Alkyl-ligand α-CH Interaction with a Rhenium–Oxygen Multiple Bond in ReO_2R_3, R = CH_2CMe_3 or CH_2SiMe_3

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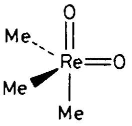
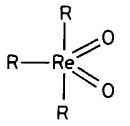
An X-ray crystallographic analysis of $ReO_2(CH_2CMe_3)_3$ and variable temperature ^1H n.m.r. studies involving ReO_2R_3, R = CH_2CMe_3 or CH_2SiMe_3, suggest that α-C–H · · · O=Re interactions occur in the complexes.

The only examples of Group VII d^0 *cis*-dioxo complexes are ReO_2R_3, R = Me or CH_2SiMe_3,[1,2] and ReO_2X_3, X = Cl or F.[3,4] Both organometallic compounds are oils at room temperature and X-ray crystallographic studies could not be performed; however, based upon n.m.r. and i.r. evidence the structures (**1**) and (**2**) have been proposed, see Figure 1.[1,2] No structural information is available for ReO_2Cl_3,[3] but spectroscopic studies[4] suggest that ReO_2F_3 has a structure similar to (**2**). We have prepared crystalline $ReO_2(CH_2CMe_3)_3$ and in order to gain some insight into the structural details we undertook an X-ray analysis. We report here the results of our study that show that $ReO_2(CH_2CMe_3)_3$ is distorted in an unusual manner. We also report the results of variable temperature ^1H n.m.r. studies for ReO_2R_3, R = CH_2CMe_3 or CH_2SiMe_3, which support our explanation that the distortions in the neopentyl ligand complex are due to α-C–H · · · O=Re interactions and suggest that similar interactions occur in the trimethylsilylmethyl ligand complex.



(**1**)



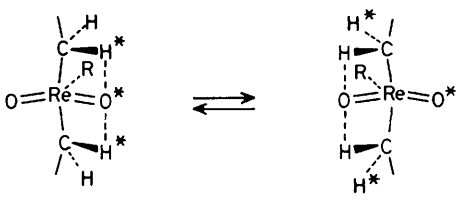
R = CH_2SiMe_3

(**2**)

Figure 1

The compound $ReO_2(CH_2CMe_3)_3$ is a co-product with the d^1–d^1 dimer $Re_2(\mu\text{-}O)_2O_2(CH_2CMe_3)_4$[5] isolated from the reaction between $ReO_3(OSiMe_3)$ and one equivalent of $Al(CH_2CMe_3)_3(thf)$ (thf = tetrahydrofuran).[†] It is extremely soluble in hydrocarbon solvents and is stable to water, but is light sensitive. In contrast to $ReO_2(CH_2SiMe_3)_3$,[2] the complex does not oxidize PPh_3 to $P(O)Ph_3$. We attribute the relative inertness of the neopentyl ligand complex compared to the trimethylsilylmethyl ligand complex to greater steric congestion in the inner co-ordination sphere from the neopentyl ligands [d(C–C) 1.54 Å *vs.* d(C–Si) 1.87 Å].

[†] To a cold solution of $ReO_3(OSiMe_3)$ (2.5 mmol) in hexane (40 ml) was added $Al(CH_2CMe_3)_3(thf)$ (2.5 mmol) dissolved in hexane (20 ml). The mixture was slowly warmed to room temperature, stirred for 12 h, and then chromatographed under an N_2 atmosphere (Al_2O_3, activity grade V, hexane eluant). A single yellow band was observed. Collection of the band, removal of the solvent under reduced pressure, and subsequent sublimation of the residue (10^{-4} torr, 45 °C, H_2O-cooled finger) produced an orange solid on the probe (0.084 g, 8%). Satifactory elemental analysis for $C_{15}H_{33}O_2Re$. ^1H n.m.r. (CD_2Cl_2, 23 °C) δ 3.36 (s, 4H, $C\mathit{H}_2CMe_3$), 2.65 (s, 2H, $C\mathit{H}_2CMe_3$), 1.15 (s, 9H, $CH_2C\mathit{Me}_3$), 1.04 (s, 18H, $CH_2C\mathit{Me}_3$). ^{13}C n.m.r. (C_7D_8, 0 °C) δ 71.4 (t, 2C, J_{CH} 136 Hz, $\mathit{C}H_2CMe_3$), 70.9 (t, 1C, J_{CH} 133 Hz, $\mathit{C}H_2CMe_3$), 36.2 (s, 1C, $CH_2\mathit{C}Me_3$), 35.6 (s, 2C, $CH_2\mathit{C}Me_3$), 34.1 (q, 3C, J_{CH} 125 Hz, $CH_2C\mathit{Me}_3$), 31.8 (q, 6C, J_{CH} 125 Hz, $CH_2C\mathit{Me}_3$). i.r. (KBr pellet, cm^{-1}): 1474 s, 1460 s, 1438 m, 1389 s, 1370 s, 1362 s, 1269 m, 1229 s, 1212 s, 1160 m, 1138 s, 1109 m, 1102 m, 1016 s, 994 s, 969 m, 944 s, 894 m, 884 m, 749 w, 710 w, 601 s, 469 w, 423 w, 397 w.



Scheme 1

Figure 2 shows an ORTEP view of the structure of $ReO_2(CH_2CMe_3)_3$.‡ The ReO_2C_3 core of the molecule can be described as a distorted trigonal bipyramid and the plane defined by Re, O(1), O(2), and C(3) taken as the equatorial plane. Within the equatorial plane the O(2)–Re–O(1) angle is 117.4(5)°, which is larger than the angles commonly observed in d^0 *cis*-dioxo complexes.[6] In the same plane the O–Re–C(3) angles are different, 133.8(6) and 108.8(5)°, which places the C(3) neopentyl ligand more *trans* to O(1) than O(2). The axial alkyl ligand methylene carbons, C(1) and C(2), are bent in the direction of the O(2) oxo ligand giving angles of 73.8(5) and 79.3(5)° for O(2)–Re–C(1) and –C(2), respectively, and 149.7(5)° for C(1)–Re–C(2). Most remarkable is the difference in Re=O bond distances, Re–O(1) 1.661(9) and Re–O(2) 1.812(11) Å. The former distance is unexceptional but the latter distance is the longest Re=O bond distance yet observed. It should be compared to the short Re–O(bridge) distances of 1.86 and 1.83 Å reported for $Re_2(\mu\text{-}O)O_2R_6$, R = CH_2SiMe_3 and Me,[7] respectively, and the short Re–OR distances of 1.86—1.90 Å reported for *trans*-$ReO(OR)X_2L_2$ complexes.[8]

There are two important intramolecular contacts in $ReO_2(CH_2CMe_3)_3$ involving O(2), the oxygen associated with the long Re=O distance, and the axial neopentyl methylene groups, that explain why the distortions described above occur. We mentioned that the axial methylene groups are bent in the direction of O(2). The Bu^t groups attached to them are also twisted such that one methylene hydrogen from each of C(1) and C(2) approach O(2) at calculated H · · · O(2) distances of 2.08 and 2.26 Å, respectively (the sum of the van der Waal's radii is 2.6 Å).§ These α-C–H · · · O=Re interactions account for the long Re=O distance and the small C(1)–Re–C(2) angle. They also explain why the equatorial neopentyl ligand is moved *trans* to O(1), since this would minimize steric repulsion between the axial neopentyl Bu^t groups that are swung around to allow for the α-C–H · · · O=Re interactions and the equatorial neopentyl Bu^t group. The variable temperature ^1H n.m.r. studies described below allow us to dismiss the explanation that steric factors are most important in determining the geometry of $ReO_2(CH_2CMe_3)_3$, and that the α-C–H · · · O=Re interactions are simply an ancillary effect.

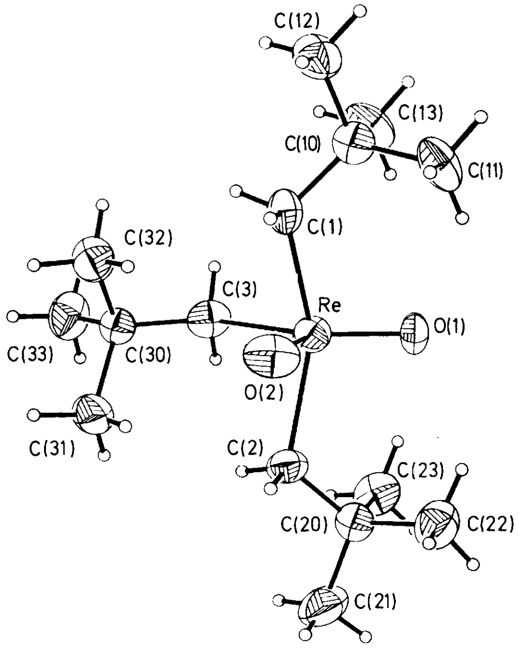


Figure 2. An ORTEP drawing of $ReO_2(CH_2CMe_3)_3$ showing 50% probability ellipsoids and atom labelling scheme. Selected bond lengths (Å) and angles (°): Re–O(1) 1.661(9), –O(2) 1.812(11), –C(1) 2.118(14), –C(2) 2.137(12), –C(3) 2.175(14); C–C(average) 1.53(3); O(1)–Re–O(2) 117.4(5), O(1)–Re–C(1) 104.3(5), O(1)–Re–C(2) 100.3(5), O(1)–Re–C(3) 133.8(6), O(2)–Re–C(1) 73.8(5), O(2)–Re C(2) 79.3(5), O(2)–Re–C(3) 108.8(5), C(1)–Re–C(2) 149.7(5), C(1)–Re–C(3) 89.4(5), C(2)–Re–C(3) 86.2(5), Re–C(1)–C(10) 118.3(10), Re–C(2)–C(20) 119.2(9), Re–C(3)–C(30) 119.6(13).

The ^1H n.m.r. spectrum recorded at +23 °C for a CD_2Cl_2 solution of $ReO_2(CH_2CMe_3)_3$ reveals two sharp singlets at δ 3.36 and 2.65 in the integral ratio of 2 : 1 assigned to the methylene protons of the neopentyl groups. As the sample is cooled the δ 3.36 resonance broadens, then collapses into the baseline at −52 °C, and finally reappears as an AB quartet ($^2J_{HH}$ 12.8 Hz) at −75 °C. The singlet at δ 2.65 broadens slightly as the sample is cooled to −75 °C, but it never disappears into the baseline. Thus, the low temperature limiting ^1H n.m.r. spectrum is consistent with expectations based upon the observed solid-state molecular structure.

Importantly, similar variable temperature ^1H n.m.r. spectra are recorded for the molecule $ReO_2(CH_2SiMe_3)_3$. In particular, the low temperature limiting spectrum for $ReO_2(CH_2SiMe_3)_3$ consists of a singlet and an AB quartet for the methylene protons, which suggests that its solution structure is similar to the structure of $ReO_2(CH_2CMe_3)_3$. Because the trimethylsilylmethyl ligand complex is less sterically congested than the neopentyl ligand complex, the proposed similarity of structure for the two compounds cannot be ascribed to steric factors common to both. Therefore, the solution limiting structures of the ReO_2R_3 compounds, and the distortions observed in the solid state for $ReO_2(CH_2CMe_3)_3$, appear to be the result of axial alkyl ligand α-C–H · · · O=Re interactions.

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‡ The 500 MHz ^1H n.m.r. spectrum recorded at 23 °C for a C_6D_6 solution prepared with the single crystal used in the diffraction study is identical to the spectrum recorded for the bulk crystals. Crystals were grown from cold saturated diethyl ether solutions. *Crystal data* for $ReO_2(CH_2CMe_3)_3$ at −79 °C: $C_{15}H_{33}O_2Re$, monoclinic, space group $P2_1$, $a = 10.879(2)$, $b = 5.8240(9)$, $c = 14.654(3)$ Å, $\beta = 107.40(1)°$, $U = 885.98$ Å^3, $D_c = 1.63$ g cm^{-3}, $Z = 2$. A total of 3114 reflections were collected (Mo-K_α radiation; $\lambda = 0.71069$ Å) in the range $3° < 2\theta < 50°$ of which 2686 were unique and 2441 with $F_o > 4.00\sigma(F_o)$ were used in the refinement. A linear decay, Lorentz, polarization, and an empirical absorption correction were applied to the data. The structure was solved by standard heavy-atom techniques. All heavy atoms were refined anisotropically with full-matrix least-squares except for the three tertiary carbon atoms C(10), C(20), and C(30), which were refined isotropically. Hydrogen atoms were included as fixed atom contributors in the final cycles [$U_{iso}(H) = 1.2U_{iso}(C)$; d(C–H) 0.96 Å]. Final residuals were R 0.0458 and R_w 0.0466. Atomic co-orindates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The nearest intermolecular contact to O(2) is with a methylene hydrogen atom at a distance of 3.22 Å.

In addition, a dynamic process involving α-C–H · · · O=Re interactions wherein at the highest symmetry point of the trajectory all three neopentyl ligands lie in a mirror plane of symmetry explains the variable temperature n.m.r. data, Scheme 1.

Further studies of the ReO_2R_3 compounds are in progress. We are especially interested to determine if the α-C–H · · · O=Re interactions result in unusual reaction chemistry and if a simple acid-base description is appropriate for the interaction.

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