# Octacarbonyl-di-$\mu$-chloro-tetra-$\mu$-diphenylphosphido-$\mu_4$-phenylphosphido-tetrarhenium(3 *Re*—*Re*) and Octacarbonyl-di-$\mu$-hydrido-tetra-$\mu$-diphenylphosphido-$\mu_4$-phenylphosphido-*quadro*-tetrarhenium(4 *Re*—*Re*) 0·5 Dichloromethane Solvate

By Nikolaos Klouras, Ulrich Flörke, Hans-Jürgen Haupt and Matthias Woyciechowski

*Anorganische und Analytische Chemie, Universität-GH-Paderborn, D-4790 Paderborn, Warburger Strasse* 100, *Federal Republic of Germany*

**Abstract.** [$Re_4(\mu\text{-Cl})_2(\mu\text{-PPh}_2)_4(\mu_4\text{-PPh})(CO)_8$] (I), $M_r = 1888\cdot6$, triclinic, $P\bar{1}$, $a = 12\cdot973$ (4), $b = 13\cdot246$ (3), $c = 20\cdot463$ (4) Å, $\alpha = 101\cdot67$ (2), $\beta = 96\cdot01$ (2), $\gamma = 112\cdot48$ (2)°, $U = 3117\cdot2$ Å$^3$, $Z = 2$, $D_x = 2\cdot012$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu(\text{Mo } K\alpha) = 8\cdot11$ mm$^{-1}$, $F(000) = 1780$, $T = 298$ (1) K, $R = 0\cdot043$ for 6666 unique observed intensities. All four Re atoms in the 66-valence-electron (VE) complex are bridged by a common $\mu_4$-PPh group and situated in a plane. They are further edge-bridged by four diphenylphosphido groups on the periphery of the plane, alternatively oriented up- and downwards. The bridging of these Re atoms is completed with two chloro ligands in opposite positions below the basal plane of the $Re_4(\mu_4\text{-P})$ polyhedron. Of these Cl-bridged Re—Re distances, one [3·382 (1) Å] is non-bonding and the other [3·192 (1) Å] is bonding. The other two Re—Re distances correspond to single bonds [av. Re—Re 2·942 (1) Å]. [$Re_4(\mu\text{-H})_2(\mu\text{-PPh}_2)_4(\mu_4\text{-PPh})(CO)_8$]. $0\cdot5CH_2Cl_2$ (II), $M_r = 1862\cdot2$, triclinic, $P\bar{1}$, $a = 12\cdot715$ (2), $b = 13\cdot446$ (2), $c = 20\cdot492$ (2) Å, $\alpha = 101\cdot96$ (1), $\beta = 94\cdot53$ (1), $\gamma = 114\cdot44$ (1)°, $U = 3066\cdot4$ Å$^3$, $Z = 2$, $D_x = 2\cdot016$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu(\text{Mo } K\alpha) = 8\cdot17$ mm$^{-1}$, $F(000) = 1758$, $T = 298$ (1) K, $R = 0\cdot036$ for 6219 unique observed intensities. The coordination of the central molecular fragment is as above, the two chloro ligands being substituted by two hydrido ligands which could be located from a $\Delta F$ map and confirmed by $\delta$ $^1$H NMR measurements. The planar arrangement of the four Re atoms in the 62-VE complex comprises four Re—Re bonds [2·969 (1), 2·961 (1), 2·928 (1) and 2·918 (1) Å] which indicates partial $\pi$ bonding.

**Introduction.** Both title substances belong to the family of phosphido-bridged transition metal cluster compounds which àre of interest as homogeneous catalysts (Haupt, Balsaa & Flörke, 1988a,b). The stereochemistry of their common $\mu_4$-PPh bridge

group favours *a priori* a planar arrangement of the four Re atoms. To fulfil the demand of the '18-electron' rule, or Effective Atomic Number rule (EAN) (Owen, 1988), in the case of a metal–metal single-bonded four-membered ring 64 valence electrons (VE) are needed. This was previously ascertained in substances like $Re_4(\mu\text{-H})(\mu\text{-}X)$-$(\mu\text{-PPh}_2)_4(\mu_4\text{-PPh})(CO)_8$ ($X = $ Cl, Br, I) (Woyciechowski, 1989). On the other hand, the electron count gives for (I) two VE in excess and for (II) two VE in deficit. On this basis, it can be proposed that two VE in excess causes an opening of the rhenium ring, whereas the lack of two VE makes possible the formation of a $\pi$-type frontier orbital or of a trans-annular Re—Re bond in the four-membered ring. To recognize the actual Re—Re bond pattern in each of these solids the X-ray structural determination was necessary. Such results might also be used to discuss $\delta$ $^{31}$P NMR data of (I) and (II) in $CDCl_3$ solution, which allow a discrimination between bonded and non-bonded Re atoms since they surprisingly show for both compounds a lack of two Re—Re bonds.

**Experimental.** Heating $Re_2(\mu\text{-PPh}_2)_2(CO)_8$ in xylene in the presence of indium(III) chloride at 493 K gave black crystals of (I). Violet crystals of (II) were obtained from the reactants $Re_2(CO)_{10}$, $HPPh_2$ and iodine at 523 K (Woyciechowski, 1989). $\delta$ $^{31}$P NMR data [Bruker FT-WH 250, $CDCl_3$ solution at 298 K; $H_3PO_4$ (85%) as standard]: (I) 223·2 ($t$, 2P), $-8\cdot2$ ($t$, 1P), $-109\cdot7$ ($dt$, 2P); (II) 206·7 ($t$, 2P), 50·6 ($t$, 1P), $-52\cdot8$ ($dt$, 2P), and $\delta$ $^1$H NMR: $-10\cdot9$ ($s$, hydrido 2H) with TMS as standard. Cyclovoltammetric data of (I) in $CH_2Cl_2$/TBAPF$_6$ solution ($c = 0\cdot36$ mmol 1$^{-1}$) with platinum as working electrode (scan velocity 20 mV s$^{-1}$): $E^f$ (*vs* NHE) = 553 mV, $\Delta E_p = 54$ mV, $E_{p,red} - E_{p,red}/2$ or $E_{p,ox} - E_{p,ox}/2 = 42$ mV and $I_{p,red}/I_{p,ox} = 1$.

Crystal size of (I) 0·15 × 0·22 × 0·31 mm, Nicolet *R*3*m*/*V* diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0\cdot71073$ Å, lattice parameters

were refined from 25 reflections, $5 \leq 2\theta \leq 25°$; $\omega$–$2\theta$ scan, 9172 intensities were collected, $3 \leq 2\theta \leq 46°$, $0 \leq h \leq 14$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$, three standards were recorded every 400 reflections, only random deviations, Lp correction, empirical absorption correction via $\psi$ scans, min./max. transmission 0·185/0·248, after merging ($R_{int} = 0·0464$) 8717 unique intensities, 6666 were considered observed, $F > 4\sigma(F)$; structure was solved by Patterson and Fourier methods, full-matrix least-squares refinement based on $F$ (282 parameters), Re, Cl and P refined anisotropically, phenyl groups were treated as rigid bodies (C—C = 1·395, C—H = 0·96 Å), H atoms were fixed in calculated positions with $U_{iso} = 0·09$ Å$^2$, max. $(\Delta/\sigma) = 0·001$, max. height in final $\Delta F$ map = 1·3 e Å$^{-3}$ near Re position, refinement converged to $R = 0·043$, $wR = 0·044$, $w = 1/[\sigma^2(F) + 0·0005F^2]$.

Crystal size of (II) $0·11 \times 0·20 \times 0·43$ mm, lattice parameters were refined from 23 reflections, $8 \leq 2\theta \leq 28°$; $\omega$–$2\theta$ scan, 8347 intensities, $3 \leq 2\theta \leq 45°$, $-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $0 \leq l \leq 22$, three standards every 400 reflections, only random deviations, corrections as above, min./max. transmission 0·353/0·694, after merging ($R_{int} = 0·016$) 8072 unique intensities, 6219 were observed, $F > 4\sigma(F)$; structure solution with Re coordinates from above structure as starting parameters, subsequent $\Delta F$ maps, full-matrix least-squares refinement on $F$ (268 parameters), Re and P refined anisotropically, phenyl groups and H atoms as above, positions of H-bridging atoms located from $\Delta F$ map but not refined, max. $(\Delta/\sigma) = 0·001$, max. height in final $\Delta F$ map = 1·1 e Å$^{-3}$ near Re position, refinement converged to $R = 0·0357$, $wR = 0·0318$, $w = 1/[\sigma^2(F) + 0·0001F^2]$. Scattering factors, structure solution and refinement by *SHELXTL-Plus* (Sheldrick, 1988) for both structures.

**Discussion.** The structures of the title compounds are shown in Figs. 1 and 2. Atomic positional parameters are given in Tables 1 and 2, bond lengths and angles in Table 3.*

The six non-metal ligand atoms of each Re coordination sphere (3P, 2C, H or Cl) are arranged in distorted octahedra. For these ligands, the stereochemical characteristics of the $\mu_4$-PPh group favour planar-positioned Re atoms, additionally bridged by a sequence of up- and downwards oriented P atoms. The bridging is completed by one hydrido or Cl

---

* Lists of structure factors, anisotropic temperature factors and H-atom parameters, and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53167 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å$^2 \times 10^3$) *of* (I)

| | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|
| Re(1) | 359 (1) | 2821 (1) | 1710 (1) | 28 (1) |
| Re(3) | 2918 (1) | 6048 (1) | 3017 (1) | 30 (1) |
| Re(2) | 3210 (1) | 4327 (1) | 1993 (1) | 30 (1) |
| Re(4) | 273 (1) | 4509 (1) | 2862 (1) | 28 (1) |
| Cl(1) | 1608 (3) | 4329 (3) | 1183 (2) | 36 (2) |
| Cl(2) | 1188 (3) | 6000 (3) | 2270 (2) | 40 (2) |
| P(1) | 1958 (3) | 2304 (3) | 1497 (2) | 31 (2) |
| P(2) | 4086 (3) | 6328 (3) | 2187 (2) | 33 (2) |
| P(3) | 1661 (3) | 5964 (3) | 3841 (2) | 31 (2) |
| P(4) | -1142 (3) | 3411 (3) | 1866 (2) | 31 (2) |
| P(5) | 1874 (3) | 3906 (3) | 2773 (2) | 36 (2) |
| C(1) | -500 (13) | 2001 (13) | 798 (8) | 44 (4) |
| O(1) | -1008 (11) | 1501 (11) | 249 (7) | 72 (4) |
| C(2) | -450 (13) | 1543 (13) | 2008 (8) | 42 (4) |
| O(2) | -967 (10) | 727 (10) | 2166 (6) | 58 (3) |
| C(3) | 4389 (13) | 4208 (13) | 2536 (8) | 44 (4) |
| O(3) | 5116 (9) | 4100 (10) | 2863 (6) | 57 (3) |
| C(4) | 3963 (13) | 4182 (13) | 1231 (8) | 44 (4) |
| O(4) | 4428 (12) | 4122 (12) | 781 (7) | 84 (4) |
| C(5) | 4212 (13) | 6228 (13) | 3618 (8) | 43 (4) |
| O(5) | 5023 (10) | 6381 (10) | 3994 (6) | 56 (3) |
| C(6) | 3432 (14) | 7650 (15) | 3240 (8) | 52 (4) |
| O(6) | 3735 (11) | 8635 (12) | 3398 (7) | 77 (4) |
| C(7) | -720 (12) | 5246 (13) | 3031 (7) | 41 (4) |
| O(7) | -1321 (10) | 5712 (10) | 3122 (6) | 65 (3) |
| C(8) | -486 (12) | 3447 (12) | 3319 (7) | 34 (3) |
| O(8) | -978 (9) | 2755 (9) | 3580 (6) | 54 (3) |
| C(11) | 2168 (8) | 1765 (9) | 641 (4) | 38 (4) |
| C(12) | 1673 | 1942 | 60 | 48 (4) |
| C(13) | 1963 | 1637 | -564 | 65 (5) |
| C(14) | 2748 | 1155 | -609 | 68 (5) |
| C(15) | 3243 | 978 | -28 | 67 (5) |
| C(16) | 2953 | 1283 | 596 | 47 (4) |
| C(21) | 1980 (8) | 1188 (8) | 1882 (5) | 36 (3) |
| C(22) | 2797 | 1366 | 2444 | 49 (4) |
| C(23) | 2741 | 469 | 2719 | 53 (4) |
| C(24) | 1868 | -606 | 2432 | 69 (5) |
| C(25) | 1050 | -784 | 1871 | 81 (6) |
| C(26) | 1106 | 113 | 1596 | 60 (5) |
| C(31) | 5598 (8) | 7208 (9) | 2465 (6) | 42 (4) |
| C(32) | 5959 | 8373 | 2557 | 67 (5) |
| C(33) | 7109 | 9094 | 2792 | 77 (6) |
| C(34) | 7900 | 8651 | 2934 | 100 (8) |
| C(35) | 7539 | 7486 | 2841 | 156 (12) |
| C(36) | 6388 | 6765 | 2606 | 95 (7) |
| C(41) | 3791 (9) | 6933 (9) | 1485 (5) | 41 (4) |
| C(42) | 4318 | 6797 | 934 | 61 (5) |
| C(43) | 4143 | 7240 | 390 | 64 (5) |
| C(44) | 3442 | 7819 | 398 | 72 (5) |
| C(45) | 2915 | 7954 | 949 | 65 (5) |
| C(46) | 3089 | 7511 | 1493 | 53 (4) |
| C(51) | 2080 (8) | 5592 (8) | 4608 (4) | 33 (3) |
| C(52) | 3167 | 6253 | 5006 | 52 (4) |
| C(53) | 3517 | 5979 | 5589 | 60 (5) |
| C(54) | 2780 | 5045 | 5773 | 75 (6) |
| C(55) | 1693 | 4385 | 5375 | 63 (5) |
| C(56) | 1343 | 4659 | 4792 | 46 (4) |
| C(61) | 1359 (9) | 7196 (7) | 4191 (5) | 36 (3) |
| C(62) | 1107 | 7789 | 3752 | 55 (4) |
| C(63) | 894 | 8732 | 4010 | 78 (6) |
| C(64) | 933 | 9084 | 4706 | 74 (6) |
| C(65) | 1185 | 8491 | 5144 | 72 (5) |
| C(66) | 1398 | 7547 | 4886 | 55 (4) |
| C(71) | -2521 (7) | 2385 (8) | 1931 (5) | 34 (3) |
| C(72) | -3036 | 2597 | 2477 | 54 (4) |
| C(73) | -4111 | 1815 | 2498 | 68 (5) |
| C(74) | -4671 | 822 | 1974 | 61 (5) |
| C(75) | -4156 | 610 | 1428 | 69 (5) |
| C(76) | -3081 | 1392 | 1407 | 51 (4) |
| C(81) | -1581 (9) | 4169 (9) | 1324 (5) | 41 (4) |
| C(82) | -2454 | 4506 | 1444 | 61 (5) |
| C(83) | -2724 | 5163 | 1061 | 69 (5) |
| C(84) | -2120 | 5483 | 558 | 74 (6) |
| C(85) | -1246 | 5146 | 438 | 76 (6) |
| C(86) | -976 | 4489 | 821 | 62 (5) |
| C(91) | 2123 (8) | 3204 (8) | 3424 (4) | 34 (3) |
| C(92) | 3173 | 3657 | 3871 | 50 (4) |
| C(93) | 3333 | 3150 | 4386 | 59 (5) |
| C(94) | 2443 | 2191 | 4452 | 71 (5) |
| C(95) | 1394 | 1739 | 4004 | 53 (4) |
| C(96) | 1234 | 2245 | 3490 | 46 (4) |

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

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\text{Å} \times 10^3$) *of* (II)

| | $x$ | $y$ | $z$ | $U_{eq}$* | | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|---|---|---|---|---|
| Re(1) | 488 (1) | 2954 (1) | 1763 (1) | 23 (1) | C(36) | 2684 | 7129 | 1483 | 49 (3) |
| Re(2) | 3081 (1) | 4290 (1) | 1992 (1) | 24 (1) | C(41) | 5580 (5) | 7115 (6) | 2359 (4) | 42 (3) |
| Re(3) | 2925 (1) | 6014 (1) | 3054 (1) | 24 (1) | C(42) | 6004 | 8275 | 2650 | 59 (4) |
| Re(4) | 368 (1) | 4597 (1) | 2905 (1) | 23 (1) | C(43) | 7212 | 8967 | 2820 | 89 (5) |
| P(1) | 1938 (2) | 2270 (2) | 1510 (1) | 26 (1) | C(44) | 7997 | 8499 | 2698 | 88 (5) |
| P(2) | 3994 (2) | 6282 (2) | 2164 (1) | 28 (1) | C(45) | 7572 | 7339 | 2406 | 77 (4) |
| P(3) | 1720 (3) | 5975 (2) | 3919 (1) | 28 (1) | C(46) | 6364 | 6648 | 2237 | 60 (4) |
| P(4) | −1003 (2) | 3563 (2) | 1893 (1) | 25 (1) | C(51) | 1495 (6) | 7230 (5) | 4271 (3) | 33 (3) |
| P(5) | 1897 (2) | 3920 (2) | 2883 (1) | 26 (1) | C(52) | 1229 | 7798 | 3835 | 43 (3) |
| C(1) | −515 (10) | 1604 (9) | 1986 (6) | 38 (3) | C(53) | 1016 | 8727 | 4095 | 53 (3) |
| O(1) | −1102 (7) | 778 (7) | 2119 (4) | 53 (2) | C(54) | 1069 | 9089 | 4791 | 57 (4) |
| C(2) | −258 (9) | 2402 (9) | 829 (6) | 36 (3) | C(55) | 1335 | 8520 | 5227 | 56 (4) |
| O(2) | −733 (7) | 2058 (7) | 267 (5) | 61 (2) | C(56) | 1548 | 7591 | 4967 | 45 (3) |
| C(3) | 3701 (10) | 4310 (9) | 1170 (6) | 38 (3) | C(61) | 2080 (6) | 5558 (6) | 4668 (3) | 29 (3) |
| O(3) | 4134 (8) | 4333 (7) | 688 (5) | 67 (3) | C(62) | 3200 | 6203 | 5066 | 40 (3) |
| C(4) | 4399 (10) | 4269 (9) | 2470 (6) | 37 (3) | C(63) | 3512 | 5914 | 5642 | 48 (3) |
| O(4) | 5205 (7) | 4229 (7) | 2769 (4) | 56 (2) | C(64) | 2704 | 4979 | 5820 | 49 (3) |
| C(5) | 4343 (10) | 6350 (9) | 3620 (6) | 36 (3) | C(65) | 1585 | 4335 | 5421 | 49 (3) |
| O(5) | 5215 (7) | 6566 (7) | 3971 (4) | 58 (2) | C(66) | 1273 | 4624 | 4845 | 39 (3) |
| C(6) | 3331 (10) | 7587 (10) | 3180 (6) | 41 (3) | C(71) | −1335 (7) | 4322 (6) | 1332 (3) | 34 (3) |
| O(6) | 3563 (8) | 8540 (7) | 3260 (4) | 65 (3) | C(72) | −454 | 4957 | 1018 | 58 (4) |
| C(7) | −602 (9) | 3527 (9) | 3330 (5) | 33 (3) | C(73) | −685 | 5560 | 595 | 90 (5) |
| O(7) | −1192 (7) | 2828 (7) | 3570 (4) | 52 (2) | C(74) | −1797 | 5529 | 485 | 80 (5) |
| C(8) | −553 (9) | 5436 (9) | 2981 (5) | 34 (3) | C(75) | −2677 | 4894 | 799 | 72 (4) |
| O(8) | −1135 (7) | 5906 (7) | 2992 (4) | 56 (2) | C(76) | −2446 | 4291 | 1222 | 53 (3) |
| C(11) | 2133 (6) | 1733 (6) | 649 (3) | 33 (3) | C(81) | −2483 (5) | 2521 (5) | 1920 (4) | 34 (3) |
| C(12) | 1764 | 2028 | 90 | 46 (3) | C(82) | −3025 | 1519 | 1400 | 51 (3) |
| C(13) | 2049 | 1705 | −538 | 62 (4) | C(83) | −4150 | 712 | 1405 | 66 (4) |
| C(14) | 2703 | 1087 | −606 | 68 (4) | C(84) | −4732 | 907 | 1930 | 65 (4) |
| C(15) | 3072 | 792 | −48 | 64 (4) | C(85) | −4191 | 1909 | 2450 | 63 (4) |
| C(16) | 2787 | 1115 | 580 | 48 (3) | C(86) | −3066 | 2716 | 2445 | 45 (3) |
| C(21) | 1910 (6) | 1172 (5) | 1899 (3) | 32 (3) | C(91) | 2122 (6) | 3211 (5) | 3512 (3) | 28 (2) |
| C(22) | 1007 | 85 | 1614 | 49 (3) | C(92) | 1191 | 2229 | 3566 | 35 (3) |
| C(23) | 919 | −798 | 1898 | 65 (4) | C(93) | 1335 | 1702 | 4062 | 44 (3) |
| C(24) | 1734 | −595 | 2466 | 62 (4) | C(94) | 2410 | 2157 | 4504 | 52 (3) |
| C(25) | 2637 | 492 | 2750 | 56 (4) | C(95) | 3341 | 3139 | 4450 | 51 (3) |
| C(26) | 2725 | 1375 | 2467 | 41 (3) | C(96) | 3197 | 3667 | 3954 | 36 (3) |
| C(31) | 3641 (6) | 6873 (6) | 1498 (3) | 36 (3) | H(1) | 1774 | 4402 | 1328 | 90 |
| C(32) | 4341 | 7072 | 1004 | 52 (3) | H(2) | 1683 | 5733 | 2308 | 90 |
| C(33) | 4084 | 7527 | 495 | 62 (4) | Cl(1) | 5586 (10) | −696 (9) | 4825 (6) | 186 (5)† |
| C(34) | 3127 | 7783 | 480 | 58 (4) | Cl(2) | 5742 (15) | 834 (13) | 4000 (9) | 222 (9)† |
| C(35) | 2427 | 7584 | 974 | 69 (4) | C(100) | 5093 (22) | 454 (21) | 4812 (15) | 101 (8)† |

\* Equivalent isotropic $U$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.
† Occupation factor 0·5.

atom (Figs. 1 and 2). Because of the well known fact that a strong $\pi$-electron-acceptor CO group prefers *trans*-positioned ligands without or with less $\pi$-electron-acceptor ability, the carbonyls are pseudo-*trans* coordinated to the H or Cl and $\mu_4$-PPh ligands. This leads to an eclipsed conformation of
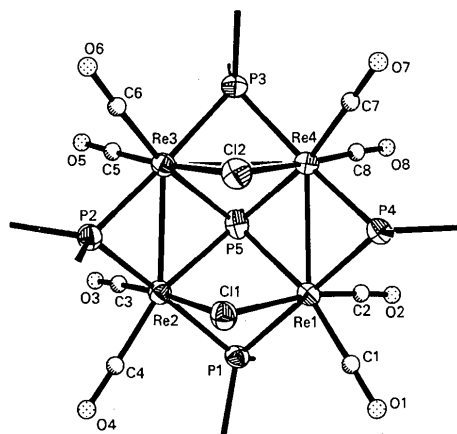


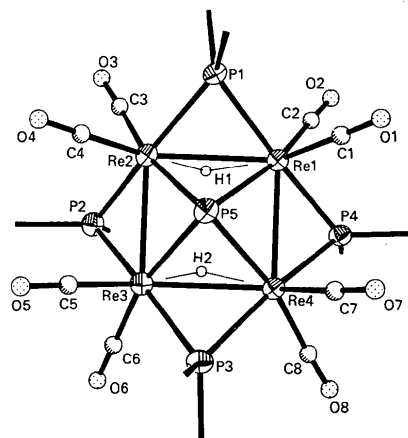Fig. 1. Molecular structure of (I). Phenyl groups have been omitted.



Fig. 2. Molecular structure of (II). Phenyl groups have been omitted.

the CO ligands in (I) and (II), viewed along the directions Re(1)···Re(2) and Re(3)···Re(4).

Striking differences appear in the Re—Re bonding pattern. In (I) (66 VE) with an excess of one valence-electron pair, one Re—Re bond is lacking as expected, although the related proof is difficult on the basis of Re—Re bond lengths. Hence three Re—Re bond lengths [Re(1)—Re(4) and Re(2)—Re(3) av. = 2·941 (1) and Re(3)—Re(4) = 3·192 (1) Å] are equivalent to those of analogous Re—Re single bonds in the 64 VE cluster Re₄(μ-Br)(μ-H)(μ-PPh₂)₄(μ₄-PPh)(CO)₈ (Haupt, Woyciechowski & Flörke, 1990) [av. 2·940 (2) and 3·152 (2) Å], but the remaining Re···Re contact [Re(1)···Re(2) = 3·382 (1) Å] with the same bridging atoms as the single bonded Re(3)—Re(4) atoms is only 0·190 (1) Å longer. The present threefold non-metallic bridging generates a shorter Re···Re contact in (I) than is the case in dirhenium compounds having two instead of three bridging groups, for example, Re···Re = 3·928 (1) Å in Re₂(μ-PPh₂)₂-(CO)₈ (Flörke, Woyciechowski & Haupt, 1988). The Re(1)···Re(2) contact length is accompanied by an enlargement of the angles at P(3) and Cl(2) vs those at P(1) and Cl(1) [by 5·2 (1)°], and at P(5) [by 7·2 (1)°]. The related bond angles at the bridging atoms Cl(1), P(1) and P(5) of the Re(1)···Re(2) distance do not obey the well known rule that such bond angles are obtuse if no metal–metal bond is present.

To support our interpretation of the Re—Re bonding pattern in (I) solutions of the substance were examined by means of cyclovoltammetric and $\delta$ ³¹P NMR analyses. The results ascertain that (I), in solution, undergoes a reversible two-electron transfer step as suggested by Nicholson & Shain (1964). The oxidative redox process generates the 64 VE cation [Re₄(μ-Cl)₂(μ-PPh₂)₄(μ₄-PPh)(CO)₈]²⁺ equivalent to Re₄(μ-Br)(μ-H)(μ-PPh₂)₄(μ₄-PPh)(CO)₈ with a four-membered ring of single-bonded Re atoms. This underlines the lack of one Re—Re bond in the starting material. For ring closure, the two electrons were removed from an antibonding orbital of the cluster compound (Owen, 1988). Besides, the negative $\delta$ ³¹P values of (I) in CDCl₃ agree with $\delta$ ³¹P NMR data in similar bridged rhenium clusters confirming the lack of two Re—Re bonds. This indicates that in the time scale of the NMR analysis both equally bridged atom pairs Re(1), Re(2) and Re(3), Re(4) should display a fluctuant behaviour. Regrettably, this assumption could not be proved by temperature-dependent NMR mesurements, since the substance is sparingly soluble below 243 K.

The bonding pattern of (II) with 62 VE consists of four Re—Re bonds. Both hydrido bridged Re—Re bonds are longer than those without such a bridging atom. Their average bond length of 2·965 (1) Å is

Table 3. Selected bond lengths (Å) and bond angles (°)

[Re₄(μ-Cl)₂(μ-PPh₂)₄(μ₄-PPh)(CO)₈] (I)

| | | | |
|---|---|---|---|
| Re(1)—Re(4) | 2·947 (1) | Re(1)—Cl(1) | 2·557 (3) |
| Re(1)—P(1) | 2·473 (2) | Re(1)—P(4) | 2·386 (2) |
| Re(1)—P(5) | 2·519 (4) | Re(3)—Re(2) | 2·937 (1) |
| Re(3)—Re(4) | 3·192 (1) | Re(3)—Cl(2) | 2·551 (3) |
| Re(3)—P(2) | 2·384 (3) | Re(3)—P(3) | 2·455 (3) |
| Re(3)—P(5) | 2·547 (3) | Re(2)—Cl(1) | 2·519 (3) |
| Re(2)—P(1) | 2·466 (3) | Re(2)—P(2) | 2·376 (3) |
| Re(2)—P(5) | 2·463 (3) | Re(3)—Cl(2) | 2·499 (3) |
| Re(4)—P(3) | 2·450 (3) | Re(4)—P(4) | 2·370 (3) |
| Re(4)—P(5) | 2·505 (2) | Re(1)···Re(2) | 3·382 (1) |
| | | | |
| Cl(1)—Re(1)—C(2) | 169·6 (3) | P(1)—Re(1)—P(4) | 175·9 (1) |
| P(5)—Re(1)—C(1) | 166·5 (3) | Cl(1)—Re(2)—C(3) | 174·8 (4) |
| P(1)—Re(2)—P(2) | 162·7 (1) | P(5)—Re(2)—C(4) | 162·4 (4) |
| Cl(2)—Re(3)—C(5) | 174·2 (4) | P(2)—Re(3)—P(3) | 172·6 (1) |
| P(5)—Re(3)—C(6) | 169·0 (3) | Cl(2)—Re(4)—C(8) | 175·7 (3) |
| P(3)—Re(4)—P(4) | 168·4 (1) | P(5)—Re(4)—C(7) | 168·8 (4) |
| Re(1)—Cl(1)—Re(2) | 83·6 (1) | Re(3)—Cl(2)—Re(4) | 78·4 (1) |
| Re(1)—P(1)—Re(2) | 86·4 (1) | Re(3)—P(2)—Re(2) | 76·2 (1) |
| Re(3)—P(3)—Re(4) | 81·2 (1) | Re(1)—P(4)—Re(4) | 76·6 (1) |
| Re(1)—P(5)—Re(2) | 85·5 (1) | Re(1)—P(5)—Re(4) | 71·8 (1) |
| Re(3)—P(5)—Re(2) | 71·8 (1) | Re(3)—P(5)—Re(4) | 78·4 (1) |

[Re₄(μ-H)₂(μ-PPh₂)₄(μ₄-PPh)(CO)₈] (II)

| | | | |
|---|---|---|---|
| Re(1)—Re(2) | 2·970 (1) | Re(1)—Re(4) | 2·928 (1) |
| Re(1)—P(1) | 2·423 (2) | Re(1)—P(4) | 2·369 (2) |
| Re(1)—P(5) | 2·520 (2) | Re(2)—Re(3) | 2·918 (1) |
| Re(2)—P(1) | 2·420 (2) | Re(2)—P(2) | 2·370 (2) |
| Re(2)—P(5) | 2·458 (2) | Re(3)—Re(4) | 2·961 (1) |
| Re(3)—P(2) | 2·359 (2) | Re(3)—P(3) | 2·427 (2) |
| Re(3)—P(5) | 2·497 (2) | Re(4)—P(3) | 2·431 (2) |
| Re(4)—P(4) | 2·346 (2) | Re(4)—P(5) | 2·464 (2) |
| | | | |
| P(1)—Re(1)—P(4) | 174·3 (1) | P(5)—Re(1)—C(2) | 166·4 (2) |
| P(1)—Re(2)—P(2) | 164·1 (1) | P(5)—Re(2)—C(3) | 167·4 (3) |
| C(3)—Re(2)—C(4) | 93·0 (4) | P(2)—Re(3)—P(3) | 170·1 (1) |
| P(5)—Re(3)—C(6) | 165·9 (2) | C(5)—Re(3)—C(6) | 91·7 (3) |
| P(3)—Re(4)—P(4) | 168·9 (1) | P(5)—Re(4)—C(8) | 168·0 (2) |
| C(7)—Re(4)—C(8) | 93·6 (3) | Re(1)—P(1)—Re(2) | 75·6 (1) |
| Re(2)—P(2)—Re(3) | 76·2 (1) | Re(3)—P(3)—Re(4) | 75·1 (1) |
| Re(1)—P(4)—Re(4) | 76·8 (1) | Re(1)—P(5)—Re(2) | 73·2 (1) |
| Re(1)—P(5)—Re(3) | 111·4 (1) | Re(1)—P(5)—Re(4) | 71·9 (1) |
| Re(2)—P(5)—Re(3) | 72·2 (1) | Re(2)—P(5)—Re(4) | 116·2 (1) |
| Re(3)—P(5)—Re(4) | 73·3 (1) | | |

however significantly shorter than that of 3·051 (1) Å in Re₂(μ-H)(μ-PPh₂)(CO)₇PPh₃ and of 3·194 (1) Å in Re₂(μ-H)(μ-PPh₂)(CO)₆(PPh₃)₂ (Haupt, Balsaa & Flörke, 1987). The average value of the non-hydrido bridged Re—Re bond length is 2·923 (1) Å, somewhat shorter than the 2·940 (1) Å of the corresponding bond in Re₄(μ-H)(μ-Br)(μ-PPh₂)₄(μ₄-PPh)(CO)₈. It is therefore reasonable to postulate, for the hydrido bridged and the other two Re—Re bonds, a contribution of a frontier orbital with partial π-bond property. The other way mentioned to become a 62 VE compound, by the formation of a transannular Re—Re bond (see Introduction), seems to be hindered by the rigid stereochemistry of the μ₄-PPh group. Regrettably, these findings have not been reflected in the $\delta$ ³¹P NMR spectrum of (II) in CDCl₃ since two Re—Re bonds are lacking. The localized μ-H positions in the $\Delta F$ map could be ascertained by $\delta$ ¹H NMR data (− 10·9, s, 2H).

Intermolecular distances in both substances do not indicate interactions greater than van der Waals forces.

### References

FLÖRKE, U., WOYCIECHOWSKI, M. & HAUPT, H.-J. (1988). *Acta Cryst.* C44, 2101–2104.

HAUPT, H.-J., BALSAA, P. & FLÖRKE, U. (1987). *Z. Anorg. Allg. Chem.* 548, 151–160.

HAUPT, H.-J., BALSAA, P. & FLÖRKE, U. (1988a). *Angew. Chem.* 100, 280–281.

HAUPT, H.-J., BALSAA, P. & FLÖRKE, U. (1988b). *Inorg. Chem.* 27, 280–286.

HAUPT, H.-J., WOYCIECHOWSKI, M. & FLÖRKE, U. (1990). *Z. Anorg. Allg. Chem.* Submitted.

NICHOLSON, R. S. & SHAIN, I. (1964). *Anal. Chem.* 36, 706–723.

OWEN, S. M. (1988). *Polyhedron*, 7, 253–283.

SHELDRICK, G. M. (1988). *SHELXTL-Plus Structure Determination Software Programs.* Nicolet Instrument Corporation, Madison, Wisconsin, USA.

WOYCIECHOWSKI, M. (1989). Dissertation, Univ. of Paderborn, Federal Republic of Germany.

# Structure of Tetrakis(diisopropyldithiocarbamato)tellurium(IV)

BY V. KUMAR AND G. ARAVAMUDAN*

*Department of Chemistry, Indian Institute of Technology, Madras 600 036, India*

M. SESHASAYEE

*Department of Physics, Indian Institute of Technology, Madras 600 036, India*

AND P. SELVAM AND K. YVON

*Laboratoire de Cristallographie aux Rayons X, Université de Genève, CH-1211, Genève-4, Switzerland*

**Abstract.** [Te(C$_7$H$_{14}$NS$_2$)$_4$], $M_r$ = 832·86, orthorhombic, $P2_12_12_1$, $a$ = 13·946 (1), $b$ = 14·833 (1), $c$ = 20·213 (3) Å, $V$ = 4181·54 Å$^3$, $Z$ = 4, $D_m$ = 1·35, $D_x$ = 1·32 Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$ = 1·119 mm$^{-1}$, $F$(000) = 1728, $T$ = 293 K, final $R(F)$ = 0·037, $S$ = 0·83 for 2920 unique reflections. The central Te atom is eight coordinated so that the S atoms form a slightly distorted dodecahedral arrangement around the metal. The lone pair of electrons on Te$^{IV}$ is found to be stereochemically inert. Interligand S···S short contacts of 3·097 (3) and 3·246 (2) Å are observed.

**Introduction.** Dithiocarbamates are known to undergo redox complexation reactions with metal ions such as Se$^{IV}$ and Te$^{IV}$, forming divalent selenium and tellurium complexes and the corresponding thiuram disulfides as the oxidation products (Fabiani, Spagna, Vaciago & Zambonelli, 1971; Schnabel, Deuten & Klar, 1980; Kumar, Aravamudan & Seshasayee, 1990). The general reaction between tellurium(IV) and dithiocarbamates ($L$) can be given as: Te$^{IV}$ + 4 $L^-$ ⇌ Te$^{IV}L_4$ ⇌ Te$^{II}L_2$ + $L$–$L$, where $L$–$L$ is the thiuram disulfide. In various solutions such as dichloromethane, carbon tetrachlo-

ride, benzene and acetonitrile, Te$^{IV}L4$ is found to undergo an autoredox reaction leading to the formation of the corresponding Te$^{II}L_2$ species and the thiuram disulfide, $L$–$L$.

The structure determination of the title compound was carried out to study whether any structural feature in the solid state can account for its facile autoredox reaction in solutions, to examine whether the lone pair of electrons on tellurium has any stereochemical significance, and also to study the effect of the bulkiness of the ligand on the stereochemistry. Other structures of Te$L_4$ complexes which have been reported are those of tetrakis(diethyldithiocarbamato)tellurium(IV) (Husebye & Svaeren, 1973); tetrakis(4-morpholinecarbodithioato)tellurium(IV) (Esperas & Husebye, 1975); tetrakis[N-(2-hydroxyethyl)-N-methyldithiocarbamato]tellurium(IV) (Husebye, 1979) and tetrakis[bis(2-hydroxyethyl)dithiocarbamato]tellurium(IV) (Rout, Seshasayee, Aravamudan & Radha, 1984).

**Experimental.** The title compound was prepared as a yellow solid on addition of 50 ml of 2$M$ acetic acid to 30 ml of 2$M$ sodium hydroxide containing 4 mmol of sodium tellurite and 100 mmol of the sodium salt of diisopropyldithiocarbamic acid. The precipitate was washed with water and air dried. 1 mmol