

Structure of (Dimethylphenylphosphine)oxotris(trimethylsilylmethyl)rhenium(V)

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Abstract. $[\text{ReO}\{\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)\}\{\text{Si}(\text{CH}_2)(\text{CH}_3)_3\}_3]$, $M_r = 602.08$, triclinic, $P\bar{1}$, $a = 11.402$ (2), $b = 16.306$ (3), $c = 16.443$ (3) Å, $\alpha = 69.03$ (1), $\beta = 80.87$ (2), $\gamma = 89.62$ (2)°, $V = 2814.0$ Å³, $Z = 4$, $D_x = 1.42$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 45.65$ cm⁻¹, $F(000) = 1215.8$, $T = 192$ (1) K, final $R = 0.0540$ for 3567 unique reflections with $F_o > 6\sigma(F_o)$ and 385 variables. The crystals have two independent molecules in the asymmetric unit. The coordination geometry about the Re atom in both molecules is approximately square pyramidal. In each case the oxo ligand occupies the apical site and the basal plane is occupied by a phosphine ligand and three alkyl ligands. Selected bond distances and angles: molecule *A*: $d(\text{Re}-\text{O}) = 1.659$ (13), $d(\text{Re}-\text{C}) = 2.128$ (20) av., $d(\text{Re}-\text{P}) = 2.415$ (6) Å, $\text{O}-\text{Re}-\text{C} = 109.7$ (8) av., $\text{O}-\text{Re}-\text{P} = 107.0$ (5)°; molecule *B*: $d(\text{Re}-\text{O}) = 1.666$ (13), $d(\text{Re}-\text{C}) = 2.128$ (22) av., $d(\text{Re}-\text{P}) = 2.430$ (5) Å, $\text{O}-\text{Re}-\text{C} = 111.4$ (7) av., $\text{O}-\text{Re}-\text{P} = 108.7$ (6)°.

Experimental. (Dimethylphenylphosphine)oxotris(trimethylsilylmethyl)rhenium(V) was prepared according to the literature method (Cai, Hoffman, Lappas, Woo & Huffman, 1987). Purple crystals were grown from a cold acetonitrile solution (253 K).

A crystal with dimensions $0.21 \times 0.15 \times 0.13$ mm was mounted under nitrogen on a glass fiber. Lattice parameters were determined by a least-squares fitting of 50 reflections ($15 < 2\theta < 30^\circ$). Nicolet R3m/V diffractometer equipped with an LT-1 low-temperature device, graphite-monochromated Mo $K\alpha$ radiation; $\theta/2\theta$ scan mode, scan width $(1.2 + \text{dispersion})^\circ$; $3.5 < 2\theta < 45^\circ$; 7402 reflections measured, 3835 unique ($R_{\text{int}} = 0.027$), 3567 observed [$F_o > 6\sigma(F_o)$]. Index range: $-12 \leq h \leq 12$, $-17 \leq k \leq 17$, $0 \leq l \leq 17$. Three intensity control reflections were monitored every 60 reflections of data collection; no crystal decay observed. Lorentz–polarization correction and empirical absorption correction (ψ scans): transmission 0.983–0.866. No extinction correction was applied. The structure was solved from Patterson and difference syntheses.

Non-H atoms refined anisotropically by full-matrix least-squares methods with the exception of the two

phenyl rings, which were refined as rigid groups. H atoms were placed in idealized positions [$\text{C}-\text{H} = 0.96$ Å, $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$]. The function $w(\Delta F)^2$ was minimized $\{w = 1/[\sigma^2(F) + 0.0036F^2]\}$. Final $R =$

Table 1. Fractional coordinates and equivalent isotropic displacement parameters (Å² × 10³) for C₂₀H₄₄OPReSi₃

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} * |
|-------|-------------|-------------|--------------|--------------------------|
| Re(1) | 0.69217 (7) | 0.26439 (6) | 0.21412 (6) | 22 (1) |
| O(1) | 0.6394 (12) | 0.2200 (9) | 0.1500 (8) | 31 (6) |
| Si(1) | 0.9241 (6) | 0.3115 (4) | 0.0455 (5) | 37 (3) |
| C(1) | 0.8585 (17) | 0.3291 (13) | 0.1505 (14) | 28 (9) |
| C(11) | 0.9516 (23) | 0.1922 (16) | 0.0691 (19) | 59 (13) |
| C(12) | 0.8273 (26) | 0.3480 (20) | -0.0430 (14) | 64 (13) |
| C(13) | 1.0707 (22) | 0.3797 (17) | -0.0011 (20) | 73 (14) |
| Si(2) | 0.8799 (6) | 0.1913 (5) | 0.3730 (5) | 42 (3) |
| C(2) | 0.7985 (17) | 0.1693 (13) | 0.2930 (14) | 28 (8) |
| C(21) | 0.8578 (21) | 0.3021 (17) | 0.3817 (17) | 55 (13) |
| C(22) | 1.0436 (21) | 0.1835 (20) | 0.3424 (20) | 72 (14) |
| C(23) | 0.8272 (28) | 0.1108 (21) | 0.0490 (19) | 79 (19) |
| Si(3) | 0.4499 (5) | 0.1559 (4) | 0.3570 (4) | 31 (3) |
| C(3) | 0.5769 (16) | 0.2375 (13) | 0.3380 (12) | 24 (8) |
| C(31) | 0.5078 (24) | 0.0439 (16) | 0.3761 (22) | 83 (17) |
| C(32) | 0.3459 (19) | 0.1576 (15) | 0.4536 (16) | 41 (11) |
| C(33) | 0.3626 (20) | 0.1776 (20) | 0.2663 (16) | 65 (14) |
| P(4) | 0.6187 (5) | 0.4102 (4) | 0.1792 (4) | 29 (2) |
| C(41) | 0.6897 (21) | 0.4692 (17) | 0.2337 (17) | 47 (12) |
| C(42) | 0.6456 (20) | 0.4736 (14) | 0.0634 (15) | 40 (10) |
| C(43) | 0.4596 (14) | 0.4196 (12) | 0.2118 (10) | 27 (5) |
| C(44) | 0.3797 (14) | 0.4040 (12) | 0.1622 (10) | 60 (8) |
| C(45) | 0.2583 (14) | 0.4132 (12) | 0.1846 (10) | 74 (9) |
| C(46) | 0.2169 (14) | 0.4379 (12) | 0.2565 (10) | 61 (8) |
| C(47) | 0.4181 (14) | 0.4443 (12) | 0.2837 (10) | 58 (7) |
| C(48) | 0.2968 (14) | 0.4534 (12) | 0.3061 (10) | 70 (9) |
| Re(2) | 0.71353 (8) | 0.76031 (6) | 0.21201 (7) | 21 (1) |
| O(2) | 0.7927 (13) | 0.7061 (9) | 0.1554 (10) | 36 (7) |
| Si(5) | 0.5630 (6) | 0.8093 (4) | 0.0399 (5) | 36 (3) |
| C(5) | 0.5742 (18) | 0.8273 (14) | 0.1452 (15) | 35 (10) |
| C(51) | 0.5099 (26) | 0.6914 (16) | 0.0657 (21) | 68 (16) |
| C(52) | 0.4493 (24) | 0.8807 (17) | -0.0135 (19) | 61 (14) |
| C(53) | 0.7058 (26) | 0.8334 (23) | -0.0404 (19) | 85 (19) |
| Si(6) | 0.4554 (6) | 0.7028 (4) | 0.3729 (5) | 33 (3) |
| C(6) | 0.5673 (17) | 0.6755 (11) | 0.2961 (13) | 22 (8) |
| C(61) | 0.4596 (22) | 0.8211 (14) | 0.3601 (16) | 42 (11) |
| C(62) | 0.4707 (21) | 0.6383 (16) | 0.4884 (15) | 45 (11) |
| C(63) | 0.3024 (21) | 0.6775 (17) | 0.3545 (18) | 56 (12) |
| Si(7) | 0.8706 (5) | 0.6485 (4) | 0.3756 (4) | 29 (3) |
| C(7) | 0.7667 (18) | 0.7461 (14) | 0.3334 (16) | 34 (10) |
| C(71) | 0.9975 (21) | 0.6383 (18) | 0.2898 (17) | 61 (13) |
| C(72) | 0.9409 (25) | 0.6690 (19) | 0.4588 (20) | 77 (15) |
| C(73) | 0.7858 (22) | 0.5382 (14) | 0.4291 (19) | 55 (12) |
| P(8) | 0.8082 (5) | 0.9060 (4) | 0.1694 (4) | 27 (2) |
| C(81) | 0.7197 (21) | 0.9766 (13) | 0.2195 (15) | 33 (10) |
| C(82) | 0.8324 (20) | 0.9704 (15) | 0.0520 (14) | 37 (10) |
| C(83) | 0.9596 (16) | 0.9090 (12) | 0.1926 (12) | 36 (5) |
| C(84) | 1.0443 (16) | 0.8636 (12) | 0.1569 (12) | 59 (8) |
| C(85) | 1.1619 (16) | 0.8660 (12) | 0.1703 (12) | 91 (11) |
| C(86) | 1.1947 (16) | 0.9137 (12) | 0.2194 (12) | 86 (10) |
| C(87) | 1.1100 (16) | 0.9591 (12) | 0.2550 (12) | 95 (11) |
| C(88) | 0.9925 (16) | 0.9568 (12) | 0.2417 (12) | 68 (8) |

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* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected bond lengths (Å) and angles (°) for C₂₀H₄₄OPReSi₃

| | | | |
|------------------|------------|------------------|------------|
| Re(1) O(1) | 1.659 (13) | Re(2) O(2) | 1.666 (13) |
| Re(1) C(1) | 2.101 (20) | Re(2) C(5) | 2.144 (22) |
| Re(1) C(2) | 2.142 (19) | Re(2) C(6) | 2.130 (19) |
| Re(1) C(3) | 2.142 (19) | Re(2) C(7) | 2.111 (21) |
| Re(1) P(4) | 2.415 (6) | Re(2) P(8) | 2.430 (5) |
| P(4) C(41) | 1.800 (22) | P(8) C(81) | 1.849 (21) |
| P(4) C(42) | 1.789 (23) | P(8) C(82) | 1.813 (22) |
| P(4) C(43) | 1.830 (16) | P(8) C(83) | 1.831 (18) |
| O(1) Re(1) C(1) | 109.4 (7) | O(2) Re(2) C(5) | 111.4 (7) |
| O(1) Re(1) C(2) | 107.2 (8) | O(2) Re(2) C(6) | 108.0 (7) |
| O(1) Re(1) C(3) | 112.6 (7) | O(2) Re(2) C(7) | 114.7 (7) |
| O(1) Re(1) P(4) | 107.0 (5) | O(2) Re(2) P(8) | 108.7 (6) |
| C(1) Re(1) C(2) | 82.9 (8) | C(5) Re(2) C(6) | 81.8 (8) |
| C(1) Re(1) C(3) | 137.9 (8) | C(5) Re(2) C(7) | 133.9 (8) |
| C(1) Re(1) P(4) | 85.4 (6) | C(5) Re(2) P(8) | 85.5 (6) |
| C(2) Re(1) C(3) | 83.4 (8) | C(6) Re(2) C(7) | 82.8 (8) |
| C(2) Re(1) P(4) | 145.8 (6) | C(6) Re(2) P(8) | 143.3 (5) |
| C(3) Re(1) P(4) | 84.0 (6) | C(7) Re(2) P(8) | 81.6 (6) |
| Re(1) C(1) Si(1) | 115.9 (9) | Re(2) C(5) Si(5) | 114.7 (10) |
| Re(1) C(2) Si(2) | 122.7 (10) | Re(2) C(6) Si(6) | 125.4 (9) |
| Re(1) C(3) Si(3) | 113.2 (10) | Re(2) C(7) Si(7) | 114.4 (9) |
| Re(1) P(4) C(41) | 109.8 (9) | Re(2) P(8) C(81) | 112.6 (8) |
| Re(1) P(4) C(42) | 113.0 (8) | Re(2) P(8) C(82) | 115.4 (7) |
| Re(1) P(4) C(43) | 117.9 (6) | Re(2) P(8) C(83) | 115.6 (6) |
| C(41) P(4) C(42) | 107.7 (12) | C(81) P(8) C(82) | 103.9 (10) |
| C(41) P(4) C(43) | 104.2 (9) | C(81) P(8) C(83) | 107.6 (9) |
| C(42) P(4) C(43) | 103.4 (9) | C(82) P(8) C(83) | 100.4 (9) |
| P(4) C(43) C(44) | 119.1 (4) | P(8) C(83) C(84) | 117.7 (5) |
| P(4) C(43) C(47) | 120.8 (4) | P(8) C(83) C(88) | 122.3 (5) |

0.0540, $wR = 0.0559$, $S = 0.9240$, $\Delta/\sigma(\max.) = 0.025$. The final difference map contained eight peaks, with heights between 2.08 and 1.20 e Å⁻³, within 1.25 Å of the two Re atoms. All remaining peaks were less than 1.01 e Å⁻³, min. = -1.8 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs used: *SHELXTL+* programs (Sheldrick, 1987).

Atom-numbering schemes for the crystallographically independent molecules *A* and *B* are given in Figs. 1(a) and 1(b), respectively. Atomic coordinates are given in Table 1,* bond lengths and angles in Table 2.

Related literature. Herrmann (1986); Herrmann, Herdtweck, Flöel, Kulpe, Küsthardt & Okuda (1987), reviews of selected organometallic rhenium-oxo chemistry with discussion of structures; Mayer, Thorn & Tulip (1985), structural and theoretical study of an organometallic rhenium-oxo compound; Stravropoulos, Edwards, Wilkinson, Motevalli, Malik & Hursthouse (1985), related rhenium-oxo structures.

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* Lists of structure factors, H-atom parameters, complete bond distances and angles, packing diagram and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44985 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

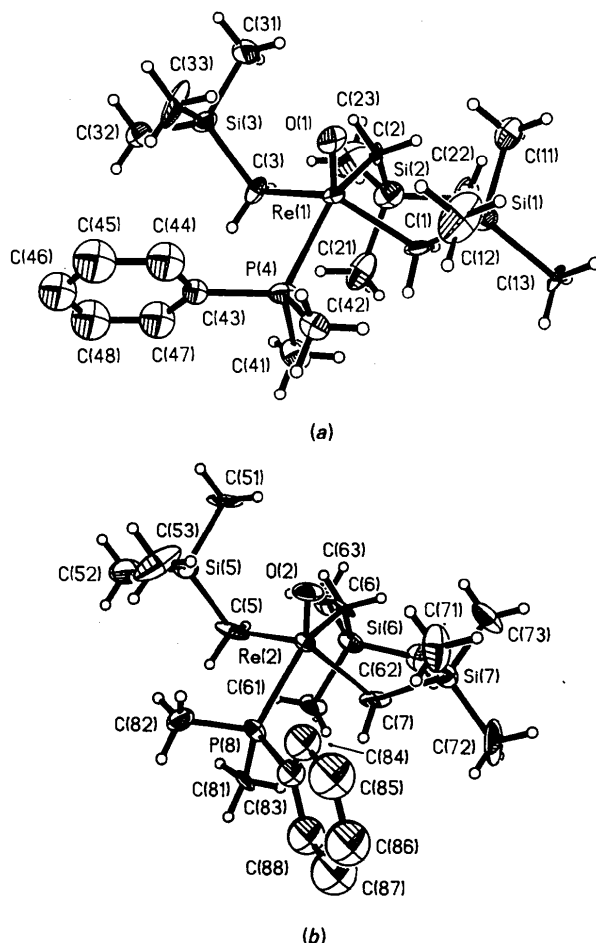


Fig. 1. (a) The molecular structure of C₂₀H₄₄OPReSi₃ (crystallographically independent molecule *A*, 50% probability level). (b) The molecular structure of C₂₀H₄₄OPReSi₃ (crystallographically independent molecule *B*, 50% probability level).

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