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A Heteronuclear Vinylacetylide Cluster as a Precursor to Allenylidene and Metallacyclopentadienyl Cluster Compounds. X-ray Structures of $Cp^*WRe_2(CO)_8(\mu\text{-}OMe)(C=C=CMe_2)$ and $Cp^*WRe_2(CO)_7(\mu\text{-}H)(CHCHCMeCH)$

Puu-Shum Cheng,[†] Yun Chi,[*,†] Shie-Ming Peng,[*,‡] and Gene-Hsiang Lee[‡]

Departments of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, ROC, and National Taiwan University, Taipei 10764, Taiwan, ROC

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Summary: Treatment of the vinylacetylide complex $Cp^*WRe_2(CO)_9[C\equiv CC(Me)=CH_2]$ *(**1**) with alcohols and with dihydrogen in refluxing toluene solution afforded allenylidene complexes* $Cp^*WRe_2(CO)_8(\mu\text{-}OR)(C=C=CMe_2)$*, R = Me (**2a**), R = Et (**2b**), and R = Ph (**2c**), and formally unsaturated metallacyclopentadienyl complexes* $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCHC(Me)CH]$ *(**3a,b**), respectively. Evidence of fluxionality of allenylidene complexes **2** in solution is presented.*

Cluster species containing allenylidene[1] or cumulene[2] fragments can be regarded as models of reactive intermediates formed from surface carbides in the catalytic heterogeneous reduction of carbon monoxide.[3] So far, the synthetic methodology for this class of polynuclear compounds is not well developed,[4] although the preparation of mononuclear[5] and dinuclear[6] complexes has been extensively examined. We report here a facile two-step preparation of heteronuclear cluster compounds containing bridging allenylidene ligands. The dynamics of the allenylidene ligands may provide crucial information regarding the fluxionality of related vinylidene and tilted ketenylidene fragments on trinuclear cluster compounds.[7]

Treatment of $Cp^*W(CO)_3[C\equiv CC(Me)=CH_2]$[8] with the dirhenium complex $Re_2(CO)_8(NCMe)_2$[9] in refluxing toluene (110 °C, 30 min) provided a trinuclear, red-orange vinylacetylide complex, $Cp^*WRe_2(CO)_9[C\equiv CC(Me)=CH_2]$ (**1**), in 31% yield. This cluster compound was characterized initially by spectroscopic methods.[10] The symmetric structure of **1** was evident from the ^{13}C NMR spectrum, which showed one W–CO and four Re–CO signals at δ 209.3 (J_{W-C} = 171 Hz), 195.4, 189.2, 187.2, and 185.7 in a ratio 2:2:2:1:2. The C_α and C_β resonances of the acetylide ligand appear at 160.8 (J_{W-C} = 134 Hz) and 94.7 (J_{W-C} = 24 Hz), which are consistent with a $\mu_3\text{-}\eta^2$ bonding mode.[11] X-ray diffraction measurements[12] reveal the above bonding features and suggest the compound's structure (Scheme I) to be similar to that of the symmetric, trinuclear acetylide complexes;[13] the acetylide ligand is perpendicular to the unique Re–Re bond. In addition, because a Re atom contains one electron less than Ru atoms in $CpWRu_2(CO)_8(C\equiv CPh)$,[13b] the WRe_2 complex possesses an extra bridging CO group on the Re–Re edge to maintain an 18-electron shell for the rhenium atoms.

Heating of vinylacetylide compound **1** in refluxing toluene with alcohol in large excess gave the brown allenylidene clusters $Cp^*WRe_2(CO)_8(\mu\text{-}OR)(C=C=CMe_2)$, R = Me (**2a**), R = Et (**2b**), R = Ph (**2c**), after TLC separation.[14] An X-ray diffraction study of **2a** was carried out to confirm their identities.[15] As presented in Figure 1, the molecule adopts an open-edge triangular geometry, in which the methoxide ligand bridges both Re atoms separated by a distance 3.3659 (7) Å. There is no direct bonding between these Re atoms because this Re–Re contact is much larger than the Re–Re distance of **1** (2.829–

[†] National Tsing Hua University.

[‡] National Taiwan University.

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(10) Spectral data for **1**: MS (FAB, ^{184}W, ^{187}Re), *m/z* 1010 (M^+); IR (C_6H_{12}) ν(CO), 2064 (m), 2025 (vs), 1987 (s, sh), 1974 (vs), 1950 (w), 1935 (w), 1891 (br, vw) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 5.35 (s, 1H, $C=CH_2$), 5.19 (s, 1H, $C=CH_2$), 2.31 (s, 3H, OMe), 2.22 (s, 15H, C_5Me_5); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) CO, δ 209.3 (J_{W-C} = 171 Hz), 195.4 (2C, br), 189.2 (2C, br), 187.2 (1C), 185.7 (2C, br); δ 160.8 (J_{W-C} = 134 Hz, $\mathit{C}\equiv CC=CH_2Me$), 140.6 ($C\equiv C\mathit{C}=CH_2Me$), 118.2 ($C\equiv CC=\mathit{C}H_2Me$), 103.0 ($\mathit{C}_5Me_5$), 94.7 ($J_{W-C}$ = 24 Hz, $C\equiv\mathit{C}C=CH_2Me$), 27.3 ($CH_3$), 12.1 ($C_5Me_5$). Anal. Calcd for $C_{24}H_{20}O_9Re_2W$: C, 28.58; H, 2.00. Found: C, 28.56; H, 2.01.

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(12) Crystal data for **1**: $C_{24}H_{20}O_9Re_2W$, M = 1008.7, monoclinic, space group Cc, a = 36.091 (9) b = 14.277 (4), c = 17.239 (3) Å, β = 115.26 (3)°, V = 8033 (3) $Å^3$, Z = 12, D_c = 2.503 mg/cm^3, $F(000)$ = 5520, μ(Mo Kα) = 13.57 mm^{-1}; 7054 unique reflections measured; 5504 reflections with $I > 2\sigma(I)$ used in refinement. R_F = 0.036 and R_w = 0.030, with GOF = 1.88.

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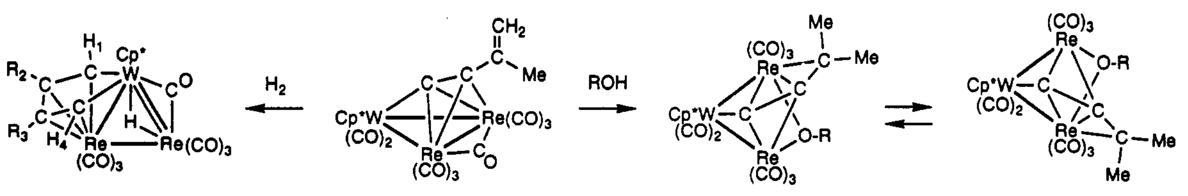
Scheme I



(3a), R_2 = H, R_3 = Me

(3b), R_2 = Me, R_3 = H

(1)

(2a), R = Me

(2b), R = Et

(2c), R = Ph

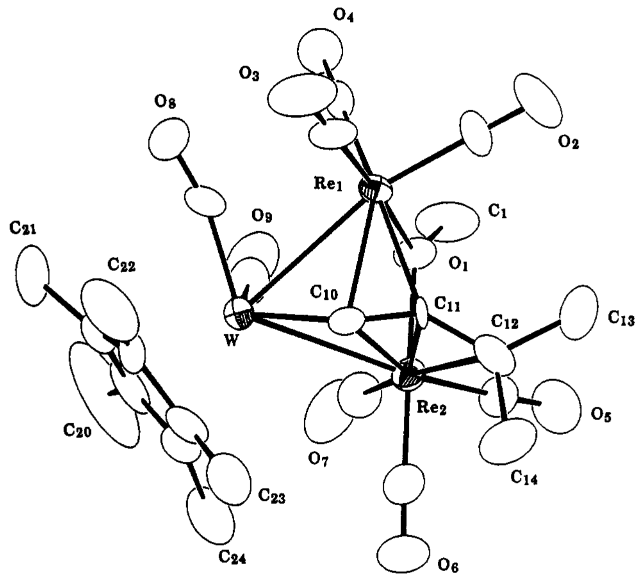


Figure 1. Molecular structure of **2a** and the atomic numbering scheme. Selected bond lengths (Å): W–Re(1) = 3.0812 (8), W–Re(2) = 3.1961 (8), Re(1)–Re(2) = 3.3659 (7), Re(1)–O(1) = 2.127 (7), Re(2)–O(1) = 2.115 (7), C(1)–O(1) = 1.38 (2), W–C(10) = 1.99 (1), Re(1)–C(10) = 2.24 (1), Re(2)–C(10) = 2.23 (1), Re(1)–C(11) = 2.28 (1), Re(2)–C(11) = 2.31 (1), Re(2)–C(12) = 2.54 (1), C(10)–C(11) = 1.27 (2), C(11)–C(12) = 1.35(2). Selected bond angles (deg): W–C(10)–C(11) = 167.0 (8), C(10)–C(11)–C(12) = 143 (1), C(13)–C(12)–C(14) = 110 (1), Re(1)–C(10)–Re(2) = 97.7 (4), Re(1)–C(11)–Re(2) = 94.3 (4), Re(1)–O(1)–Re(2) = 105.0 (3).

2.869 Å). This bond elongation has been observed in several triosmium clusters with bridging alkoxide ligand[16] and dirhenium alkoxide compounds as well.[17] For the allenylidene ligand, the C_3 chain forms an angle 143 (1)° with both α and β carbons connected to all three metal atoms; the γ carbon is linked to only one Re atom. The C(10)–C(11) distance (1.27 (2) Å) is slightly shorter than the C(11)–C(12) distance (1.35 (2) Å) but is comparable to the acetylide C_α–C_β distance in 1 (1.25–1.28 Å). Apparently, the C(10)–C(11) fragment has retained some contribution of acetylide triple-bond character. This structural feature is reminiscent of that found in several mono- and dinuclear allenylidene complexes.[18]

The solution dynamics of these WRe_2 allenylidene complexes are of particular interest. The ^1H NMR spectrum at 300 MHz shows the presence of two broad methyl resonances at 297 K for all three derivatives, in addition to the expected proton signals of alkoxide and Cp* ligands. These Me signals coalesce to a broad signal on increasing the temperature and turn to two sharp singlets when the temperature is lowered. The fluxional behavior is due to the parallel movement of the allenylidene ligand from one Re atom to the second (Scheme I), which exchanges the environment of nonequivalent methyl substituents, and is not coupled with the rotational motion of Cp*W(CO)$_2$ unit because the ^{13}C NMR spectrum of **2a** shows only one broad W–CO signal instead of two CO signals at even 223 K. For the ethoxide derivative **2b**, we also observed that the methylene quartet turned to a broad, featureless hump on lowering the temperature to 240 K. This broadening is attributed to the fact that the slow movement of the allenylidene ligand prevents the interchanging of the nonequivalent magnetic environments of the methylene protons. The variation of alkoxide ligand has little effect on the migration of allenylidene ligand since all these three compounds show very similar energy barrier of activation. For compound **2b**, we obtain a kinetic barrier ($\Delta G^{\ddagger}$ = 59 kJ/mol) by using the ^1H NMR data, $\Delta\nu$ = 86.8 Hz and T_c = 300 K, at 400 MHz.

On the other hand, treatment of 1 with molecular hydrogen generated not the expected hydrido–allenylidene complex $Cp^*WRe_2(CO)_8(\mu\text{-}H)(C{=}C{=}CMe_2)$ but instead an unsaturated, metallacyclopentadienyl cluster $Cp^*WRe_2(CO)_7(\mu\text{-}H)[CHCHC(Me)CH]$ as a mixture of two noninterchangeable isomers (**3a,b**) with a ratio 48:52.[19] The

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(14) Spectral data for **2a**: MS (FAB, ^{184}W, ^{187}Re), *m/z* 1014 (M^+); IR (C_6H_{12}) ν(CO), 2034 (m), 2010 (vs), 1974 (vs), 1937 (m), 1919 (s), 1901 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 2.87 (s, 3H, OMe), 2.63 (s, br, 3H, Me), 2.42 (s, br, 3H, Me), 2.25 (s, 15H, C_5Me_5); ^{13}C NMR (100 MHz, $CDCl_3$, 294K) CO, δ 215.9 (2C, J_{W-C} = 173 Hz), 200.4 (2C, br), 197.5 (4C, br); δ 186.7 (*C*CCMe$_2$, J_{W-C} = 163 Hz), 140.3 (C*C*CMe$_2$, J_{W-C} = 32 Hz), 116.1 (CC*C*Me$_2$), 106.1 (*C*$_5$Me$_5$), 70.9 (OMe), 36.2 (Me, br), 29.5 (Me, br), 11.9 (C_5Me_5). Anal. Calcd for $C_{24}H_{24}O_9Re_2W$: C, 28.46; H, 2.23. Found: C, 28.50; H, 2.46.

(15) Crystal data for **2a**: $C_{24}H_{24}O_9Re_2W$, M = 1012.73, monoclinic, space group $P2_1/c$, a = 16.496 (1), b = 15.863 (2), c = 10.409 (2) Å, β = 97.05 (1°), V = 2703.2 (7) Å^3, Z = 4, D_c = 2.489 mg/cm^3, $F(000)$ = 1856, μ(Mo Kα) = 13.44 mm^{-1}; 3524 unique reflections measured; 2772 reflections with $I > 2\sigma(I)$ used in refinement. R_F = 0.029 and R_w = 0.025, with GOF = 1.88.

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(19) Spectal data for **3**: MS (FAB, ^{184}W, ^{187}Re), *m/z* 956 (M^+); IR(CH_2Cl_2) ν(CO), 2037 (vs), 2002 (s), 1959 (vs, br), 1906 (w, br) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 6.53 (dd, J_{H-H} = 2.9 and 6.1 Hz, R_2, **a**), 6.43 (dd, J_{H-H} = 2.1 and 5.8 Hz, R_3, **b**), 6.10 (dd, J_{H-H} = 3.5 and 5.8 Hz, H_4, **b**), 5.97 (d, J_{H-H} = 6.1 Hz, H_1, **a**), 5.86 (t, J_{H-H} = 2.9 and 3.2 Hz, H_4, **a**), 5.71 (d, J_{H-H} = 2.1 Hz, H_1, **b**), 2.64 (s, Me, **a**), 2.62 (s, Me, **b**), 2.00 (s, C_5Me_5, **b**), 1.99 (s, C_5Me_5, **a**), −5.74 (d, J_{H-H} = 3.5 Hz, J_{W-H} = 99 Hz, **b**), −5.77 (d, J_{H-H} = 3.2 Hz, J_{W-H} = 99 Hz, **a**); ^{13}C NMR (100 MHz, THF-d_8, 294 K) CO, δ 238.1 (J_{W-C} = 126 Hz, **a**), 237.9 (J_{W-C} = 126 Hz, **b**), 201.2 (3C, **a** and **b**), 196.3 (1C, br, **a** and **b**), 191.9 (2C, br, **a** and **b**); δ 146.6 (CH, J_{W-C} = 64 Hz, **a**), 145.8 (CH, J_{W-C} = 67 Hz, **b**), 135.9 (CH, J_{W-C} = 65 Hz, **b**), 134.6 (CH, J_{W-C} = 67 Hz, **a**), 126.2 (*C*Me, **a**), 120.6 (*C*Me, **b**), 108.5 (CH, **a**), 106.3 (*C*$_5$Me$_5$, **a** and **b**), 103.7 (CH, **b**), 22.0 (Me, **b**), 21.9 (Me, **a**), 13.1 (C_5Me_5, **b**), 13.0 (C_5Me_5, **a**). Anal. Calcd for $C_{22}H_{22}O_7Re_2W$: C, 27.68; H, 2.32. Found: C, 27.56; H, 2.40.

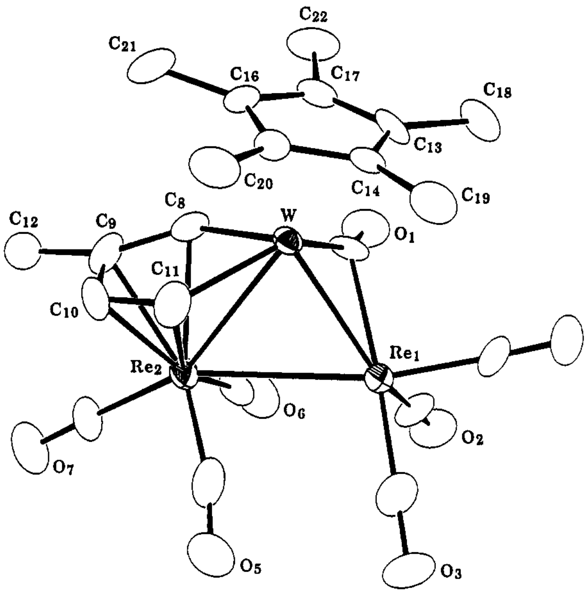

Figure 2. Molecular structure of **3** and the atomic numbering scheme. For clarity, only the methyl group of isomer **3b** is presented. Selected bond lengths (Å): Re(1)–Re(2) = 3.151 (2), Re(1)–W = 2.672 (1), Re(2)–W = 2.898 (1), W–C(1) = 2.00 (2), Re(1)–C(1) = 2.34 (2), W–C(8) = 2.12 (2), W–C(11) = 2.11 (2), Re(2)–C(8) = 2.33 (2), Re(2)–C(9) = 2.28 (2), Re(2)–C(10) = 2.26 (2), Re(2)–C(11) = 2.28 (2), C(8)–C(9) = 1.43 (3), C(9)–C(10) = 1.45 (4), C(10)–C(11) = 1.36 (3), C(9)–C(12) = 1.46 (5), C(10)–C(12′) = 1.39 (4).

molecular structure of **3**, determined from X-ray diffraction,[20] is presented in Figure 2. The structure corresponds to the valence-bond description shown in Scheme I, and the cluster has 46 cluster valence electrons. To our knowledge, this molecule provides a unique example of a cluster molecule containing both Re–W single and double bonds. The double-bond distance (2.672 (1) Å) is substantially shorter than the respective single-bond distance (2.898 (1) Å) and is comparable to the Re=Re length (2.723 Å) of dinuclear complex $Cp^*{}_2Re_2(CO)_4$[21] and the W=W length (2.747–2.592 Å) observed in several heterometallic clusters prepared by Stone and co-workers and by Chi and co-workers.[22] Another notable feature is the cyclic C_4H_3Me fragment, on which the C(10)–C(11) distance (1.36 (3) Å) is shorter than the C(8)–C(9) (1.43 (3) Å) and the C(9)–C(10) distances (1.45 (4) Å), and that the methyl substituent is disordered in its distribution between the C(9) and C(10) atoms. The bridging hydride was not located on the difference Fourier map, but we propose that it is associated with the short W=Re double bond in a position opposite to the unique bridging CO ligand, because of the tilted arrangement of CO ligands on Re(1) and the observation of large $^1J_{W-H}$ coupling and small $^3J_{H-H}$ coupling to the adjacent proton (H_4) in its ^1H NMR spectrum. The unambiguous assignment of the olefinic hydrogen atoms and bridging hydrides was achieved by means of the ^1H NMR decoupling technique and NOE experiments.

The mechanism for the formation of **3** is unclear at present; however, treatment of **1** with deuterium gas afforded a similar mixture, in which the protons occupy the bridging hydride position to the extent of 45% in both isomers, and the proton isotope amounts at positions H_1, R_2, and H_4 of **3a** and positions H_4, R_3, and H_1 of **3b** are approximately 25%, 5%, and 40%, respectively. This observation suggests that hydrogen isotope has a higher tendency to move to the α-carbon of the vinylacetylide ligand instead of the β-carbon and that the molecule has undergone rapidly multiple H–D scrambling since the total hydrogen isotope amounts attached to these four sites are equivalent to 1.15H, significantly less than the value (2H) anticipated for the simple D_2 addition. This H–D scrambling occurs prior to formation of **3**, as treatment of **3** with D_2 under identical conditions produces unnoticeable H–D exchange at all sites.

In summary, these experiments provide the first observations of the solution dynamics of allenylidene cluster compounds. The rhenium atoms play an important role in activating the O–H bond of alcohols and the H–H bond of molecular hydrogen via formation of strong rhenium–alkoxide interactions and the tungsten–rhenium multiple bond, respectively. In contrast, the related tungsten–ruthenium complex $Cp^*WRu_2(CO)_8[C{\equiv}CC(Me){=}CH_2]$ exhibits no such reactivity toward both alcohols and hydrogen gas under similar conditions. Research on isolation of the intermediate in the hydrogenation reaction and on reactions of these cluster compounds through introduction of small, unsaturated hydrocarbon molecules is in progress.

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Supplementary Material Available: Text conveying experimental procedures for the synthesis of complexes **1**–**3** and spectral and analytical data for **2b,c**, an ORTEP diagram of **1**, and tables of crystal data, bond distances, calculated positions of hydrogen atoms, and anisotropic thermal parameters for **2a** and **3** (17 pages). Ordering information is given on any current masthead page.

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(20) Crystal data for **3**: $C_{22}H_{22}O_7Re_2W$, $M = 953.69$, triclinic, space group $P\bar{1}$, $a = 8.794$ (2), $b = 9.656$ (3), $c = 15.417$ (4) Å, $\alpha = 92.05$ (2), $\beta = 103.04$ (2), $\gamma = 109.54$ (2)°, $V = 1193.0$ (5) Å^3, $Z = 2$, $D_c = 2.655$ mg/cm^3, $F(000) = 866$, μ(Mo Kα) = 15.21 mm^{-1}; 4219 unique reflections measured; 2857 reflections with $I > 2\sigma(I)$ used in refinement. $R_F = 0.047$ and $R_w = 0.049$, with GOF = 1.84.

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