-C$_6$H$_6$)(P*i*Pr$_3$)]$^+$, where for the bonding pattern of the heterocycle the two resonance forms shown in Scheme IV have been suggested.[22]

The Os–C(6) length (1.977 (4) Å) is consistent with a single bond from Os(II) to a C(sp) atom (sum of covalent radii 1.95 Å) and indicates a low degree of metal-to-ligand back-bonding.[23] The C(6)–C(7) distance and the mean C(6)–C(7)–C(8) angle are 1.212 (6) Å and 164.6 (6)°, respectively. A slight bending in the Os–C(6)–C(7) moiety is present (Os–C(6)–C(7) = 176.9 (4)°); similar values have been found for related complexes containing terminal alkynyl groups.[18c,d,24] The Os–P and Os–CO distances are clearly in the range expected and deserve no further comments.

Concluding Remarks. This study has shown that the tetrahydride OsH$_4$(CO)(P*i*Pr$_3$)$_2$ (1) reacts with PhC$_2$H to give the σ-alkynyl–dihydrogen complex OsH(C$_2$Ph)(η^2-H$_2$)(CO)(P*i*Pr$_3$)$_2$ (2), which evolves under hydrogen atmosphere to OsH$_2$(η^2-H$_2$C=CHPh)(CO)(P*i*Pr$_3$)$_2$ (4) and subsequently to 1 and styrene. In the presence of 2-propanol under argon atmosphere, 2 gives rise to a hydrogen-transfer reaction, where 2 is converted into 4 and 2-propanol is dehydrogenated to acetone.

1 reacts with Me$_3$SiC$_2$H in the same way as with PhC$_2$H, while the reaction between 1 and MeO$_2$CC$_2$H leads to the alkynyl-vinyl derivative Os(C$_2$CO$_2$Me)(CH=C(H)-C(OMe)=O)(CO)(P*i*Pr$_3$)$_2$ (16).

In general, the reaction of alkynes with transition-metal hydrides complexes leads to vinyl derivatives by an insertion reaction of the alkyne into the M–H bond. However, it is also true, in light of these results, that the reactions of some transition metal hydrides with alkynes give rise to alkynyl–dihydrogen compounds. Similarly to the vinyl derivatives, the alkynyl–dihydrogen complexes can play a main role in the reduction of terminal alkynes by hydrogen-transfer reactions and by hydrogenation with molecular hydrogen.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air by using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. Phenylacetylene (Merck) was purified by distillation.

The starting material OsH$_4$(CO)(P*i*Pr$_3$)$_2$ was prepared in situ by decomposition of OsH(η^2-H$_2$BH$_2$)(CO)(P*i*Pr$_3$)$_2$ in methanol.[1]

Physical Measurements. NMR spectra were recorded on a Varian UNYT 300 spectrophotometer. Chemical shifts are expressed in ppm upfield from Me$_4$Si (^{13}C, ^{1}H) and 85% H$_3$PO$_4$ (^{31}P). The T_1 measurements were performed at 20 °C on a 200-MHz Varian XL with a standard 180°–τ–90° pulse sequence. Infrared spectra were recorded with a Perkin-Elmer 783 spectrophotometer. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer.[25]

The amount of acetone produced from the reaction of 2 with 2-propanol was measured with an FFAP on Chromosorb GHP 80/100 mesh column at 40 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector.

Preparation of OsH(C$_2$Ph)(η^2-H$_2$)(CO)(P*i*Pr$_3$)$_2$ (2). A solution of 1 (114 mg, 0.21 mmol) in 6 mL of methanol was treated with phenylacetylene (22.5 μL, 0.22 mmol). After 2 h the solution was concentrated to ca. 2 mL and the argon atmosphere replaced by a hydrogen atmosphere. The white solid formed was filtered off, repeatedly washed with methanol, and dried under a hydrogen stream. Yield: 114.7 mg (85%).

Preparation of OsH(C$_2$Ph)(CO)(P*i*Pr$_3$)$_2$ (3). Method a. A solution of 1 (114 mg, 0.21 mmol) in 5 mL of methanol was treated with phenylacetylene (22.5 μL, 0.2 mmol). After 2 h the solution was concentrated to ca. 2 mL. The solid formed was filtered off, repeatedly washed with methanol, and dried under vacuo. A green-brown solid formed. Yield: 94 mg (70%).

Method b. In an NMR tube and at room temperature 25 mg of 2 (0.04 mmol) was dissolved in 0.8 mL of benzene-*d*$_6$. The mixture was degassed and refilled with argon two times. Then the ^{1}H NMR and ^{31}P NMR spectra were recorded. The signals observed were assigned to complex 3, by comparison of these spectra with those measured for the solid obtained by method a.

Preparation of OsH$_2$(η^2-H$_2$C=CHPh)(CO)(P*i*Pr$_3$)$_2$ (4). A solution of 2 (90 mg, 0.14 mmol) in 2 mL of 2-propanol was stirred at room temperature under argon atmosphere. After 15 h, 0.2 μL of the solution was injected in the gas chromatograph. The analysis shows the presence of acetone in a concentration of 0.055 M. Then, the solution was concentrated to dryness and the residue was treated with 0.6 mL of benzene-*d*$_6$ and characterized by IR, ^{1}H NMR, and ^{31}P{^{1}H} NMR spectroscopy as OsH$_2$(η^2-H$_2$C= CHPh)(CO)(P*i*Pr$_3$)$_2$. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.4–7.0 (m; C$_6$H$_5$), 3.8 (m; =CHPh), 3.0 (vt, *J*(HH) = 18.8; H$_2$C=), 2.5 (d, *J*(HH) = 9.6; H$_2$C=), 2.4 (m; PCH), 1.2 (dvt, *N* = 11.0, *J*(HH) = 7.4; PCCH$_3$), 1.1 (dvt, *N* = 18, *J*(HH) = 8.5; PCCH$_3$), –9.5 (td, *J*(HP) = 32, *J*(HH) = 5.4; OsH, H trans to CO), –11.05 (td, *J*(HP) = 20.2, *J*(HH) = 5.4; OsH, H trans to olefin).

Preparation of OsH(C$_2$Ph)(CO)$_2$(P*i*Pr$_3$)$_2$ (5). Carbon monoxide was bubbled through a suspension of 2 (100 mg, 0.16 mmol) in 4 mL of methanol. After 15 min the suspension was concentrated to ca. 1 mL. The white solid formed was filtered off, repeatedly washed with methanol, and dried in vacuo. Yield: 90 mg (84%). Anal. Calcd for OsC$_{28}$H$_{48}$O$_2$P$_2$: C, 50.25; H, 7.23. Found: C, 49.80; H, 7.61. IR (Nujol): ν(C≡C) 2095 (m), ν(OsH) 2000 (w), ν(C≡O) 1955, 1895 (s) cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.14 (m; C$_6$H$_5$), 2.48 (m; PCH), 1.23 (dvt, *N* = 13.4, *J*(HH) = 6.6; PCCH$_3$), –7.64 (t, *J*(HP) = 20.9; OsH). ^{31}P{^{1}H}NMR (80.9 MHz, C$_6$D$_6$): δ 25.41 (s).

Preparation of OsH(C$_2$Ph)(CO)(P*i*Pr$_3$)$_2$(P(OMe)$_3$) (6). A suspension of 2 (100 mg, 0.16 mmol) in 4 mL of methanol was treated with trimethyl phosphite (19.8 μL, 0.16 mmol). After the mixture was stirred for 15 min at room temperature, the suspension was concentrated to ca. 2 mL. The pale orange solid formed was filtered off, repeatedly washed with methanol, and dried in vacuo. Yield: 98 mg (80%). Anal. Calcd for OsC$_{30}$H$_{57}$O$_4$P$_3$: C, 47.11; H, 7.51. Found: C, 47.49; H, 8.06.

Preparation of OsH(C$_2$Ph)(CO)(Hpz)(P*i*Pr$_3$)$_2$ (7). This compound was prepared analogously as described for 6 starting from 2 (100 mg, 0.16 mmol) and pyrazole (10.9 mg, 0.16 mmol).

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(25) Elemental analyses of complexes 2, 3, 4, 10, and 13 were precluded because the samples were extremely air-sensitive.

A white solid formed. Yield: 94 mg (83%). Anal. Calcd for $OsC_{30}H_{52}N_2OP_2$: C, 50.84; H, 7.39, N, 3.95. Found: C, 51.16; H, 7.92; N, 3.78.

Preparation of $Os(C_2Ph)_2(CO)(PiPr_3)_2$ (8). A solution of 2 (100 mg, 0.16 mmol) in 6 mL of methanol was treated with phenylacetylene (17.4 μL, 0.17 mmol). After being stirred for 10 min at room temperature, the solution was concentrated to ca. 2 mL. The dark red solid formed was filtered off, repeatedly washed with methanol, and dried in vacuo. Yield: 95 mg (85%). Anal. Calcd for $OsC_{35}H_{52}OP_2$: C, 56.74; H, 7.07. Found: C, 57.06; H, 7.51. IR (Nujol): $\nu(C{\equiv}C)$ 2060 (m), $\nu(C{\equiv}O)$ 1905 (s). ^1H NMR (300 MHz, C_6D_6): δ 7.4–7.1 (m; C_6H_5), 3.25 (m; PCH), 1.42 (dvt, N = 14.0, J(HH) = 6.0; $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 37.13 (s).

Preparation of $Os(C_2Ph)_2(CO)(Hpz)(PiPr_3)_2$ (9). A suspension of 8 (100 mg, 0.14 mmol) in 4 mL of hexane was treated with pyrazole (10.2 mg, 0.15 mmol). After being stirred for 30 min, the solution was concentrated to ca. 2 mL. The white solid formed was filtered off, repeatedly washed with hexane, and dried in vacuo. Yield: 90 mg (84%). Anal. Calcd for $OsC_{38}H_{56}N_2OP_2$: C, 56.42; H, 6.97, N, 3.46. Found: C, 56.41; H, 7.33; N, 3.29. $^{13}C\{^1H\}$ NMR (75.33 MHz, C_6D_6): δ 187.9 (t, J(CP) = 10.1; OsCO), 144, 132 (s; C^3, C^5 of Hpz), 130 (s; $\equiv CC_6H_5$), 126, 124, 116, 115 (s; C_6H_5), 112 (t, J(CP) = 12.0; $OsC\equiv$), 107.5 (s; C^4 of Hpz), 26 (vt, N = 20; PCH), 19.54 (s; $PCCH_3$).

Preparation of $OsH(C_2SiMe_3)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (10). A solution of 1 (135 mg, 0.25 mmol) in 6 mL of methanol was treated with (trimethylsilyl)acetylene (36.5 μL, 0.26 mmol). After being stirred for 30 min at room temperature, the solution was concentrated to ca. 2 mL of cooled to −20 °C for 12 h. A white solid was formed, which was filtered off, washed with cold methanol, and dried by a hydrogen stream. Yield: 130 mg (82%).

Preparation of $OsH(C_2SiMe_3)(CO)(PiPr_3)_2(P(OMe)_3)$ (11). This compound was prepared analogously as described for 6 starting from 10 (102 mg, 0.16 mmol) and trimethyl phosphite (20 μL, 0.16 mmol). It is a white solid. Yield: 96 mg (79%). Anal. Calcd for $OsC_{27}H_{61}O_4P_3Si$: C, 42.61; H, 8.08. Found: C, 42.61; H, 8.59.

Preparation of $OsH(C_2SiMe_3)(CO)(Hpz)(PiPr_3)_2$ (12c). This compound was prepared analogously as described for 6 starting from 10 (100 mg, 0.16 mmol) and pyrazole (10.9 mg, 0.16 mmol). It is a white solid. Yield: 93 mg (83%). Anal. Calcd for $OsC_{27}H_{56}N_2OP_2Si$: C, 46.00; H, 8.0; N, 3.97. Found: C, 45.56; H, 8.57; N, 3.58.

Formation of the Isomers 12a and 12b. In an NMR tube and at room temperature 28 mg (0.04 mmol) of **12c** was dissolved in 0.5 mL of benzene-d_6. The formation of the isomeric mixture of **12a**, **12b**, and **12c** was followed by ^1H NMR and ^{31}P NMR as a function of time.

Preparation of $Os(C_2SiMe_3)_2(CO)(PiPr_3)_2$ (13). This compound was prepared analogously as described for 8 starting from 10 (100 mg, 0.16 mmol) and (trimethylsilyl)acetylene (22.4 μL, 0.16 mmol). It is a dark red solid. Yield: 94 mg (80%).

Preparation of $Os(C_2SiMe_3)_2(CO)(PiPr_3)_2(P(OMe)_3)$ (14). A solution of 13 (100 mg, 0.14 mmol) in 6 mL of methanol was treated with trimethyl phosphite (17.4 μL, 0.14 mmol). After being stirred for 30 min at room temperature, the solution was concentrated to ca. 2 mL and cooled to −20 °C for 12 h. A yellow solid precipitated, which was filtered off, washed with cold methanol, and dried in vacuo. 14 is a reddish solid. Yield: 100 mg (82%). Anal. Calcd for $OsC_{34}H_{69}O_4P_3Si_2$: C, 46.34; H, 7.89. Found: C, 45.95; H, 8.9.

Preparation of $Os(C_2SiMe_3)_2(CO)(Hpz)(PiPr_3)_2$ (15). This compound was prepared analogously as described for 14 starting from 13 (100 mg, 0.14 mmol) and pyrazole (9.5 mg, 0.14 mmol). It is a pale orange solid. Yield: 83 mg (74%). Anal. Calcd for $OsC_{32}H_{65}N_2OP_2Si_2$: C, 47.92; H, 8.16; N, 3.35. Found: C, 47.47; H, 8.58; N, 3.35.

Preparation of $Os(C_2CO_2Me)(CH{=}C(H)C(OMe){=}O)(CO)(PiPr_3)_2$ (16). Method a. A solution of 1 (150 mg, 0.28 mmol) in 10 mL of methanol was treated with methyl propiolate (26.8 μL, 0.30 mmol). After 70 min the solution was concentrated to ca. 2 mL. A yellow solid was formed, which was filtered off, repeatedly washed with methanol, and dried in vacuo. Yield: 77 mg (39%).

Table IV. Atomic Coordinates (×10⁴; ×10⁵ for the Os Atom) and Equivalent Isotropic Displacement Coefficients (Å² × 10³; Å² × 10⁴ for the Os Atom) for the Compound $Os(C_2CO_2Me)(CH{=}C(H)C(OMe){=}O)(CO)(PiPr_3)_2$

atom	x/a	y/b	z/c	$U_{eq}{}^a/U_{iso}$
Os	21485 (1)	12269 (1)	0	374 (1)
P(1)	2184 (2)	1160 (2)	1708 (3)	38 (1)
P(2)	2187 (2)	1163 (2)	−1710 (3)	39 (1)
O(1)	226 (2)	526 (2)	24 (9)	64 (1)
O(2)	1966 (2)	4109 (2)	−25 (9)	50 (1)
O(3)	1603 (2)	2616 (2)	10 (8)	38 (1)
O(4a)	4752 (5)	−1153 (5)	294 (5)	75 (2)[b]
O(4b)	3124 (10)	−2276 (9)	−149 (19)	92 (5)[b]
O(5a)	3689 (4)	−2150 (4)	−94 (9)	57 (2)[b]
O(5b)	4415 (11)	−1639 (11)	−137 (20)	104 (6)[b]
C(1)	974 (3)	725 (3)	−18 (12)	45 (2)
C(2)	3284 (3)	2081 (3)	6 (12)	40 (1)
C(3)	3129 (3)	2991 (3)	33 (12)	42 (1)
C(4)	2192 (3)	3219 (3)	12 (13)	39 (1)
C(5)	1026 (3)	4328 (3)	38 (14)	63 (2)
C(6)	2824 (3)	62 (3)	−17 (14)	42 (1)
C(7)	3270 (3)	−631 (3)	−2 (13)	53 (2)
C(8a)	3959 (6)	−1296 (5)	105 (11)	44 (2)[b]
C(8b)	3569 (15)	−1618 (16)	100 (37)	84 (7)[b]
C(9a)	4322 (5)	−2896 (5)	124 (11)	53 (2)[b]
C(9b)	4736 (8)	−2660 (8)	176 (11)	32 (3)[b]
C(10)	1442 (9)	1946 (9)	2342 (10)	49 (4)
C(11)	1739 (11)	2928 (10)	2305 (9)	61 (4)
C(12)	451 (10)	1861 (10)	1966 (10)	57 (5)
C(13)	3298 (10)	1457 (10)	2218 (9)	47 (4)
C(14)	3342 (13)	1493 (12)	3320 (9)	70 (6)
C(15)	4040 (9)	847 (8)	1967 (10)	59 (4)
C(16)	1939 (9)	−11 (8)	2235 (10)	55 (5)
C(17)	1603 (11)	12 (10)	3294 (9)	78 (6)
C(18)	1312 (9)	−587 (9)	1672 (9)	65 (4)
C(19)	1382 (8)	1947 (9)	−2337 (9)	42 (4)
C(20)	1691 (10)	2978 (9)	−2370 (10)	52 (4)
C(21)	445 (9)	1854 (10)	−1952 (10)	63 (5)
C(22)	3301 (9)	1445 (9)	−2263 (10)	52 (4)
C(23)	3326 (13)	1589 (13)	−3327 (11)	76 (6)
C(24)	4042 (7)	745 (10)	−1835 (10)	67 (4)
C(25)	1931 (9)	34 (9)	−2219 (9)	52 (4)
C(26)	1373 (8)	−635 (9)	−1566 (9)	56 (4)
C(27)	1557 (10)	13 (8)	−3212 (9)	67 (5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic thermal parameters have been used for disordered atoms.

Method b. This compound was prepared analogously as described in method a starting from 1 (150 mg, 0.28 mmol) and methyl propiolate (54 μL, 0.60 mmol). It is a yellow solid. Yield: 178 mg (90%). Anal. Calcd for $OsC_{27}H_{50}O_5P_2$: C, 45.87; H, 7.13. Found: C, 46.05; H, 7.76. ^1H NMR (300 MHz, C_6D_6): δ 11.2 (d, J(HH) = 10.1; $OsCH{=}$), 6.8 (dt, J(HH) = 10.1, J(HP) = 2.1; $=CH-$), 3.6, 3.44 (both s; CO_2CH_3), 2.45 (m; PCH), 1.4 (dvt, N = 13.9, J(HH) = 7.1; $PCCH_3$), 1.1 (dvt, N = 12.8, J(HH) = 6.7; $PCCH_3$). $^{13}C\{^1H\}$ NMR (75.33 MHz, C_6D_6): δ 225.35 (t, J(CP) = 10.1; $OsCH{=}$), 194.3 (t, J(CP) = 9.2; OsCO), 185.32 (s; $=CHC({=}O)$), 154 (s; $\equiv CC({=}O)$), 121.7 (s; $=CH-$), 106.6 (t, J(CP) = 12.4; $OsC\equiv$), 104.7 (s; $\equiv CC({=}O)$), 52.5, 50.7 (both s; OCH_3), 25.33 (vt, N = 25.31; PCH), 20.57, 19.54 (both s; $PCCH_3$).

Reaction of $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (2) and $Os(C_2Ph)_2(CO)(PiPr_3)_2$ (8) with H_2. In an NMR tube and at room temperature 0.04 mmol (25 mg (2), 30 mg (8)) was dissolved in 0.8 mL of toluene-d_8, and H_2 was bubbled for 2 min. NMR tubes were capped under hydrogen at atmospheric pressure. The ^1H NMR was measured as a function of time. All the signals of the spectra were assigned by comparison with pure samples.

X-ray Structure Analysis of 16. Collection and Reduction of Data. Crystals suitable for an X-ray diffraction experiment were obtained by slow evaporation of methanol from a concentrated solution of 16 in this solvent. Atomic coordinates and U_{eq} values are listed in Table IV. A summary of crystal data, intensity

Table V. Crystal Data and Data Collection and Refinement for $\overline{\mathrm{Os}(C_2CO_2Me)(CH{=}C(H)C(OMe){=}O})(CO)(P\mathit{i}Pr_3)_2$ (16)

	Crystal Data
formula	$C_{27}H_{50}O_5OsP_2$
mol wt	706.84
color and habit	yellow, orthorhombic prism
cryst size, mm	0.494 × 0.274 × 0.182
cryst syst	orthorhombic
space group	$Pna2_1$ (No. 33)
a, Å	14.9009 (6)
b, Å	14.6152 (5)
c, Å	14.0339 (6)
V, Å^3	3056.3 (2)
Z	4
D(calcd), g cm^{-3}	1.536
	Data Collection and Refinement
diffractometer	4-circle Siemens AED
λ((Mo Kα) radiation), Å; technique	0.710 69, bisecting geometry
monochromator	graphite oriented
μ, cm^{-1}	43.11
scan type	ω–2θ
2θ range, deg	3–50
no. of data collcd	6090
no. of unique data	5371
unique observed data	4589; $F_o \geq 5\sigma(F_o)$
no. of params refined	313
R, R_w[a]	0.022, 0.022
max/min transm fact	0.458, 0.376

[a] $w^{-1} = \sigma^2(F)$.

collection procedure, and refinement data is reported in Table V. The primatic crystal studied was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 50 reflections in the range $20 \leq 2\theta \leq 35°$. The 6090 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitorized every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by a numerical method based on indexed morphological faces.

Structure Solution and Refinement. The structure was solved by Patterson (Os atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. The more external part of the alkynyl ligand, that is C(8), O(4), O(5), and C(9), was observed disordered in two positions related approximately by rotation around the C(7)–C(8) bond. The complementary occupancy factors were assigned on the basis of thermal parameters, 0.65 for the *a*-labeled atoms, and 0.35 for the *b*-labeled ones. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms excepting those involved in disorder. Hydrogen atoms were partially located from difference Fourier maps and included in the refinement (some of them in calculated positions; C–H = 0.97 Å) riding on carbon atoms with a common isotropic thermal parameter. Hydrogen atoms bonded to disordered atoms were not included in the refinement. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were taken from ref 26. The function minimized was $\sum w([F_o] - [F_c])^2$ with the weight defined as $w = 1/[\sigma^2(F_o)]$. Final R and R_w values were 0.022. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[27]

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (19 pages). Ordering information is given on any current masthead page.

OM920457K

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