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Oxo Ligand Reactivity and Bonding in the Dinuclear W−Re Oxo−Acetylide Complex (η^5-C$_5$Me$_5$)W(O)Re(CO)$_4$(μ-H)(CCPh)

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The trinuclear oxo−acetylide metal cluster (η^5-C$_5$Me$_5$)W(O)Re$_2$(CO)$_8$(μ-CCPh) (**1**) reacts with thiophenol in refluxing toluene to afford the dinuclear metal complex (η^5-C$_5$Me$_5$)W(O)Re(CO)$_4$(μ-H)(μ-CCPh) (**2**) in 90% yield. Upon treatment with Me$_3$NO in acetonitrile, complex **2** loses one CO ligand and is converted initially to an acetonitrile derivative, (η^5-C$_5$Me$_5$)W(O)Re(CO)$_3$(NCMe)(μ-H)(μ-CCPh) (**4**), and then to a head-to-tail dimer, [(η^5-C$_5$Me$_5$)WRe(CO)$_3$(μ-O)(μ-H)(μ-CCPh)]$_2$ (**5**), through the formation of two W≡O−Re bridges. Extended Hückel MO calculations indicate that the most likely site of electrophilic attack is the oxo oxygen atom, and in agreement with this prediction, protonation of **2** with CF$_3$CO$_2$H is suggested to give the unstable hydroxy complex **6**.

Studies on organometallic oxo complexes[1] have intensified in recent years as a result of the implication of such species in catalytic oxidations or as reagents in oxidation of organic molecules.[2] We are interested in the chemistry of polynuclear oxo cluster compounds as they may provide some connection between organometallic oxides, inorganic oxides and polyoxy anions.[3] Therefore, elucidation of the reactivity and structural features of these oxo clusters is crucial to a further understanding of how oxo ligands bond to the metal atoms[4] and how they react with adjacent hydrocarbon ligands[5] and serve as intimate reagents for the oxygen transfer reactions.[6] For these reasons we have prepared the oxo−acetylide cluster compound (η^5-C$_5$Me$_5$)W(O)Re$_2$(CO)$_8$(μ-CCPh) (**1**) and investigated the subsequent reaction with both H$_2$ and CO gas.[7] Herein we wish to report the synthesis and characterization of a related dinuclear metal compound (η^5-C$_5$Me$_5$)W(O)Re(CO)$_4$(μ-H)(CCPh) (**2**) and its tetrametallic dimer complex [(η^5-C$_5$Me$_5$)WRe(CO)$_3$(μ-O)(μ-H)(CCPh)]$_2$ (**5**), obtained by the direct treatment of **1** with thiophenol, followed by reaction with Me$_3$NO. Furthermore, EHMO calculations and protonation reactions were carried out in order to help interpret the basicity and bonding of the oxo ligand in these complexes.

Experimental Procedure

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker AM-400, a Varian Gemini-300, or a Varian Unity-400 instrument. ^{1}H and ^{13}C NMR chemical shifts are quoted with respect to internal standard tetramethysilane. Mass spectra were obtained on a JEOL-HX110 instrument operating in the fast atom bombardment (FAB) mode. The metal acetylide complex (η^5-C$_5$Me$_5$)W(O)Re$_2$(CO)$_8$(CCPh) was prepared according to literature procedures.[7] All reactions were performed under nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F$_{254}$, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F$_{254}$, E. Merck). Elemental analyses were carried out at the regional instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of (η^5-C$_5$Me$_5$)W(O)Re$_2$(CO)$_8$(CCPh) with Thiophenol. A toluene solution (60 mL) of **1** (213 mg, 0.206 mmol) and thiophenol (43 μL) was heated under 1 atm of CO at reflux for 30 min, during which the color changed from yellow-orange to yellow. After the solution was allowed to cool to room temperature, the solvent was evaporated and the residue was separated by thin layer chromatography (dichloromethane:hexane = 1:2), giving 51.6 mg of light yellow [Re(CO)$_4$(μ-SPh)]$_2$ (**3**, 0.063 mmol, 62%) and 136 mg of light orange (η^5-C$_5$Me$_5$)W(O)Re(CO)$_4$(μ-H)(μ-CCPh) (**2**, 0.184 mmol, 89.5%). Crystals of **2** suitable for X-ray diffraction study were obtained from a layered solution of dichloromethane−heptane at room temperature.

Spectroscopic Data for 3. MS (FAB, ^{187}Re): *m/z* 816 (M$^+$). IR (C$_6$H$_{12}$): ν (CO), 2098 (m), 2018 (vs), 1993 (m, br), 1959 (s, br) cm^{-1}. ^{1}H NMR (CDCl$_3$, 294 K): δ 7.46 (d, 4H, $J_{\text{H-H}}$ = 7.6 Hz), 7.33 (t, 4H, $J_{\text{H-H}}$ = 7.6 Hz), 7.19 (t, 2H, $J_{\text{H-H}}$ = 7.6 Hz). ^{13}C NMR (CDCl$_3$, 294 K): 188.6 (4C), 186.5 (4C), 136.7 (*i*-C$_6$H$_5$), 131.1 (*p*-C$_6$H$_5$), 128.9 (*o,m*-C$_6$H$_5$), 126.6 (*m,o*-C$_6$H$_5$). Anal. Calcd for C$_{20}$H$_{10}$O$_8$S$_2$Re$_2$: C, 29.48; H, 1.24. Found: C, 29.37; H, 1.33.

Spectroscopic Data for 2. MS (FAB, ^{184}W, ^{187}Re): *m/z* 738 (M$^+$). IR (C$_6$H$_{12}$): ν(CO), 2096 (m), 2005 (vs), 1982 (s), 1952 (vs) cm^{-1}; IR (KBr): ν(W≡O), 930 (br) cm^{-1}. ^{1}H NMR (CDCl$_3$, 294 K): δ 7.77 (d, 2H, $J_{\text{H-H}}$ = 7.7 Hz), 7.50 (t, 2H, $J_{\text{H-H}}$ = 7.7 Hz), 7.38 (t, 1H, $J_{\text{H-H}}$ = 7.7 Hz), 2.03 (s, 15H, C$_5$Me$_5$), −4.32 (s, 1H, $J_{\text{W-H}}$ = 130 Hz). ^{13}C

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NMR ($CDCl_3$, 294K): CO, δ 190.1 ($J_{C-H} = 3.2$ Hz), 187.3 ($J_{C-H} = 2.6$ Hz), 186.6, 181.0; δ 169.2 (*C*CPh), 149.2 ($J_{W-C} = 70$Hz, C*C*Ph), 137.7 (*i*-C_6H_5), 131.3 (*o,m*-C_6H_5), 128.5 (*m,o*-C_6H_5), 127.9 (*p*-C_6H_5), 111.6 (C_5Me$_5$), 11.4 (C_5*Me*$_5$). Anal. Calcd for $C_{22}H_{21}O_5Re_1W_1$: C, 35.93; H, 2.88. Found: C, 35.84; H, 2.86.

Reaction of (η^5-C_5Me_5)W(O)Re(CO)$_4$(μ-H)(μ-CCPh) with Me_3NO. An acetonitrile (30 mL) solution of **2** (33.3 mg, 0.045 mmol) and freshly sublimed Me_3NO (4.73 mg, 0.063 mmol) was heated at reflux for 40 min, during which the color changed from yellow-orange to orange. After the solution was allowed to cool to room temperature, the solvent was evaporated under vacuum and the residue was separated by thin layer chromatography with dichloromethane as eluent, giving 19.6 mg of orange (η^5-C_5Me_5)W(O)Re(CO)$_3$(NCMe)(μ-H)(μ-CCPh) (**4**, 0.026 mmol, 58%). Complex **4** was further purified by recrystallization from dichloromethane−heptane solution at −20 °C. If the recrystallization was carried out at room temperature, then crystals of **5**, formed by elimination of the coordinated acetonitrile, were obtained instead.

Spectroscopic Data for 4. MS (FAB, ^{184}W, ^{187}Re): *m/z* 749 (M^+). IR(C_6H_{12}): ν(CO), 2017 (s), 2003 (w), 1921 (s, br) cm^{-1}. IR (KBr): ν(W≡O), 928 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 K): δ 7.75 (d, 2H, $J_{H-H} = 7.4$ Hz), 7.46 (t, 2H, $J_{H-H} = 7.4$ Hz), 7.33 (t, 1H, $J_{H-H} = 7.4$ Hz), 1.89 (s, 15H), 1.82 (s, 3H), −3.69 (s, 1H, $J_{W-H} = 136$ Hz). ^{13}C NMR ($CDCl_3$, 200K): δ 197.7, 194.1, 193.0, 181.7 (*C*CPh), 151.4 ($J_{W-C} = 71$ Hz, C*C*Ph), 137.8 (*o,m*-C_6H_5), 131.7 (*m,o*-C_6H_5), 128.6 (*p*-C_6H_5), 127.7 (*i*-C_6H_5), 121.0 (MeCN), 110.8 (C_5Me$_5$), 11.6 (C_5*Me*$_5$), 3.9 (*Me*CN).

Spectroscopic Data for 5. MS (FAB, ^{184}W, ^{187}Re): *m/z* 1416 (M^+). IR(C_6H_{12}): ν(CO), 2004 (vs), 1919 (s, br), 1907 (s, br) cm^{-1}. IR (KBr): ν(W≡O), 934 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 294 K): δ 7.95 (d, 4H, $J_{H-H} = 7.4$ Hz), 7.62 (t, 4H, $J_{H-H} = 7.4$ Hz), 7.46 (t, 2H, $J_{H-H} = 7.4$ Hz), 1.80 (s, 30H). −2.95 (s, 2H, $J_{W-H} = 135$ Hz). ^{13}C NMR ($CDCl_3$, 294 K): 200.2, 200.1, 195.9, 193.7 (*C*CPh), 159.9 ($J_{W-C} = 69$ Hz, C*C*Ph), 138.2 (*i*-C_6H_5), 131.9 (*o,m*-C_6H_5), 128.7 (*m,o*-C_6H_5), 128.3 (*p*-C_6H_5), 111.6 (C_5Me$_5$), 11.2 (C_5*Me*$_5$). Anal. Calcd for $C_{42}H_{42}O_8Re_2W_2$: C, 35.30; H, 2.96. Found: C, 35.32; H, 2.96.

Reaction of [(η^5-C_5Me_5)WRe(CO)$_3$(μ-O)(μ-H)(μ-CCPh)]$_2$ with CO. A toluene solution (30 mL) of **5** (11 mg, 0.0078 mmol) was heated under 1 atm of CO at reflux for 80 min. The solvent was evaporated under vacuum and the residue was separated by thin layer chromatography (dichloromethane:hexane = 1:1), giving 9.4 mg of **2** (0.013 mmol, 82%).

Protonation of (η^5-C_5Me_5)W(O)Re(CO)$_4$(μ-H)(μ-CCPh). In a typical reaction, 12 mg to 15 mg of **2** was dissolved in 0.45 mL of $CDCl_3$ solvent and loaded into a 5-mm NMR tube capped with a rubber septum. A predetermined amount of CF_3CO_2H in $CDCl_3$ solution was then added using a microsyringe. The mixture was shaken briefly before inserting the tube into the NMR probe maintained at −30°C.

Spectral Data for 6. ^{1}H NMR ($CDCl_3$, 243 K): δ 8.03 (br, 2H), 7.74 (d, 2H, $J_{H-H} = 7.2$ Hz), 7.51 (t, 2H, $J_{H-H} = 7.2$ Hz), 7.40 (t, 1H, $J_{H-H} = 7.2$ Hz), 2.03 (s, 15H), −4.31 (s, 1H, $J_{W-H} = 127$ Hz).

X-ray Crystallography. Diffraction measurements of complexes **2** and **5** were carried out on a Enraf-Nonius CAD-4 diffractometer. All reflections were corrected for Lorentz, polarization, and absorption effects. Data deduction and refinement were performed using the NRCC-SDP-VAX packages. Lattice parameters of **2** were determined from 25 randomly selected high angle reflections with 2θ angles in the range 18.90−34.00°. The space group $P2_1/n$ was identified on the basis of systematic absences and confirmed by successful solution of the crystal structure. Absorption corrections were made by the Ψ scan method; the minimum and maximum transmission factors were 0.323 and 1.00, respectively. Anisotropic thermal parameters were used for all non-hydrogen atoms. The bridging hydride ligand was located from a difference Fourier map and was included in the structure factor calculations. Full matrix least-squares refinement with 50 atoms and 266 parameters gave $R_F = 0.027$ and $R_w = 0.027$, for 3376 reflections with $I > 2\sigma(I)$.

Table 1. Experimental Data for the X-ray Diffraction Studies[a]

	2	**5**
formula	$C_{22}H_{21}O_5ReW$	$C_{42}H_{42}O_8Re_2W_2$
mol wt	735.46	1414.91
cryst syst	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	8.119(2)	8.866(1)
b (Å)	18.784(2)	11.205(2)
c (Å)	14.602(1)	11.220(3)
α (deg)	77.42(8)	
β (deg)	92.99(2)	77.63(8)
γ (deg)	81.63(1)	
V (Å^3)	2223.9(7)	1056.9(3)
Z	4	1
D_c (g/cm^3)	2.197	2.223
F(000)	1368	656
2θ(max) (deg)	50°	50°
h, *k*, *l* ranges	−9 to 9, 0 to 22, 0 to 17	−10 to 10, 0 to 13, −12 to 13
cryst size, mm.	0.20 × 0.40 × 0.40	0.17 × 0.25 × 0.45
μ(Mo Kα) cm^{-1}	108.2	113.8
transm: max, min.	1.00, 0.32	1.00, 0.67
no. of unique data	3918	3733
no. of data with $I > 2\sigma(I)$	3376	2688
no. of atoms and params	50, 266	49, 245
weight modifier	0.000 02	0.000 06
max Δ/σ ratio	0.000	0.011
R_F; R_w	0.027; 0.027	0.032; 0.032
GOF	1.93	1.63
D-map, max/min, e/Å^3	2.11/−1.00	1.13/−1.65

[a] Features common to all determinations: Nonius CAD-4 diffractometer; λ(Mo Kα) = 0.7107 Å; 25 °C; minimize function $\sum(w|F_o - F_c|^2)$, weighting scheme $(1/\sigma^2)(F_o)$; $w = 1/\sigma^2(F_o)$; GOF = $[\sum w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **2**

W−Re	3.0333(5)	W−O(5)	1.696(4)
W−C(5)	2.152(7)	W−C(6)	2.126(6)
Re−C(5)	2.052(8)	W−H(1)	1.57(5)
Re−H(1)	1.92(5)	C(5)−C(6)	1.28(1)
∠Re−C(5)−C(6)	163.3(5)	∠C(5)−C(6)−C(7)	146.8(6)
∠O(5)−W−C(5)	110.1(2)	∠O(5)−W−C(6)	104.0(2)
Parameters Associated with the Cp* Ligands			
W−C(13)	2.326(7)	W−C(14)	2.324(7)
W−C(15)	2.473(6)	W−C(16)	2.477(6)
W−C(17)	2.371(7)	C(13)−C(14)	1.42(1)
C(14)−C(15)	1.43(1)	C(15)−C(16)	1.40(1)
C(16)−C(17)	1.43(1)	C(13)−C(17)	1.40(1)
Parameters Associated with CO Ligands			
Re−C(1)	1.923(8)	Re−C(2)	2.002(7)
Re−C(3)	1.992(7)	Re−C(4)	1.946(8)

Lattice parameters of **5** were determined from 25 selected reflections with 2θ angles in the range 17.32−23.76°. Empirical absorption corrections were performed and the minimum and maximum transmission factors were 0.669 and 1.000, respectively. The hydrogen atoms of the η^5-C_5Me_5 and phenyl groups were included at idealized positions with fixed temperature coefficients. Full-matrix least squares refinement with 49 atoms and 245 parameters converged at $R_F = 0.032$ and $R_w = 0.032$ for 2688 reflections with $I > 2\sigma(I)$. The combined data collection and refinement parameters are summarized in Table 1. The selected bond angles and lengths of **2** and **5** are listed in Tables 2 and 3, respectively.

Extended Hückel Molecular Orbital (EHMO) Calculations. These were carried out using the CACAO package of Mealli et al.[8] on the model complexes CpW(O)Re(CO)$_4$(μ-H)(CCMe) and [CpWRe(CO)$_3$(μ-O)(μ-H)(CCMe)]$_2$. The Cp rings were idealized to C_{5h} geometry, and the phenyl rings replaced with idealized methyl groups, but otherwise the crystallographic coordinates were used. The sym-

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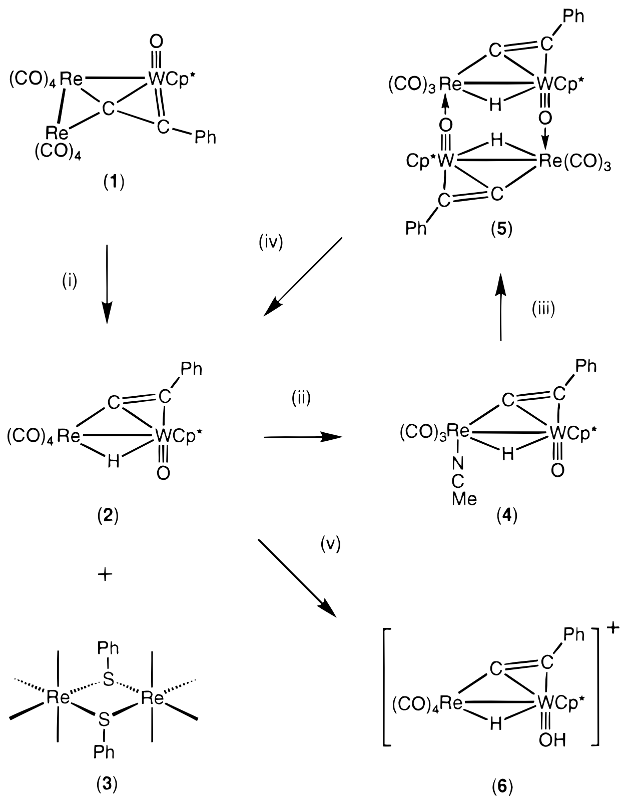
Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **5**

W−Re	3.0043(7)	W−O(4)	1.728(6)
Re−O(4)	2.162(6)	W−C(4)	2.16(1)
W−C(5)	2.06(1)	Re−C(4)	2.06(1)
C(4)−C(5)	1.30(2)		
∠Re−C(4)−C(5)	160.9(8)	∠C(4)−C(5)−C(6)	142(1)
∠W−O(4)−Re	173.0(4)		
Parameters Associated with the Cp* Ligands			
W−C(12)	2.36(1)	W−C(13)	2.38(1)
W−C(14)	2.39(1)	W−C(15)	2.37(1)
W−C(16)	2.34(1)		
Parameters Associated with CO Ligands			
Re−C(1)	1.86(1)	Re−C(2)	1.93(1)
Re−C(3)	1.93(1)		

Scheme 1



(i) PhSH, 110°C, 30 min. (ii) $Me_3NO/NCMe$, 81°C, 40 min. (iii) RT. (iv) CO, 110°C, 80 min. (v) CF_3CO_2H, −30°C.

metry was thus C_1 for $CpW(O)Re(CO)_4(\mu\text{-}H)(CCMe)$ and C_i for $[CpWRe(CO)_3(\mu\text{-}O)(\mu\text{-}H)(CCMe)]_2$.

Results and Discussion

Earlier we reported the synthesis of the trinuclear oxo-acetylide complex $(\eta^5\text{-}C_5Me_5)W(O)Re_2(CO)_8(\mu\text{-}CCPh)$ (**1**) and the products obtained from hydrogenation reactions.[7] In an attempt to further examine the reactivity pattern, complex **1** was reacted with thiophenol in refluxing toluene under CO atmosphere. Two complexes $(\eta^5\text{-}C_5Me_5)W(O)Re(CO)_4(\mu\text{-}H)(CCPh)$ (**2**) and $[Re(CO)_4(\mu\text{-}SPh)]_2$ (**3**) were isolated from this fragmentation reaction according to Scheme 1. Their relative yields decreased substantially in the absence of CO, and no reaction intermediate was observed upon lowering the temperature and shortening the reaction time. Both complexes **2** and **3** were obtained as stable crystalline solids, and they presumably result from cleavage of an "$Re(CO)_4(\mu\text{-}SPh)$" unit after the initial coordination of thiophenol. The rhenium dimer **3** was characterized by routine spectroscopic analysis, for which the data are fully consistent with an authentic sample independently prepared from photolysis of $Re_2(CO)_{10}$ and PhSSPh.[9] For complex **2** the IR spectrum showed an intense stretching band at 930 cm^{-1} due to the terminal oxo ligand, which falls in the region typical for a W≡O functional group.[10] In addition, the ^1H NMR spectrum showed a singlet at δ −4.32 ($J_{W-H} = 130$ Hz) assigned to the hydride ligand. The downfield chemical shift and the large $^{183}W-H$ coupling constant are possibly caused by the electron-withdrawing effect of the terminal oxo ligand and the presence of some terminal bonding character for the hydride ligand.[11]

The reactivity of complex **2** was examined. It failed to react with gaseous reagents such as hydrogen, carbon monoxide, or oxygen. However, upon treatment with Me_3NO in refluxing acetonitrile solution, it lost a CO ligand to form the acetonitrile-substituted complex **4**. Complex **4** was found to be stable at −20 °C and could be characterized from ^1H and ^{13}C NMR spectroscopic data. In addition to signals due to the phenyl, C_5Me_5, and hydride, the ^1H NMR spectrum showed an additional peak at δ 1.82 assigned to the methyl group of the coordinated acetonitrile ligand. The ^{13}C NMR spectrum exhibited three resonances due to the Re−CO ligands at δ 197.7, 194.1, and 193.0, as well as signals from the acetonitrile ligand at δ 121.0 and 3.9.

Complex **4** then underwent a clean transformation to $[(\eta^5\text{-}C_5Me_5)WRe(CO)_3(\mu\text{-}O)(\mu\text{-}H)(CCPh)]_2$ (**5**) at room temperature and in the absence of acetonitrile solvent. Upon treatment with CO in refluxing toluene, complex **5** was found to convert back to **2** in 82% yield. The FAB mass analysis of **5** gave a parent ion at *m/z* 1416, which is consistent with the formula $C_{42}H_{42}O_8Re_2W_2$. The IR spectrum exhibits three ν(CO) stretching bands at 2004, 1919, and 1907 cm^{-1} and one ν(W≡O) band at 934 cm^{-1} as expected. The ^1H and ^{13}C NMR data were also very similar to those of **4** described previously, except for the disappearance of signals due to the acetonitrile ligand. On the basis of this information, we propose that complex **5** is produced by the loss of the weakly coordinated acetonitrile ligand and the coupling of the resulting unsaturated "$(\eta^5\text{-}C_5Me_5)W(O)Re(CO)_3(\mu\text{-}H)(CCPh)$" fragment. In order to confirm these proposed structures, we have carried out single-crystal X-ray structural determinations on complexes **2** and **5**.

Crystal Structure of 2. An ORTEP diagram of **2** is shown in Figure 1, and selected bond parameters are presented in Table 2. The W atom, which possesses a pianostool arrangement, is linked to the Re atom which can be considered to adopt a *pseudo*octahedral geometry. The hydride ligand, which was located from a difference Fourier map, bridges the W−Re edge in an asymmetric fashion, W−H(1) = 1.57(5) Å and Re−H(1) = 1.92(5) Å. The W−Re distance of 3.0333(5) Å is slightly longer than has been observed for other W−Re heterometallic compounds, due to the presence of the bridging hydride ligand.[12] In addition, the unique oxo ligand, which is located on the W atom with short W−O distance of 1.696(4) Å, exhibits a strong weakening effect on the trans W−C bonding of the adjacent

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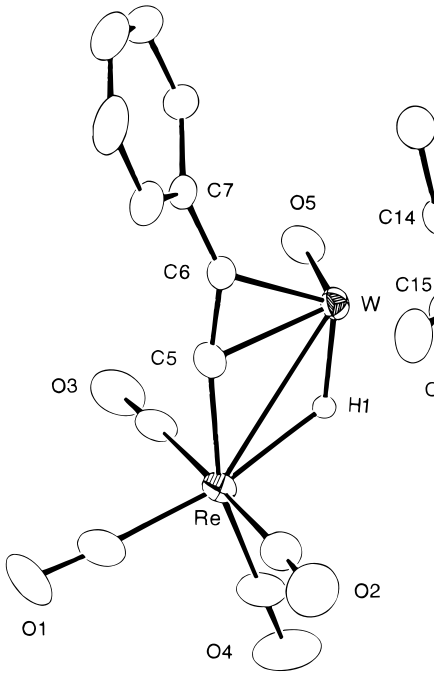

Figure 1. Molecular structure of (η^5-C_5Me_5)W(O)Re(CO)$_4$(μ-H)(μ-CCPh) (**2**) showing the crystallographic labeling scheme with thermal ellipsoids at the 30% probability level.

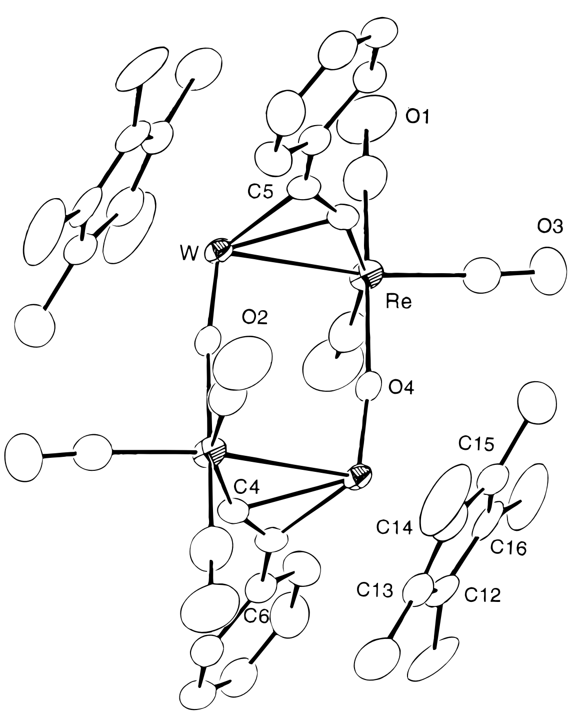

Figure 2. Molecular structure of [(η^5-C_5Me_5)WRe(CO)$_3$(μ-O)(μ-H)(μ-CCPh)]$_2$ (**5**) showing the crystallographic labeling scheme with thermal ellipsoids at the 30% probability level.

C_5Me_5 ligand. This trans influence is indicated by the lengthening of the W−C(15) and W−C(16) distances, 2.473(6) and 2.477(6) Å, which are located at positions trans to the oxo ligand, in comparison with the rest of the W−C distances of 2.324(7)−2.371(7) Å. Other examples of oxo ligands exerting a strong trans influence are provided by the structures of (η^5-C_5Me_5)Re(O)Cl_2 and (η^5-C_5Me_5)Re(O)Me_2.[13] In these compounds and complex **2**, the metal−C_5Me_5 ligand interaction may thus be more aptly described as a typical η^5-interaction with some significant η^2,η^3-character.

Furthermore, the acetylide is σ-bonded to the Re atom and π-bonded to the W atom, respectively. The Re−C(5) distance, 2.052(8) Å, is slightly shorter that the corresponding W−C distances of the π-interaction, 2.152(7) and 2.126(6) Å, while the C(5)−C(6) bond (1.28(1) Å) is comparable to those observed for the mononuclear alkyne complexes, in which the alkyne ligand serves as a two-electron-donor and uses only one set of π-orbitals to bond with the metal atoms.[14] In addition, the acetylide π-bond is virtually perpendicular to the W−O vector with angles O(5)−W−C(5) = 110.1(2)° and O(5)−W−C(6) = 104.0(2)°. This overall molecular geometry closely resembles that observed for the complexes CpMo(O)(PhC_2Ph)(Ru(CO)$_2$Cp), CpW(O)(HC_2Ph)(CH_2CO_2Et), and CpMo(O)($CF_3C_2CF_3$)(SC_6F_5)[15] owing to the maximization of the metal-to-acetylide back bonding and the dative π-interaction from the terminal oxo ligand to the central metal atom.

Crystal Structure of 5. As indicated in Figure 2, compound **5** possesses a centrosymmetric structure with a planar $W_2Re_2O_2$ six-membered ring, of which the bridging oxygen atoms are linked to the Re atoms and have a nearly linear W≡O−Re arrangement with a W−O(4)−Re angle of 173.0(4)°; see Table 3. Alternatively, this complex can be viewed as a head-to-tail dimer of **2** which is formed by removal of a CO ligand from the Re(CO)$_4$ vertex, where the terminal oxo ligand is coordinated to the vacant site of the departed CO ligand. This description is further supported by the overall coordination geometry around each monomeric W−Re unit, which is quite similar to that found for **2**, except that the Re−C(carbonyl) distance *trans* to the oxo ligand (Re−C(1) = 1.86(1) Å) is slightly shorter than the other Re−CO distances (Re−C(2) and Re−C(3) = 1.93(1) Å). The shortening of this Re−C distance is presumably a result of π-bond competition, which implies that the oxo ligand is a good σ-donor but a poor π-acceptor. Therefore, the *trans*-carbonyl ligand, which is a good π-acceptor, receives most of the back-donated π-electron from the Re metal and produces a much stronger Re−C interaction. Similar variation in M-C(carbonyl) distances has been noted for the CO ligands trans to the weakly coordinated acetonitrile in the osmium cluster derivatives Os_3(CO)$_9$(NCMe)(μ-H)(μ-SMe), Os_3(CO)$_{10}$(NCMe)$_2$, and Os_3(CO)$_{11}$(NCMe).[16] In these molecules, the acetonitrile ligands are also considered as good σ-donors but poorer π-acceptors.

Molecular Orbital Calculations. In order to gain further insight into the bonding in, and the chemical reactivity of these complexes, EHMO calculations were carried out on the model complexes CpW(O)Re(CO)$_4$(μ-H)(CCMe) (**A**) and [CpWRe(CO)$_3$(μ-O)(μ-H)(CCMe)]$_2$ (**B**). In view of the complexity and low symmetry of both molecules, a detailed investigation on

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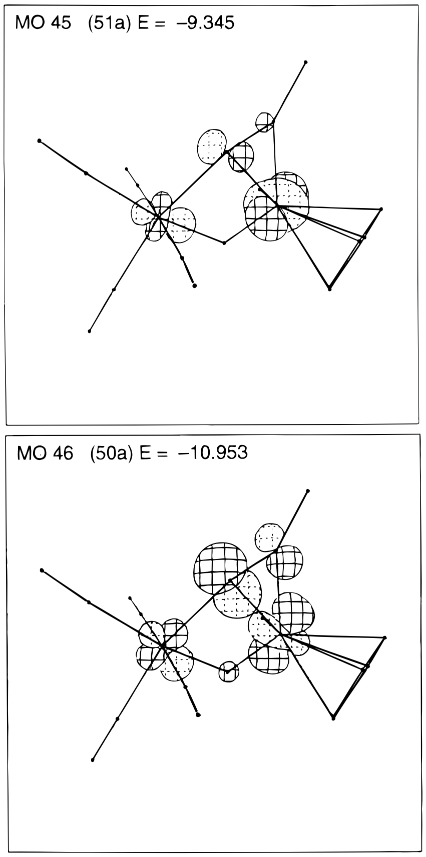

Figure 3. View of the HOMO (MO46) and the LUMO (MO45) of the complex CpW(O)Re(CO)$_4$(μ-H)(CCMe) (**A**).

the constitution of the molecular MO's by fragment analysis was not undertaken, but the study focused instead on two aspects, (a) possible sites of chemical reactivity and (b) the nature of the W−O bond.

Our calculations indicate there is little electronic interaction between the two WRe units in the dimer complex **B**, and they behave as essentially independent monomer units. For this reason, discussion will be mainly restricted to the model dimetallic complex **A**. The relatively isolated HOMO of **A** is separated from the next lowest lying orbitals by about 1.25 eV, while the LUMO lies about 1.6 eV higher. This situation is mirrored in **B** except that in this case we observe a pair of virtually degenerate orbitals from each WRe subunit for both the HOMO and LUMO. The HOMO (MO 46) and LUMO (MO 45) for **A** are illustrated in Figure 3.

The HOMO has considerable W−alkynyl π-bonding character and is more localized on the α-carbon. This suggests that, in the case of frontier orbital control, electrophilic attack should occur at this carbon atom, rather than the β-carbon. Nevertheless, the most negatively charged site in the molecule is the oxo oxygen atom (charge −1.37) and in the event of charge control, this atom ought to be the most likely site of electrophilic attack. For an electrophile such as H$^+$ the latter situation is much more likely, and this is borne out by the experimental evidence cited below. It should be noted that the EHMO calculations were carried out without charge iteration, so that the calculated charges presented here are almost certainly too high, although the relative order of atomic charges is likely to be reasonably correct. The Re atoms bears the next highest negative charge (−0.95), while the carbonyl oxygens have calculated charges in the range −0.72 to −0.55. By a considerable margin, the site of highest positive charge is the W center (+2.57) which suggest that nucleophilic attack by a charged nucleophile should occur here, and the localization in the LUMO (Figure 3) is also consistent with this suggestion. However the LUMO is quite delocalized, with considerable virtual density on the carbonyl ligands (not shown in Figure 3), so that prediction of the site of nucleophilic attack is difficult.

With regard to the bond order in the W−oxo bond, it is clear from the EHMO studies that this is a strong bond. The reduced overlap population (0.72) compares with the W−C(carbonyl) overlap populations (0.71−0.88), and is larger than the overlap populations between the alkynyl α-carbon and either the Re atom (0.63) or the W atom (0.28). There are three low lying orbitals which may be identified at contributing significantly toward one W−O σ-bond and two W−O π-bonds, while there are no populated orbitals with any substantial W−O antibonding character. This analysis thus leads to the conclusion of a formal triple W≡O bond, in line with many other studies on metal−oxo complexes containing one oxo ligand.[2a,17] The actual bond order is likely to be intermediate between 2 and 3. Interestingly, in the dimer complex **B**, there is no noticeable reduction in the W−O overlap population (0.71), though of course there is now a significant Re−O overlap population (0.29). There is thus little theoretical justification for a diminuation in the strength of the W−O bond on dimer formation, and this is borne out by our experimental evidence. The W−O stretching frequencies in **2** (930 cm^{-1}) and **5** (934 cm^{-1}) are almost identical, and there is only a marginal increase in the W−O distance in going from **2** to **5** (from 1.696(4) to 1.728(6)Å, *i.e.* an increase of $\sim 5\sigma$).

Protonation of 2. The successful isolation of the dimer **5** indicates that the terminal oxo ligand in complexes **2** and **4** is capable of replacing the coordinated acetonitrile on the Re atom by forming a bridging W≡O−Re linkage. The property may be rationalized in terms of the high basicity of the oxo ligand. As indicated by our EHMO studies, this oxo ligand may be expected to be the center for protonation, a process that has been recently demonstrated in the oxo complexes Re(O)(R)(R′CCR′), R; R′ = Me, Et, and ^{i}Pr,[18] and the oxo cluster complex Ru$_3$(CO)$_4$(μ_3-O)(μ-dppm)$_3$.[19]

In accordance with the above predictions, complex **2** reacts with CF$_3$CO$_2$H to give **6** by protonation of the terminal W≡O ligand. In one experiment, after the addition of 2 equiv of CF$_3$CO$_2$H into the CDCl$_3$ solution of **2**, the ^{1}H NMR spectra at −30 °C exhibited an additional broad signal at δ 8.03 assigned to the W≡OH$^+$ hydroxo grouping, while the chemical shifts of other hydrogen signals varied only slightly. The chemical shift of this hydroxo signal moved to the downfield region upon lowering the temperature and addition of more CF$_3$CO$_2$H into the solution, and the relative intensity was also proportional to the amount of CF$_3$CO$_2$H introduced. These observations suggests that there are some kind of complex ion-paired interactions between **2** and **6** and between **6** and CF$_3$CO$_2$H. Furthermore, two broad signals at δ 11.21 and 9.52 were observed after the addition of 7 equiv of CF$_3$CO$_2$H and lowering the probe temperature to −60 °C, suggesting that the proton exchange is slow under such conditions. The newly formed signal at δ 11.21 is due to the unreacted CF$_3$CO$_2$H as its chemical shift is very close to the proton signal of pure CF$_3$CO$_2$H at room temperature (δ 11.42).

Therefore, these ^{1}H NMR data provide evidence for the formation of **6** through the proton addition at the terminal oxo

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group. Unfortunately, all attempts to isolate complex **6** proved fruitless because it was very unstable and decomposes rapidly even at room temperature. This poor stability is also revealed in an independent experiment involving consecutive protonation and deprotonation. Thus, addition of triethylamine to a $CDCl_3$ solution of **6** that had been kept at room temperature for 1 h produced only a minimal amount of **2**.

Conclusion. The synthesis of binuclear metal complex containing the oxo ligand coordinated to the (η^5-C_5Me_5)W fragment is achieved. The isolation of **2**, which is much simpler than its trinuclear metal precursor **1** in the respect of molecular geometry, has facilitated an investigation into the nature of the tungsten−oxygen multiple bonding. The EHMO calculation is in agreement with the electron counting which suggests the existence of a formal W≡O bond. The W≡O interaction in **2** requires considerable O→M dative interaction involving donation of electrons on oxygen into the empty orbitals on the tungsten atom. This contrasts with the situation observed in the mononuclear dioxo complex $CpW(O)_2(CH_2SiMe_3)$, in which Legzdins and co-workers propose the existence of W═O double bonds with the tungsten atom adopting a 16-electron configuration.[20]

Interestingly, despite the high tungsten-oxygen bond order and the obvious O→W dative interaction, the oxo ligand still exhibits considerable basic character. As such, the remaining electrons on oxygen react with incoming electrophiles, such as the potentially unsaturated rhenium center "$Re(CO)_3(NCMe)$" in **4** or a proton to afford the dimer **5** and the unstable cationic complex **6**, respectively. During the formation of such donor−acceptor interactions, the nature of the W≡O bond is essentially unchanged. This is established by comparison of the solid-state structures of **2** and **5**, which show only a marginal increase in the W−O distance. Finally, the coordination mode of the oxo ligands in **5** is unique, providing an example in which all six valence electrons on oxygen are utilized in forming the linear, asymmetric W≡O−Re interaction. This coordination mode has never been observed for the related carbonyl compounds containing the oxo ligand.[21]

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Supporting Information Available: Full details of crystal structure analyses including crystal and refinement data, tables of atomic coordinates, and anisotropic thermal parameters for **2** and **5** (8 pages). Ordering information is given on any current masthead page.

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