[(silox)$_2$ReO]$_2$ (silox = ^{t}Bu$_3$SiO) contains a Re≡Re bond and terminal oxo ligands

Richard E. Douthwaite, Peter T. Wolczanski* and Erika Merschrod

Cornell University, Baker Laboratory, Department of Chemistry, Ithaca, New York, USA 14853.
E-mail: ptw2@cornell.edu

Received (in Bloomington, IN, USA) 14th September 1998, Revised manuscript received 19th October 1998. Accepted 23rd October 1998

The preference for terminal rather than bridging {*i.e.* [(silox)$_2$Re]$_2$(μ-O)$_2$} oxo ligands in C_2 (silox)$_2$(O)Re≡Re-(O)(silox)$_2$ is electronic, not steric, in origin.

Use of the bulky siloxide ^{t}BuSiO$^-$ (silox) ligand has enabled investigations of several low coordinate, monomeric complexes of groups 4–6,[1–4] but metal–metal bond formation cannot always be averted. [(silox)$_2$MH$_2$]$_2$ (M^{IV} = Nb, Ta)[5] dimers form upon reduction of (silox)$_2$MCl$_3$ under H$_2$ when M^V trihydride derivatives were expected, and while sterically protected (silox)$_2$W=N^{t}Bu,[4] an unusual three-coordinate W^{IV} derivative, was isolable, a less hindered W^{III} environment encouraged triple-bond formation, *i.e.* (silox)$_2$XW≡WX(silox)$_2$ (X = Cl, H, Me, Et).[6] Attempts to extend the theme of low-coordination to Re[7] have instead resulted in the synthesis of C_2 (silox)$_2$(O)Re≡Re(O)(silox)$_2$, whose terminal oxo groups are an apparent oddity.

In contrast to metatheses within groups 4–6, treatments of various rhenium chlorides with Na(silox) were ineffective. Utilization of Tl(silox), prepared *via* metathesis of Hsilox with TlOEt, mitigated some of the undesired redox processes. Addition of Tl(silox) to ReCl$_3$(PEt$_3$)$_3$[8] (100 °C, 12 h, C$_6$H$_6$) afforded orange (silox)ReCl$_2$(PEt$_3$)$_2$ **1** (60%), and a similar treatment (100 °C, 2 d, C$_6$H$_6$) of Cl$_4$ReL$_2$ (L = THT,[9] THF)[10] gave the blue, trigonal bipyramidal (X-ray) Re^V complex, (silox)$_3$ReCl$_2$ **2** (33%) upon chromatographic work-up in air. Metathesis of Re$_3$Cl$_9$ with 3 equiv. Tl(silox) (100 °C, 12 h, C$_6$H$_6$) provided dark green, C_s (X-ray) [(silox)ReCl]$_3$(μ-Cl)$_3$ **3** (85%); further incorporation of silox into **1–3** could not be effected.

Treatment of *cis*-ReOCl$_3$(PEt$_3$)$_2$[11] with 3 equiv. of Tl(silox) afforded orange (silox)$_2$(O)Re≡Re(O)(silox)$_2$ **4** [eq (1)] in moderate yield (38%) after extensive trituration with hydrocarbons and crystallization from THF. Two singlets in its ^{1}H NMR spectrum suggested C_2 symmetry, and IR spectroscopy revealed a moderate band at 944 cm^{-1} tentatively assigned to ν(ReO). An X-ray diffraction study of **4** confirmed the molecular C_2 symmetry, terminal oxo and silox ligands, and distorted tetrahedral geometry about each Re (Fig. 1). Inter-silox angles O1–Re1–O4 [124.9(2)°] and O2–Re2–O3 [123.1(2)°] are significantly splayed due to a steric interaction. While O4–Re1–Re2 110.8(2)° and O3–Re2–Re1 112.5(2)° are relatively normal, they contrast with O1–Re1–Re2 [92.8(2)°] and O2–Re2–Re1 [93.0(2)°], which cant toward more open space between the silox and oxo groups. The d(Re≡Re) of 2.3593(6) Å is long compared to common Re^{II} d^5–d^5 ($\sigma^2\pi^4\delta^2\delta^{*2}$) triple bonds and related C_2 ditungsten species.[12] The Re–oxo bond lengths of 1.690(5) and 1.729(6) Å are slightly longer than average, but most comparisons are with oxo ligands on higher valent derivatives,[13,14] where shorter bonds are expected. Two Re-silox distances are normal [d(Re1–O1) = 1.822(5), d(Re2–O2) = 1.819(5) Å], while the remaining Re1–O4 [1.875(6) Å] and Re2–O3 [1.909(6) Å] linkages are quite long due to the respective *trans*-influences of the O6 and O5 oxo groups transmitted through the Re≡Re bond.

$$\textit{cis}\text{-ReOCl}_3(\text{PEt}_3)_2 \;+\; 3\ \text{Tl(silox)} \xrightarrow[\text{benzene, -3 TlCl}]{160\ ^\circ\text{C, 3 d}} \underset{\textbf{4}}{(\text{silox})_2(\text{O})\text{Re}{\equiv}\text{Re}(\text{O})(\text{silox})_2} + \ldots. \quad (1)$$

(silox)$_2$(O)Re≡Re(O)(silox)$_2$ **4** was remarkably inert toward simple donors (*e.g.* CO, py, alkenes), reducing agents (*e.g.* H$_2$, Me$_3$SiH), common oxidants (*e.g.* I$_2$, BrCH$_2$CH$_2$Br, pyO, Me$_3$NO, H$_2$CCH$_2$O, N$_2$O) and heterocumulenes (*e.g.* CS$_2$, PhN=C=O), and reacted with a few substrates or reagents (*e.g.* PhPH$_2$, Na/Hg, O$_2$) to give mixtures. Terminal rhenium–oxo bonds have been noted to be strong and inert in mononuclear complexes [*cf.* (MeC$_2$Me)$_2$RReO],[14] yet aggregation *via* μ-oxo formation is common.[15] Since **4** could have adopted a [(silox)$_2$Re]$_2$(μ-O)$_2$ **5** configuration without undue steric strain {*cf.* [(silox)$_2$W]$_2$(μ-CMe)$_2$},[16] calculations were employed to assess the terminal oxo electronic structure preference.

Fig. 2 illustrates truncated extended Hückel MO diagrams for the model complex (HO)$_2$(O)Re≡Re(O)(OH)$_2$ **4′**, which was given the structural parameters of **4** and adjusted to be C_2, and [(HO)$_2$Re]$_2$(μ-O)$_2$ **5′**, whose optimized geometry [*e.g.* d(ReRe) $\doteq$ 2.53 Å, d(Re–O$_b$) = 1.94 Å] was determined from density functional theory (DFT). The EHMO calculations revealed **5′** to be *ca.* 4 eV less stable than the observed **4′** system, with a very small HOMO–LUMO gap of *ca.* 0.5 eV. The extreme discrepancy in total energy is due to a tremendous increase of Re–O and Re–Re π* character realized in the three highest occupied orbitals of **5′**. In the unbridged geometry **4′**, the Re≡Re bond is comprised of the usual σ- and two π-bonding orbitals,[17] and while the d^3 fragment MOs have a significant amount of Re–O π*-character, it is largely dissipated upon forming the

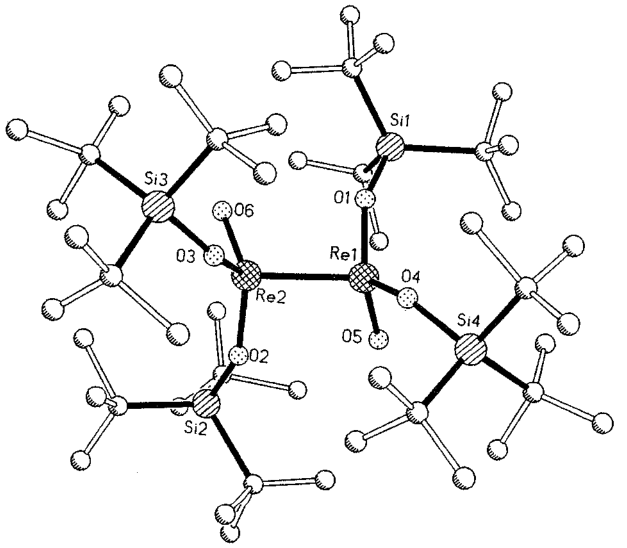

Fig. 1 Molecular view of (silox)$_2$(O)Re≡Re(O)(silox)$_2$ **4**. Selected (see text) interatomic distances (Å) and angles (°): Si1–O1 1.629(5), Si2–O2 1.637(5), Si3–O3 1.704(6), Si4–O4 1.728(6); O1–Re1–O5 112.4(2), O4–Re1–O5 109.8(2), O2–Re2–O6 115.9(2), O3–Re2–O6 104.6(3), O5–Re1–Re2 104.9(2), O6–Re2–Re1 106.4(2), Re1–O1–Si1 156.9(4), Re1–O4–Si4 146.7(4), Re2–O2–Si2 153.3(4), Re2–O3–Si3 149.4(4).

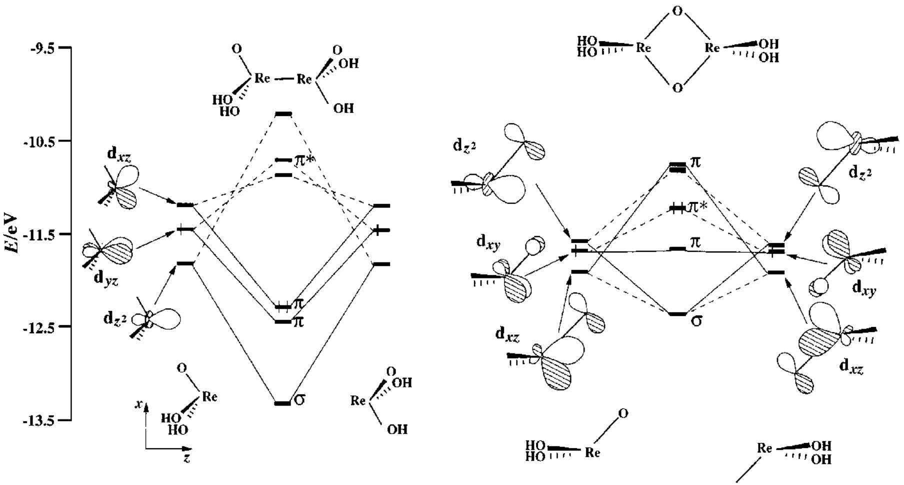

Fig. 2 Truncated MO diagrams for $(HO)_2(O)Re{\equiv}Re(O)(OH)_2$ **4′** and $[(HO)_2Re]_2(\mu{-}O)_2$ **5′**, modeling $(silox)_2(O)Re{\equiv}Re(O)(silox)_2$ **4** and hypothetical $[(silox)_2Re]_2(\mu{-}O)_2$ **5**, respectively.

metal–metal bond. In the μ-oxo version **5′**, dimerization of the $(HO)_2ReO$ fragments affords a Re–Re σ-bonding (σ) orbital that is principally d$_{z^2}$ and a Re–Re π-bonding (π) orbital based on d$_{xy}$, but both have significant Re–O π* character, and the latter is rendered virtually non-bonding relative to the fragment MOs. Another Re–Re π-bonding orbital derived from d$_{xz}$ contains so much Re–O π* character that it is destabilized relative to a Re–Re π* orbital that is populated instead. The net $\sigma^2\pi^2\pi^{*2}$ ordering describes a single Re–Re bond, and an assessment of the core orbitals (not shown) indicates that the Re–O antibonding π-interactions are not compensated enough by the two additional Re–O σ-interactions. Interestingly, the calculated minimum energy configuration of **4′** does not have a classical ethane-like geometry,[17] but optimizes with an HO–Re–Re angle near 90°, as in the crystal structure of **4**.

The cylindrical symmetry accorded the terminal oxos in **4** permits four significant π-bonds, whereas disruption of virtually all Re–O π-bonding in the bridged form is poorly balanced by additional σ-interactions; the terminal oxo structural preference of **4** is electronic in character. Thermodynamic preferences of $[(EtC_2Et)_2(O)Re]_2$ over $[(EtC_2Et)_2Re](\mu{-}O)(\mu{-}EtC_2Et)[Re(O)(EtC_2Et)]$,[18] and $(RO)_2(^tBuC{\equiv})Re=Re({\equiv}C{-}^tBu)(OR)_2$[19] over μ-alkylidyne bridged forms, may be similarly ascribed. In compounds that lack additional terminal π-donors, or contain two less electrons {*e.g.* d^2-d^2 $[(Me_3SiCH_2)_2Re]_2(\mu{-}CSiMe_3)_2$},[20] the bridged form of multiple metal–ligand bond may prevail.[15]

Financial support from the National Science Foundation (CHE-9528914), Cornell University and The English-Speaking Union, for a Lindemann Trust Fellowship (R. E. D.), is gratefully acknowledged. We thank Ana-Rita Mayol and Emil Lobkovsky for experimental assistance, and Chase A. Munson for the initial calculations.

Notes and references

Selected analytical data: **1** (C_6D_6), δ_H δ1.58 (12 H, br q, CH_2), 7.00 (18 H, br t, CH_3), 8.07 (27 H, s, ^{t}Bu); δ_C δ10.31 (CH_2), 48.78 (CMe_3), 112.81 [$C(CH_3)_3$], 121.44 (CH_3). Anal. Calc. for $C_{24}H_{57}OSiP_2Cl_2Re$, C, 40.7, H, 8.1. Found: C, 40.8, H, 8.3%. **2** (C_6D_6), δ_H 6.70 (br, ^{t}Bu); δ_C 44.64 [$C(CH_3)_3$], 167.30 (CMe_3); UV–VIS (CH_2Cl_2) 700 nm (ε = 50 dm^3 mol^{-1} cm^{-1}), 577 [170, $e''(^3A_2') \rightarrow e'(^3A_2'')$], 345 (3100), 283 (5900). Anal. Calc. for $C_{36}H_{81}O_3Si_3Cl_2Re$, C, 47.9, H, 9.0. Found C, 47.6, H, 8.6%. **3** (C_6D_6), δ_H 1.12 (27 H, s, ^{t}Bu), 1.17 (54 H, s, ^{t}Bu); δ_C 22.51 (CMe_3), 23.56 (2xCMe_3), 30.37 [$C(CH_3)_3$], 30.62 [2x$C(CH_3)_3$]. Anal. Calc. for $C_{36}H_{81}O_3Si_3Cl_6Re_3$: C, 30.5; H, 5.7. Found: C, 31.1; H, 5.9%. **4** (C_6D_6), δ_H 1.26 (s, ^{t}Bu), 1.30 (s, ^{t}Bu); δ_C 24.20 (CMe_3), 24.86 (CMe_3), 30.74 [$C(CH_3)_3$], 30.79 [$C(CH_3)_3$]. Anal. Calc. for $C_{48}H_{108}O_6Si_4Re_2$: C, 46.6; H, 9.1. Found: C, 45.5, H, 8.6%.

Crystallographic data: **4**. 4 THF, $C_{64}H_{140}O_{10}Re_2Si_4$, M = 1554.58, D_c = 1.500 g cm^{-3}, μ = 3.66 mm^{-1}; orthorhombic, space group $Pca2_1$, a = 22.927(5), b = 12.552(3), c = 23.922(5) Å, U = 6844(2) Å^3, Z = 4, T = 293(2) K, 2923 independent reflections, R_1 = 0.1024, GOF(F^2) = 1.085% CCDC 182/1073.

References

1 P. T. Wolczanski, *Polyhedron*, 1995, **14**, 3335.
2 K. J. Covert, D. R. Neithamer, M. C. Zonnevylle, R. E. LaPointe, C. P. Schaller and P. T. Wolczanski, *Inorg. Chem.* 1991, **30**, 2494; K. J. Covert, P. T. Wolczanski, S. A. Hill, S.A. and P. J. Krusic, *Inorg. Chem.*; 1992, **31**, 66; K. J. Covert, A.-R. Mayol and P. T. Wolczanski, *Inorg. Chim. Acta*, 1997, **263**, 263.
3 J. B. Bonanno, T. P. Henry, D. R. Neithamer, P. T. Wolczanski and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1996, **118**, 5132; J. B. Bonanno, P. T. Wolczanski and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1994, **116**, 11 159; D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. Van Duyne and P. T. Wolczanski, *J. Am. Chem. Soc.* 1989, **111**, 9056-9072.
4 D. F. Eppley, P. T. Wolczanski and G. D. Van Duyne, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 584.
5 R. E. LaPointe and P. T. Wolczanski, *J. Am. Chem. Soc.* 1986, **108**, 3535; R. L. Miller, R. Toreki, R. E. LaPointe, P. T. Wolczanski, G. D. Van Duyne and D. C. Roe, *J. Am. Chem. Soc.*, 1993, **115**, 5570.
6 R. L. Miller, K. A. Lawler, J. L. Bennett and P. T. Wolczanski, *Inorg. Chem.* 1996, **35**, 3242; R. L. Miller, P. T. Wolczanski and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 10 422.
7 M. Weidenbruck, C. Pierrard and H. Pesel, *Z. Naturforsch., Teil B*, 1978, **33**, 1468.
8 G. W. Parshall, *Inorg. Synth.*, 1965, **17**, 111.
9 I. M. Gardener, M. A. Bruck, P. A. Wexler and D. E. Wigley, *Inorg. Chem.* 1989, **28**, 3688.
10 E. A. Allen, N. P. Johnson, D. T. Resevear and W. Wilkinson, *J. Chem. Soc. A*, 1969, 788.
11 J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc.*, 1964, 601; J. Chatt and G. A. Rowe, *J. Chem. Soc.* 1962, 4019.
12 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, New York, 2nd edn., 1993.
13 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley Interscience, New York, 1988.
14 E. Spaltenstein, T. K. G. Erikson, S. C. Critchlow and J. M. Mayer, *J. Am. Chem. Soc.*, 1989, **111**, 617.
15 D. M. Hoffman, *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. R. Stone and G. Wilkinson, Pergamon, Exeter, UK, 1995, vol. 6, pp 231–235.; K. P. Gable, F. A. Zhuravlev and A. F. T. Yokochi, *Chem. Commun.*, 1998, 799 and references therein.
16 R. L. Miller, Ph.D. Thesis, Cornell University, 1993.
17 A. Dedieu, T. A. Albright and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **111**, 3141; M. H. Chisholm, D. L. Clark, M. J. Hampden-Smith and D. M. Hoffman, *Angew Chem. Int. Ed. Engl.*, 1989, **28**, 432.
18 E. Spaltenstein and J. M. Mayer, *J. Am. Chem. Soc.*, 1991, **113**, 7744.
19 R. Toreki, R. R. Schrock and M. G. Vale, *J. Am. Chem. Soc.* 1991, **113**, 3610.
20 M. Bochmann, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1797.

Communication 8/08306A