Reactions of Osmium Hydride Complexes with Terminal Alkynes: Synthesis and Catalytic Activity of $OsH(\eta^2\text{-}O_2CCH_3)(C{=}CHPh)(PiPr_3)_2$

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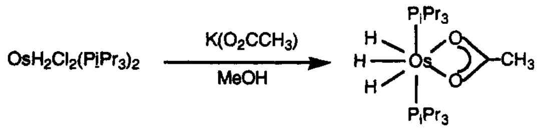
Summary: The reaction of the complex $OsH_2Cl_2(PiPr_3)_2$ with $K(CH_3CO_2)$ in methanol affords the trihydride $OsH_3(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2$. This complex reacts with PhC_2H to give the hydride–vinylidene complex $OsH(\eta^2\text{-}O_2CCH_3)(C{=}CHPh)(PiPr_3)_2$, which catalyzes the dimerization of phenylacetylene to give a mixture of trans-$PhC{\equiv}CCH{=}CHPh$ and cis-$PhC{\equiv}CCH{=}CHPh$ in a 2:5 molar ratio.

We have observed that three different types of organometallic compounds could be obtained by reaction of terminal alkynes with osmium–hydride complexes. Thus, some years ago, we reported that the monohydrides $OsHCl(CO)(PiPr_3)_2$ and $[OsH(\eta^1\text{-}OCMe_2)(CO)(PiPr_3)_2]^+$ react with alkynes such as PhC_2H, C_2H_2, and HC_2CO_2Me to give the corresponding vinyl derivatives by insertion of the alkynes into the Os–H bond of these complexes.[1] Subsequently, it was found that the dihydride complex $OsH_2(CO)(PiPr_3)_2$, generated *in situ* by loss of a hydrogen molecule from the tetrahydride $OsH_4(CO)(PiPr_3)_2$, reacts with PhC_2H and Me_3SiC_2H to give hydride–alkynyl-dihydrogen complexes of formula $OsH(C_2R)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (R = Ph, Me_3Si).[2] Most recently, the synthesis of new hydride–carbyne and hydride–vinylcarbyne compounds of osmium(II) have been described. They were obtained by reaction of the dihydride–dichloro complex $OsH_2Cl_2(PiPr_3)_2$ with the corresponding terminal alkynes.[3] As a continuation of our work on the reactivity of hydride–osmium complexes toward terminal alkynes, we have carried out the reaction of the trihydride $OsH_3(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2$ complex with PhC_2H, which affords the hydride–vinylidene $OsH(\eta^2\text{-}O_2CCH_3)(C{=}CHPh)(PiPr_3)_2$ compound.

Results and Discussion

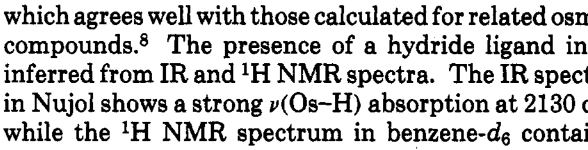
The complex $OsH_3(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2$ (1) was prepared by reaction of $OsH_2Cl_2(PiPr_3)_2$ with $K(CH_3CO_2)$ in methanol at room temperature (eq 1). Under the same experimental conditions the reactions of $OsH_2Cl_2(PiPr_3)_2$ with $K(EtOCS_2)$ and $K(CH_3COS)$ lead to the dihydrogen compounds $Os(\eta^2\text{-}S_2COEt)(\eta^1\text{-}SC(S)OEt)(\eta^2\text{-}H_2)(PiPr_3)_2$ and $Os(\eta^2\text{-}OSCCH_3)(\eta^1\text{-}SC(O)CH_3)(\eta^2\text{-}H_2)(PiPr_3)_2$, respectively.[4]



(1)

The ${}^1H$ NMR spectrum of 1 in toluene is temperature-dependent (Figure 1). At room temperature it contains in the hydride region a triplet at −14.57 ppm with a P–H coupling constant of 11.7 Hz. At temperatures lower than 40 °C an AB_2 splitting pattern is observed. The ${}^{31}P\{{}^1H\}$ NMR spectrum, in contrast to the ${}^1H$ NMR spectrum, is temperature-invariant. From room temperature −80 °C, it shows a singlet at 40.66 ppm that under off-resonance conditions due to the P–H coupling is split into a quartet.

Complex 1 reacts with PhC_2H in toluene at room temperature to give, after 5 h, the hydride–vinylidene compound $OsH(\eta^2\text{-}O_2CCH_3)(C{=}CHPh)(PiPr_3)_2$ (2) (eq 2),[5] which was isolated as an orange solid in 60% yield.



(2)

This compound was fully characterized by elemental analysis and IR and ${}^1H$, ${}^{31}P\{{}^1H\}$, and ${}^{13}C\{{}^1H\}$ NMR spectroscopy. The acetate ligand is formulated as bidentate on the basis of the value calculated for $\Delta\nu$ (95 cm⁻¹), which agrees well with those calculated for related osmium compounds.[8] The presence of a hydride ligand in 2 is inferred from IR and ${}^1H$ NMR spectra. The IR spectrum in Nujol shows a strong ν(Os–H) absorption at 2130 cm⁻¹, while the ${}^1H$ NMR spectrum in benzene-d_6 contains a triplet at −11.51 ppm with a P–H coupling constant of 15.6 Hz. The vinylidene group is characterized in the ${}^1H$ NMR spectrum by a triplet at 2.25 ppm with a P–H coupling constant of 2.5 Hz and in the ${}^{13}C\{{}^1H\}$ NMR spectra by two triplets, one due to the α-carbon atom at 291.5 ppm with a P–C coupling constant of 10.5 Hz and the other due to the β-carbon atom at 107.51 ppm with a P–C coupling constant of 2.8 Hz. The ${}^{31}P\{{}^1H\}$ spectrum shows

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[5] The addition of terminal alkynes to transition-metal complexes to give vinylidene compounds, via a formal 1,2-hydrogen shift, is a general method to prepare this type of compound.[6] However, when the transition-metal complex contains hydride ligands, the alkyne generally undergoes insertion into the M–H bond leading to vinyl compounds.[7]

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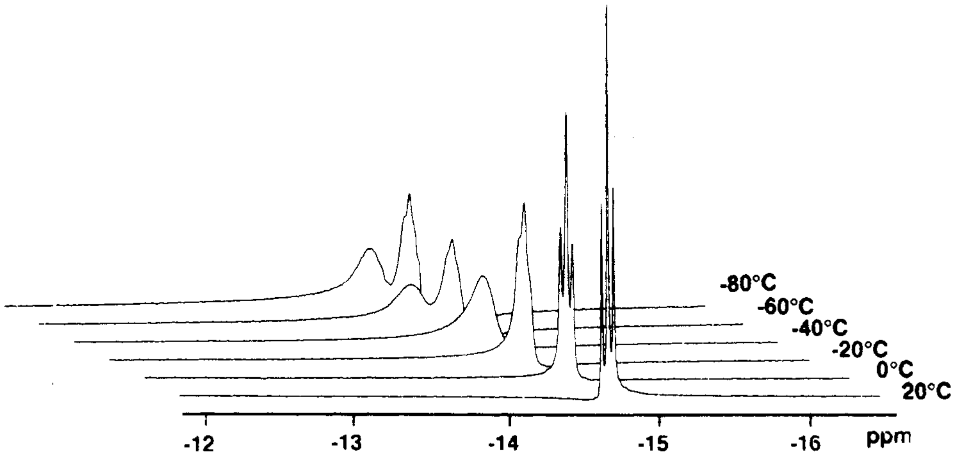

Figure 1. Variable-temperature 300-MHz ^1H NMR spectra in the high-field region of $OsH_3(\eta^2\text{-}O_2CCH_3)(P\textit{i}Pr_3)_2$, in toluene-$d_8$.

a singlet at 26.8 ppm, which under off-resonance conditions due to the P–H coupling is split into a doublet.

We note that the synthesis of the hydride–vinylidene complex $Cp^*_2TaH(C{=}CH_2)$ has been previously reported by Bercaw *et al.* This compound was prepared by reaction of $Cp^*_2TaCl_2$ with vinylmagnesium bromide in THF.[9]

Complex 2 is found to be an active catalyst (or catalyst precursor) for the dimerization of phenylacetylene (eq 3).

$$2PhC{\equiv}CH \xrightarrow{2} PhC{\equiv}CCH{=}CHPh \qquad (3)$$

Thus, the formation of 0.10 M *trans*-$PhC{\equiv}CCH{=}CHPh$ and 0.24 M *cis*-$PhC{\equiv}CCH{=}CHPh$ is observed after 2 h, by treatment of 1.4 M $PhC{\equiv}CH$ with 1.4×10^{-2} M of 2 in toluene at 111 °C.

From a mechanistic point of view, it has been proposed that the dimerization of terminal alkynes catalyzed by transition-metal complexes could involve either alkynyl–vinyl[10] or alkynyl–vinylidene[11] intermediates. According to the alkynyl–vinylidene mechanism, the intramolecular coupling of both ligands leads to the formation of $M(\eta^3\text{-}RC_3CHR)$ species, some of which have been isolated and characterized by X-ray diffraction analysis.[11,12]

Bianchini et al. have recently observed that the complex $[(PP_3)OsH(N_2)]BPh_4$ catalyzes the dimerization of terminal alkynes to disubstituted but-3-en-1-ynes. Interestingly, at 0 °C, this complex reacts with the stoichiometric amount of (trimethylsilyl)acetylene to give a mixture of the cationic compounds $[(PP_3)OsH(C{=}CHSiMe_3)]BPh_4$ and (*E*)-$[(PP_3)Os\{\eta^3\text{-}(SiMe_3)C_3{=}CH(SiMe_3)\}]BPh_4$.[13]

The reactions of alkynes with transition-metal hydride complexes generally lead to vinyl derivatives.[7] The osmium monohydrides seem to follow this trend.[1] However, the osmium dihydrides can give different types of compounds, depending on the electronic nature of the metallic fragment. Thus, when the metallic fragment is rich in electrons a formal oxidative addition of the alkyne can take place to give hydride–alkynyl–dihydrogen complexes,[2b] while, when the metallic fragment is poor in electrons, the formation of hydride–carbyne derivatives is observed.[3] The present study reports a new reaction pattern between a transition-metal hydride complex and a terminal alkyne. The trihydride complex $OsH_3(\eta^2\text{-}O_2CCH_3)(P\textit{i}Pr_3)_2$ reacts with PhC_2H to give the hydride–vinylidene $OsH(\eta^2\text{-}O_2CCH_3)(C{=}CHPh)(P\textit{i}Pr_3)_2$ compound.

In connection with the homogeneous catalysis, it is interesting to note that the vinyl–osmium derivatives can play main roles in hydrogenation reactions as key intermediates,[1a] and as side catalytic intermediates in hydrosilylation reactions.[14] Similarly, it has been proved that the hydride–alkynyl–dihydrogen compounds can also play the main role in the reduction of terminal alkynes by hydrogen-transfer reactions and hydrogenation with molecular hydrogen.[2b] Now, we show that the hydride–vinylidene complex 2 is an active catalyst for the dimerization of PhC_2H.

In conclusion, the reactions of osmium hydride complexes with terminal alkynes allow the preparation of specific organometallic compounds, if the number of hydride ligands and the electronic properties of the starting complexes are appropriately selected (Scheme 1). In general, the organometallic compounds prepared in this way play leading roles in homogeneous catalytic processes.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere by using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. Phenylacetylene (Merck) was purified by distillation. The starting complex $OsH_2Cl_2(P\textit{i}Pr_3)_2$ was prepared by a published method.[15]

Physical Measurements. NMR spectra were recorded on a Varian 200 XL or on a Varian UNITY 300 spectrophotometer at room temperature. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ (^1H and $^{13}C\{^1H\}$ NMR spectra) and 85% H_3PO_4 ($^{31}P\{^1H\}$ NMR spectra). Coupling constants *J* and *N* ($N = J(PH) + J(P'H)$) are given in hertz. Infrared spectra

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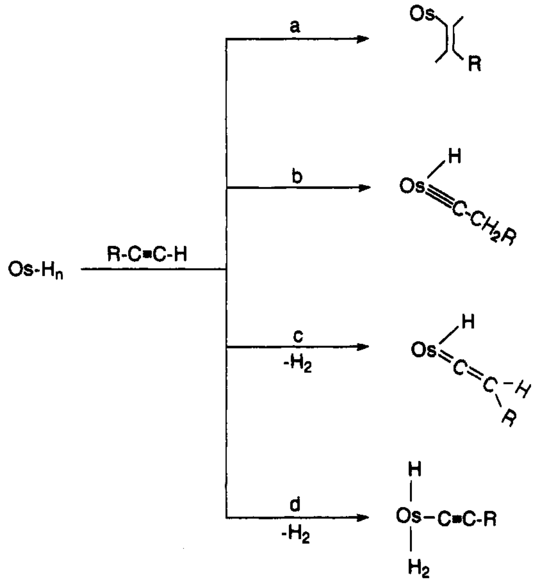
Scheme I[a]



[a] Legend: Os–H$_n$ = (a) $OsHCl(CO)(P\textit{i}Pr_3)_2$, (b) $OsH_2Cl_2(P\textit{i}Pr_3)_2$, (c) $OsH_3(\eta^2\text{-}O_2CCH_3)(P\textit{i}Pr_3)_2$, (d) $OsH_4(CO)(P\textit{i}Pr_3)_2$.

were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls on polyethylene sheets. C, H analyses were carried out on a Perkin-Elmer 240 microanalyzer.

Preparation of $OsH_3(\eta^2\text{-}O_2CCH_3)(P\textit{i}Pr_3)_2$ (1). A suspension of $OsH_2Cl_2(P\textit{i}Pr_3)_2$ (150 mg, 0.26 mmol) in 10 mL of methanol was treated with potassium acetate (75.7 mg, 0.78 mmol). After it was stirred for 5 min, the solution was concentrated to dryness; then 10 mL of dichloromethane was added and the solution was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL; addition of methanol caused the precipitation of a yellow solid after storing at −78 °C for 3 h. The resulting yellow solid was decanted, washed with methanol, stored at −78 °C and dried in vacuo; yield 93 mg (63%). Anal. Calcd for $C_{20}H_{48}O_2OsP_2$: C, 41.96; H, 8.73. Found: C, 42.34; H, 9.01. IR (Nujol, cm^{-1}): ν(OsH) 2145, 2120; ν(OCO) 1540, 1460. ^{1}H NMR (300 MHz, C_6D_6): δ 1.97 (m, 6 H, PC*H*CH$_3$), 1.70 (s, 3 H, CH$_3$), 1.21 (dvt, N = 12.7, J(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$), −14.57 (t, J(PH) = 11.7 Hz, 3 H, OsH). ^{31}P{^{1}H} NMR (80.98 MHz, C_6D_6): δ 40.66 (s; q under off-resonance conditions).

Preparation of $OsH(\eta^2\text{-}O_2CCH_3)(C{=}CHPh)(P\textit{i}Pr_3)_2$ (2). A suspension of 1 (150 mg, 0.26 mmol) in 12 mL of toluene was treated with phenylacetylene (34.5 μL, 0.31 mmol). After it was stirred for 5 h, the solution was concentrated to dryness. Addition of methanol caused the precipitation of an orange solid. The resulting orange solid was decanted, washed with methanol, and dried in vacuo: yield 106 mg (60%). Anal. Calcd for $C_{28}H_{52}O_2OsP_2$: C, 49.97; H, 7.80. Found: C, 49.62; H, 8.47. IR (Nujol, cm^{-1}): ν(OsH) 2130; ν(OCO) 1555, 1460. ^{1}H NMR (300 MHz, C_6D_6): δ 7.25–6.83 (5 H, Ph), 2.59 (m, 6 H, PC*H*CH$_3$), 2.25 (t, 2 H, J(PH) = 2.5 Hz, 1 H, =CH), 1.67 (s, 3 H, CH$_3$), 1.33 (dvt, N = 13.3, J(HH) = 7.1 Hz, 18 H, PCHC*H*$_3$), 1.30 (dvt, N = 12.8, J(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$), −11.51 (t, J(PH) = 15.6 Hz, 1 H, OsH). ^{31}P{^{1}H} NMR (80.98 MHz, C_6D_6): δ 26.84 (s; d under off-resonance conditions). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 291.5 (t, J(PC) = 10.5 Hz, Os=C), 182.57 (s, OCO), 132.1, 123.25 and 122.03 (each s, Ph), 107.51 (t, J(PC) = 2.8 Hz, =CH), 25.32 (s, CH$_3$), 24.97 (vt, N = 23.9 Hz, PCHCH$_3$), 19.94 and 19.53 (both s, PCHCH$_3$).

Catalytic Study. The catalytic reaction was carried out under an atmosphere of argon in a 50-mL round-bottomed flask fitted with a condenser and provided with a serum cap. Phenylacetylene (34 mmol) in 10 mL of toluene was added to a solution of the catalyst (0.34 mmol) in 15 mL of toluene, and this mixture was stirred for 2 h at 111 °C. The process of the reaction was monitored by using a Perkin-Elmer 8900 gas chromatograph with a flame ionization detector and an FFAP on Chromosorb GHP 80/100 mesh (3.6 × $^1/_8$ in.) column at 130 °C. After 2 h the solvent was evaporated off, and the residual mixture was separated by column chromatography (silica gel 60, hexane) and was characterized by using a VG AutoSpec mass spectrometer connected to a Konik HRGC-3000C gas chromatograph. The ratio of isomers was determined by ^{1}H NMR in CDCl$_3$ of the organic mixture isolated by column chromatography.

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