Intermolecular Coupling of the Allenyl Ligand on Tungsten to form Hexa-1,5-diene aided by Triosmium Clusters

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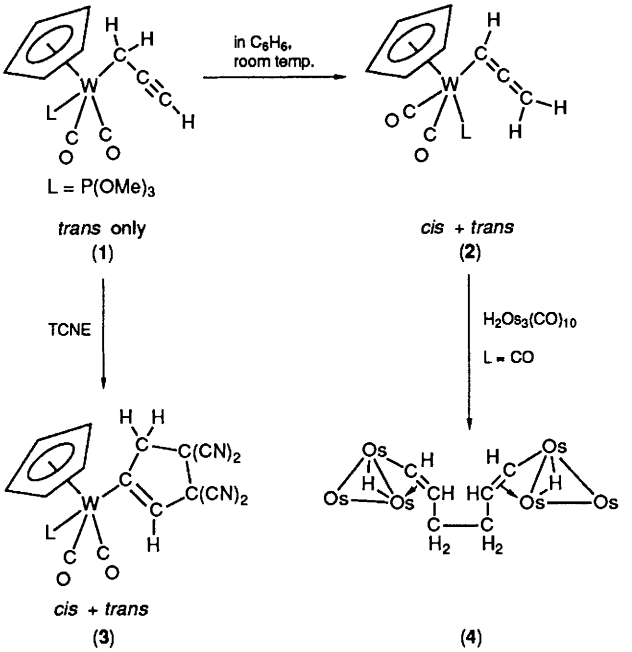
The propynyl ligand of the trimethyl phosphite substituted tungsten complex $[(\eta^5\text{-}C_5H_5)W(CO)_2\{P(OMe)_3\}(CH_2C{\equiv}CH)]$ is converted to an allenyl ligand at room temperature and the reaction of $[(\eta^5\text{–}C_5H_5)W(CO)_3(CH{=}C{=}CH_2)]$ with $[H_2Os_3(CO)_{10}]$ yields the coupling product $[H_2Os_6(CO)_{20}(C_6H_8)]$ (**4**); the structure of (**4**), established by *X*-ray crystallography, confirms the presence of a hexa-1,5-diene ligand with two alkene groups bound to two triosmium clusters in a μ,η^2-fashion.

The use of stoicheiometric reagents for carbon–carbon bond formation is a promising synthetic method. Particular attention has been given to research on π-allyl ligands in nickel complexes; *e.g.*, hexa-1,5-diene formation or formation of ketones by CO insertion during coupling.[1—3] However, the alternative σ-bonding mode of the allenyl ligand in metal complexes has been studied in relatively few cases.[4—6] We recently reported that the reaction of an allenyl tungsten complex and the iron methylene complex $[Fe_2(CO)_8(CH_2)]$ yields a tungsten-substituted trimethylenemethane iron com



plex.[7] To understand further the mechanism of the formation of the σ-allenyl ligand, and its chemical reactivity, we report herein the preparation of the phosphite-substituted tungsten propynyl complex [(η^5-Cp)W(CO)$_2${P(OMe)$_3$}(CH$_2$C≡CH)] **(1)** (Cp = cyclopentadienyl), its transformation to the allenyl complex [(η^5-Cp)W(CO)$_2${P(OMe)$_3$}(CH=C=CH$_2$)] **(2)**, and the reaction of [$H_2Os_3(CO)_{10}$] with [(η^5-Cp)W(CO)$_3$-(CH=C=CH$_2$)] to yield, to the best of our knowledge, the first example of an allenyl coupled product.

The *trans*- and *cis*-phosphite-substituted tungsten propynyl complexes [(η^5-Cp)W(CO)$_2${P(OMe)$_3$}(CH$_2$C≡CH)] **(1)**,† in

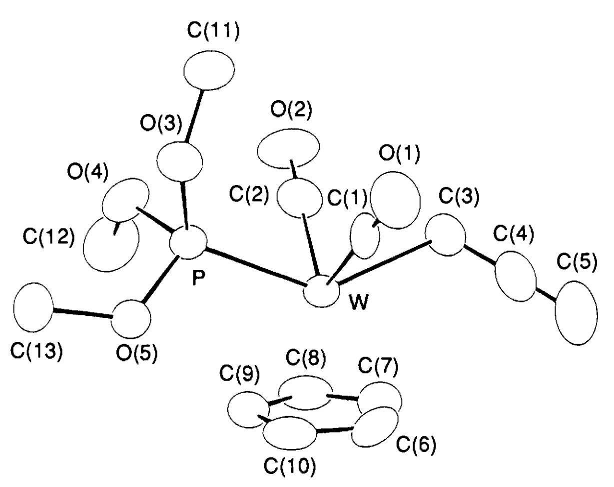


Figure 1. Molecular structure of [(Cp)W(CO)$_2${P(OMe)$_3$}(C$_3$H$_3$)] **(1)**. Important bond lengths (Å) and bond angles (°): W–P, 2.385(2); W–C(1), 1.955(5); W–C(2), 1.958(6); W–C(3), 2.348(6); C(3)–C(4), 1.428(10); C(4)–C(5), 1.174(11). C(3)–C(4)–C(5), 178.9(7); P–W–C(1), 79.93(16); P–W–C(2), 78.80(19); P–W–C(3), 137.78(16).

Table 1. P–H Coupling constants (*J*/Hz) in **(1)**, **(2)**, and **(3)**.

	(1)		(2)		(3)
Compound	Cp	α-CH$_2$	Cp	α-CH	Cp
trans	1.5	4.1	1.5	2.8	1.4
cis	0	8.3	0	13.8	0

a 12:1 ratio, were prepared by the reaction of prop-2-ynyl bromide with [(η^5-Cp)(CO)$_2${P(OMe)$_3$}W]$^-$. The anion was prepared by the reduction of the mercury derivative of the tungsten dimer [{(η^5-Cp)(CO)$_2${P(OMe)$_3$}W}$_2$Hg].[8] The *trans*-isomer of complex **(1)**, isolated by recrystallization, was converted to a *cis*- and *trans*-isomeric mixture (3:1) of the allenyl complex [(η^5-Cp)W(CO)$_2${P(OMe)$_3$}(CH=C=CH$_2$)] **(2)** in a relatively high NMR yield (Scheme 1). The fact that a single *trans*-isomer is transformed to *trans*- and *cis*-isomers provides further evidence that such a transformation may proceed through tungsten migration instead of a 1,3 hydrogen shift.[9] In the corresponding non-phosphite substituted complex, such a transformation has been observed,[7] at a faster rate. From the rate constant of the transformation, the 1,3 hydrogen shift pathway is unlikely.[10]

For complex *trans*-**(1)**, the Cp ^{1}H NMR signal is a doublet with $J_{H(Cp)\text{-}P}$ 1.5 Hz, and the α proton shows a relatively small coupling constant, $J_{H\text{-}P}$ 4.1 Hz. In contrast, the Cp resonance of *trans*-**(1)** shows the correct configuration.‡ The molecular structure and selected metrical data are presented in Figure 1. of *trans*-**(1)** shows the correct configuration. The molecular structure and selected metrical data are presented in Figure 1. The geometry around the tungsten is typical for a piano stool complex. The structural assignments of the *cis*- and *trans*-isomers of **(2)** are based on their NMR data; in the

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† *Spectroscopic data*: *trans*-**(1)**: ^{1}H NMR (C_2D_6CO): δ 5.27 (d, 5H, Cp, $J_{P\text{-}H}$ 1.5 Hz), 3.60 [d, 9H, P(OMe)$_3$, $J_{P\text{-}H}$ 11.7 Hz], 1.75 (dd, 2H, CH$_2$, $J_{P\text{-}H}$ 4.1, $J_{H\text{-}H}$ 2.8 Hz), and 2.08 (t, 1H, $J_{H\text{-}H}$ 2.8 Hz); ^{13}C NMR (C_6D_6): δ 226.3 (d, $J_{C\text{-}P}$ 25 Hz, 2 CO) 95.5 (s, ≡C–C), 91.1 (s, Cp), 65.8 (s, ≡C–H), 52.5 (d, $J_{C\text{-}P}$ 3.8 Hz, OMe), and −33.0 (d, $J_{C\text{-}P}$ 11.6 Hz, W–CH); ^{31}P NMR (C_2D_6CO): 160.7 ($J_{W\text{-}P}$ 384.7 Hz); ν_{CO} (CHCl$_3$): 1941m, and 1854s cm^{-1}; *m/z* 470 (M^+, ^{186}W), 431 (M^+ −C$_3$H$_3$), 414 (M^+ −2 CO), and 346 [M^+ −P(OMe)$_3$].

cis-**(1)**: ^{1}H NMR (C_2D_6CO): δ 5.46 (s, 5H, Cp), 3.60 [d, 9H, P(OMe)$_3$, $J_{P\text{-}H}$ 11.8 Hz], 2.12 (td, 1H, CH, $J_{P\text{-}H}$ 0.6, $J_{H\text{-}H}$ 2.9 Hz), 1.59 (dd, 1H, $J_{P\text{-}H}$ 8.3, $J_{H\text{-}H}$ 2.9 Hz), and 1.54 (dd, 1H, $J_{P\text{-}H}$ 7.9, $J_{H\text{-}H}$ 2.9 Hz); ^{31}P NMR (C_2D_6CO): 152.1 ($J_{W\text{-}P}$ 474.7 Hz).

trans-**(2)**: ^{1}H NMR (CDCl$_3$): δ 6.01 (dt, 1H, CH, $J_{P\text{-}H}$ 2.8, $J_{H\text{-}H}$ 6.5 Hz), 4.78 (d, 5H, Cp, $J_{P\text{-}H}$ 1.5 Hz), 4.26 (dd, 2H, CH$_2$, $J_{P\text{-}H}$ 2.1, $J_{H\text{-}H}$ 6.5 Hz), and 3.23 [d, 9H, P(OMe)$_3$, $J_{P\text{-}H}$ 11.5 Hz].

cis-**(2)**: ^{1}H NMR (CDCl$_3$): δ 5.68 (dt, 2H, CH, $J_{P\text{-}H}$ 13.8, $J_{H\text{-}H}$ 6.6 Hz), 4.87 (s, 5H, Cp), 4.09 (dd, 2H, CH$_2$, $J_{P\text{-}H}$ 2.0, $J_{H\text{-}H}$ 6.6 Hz), 4.06 (dd, 2H, CH$_2$, $J_{P\text{-}H}$ 2.0, $J_{H\text{-}H}$ 6.6 Hz), and 3.23 [d, 9H, P(OMe)$_3$, $J_{P\text{-}H}$ 11.5 Hz].

trans-**(3)**: ^{1}H NMR (CDCl$_3$): δ 5.10 (t, 1H, CH, $J_{H\text{-}H}$ 1.6 Hz), 4.51 (d, 5H, Cp, $J_{P\text{-}H}$ 1.4 Hz), 3.15 (d, 2H, CH$_2$, $J_{H\text{-}H}$ 1.6 Hz), and 3.08 [d, 9H, P(OMe)$_3$, $J_{P\text{-}H}$ 11.5 Hz]; ^{13}C NMR (C_2D_6CO): 225.3 (d, $J_{C\text{-}P}$ 29.5 Hz, 2 × CO), 152.7 (d, $J_{C\text{-}P}$ 5 Hz, W–C), 124.2 (d, $J_{C\text{-}P}$ 1.5 Hz, =CH), 111.8, 110.8 (4 × CN), 90.7 (s, Cp), 59.6 (d, $J_{C\text{-}P}$ 1.7 Hz, CH$_2$), 53.4 (d, $J_{C\text{-}P}$ 6.5 Hz, POMe$_3$), 51.0, 45.6 [s, 2C(CN)$_2$]; ^{31}P NMR (C_6D_6): 152.7 ($J_{W\text{-}P}$ 351.3 Hz); ν_{CO} (CHCl$_3$): 1957m and 1973s cm^{-1}; *m/z* 598 (M^+), 570 (M^+ −CO), 542 (M^+ −2CO), 442, (M^+ −CO −L), and 414 (M^+ −2CO −L).

cis-**(3)**: ^{1}H NMR (CDCl$_3$): δ 4.68 (t, 1H, CH, $J_{H\text{-}H}$ 1.6 Hz), 4.55 (s, 5H, Cp), 2.57 (d, 2H, CH$_2$, $J_{H\text{-}H}$ 1.6 Hz), and 3.55 [d, 9H, P(OMe)$_3$, $J_{P\text{-}H}$ 12.6 Hz]; ^{31}P NMR (C_6D_6): 140.2.

(4): ν_{CO} (C$_2$Cl$_4$): 2100w, 2081m, 2071m, 2059s, 2052s, 2021s, 2011s, 2003s 1998m,sh, 1987w,sh), and 1975w cm^{-1}.

‡ *Crystal data* for **(1)**: $C_{13}H_{17}O_5PW$, M = 468.1, a = 8.092(3), b = 9.721(1), c = 11.222(6) Å, α = 98.38(3), β = 97.77(4), γ = 114.33(2)°, V = 776.9(5) Å^3, space group $P\bar{1}$, Z = 2, D_c = 2.001 g cm^{-3}, μ(Mo-K_α = 7.71 mm^{-1}, F(000) = 448, λ = 0.7107 Å. The structure was solved by Patterson and Fourier methods. Of the 2741 unique reflections measured, 2508 were considered significant [$I > 2\sigma(I)$] and used in the refinement with 182 parameters to give R = 0.023 and R_w = 0.021; weights were calculated from counting statistics.

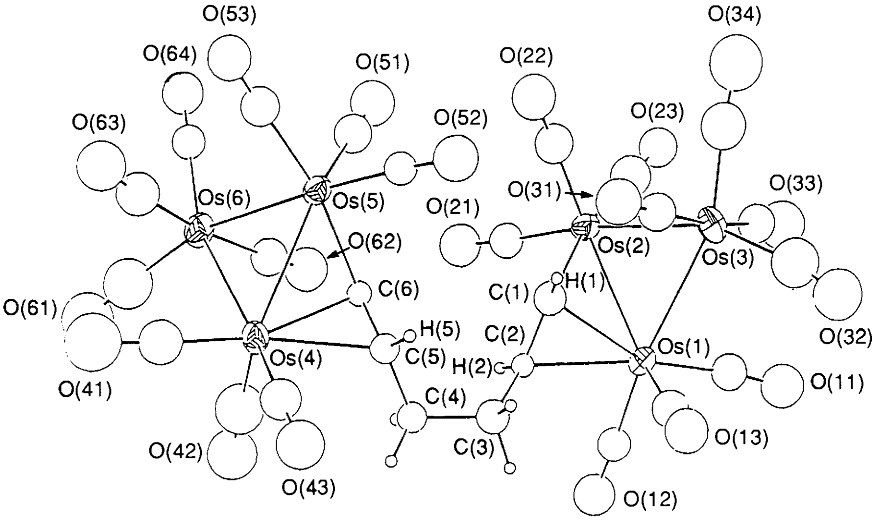

Figure 2. Molecular structure of $[H_2Os_6(CO)_{20}(C_6H_8)]$ (**4**). Important bond lengths (Å) and bond angles (°): Os(1)–Os(2), 2.835(2); Os(1)–Os(3), 2.898(2); Os(2)–Os(3), 2.839(2); Os(4)–Os(5), 2.834(2); Os(4)–Os(6), 2.900(2); Os(5)–Os(6), 2.844(2); C(4)–C(5), 1.47(5); Os(2)–C(1), 2.12(3); C(5)–C(6), 1.33(4); Os(4)–C(6), 2.26(3); Os(4)–C(5), 2.38(3); Os(5)–C(6), 2.15(3); C(1)–C(2), 1.37(4); C(2)–C(3), 1.47(4); C(3)–C(4), 1.50(5). C(2)–C(3)–C(4), 114(3); C(3)–C(4)–C(5), 110(3); C(4)–C(5)–C(6), 124(3); Os(4)–C(6)–Os(5), 79.9(10); Os(4)–C(6)–C(5), 78.4(19); Os(5)–C(6)–C(5), 123.3(22); Os(1)–C(1)–Os(2), 80.5(12); Os(1)–C(1)–C(2), 76.3(20); Os(2)–C(1)–C(2), 121.8(24); C(1)–C(2)–C(3), 123(3).

trans-isomer, the Cp resonance is a doublet with $J_{H(Cp)\text{-}P}$ 1.5 Hz and the coupling constant between the P and α proton is 2.8 Hz. For the *cis*-isomer, the Cp resonance is a singlet and the coupling constant $J_{P\text{-}H\alpha}$ is 13.8 Hz. Reaction of *trans*-(**1**) with tetracyanoethylene (TCNE) also gave the [3 + 2] cyclization[12] product $[(\eta^5\text{-}Cp)W(CO)_2\{P(OMe)_3\}\{C_5H_3(CN)_4\}]$ (**3**). Again, such a reaction involves the migration of the W atom, and therefore the *trans*- and *cis*-isomers of complex (**3**) were both observed in the NMR spectrum.

The non-phosphite substituted tungsten allenyl complex $[(\eta^5\text{-}Cp)W(CO)_3(CH{=}C{=}CH_2)]$ (**2a**) was treated with $H_2Os_3(CO)_{10}$ at room temperature to yield the coupling product $[H_2Os_6(CO)_{20}(C_6H_8)]$ (**4**) after column chromatography. Two allenyl ligands coupled intermolecularly to form a hexa-1,5-diene ligand with two double bonds bound to two triosmium clusters in a μ,η^2-fashion. Several intermediates were observed when the reaction was carried out in an NMR tube. Identification of these species is currently underway. An *X*-ray crystallographic study established the structure of complex (**4**) (Figure 2).§ In (**4**), the two Os atoms attain an 18 electron configuration by co-ordination of two μ–η^2 unsaturated groups of the newly formed hexa-1,5-diene. The length of the two double bonds in the hexadiene is 133 and 137 pm. The alkene protons are in a *trans*-configuration. Hydride ligands were not located in the difference map and, based on the 18 electron rule, were presumably between the Os metal atoms bridged by the two alkene ligands.

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§ *Crystal data* for (**4**): $C_{26}H_{10}O_{20}Os_6$, M = 1783.5, monoclinic, a = 14.448(7), b = 13.689(4), c = 19.224(4) Å, β = 107.14(3)°, V = 3633(2) Å^3, space group $P2_1/c$, Z = 4, D_c = 3.257 g cm^{-3} μ(Mo-K_α) = 21.0 mm^{-1}, F(000) = 3119, λ = 0.7107 Å. The structure was solved by Patterson and Fourier methods. Of the 4748 unique reflections measured, 2860 were considered significant [$I > 2\sigma(I)$] and used in the refinement with 240 parameters to give R = 0.054 and R_w = 0.048; weights were calculated from counting statistics. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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