The First Rhenium Oxo–Alkylidene Complex. *X*-Ray Structure of $ReO_2[C(H)CMe_3](CH_2CMe_3)$

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Photolysis of $ReO_2(CH_2CMe_3)_3$ in pyridine gives the alkylidene complex $ReO_2[C(H)CMe_3](CH_2CMe_3)$ in 76% yield; an *X*-ray crystallographic study shows $ReO_2[C(H)CMe_3](CH_2CMe_3)$ has a distorted tetrahedral structure.

Several heterogeneous olefin metathesis catalysts based upon rhenium oxide are known,[1] and Herrmann and co-workers have recently shown that $Re(Me)O_3$ and $Re(OSnMe_3)O_3$ are the catalytic precursors in a $Re_2O_7/SnMe_4$ system.[2] Oxo–alkylidene compounds are reasonably assumed to be the active catalysts in some of the metathesis systems, yet no rhenium oxo–alkylidene complexes have been prepared.[3] In this regard, we report the synthesis, spectroscopic, and *X*-ray crystallographic characterization of the first example of a rhenium oxo–alkylidene complex.

Photolysis of the Re^{VII} *cis*-dioxo complex $ReO_2(CH_2CMe_3)_3$[4,5] in pyridine (py) for 1 hour, using Pyrex glass-filtered light from a medium-pressure mercury lamp, produces $ReO_2[C(H)CMe_3](CH_2CMe_3)$ (**1**) and neopentane as the only identifiable products, equation (1). Isolation of (**1**) is accomplished by sublimation [40 °C, 10^{-4} torr (torr = 133.322 Pa), yield 76%]. Acetonitrile can also be used as a solvent for the reaction, but photolysis of $ReO_2(CH_2CMe_3)_3$ in hydrocarbon solvents gives a mixture of (**1**) and Re^{VI} $[Re(\mu\text{-}O)O(CH_2CMe_3)_2]_2$.[6] One possible explanation for the solvent dependence is that co-ordinating solvents weakly associate with $ReO_2(CH_2CMe_3)_3$ thereby increasing steric congestion and inducing α-hydrogen elimination.

$$ReO_2(CH_2CMe_3)_3 \xrightarrow[\text{pyridine}]{h\nu,\ 1\ \text{h}} \underset{(\mathbf{1})}{ReO_2[C(H)CMe_3](CH_2CMe_3)} + CMe_4 \quad (1)$$

Compound (**1**) is a yellow solid which is very soluble in common solvents. It is moderately air-stable in the solid state and solution.

A single crystal *X*-ray diffraction study shows (**1**) has a distorted tetrahedral geometry (Figure 1).[†] The Re=C(1) distance [1.869(9) Å] is within experimental error of the Re=C distance [1.873(9) Å] reported in $Re(\equiv CCMe_3)[C(H)CMe_3]I_2(py)_2$ by Schrock, Churchill, and co-workers,[3a] and the Re–O(1) and Re–O(2) distances, 1.706(7) and 1.696(7) Å, respectively, are similar to the Re=O distances [1.688(7) Å av.] in $ReO_2(CH_2CMe_3)_2Br(py)$, which has *cis*-dioxo and *trans*-alkyl groups.[5] The C(2)–Re–O(1) and C(2)–Re–O(2) angles of 106.9(3) and 105.0(4)° are close to the expected tetrahedral values, but the C(1)–Re–C(2) angle is only 94.8(4)° and O(1)–Re–O(2) is 124.6(4)°, the latter being larger than the usual 100—110° angles observed in d^0 *cis*-dioxo compounds [*e.g.*, <O=M=O 108.5(2), 110.5(3), and 107.4(3)° in tetrahedral CrO_2Cl_2,[7] trigonal bipyramidal $MoO_2(L\text{-}NS_2)$,[8] and octahedral $ReO_2(CH_2CMe_3)_2Br(py)$,[5] respectively]. It is unclear whether the closed C(1)–Re–C(2) and opened O(1)–Re–O(2) angles in (**1**) are primarily the result of steric interactions or electronic effects.[6a] A theoretical study using extended Hückel and molecular mechanics calculations is in progress to determine the cause of the distortions.

Spectroscopic data for (**1**) are consistent with the solid state structure. Specifically, $Re{=}C_\alpha$ appears as a doublet in the ^{13}C n.m.r. spectrum (δ 283.5, J_{CH} 138 Hz), and $Re{=}CH_\alpha$ is observed as a singlet in the ^1H n.m.r. spectrum (δ 12.1).[3] The

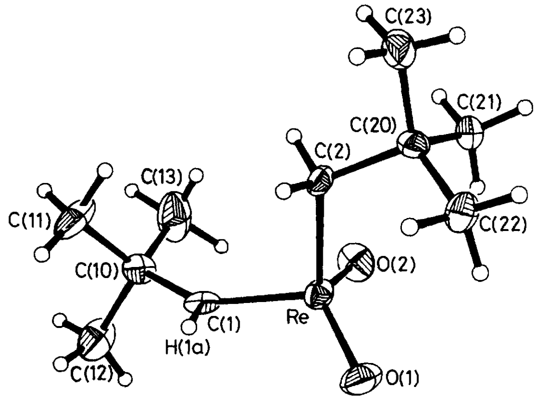
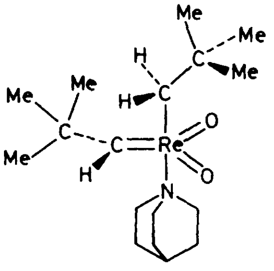


Figure 1. An ORTEP drawing of $ReO_2[C(H)CMe_3](CH_2CMe_3)$ (**1**) showing 50% probability ellipsoids and atom-labelling scheme. Selected bond lengths (Å) and angles (°): Re–C(1) 1.869(9), –C(2) 2.114(9), –O(1) 1.706(7), –O(2) 1.696(7); C(2)–Re–C(1) 94.8(4), C(2)–Re–O(1) 106.9(3), C(2)–Re–O(2) 105.0(4), C(1)–Re–O(1) 109.3(4), C(1)–Re–O(2) 111.7(4), O(1)–Re–O(2) 124.6(4), Re–C(1)–C(10) 136.6(8), Re–C(1)–H(1A) 96(6).



(**2**)

[†] *Crystal data* for $ReO_2[C(H)CMe_3](CH_2CMe_3)$ at −80(1) °C: $C_{10}H_{21}O_2Re$, orthorhombic, space group *Pbca*, $a = 11.038(2)$; $b = 20.168(4)$, $c = 11.290(2)$ Å, $U = 2513.3(8)$ Å^3, $D_c = 1.90$ g cm^{-3}, $Z = 8$. A total of 3678 reflections were collected (Mo-K_α radiation; $\lambda = 0.71073$ Å) in the range $4° < 2\theta < 50°$ of which 1646 were unique and 1369 with $F_o > 4.00\sigma(F_o)$ were used in the refinement. Lorentz–polarization and an empirical absorption correction were applied. The structure was solved by standard heavy-atom techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms attached to C(2) and C(21) were included as fixed atom contributors in the final cycles of refinement [$U_{iso}(H) = 1.2U_{iso}(C)$; d(C–H) 0.96 Å]. All other hydrogen atoms were refined isotropically. Final residuals were R 0.0384 and R_w 0.0394. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

methylene protons of the neopentyl alkyl ligand appear as an AB quartet in the ^1H n.m.r. spectrum, indicating that the neopentylidene plane remains perpendicular to the Re–CH_2 bond vector in solution. The i.r. spectrum has strong bands at 986 and 947 cm^{-1}, which are characteristic of a *cis*-$M(=O)_2$ moiety.[9]

Addition of quinuclidine to the crude reaction mixture from reaction (1) produces the yellow 1:1 quinuclidine (quin) adduct $ReO_2[C(H)CMe_3](CH_2CMe_3)(quin)$ (**2**), which is isolated by removing the pyridine solvent and neopentane *in vacuo* and crystallizing from acetonitrile solution. The isolated yield of the adduct is 54% based on $ReO_2(CH_2CMe_3)_3$. Spectroscopic data for (**2**) are similar to those for (**1**) and an *X*-ray crystallographic study has confirmed the trigonal bipyramidal structure shown in structure (**2**).

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