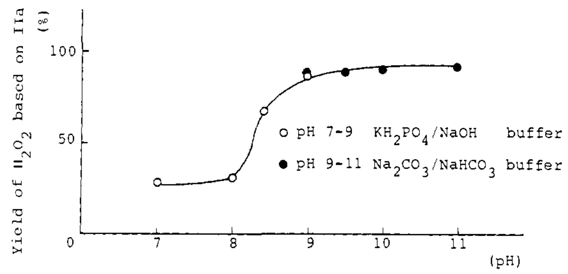
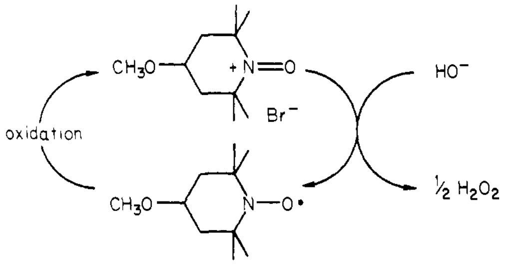


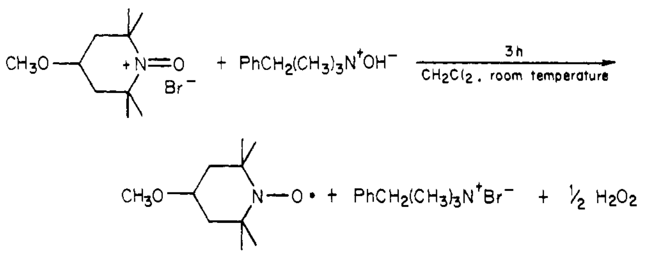
Figure 1. Influence of pH in the oxidation of H_2O by use of IIa.

During examination of II as an oxidizing agent for organic compounds such as amines and alcohols, we found that hydroxide ion undergoes one-electron oxidation by IIa to produce hydrogen peroxide,[4] and >N-O· was afforded quantitatively from IIa.

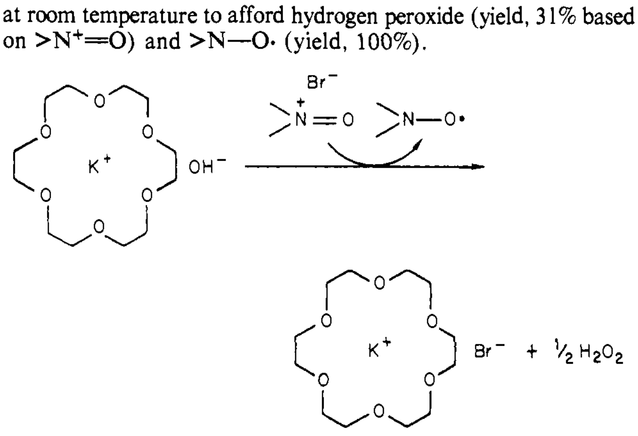


As shown in Figure 1, the amount of the produced hydrogen peroxide was only dependent on the pH and not the buffer composition. Especially in the range of pH 9-11 it was obtained in higher yields and >N-O· was recovered quantitatively.

Further, the oxidation of hydroxide ion was carried out in nonaqueous solvent. The hydroxide ion of anhydrous benzyltrimethylammonium hydroxide (Triton B) in methylene chloride[5] was oxidized by $>N^+{=}O$ at room temperature for 3 h to give hydrogen peroxide in 38% yield based on IIa.



The oxidation of potassium hydroxide,[6] which solubilized with 18-crown-6-ether into methylene chloride, was also carried out at room temperature to afford hydrogen peroxide (yield, 31% based on $>N^+{=}O$) and >N—O· (yield, 100%).



This method might be important in the chemical field using hydroxyl radical, because its generation from hydroxide ion in nonaqueous solvent should be useful in the organic chemistry.

Registry No. IIa·Br^-, 90246-27-8; HO^-, 14280-30-9; H_2O_2, 7722-84-1; $PhCH_2(CH_3)_3N^+OH^-$, 100-85-6; potassium hydroxide, 1310-58-3.

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(2) Ia was obtained by the reaction of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl and methyl iodide. Ia: mp 35-36 °C; mass spectrum, *m/e* 186; IR (KBr) 2980, 2940, 2820, 1470, 1390, 1360, 1350, 1315, 1180, 1100 cm^{-1}. Anal. Calcd for $C_{10}H_{20}NO_2$: C, 64.48; H, 10.82; N, 7.52. Found: C, 64.11; H, 10.59; N, 7.64.

(3) IIa was obtained by the oxidation of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl with bromine in CCl_4. IIa: mp 206-207 °C dec; IR (KBr) 2940, 2730, 2590, 2540, 1600, 1460, 1410, 1390, 1320, 1280, 1215, 1160, 1100 cm^{-1}. Anal. Calcd for $C_{10}H_{20}NO_2Br$: C, 45.12; H, 7.57; N, 5.26; Br, 30.02. Found: C, 45.11; H, 7.45; N, 5.29; Br, 29.59.

(4) After IIa (100 mg, 3.8 mmol) was dissolved in 50 mL of buffer solution (KH_2PO_4/NaOH or $Na_2CO_3/NaHCO_3$), the solution was stirred for 3 h at room temperature. The reaction mixture was washed with ether 3 times to remove the obtained nitroxyl radical (Ia), and the water layer was treated by iodometric titration to estimate the yield of hydrogen peroxide. Hydrogen peroxide derived from this method was detected by the mass spectrometry. The molecular ion peak at 34 was clearly observed.

(5) To a stirred solution of 940 mg (5.6 mmol) of anhydrous Triton B in 10 mL of methylene chloride was added 170 mg (0.64 mmol) of IIa at room temperature under nitrogen. After it was stirred for 3 h at room temperature, hydrogen peroxide was extracted with water from the methylene chloride solution and its amount was estimated by iodometry.

(6) IIa (69 mg, 0.26 mmol) was added to 5 mL of the supernatant of the KOH solution prepared from vigorous stirring of anhydrous 18-crown-6-ether (1.54 g, 5.8 mmol) and powdered KOH (3.25 g, 58 mmol) in 60 mL of methylene chloride. The obtained hydrogen peroxide was extracted with water from the reaction mixture and its amount was estimated by iodometry.

Synthesis, Reactivity, and Crystal and Molecular Structure of $\mathrm{Re(O)I(MeC{\equiv}CMe)_2}$

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Oxide compounds are known for all of the transition metals, in fact for all the elements except the lighter noble gases.[1] However, transition-metal complexes with terminal, multiply bonded oxo ligands have been characterized only for Ti,[2] the elements in groups 5-7, and the iron triad.[1,3] These complexes have also been restricted to d^0, d^1, and d^2 electron configurations and therefore to the highest oxidation states of these elements. We wish to report the synthesis, structure, and reactivity of oxoiodobis(2-butyne)rhenium(III), $\mathrm{Re(O)I(MeC{\equiv}CMe)_2}$ (**1**), the first well-characterized low-valent oxo complex.

Compound **1** is formed when excess 2-butyne is added to benzene solutions of $ReO_2I(PPh_3)_2$[4] or $ReOI_3(AsPh_3)_2$[5,6] (eq 1

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(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980.

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(5) (a) $ReOI_3(AsPh_3)_2$ was prepared from $KReO_4$, aqueous HI, and $AsPh_3$, following the published procedure for $ReOBr_3(AsPh_3)_2$.[5b] Although we have as yet been unable to obtain analytically pure $ReOI_3(AsPh_3)_2$, the IR spectra of the iodide and bromide deriviatives are very similar (ν_{ReO}: 975 cm^{-1}). $Re(O)I(MeCCMe)_2$ was prepared by adding 1.5 g (28 mmol) of 2-butyne to a 10-mL benzene solution of 2 g (1.7 mmol) of $ReOI_3(AsPh_3)_2$ in a drybox. After stirring for 2 h 0.46 g (1.8 mmol) of I_2 in 50 mL of benzene was added and the mixture stirred another 0.5 h. After filtration the volatiles were removed and the residue recrystallized from hexane, yield 0.34 g of yellow crystals (47%). Anal. Calcd for $C_8H_{12}IORe$: C, 21.97; H, 2.77. Found: C, 22.22, 21.94; H, 2.76, 2.88. (b) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054-1066.

and 2). The reactions of $ReO(OC_2H_5)I_2(EPh_3)_2$ (E = P, As)[7]

$$ReO_2I(PPh_3)_2 + 2MeCCMe \rightarrow Re(O)I(MeCCMe)_2 + OPPh_3 + PPh_3 \quad (1)$$

$$ReOI_3(AsPh_3)_2 + 2MeCCMe \rightarrow \underset{(\mathbf{1})}{Re(O)I(MeCCMe)_2} + I_2AsPh_3 + AsPh_3 \quad (2)$$

with 2-butyne also form **1**, although in lower yield. These reactions involve reduction of rhenium(V) (d^2) to Re(III) (d^4), with concomitant oxidation of a coordinated ligand. Since the starting materials do not oxidize triphenylphosphine or arsine in the absence of the acetylene, the organic ligand appears to make the rhenium(V) center a better oxidant.

Crystals of **1** were grown by slow cooling of a hexane solution; the structure was solved by the heavy-atom method and refined to final residuals of $R = 0.027$, $R_w = 0.029$.[8] The structure consists of isolated molecules (Figure 1) with virtual mirror symmetry. The rhenium adopts a pentagonal-pyramid geometry with the oxygen atom at the apex. An alternative description of the Re coordination is as a slightly distorted tetrahedron in which the acetylene midpoints occupy two vertices (bond angles 109 ± 7°). The geometry of the 2-butyne ligands is unexceptional: the C≡C distances (1.278–1.288 (7) Å) and CCC angles (144.0–145.8 (5)°) are, for example, intermediate between the parameters for Pt(0) and Pt(II) acetylene complexes.[9] The structural data do *not* support the suggestion that **1** is better described as Re(V) with reduced acetylene ligands. Despite the low oxidation state, the Re–O distance is quite short (1.697 (3) Å), within the range found for high-valent rhenium oxo compounds (1.65–1.78 Å).[10] Since **1** is diamagnetic based on sharp, unshifted NMR spectra, it appears to be a rare example of a low-spin tetrahedral d^4 molecule.[11] A more detailed discussion of the electronic structure of this unusual compound will appear in a future publication.[12]

The solution structure of **1** appears to be similar to that found in the solid state, because the methyl groups and acetylene carbons of each 2-butyne ligand are inequivalent by NMR spectroscopy.[13]

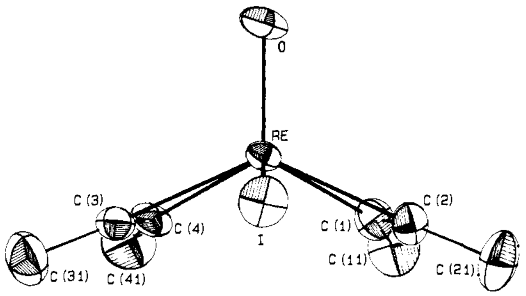

Figure 1. Perspective drawing of $Re(O)I(MeC{\equiv}CMe)_2$ (**1**). The vibrational ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Bond distances not reported in the text: Re–I 2.691 (1), Re–C 2.038–2.066 (5) Å.

The IR spectrum of **1** shows a strong band at 975 and a weak doublet at 1810, 1800 cm^{-1}, which we tentatively assign to the ReO and CC stretching modes.

$Re(O)I(MeCCMe)_2$ (**1**) is remarkably inert considering its unusual oxidation state and structure. It dissolves, apparently without chemical change, in methanol, acetonitrile, THF, methylene chloride, and hydrocarbon solvents. It sublimes at 40 °C (10^{-4} torr); mass spectrum calcd for $C_8H_{12}IORe$ 437.9496, found 437.9506. In light of the stability of Re(V) oxo complexes[10] (and tungsten(IV) oxo acetylene complexes[14]), it is surprising that **1** is difficult to oxidize: at ambient temperatures benzene solutions of **1** are stable to O_2, I_2, H_2, and MeI, as well as CO and ethylene. Compound **1** is a mild oxidant, taking trimethylphosphine to Me_3PO and an as yet unidentified rhenium product, but it is inert to PPh_3 (cf. eq 1) and iodide ions. The 2-butyne ligands exchange at 80 °C with methylphenylacetylene (eq 3).[15] In acetonitrile

$$Re(O)I(MeCCMe)_2 + MeCCPh \rightleftharpoons Re(O)I(MeCCMe)(MeCCPh) + MeCCPh \rightleftharpoons Re(O)I(MeCCPh)_2 \quad (3)$$

or THF solution, the iodide ligand can be removed by silver ion to give a solvato cation which on addition of potassium iodide regenerates **1**. These reactions are being examined as routes to other rhenium(III) oxo compounds.

A few other transition-metal complexes that appear to have terminal oxo ligands and more than two d electrons have been discussed in the recent literature. The work of Groves and others suggests that the active species in cytochrome P-450 (and in various model systems) is an iron(IV) (d^4) oxo porphyrin complex; this hydroxylates alkanes and epoxidizes olefins.[16] Meyer and co-workers have electrochemically prepared and characterized some polypyridine oxoruthenium(IV) (d^4) complexes, which are also strong oxidants.[17] The high reactivity of these species is an interesting contrast to the relative inertness of compound **1**. Further work is in progress to explore the generality and chemical properties of low-valent transition-metal oxo complexes.

Acknowledgment. The technical assistance of G. E. Barkley, E. A. Conaway, and L. Lardear is gratefully acknowledged.

Supplementary Material Available: Listing of positional and thermal parameters for heavy atoms and for hydrogen atoms and a list of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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[6] Ph_3PO and Ph_3AsI_2 have been identified by comparison of their IR and NMR spectra with authentic samples, the latter prepared by the method of: Beveridge, A. D.; Harris, G. S. *J. Chem. Soc.* **1964**, 6076–6084.

[7] $ReO(OEt)I_2(PPh_3)_2$ has been previously reported;[5b] the arsine derivative was prepared by refluxing $ReOI_3(AsPh_3)_2$ in ethanol (work in progress).

[8] Complex **1**: $C_8H_{12}IORe$; *M* 437.29. Crystal data: monoclinic; C^5_{2h}-$P2_1/c$ (No. 14); $a = 9.749$ (3) Å, $b = 7.307$ (3) Å, $c = 16.106$ (7) Å; $\beta = 106.42$ (3)°; $V = 1111$ (2) Å^3; $Z = 4$; D(calcd) = 2.639 g cm^{-3}. Intensity data: Syntex P3 diffractometer, Mo K_α ($\lambda = 0.71069$ Å) radiation, graphite monochromator; −100 °C; ω scans of 2.2°; $4° < 2\theta < 55°$; 2821 reflections; absorption correction, applied, $\mu = 139.23$ cm^{-1}; transmission factors 0.37–0.99. Solution and refinement (PDP-11 computer, local modifications of SDP-Plus software supplied by the Enraf-Nonius Corp.): Patterson synthesis and usual combination of least-squares refinements and Fourier syntheses. H atoms found and included in idealized positions ($B_H = 4.0$) as a fixed contribution, full-matrix least-squares refinement, 11 anisotropic atoms, 100 variables, 2087 observations [$F_o^2 > 3\sigma(F_o^2)$], $R = 0.027$, $R_w = 0.029$; Fourier residuals ≤ 1.09 e$^-$ Å^{-3}, associated with Re and I atoms.

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[10] (a) Rouschias, G. *Chem. Rev.* **1974**, *74*, 531–566. (b) Lock, C. J. L.; Wan, C. *Can. J. Chem.* **1975**, *53*, 1548. Lock, C. J. L.; Turner, G. *Ibid.* **1977**, *55*, 333; **1978**, *56*, 179; *Acta Crystallogr., Sect B* **1978**, *B34*, 923. Lis, T., et al. *Ibid.* **1977**, *B33*, 944, 1248; **1976**, *B32*, 2707; **1979**, *B35*, 3041. Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2467. Sergienko, V. S. et al. *Koord. Khim.* **1977**, *3*, 1060. Mattes, R.; Weber, H. *Z. Anorg. Allg. Chem.* **1981**, *474*, 216. Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 279. (c) See also ref 3a, 4b.

[11] To our knowledge, the only other diamagnetic d^4 tetrahedral species is $Re[P(C_6H_{11})_2]_4Li(MeOCH_2CH_2OMe)$; Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763–6765.

[12] Mayer, J. M.; Thorn, D. L.; Tulip, T. H., work in progress.

[13] ^{1}H NMR (C_6D_6, 25 °C) δ 2.92 q, 2.30 q ($J_{HH} = 1$ Hz, $CH_3CCCH'_3$). ^{13}C NMR δ 142.32 s, 138.21 s, (MeCC′Me), 17.09 q ($^1J_{CH} = 130$ Hz), 14.95 q ($^1J_{CH} = 130$ Hz, $CH_3CCC'H_3$). From ref 13a, the chemical shifts of the acetylene carbons are consistent with either two or three electron donor acetylenes. (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290.

[14] Templeton, J. L.; Ward, B. C.; Chen, C. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248–1253 and references therein.

[15] Re(O)I(MeCCMe)(MeCCPh) (two isomers) and $Re(O)I(MeCCPh)_2$ (three isomers) have been identified by their NMR spectra.[12]

[16] Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786–5791, 6243–6248. Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *Ibid.* **1981**, *103*, 2884–2886. Boso, B.; Lang, G.; McMurray, T. J.; Groves, J. T. *J. Chem. Phys.* **1983**, *79*, 1122–1126. Penner-Hahn, J. E.; Hodgson, K. O. et al. *J. Biol. Chem.* **1983**, *258*, 12761–12764.

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