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Intermetal Oxo Transfer: Isomerization of Tungsten–Rhenium Carbonyl Complexes Containing Oxo and Acetylide Ligands

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Summary: The heterometallic oxo–acetylide complex $Cp^*Re(O)(\mu\text{-}C_2Ph)W(CO)_2Cp$ *(**1**), possessing an oxo ligand bound to the Re atom, was prepared by treatment of* $[Cp^*Re(O)(\mu\text{-}O)]_2$ *with the acetylide complex* $CpW(CO)_3(CCPh)$ *in refluxing toluene. Further thermolysis of **1** afforded the isomeric complex* $Cp^*Re(CO)_2(\mu\text{-}C_2Ph)W(O)Cp$ *(**2**), showing an intermetal transfer of oxygen atom from Re to W atoms.*

Organometallic complexes containing oxo and hydrocarbyl ligands serve as realistic models for metal-mediated oxidations and other homogeneous and heterogeneous reactions with high-valent metal species as catalysts.[1] As a result, a large number of oxometal complexes has been synthesized; their reactivities with other metal complexes and the organic substrates have been thoroughly explored.[2] One particularly interesting subject relevant to this topic is oxygen atom transfer, which covers a rather broad spectrum, including intermetal oxygen transfer,[3] terminal-to-bridging oxo exchange on metal complexes,[4] and intramolecular oxo transfer from phosphorus to metal atoms.[5] However, no illustrative example has been observed that demonstrates the intermetal oxygen migration within the same molecule. In this study, we report preliminary experimental results on the structure and reactivity of the W–Re oxo–acetylide complexes, which offer such an opportunity for detailed investigation of this phenomenon.

The rhenium dioxo dimer $[Cp^*Re(O)(\mu\text{-}O)]_2$, generated from *in situ* treatment of 1:1 molar equiv of Cp^*ReO_3 and PPh_3,[6] reacts with the tungsten acetylide complex $CpW(CO)_3(CCPh)$ in toluene (110 °C, 20 min) to afford the dark green oxo–acetylide compound $Cp^*Re(O)(\mu\text{-}C_2Ph)W(CO)_2Cp$ (**1**) in 52% yield, in addition to a small amount of a second oxo–acetylide compound, $Cp^*Re(CO)_2(\mu\text{-}C_2Ph)W(O)Cp$ (**2**) (Scheme 1). These isomers were characterized by structural and spectroscopic methods.[7]

As indicated by an X-ray crystallographic analysis,[8] **1** shows a 16-electron $CpW(CO)_2(CCPh)$ fragment, in which the W atom and the acetylide fragment are linked to the oxo-containing $Cp^*Re(O)$ unit through Re→W dative bonding and an alkyne to rhenium π-interaction (Figure 1). The Re–O bond length (1.69(1) Å) resembles that found for Re=O distances exhibited in $(C_5Me_4Et)ReO_3$.[9] The IR spectrum of **1** shows a broad absorption at 898 cm^{-1}, which lies in the expected range for "class b" Re=O derivatives.[10] The Re–O vector is perpendicular to the Re–C(3)–C(4) plane. This ligand arrangement around the Re atom is similar to that proposed for mononuclear complexes $Cp^*Re(O)(RC_2R)$ (R = Me, Et).[11] The ^{13}C NMR signals of the acetylide ligand resonate at δ 214.7 ($J_{W-C} = 134$ Hz, C_α) and 155.4 ($J_{W-C} = 13$ Hz, C_β). The deshielded chemical shifts are consistent with alkynes donating four electrons to the metal atom, via an interaction incorporating both sets of π-orbitals.[12]

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(7) Spectral data for **1** are as follows. IR (CH_2Cl_2): ν(CO), 1934 (s), 1867 (m) cm^{-1}. IR (KBr): ν(C≡C), 1670 cm^{-1}, ν(Re=O), 898 (br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 294 K): δ 7.70 (d, 2H, $J_{H-H} = 7.1$ Hz), 7.47 (t, 2H, $J_{H-H} = 7.1$ Hz), 7.28 (t, 1H, $J_{H-H} = 7.4$ Hz), 5.60 (s, 5H), 1.83 (s, 15H). ^{13}C NMR (75 MHz, $CDCl_3$, 294 K): CO, δ 236.1 ($J_{W-C} = 176$ Hz), 219.9 ($J_{W-C} = 185$ Hz); δ 214.7 (*C*CPh, $J_{W-C} = 134$ Hz), 155.4 (C*C*Ph, $J_{W-C} = 13$ Hz), 137.7 (*i*-C_6H_5), 131.0 (2C, *o,m*-C_6H_5), 128.3 (2C, *m,o*-C_6H_5), 126.9 (*p*-C_6H_5), 108.1 (C_5Me_5), 89.3 (C_5H_5), 11.6 (C_5Me_5). ^{17}O NMR (47.4 MHz, $CDCl_3$, 293 K): δ 669. Anal. Calcd for $C_{25}H_{25}O_3ReW$: C, 40.32; H, 3.39. Found: C, 39.98; H, 3.45. Spectral data for **2** are as follows. IR (CH_2Cl_2): ν(CO), 1920 (s), 1791 (m) cm^{-1}. IR (KBr): ν(C≡C), 1737 cm^{-1}; ν(W=O), 931 (br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 294 K): δ 8.06 (d, 2H, $J_{H-H} = 7.2$ Hz), 7.52 (t, 2H, $J_{H-H} = 7.6$ Hz), 7.30 (t, 1H, $J_{H-H} = 7.4$ Hz), 5.88 (s, 5H), 2.12 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$, 251 K): CO, δ 237.1, 200.9; δ 181.5 (*C*CPh, $J_{W-C} = 13$ Hz), 140.2 (C*C*Ph, $J_{W-C} = 63$ Hz), 138.5 (*i*-C_6H_5), 132.2 (2C, *o,m*-C_6H_5), 128.6 (2C, *m,o*-C_6H_5), 127.1 (*p*-C_6H_5), 102.7 (C_5H_5), 99.8 (C_5Me_5), 10.2 (C_5Me_5). ^{17}O NMR (47.4 MHz, $CDCl_3$, 293 K): δ 733. Anal. Calcd for $C_{25}H_{25}O_3ReW$: C, 40.32; H, 3.39. Found: C, 40.25; H, 3.42.

(8) Crystal data for **1**: $C_{25}H_{25}O_3ReW$, triclinic, $P\bar{1}$, $a = 9.077(3)$ Å, $b = 11.541(9)$ Å, $c = 11.742(3)$ Å, $\alpha = 89.35(3)°$, $\beta = 68.27(2)°$, $\gamma = 80.73(4)°$, $F(000) = 700$, $\mu(\text{Mo K}_\alpha) = 106.8\ cm^{-1}$, 3518 reflections with $I > 2\sigma(I)$, $R = 0.047$, $R_w = 0.057$, GOF = 2.79.

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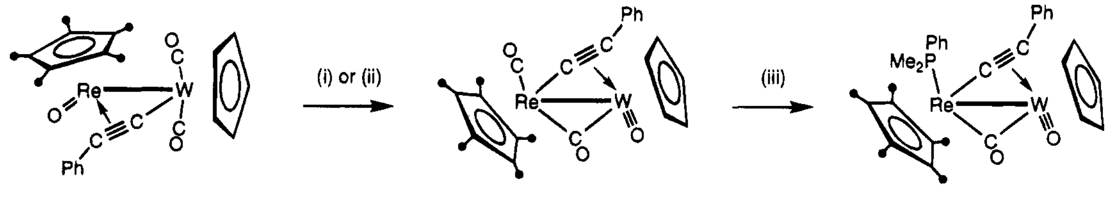
Scheme 1



(1) (2) (3)

^{a} Legend: (i) without O_2, 110 °C, 36 h, 65%; (ii) O_2, 110 °C, 15 min, 52%; (iii) PMe_2Ph, $h\nu$, 46%.

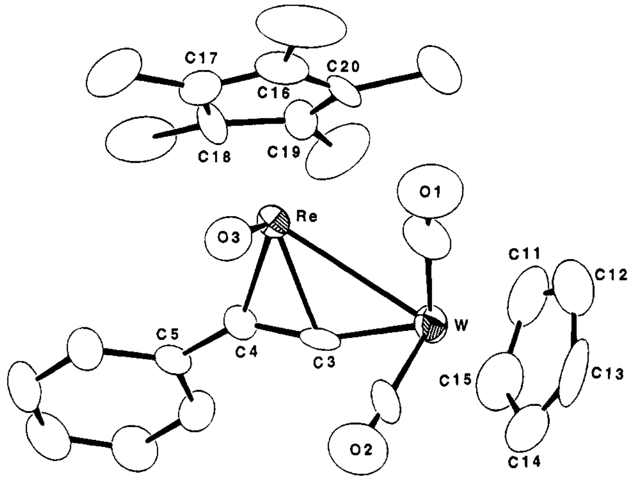


Figure 1. View of the molecular structure of **1**. Selected bond lengths (Å): W−Re = 2.895(2), Re−O(3) = 1.69(1), W−C(3) = 1.96(2), Re−C(3) = 2.07(1), Re−C(4) = 2.02(1), C(3)−C(4) = 1.34(2). Selected bond angles (deg): W−C(3)−C(4) = 161(1), C(3)−C(4)−C(5) = 141(1).

Furthermore, heating of a toluene solution of **1** under nitrogen afforded the orange isomer **2** (110 °C, 36 h) in 65% yield. This reaction proceeds formally via a transfer of the oxo ligand from rhenium to tungsten, CO migration from tungsten to rhenium atoms and a concomitant acetylide $\sigma \rightarrow \pi$, $\pi \rightarrow \sigma$ rearrangement. The structure of **2** was established on the basis of the X-ray structure of the PMe_2Ph derivative (**3**).[13] The latter was obtained by photolysis of **2** in the presence of a slight excess of PMe_2Ph, and the structure of **3** is proposed to be similar to that of **2** according to the spectral data.[14]

As depicted in Figure 2, the phosphine ligand lies on the rhenium atom and the oxo ligand is now located at the tungsten center. Additionally, the W−Re edge bears a *semi*bridging CO ligand, while the acetylide is σ-bonded to the Re and π-bonded to the W atoms, respectively. The C(2)−C(3) bond (1.30(2) Å) is shorter than the alkyne C−C distance in **1** (1.34(2) Å), indicating a weakened back-donation from the acetylide π-orbitals to the W atom.[12] This gross molecular geometry resembles that of the alkyne complex $CpRu(CO)_2Mo(O)(PhC_2Ph)Cp$,[15] whereas the acetylide−tungsten interaction in **3** is related to the alkyne-metal π-bonding observed in the oxo−alkyne complexes $CpW(O)(HC_2Ph)(CH_2CO_2Et)$ and $CpMo(O)(CF_3C_2CF_3)(SC_6F_5)$.[16] Moreover, the acetylide ligands of **2** and the PMe_2Ph derivative **3** show signals at δ 181.5 (J_{W-C} = 13 Hz) and 140.2 (J_{W-C} = 63 Hz), and at δ 199.5 (J_{P-C} = 10 Hz) and 143.7 (J_{W-C} = 72 Hz) in the ^{13}C NMR spectra, respectively, exhibiting the expected high-field shifting with respect to that of **1**.[12] Apparently, an increasing lone-pair donation from oxygen would compensate this unfavorable reduction of electron density on the tungsten center. The high-frequency terminal W−O stretching vibration at 931 cm^{-1} for **2** and 917 cm^{-1} for **3** confirms this postulate. Competition of π-bonding between oxo and acetylene ligands has been observed in the rhenium acetylene complexes $Re(O)(C_2R_2)_2Na$ (R = Me, Et, Ph).[17]

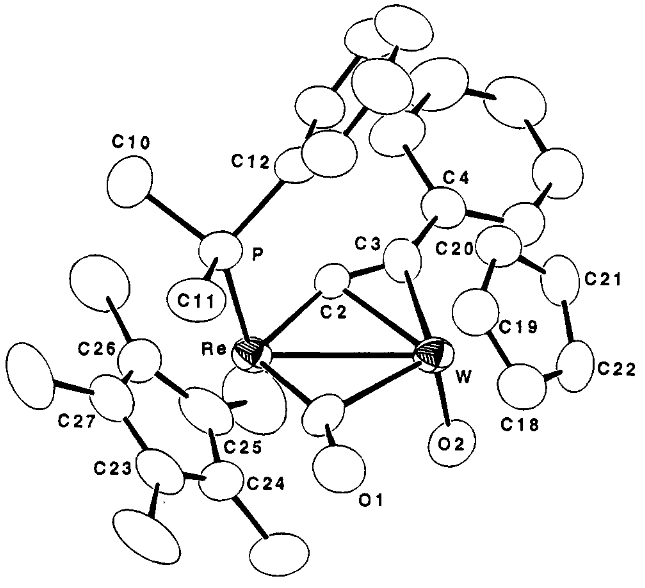


Figure 2. View of the molecular structure of **3**. Selected bond lengths (Å): W−Re = 2.862(1), Re−P = 2.360(4), W−O(2) = 1.66(1), W−C(1) = 2.38(2), Re−C(1) = 1.90(1), W−C(2) = 2.13(1), Re−C(2) = 1.94(1), W−C(3) = 2.09(1), C(2)−C(3) = 1.30(2). Selected bond angles: Re−C(1)−O(1) = 155(1), Re−C(2)−C(3) = 157(1), C(2)-C(3)-C(4) = 146(1).

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(14) Spectral data for **3** are as follows: MS (FAB, ^{184}W, ^{187}Re): *m/z* 854 (M^+). IR (CH_2Cl_2): ν(CC), 1722 (w) cm^{-1}; ν(CO), 1692 (m) cm^{-1}. IR (KBr): ν(C≡C), 1737 cm^{-1}; ν(W=O), 917 (br) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 294 K): δ 8.05 (d, 2H, J_{H-H} = 8.0 Hz), 7.54−7.49 (m, 4H), 7.33 (t, 2H, J_{H-H} = 6.8 Hz), 7.31 (d, 1H, J_{H-H} = 7.5 Hz), 7.19 (t, 1H, J_{H-H} = 4.4 Hz), 5.79 (s, 5H), 1.78 (s, 15H), 1.40 (d, 3H, J_{P-H} = 8.4 Hz), 1.30 (d, 3H, J_{P-H} = 9.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 294 K): CO, δ 233.6 (d, J_{P-C} = 7 Hz); δ 199.5 (d, *C*CPh, J_{P-C} = 10 Hz), 143.7 (C*C*Ph, J_{W-C} = 72 Hz), 141.3 (*i*-C_6H_5), 139.5 (d, J_{P-C} = 44 Hz, *i*-C_6H_5), 131.2 (2C), 130.1 (d, 2C, J_{P-C} = 9 Hz), 129.2 (*p*-C_6H_5), 128.5 (2C), 128.1 (d, 2C, J_{P-C} = 9 Hz), 125.4 (*p*-C_6H_5), 103.1 (C_5H_5), 96.1 (C_5Me_5), 22.2 (d, Me, J_{P-C} = 33 Hz), 21.8 (d, Me, J_{P-C} = 31Hz), 9.6 (C_5Me_5); ^{31}P NMR (121 MHz, $CDCl_3$, 294 K): δ −16.3 (s). Anal. Calcd for $C_{32}H_{36}O_2PReW$: C, 45.02; H, 4.25. Found: C, 44.78; H, 4.21.

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The ^{17}O labeling studies were carried out to illustrate some characteristics of this oxygen migration process. The required ^{17}O-enriched [Cp*Re(O)(μ-O)]$_2$ dimer was obtained from the deoxygenation of 15% ^{17}O-enriched Cp*ReO$_3$. The latter was in turn generated by exposure of regular [Cp*Re(O)(μ-O)]$_2$ under a 45% ^{17}O-enriched dioxygen atmosphere.[18] Using this ^{17}O-enriched [Cp*Re(O)(μ-O)]$_2$, we have successfully prepared the expected ^{17}O-labeled **1** and **2** from the direct reaction with CpW(CO)$_3$(CCPh) and from the subsequent thermolysis of ^{17}O-labeled **1** in a sealed tube under vacuum. The ^{17}O NMR integration indicated that nearly 96% of the ^{17}O isotopes in **1** were preserved during the conversion to **2**. This result confirms that the isomerization predominantly proceeds via a direct oxygen atom transfer.

However, when thermolysis of **1** was carried out in air (3 h) or under O$_2$ (15 min), a dramatic enhancement in rate and a slight decrease in yield were observed with respect to the reaction conducted in vacuo or under N$_2$. The enhanced activity is consistent with a second labeling experiment in which complex **2**, generated from heating of nonlabeled **1** under 45% ^{17}O-enriched dioxygen, showed the presence of an additional W≡^{17}O stretch at 908 cm^{-1} and a broad ^{17}O NMR signal at δ 733, in the range expected for the terminal oxo ligands of oxo complexes Cp*W(O)$_2$—O—ML$_n$.[19] The exchange of isotopes indicates that complex **2** may arise from a different pathway under this extreme circumstance, such that an unstable oxo–peroxo complex is produced from the direct attack of a ^{17}O$_2$ molecule. This putative oxo–peroxo intermediate may exhibit rapid oxo/peroxo scrambling, oxygen transfer to tungsten, and removal of a mixed ^{16}O^{17}O molecule, generating the observed ^{17}O-enriched **2**. Formations of the mononuclear rhenium and tungsten oxo–peroxo derivatives have already been documented.[20]

In summary, the described reactions represent the first synthesis of W–Re oxo–acetylide complexes and the conversion to a thermodynamically more stable isomer via the intermetal migration of an oxo ligand. In the absence of O$_2$, this oxo transfer is presumed to involve formation of a bridging oxo ligand, which may be structurally related to the bridging oxo ligand observed in the clusters Cp$_2$W$_2$Re(CO)$_3$(μ-O)(μ-Br)(μ_3-CTol) and Cp*WRe$_2$(CO)$_6$(μ-O)(μ-H)$_2$(CCPh).[21] It is notable that the W–O bonds of these bridging oxo ligands (1.77–1.78 Å) are always markedly shorter and stronger than the corresponding Re–O bonding (2.14–2.28 Å). Similarly, the W–O multiple-bond interaction in **2** is also stronger than the Re–O bonding in **1**, as revealed by our IR ν(M=O) data (*vide supra*). These two experimental facts strongly indicate that the isomerization **1** → **2** is driven by the difference in M–O bond strengths. However, on the basis of our current evidence, the latent contribution from the CO and the acetylide ligands cannot be eliminated completely.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, atomic coordinates, and anisotropic thermal parameters for **1** and **3** (12 pages). Ordering information is given on any current masthead page.

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