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Insertion Reactions of the 16-Electron Complexes $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) with Alkynes. The X-ray Crystal Structure of $Os((E)\text{-}CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$

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The carbonyl hydrido complexes $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) react with alkynes $HC{\equiv}CR$ (R = Ph, H) by insertion to give the five-coordinate vinylmetal compounds $M(CH{=}CHR)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**3**–**6**) in nearly quantitative yields. Addition of CO or displacement of the chloride ligand in **3**–**6** by acetate or acetylacetonate produces the six-coordinate complexes $M(CH{=}CHR)Cl(CO)_2(P\text{-}i\text{-}Pr_3)_2$ (R = Ph; **7**, **8**), $M(CH{=}CHR)(\eta^2\text{-}O_2CMe)(CO)(P\text{-}i\text{-}Pr_3)_2$ (R = Ph; **9**, **10**) and $M(CH{=}CHR)(\eta^2\text{-acac})(CO)(P\text{-}i\text{-}Pr_3)_2$ (R = H, Ph; **11**–**14**), respectively. Treatment of $RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ with $HC{\equiv}CPh$ and KOH in methanol leads to a mixture of $Ru(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (**15**) and $Ru(C{\equiv}CPh)(CH{=}CHPh)(CO)(P\text{-}i\text{-}Pr_3)_2$ (**16**), the latter of which reacts with CO to form the octahedral compound $Ru(C{\equiv}CPh)(CH{=}CHPh)(CO)_2(P\text{-}i\text{-}Pr_3)_2$ (**17**). The molecular structure of $Os(CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**4**) has been determined by X-ray investigation. **4** crystallizes in the space group $P2_1/n$ with a = 16.437 (5) Å, b = 10.980 (4) Å, c = 17.086 (4) Å, and β = 105.56 (2)°. The osmium atom has a nearly perfect square-pyramidal coordination with the vinyl ligand in the apical position and the two phosphines trans to each other in the base of the pyramid. With regard to the stereochemistry at the vinyl C=C bond, only the E isomer is formed. A stereo ORTEP diagram illustrates that the metal atom, although coordinatively unsaturated, nevertheless is well shielded at the sixth position of the (uncompleted) octahedron by four of the 12 methyl groups of the phosphine ligands. IR as well as ^1H, ^{13}C, and ^{31}P NMR data of the complexes **3**–**17** are reported.

Introduction

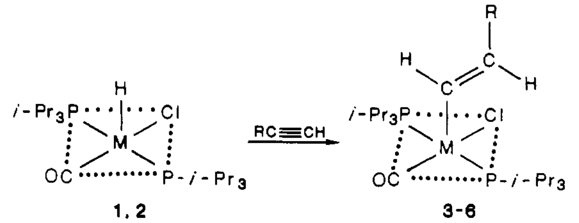
One of the most typical reactions of transition-metal hydrides is the insertion of olefins and alkynes into the metal–hydride bond.[1] This insertion process is in general kinetically highly favored, and, therefore, the primary products of general composition $MH(C{=}C)L_n$ or $MH(C{\equiv}C)L_n$ formed on coordination of the olefin or alkyne to the transition-metal center can rarely be isolated.

During investigations directed toward the synthesis of coordinatively unsaturated ruthenium and osmium compounds which could possibly activate aromatic or aliphatic C–H bonds,[2] we recently observed that the five-coordinate 16-electron osmium(II) complex $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ reacts with olefins such as ethylene, methyl acrylate, acrylonitrile, and methyl vinyl ketone to give the six-coordinate 18-electron compounds $OsHCl(CO)(CH_2{=}CHR)(P\text{-}i\text{-}Pr_3)_2$ (R = H, CO_2Me, CN, COMe) in excellent yields.[3] These compounds do not form the corresponding alkylosmium(II) complexes by intramolecular insertion of the olefin into the Os–H bond which is probably due to the trans position of the hydride and olefin ligands.

In continuing this work we were interested to determine whether alkynes would behave in a similar manner to olefins toward $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ and the ruthenium analogue $RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ or whether in this case an insertion process is more favored. The insertion should lead to vinylosmium(II) and -ruthenium(II) complexes which could be suitable starting materials for the synthesis of hitherto unknown four- or five-coordinate (vinylidene)osmium(0) and -ruthenium(0) derivatives. Evidence for the possibility of preparing compounds of the general type $M({=}C{=}CHR)L_n$ by HX elimination of the corresponding vinyl precursors $MX(CH{=}CHR)L_n$ has recently been provided from our laboratory for $ML_n{=}Rh(P\text{-}i\text{-}Pr_3)C_5H_5$[4] and $Os(P\text{-}i\text{-}Pr_3)C_6H_6$,[5] respectively.

Results

Treatment of a suspension of $RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**1**) or $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**2**) with phenylacetylene in hexane results in an almost instantaneous precipitation of a dark red (Ru) or dark blue (Os) solid which according to the elemental analysis corresponds to a 1:1 adduct of the starting material and the alkyne. A similar reaction occurs by bubbling acetylene through a suspension of **1** or **2** in hexane giving a red precipitate (Ru) or a dark red solution (Os) from which after concentration and addition of methanol red crystals are isolated. In all cases the yield is almost quantitative. Under similar conditions, diphenylacetylene does not react with **1** or **2**; even on heating the five-coordinate starting materials remain inert toward C_2Ph_2.



(1)

1, 3, and 5, M=Ru; 2, 4, and 6, M=Os; 3 and 4, R=Ph; 5 and 6, R=H

The IR and ^1H NMR spectra of **3**–**6** (Table I) confirm that the products obtained according to eq 1 are not analogues of the hydrido olefin compounds $OsHCl(CO)(CH_2{=}CHR)(P\text{-}i\text{-}Pr_3)_2$ but instead are vinylmetal complexes formed by insertion of the alkyne into the metal–hydride bond. The trans stereochemistry at the C=C bond is strongly supported by the large proton–proton coupling constant,[6] which is in the range of 14–18 Hz. ^1H

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Table I. ^{1}H NMR, ^{31}P NMR, and IR Data of 3–17

	^{1}H NMR^a					IR^a	
	$\delta(\mathrm{PCHC}\mathit{H}_3)$ [N; J(HH)]	$\delta(\mathrm{PC}\mathit{H}\mathrm{CH}_3)$	$\delta(\mathrm{H}_\alpha)^b$ [J(PH); J(HH)]	$\delta(\mathrm{H}_\beta)^{b,c}$ [J(PH); J(HH)]	^{31}P NMR^a δ	ν(C≡O)	ν(OAc) or ν(acac)
3	1.30 (dvt) [13.0; 7.0]	2.72 (m)	8.72 (dt) [0.7; 14.0]	6.34 (dt) [2.0; 14.0]	37.70 (s)	1905	
4	1.28 (dvt), 1.27 (dvt) [14.0; 7.0]	2.87 (m)	8.66 (d) [...; 14.0]	6.02 (dt) [2.0; 14.0]	23.28 (s)	1890	
5	1.19 (dvt), 1.17 (dvt) [13.0; 7.0]	2.67 (m)	8.00 (ddt) [1.0; 14.0, 6.0]^d	4.94 (ddt)^e [2.0; 14.0, 1.0] 5.25 (ddt)^f [3.0; 6.0, 1.0]	37.01 (s)	1898	
6	1.21 (dvt) [13.0; 6.0]	2.84 (m)	7.42 (dd) [...; 14.0, 7.0]^d	4.46 (dt) [2.0; 14.0] 5.06 (dt) [3.0; 7.0]	22.34 (s)	1885	
7	1.32 (dvt), 1.08 (dvt) [13.5; 7.0]	2.57 (m)	8.60 (dt) [1.0; 18.0]	*g*	35.21 (s)	2007, 1940	
8	1.27 (dvt), 1.07 (dvt) [13.5; 7.0]	2.63 (m)	8.67 (dt) [2.0; 18.0]	*g*	2.25 (s)	2000, 1925	
9^h	1.27 (dvt), 1.18 (dvt) [13.0; 6.0]	2.33 (m)	8.78 (dt) [1.0; 16.0]	6.42 (dt) [2.0; 16.0]	36.84 (s)	1895	1525, 1450
10^i	1.42 (dvt); 1.38 (dvt) [12.5; 7.0]	2.63 (m)	9.06 (dt) [0.7; 16.0]	6.36 (dt) [2.0; 16.0]	14.95 (s)	1880	1525, 1455
11^j	1.24 (dvt); 1.13 (dvt) [13.0; 6.0]	2.34 (m)	9.11 (dt) [2.0; 16.0]	6.74 (dt) [2.0; 16.0]	34.68 (s)	1895	1587, 1505
12^k	1.37 (dvt); 1.25 (dvt) [13.5; 6.0]	2.52 (m)	9.36 (dt) [0.7; 16.0]	6.56 (dt) [2.0; 16.0]	11.93 (s)	1880	1580, 1525
13^l	1.42 (dvt); 1.33 (dvt) [12.5; 6.0]	2.38 (m)	8.43 (ddt) [1.5; 18.0, 8.0]^d	5.50 (ddt)^e [2.0; 18.0, 2.0] 6.00 (ddt)^f [3.0; 8.0, 2.0]	34.19 (s)	1895	1585, 1505
14^m	1.42 (dvt); 1.30 (dvt) [12.0; 6.0]	2.68 (m)	8.63 (dd) [...; 18.0, 11.0]^d	5.42 (ddt)^e [2.0; 18.0, 4.0] 6.23 (ddt)^f [2.0; 11.0, 4.0]	11.31 (s)	1880	1580, 1500
15	1.40 (dvt) [14.0; 7.0]	3.05 (m)			51.46 (s)	1925^n	
16	1.35 (dvt); 1.32 (dvt) [14.0; 6.0]	2.75 (m)	8.73 (dt) [1.0; 14.0]	6.47 (dt) [2.0; 14.0]	42.40 (s)	1905^o	
17	1.37 (dvt); 1.23 (dvt) [14.0; 6.5]	2.37 (m)	8.30 (dt) [1.0; 16.0]	6.90 (dt) [2.0; 16.0]	40.15 (s)	1998, 1937^p	

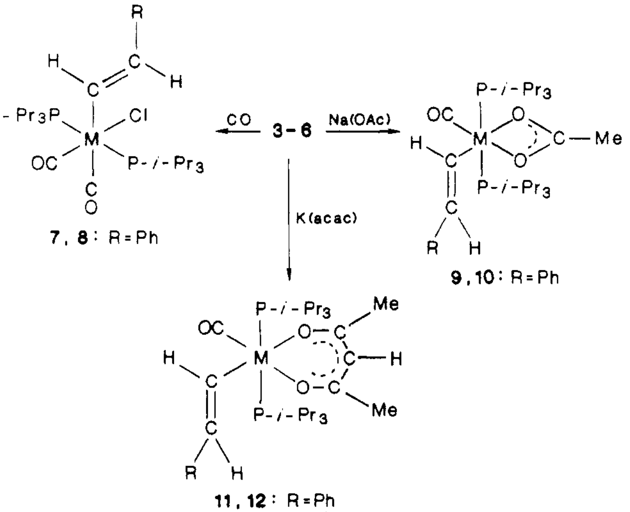
[a] ^{1}H: δ in ppm, Me$_4$Si internal standard. ^{31}P: δ in ppm, 85% H_3PO_4 external standard. J and N in Hz. IR: ν in cm^{-1}. Abbreviations used: s = singlet, d = doublet, t = triplet, m = multiplet, vt = virtual triplet. ^{1}H and ^{31}P NMR in C_6D_6; IR in C_6H_6. [b] H_α = proton at α-C atm; H_β = proton(s) at β-C atom of vinyl ligand CH=CHR (R = H, Ph). [c] For R = Ph: multiplet for C_6H_5 protons between δ 7.0 and δ 7.5. [d] Larger H–H coupling to H_β in the trans position; smaller H–H coupling to H_β in the cis position. [e] H_β trans to H_α. [f] H_β cis to H_α. [g] Not observed. [h] $\delta(CH_3CO_2)$ 1.75 (s). [i] $\delta(CH_3CO_2)$ 1.87 (s). [j] $\delta(CCH_3)$ 1.88 (s) and 1.79 (s); δ(CH) 5.22 (s). [k] $\delta(CCH_3)$ 1.89 (s) and 1.75 (s); δ(CH) 5.28 (s). [l] $\delta(CCH_3)$ 1.83 (s) and 1.70 (s); δ(CH) 5.18 (s). [m] $\delta(CCH_3)$ 1.82 (s) and 1.72 (s); δ(CH) 5.25 (s). [n] ν(C≡C) 2060 cm^{-1}. [o] ν(C≡C) 2065 cm^{-1}. [p] ν(C≡C) 2098 cm^{-1}.

NMR measurements in different solvents gave no indication that in solution an equilibrium between the vinyl and the isomeric alkyne hydrido complexes exists.

Although compounds **3–6** are coordinatively unsaturated, they are monomeric in benzene and thus resemble the well-known five-coordinate triarylphosphine complexes $MCl_2(PR_3)_3$.[7] It appears that in both cases dimerization via Cl bridges, which would provide an 18-electron configuration at the metal, is hindered for steric reasons.

The coordination number six for ruthenium and osmium can be achieved, however, either by addition of CO or displacement of the chloride ligand with acetate or acetylacetonate anions. The corresponding compounds **7–14** (Scheme I) are isolated in good to excellent yields. The IR spectra indicate that the OAc and acac groups in **9–14** are coordinated via both oxygen atoms, i.e., as chelating ligands. The observation of two C–O stretching frequencies at ca. 1525 and 1450 cm^{-1} (for **9** and **10**) and 1585 and 1505 cm^{-1} (for **11–14**) is in accord with this structural proposal.[8,9] It is also worth mentioning that the hydridometal compounds **1** and **2** used in this work react with Na(OAc) and K(acac) to produce the corresponding chelate complexes.[3]

Scheme I



7, 9, 11, and 13, M = Ru; 8, 10, 12, and 14; M = Os

Attempts to use the dicarbonyl compounds **7** and **8** as precursors for the synthesis of (phenylvinylidene)ruthenium(0) and -osmium(0) complexes have remained unsuccessful as yet. The octahedral starting materials do not react, e.g., with NEt_3 or n-BuLi, by HCl elimination and thus behave differently to the half-sandwich type com-

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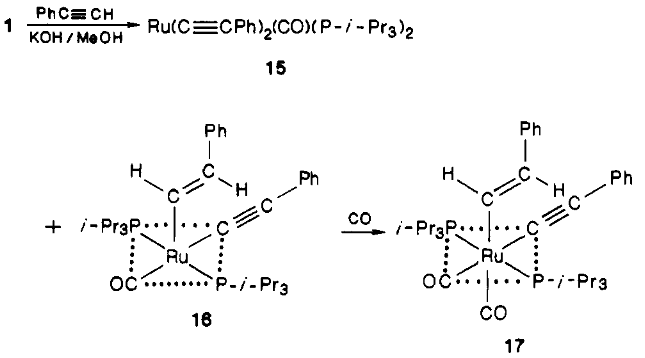
Table II. ^{13}C NMR Data of 3–14, 16, and 17[a,m]

	$\delta(PCHCH_3)$	$\delta(PCH)$	*N*	$\delta(CO)$	*J*(PC)	$\delta(C_\alpha)$[a]	*J*(PC)	$\delta(C_\beta)$[a]	$\delta(C_6H_5)$[b]
3	20.06 (s), 19.86 (s)	24.82 (vt)	22.0	203.64 (t)	13.0	150.23 (t)	11.0	*c*	139.33, 135.22, 128.75, 124.34
4	20.02 (s), 19.63 (s)	24.80 (vt)	24.0	182.77 (t)	9.0	119.83 (t)	8.5	124.63 (s)	140.10, 134.65, 128.51, 124.51
5	20.05 (s), 19.96 (s)	24.66 (vt)	18.0	203.71 (t)	12.0	153.05 (t)	10.5	120.27 (s)	
6	20.05 (s), 19.84 (s)	24.85 (vt)	23.0	182.86 (t)	9.0	120.96 (t)	7.5	118.99 (s)	
7	20.29 (s), 19.59 (s)	25.23 (vt)	21.0	202.40 (t), 198.50 (t)	13.0, 13.0	160.46 (t)	13.0	125.24 (s)	142.03, 139.62, 128.85, 124.91
8	20.23 (s), 19.18 (s)	24.84 (vt)	24.0	185.66 (t), 181.08 (t)	9.0, 9.0	150.17 (t)	12.0	125.27 (s)	143.16, 140.45, 128.79, 124.91
9[d]	19.86 (s), 19.80 (s)	25.05 (vt)	18.0	209.14 (t)	13.5	159.36 (t)	11.0	123.78 (s)	141.19, 134.27, 128.70, 124.11
10[e]	19.71 (s)	24.84 (vt)	24.0	186.17 (t)	9.0	137.04 (t)	8.0	123.36 (s)	142.60, 132.79, 128.57, 124.08
11[f]	19.87 (s), 19.71 (s)	24.69 (vt)	16.0	209.92 (t)	13.5	159.30 (t)	12.0	123.54 (s)	142.30, 135.28, 128.64, 124.15
12[g]	19.77 (s), 19.65 (s)	24.42 (vt)	21.0	188.26 (t)	11.0	143.83 (t)	9.0	123.08 (s)	143.66, 134.12, 128.42, 124.15
13[h]	20.04 (s), 19.77 (s)	24.44 (vt)	18.0	209.95 (t)	16.0	166.82 (t)	12.0	120.24 (s)	
14[i]	19.93 (s), 19.72 (s)	24.17 (vt)	24.0	188.69 (t)	9.0	146.41 (t)	8.0	118.20 (s)	
16[j]	20.06 (s), 19.96 (s)	25.88 (vt)	18.0	205.52 (t)	12.0	150.38 (t)	10.0	124.34 (s)	128.76[k]
17[l]	20.35 (s), 19.26 (s)	25.81 (vt)	18.0	203.58 (t), 199.64 (t)	9.0, 9.0	154.93 (t)	12.0	124.31 (s)	142.65, 140.58, 130.63, 129.81, 128.42, 125.02

[a] C_α and C_β are the α- and β-carbon atoms of the vinylic ligand. [b] All signals of the phenyl carbon atoms are singlets. [c] Not observed. [d] $\delta(CH_3CO_2)$ 24.51 (s); $\delta(CH_3CO_2)$ 182.23 (s). [e] $\delta(CH_3CO_2)$ 25.26 (s); $\delta(CH_3CO_2)$ 183.60 (s). [f] acac: δ(OC) 188.54 (s) and 186.69 (s); δ(CH) 100.28 (s); $\delta(CH_3)$ 28.57 (s). [g] acac: 186.72 (s) and 184.54 (s); δ(CH) 102.31 (s); $\delta(CH_3)$ 28.06 (s). [h] acac: δ(OC) 188.35 (s) and 186.56 (s); δ(CH) 100.09 (s); $\delta(CH_3)$ 28.55 (s). [i] acac: δ(OC) 186.55 (s) and 184.48 (s); δ(CH) 102.16 (s); $\delta(CH_3)$ 28.03 (s). [j] δ(C≡CPh) 139.33 (t), *J*(PC) 2.0 Hz; δ(C≡CPh) 132.60 (s). [k] Other signals of phenyl carbon atoms not exactly located. [l] δ(C≡CPh) 116.80 (t), *J*(PC) = 2.0 Hz; δ(C≡CPh) 113.20 (s). [m] Me_4Si internal standard; *J* and *N* in Hz; abbreviations used: s = singlet, t = triplet, vt = virtual triplet.

Scheme II



pounds $C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)X$ and $C_6H_6Os(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)X$, respectively.[4,5]

The reaction of **1** with phenylacetylene in the presence of stoichiometric amounts of KOH in methanol proceeds differently to that of **1** with PhC_2H in hexane. Two products are formed which are deeply colored and can easily be separated from benzene–hexane. The elemental analyses and spectroscopic data are consistent with the formation of $Ru(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (**15**) and $Ru(C{\equiv}CPh)(CH{=}CHPh)(CO)(P\text{-}i\text{-}Pr_3)_2$ (**16**), respectively. When the ^1H and ^{13}C NMR data are compared there is no doubt that in **16** two different σ-bonded unsaturated ligands are present which presumably are in cis position to each other. As the alkynyl vinyl complex is also obtained from **3** and LiC_2Ph in benzene, we assume that the mechanism of formation of **16** involves the primary insertion of the alkyne into the Ru–H bond followed by displacement of the chloride ligand by the alkynyl anion. On reaction with CO, the dark green five-coordinate compound **16** is readily transformed into the six-coordinate complex $Ru(C{\equiv}CPh)(CH{=}CHPh)(CO)_2(P\text{-}i\text{-}Pr_3)_2$ (**17**) (Scheme II) which forms white crystals. The spectroscopic data are summarized in Tables I and II.

Table III. Positional Parameters and Their Estimated Standard Deviations for Non-Hydrogen Atoms in 4

	x	*y*	*z*	B_{eq}, Å^2
Os	0.73117 (2)	0.70638 (2)	0.99333 (2)	2.04 (1)
Cl	0.6187 (1)	0.7076 (2)	1.0623 (1)	4.8 (1)
P(1)	0.6610 (1)	0.8693 (2)	0.9082 (1)	2.23 (8)
P(2)	0.7801 (1)	0.5159 (2)	1.0570 (1)	2.58 (9)
O	0.8418 (5)	0.6761 (5)	0.8929 (4)	3.8 (3)
C(1)	0.8059 (6)	0.6880 (8)	0.9264 (7)	3.6 (5)
C(2)	0.8113 (5)	0.8161 (6)	1.0695 (5)	2.7 (3)
C(3)	0.8833 (6)	0.8642 (8)	1.0726 (5)	4.1 (4)
C(4)	0.9249 (5)	0.9604 (8)	1.1347 (5)	3.5 (4)
C(5)	0.9963 (5)	1.0119 (8)	1.1231 (5)	4.2 (5)
C(6)	1.0401 (5)	1.1004 (9)	1.1731 (7)	4.9 (5)
C(7)	1.0095 (7)	1.1376 (9)	1.2393 (6)	5.0 (5)
C(8)	0.9376 (7)	1.088 (1)	1.2488 (6)	5.2 (5)
C(9)	0.8979 (5)	1.0002 (9)	1.1971 (6)	4.7 (5)
C(10)	0.5969 (4)	0.9736 (7)	0.9522 (4)	2.7 (3)
C(11)	0.6457 (5)	1.0300 (8)	1.0332 (5)	3.8 (4)
C(12)	0.5486 (5)	1.0728 (8)	0.8952 (5)	3.9 (4)
C(13)	0.7289 (5)	0.9605 (7)	0.8594 (5)	3.5 (4)
C(14)	0.7826 (5)	1.0556 (8)	0.9158 (5)	4.2 (4)
C(15)	0.6880 (6)	1.0195 (8)	0.7768 (5)	5.0 (5)
C(16)	0.5812 (5)	0.8032 (7)	0.8211 (4)	3.0 (3)
C(17)	0.5115 (6)	0.7350 (9)	0.8482 (6)	4.5 (5)
C(18)	0.6238 (6)	0.7204 (8)	0.7710 (5)	4.7 (5)
C(19)	0.7124 (5)	0.3939 (8)	0.9976 (5)	3.9 (4)
C(20)	0.7149 (7)	0.4002 (9)	0.9087 (5)	5.2 (5)
C(21)	0.6222 (6)	0.400 (1)	1.0016 (8)	7.1 (7)
C(22)	0.7695 (6)	0.4933 (7)	1.1614 (5)	3.9 (4)
C(23)	0.7925 (8)	0.3676 (10)	1.1964 (6)	7.4 (7)
C(24)	0.8130 (7)	0.5884 (9)	1.2205 (5)	5.6 (5)
C(25)	0.8883 (5)	0.4738 (8)	1.0539 (5)	3.7 (4)
C(26)	0.9549 (6)	0.5449 (9)	1.1084 (6)	5.2 (5)
C(27)	0.9108 (7)	0.3388 (10)	1.0567 (7)	5.9 (5)
H(2)	0.7772 (0)	0.8257 (0)	1.1185 (0)	5.0 (0)

Crystal Data and Structure Determination of 4

In contrast to our attempts with **1** and **2**, we succeeded in obtaining suitable single crystals of **4** from hexane. They are monoclinic with *a* = 16.437 (5) Å, *b* = 10.980 (4) Å, *c* = 17.086 (4) Å, β = 105.56 (2)°, and *V* = 2970.7 Å^3. The space group is $P2_1/n$ from systematic absences, *Z* = 4, *d*(calcd) = 1.51 g/cm^3, *d*(exptl) = 1.52 g/cm^3. One crystal with the dimensions of 0.3 × 0.4 × 0.4 mm was used for the structure determination, and a total of 4799 independent reflections were collected on a Syntex $P2_1$ four-circle automatic diffractometer at −48 °C (Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator, ω scan) in the range $4.5° \leq 2\theta \leq 48.5°$. An empirical correction for absorption was applied (μ_{Mo} = 47.6 cm^{-1}); the range of absorption correction factors was 0.72–1.00. The structure was solved by the Patterson method (Syntex XTL). The hydrogen atoms were located from difference Fourier maps. Refinement of the non-hydrogen atoms by full-matrix least squares with anisotropic thermal parameters resulted in *R* = 0.038 and R_w = 0.044 ($1/w = \sigma F_o^2$)) for 4136 structure factors with $F_o \geq 5.92\sigma(F_o)$. Structure factors for uncharged atoms according to ref 15 were used, cor-

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations

Bond Distances			
Os-Cl	2.444 (3)	C(3)-C(4)	1.52 (1)
Os-P(1)	2.398 (2)	P(1)-C(10)	1.85 (1)
Os-P(2)	2.395 (2)	P(1)-C(13)	1.86 (1)
Os-C(1)	1.89 (1)	P(1)-C(16)	1.85 (1)
Os-C(2)	1.99 (1)	P(2)-C(19)	1.86 (1)
C(1)-O	0.94 (1)	P(2)-C(22)	1.86 (1)
C(2)-C(3)	1.29 (1)	P(2)-C(25)	1.85 (1)
Bond Angles			
Cl-Os-P(1)	89.1 (1)	P(2)-Os-C(1)	89.5 (3)
Cl-Os-P(2)	89.5 (1)	P(2)-Os-C(2)	98.5 (2)
Cl-Os-C(1)	170.4 (3)	C(1)-Os-C(2)	91.8 (4)
Cl-Os-C(2)	97.7 (2)	Os-C(1)-O	177 (1)
P(1)-Os-P(2)	167.4 (1)	Os-C(2)-C(3)	135.7 (7)
P(1)-Os-C(1)	89.8 (3)	C(2)-C(3)-C(4)	123.3 (9)
P(1)-Os-C(2)	94.1 (2)		

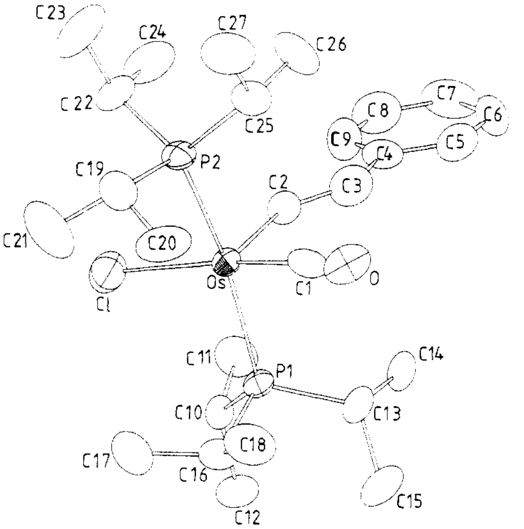


Figure 1. X-ray crystal structure of 4. Heavy atoms are represented by thermal ellipsoids drawn to encompass 50% of the electron density.

rected for anomalous dispersion. The largest peaks in the final difference Fourier map were 0.6–0.8 e/Å^3. Final positional parameters are given in Table III and selected intramolecular bond lengths and angles in Table IV.

The molecular structure of 4 is shown in Figure 1. The most remarkable features are, first, the square-pyramidal coordination of the metal and, second, the trans position of the two substituents C_6H_5 and $OsCl(CO)(P\text{-}i\text{-}Pr_3)_2$ at the C=C double bond. The four atoms P(1), P(2), Cl, and C(1) forming the basis of the pyramid are approximately in one plane, whereas the osmium atom is located 0.26 Å above this plane toward the apical position. The C(1)–O distance is unusually short (presumably due to absorption effects), but there is no evidence that the Cl–Os–C(1)–O unit is disordered. The highest peaks obtained from the final difference Fourier synthesis are at the metal, but certainly not directly on the Cl–Os–C(1) axis.

Although 4 undoubtedly is a 16-electron complex and thus coordinatively unsaturated, the stereo ORTEP diagram of the molecule shown in Figure 2 illustrates that also in the sixth (formally unoccupied) position of the octahedron the osmium atom is well-shielded. Four of the 12 methyl groups of the phosphine ligands surround the metal like an umbrella which may also explain why compound 4 does not readily react in solution with ligands such as PMe_3 or $P\text{-}i\text{-}Pr_3$ being more bulky than carbon monoxide. The shielding effect of the methyl groups is certainly supported by the bending of the phosphorus–osmium–phosphorus axis resulting in an P(1)–Os–P(2) angle of 167.4 (1)°.

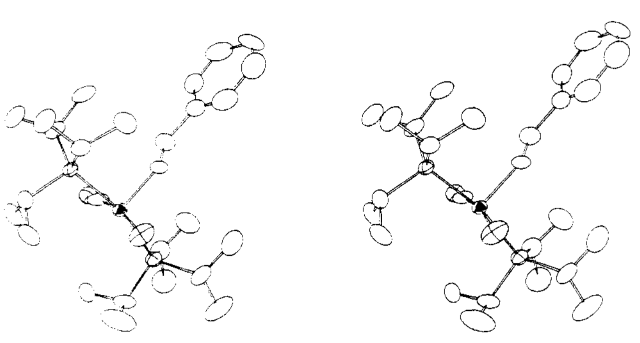


Figure 2. Stereo ORTEP diagram of 4.

Conclusion

The present study has confirmed that the preferred pathway for the reaction of the 16-electron complexes $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**1**, **2**) with C_2H_2 and PhC_2H is the insertion of the alkyne into the metal–hydride bond. Owing to the high reactivity of **1** and **2** toward Lewis bases such as CO, PMe_3, $P(OMe)_3$, $CH_2{=}CHR$, etc.,[3] it is assumed that in the reactions leading to the formation of $M(CH{=}CHR)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**3**–**6**) addition of the alkyne to the metal first occurs followed by rapid migration of the hydride from the metal to the carbon atom. The same type of reaction has recently been considered by Stolzenberg and Muetterties as the crucial step in the hydrogenation of alkynes to form alkenes using $RuHCl(PPh_3)_3$ as the catalyst.[10] The osmium compound $OsHBr(CO)(PPh_3)_3$ behaves similarly.[11] It should be mentioned that the regioselectivity observed in the formation of **3** and **4** (as well as in the analogous reactions of $MH(O_2CCF_3)(CO)(PPh_3)_2$ (M = Ru and Os) with $RC{\equiv}CPh$)[12] does not seem to be a general phenomenon as the insertion of alkynes $RC{\equiv}CH$ (R = CN, CF_3) into the metal–hydride bond of the complexes $(C_5H_5)_2MH(CO)$ (M = Nb, Ta) only produces vinyl metal compounds having the substituent R in the α-position.[13] Recent results obtained in our laboratory on the reactions of $IrH_5(P\text{-}i\text{-}Pr_3)_2$ with alkynes show[14] that, e.g., propyne reacts to give an $Ir(CMe{=}CH_2)$ complex, again indicating that one can not predict whether the alkyne insertion leads to α-R- or β-R-substituted vinyl compounds.

Experimental Section

NMR spectra were recorded on a Varian EM 360 L (^1H), a Bruker WH 90 FT (^{31}P), and a Bruker Cryospec WM 400 (^1H and ^{13}C) spectrometer, IR spectra on a Perkin-Elmer 457 spectrometer, and mass spectra on a Varian MAT CH 7 instrument (70 eV). The starting materials $RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**1**) and $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**2**) were prepared by published methods.[3]

Preparation of $Ru(CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (3). A suspension of **1** (77.4 mg, 0.16 mmol) in 5 mL of hexane was treated with PhC_2H (18.7 μL, 0.17 mmol) and stirred for 30 min at room temperature. The dark red precipitate was filtered off, repeatedly washed with hexane, and dried in vacuo; yield 79 mg

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(85%). Anal. Calcd for $C_{27}H_{49}ClOP_2Ru$: C, 55.14; H, 8.40; M_r, 588.13. Found: C, 55.18; H, 8.54; M_r 558 (osmometric in benzene).

Preparation of Os(CH=CHPh)Cl(CO)(P-*i*-Pr$_3$)$_2$ (4) was prepared analogously as described for **3**, starting with **2** (82.9 mg, 0.15 mmol) and PhC_2H (16.6 μL, 0.15 mmol): dark blue crystals; yield 80 mg (82%). Anal. Calcd for $C_{27}H_{49}ClOOsP_2$: C, 47.88; H, 7.29; M_r, 677.26. Found: C, 48.50; H, 7.82; M_r 678 (osmometric in benzene).

Preparation of Ru(CH=CH$_2$)Cl(CO)(P-*i*-Pr$_3$)$_2$ (5). Acetylene was bubbled through a suspension of **1** (553.7 mg, 1.14 mmol) in 10 mL of hexane for 15 min at room temperature. The red precipitate was filtered off, washed with methanol and pentane, and dried in vacuo; yield 560 mg (96%). Anal. Calcd for $C_{21}H_{45}ClOP_2Ru$: C, 49.26; H, 8.86; M_r 512.03. Found: C, 49.67; H, 9.45; M_r, 478 (osmometric in benzene).

Preparation of Os(CH=CH$_2$)Cl(CO)(P-*i*-Pr$_3$)$_2$ (6). Acetylene was bubbled through a solution of **2** (284.2 mg, 0.49 mmol) in 20 mL of benzene for 15 min at room temperature. The solution was concentrated in vacuo to ca. 3 mL, and 15 mL of methanol was added. A red precipitate was formed which was filtered off, washed with methanol and pentane, and dried in vacuo; yield 238 mg (80%). Anal. Calcd for $C_{21}H_{45}ClOOsP_2$: C, 41.96; H, 7.55; M_r, 601.16. Found: C, 42.02; H, 7.90; M_r, 602 (MS), 560 (osmometric in benzene).

Preparation of Ru(CH=CHPh)Cl(CO)$_2$(P-*i*-Pr$_3$)$_2$ (7). Carbon monoxide was bubbled through a suspension of **3** (117.6 mg, 0.20 mmol) in 20 mL of hexane which led to solution of the starting material and formation of a gray precipitate. After removal of the solvent in vacuo, the residue was treated with 20 mL of benzene, and the resulting suspension was filtered. The filtrate was concentrated in vacuo to ca. 0.5 mL, and 10 mL of methanol was added. A white solid was formed which was filtered off, repeatedly washed with methanol, and dried in vacuo; yield 92 mg (75%). Anal. Calcd for $C_{28}H_{49}ClO_2P_2Ru$: C, 54.58; H, 8.02; M_r, 616.14. Found: C, 54.56; H, 8.47; M_r, 602 (osmometric in benzene).

Preparation of Os(CH=CHPh)Cl(CO)$_2$(P-*i*-Pr$_3$)$_2$ (8). Carbon monoxide was bubbled through a suspension of **4** (135.1 mg, 0.20 mmol) in 20 mL of hexane, and the same workup procedure was used which was described for **7**; yield 100 mg (71%). Anal. Calcd for $C_{28}H_{49}ClO_2OsP_2$: C, 47.68; H, 7.00; M_r, 705.27. Found: C, 47.64; H, 7.31; M_r, 706 (MS).

Preparation of Ru(CH=CHPh)(η^2-O$_2$CMe)(CO)(P-*i*-Pr$_3$)$_2$ (9). A suspension of **3** (147.1 mg, 0.25 mmol) in 20 mL of methanol was treated with sodium acetate (20.5 mg, 0.25 mmol) and stirred for 1 h at room temperature. The solvent was removed, and the solid residue was treated with 20 mL of benzene. The resulting suspension was filtered, the filtrate was concentrated in vacuo to ca. 0.5 mL, and 10 mL of methanol was added. After the solution was concentrated to ca. 5 mL and cooled to −78 °C yellow crystals were formed which were filtered off, repeatedly washed with methanol, and dried in vacuo; yield 132 mg (86%). Anal. Calcd for $C_{29}H_{52}O_3P_2Ru$: C, 56.94; H, 8.57; M_r, 611.72. Found: C, 56.52; H, 8.69; M_r, 612 (MS).

Preparation of Os(CH=CHPh)(η^2-O$_2$CMe)(CO)(P-*i*-Pr$_3$)$_2$ (10) was prepared analogously as described for **9**, starting with **4** (413.3 mg, 0.61 mmol) and sodium acetate (50 mg, 0.61 mmol): yellow crystals; yield 240 mg (53%). Anal. Calcd for $C_{29}H_{52}O_3OsP_2$: C, 49.70; H, 7.48; M_r 700.85. Found: C, 49.60; H, 7.59; M_r, 666 (osmometric in benzene).

Preparation of Ru(CH=CHPh)(η^2-acac)(CO)(P-*i*-Pr$_3$)$_2$ (11). A stoichiometric amount of **3** (270.5 mg, 0.46 mmol) was added to a solution of KOH (26.2 mg, 0.46 mmol) in 4 mL of methanol. The mixture was treated with 2,4-pentanedione (47.5 μL, 0.46 mmol) and stirred for 2 h at room temperature. The solvent was removed, the solid residue was treated with 10 mL of benzene, and the resulting suspension was filtered. The filtrate was concentrated in vacuo to ca. 0.5 mL, and 10 mL of methanol was added. A yellow precipitate was formed which was filtered off, repeatedly washed with methanol, and dried in vacuo; yield 258 mg (86%). Anal. Calcd for $C_{32}H_{56}O_3P_2Ru$: C, 58.61; H, 8.61; Ru, 15.41. Found: C, 58.91; H, 8.69; Ru, 15.86.

Preparation of Os(CH=CHPh)(η^2-acac)(CO)(P-*i*-Pr$_3$)$_2$ (12) was prepared analogously as described for **11**, starting with **4** (419.1 mg, 0.62 mmol) and stoichiometric amounts of KOH and 2,4-pentanedione: yellow crystals; yield 331 mg (72%). Anal. Calcd for $C_{32}H_{56}O_3OsP_2$: C, 51.59; H, 7.58; Os, 25.53; M_r, 744.95. Found: C, 51.89; H, 7.86; Os, 25.89; M_r, 697 (osmometric in benzene).

Preparation of Ru(CH=CH$_2$)(η^2-acac)(CO)(P-*i*-Pr$_3$)$_2$ (13) was prepared analogously as described for **11**, starting with **5** (189.4 mg, 0.37 mmol) and stoichiometric amounts of KOH and 2,4-pentanedione: yellow crystals; yield 138 mg (65%). Anal. Calcd for $C_{26}H_{52}O_3P_2Ru$: C, 53.87; H, 9.04; M_r, 579.72. Found: C, 54.66; H, 9.32; M_r, 558 (osmometric in benzene).

Preparation of Os(CH=CH$_2$)(η^2-acac)(CO)(P-*i*-Pr$_3$)$_2$ (14) was prepared analogously as described for **11**, starting with **6** (300.5 mg, 0.50 mmol) and stoichiometric amounts of KOH and 2,4-pentanedione: yellow crystals; yield 233 mg (70%). Anal. Calcd for $C_{26}H_{52}O_3OsP_2$: C, 46.69; H, 7.84; Os, 28.44; M_r, 668.85. Found: C, 47.47; H, 8.46; Os, 28.73; M_r, 623 (osmometric in benzene).

Preparation of Ru(C≡CPh)$_2$(CO)(P-*i*-Pr$_3$)$_2$ (15) and Ru(C≡CPh)(CH=CHPh)(CO)(P-*i*-Pr$_3$)$_2$ (16). A stoichiometric amount of **1** (296.8 mg, 0.65 mmol) was added to a solution of KOH (37.0 mg, 0.65 mmol) in 6 mL of methanol. The mixture was treated with PhC_2H (71.4 μL, 0.65 mmol) and stirred for 1 h at room temperature. The solvent was removed, the solid residue was treated with 10 mL of benzene, and the resulting suspension was filtered. The filtrate was concentrated in vacuo to ca. 0.5 mL, and 10 mL of hexane was added. After the solution was cooled to −20 °C, a dark red precipitate of **15** was formed which was filtered off, washed with hexane, and dried in vacuo; yield 87 mg (22%). Anal. Calcd for $C_{35}H_{52}OP_2Ru$: C, 64.50; H, 8.04; M_r, 651.79. Found: C, 63.89; H, 7.95; M_r 652 (MS). The dark filtrate was concentrated in vacuo to ca. 5 mL and cooled to −20 °C. After the filtrate was stored for 2 days, dark green crystals of **16** were formed which were filtered off, washed with cold hexane, and dried in vacuo; yield 76 mg (19%). Anal. Calcd for $C_{35}H_{54}OP_2Ru$: C, 64.30; H, 8.33; M_r, 653.81. Found: C, 64.78; H, 8.35; M_r, 654 (MS).

Preparation of Ru(C≡CPh)(CH=CHPh)(CO)$_2$(P-*i*-Pr$_3$)$_2$ (17). Carbon monoxide was bubbled through a solution of **16** (136.2 mg, 0.21 mmol) in 25 mL of hexane. After removal of the solvent, the residue was treated with 10 mL of methanol, and the mixture was stirred for 15 min. A colorless precipitate was formed which was filtered off, repeatedly washed with methanol, and dried in vacuo. It was recrystallized from hexane at −30 °C; yield 88 mg (62%). Anal. Calcd for $C_{36}H_{54}O_2P_2Ru$: C, 63.42; H, 7.98; Ru, 14.82. Found: C, 63.29; H, 8.21; Ru, 15.17.

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Supplementary Material Available: A listing of structure factors for 4 (25 pages). Ordering information is given on any current masthead page.