# Low-Valent Binuclear Rhenium–Oxo–Acetylene Complexes: Comparison of Symmetrical Dimers Containing an Unsupported Re–Re Bond with Asymmetric Dimers with Bridging Oxo and Acetylene Ligands[1]

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**Abstract:** Reduction of the rhenium(III)–oxo–bis(acetylene) complexes Re(O)I(RC≡CR)$_2$ (1) yields mixtures of two isomeric rhenium dimers Re$_2$(O)$_2$(RC≡CR)$_4$ (R = Me, Et, Ph, and 'Bu/H). A wide variety of reducing agents can be used, including 'BuZnCl, NaC$_{10}$H$_8$, and Cp$_2$Co. One of the isomers has $C_2$ symmetry (the "symmetric" dimers 2) and consists of two Re(O)(RC≡CR)$_2$ fragments connected by an unsupported Re–Re bond (2.686 (1) Å in the structure of 2a, R = Me). The structural and spectroscopic properties of the Re(O)(RC≡CR)$_2$ groups in 2 are very similar to those of Re(O)X(RC≡CR)$_2$ compounds, for instance, with rhenium–terminal oxo distances of 1.693 (11) Å (av). The other isomer (3) is asymmetric, with one bridging and one terminal oxo group, as revealed by the structure of (EtC≡CEt)(O)Re($\mu$-O)($\mu$-EtC≡CEt)Re-(EtC≡CEt)$_2$ (3b). The unusual bridging acetylene ligand in 3b is twisted roughly 34° with respect to the Re–Re bond, with Re–C distances that vary from double bond to longer than single bond distances (1.89 (2) to 2.52 (3) Å). Compounds 3 are best described as Re(III)/Re(I) mixed-valence species, the Re(III) side resembling Re(O)X(RC≡CR)$_2$ compounds and the Re(I) side close to ReX(RC≡CR)$_3$, with X = $\mu$-O and one acetylene shared between the two. On heating, compounds 3 cleanly convert to 2, indicating that the symmetric isomers are thermodynamically more stable. This is surprising in light of the normal preference for bridging oxo ligands in low-valent compounds. The Re–Re bond in 2 is cleaved by I$_2$ to regenerate 1. Compounds 2 are rigid on the NMR time scale (like 1), but 3 are fluxional. The fluxional process involves only the two acetylene ligands on the Re(I) side, and is concluded to be a "turnstile" rotation that exchanges the end of one acetylene for the opposite end of another. The symmetric dimers are thought to be formed by combination of two [Re(O)(RC≡CR)$_2$]· radicals while the asymmetric dimers can result from reaction of Re(I)- and Re(III)–oxo–bis(acetylene) complexes.

Compounds with two transition metals (dimeric complexes) have been intensively studied for some time, to understand both how the metals interact and how the chemistry of bridging ligands differs from terminal ones.[4,5] The bonding mode is particularly important for ligands with multiple donor orbitals such as oxo or acetylene ligands because, as terminal ligands, they can form multiple bonds to metal centers. The presence of multiple donor orbitals on the ligands also often leads to unusually low coordination numbers for the metal centers and to a variety of possible structural types. We report here comparative studies of two novel types of dimers, symmetric and asymmetric isomers of the stoichiometry Re$_2$(O)$_2$(RC≡CR')$_4$ (Scheme I).[6] In the symmetric dimers, there are no bridging ligands while the asymmetric dimers have bridging oxo and acetylene groups.

The preference for terminal vs bridging ligation of an oxo group has implications in the chemistry of oxide materials (osmium tetroxide vs zirconia),[7] reagents (permanganate vs MnO$_2$),[8] catalysts (different crystal faces of MoO$_3$),[9] and metalloenzymes

**Scheme I.** Formation of Symmetric (2) and Asymmetric (3) Dimers
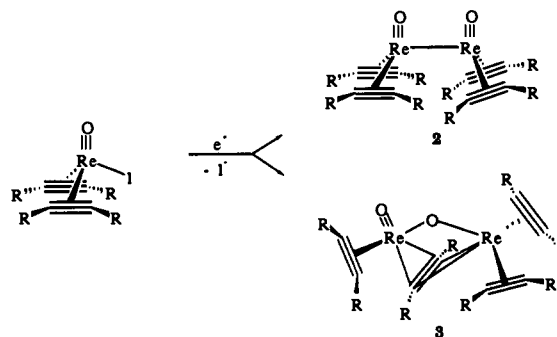


(cytochrome P-450 vs hemerythrin).[10] Compounds with bridging oxygens are known for all of the transition elements (e.g., the binary oxides), but terminal oxo complexes are common only for metals in the center–left area of the transition series.[11] The large majority of stable terminal oxo complexes have high metal oxidation states ($\geq$+4) and low d electron counts (d$^0$, d$^1$, or d$^2$) in order to allow the oxygen p$\pi$ electrons to donate into empty metal d$\pi$ orbitals.[11] In low oxidation states, multiple bonding becomes unfavorable as electrons occupy metal d$\pi$ orbitals (the metal–oxygen $\pi$-antibonding orbitals) and oxo-bridged structures (M–O–M) with single bonds become dominant. For instance, reduction of permanganate in neutral solution yields manganese dioxide, an insoluble material with bridging oxide ions.[12] The rhenium–oxo–acetylene compounds Re(O)X(RC≡CR')$_2$ have

(1) Low-Valent Rhenium–Oxo Complexes. 10. Part 9: ref 18. Part 11: ref 19.

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been a focus of research in our laboratories for some time[6,13-19] because the +3 formal oxidation state and $d^4$ electron count are unusual for terminal oxo complexes.[11,20,21] The present study of the reduction of the $Re(O)I(RC\equiv CR')_2$ compounds was undertaken to investigate the effects of an added electron on their structure and reactivity.

## Experimental Section

General procedures were as previously described.[17] Compounds **1a**, **1b**, and **1d**[13] were prepared as described in ref 22; **1c** is reported in ref 19. Sodium naphthalenide solutions were prepared fresh every 3–4 weeks by literature methods;[23] solutions were stored under $N_2$ at 10 °C and routinely titrated with 0.1000 ± 0.0002 N HCl (VWR).

**[Re(O)(MeC≡CMe)₂]₂ (2a). Method A.** A solution of anhydrous $ZnCl_2$ (0.12 g, 0.82 mmol) in 15 mL of $Et_2O$ at −78 °C was treated with 0.25 mL of $^t$BuLi (2.0 M, 0.5 mmol) and stirred for 1 h. After slow warming to 25 °C, the solution was recooled to −78 °C and the supernatant was transferred via cannula to a −78 °C solution of **1a** (0.23 g, 0.52 mmol) in 25 mL of $Et_2O$. Upon warming to room temperature, the volatiles were removed, and the crude product was redissolved in a minimum amount of $CH_2Cl_2$ in the air and filtered through a short wide column of silica gel (1:4 EtOAc/hexanes) to afford 146 mg of **2a** (93%) as a tan solid. **Method B.** A solution of **1a** (0.20 g, 0.46 mmol) in 15 mL of THF was cooled to −78 °C, and 1.4 mL of a 0.33 M solution of $Na/C_{10}H_8$ in THF (1.1 equiv) was syringed in. The yellow solution turned blue and then quickly red-orange. It was allowed to reach room temperature slowly, and the final tan-colored solution was stripped of solvent in vacuo. Workup on silica gel required hexane solvent to first remove naphthalene followed by 1:4 EtOAc/hexanes to afford 116 mg of **2a** (82%): $^1$H NMR δ 3.16, 3.06, 2.80, 1.03 (each 6 H, q, 1 Hz, $CH_3C\equiv CCH_3'$); $^{13}C$ {$^1$H} NMR δ 148.01, 146.50, 143.33, 140.78 (MeC≡*C*Me), 23.10, 15.30, 15.13, 13.17 ($CH_3C\equiv CCH_3$); IR (Nujol) 1766 (w) $\nu$(C≡C), 1155, 1035, 951 (s), 941 (s) both $\nu$(ReO), 805 cm$^{-1}$ (w); MS $m/e$ 618, 620, 622 (M$^+$). Anal. Calcd for $Re_2O_2C_{16}H_{24}$: C, 30.96; H, 3.90. Found: C, 30.94; H, 3.82.

**[Re(O)(EtC≡CEt)₂]₂ (2b).** A solution of anhydrous $ZnCl_2$ (0.10 g, 0.75 mmol) in 15 mL of $Et_2O$ at −78 °C was treated with 0.78 mL of $^t$BuLi (1.9 M, 1.5 mmol) and stirred for 0.5 h at −40 °C. Following a procedure similar to method A for **2a** above, the zinc reagent was transferred at −78 °C via cannula to a frozen solution of **1b** (0.25 g, 0.51 mmol) in 50 mL of benzene at 0 °C; workup on a short wide column of silica gel (1:9 EtOAc/hexanes) afforded 148 mg of **2b** (88%) as a pale gold oil: $^1$H NMR ($C_6D_6$) δ 3.77 (4 H), 3.45, 3.30, 3.17, 3.02 (each 2 H, dq, 15, 7 Hz), 1.14 (4 H, q, 7 Hz, all Me$CHH'$C≡CC$HH'$Me), 1.45, 1.43, 1.19, 0.69 (each 6 H, t, 7 Hz $CH_3CH_2C\equiv CCH_2CH_3'$); $^{13}C$ {$^1$H} NMR ($C_6D_6$) δ 150.8, 150.3, 147.2, 144.0 (Et*C*≡*C*Et), 33.25, 25.15, 24.78, 24.01 (Me$CH_2$C≡C$C'H_2$Me), 15.10, 14.55, 14.30 (2 signals unresolved, $CH_3CH_2C\equiv CCH_2C'H_3$); IR (neat) 2965, 2940, 2865, 1758 $\nu$(C≡C), 1455, 1372, 1251, 1138, 1090, 1050, 955 (s), $\nu$(ReO) 934 (w), 803, 770 cm$^{-1}$ (w); MS $m/e$ 730, 732, 734 (M$^+$).

**[Re(O)(PhC≡CPh)₂]₂ (2c).** Following method B for **2a** above, **1c** (0.052 g, 0.076 mmol) in 15 mL of THF and 0.12 mL of a 0.73 M solution of $Na/C_{10}H_8$ in THF (1.1 equiv) gave 43 mg of a 1.0:1.1 mixture of **2c/3c** (100% combined). The products were separated on silica gel by using 05:95 EtOAc/hexanes: **2c** eluted first and was obtained as an off-white solid after solvent removal in vacuo: $^1$H NMR ($C_6D_6$) δ 8.45, 6.36 (each 4 H), 7.21 (8 H, d, 7 Hz, $H_o$), 7.38, 6.90, 6.70 (each 4 H, t,

7 Hz, $H_m$), 7.12, 6.92, 6.77 (each 2 H, t, 7 Hz, $H_p$), 6.99 (6 H, t, 7 Hz, $H_m$ and $H_p$); $^{13}C$ {$^1$H} NMR ($CD_2Cl_2$) δ 154.2, 150.6, 149.6, 142.2 (Ph*C*≡*C*Ph), 135.0, 134.4, 134.0, 133.3 ($C_{ipso}$), 131.7–127.0 ($C_6H_5C\equiv CC'_6H_5$); IR (neat) 3080, 3058, 3020, 2920, 1590, 1550, 1480, 1440, 1270, 1180, 1072, 1028, 972 (s), 925, 910, 720, 700, 695 cm$^{-1}$ (s).

**[Re(O)(HC≡CCMe₃)₂]₂ (2d, 2g).** Following method A for **2a** above, $ZnCl_2$ (0.34 g, 2.5 mmol) in 10 mL of $Et_2O$, 1.3 mL of $^t$BuLi (1.9 M, 2.4 mmol), and **1d** (0.60 g, 1.21 mmol) in 25 mL of $Et_2O$ gave, after workup on silica ($CH_2Cl_2$ to isolate **2d** followed by 1:4 EtOAc/hexanes to elute **3d**), 82 mg of **2d** (19%) as pale tan solids, 117 mg of **3d** (26%) as bright yellow solids, and a small amount of **2g** (an isomer of **2d**): $^1$H NMR δ 9.66, 5.20 (each 2 H, s, $HC\equiv CCMe_3$), 1.52, 1.41 (each 18 H, s, $HC\equiv CC(CH_3)_3$); $^{13}C$ NMR ($CD_2Cl_2$) δ 175.11, 156.3 (both s, $HC\equiv CC(Me)_3$), 130.4 (d, 207 Hz, $HC\equiv CC(Me)_3$), 125.8 (d, 214 Hz, $HC\equiv CC(Me)_3$), 37.2, 37.0 (both s, $HC\equiv CC(Me)_3$), 31.4, 30.8 (both q, 128 Hz, $HC\equiv CC(CH_3)_3$); IR (neat) 2960, 2900, 1655 (w) $\nu$(C≡C), 1462, 1465, 1360, 1235, 1215, 1038, 965 (s) $\nu$(ReO), 782 cm$^{-1}$; MS $m/e$ 732, 734 (M$^+$). Anal. Calcd for $Re_2O_2C_{24}H_{40}$: C, 39.33; H, 5.50. Found: C, 39.42; H, 5.47. Data for **2g**: $^1$H NMR δ 10.26, 9.89, 9.88, 5.95 (each 1 H, s, $HC\equiv CCMe_3$), 1.67, 1.69, 1.46, 0.66 (each 9 H, s, $HC\equiv CC(CH_3)_3$).

**(MeC≡CMe)₂(O)ReRe(O)(PhC≡CPh)₂ (2e).** An NMR tube was loaded with 50 mg of **3e** dissolved in $CD_2Cl_2$, and the tube was sealed under vacuum and heated at 110 °C for 3.0 h. After this time, 25% of **3e** was converted to **2e** and the isomers were separated on silica gel by using $CH_2Cl_2$, with **2e** collected first as an off-white solid after solvent removal: $^1$H NMR ($C_6D_6$) δ 8.15, 7.19 (each 2 H, d, 7 Hz), 7.33, 6.19 (each 5 H, m), 6.88, 6.77 (each 4 H, m, all $C_6H_5C\equiv CC_6H'_5$), 3.55, 2.28, 2.06, 1.64 (each 3 H, q, 1 Hz, $CH_3C\equiv CCH_3'$); $^{13}C$ {$^1$H} NMR ($CD_2Cl_2$) δ 154.2, 149.9, 148.4, 146.7, 145.9, 144.9, 141.9, 141.17 (R*C*≡*C*R), 135.0–127.0 ($C_6H_5C\equiv CC'_6H_5$), 24.53, 15.6, 15.3, 15.0 ($CH_3C\equiv CC'H_3$); IR (neat) 1752, 1592, 1675, 1480, 1440, 1360, 1270, 1152, 1070, 1025, 958 (s) $\nu$(ReO), 808, 765, 740, 688 cm$^{-1}$.

**(MeC≡CMe)₂(O)ReRe(O)(EtC≡CEt)₂ (2f).** A solution of **1a** (0.150 g, 0.345 mmol) and **1b** (0.171 g, 0.345 mmol) in 25 mL of benzene was cooled to 5 °C, and 1.5 mL of a 0.6 M solution of $Na/C_{10}H_8$ in THF (1.3 equiv) was syringed in. The solution was warmed to room temperature, and then the solvent was removed in vacuo. Workup on silica gel (hexane to remove naphthalene, followed by $CH_2Cl_2$) afforded 55 mg of **2a**, 65 mg of **2b**, and 55 mg of **2f** (25%): $^1$H NMR ($CD_3CN$) δ 3.70, 3.50, 3.22, 1.06, 0.93 (each 1 H), 3.45 (3 H, all m, Me$CHH'$C≡C$CHH'$Me), 3.13, 2.95, 2.80, 1.10 (each 3 H, q, 1 Hz, $CH_3C\equiv CCH_3'$), 1.54, 1.33, 1.26, 0.71 (each 3 H, t, 7 Hz, $CH_3CH_2C\equiv CCH_2CH_3'$); $^{13}C$ {$^1$H} NMR ($C_6D_6$) δ 150.8, 150.4, 147.4, 143.7 (Et*C*≡*C*Et), 147.1, 146.5, 143.0, 140.6 (Me*C*≡*C*Me), 33.0, 24.9, 24.7, 23.9 (Me$CH_2$C≡C$C'H_2$Me), 15.0, 14.6, 14.3, 14.2 ($CH_3CH_2C\equiv CCH_2C'H_3$), 23.4, 15.3, 15.2, 14.1 ($CH_3C\equiv CC'H_3$) (assignments tentative); IR (Nujol) 1761 $\nu$(C≡C), 1304, 1252, 1158, 1048, 963 cm$^{-1}$ (s) $\nu$(ReO); MS $m/e$ 674, 676, 678 (M$^+$).

**(EtC≡CEt)(O)Re($\mu$-O)($\mu$-EtC≡CEt)Re(EtC≡CEt)₂ (3b).** Following method A for **2a**, $ZnCl_2$ (0.27 g, 1.95 mmol) in 10 mL of $Et_2O$, 0.51 mL of BuLi (1.9 M, 0.97 mmol), and **2b** (0.45 g, 0.91 mmol) in 25 mL of $Et_2O$ yielded, after filtration through silica gel (1:9 EtOAc/hexanes) and separation on silica gel (5:95 hexanes/EtOAc), 130 mg of **2b** (39%) as a golden oil and 125 mg of **3b** (37%) as a bright yellow solid: $^1$H NMR ($CD_2Cl_2$, −40 °C) δ 3.97, 3.51, 3.40, 2.97, 1.96, 1.76 (each 1 H, m), 3.60, 3.25 (each 3 H, m), 3.12, 2.80 (each 2 H, m, all Me$CHH'$C≡C$CHH'$Me), 1.63, 1.51, 1.42, 1.08, 1.05, 0.95, 0.84, 0.46 (each 3 H, t, 7 Hz, $CH_3CH_2C\equiv CCH_2CH_3'$); $^{13}C$ {$^1$H} NMR ($CD_2Cl_2$, −40 °C) δ 196.47, 192.90, 180.75, 169.71, 168.62, 165.06, 153.52, 150.09 (Et*C*≡*C*Et), 31.89, 30.54, 29.79, 27.67, 24.82, 23.82, 22.87, 21.78 (Me$CH_2$C≡C$C'H_2$Me), 15.43, 14.69, 14.54, 14.40, 12.89, 14.17 ($CH_3CH_2C\equiv CCH_2C'H_3$, the last resonance believed to be three carbons, unresolved); IR (neat) 2962, 2935, 2865, 1759, 1455, 1370, 1302, 1245, 1145, 1085, 1056, 928 (s) $\nu$(ReO), 700 cm$^{-1}$; MS $m/e$ 674, 676, 678 (M$^+$). Anal. Calcd for $Re_2O_2C_{24}H_{40}$: C, 39.33; H, 5.50. Found: C, 39.73; H, 5.52. **3b**-$^{18}O$ was prepared by exchange with $H_2^{18}O$ in $CH_2Cl_2$: IR $\nu$(Re$^{18}O$) 880 cm$^{-1}$.

**(PhC≡CPh)(O)Re($\mu$-O)($\mu$-PhC≡CPh)Re(PhC≡CPh)₂ (3c).** The procedure given for the preparation of **2c** was followed. Complex **3c** was obtained as a bright yellow solid: $^1$H NMR ($CD_2Cl_2$, −80 °C) δ 8.91, 8.22 (2 H, d, 7 Hz, $H_o$), 7.86 (2 H, t, 7 Hz, $H_m$), 7.77 (3 H, m, $H_m$ and $H_p$), 7.60 (2 H, m, $H_o$), 7.47 (1 H, t, 7 Hz, $H_p$), 7.41–6.91 (21 H, $C_6H_5C\equiv CC'_6H_5$), 6.97, 6.38 (each 2 H, t, 7 Hz, $H_m$), 6.59 (1 H, t, 7 Hz, $H_p$), 6.18 (2 H, d, 7 Hz, $H_o$); $^1$H NMR ($CD_2Cl_2$, 25 °C) δ 8.90 (2 H, d, 7 Hz, $H$), 7.89 (4 H, t, 7 Hz, $H$), 7.77 (1 H, t, 7 Hz, $H$), 7.59 (2 H, m, $H$), 7.45–6.90 (26 H, $C_6H_5C\equiv CC'_6H_5$, mostly resonances are broad), 6.74 (1 H, t, 7 Hz, $H$), 6.61 (2 H, t, 7 Hz, $H$), 7.86, 6.44 (2 H, d, 7 Hz, $H$); IR (neat) 3070, 3010, 2920, 1958, 1895, 1804, 1745, 1660 (w), 1590, 1570, 1470, 1440, 1280 (s), 1175, 1155, 1065, 1020, 995 (w),

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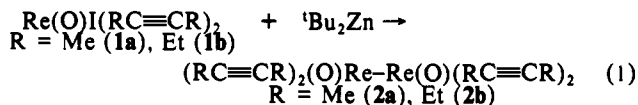
925 (s), 835, 760 (s), 682 cm$^{-1}$ (s). Anal. Calcd for $Re_2O_2C_{56}H_{40}$: C, 60.20; H, 3.61. Found: C, 59.98; H, 3.79.

(HC≡CCMe$_3$)(O)Re($\mu$-O)($\mu$-HC≡CCMe$_3$)Re(HC≡CCMe$_3$)$_2$ (3d). The procedure given for the preparation of 2d was followed: $^1$H NMR (CD$_2$Cl$_2$, –40 °C) $\delta$ 10.74, 10.16, 10.08, 9.85 (each 1 H, s, *HC*≡ CCMe$_3$), 1.73, 1.69, 1.25, 0.62 (each 9 H, s, HC≡CC(C$H_3$)$_3$); $^1$H NMR (CD$_2$Cl$_2$, 25 °C) 10.72, 9.99 (each 1 H, s, *HC*≡CC(Me)$_3$), 1.82, 1.30 (each 9 H, s, sharp, HC≡CC(C$H_3$)$_3$), 1.58, 0.88 (each 9 H, br s, HC≡CC(C$H_3$)$_3$); $^{13}$C NMR (CD$_2$Cl$_2$, –40 °C) $\delta$ 183.8, 183.1, 180.0, 163.9 (each s, HC≡*C*CMe$_3$), 170.1 (d, 185 Hz), 166.4 (d, 204 Hz), 134.5 (d, 209 Hz), 156.7 (d, 201 Hz, H*C*≡CCMe$_3$); $^{13}$C NMR (CD$_2$Cl$_2$, 25 °C) $\delta$ 184.3, 164.2 (both s, HC≡*C*CMe$_3$), 171.1 (d, 185 Hz), 134.5 (d, 214 Hz) (both sharp), HC≡CC(Me)$_3$), 156.9 (br d, 197 Hz, H*C*≡ CCMe$_3$); IR (neat) 2990, 2920, 1480, 1460, 1365, 1240, 1215, 1040, 980, 945 (s), 905 cm$^{-1}$; MS *m/e* 732, 734 (M$^+$).

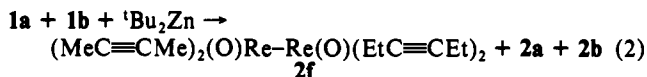(MeC≡CMe)(O)(Re)($\mu$-O)($\mu$-MeC≡CMe)Re(PhC≡CPh)$_2$ (3e). A solution of 1c (0.30 g, 0.44 mmol) in 20 mL of THF was cooled to –78 °C, and 1.3 mL of a 0.73 M solution of Na/C$_{10}$H$_8$ in THF (2.1 equiv) was syringed in to give a deep red-purple color. To this solution, 0.192 g of 1a (0.44 mmol) in 20 mL of THF at –78 °C was transferred (via cannula) and the whole was allowed to reach room temperature slowly. Workup on silica using CH$_2$Cl$_2$ afforded 240 mg of 3e (67%) as a bright yellow solid: $^1$H NMR (CD$_2$Cl$_2$, –40 °C) $\delta$ 7.98, 7.84, 6.94, 6.92 (each 2 H, d, 7 Hz), 7.54 (2 H, t, 7 Hz), 7.40 (3 H, br m), 7.23–6.10 (7 H, m), 3.49, 2.84, 2.59, 2.51 (each 3 H, q, 1 Hz, C$H_3$C≡C C$H_3$'); $^1$H NMR (CD$_2$Cl$_2$, 25 °C) $\delta$ 7.87, 7.01 (each 4 H, br), 7.50–7.36 and 7.30–6.10 (each 6 H, br), 3.47, 2.90, 2.61, 2.54 (each 3 H, q, 1 Hz, C$H_3$C≡ CC$H_3$'); $^{13}$C NMR (CD$_2$Cl$_2$, –60 °C) $\delta$ 194.1, 164.7, 152.8, 145.6 (each q, Me*C*≡*C*'Me), 190.0, 176.4, 166.9, 163.9 (each s, Ph*C*≡*C*'Ph), 139.8–125.7 (C$_6$H$_5$C≡C$C'_6$H$_5$), 21.1, 18.6, 16.1, 14.3 (each q, *C*H$_3$C≡ CC'H$_3$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 25 °C) $\delta$ 195.6, 165.1, 152.5, 145.3 (Me*C*≡*C*'Me), 131.6–127.6 (C$_6$H$_5$C≡CC$_6$H$_5$), 21.5, 18.9, 15.6, 15.1 (*C*H$_3$C≡CC'H$_3$); IR (neat) 3060, 2910, 1590, 1480, 1440, 1275, 1178, 1160, 1072, 1050 (br), 1030, 968 (s), 932 (s), 770, 692 cm$^{-1}$.
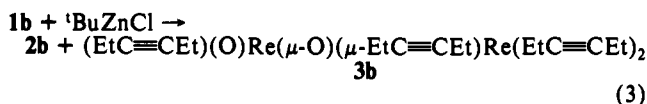
## Results

**Synthesis of Symmetric and Asymmetric Dimers 2 and 3.** The symmetrical dimers with 2-butyne and 3-hexyne supporting ligands [Re(O)(MeC≡CMe)$_2$]$_2$ (2a) and [Re(O)(EtC≡CEt)$_2$]$_2$ (2b) were first prepared by addition of excess di-*tert*-butylzinc to Re(O)I(RC≡CR)$_2$ (R = Me (1a), Et (1b)) in benzene solution at 0 °C followed by slow warming to room temperature (eq 1). Compounds 2a and 2b are isolated in 85–95% yield after filtration through silica gel.

$$\begin{array}{c} \text{Re(O)I(RC} \equiv \text{CR)}_2 \\ \text{R = Me (1a), Et (1b)} \end{array} + \text{'Bu}_2\text{Zn} \rightarrow$$
$$\begin{array}{c} \text{(RC} \equiv \text{CR)}_2\text{(O)Re–Re(O)(RC} \equiv \text{CR)}_2 \\ \text{R = Me (2a), Et (2b)} \end{array} \quad (1)$$

The mixed acetylene dimer (MeC≡CMe)$_2$(O)Re–Re(O)-(EtC≡CEt)$_2$ (2f) is obtained, together with 2a and 2b, upon addition of excess 'Bu$_2$Zn to a 1:1 mixture of 1a and 1b in benzene (eq 2); the roughly equimolar mixture is easily separated by chromatography on silica.

$$\text{1a} + \text{1b} + \text{'Bu}_2\text{Zn} \rightarrow$$
$$\underset{\text{2f}}{\text{(MeC} \equiv \text{CMe)}_2\text{(O)Re–Re(O)(EtC} \equiv \text{CEt)}_2} + \text{2a} + \text{2b} \quad (2)$$

In THF or Et$_2$O solvent, reductions of Re(O)I(RC≡CR')$_2$ (1) with a variety of reducing agents, including bulk electrolysis, in general yield not only the symmetric rhenium dimers 2, but also unsymmetrical dimers (RC≡CR)(O)Re($\mu$-O)($\mu$-RC≡CR)Re-(RC≡CR)$_2$, 3 (Scheme I). For instance, addition of excess 'BuZnCl to 1b at –78 °C in Et$_2$O followed by slow warming to room temperature gives a roughly 1:1 mixture of 2b and 3b (eq 3), isolated in 80% combined yield after chromatography on silica gel. Compounds 2 and 3 are isomers, as indicated by analytical and spectroscopic data, X-ray crystal structures of 2a and 3b, and the thermal conversion of 3 to 2 (see below). A similar mixture

$$\text{1b} + \text{'BuZnCl} \rightarrow$$
$$\underset{\text{3b}}{\text{2b} + \text{(EtC} \equiv \text{CEt)(O)Re(} \mu \text{-O)(} \mu \text{-EtC} \equiv \text{CEt)Re(EtC} \equiv \text{CEt)}_2}$$
$$(3)$$

of the two isomeric dimers 2b and 3b (≈0.75:1) is obtained from 1b and excess sodium amalgam (5%) or sodium metal, or 1 equiv



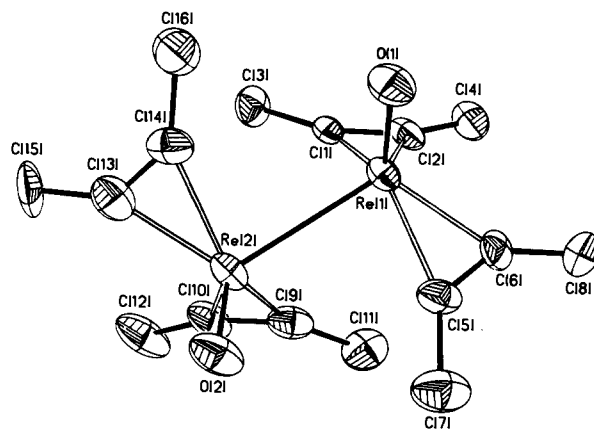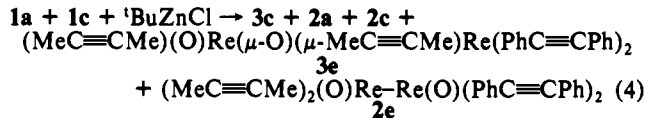**Figure 1.** Perspective drawing of (MeC≡CMe)$_2$(O)Re–Re(O)(MeC≡ CMe)$_2$ (2a), with hydrogen atoms omitted for clarity.

of NaC$_{10}$H$_8$ in THF. In reactions with NaC$_{10}$H$_8$, the ratio of products was found to be independent of reaction temperature from –78 to +25 °C. An initial blue color is observed in most of these reductions, which fades to tan within seconds at ambient temperatures (1–3 min at –78 °C).

Reduction of Re(O)I(PhC≡CPh)$_2$ (1c) and Re(O)I('BuC≡ CH)$_2$ (1d) with 'BuZnCl yields both symmetric and asymmetric dimers with diphenylacetylene (2c, 3c) and *tert*-butylacetylene ligands (2d, 3d). A 1:1 mixture of 2c and 3c is also formed on addition of 1 equiv of NaC$_{10}$H$_8$ to 1c in THF. However, we have never observed a 2-butyne asymmetric dimer: Reduction of 1a yields only 2a (and an asymmetric isomer of 2f has not been observed). Mixed acetylene dimers, both symmetric and asymmetric, are prepared by treatment of a mixture of 1a and 1c with excess 'BuZnCl reagent (eq 4) or with 1 equiv of NaC$_{10}$H$_8$ in THF.

$$\text{1a} + \text{1c} + \text{'BuZnCl} \rightarrow \text{3c} + \text{2a} + \text{2c} +$$
$$\underset{\text{3e}}{\text{(MeC} \equiv \text{CMe)(O)Re(} \mu \text{-O)(} \mu \text{-MeC} \equiv \text{CMe)Re(PhC} \equiv \text{CPh)}_2}$$
$$+ \underset{\text{2e}}{\text{(MeC} \equiv \text{CMe)}_2\text{(O)Re–Re(O)(PhC} \equiv \text{CPh)}_2} \quad (4)$$

The asymmetric dimer (MeC≡CMe)(O)Re($\mu$-O)($\mu$-MeC≡ CMe)Re(PhC≡CPh)$_2$ (3e) is the major product of reaction 4, followed by a smaller amount of 3c and trace amounts of the symmetric dimers 2a, 2c, and (MeC≡CMe)$_2$(O)Re–Re(O)-(PhC≡CPh)$_2$ (2e) (<5% combined). The synthesis of 3e is the only case in which the asymmetric isomer is the predominant product. Reductions of 1c, either alone or with 1a, give an initial deep red color, with no indication of the blue intermediate observed in reactions of dialkylacetylene compounds.

The dimers are all diamagnetic, air-stable solids, except for 2b, which is isolated as an oil. The symmetric dimers 2 are white or tan in color, the asymmetric dimers bright yellow. All are soluble in C$_6$H$_6$ and CH$_2$Cl$_2$ and at least sparingly soluble in CHCl$_3$ and CH$_3$CN. 2a and 2f can be stored for months in air at 0 °C without degradation, while 2b darkens under these conditions.

**X-ray Crystal Structures of 2a and 3b.** Crystals of 2a and 3b both contain isolated molecules with the stoichiometry Re$_2$-(O)$_2$(RC≡CR)$_4$. Views of the molecules are presented in Figures 1–3, relevant bond lengths and angles in Tables I and II. Compound 2a, an example of the symmetric isomers, is composed of two Re(O)(MeC≡CMe)$_2$ fragments connected by an unsupported rhenium–rhenium bond. The two fragments are related by an approximate 2-fold axis perpendicular to the Re–Re bond. The coordination about each rhenium is roughly tetrahedral with the Re–Re bond, an oxo group, and the acetylene midpoints occupying the four sites. The bond angles are within 12° of the tetrahedral value, with the largest deviations in the Re–Re–(CC midpoint) angles (av 97.8 (7)°). The two acetylenes bound to each rhenium lie in a plane approximately perpendicular to the terminal oxo group. This geometry—and the metrical data—is
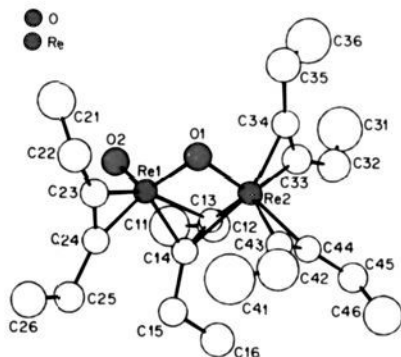
*Low-Valent Binuclear Rhenium-Oxo-Acetylene Complexes*

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**Figure 2.** Perspective drawing of (EtC≡CEt)(O)Re(μ-O)(μ-EtC≡CEt)Re(EtC≡CEt)₂ (**3b**), with hydrogen atoms omitted for clarity.
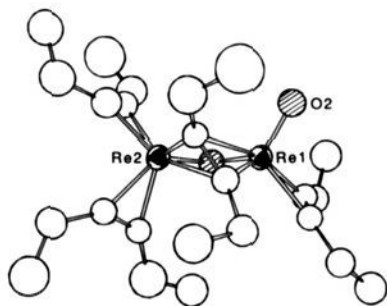


*Figure 3.* Perspective drawing of (EtC≡CEt)(O)Re(μ-O)(μ-EtC≡CEt)Re(EtC≡CEt)₂ (**3b**), showing the twist of the bridging acetylene ligand.

**Table I.** Selected Bond Distances (Å) in (MeC≡CMe)₂(O)ReRe(O)(MeC≡CMe)₂ (**2a**), (EtC≡CEt)(O)Re(μ-O)(μ-EtC≡CEt)Re(EtC≡CEt)₂ (**3b**), and Re(O)I(MeC≡CMe)₂ (**1a**)[a]

| | 2a | | 3b | | 1a |
|---|---|---|---|---|---|
| Re1–Re2 | 2.686 (1) | Re1–Re2 | 2.677 (2) | | |
| Re1–O1 | 1.712 (11) | Re1–O2 | 1.64 (2) | | 1.697 (3) |
| Re2–O2 | 1.674 (10) | | | | |
| | | Re1–O1 | 1.84 (2) | | |
| | | Re2–O1 | 2.08 (2) | | |
| Terminal Acetylenes | | | | | |
| Re1–C1 | 2.063 (17) | Re1–C23 | 2.01 (3) | | 2.038 (5) |
| Re1–C2 | 2.051 (14) | Re1–C24 | 2.05 (3) | | 2.061 (5) |
| Re1–C5 | 2.052 (15) | | | | |
| Re1–C6 | 2.02 (3) | | | | |
| Re2–C9 | 2.119 (17) | Re2–C33 | 1.96 (3) | | 2.066 (5) |
| Re2–C10 | 2.04 (2) | Re2–C34 | 2.02 (3) | | 2.040 (5) |
| Re2–C13 | 2.04 (3) | Re2–C43 | 1.98 (3) | | |
| Re2–C14 | 2.075 (17) | Re2–C44 | 2.02 (3) | | |
| C1–C2 | 1.28 (4) | C23–C24 | 1.24 (3) | | 1.278 (7) |
| C5–C6 | 1.34 (3) | | | | 1.288 (7) |
| C9–C10 | 1.29 (3) | C33–C34 | 1.33 (4) | | |
| C13–C14 | 1.38 (4) | C43–C44 | 1.29 (3) | | |
| Bridging Acetylene | | | | | |
| | | Re1–C13 | 2.52 (3) | | |
| | | Re1–C14 | 2.04 (3) | | |
| | | Re2–C13 | 1.89 (2) | | |
| | | Re2–C14 | 2.32 (3) | | |
| | | C13–C14 | 1.34 (3) | | |

[a] Data for **1a** from ref 13.

very similar to that of four Re(III) oxo complexes: **1a**,[13] Re-(O)Et(MeC≡CMe)₂,[17] Re(O)OPh(MeC≡CMe)₂,[15] and [Re-(O)(MeC≡CMe)₂(py)]SbF₆;[14] for comparison, the data for **1a** are included in Tables I and II. The average rhenium–oxygen bond distance of 1.693 (11) Å in **2a** is typical of Re–O multiple bond lengths,[24] and is essentially the same as those in Re(III) oxo species (1.692 (3) to 1.712 (13) Å). The rhenium–carbon distances fall into two groups, for the carbons near the Re–Re bond (av 2.077 (17) Å) and those away (av 2.037 (22) Å), very similar to those found in **1a** (2.064 (5), 2.039 (5) Å).

The Re(O)(MeC≡CMe)₂ group is a 17-electron unit in tetrahedral Re(O)X(RC≡CR)₂ complexes.[13] Since the dimer is structurally and spectroscopically similar to **1a** and its derivatives, the two rhenium–oxo units of **2a** should be connected by a Re–Re single bond. This is consistent with the chemical properties of **2a** (see below). The Re–Re distance of 2.686 (1) Å is at the short end of the reported range of single bond lengths (2.56–3.11 Å).[25] The unsupported single bonds in Re₂(CO)₁₀ (3.041 (1) Å)[26] and Re₂(CO)₈(PMe₂Ph)₂ (3.044 (1) Å)[27] are significantly longer while dimers with bridging ligands like Cp*₂Re₂(μ-O)(CO)₄ (2.817 (1) Å)[28] and Re₂(O)₂(μ-O)₂(CH₂CMe₂Ph)₄ (2.612 (1) Å)[29] are more similar.

Compound **2a** adopts an ethane-like structure, with the two tetrahedral Re(O)(MeC≡CMe)₂ fragments in a staggered gauche arrangement. The O–Re–Re–O torsion angle is 74.2°. There is no evidence from the crystal structure or from NMR spectra for any of the anti isomer. In the gauche conformation, one acetylene methyl group lies in between the two acetylene methyls

on the other rhenium, which should restrict rotation about the Re–Re bond. NMR spectra of **2a** and **2b** indicate that this conformation is retained in solution and that rotation about the Re–Re bond is slow on the NMR time scale, even at 90 °C.

The structure of **3b** (Figure 2) is remarkably asymmetric, particularly in comparison with that of the essentially isomeric **2a**. *The two rhenium centers in* **3b** *have different ligand sets*, with only Re1 being bound to a terminal oxo ligand (Re1–O2 = 1.64 (2) Å), and the bridging oxo and acetylene ligands are bound quite asymmetrically. The bridging oxygen, O1, is 0.2 Å closer to Re1 (1.84 (2) Å) than to Re2 (2.08 (2) Å) (compare 1.934 (6) and 1.903 (6) Å in [Re(O)(μ-O)(CH₂CMe₂Ph)₂]₂[29]). The Re2–O1 distance is normal for a Re–O single bond length,[30] whereas the shorter Re1–O1 distance indicates Re1–O1 π bonding (compare Re–OPh = 1.966 (14) Å in Re(O)OPh(MeC≡CMe)₂, where there is evidence for some O → Re π bonding[15]). The Re1–O1–Re2 angle of 86.1° in **3b** is much the same as those found in Cp*(O)Re(μ-O)₂ReCp*(ReO₄)₂,[28] [Re(O)(μ-O)(CH₂CMe₂Ph)₂]₂,[29] and [Re(O)(μ-O)(CH₂CMe₃)₂]₂[31] (av. 86.4 (4)°, 85.8 (3)°, and 84.6 (7)°). The rhenium–rhenium distance in **3b** of 2.677 (2) Å is very close to the unsupported Re–Re bond in **2a** (2.686 (1) Å). However, metal–metal bond lengths are strongly influenced by the presence of bridging ligands, usually with shorter M–M distances in bridged structures.[28,29]

A most unusual feature of **3b** is the bridging acetylene ligand, which is twisted roughly 34° away from an orientation perpendicular to the Re–Re axis (Figure 3).[32] In addition to being twisted, the μ-EtC≡CEt ligand bridges the rhenium centers very unsymmetrically, with four quite different Re–C distances. The Re2–C13 bond of 1.89 (2) Å is typical of a double bond, Re1–C14

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**Table II.** Selected Bond Angles (deg) for $(MeC\equiv CMe)_2(O)ReRe(O)(MeC\equiv CMe)_2$ (**2a**),
$(EtC\equiv CEt)(O)Re(\mu\text{-}O)(\mu\text{-}EtC\equiv CEt)Re(EtC\equiv CEt)_2$ (**3b**), and $Re(O)I(MeC\equiv CMe)_2$ (**1a**)[a]

| 2a | | 3b | | 1a | |
|---|---|---|---|---|---|
| O1–Re1–Re2 | 113.8 (6) | O2–Re1–Re2 | 117.4 (6) | | |
| | | O1–Re1–O2 | 122.1 (8) | O–Re–I | 109.4 (1) |
| | | Re1–O1–Re2 | 86.1 (7) | | |
| | | Re2–Re1–O1 | 50.7 (5) | | |
| | | Re1–Re2–O1 | 43.2 (4) | | |
| O1–Re1–C1 | 110.2 (6) | O2–Re1–C13 | 90.7 (8) | O–Re–C | 114.8 (2) |
| O1–Re1–C2 | 112.5 (5) | O2–Re1–C14 | 108.3 (10) | O–Re–C | 109.1 (2) |
| O1–Re1–C5 | 111.4 (7) | O2–Re1–C23 | 105.7 (10) | O–Re–C | 114.2 (2) |
| O1–Re1–C6 | 112.3 (9) | O2–Re1–C24 | 112.0 (8) | O–Re–C | 108.8 (2) |
| O2–Re2–Re1 | 115.0 (6) | | | | |
| O2–Re2–C9 | 111.5 (6) | O1–Re2–C33 | 126.2 (10) | | |
| O2–Re2–C10 | 112.4 (6) | O1–Re2–C34 | 89.2 (10) | | |
| O2–Re2–C13 | 110.3 (8) | O1–Re2–C43 | 92.9 (9) | | |
| O2–Re2–C14 | 110.6 (6) | O1–Re2–C44 | 130.0 (9) | | |
| | | O1–Re2–C13 | 106.7 (8) | | |
| | | O1–Re2–C14 | 87.9 (8) | | |
| Re2–Re1–C1 | 83.4 (6) | O1–Re1–C23 | 89.4 (9) | I–Re–C | 85.2 (1) |
| Re2–Re1–C2 | 113.3 (7) | O1–Re1–C24 | 111.7 (9) | I–Re–C | 119.6 (2) |
| Re2–Re1–C5 | 81.0 (7) | O1–Re1–C13 | 92.5 (7) | I–Re–C | 85.2 (1) |
| Re2–Re1–C6 | 113.6 (6) | O1–Re1–C14 | 104.0 (9) | I–Re–C | 119.7 (2) |
| Re1–Re2–C9 | 81.9 (7) | O1–Re2–C13 | 106.7 (8) | | |
| Re1–Re2–C10 | 112.1 (7) | O1–Re2–C14 | 87.9 (8) | | |
| Re1–Re2–C14 | 82.0 (7) | O1–Re2–C33 | 126.2 (10) | | |
| Re1–Re2–C13 | 115.3 (6) | O1–Re2–C34 | 89.2 (10) | | |
| | | O1–Re2–C43 | 92.9 (9) | | |
| | | O1–Re2–C44 | 130.0 (9) | | |
| C1–Re1–C5 | 138.4 (6) | C13–Re1–C23 | 159.3 (9) | C–Re–C | 130.5 (2) |
| C2–Re1–C6 | 88.8 (8) | C14–Re1–C24 | 94.6 (10) | C–Re–C | 88.3 (2) |
| C9–Re2–C14 | 137.9 (6) | C14–Re2–C34 | 148.3 (10) | | |
| C10–Re2–C13 | 89.0 (10) | C14–Re2–C43 | 91.4 (9) | | |
| | | C34–Re2–C43 | 120.3 (10) | | |
| | | C13–Re2–C33 | 92.1 (10) | | |
| | | C13–Re2–C44 | 105.3 (10) | | |
| | | C33–Re2–C44 | 89.6 (12) | | |
| C1–C2–C4 | 143.3 (19) | C12–C13–C14 | 126 (3) | C–C–C | 145.8 (5) |
| C2–C1–C3 | 140.4 (15) | C13–C14–C15 | 136 (3) | C–C–C | 144.3 (5) |
| C5–C6–C8 | 144.7 (17) | C22–C23–C24 | 146 (3) | C–C–C | 144.9 (5) |
| C6–C5–C7 | 134.5 (23) | C23–C24–C25 | 140 (3) | C–C–C | 144.0 (5) |
| C9–C10–C12 | 142.7 (18) | C32–C33–C34 | 138 (3) | | |
| C10–C9–C11 | 142.7 (19) | C33–C34–C35 | 160 (3) | | |
| C13–C14–C16 | 140.8 (26) | C42–C43–C44 | 138 (3) | | |
| C14–C13–C15 | 139.3 (19) | C43–C44–C45 | 145 (3) | | |
| | | Re1–C13–C14 | 54 (2) | | |
| | | Re1–C14–C13 | 94 (2) | | |
| | | Re2–C13–C14 | 90 (2) | | |
| | | Re2–C14–C13 | 55 (1) | | |

[a] Data for **1a** from ref 13.

(2.04 (3)) is consistent with a single bond, and Re2–C14 and Re1–C13 (2.32 (3) and 2.52 (3) Å) are much longer. Re≡C and Re—C distances are 1.869 (9) and 2.144 (9) Å in $ReO_2$-$(CHCMe_3)(CH_2CMe_3)$;[33] distances for $Re\text{-}CH_2CH_3$ and Re–acetylene carbons average 2.161 (8) and 2.037 (7) Å in $Re(O)$-$Et(MeC\equiv CMe)_2$.[17] Only three other examples of twisted $\mu$-acetylene ligands have been reported,[34] all with similar twist angles of 31–35° but much more symmetric bonding of the acetylene (e.g., for $W_2(\mu\text{-}NMe_2)_2(\mu\text{-}MeC\equiv CMe)Cl_4(py)_4$, W–C = 2.447 (9), 2.020 (11), 2.438 (9), and 2.024 (11)[34a]). The ethyl substituents of the $\mu$-EtC≡CEt ligand in **3b** are also twisted, with a C12–C13–C14–C15 torsion angle of 37° that deviates from the expected 0°.

**Spectroscopic Characterization.** The $^1H$ and $^{13}C$ NMR spectra of the symmetric dimers $[Re(O)(RC\equiv CR)_2]_2$ (**2a–c**) show four sets of acetylenic substituents; the $^{13}C$ NMR spectra also show four different acetylenic carbons. In **2b**, the methylene protons
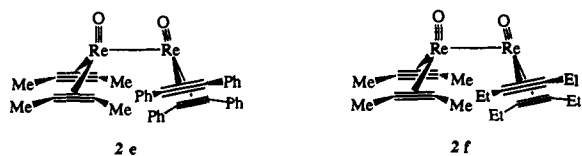
of the 3-hexyne ligands are diastereotopic. These data are consistent with **2a–c** adopting structures in solution with $C_2$ symmetry, similar to the structure of **2a** in the solid state. Three of the methyl resonances of the 2-butyne ligands in **2a** appear between 3.19 and 2.44 ppm ($C_6D_6$), close to the chemical shifts of **1a** ($\delta$ 2.92, 2.30),[13] but the fourth set of methyl groups is found upfield at $\delta$ 0.80. This may be due to the two methyl groups that lie in between the acetylene ligands on the other rhenium (C3 and C11 in **2a**), in the shielding cone of the C≡C bonds. Similarly, one set of ethyl resonances is shifted upfield in the $^1H$ NMR of **2b**.

The mixed acetylene symmetric dimers **2e** and **2f** exist as only one isomer (as does the asymmetric dimer **3e**). The NMR of **2e** and **2f** each show eight acetylenic $^{13}C$ resonances, and the $^1H$ NMR spectrum of **2f** displays four methyl and four ethyl signals, with one methyl and one set of ethyl resonances shifted upfield from the others. This and their chemical reactivity (see below) are consistent with the structures shown below, in which there has been no scrambling of acetylenes between the rhenium centers during synthesis.

The *tert*-butylacetylene dimer **2d** is formed predominantly as one isomer that retains the $C_2$ symmetry of the basic structure. Two $^1Bu$ and two acetylenic hydrogen resonances are observed, with one ≡C$H$ signal upfield, as above (in **2d**, $\delta$ 9.66 and 5.20; compare $\delta$ 9.64 and 9.18 in **1d**). This is the least sterically en-

(33) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Comm.* **1988**, 1489–1450.

(34) (a) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2171–2181. (b) Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990**, *29*, 508–514. (c) Hitchcock, P. B.; Lappert, M. F.; McGeary, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 5658–5660.

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2 e                                    2 f

cumbered structure for the dimer because the acetylenes on each rhenium are antiparallel (as found in **1d**) and the *tert*-butyl groups do not have to lie between the acetylenes of the other rhenium. The reaction of **1d** with 'BuZnCl does give a small amount of a minor isomer (**2g**) (**2d:3d:2g** ≈ 1.0:1.0:0.1), which is believed to have the structure shown on the basis of its NMR (four sets of 'BuC≡CH resonances) and chemical properties.



2 d                                    2 g
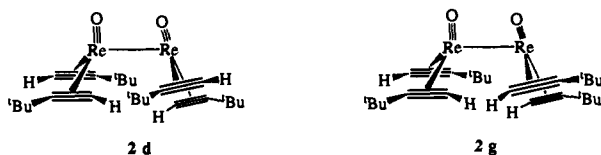
The $^{13}$C NMR chemical shifts for the acetylenic carbons in **2a,b,f** are in the range 140–151 ppm, characteristic of three-electron donor acetylenes[35] and very similar to the shifts in compounds **1**.[13] The $^1J_{CH}$ coupling constants for the acetylenic CH bonds in **2d** average 211 Hz, only slightly smaller than those found for **1d** (220 Hz)[13] and Re(O)OPh('BuC≡CH)$_2$ (215 Hz).[15] This suggests that the d$^5$ Re(II) center is, at most, slightly more electron rich than the related d$^4$ Re(III) centers, since lower values of $^1J_{CH}$ indicate more [RC≡CR]$^{2-}$ character.[36]

The IR spectra of compounds **2** all show strong absorptions in the range 930–970 cm$^{-1}$, typical of rhenium–terminal oxo compounds[5,11,37] and similar to the frequencies in compounds **1**.[13] The spectra of **2a** and **2b** also show acetylenic C≡C stretches at 1766 and 1758 cm$^{-1}$, roughly 30 cm$^{-1}$ lower than observed in **1a** and **1b** and again consistent with a slightly more electron rich metal center in **2** than in **1**. Overall, however, the spectroscopic properties of **2** are very close to those of **1**, indicating (together with the structure of **2a**) that the Re(O)(RC≡CR)$_2$ moiety is preserved and little affected by reduction.

The asymmetric dimers **3** all have very similar spectroscopic properties, suggesting that they are structurally similar. Their IR spectra all show strong bands in the region 925–945 cm$^{-1}$, assigned to the Re≡O terminal oxo stretch. For **3b**, this assignment was confirmed by $^{18}$O labeling: $\nu$(Re$^{18}$O) = 882. A band present at 700 cm$^{-1}$ is assigned to the Re—O—Re stretch, by comparison with other Re—O—Re bridged M—M and M≡M dimers (e.g. [Re(O)($\mu$-O)(CH$_2$CMe$_2$Ph)$_2$]$_2$,[29] 740 cm$^{-1}$ and [Cp*Re(O)($\mu$-O)]$_2$,[28] 634, 614 cm$^{-1}$).

$^1$H and $^{13}$C NMR spectra show that compounds **3** are all fluxional on the NMR time scale. At low temperatures (–40 to –80 °C), eight acetylene substituents and eight acetylenic carbon resonances are observed, consistent with the asymmetric solid-state structure of **3b**. At ambient temperatures, however, only four of the eight signals are clear, with the other four quite broad; above 25 °C, the four broad resonances begin to coalesce into two. The changes in the NMR spectra are completely reversible with temperature, although the high temperature limits are difficult to reach because of decomposition (see below) and because other fluxional processes seem to be occurring (particularly for **3c** and **3e**). Addition of free alkyne to the solution has no effect on the spectra, ruling out a dissociative process.

The $^1$H NMR spectra of **3b** illustrate these changes: Eight triplets for the methyl groups are observed at –40 °C, four of which are unaffected by increasing temperature. The other four triplets coalesce (at 25 °C) into the two broad triplets that are seen at 80 °C. The methylene region of these spectra ($\delta$ 2.5–4) is com-
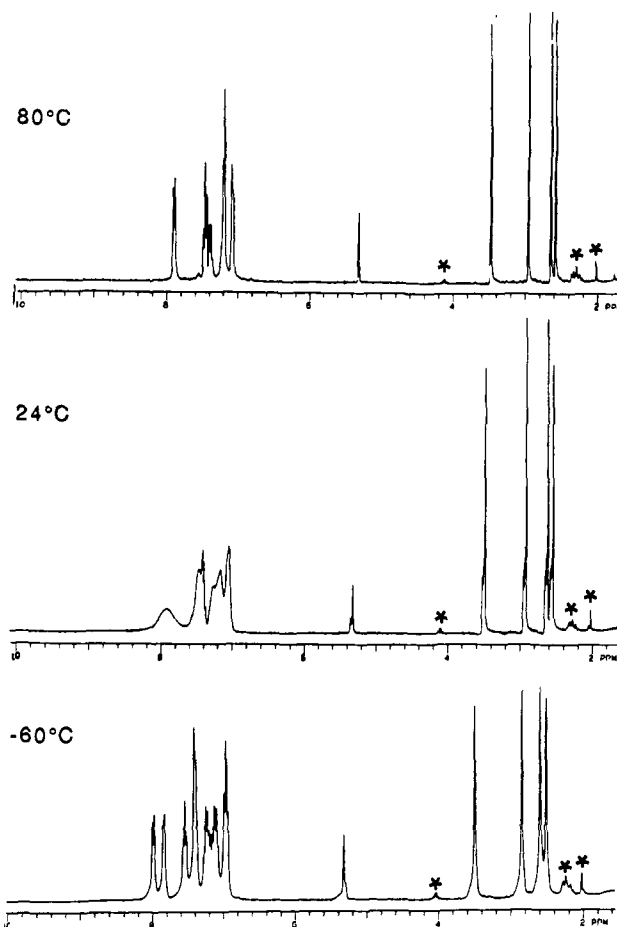


**Figure 4.** $^1$H NMR spectra of (MeC≡CMe)(O)Re($\mu$-O)($\mu$-MeC≡CMe)Re(PhC≡CPh)$_2$ (**3e**) in CD$_2$Cl$_2$, at 80, 24, and –60 °C. Peaks arising from impurities are marked with an asterisk.

plicated by the hydrogens all being diastereotopic. The fluxional process can also be followed by $^{13}$C NMR: Four of the acetylenic carbon resonances observed at –40 °C in C$_7$D$_8$ are not affected, two ($\delta$ 168.0 and 165.4) coalesce to one sharp singlet ($\delta$ 167) at 80 °C, and the last two ($\delta$ 194.9 and 182.4) coalesce but have not reappeared as a new signal at 80 °C.[38] On the basis of the coalescence of ethyl resonances in the $^1$H NMR, the barrier for the fluxional process in **3b** is estimated to be $\Delta G^{\ddagger}$ = 15 kcal/mol; the same value is calculated for **3e**, by using the coalescence of the ortho signals.[39]

The two acetylenes that are fluxional are most likely the two bound to the rhenium center which does not have a terminal oxo (Re2 in the structure of **3b**), and the rigid acetylenes are the bridging acetylene and the acetylene on Re1. (Bridging acetylenes are rarely fluxional.[40]) In **3d**, the bridging acetylene is identified by a low C–H coupling constant of 185 Hz (vs $^1J_{CH}$ = 201–220 Hz in **1d**, **2d**, and the other three CH groups in **3d**), and this resonance is a nonfluxional one. The acetylenic chemical shifts for **3** appear over a wide range ($\delta$ 197–134); the two furthest upfield of the nonfluxional signals are close to those of the related compounds **1b–e** (Table III) and are assigned to the acetylene on the rhenium with the terminal oxo. In **3b**, for instance, the nonfluxional resonances at $\delta$ 153.4 and 150.1 are due to the acetylene on Re1 (compare **1b**, $\delta$ 146.2, 142.8) and the other nonfluxional signals at 193.6 and 169.9 are assigned to the bridging

(35) (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290. (b) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248–1253.

(36) McGreary, M. J.; Gamble, A. S.; Templeton, J. L. *Organometallics* **1988**, *7*, 271–279.

(37) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459–517.

(38) Acetylenic $^{13}$C NMR chemical shifts for **2b** in C$_7$D$_8$: (at –40 °C) $\delta$ 194.9, 194.6, 182.4, 168.9, 168.0, 165.4, 151.2, and 147.0 (25 °C): $\delta$ 195.5, 168.9, 151.0, and 147.2 (80 °C) $\delta$ 196.0, 168.9, 167.0, 151.0 and 147.4.

(39) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 96.

(40) Hoffman, D. M.; Hoffman, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858–3875. Hoffman, D. M.; Hoffman, R. *Organometallics* **1982**, *1*, 1299–1302. Hoffman, D. M.; Hoffman, R. *J. Chem. Soc., Dalton Trans.* **1982**, 1471–1482.

**Table III.** Selected $^{13}$C NMR Data for the Asymmetric Dimers $(RC\equiv CR)(O)Re(\mu\text{-}O)(\mu\text{-}RC\equiv CR)Re(RC\equiv CR)_2$ (3) and Comparison with Compounds 1[a]

| | RC≡CR′ | | |
| compound | low temperature | 25 °C[b] | comparison with Re(O)I(RC≡CR′)$_2$[b] |
|---|---|---|---|
| Re$_2$O$_2$(EtC≡CEt)$_4$ (3b) | 196.5[c] | | |
| | 192.9 | 193.6 | |
| | 180.8 | | |
| | 169.7 | 169.9 | |
| | 168.6 | | |
| | 165.1 | | Re(O)I(EtC≡CEt)$_2$ (1b) |
| | 153.5 | 153.4 | 146.2 |
| | 150.1 | 150.1 | 142.8 |
| Re$_2$O$_2$(PhC≡CPh)$_4$ (3c) | 195.2[d] | 195.4 | |
| | 194.4 | | |
| | 182.6 | | |
| | 166.5 | | |
| | 161.4 | 162.6 | |
| | 159.7 | | Re(O)I(PhC≡CPh)$_2$ (1c) |
| | 157.9 | 157.6 | 147.6 |
| | 149.2 | 149.9 | 144.7 |
| Re$_2$O$_2$(ᵗBuC≡CH)$_4$ (3d) | 183.8[e] | 184.3[f] | |
| | 183.1 | | |
| | 180.0 | | |
| | 170.1 (d, 184 Hz) | 171.1 (d, 185 Hz) | |
| | 166.4 (d, 204 Hz) | | Re(O)I(ᵗBuC≡CH)$_2$ (1d)[f] |
| | 163.9 | 164.2 | 164.5, 157.3 |
| | 156.7 (d, 201 Hz) | | |
| | 135.1 (d, 209 Hz) | 134.5 (d, 212 Hz) | 128.7 (d, 223 Hz) |
| | | | 127.0 (d, 217 Hz) |
| MeC≡CMe)(O)Re(μ-O)- | 194.1[e] | 195.6[g] | |
| (μ-MeC≡CMe)Re(PhC≡CPh)$_2$ (3e)[g] | 190.1 | | |
| | 176.4 | | |
| | 166.9 | | |
| | 164.7 | 165.1 | |
| | 163.9 | | Re(O)I(MeC≡CMe)$_2$ (1a) |
| | 152.8 | 152.5 | 142.0 |
| | 145.6 | 143.3 | 139.0 |

[a] $^{13}$C{H} NMR spectra taken in CD$_2$Cl$_2$ at 300 MHz; chemical shifts are reported in parts per million and referenced to the NMR solvent. [b] Spectra obtained at ambient temperature. [c] Spectrum obtained at –40 °C. [d] Spectrum obtained at –80 °C. [e] Spectrum obtained at –60 °C. [f] $^{13}$C NMR spectrum; $^1J_{CH}$ values are given. [g] Resonances observed at 25 °C are due to *C*Me carbons, assigned by observation of $^2J_{CH}$.

acetylene. The two sets of chemical shifts for the fluxional acetylenes are close to those for d$^6$ tris(acetylene) complexes: Compare δ 196.5 and 169.7 and δ 180.8 and 168.6 in 3b with δ 178.7 and 165.2 for Re(OSiMe$_3$)(EtC≡CEt)$_3$.[18]

In the spectra of 3e, the resonances due to the diphenylacetylene ligands are fluxional while the 2-butyne groups are unaffected by temperature (Figure 4), showing that the fluxional process does not exchange acetylenes between rhenium centers. Complex 3d also shows two fluxional and two rigid acetylenes; the fluxional process equilibrates one pair of ᵗBuC groups and one pair of CH signals (by both $^1$H and $^{13}$C NMR). This shows that the fluxional process is *not* due to simple rotation of individual acetylene ligands, which would equilibrate the ends of the acetylenes but would not equilibrate a *tert*-butyl signal of one acetylene with that of another. The effect of the fluxionality is to equilibrate one end of one acetylene with one end of another. The simplest motion that would accomplish this is coupled rotation of the two acetylene ligands on the rhenium without a terminal oxo (Re2). This movement, best described as a turnstile rotation, makes the A sites equivalent and the B sites equivalent, but does not interconvert A and B. It does not introduce any symmetry into the molecule, consistent with the observation of diastereotopic methylene resonances in 3b even at +80 °C.



3
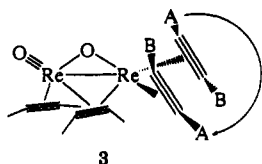
**Reactivity of Re$_2$(O)$_2$(RC≡CR′)$_4$ Compounds 2a–g and 3b–e.** The symmetric dimers, compounds 2, are thermally quite stable

**Scheme II**
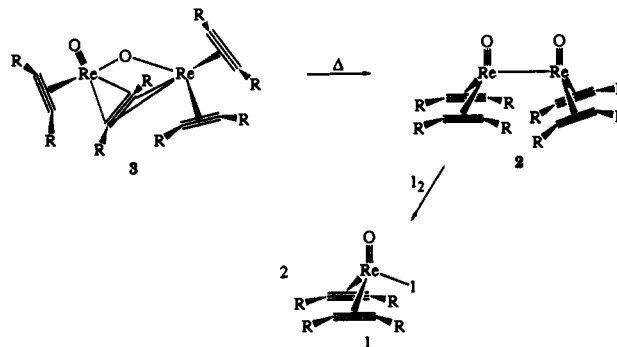


in solution in the absence of air. Thermolyses of 2a and 2b in C$_6$D$_6$ for 14 h at 120 °C results in only a slight darkening of the solutions without change in the NMR spectra. Heating a 1:1 mixture of 2a and 2b for 7 days at 120 °C in C$_6$D$_6$ does not yield the mixed acetylene dimer 2f, and similarly, 2f does not disproportionate into 2a and 2b over 16 h at 105 °C in C$_6$D$_6$. The isomers of the *tert*-butyl acetylene dimer 2d and 2g do not interconvert in 1 h at 70 °C. Thus, homolytic Re–Re bond cleavage to [Re(O)(RC≡CR)$_2$]· fragments does not occur under these conditions.

The asymmetric dimers 3, on the other hand, convert to their isomeric symmetric dimers 2 on heating (Scheme II). Thus, 3b stoichiometrically converts to 2b within 1 h at 100 °C in benzene solution. The diphenylacetylene dimer 3c is the exception, as it is recovered unchanged after 4 days at 100 °C. Thermolysis of 3d yields exclusively 2d, with no evidence for the other "symmetric" isomer, 2g. The butyne/diphenylacetylene dimer 3e converts cleanly to its isomer 2e without the formation of 2a and 2c,

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indicating both that monomeric intermediates are not formed and that isomerization occurs without exchange of acetylenes between the two rhenium centers. Heating **3b** in the presence of excess 2-butyne yields **2b** without the formation of mixed acetylene products, so alkyne dissociation is not occurring. Thus, the rearrangement is an intramolecular isomerization. The relative rates of conversion of **3** → **2** are **3d** > **3b** > **3e** ≫ **3c**.

Both forms of rhenium oxo dimers are stable to air and can be readily handled without precautions to exclude air, but under an atmosphere of $O_2$, a benzene solution of **2a** slowly forms hexamethylbenzene at 25 °C.[41] Stirring a $CH_2Cl_2$ solution of **3b** with $H_2^{18}O$ for 3 days resulted in exchange of the terminal oxo group—$\nu_{Re O}$ at 928 cm$^{-1}$ decreased in intensity and $\nu_{Re^{18}O}$ appeared at 882 cm$^{-1}$—but the bridging oxygen is not affected. Thermolysis of this sample of **3b**, roughly 50% $^{18}O$ labeled at the terminal oxo site, gave isomer **2b** approximately 25% labeled in the terminal oxo groups (by IR and MS).

The symmetric dimers react quantitatively with $I_2$ to give Re(O)I(RC≡CR')$_2$ compounds **1** (Scheme II). $Br_2$ reacts analogously, albeit much faster, to give Re(O)Br(RC≡CR)$_2$. Compounds **2e** and **2f** are cleaved by $I_2$ back to their starting materials, **1a** + **1c** from **2e** and **1a** + **1b** from **2f**, without formation of mixed complexes Re(O)I(RC≡CR)(R'C≡CR'). Thus, alkynes are not exchanged from one rhenium center to the other in this process. In the reaction of **2d** with $I_2$, only the asymmetric form of **1d** is obtained, while reaction of the minor isomer **2g** gives both this and a $C_s$ form of **1d**, in close to equal amounts (eq 5). These reactions are consistent with the structural assignments made earlier and indicate that the reactions with $I_2$ occur without loss of stereochemistry about the rhenium center.



(5)
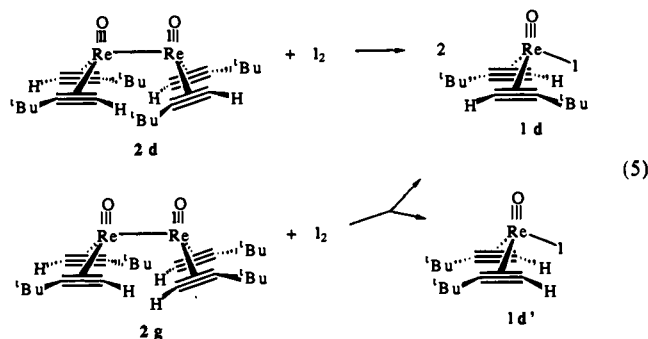
The relative rates of iodine oxidation are **2a** > **2f** > **2b** > **2e** ≫ **2d** > **2c**; for instance, 50% of **2a** is consumed versus less than 5% of **2d** under the same conditions (1.5 h, excess $I_2$, $CDCl_3$ at 25 °C). Complexes of diphenylacetylene, the most electron withdrawing of these ligands, are the hardest to oxidize. An outer-sphere electron-transfer pathway is unlikely, as no oxidation of **2** is observed by cyclic voltammetry. For the dialkylacetylene species, steric bulk inhibits reaction, suggesting an associative process (consistent with reactions of **2a** being faster at higher $I_2$ concentrations).[42] The asymmetric dimer **3c** also reacts cleanly with $I_2$ to give **1c**, but **3b** reacts to give a mixture of at least 10 products, of which **1b** was the major product. **3d** plus $I_2$ gives exclusively the asymmetric form of **1d**. Reactions of compounds **3** with $I_2$ are faster than reactions of **2**.

Dimers **2a** and **2b** react with the strong acids $HSO_3CF_3$ and HCl but are unreactive with $H_2$, $^nBu_3SnH$, $CH_3COOH$, or $CF_3COOH$. The addition of excess HCl(g) to **2b** in toluene-$d_8$

resulted in an initial broadening of the EtC≡CEt signals in the $^1H$ NMR, the same effect as observed on protonation of the oxo groups in rhenium(III) complexes such as **1b**.[17] While a number of products grow in, broad signals consistent with [Re(OH)Cl(EtC≡CEt)$_2$]$^+$ were observed and the rhenium(III) complex Re(O)Cl(EtC≡CEt)$_2$ was isolated after chromatography on silica gel. Re(O)H(EtC≡CEt)$_2$, which should be stable to these conditions,[17] was not observed. **2a** and **2b** do not react with MeI or $MeSO_3CF_3$; **3b** reacts to give as yet unidentified products.

## Discussion

The **symmetric dimers 2a–f** have an unusually low oxidation state (+2, d$^5$) for terminal oxo species.[43] An alternative assignment as Re(VI), considering the acetylene ligands as dianions, is ruled out by the structural, spectroscopic, and chemical properties of **2**:[13] In particular, their hydrolytic and protic stability contrasts with the very facile hydrolysis of RC≡CR$^{2-}$ complexes.[44] All of the previously known rhenium dimers with terminal oxo ligands have oxidation states of +5 or higher,[5,11] and previously reported low-valent rhenium–oxo dimers have only $\mu$-oxo groups.[45] Complex **2** and the unusual mixed-valence trimer $(Me_3SiCH_2)_2(O)Re(\mu-O)(PMe_3)_4Re=Re(O)_2(CH_2SiMe_3)$[46] are also the only examples of unsupported Re–Re bonds in rhenium–oxo complexes—all other rhenium–oxo dimers have at least one $\mu$-oxo ligand (e.g., $Re_2(O)_3Cl_4(en)_2$ and $Re_2(O)_3Me_6$).[47] Not only is the absence of a $\mu$-oxo ligand in **2** unusual, but in addition, these species with two terminal oxo ligands are thermodynamically more stable than **3**, with one bridging and one terminal oxo (**3** → **2** on heating). Although it is too simplistic to focus solely on the oxo ligands in **2** and **3**, it is clear that strong, stable rhenium–oxo multiple bonds are formed and that bridging is not always favored over terminal oxo ligation, even in low oxidation states.

The symmetric dimers **2** are an exception to the trend for the same reasons that favor Re–O multiple bonding in the rhenium-(III)–oxo–bis(acetylene) complexes Re(O)X(RC≡CR)$_2$, including the pseudotetrahedral geometry and the presence of the acetylene coligands.[13] **2** are isoelectronic with Re(O)X(RC≡CR)$_2$ compounds and can be considered another member of this series, in which X = [Re(O)(RC≡CR)$_2$].[48] The similarity between **2** and other Re(O)X(RC≡CR)$_2$ compounds is seen in their structure, spectra, and chemical properties. The compounds are all thermally robust and chemically quite inert (e.g., protonation occurs only with strong acids); they are all rigid on the NMR time scale. Spectroscopically, the dimers **2** appear to be slightly more electron rich than **1**, perhaps reflecting their formal Re(II) oxidation state.

The assignment of the Re–Re bond in **2** as a single bond is consistent with their cleavage by halogens and the description of Re(O)X(RC≡CR)$_2$ compounds as 18-e$^-$ complexes.[13] The bond distance of 2.686 (1) Å is at the short end of reported single bond distances, possibly indicating some rhenium–rhenium double bond character.[49,50] On the basis of the MO picture for **1**,[13] the rhenium

(41) Formation of hexaalkyl benzenes has also been observed from Re-(O)R'(RC≡CR)$_2$ and [Re(O)py(RC≡CR)$_2$]SbF$_6$.

(42) The mechanism may involve initial formation of an $I_2$ adduct followed by Re–Re bond fission, as observed in $I_2$ oxidation of some rhenium carbonyl—phosphine compounds: Poe, A. J. In *Reactivity of Metal-Metal Bonds*; Chisholm, M. H., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1981; Chapter 7 and references therein. Kramer, G.; Patterson, J.; Poe, A. J.; Ng, L. *Inorg. Chem.* **1980**, *19*, 1161–1169. Reactions of $I_2$ with Mn$_2$(CO)$_{10}$ and Re$_2$(CO)$_{10}$ proceed by both [$I_2$]-dependent and -independent (M–M homolytic fission) paths: Haines, L. I. B.; Hopgood, D.; Poe, A. J. *J. Chem. Soc. A* **1968**, 421–428. (d) Haines, L. I. B.; Poe, A. J. *J. Chem. Soc. A* **1969**, 2826–2833.

(43) [Re(O)(OH)(py)$_4$]$^-$ has been generated electrochemically in solution. See also refs 11, 18, and 20.

(44) As a reviewer pointed out, there is clearly an electronic similarity between low-valent acetylene and high-valent oxo complexes, as illustrated by the series of known compounds ReMe(O)$_3$, ReMe(O)$_2$(RCCR), ReMe-(O)(RCCR)$_2$, and ReMe(RCCR)$_3$.

(45) For instance, [Re$^{IV}_2(\mu-O)X_{10}$]$^{4-}$ (Lis, T.; Glowiak, T.; Jezowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1975**, *23*, 739. Lis, T.; Jezowska-Trzebiatowska, B. *Acta Crystallogr., Sect. B* **1976**, *32*, 867–9) or Cp*$_2$Re$^{II}_2(\mu-O)$(CO)$_4$.[28] See also ref 5b, p 171–2.

(46) Chiu, K. W.; Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 31–36.
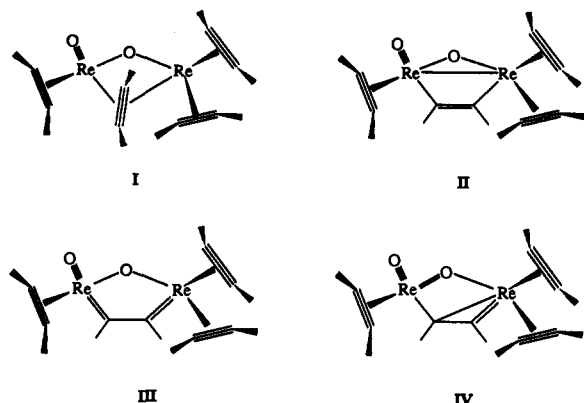
(47) Reference 5b, p 171–2. Glowiak, T.; Lis, T.; Jezowska-Trzebiatowska, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1972**, *20*, 199. Toppen, D. L.; Murmann, R. K. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 139. Shandles, R.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1971**, *10*, 2785–9. Stavropoulos, P.; Edwards, P. G.; Wilkinson, G.; Motevalli, M.; Abdul Malik, K. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 2167–2175. Calvo, C.; Frais, P. W.; Lock, C. J. L. *Can. J. Chem.* **1972**, *50*, 3607–3618.

(48) The formal d$^5$ configuration for **2** is different than the d$^4$ configuration for the other Re(O)X(RC≡CR)$_2$ complexes because of the way metal–metal bonds are counted in the oxidation state formalism.

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**Scheme III.** Suggested Valence Bond Contributors to the Structure of **3**



I

II

III

IV

d orbitals parallel to the Re–O bond are empty ($d_{xz}$, $d_{yz}$, and $d_{z^2}$, taking the z axis to be along the Re–O bond) while those perpendicular to it are filled ($d_{xy}$ and $d_{x^2-y^2}$). If the two rhenium centers are twisted 90° relative to each other, filled–empty overlap can occur. The observed torsion angle, $\angle$O–Re–Re–O = 74.2°, is close to the predicted 90°. This may also explain why only the gauche rotamer of compounds **2** is observed, although the anti form might be sterically less encumbered. A similar argument has been used to rationalize the orientation of the $\pi$-donor phenoxide ligand in Re(O)OPh(MeC≡CMe)$_2$ ($\angle$O–Re–O–C = 69°).[15]

**The asymmetric dimers 3b–f** have a unique and complex structure, in which the coordination spheres about Re1 and Re2 are quite different and do not closely resemble any idealized geometry. Clearly, a single valence bond structure will not provide a complete picture of the structure and bonding in compounds **3**. However, valuable insights can be obtained by examining the two halves of these dimers.

The half of the asymmetric dimers containing the terminal oxo group, the left half in Figure 2, is in many ways similar to the rhenium(III) complexes Re(O)X(RC≡CR)$_2$.[13–18] The bond angles about Re1 in **3b** are similar to those in Re(O)X(RC≡CR)$_2$ structures: Compare O2–Re1–C23,24 = 105.7 (10), 112.0 (8)° vs O–Re–C = 110–115° in **2a**, and O2–Re1–Re2 and O2–Re1–O1 = 117.4 (6)° and 122.1 (8)° vs 114.4 (6)° for the average O–Re–Re angles in **2a**. The Re(O)(RC≡CR)($\mu$-RC≡CR) portion of the asymmetric dimers is rigid on the NMR time scale, as are Re(O)X(RC≡CR)$_2$, and the $^{13}$C chemical shifts for the carbons of the nonbridging acetylene are close to the shifts observed in the analogous compounds **1** (Table III).

The other half of the asymmetric dimers resembles rhenium-(I)–tris(acetylene) complexes of the type ReX(RC≡CR)$_3$, which we have recently characterized[22,51] and which have close group VI analogues such as WL(RC≡CR)$_3$.[52] Both this half of **3** and the tris(acetylene) species are fluxional, and the $^{13}$C chemical shifts
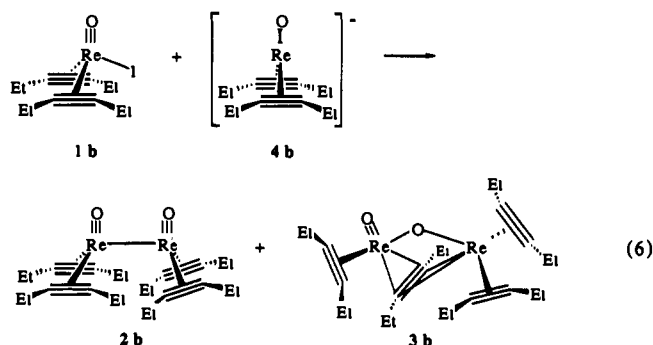
are similar. Structurally, the acetylene ligands on Re2 in **3b** are almost parallel to Re2–O1, which is characteristic of the $C_{3v}$ MX(RC≡CR)$_3$ geometry but opposite to that found in Re(O)-X(RC≡CR)$_2$ (and that found at Re1). Bond angles relating the two terminal acetylenes in **3b** (e.g., $\angle$C43–Re2–C34 = 120.3 (10)° and $\angle$C44–Re2–C33 = 89.6 (12)°) are quite similar to related angles in Re(OSiMe$_3$)(MeC≡CMe)$_3$ (av 119.8 (5)° and 90.5 (5)°).[51a]

Thus, the best simple description of the asymmetric dimers is that they are mixed valence, Re(III)/Re(I) species. The Re(III) half is an unusual Re(O)X(RC≡CR)$_2$ structure in which one acetylene is bridging and the X group is the $\mu$-oxo (similar to Re(O)OR'(RC≡CR)$_2$), and the Re(I) half, Re($\mu$-O)($\mu$-RC≡CR)(RC≡CR)$_2$, is related to Re(OSiMe$_3$)(RC≡CR)$_3$. In this description (I in Scheme III), the bridging acetylene is considered to be a neutral four-electron donor and a Re–Re bond is not invoked. It is interesting that 2-butyne is ineffective in displacing the $\mu$-EtC≡CEt ligand of **3b** to give a singly bridged dimer, "[(EtC≡CEt)$_2$(O)Re-O-Re(EtC≡CEt)$_2$(MeC≡CMe)]", which would be directly analogous to the rhenium(III) and rhenium(I) species discussed above.

Structure I is a valuable simple picture, but other resonance forms (II–IV in Scheme III) are helpful to discuss the details of the structure. The twisting of the bridging acetylene and the short Re–Re distance suggest a contribution from II (in which the parallel acetylene is described as [$\mu$-RC≡CR]$^{2-}$, as is typical[40]). Forms III and IV might be included to describe the asymmetry of both the bridging oxo and acetylene ligands and the short Re2–C13 and Re1–O1 bond lengths. The shorter bonds to the bridging acetylene are from the Re($\mu$-O)(RC≡CR)$_2$ fragment, probably reflecting greater back-bonding from the more electron rich, lower oxidation state rhenium center. Thus, the origin of the twist of the bridging acetylene seems to be in the different electronic demands of the two quite different rhenium centers. This may also be the case in a mixed-valence tungsten sulfido complex with a twisted bridging Me$_2$NC≡CNMe$_2$ ligand,[34c] but the two other examples have equivalent metal centers and therefore have different reasons for the twisting of the acetylene.[53]

The isomerization of **3** to **2** seems to involve movement of the $\mu$-oxo to the low-valent rhenium and movement of the $\mu$-acetylene to the rhenium–oxo center, with cleavage of the short Re1–O1 and Re2–C13 bonds. The higher thermal stability of **3c** and **3e** versus **3b** could be due to ground-state stabilization of the electron-rich rhenium center by the more $\pi$-acidic diphenylacetylene ligand or, alternatively, to destabilization of an electron-deficient transition state.

**Mechanistic Aspects of Dimer Formation.** The rhenium dimers **2** and **3** are formed whenever the oxidation state of rhenium in this system is adjusted to +2. This can be accomplished by reduction of **1** electrochemically or by $^t$Bu$_2$Zn, $^t$BuZnCl, sodium metal, NaC$_{10}$H$_8$, or Cp$_2$Co and by oxidation of rhenium(I)-oxo–bis(acetylene) anions, NaRe(O)(RC≡CR)$_2$ (**4**),[18] with almost any one-electron acceptor, including air, Cp$_2$Fe$^+$, PhI, and $^t$BuI.[19] Dimers are also formed on reaction of **1** with **4**, by conproportionation of Re(III) and Re(I) (e.g., eq 6).



$$(6)$$

1b     4b

2b     3b

(49) Re–Re double bonds are typically in the range 2.38–2.65 Å, although some longer distances have been reported. Cotton, F. A. In *Reactivity of Metal-Metal Bonds*; M. H. Chisholm, Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1981; Chapter 1; see also ref 28. Bennet, M. J.; Graham, W. A. G.; Hoyano, K. J.; Hutcheon, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 6232. Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171–173.

(50) The short Re–Re bond could also be due to the overlap of two directional, half-occupied $\sigma$ orbitals of [Re(O)(RC≡CR)$_2$]· fragments, as has been suggested to explain short single bonds in other systems: Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. Goldberg, S. Z.; Eisenburg, R. *Inorg. Chem.* **1976**, *15*, 535. Jarchow, O. Z. *Anorg. Allg. Chem.* **1971**, *383*, 40.

(51) (a) Conry, R. R., Ph.D. Thesis, University of Washington, 1991. (b) Re(OSiMe$_3$)(RC≡CR)$_3$ synthesis[18] structure.[51a]

(52) (a) Tate, D. P.; Augl, J. M. *J. Am. Chem. Soc.* **1963**, *85*, 2174–2175. (b) Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Ross, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261–3265. (c) Laine, R. M.; Moriarity, R. E.; Bau, R. *J. Am. Chem. Soc.* **1972**, *94*, 1402–1403. (d) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044–6. (e) Maher, J. M.; Fox, J. R.; Foxman, B. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 2347–2353. (f) Wink, D. J.; Creagan, B. T. *Organometallics* **1990**, *9*, 328–334 and references therein.

(53) Calhorda, M. J.; Hoffmann, R. *Organometallics* **1986**, *5*, 2181–2187. Cotton, F. A.; Feng, X. *Inorg. Chem.* **1990**, *29*, 3187–3192.

The effectiveness of outer-sphere redox reagents suggest that many of the reactions proceed via electron transfer. Electrochemical reductions of **1a–c** are irreversible and show the formation of dimers on the cyclic voltammetry time scale,[54] suggesting that reduction leads to rapid loss of I⁻ and the resulting rhenium(II) radical [Re(O)(RC≡CR)₂]⁻ (**5**) dimerizes.[55] Similarly, one-electron oxidation of **4** should yield **5**.

Most reactions yield both the symmetric and asymmetric dimers, with the ratio of **2:3** usually between 10:1 and 0.75:1. Dimerization of **5** seems likely to give the symmetric dimers **2**. A clue to the pathway to asymmetric dimers may be the one case in which it is the predominant isomer: the formation of the mixed dimer **3e**, either by reduction of **1a** + **1c** (eq 4 above) or on reaction of **1a** with **4c** (eq 7). In contrast, the reaction of **1c** with **4a** yields quite different products (eq 8).



(7)



(8)
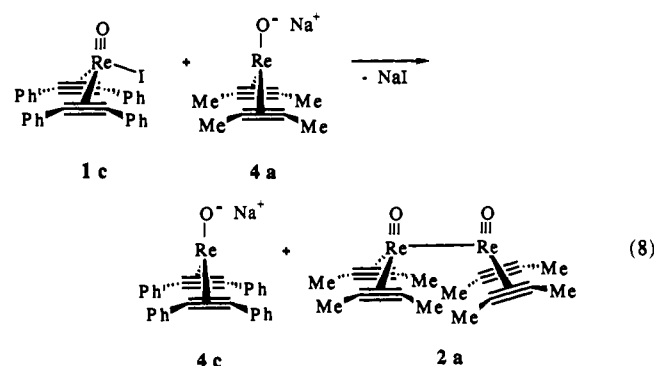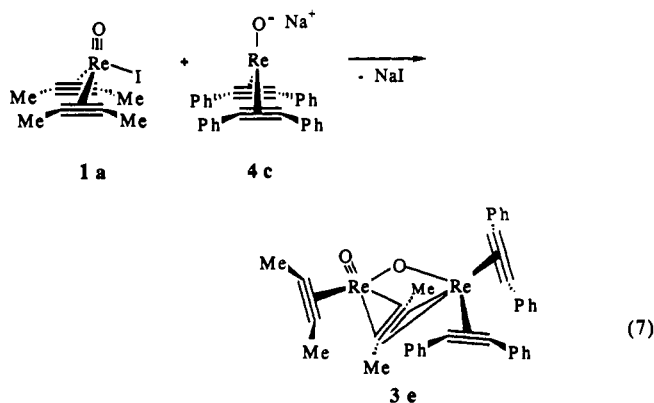
Reaction 7 is unique because it does not occur by electron transfer, since anion **4c** is not a strong enough reductant to reduce **1a** (due to the electron-withdrawing PhC≡CPh ligands). In the reduction of a mixture of **1a** and **1c** (eq 4), the diphenylacetylene complex is reduced first, leading to conditions much like eq 7. Other conproportionation reactions, such as eqs 6 and 8, proceed by electron transfer and give the same products as if an outer-sphere reagent had been used. Reaction 7 appears to be simple metathesis of the iodide ligand in **1a** by the (quite nucleophilic[19]) oxo ligand of **4c**, analogous to the formation of Re(O)(OR)-(RC≡CR)₂ from **1** and thallium alkoxides.[15] Initial substitution to create the μ-oxo ligand is likely followed by a 2-butyne ligand shifting into the bridging position, analogous to the silylation of

the oxo of **4c**, which is rapidly followed by the binding of a third acetylene ligand.[18,51a]

Formation of the asymmetric dimers from Re(III) and Re(I) precursors is an attractive mechanism because of the description of **3** as Re(III)/Re(I) mixed-valence species. It is possible that this is a general mechanism for the production of **3**, that some **4** is formed on reduction of **1**,[56] and that oxidation of **4** yields some [Re^III(O)(RC≡CR)₂(S)]⁺ (**6**, where S is a solvent or other available ligand).[13] Re(III) and Re(I) compounds could also be formed by disproportionation of the Re(II) radical **5** to **4** and **6** in the presence of a coordinating solvent.[57] Consistent with this suggestion, yields of **3** are usually higher—sometimes substantially—in better coordinating solvents (THF or acetonitrile vs benzene). The presence of **4** in the reduction of **1** to dimers is consistent with a trapping experiment: In the presence of MeI,[58] the reaction of **1b** with 1 equiv of NaC₁₀H₈ (THF, –78 → 25 °C) forms, instead of dimers, a 1:1 ratio of starting **1b** and Re(O)-Me(EtC≡CEt)₂ (the product of **4b** + MeI[19]). The Re(III)/Re(I) mechanism is, however, hard to reconcile with all of the data on the formation of **3**. For instance, reduction of **1b** yields essentially the same ratio of **2b** to **3b** with ¹BuZnCl, sodium metal, and NaC₁₀H₈ (0.5 or 1.0 equiv); if **4b** is a key intermediate, the nature and quantity of reductant should be important. Other pathways cannot be ruled out, such as the combination of Re(II) radicals **5** to form both **2** and **3**, or the involvement (particularly in reactions of **4**) of the dimer radical anion [Re₂(O)₂(RC≡CR)₄]⁻, which appears to be stable on the cyclic voltammetry time scale.

## Conclusions

Rhenium dimers Re₂(O)₂(RC≡CR)₄ are formed on reduction of Re(III) complexes Re(O)I(RC≡CR)₂ (**1**) and on oxidation of Re(I) anions NaRe(O)(RC≡CR)₂ (**4**) by a variety of reagents. Two quite different isomers are isolated, a symmetric form with two terminal oxo groups and an unsupported Re–Re bond (**2**) and an asymmetric isomer (**3**) with one terminal and one bridging oxo ligand and an unusual twisted bridging acetylene ligand. The asymmetric isomers **3** are best described as mixed-valence Re-(III)/Re(I) complexes. They convert to the symmetric form **2** on heating, and **2** react with I₂ to form **1**, all without scrambling the acetylene ligands between rhenium centers. The acetylene ligands on the Re(I) side of **3** are fluxional on the NMR time scale, undergoing a "turnstile" rotation that exchanges the ends of two different acetylenes. The symmetric dimers are likely the product of coupling of two Re(II) radicals; the asymmetric dimers, at least in one case, can be formed by the reaction of Re(III) and Re(I) compounds (**1** + **4**).

(54) Spaltenstein, E. Ph.D. Thesis, University of Washington, 1989.

(55) The initial blue color observed during reductions of **1a,b,d** (red for **1c**) could be due to **5** or possibly to [Re(O)I(RC≡CR)₂]⁻. The color persists for a few seconds at ambient temperatures, a few minutes at –78 °C.

(56) **4** is formed on reduction of **1** with NaC₁₀H₈ but not with Na metal or Cp₂Co.

(57) Disproportionation is a common reaction of 17e⁻ organometallic radicals, and solvent effects similar to those observed here have been reported: Steigman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217–240. Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4434–4436. Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253–8. Bond, A. M.; Colton, R. *Inorg. Chem.* **1976**, *15*, 446–8. Bond, A. M.; Bowden, J. A.; Colton, F. *Inorg. Chem.* **1974**, *13*, 602–8.

(58) The reduction potential of MeI is more negative than that of **1b** by ~1.0 V.