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 $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\text{CH}_2\text{C}\equiv\text{CH})]$ is converted to an allenyl ligand at room temperature and the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{CH}=\text{C}=\text{CH}_2)]$ with $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ yields the coupling product $[\text{H}_2\text{Os}_6(\text{CO})_{20}(\text{C}_6\text{H}_8)]$ (**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 stoichiometric 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 $[\text{Fe}_2(\text{CO})_8(\text{CH}_2)]$ 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 $[(\eta^5\text{-Cp})\text{W}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\text{CH}_2\text{C}\equiv\text{CH})]$ (1) (Cp = cyclopentadienyl), its transformation to the allenyl complex $[(\eta^5\text{-Cp})\text{W}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\text{CH}=\text{C}=\text{CH}_2)]$ (2), and the reaction of $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ with $[(\eta^5\text{-Cp})\text{W}(\text{CO})_3(\text{CH}=\text{C}=\text{CH}_2)]$ 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 $[(\eta^5\text{-Cp})\text{W}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\text{CH}_2\text{C}\equiv\text{CH})]$ (1),[†] in

[†] Spectroscopic data: *trans*-(1): ^1H NMR ($\text{C}_2\text{D}_6\text{CO}$): δ 5.27 (d, 5H, Cp, $J_{\text{P-H}}$ 1.5 Hz), 3.60 [d, 9H, $\text{P}(\text{OMe})_3$, $J_{\text{P-H}}$ 11.7 Hz], 1.75 (dd, 2H, CH_2 , $J_{\text{P-H}}$ 4.1, $J_{\text{H-H}}$ 2.8 Hz), and 2.08 (t, 1H, $J_{\text{H-H}}$ 2.8 Hz); ^{13}C NMR (C_6D_6): δ 226.3 (d, $J_{\text{C-P}}$ 25 Hz, 2 CO) 95.5 (s, $\equiv\text{C-C}$), 91.1 (s, Cp), 65.8 (s, $\equiv\text{C-H}$), 52.5 (d, $J_{\text{C-P}}$ 3.8 Hz, OMe), and -33.0 (d, $J_{\text{C-P}}$ 11.6 Hz, W-CH); ^{31}P NMR ($\text{C}_2\text{D}_6\text{CO}$): 160.7 ($J_{\text{W-P}}$ 384.7 Hz); ν_{CO} (CHCl_3): 1941m, and 1854s cm^{-1} ; m/z 470 (M^+ , ^{186}W), 431 ($M^+ - \text{C}_3\text{H}_3$), 414 ($M^+ - 2\text{CO}$), and 346 [$M^+ - \text{P}(\text{OMe})_3$].

cis-(1): ^1H NMR ($\text{C}_2\text{D}_6\text{CO}$): δ 5.46 (s, 5H, Cp), 3.60 [d, 9H, $\text{P}(\text{OMe})_3$, $J_{\text{P-H}}$ 11.8 Hz], 2.12 (td, 1H, CH, $J_{\text{P-H}}$ 0.6, $J_{\text{H-H}}$ 2.9 Hz), 1.59 (dd, 1H, $J_{\text{P-H}}$ 8.3, $J_{\text{H-H}}$ 2.9 Hz), and 1.54 (dd, 1H, $J_{\text{P-H}}$ 7.9, $J_{\text{H-H}}$ 2.9 Hz); ^{31}P NMR ($\text{C}_2\text{D}_6\text{CO}$): 152.1 ($J_{\text{W-P}}$ 474.7 Hz).

trans-(2): ^1H NMR (CDCl_3): δ 6.01 (dt, 1H, CH, $J_{\text{P-H}}$ 2.8, $J_{\text{H-H}}$ 6.5 Hz), 4.78 (d, 5H, Cp, $J_{\text{P-H}}$ 1.5 Hz), 4.26 (dd, 2H, CH_2 , $J_{\text{P-H}}$ 2.1, $J_{\text{H-H}}$ 6.5 Hz), and 3.23 [d, 9H, $\text{P}(\text{OMe})_3$, $J_{\text{P-H}}$ 11.5 Hz].

cis-(2): ^1H NMR (CDCl_3): δ 5.68 (dt, 2H, CH, $J_{\text{P-H}}$ 13.8, $J_{\text{H-H}}$ 6.6 Hz), 4.87 (s, 5H, Cp), 4.09 (dd, 2H, CH_2 , $J_{\text{P-H}}$ 2.0, $J_{\text{H-H}}$ 6.6 Hz), 4.06 (dd, 2H, CH_2 , $J_{\text{P-H}}$ 2.0, $J_{\text{H-H}}$ 6.6 Hz), and 3.23 [d, 9H, $\text{P}(\text{OMe})_3$, $J_{\text{P-H}}$ 11.5 Hz].

trans-(3): ^1H NMR (CDCl_3): δ 5.10 (t, 1H, CH, $J_{\text{H-H}}$ 1.6 Hz), 4.51 (d, 5H, Cp, $J_{\text{P-H}}$ 1.4 Hz), 3.15 (d, 2H, CH_2 , $J_{\text{H-H}}$ 1.6 Hz), and 3.08 [d, 9H, $\text{P}(\text{OMe})_3$, $J_{\text{P-H}}$ 11.5 Hz]; ^{13}C NMR ($\text{C}_2\text{D}_6\text{CO}$): 225.3 (d, $J_{\text{C-P}}$ 29.5 Hz, 2 $\times$ CO), 152.7 (d, $J_{\text{C-P}}$ 5 Hz, W-C), 124.2 (d, $J_{\text{C-P}}$ 1.5 Hz, $=\text{CH}$), 111.8, 110.8 (4 $\times$ CN), 90.7 (s, Cp), 59.6 (d, $J_{\text{C-P}}$ 1.7 Hz, CH_2), 53.4 (d, $J_{\text{C-P}}$ 6.5 Hz, POMe_3), 51.0, 45.6 [s, 2C(CN) $_2$]; ^{31}P NMR (C_6D_6): 152.7 ($J_{\text{W-P}}$ 351.3 Hz); ν_{CO} (CHCl_3): 1957m and 1973s cm^{-1} ; m/z 598 (M^+), 570 ($M^+ - \text{CO}$), 542 ($M^+ - 2\text{CO}$), 442, ($M^+ - \text{CO} - \text{L}$), and 414 ($M^+ - 2\text{CO} - \text{L}$).

cis-(3): ^1H NMR (CDCl_3): δ 4.68 (t, 1H, CH, $J_{\text{H-H}}$ 1.6 Hz), 4.55 (s, 5H, Cp), 2.57 (d, 2H, CH_2 , $J_{\text{H-H}}$ 1.6 Hz), and 3.55 [d, 9H, $\text{P}(\text{OMe})_3$, $J_{\text{P-H}}$ 12.6 Hz]; ^{31}P NMR (C_6D_6): 140.2.

(4): ν_{CO} (C_2Cl_4): 2100w, 2081m, 2071m, 2059s, 2052s, 2011s, 2003s 1998m,sh, 1987w,sh), and 1975w cm^{-1} .

Figure 1. Molecular structure of $[(\text{Cp})\text{W}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\text{C}_3\text{H}_3)]$ (1). Important bond lengths ($\text{\AA}$) and bond angles ($^\circ$): 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).

Compound	(1)		(2)		(3)
	Cp	$\alpha\text{-CH}_2$	Cp	$\alpha\text{-CH}$	Cp
<i>trans</i>	1.5	4.1	1.5	2.8	1.4
<i>cis</i>	0	8.3	0	13.8	0

a 12:1 ratio, were prepared by the reaction of prop-2-ynyl bromide with $[(\eta^5\text{-Cp})(\text{CO})_2\{\text{P}(\text{OMe})_3\}\text{W}]^-$. The anion was prepared by the reduction of the mercury derivative of the tungsten dimer $[(\eta^5\text{-Cp})(\text{CO})_2\{\text{P}(\text{OMe})_3\}\text{W}]_2\text{Hg}$.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 $[(\eta^5\text{-Cp})\text{W}(\text{CO})_2\{\text{P}(\text{OMe})_3\}(\text{CH}=\text{C}=\text{CH}_2)]$ (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 ^1H NMR signal is a doublet with $J_{\text{H(Cp)-P}}$ 1.5 Hz, and the α proton shows a relatively small coupling constant, $J_{\text{H-P}}$ 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

[‡] Crystal data for (1): $\text{C}_{13}\text{H}_{17}\text{O}_5\text{PW}$, $M = 468.1$, $a = 8.092(3)$, $b = 9.721(1)$, $c = 11.222(6)$ $\text{\AA}$, $\alpha = 98.38(3)$, $\beta = 97.77(4)$, $\gamma = 114.33(2)^\circ$, $V = 776.9(5)$ $\text{\AA}^3$, space group $P\bar{1}$, $Z = 2$, $D_c = 2.001$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 7.71$ mm^{-1} , $F(000) = 448$, $\lambda = 0.7107$ $\text{\AA}$. 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 $[\text{H}_2\text{Os}_6(\text{CO})_{20}(\text{C}_6\text{H}_8)]$ (4). Important bond lengths (Å) and bond angles ($^\circ$): 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 $J_{\text{H}(\text{Cp})-\text{P}}$ 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 $J_{\text{P}-\text{H}\alpha}$ is 13.8 Hz. Reaction of *trans*-(1) with tetracyanoethylene (TCNE) also gave the [3 + 2] cyclization¹² product $[(\eta^5\text{-Cp})\text{W}(\text{CO})_2\{\text{P}(\text{OMe})_3\}\{\text{C}_5\text{H}_3(\text{CN})_4\}]$ (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 $[(\eta^5\text{-Cp})\text{W}(\text{CO})_3(\text{CH}=\text{C}=\text{CH}_2)]$ (2a) was treated with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ at room temperature to yield the coupling product $[\text{H}_2\text{Os}_6(\text{CO})_{20}(\text{C}_6\text{H}_8)]$ (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 $\mu\text{-}\eta^2$ 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): $\text{C}_{26}\text{H}_{10}\text{O}_{20}\text{Os}_6$, $M = 1783.5$, monoclinic, $a = 14.448(7)$, $b = 13.689(4)$, $c = 19.224(4)$ Å, $\beta = 107.14(3)^\circ$, $V = 3633(2)$ Å³, space group $P2_1/c$, $Z = 4$, $D_c = 3.257$ g cm⁻³ ($\mu\text{-K}\alpha$) = 21.0 mm⁻¹, $F(000) = 3119$, $\lambda = 0.7107$ 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.