

The structure is held together by van der Waals interactions and hydrogen bonds; short intermolecular contacts C13...C8, C14...C22 and O5...O2 correspond to the sum of van der Waals radii of the atoms involved (Huheey, 1983).

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A Comparison of Phosphido-Bridged Triangular Rhenium Carbonyl Derivatives with 44, 46 and 48 Valence Electron Counts

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Abstract. Hexacarbonyl-tris(μ -cyclohexylphosphido)-bis(μ_3 -hydrido)-triangulo-trirhenium(3Re-*Re*), $C_{42}H_{68}O_6P_3Re_3$, $Re_3(CO)_6(\mu_3-H)_2[\mu-P(C_6H_{11})_2]_3$ (I), $M_r = 1320.5$, monoclinic, $P2_1/n$, $a = 10.361$ (2), $b = 19.729$ (4), $c = 23.254$ (5) Å, $\beta = 92.85$ (2)°, $U = 4747.5$ Å³, $Z = 4$, $D_x = 1.847$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 7.88$ mm⁻¹, $F(000) = 2552$, $T = 298$ (1) K, $R = 0.0688$ for 4169 unique reflections. The molecular structure has a central Re_3 ring which has three edge-bridging μ -PCy₂ groups (Cy = cyclohexyl) and two μ_3 -H ligands. The mean value of the metal-metal bonds is 2.756 (2) Å, the corresponding angles 60.0°. Hexacarbonyl-tris(μ -diphenylmethylphosphido)-(μ_3 -hydrido)-triangulo-rhenium(3Re-*Re*), $C_{27}H_{25}O_6P_4Re_3$, $Re_3(CO)_6(\mu_3-H)(\mu_3-P)[\mu-P(C_6H_5)(CH_3)]_3$ (II), $M_r = 1129.0$, monoclinic, $P2_1/a$, $a = 15.477$ (6), $b = 12.553$ (4), $c = 18.109$ (6) Å, $\beta = 114.22$ (2)°, $U = 3208.6$ Å³, $Z = 4$, $D_x = 2.337$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 11.68$ mm⁻¹, $F(000) = 2084$, $T = 296$ (1) K, $R = 0.0741$ for 3008 unique reflections. The central Re_3 ring is edge bridged by three μ -PPhMe groups (Ph = phenyl, Me = methyl) and capped by one μ_3 -H and one μ_3 -P ligand. The mean Re—Re bond distance is 2.804 (2) Å and the enclosed angles are 58.8, 60.5 and 60.7°. Hexacarbonyl-tris(μ -dicyclohexylphosphido)-(μ_3 -hydrido)-(μ_3 -phosphino)-triangulo-rhenium(3Re-*Re*), $C_{42}H_{67}O_6P_4Re_3$, $Re_3(CO)_6(\mu_3-H)(\mu_3-P)[\mu-P(C_6H_{11})_2]_3$ (III), $M_r = 1351.5$, monoclinic, $P2_1/n$, $a = 10.083$ (2), $b = 21.220$ (6), $c =$

22.441 (7) Å, $\beta = 100.43$ (2)°, $U = 4722.2$ Å³, $Z = 4$, $D_x = 1.901$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 7.95$ mm⁻¹, $F(000) = 2612$, $T = 298$ (1) K, $R = 0.0645$ for 4766 unique reflections. The central molecular fragment is an Re_3 ring capped by one μ_3 -H and one μ_3 -P ligand, the Re—Re bonds are bridged by three μ -PCy₂ groups. The mean Re—Re bond distance is 2.815 (1) Å and the enclosed angles are 59.6, 60.1 and 60.3°. Nonacarbonyl-tris(μ -dicyclohexylphosphido)-triangulo-rhenium(3Re-*Re*), $C_{45}H_{66}O_9P_3Re_3$, $Re_3(CO)_9[\mu-P(C_6H_{11})_2]_3$ (IV), $M_r = 1402.5$, orthorhombic, $Pbcn$, $a = 11.790$ (3), $b = 24.005$ (8), $c = 17.833$ (4) Å, $U = 5046.8$ Å³, $Z = 4$, $D_x = 1.846$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 7.42$ mm⁻¹, $F(000) = 2712$, $T = 296$ (1) K, $R = 0.0595$ for 2869 unique intensities. The central Re_3 ring is edge bridged by three μ -PCy₂ groups, each Re atom has three CO ligands. The mean Re—Re bond distance is 2.913 (1) Å and the angles are 59.9 (× 2) and 60.3°.

Introduction. As a requirement of the so-called effective atomic number (EAN) rule, Re atoms need, in a three-membered ring of three σ Re—Re bonds, 48 valence electrons (VE) (Lauher, 1978). Furthermore, this means that such a rhenium ring is unfold unsaturated with 46 and twofold unsaturated with 44 VE. The last VE count for a three-membered transition metal ring was obtained for the first time in $Re_3(CO)_6(\mu_3-H)_2(\mu-PPh_2)_3$ (Haupt, Flörke & Balsaa,

1988a) which shows a π -delocalization effect along the Re—Re edges. To study the complex dependence of bridged Re—Re bonds in Re₃ triangles on Ph vs Cy (cyclohexyl) substitution in 44 VE clusters, a transfer from 44 into 46 VE clusters and finally, into a 48 VE cluster was undertaken and the following substances identified by structural determinations: Re₃(CO)₆(μ_3 -H)₂(μ -PCy₂)₃ (I), Re₃(CO)₆(μ_3 -H)(μ_3 -P)(μ -PPhMe)₃ (II), Re₃(CO)₆(μ_3 -H)(μ_3 -P)(μ -PCy₂)₃ (III) and Re₃(CO)₉(μ -PCy₂)₃ (IV). Of further interest are their cyclovoltammetric and catalytic properties for hydrogenation (Haupt, Balsaa & Flörke, 1988b).

Experimental. Yellow crystals of Re₃(CO)₆(μ_3 -H)₂(μ -PCy₂)₃ (I) and yellow crystals of Re₃(CO)₆(μ_3 -H)(μ_3 -P)(μ -PCy₂)₃ (III) were prepared by hydrogenation of Re₂(CO)₈(μ -H)(μ -PCy₂) in xylene solution at 473 K and 2×10^5 Pa hydrogen pressure for 50 h. Orange-red crystals of Re₃(CO)₆(μ_3 -H)(μ_3 -P)(μ -PPhMe)₃ (II) were prepared by hydrogenation of Re₂(CO)₈(μ -PPhMe)₂ in xylene solution at 503 K and 2×10^5 Pa hydrogen pressure for 50 h. Red crystals of Re₃(CO)₉(μ -PCy₂)₃ (IV) were prepared in xylene solution by reaction of (I) and Re₂(CO)₁₀ at 543 K for 2 h in a glass tube.

Crystal size of (I) $0.03 \times 0.14 \times 0.43$ mm, Nicolet R3m/V diffractometer, graphite-monochromated Mo K α radiation, lattice parameters refined from 25 reflections $10 \leq 2\theta \leq 25^\circ$, ω - 2θ scan, scan speed $2.6^\circ \text{ min}^{-1}$, 10 491 reflections collected $3 \leq 2\theta \leq 54^\circ$, $-13 \leq h \leq 13$, $0 \leq k \leq 25$, $0 \leq l \leq 29$, three standards recorded every 400 reflections, 5% decrease in intensities scaled on standards, Lp correction, empirical absorption correction via ψ scans, min./max. transmission 0.500/0.862, after merging ($R_{\text{int}} = 0.066$) 9941 unique reflections, 4169 considered observed $F > 5\sigma(F)$. Structure solved by direct and Fourier synthesis methods, full-matrix least-squares refinement based on F (247 parameters), Re and P refined anisotropically, H atoms fixed in idealized positions with common isotropic displacement parameter, μ_3 -H positions not located from ΔF maps but ascertained from ¹H NMR measurements, $(\Delta/\sigma)_{\text{max}} = 0.001$, max. height in final ΔF map $1.1 \text{ e } \text{Å}^{-3}$ near Re position, refinement converged to $R = 0.069$, $wR = 0.052$, $1/w = \sigma^2(F) + 0.0001F^2$, $S = 1.588$. Complex neutral-atom scattering factors corrected for anomalous dispersion and all calculations from and with *SHELXTL-Plus* (Sheldrick, 1988).

Crystal size of (II) $0.04 \times 0.14 \times 0.35$ mm, lattice parameters refined from 32 reflections $10 \leq 2\theta \leq 32^\circ$, ω - 2θ scan, 7226 reflections collected $3 \leq 2\theta \leq 53^\circ$, $-19 \leq h \leq 19$, $0 \leq k \leq 15$, $0 \leq l \leq 22$, three standards every 400, only random deviations, corrections as above, min./max. transmission 0.225/0.740, after merging ($R_{\text{int}} = 0.052$) 6684 unique reflections, 3008 considered observed $F > 4\sigma(F)$. Structure solution

and refinement as above, 235 parameters, all but H atoms and phenyl C refined anisotropically, phenyl groups treated as rigid bodies (C—C 1.395, C—H 0.96 Å), H atoms and μ_3 -H position as above, $(\Delta/\sigma)_{\text{max}} = 0.001$, max. heights in final ΔF map $1.4 \text{ e } \text{Å}^{-3}$ near Re position, refinement converged to $R = 0.074$, $wR = 0.052$, $1/w = \sigma^2(F) + 0.001F^2$, $S = 1.558$. Further details of the structural analysis as above.

Crystal size of (III) $0.05 \times 0.18 \times 0.31$ mm, lattice parameters refined from 25 reflections $10 \leq 2\theta \leq 31^\circ$, ω - 2θ scan, 8234 reflections collected $3 \leq 2\theta \leq 50^\circ$, $-12 \leq h \leq 12$, $0 \leq k \leq 25$, $0 \leq l \leq 26$, three standards every 400, 5% decrease in intensities scaled on standards, corrections as above, min./max. transmission 0.241/0.766, after merging ($R_{\text{int}} = 0.0355$) 7788 unique reflections, 4766 considered observed $F > 4\sigma(F)$. Structure solution and refinement as above, 316 parameters, Re, P, and carbonyl groups refined anisotropically, H atoms and μ_3 -H position as above, $(\Delta/\sigma)_{\text{max}} = 0.005$, max. height in final ΔF map $1.6 \text{ e } \text{Å}^{-3}$ near Re position, refinement converged to $R = 0.064$, $wR = 0.053$, $1/w = \sigma^2(F) + 0.0004F^2$, $S = 1.397$. Further details of the structural analysis as above.

Crystal size of (IV) $0.12 \times 0.38 \times 0.40$ mm, lattice parameters refined from 29 reflections $13 \leq 2\theta \leq 33^\circ$, ω - 2θ scan, 6019 reflections collected $3 \leq 2\theta \leq 55^\circ$, $0 \leq h \leq 15$, $0 \leq k \leq 31$, $0 \leq l \leq 23$, three standards every 400, only random deviations, corrections as above, min./max. transmission 0.370/0.756, 2869 unique observed reflections $F > 4\sigma(F)$. Structure solution and refinement as above, 272 parameters, all but H atoms refined anisotropically, H atoms as above, O(4) slightly disordered around twofold axis, small disorder of O(3) not resolved, $(\Delta/\sigma)_{\text{max}} = 0.001$, max. height in final ΔF map $1.1 \text{ e } \text{Å}^{-3}$ near Re position, refinement converged to $R = 0.060$, $wR = 0.048$, $1/w = \sigma^2(F) + 0.0003F^2$, $S = 1.430$. Further details of the structural analysis as above.

Discussion. The structures of (I)–(IV) are shown in Figs. 1–4. Selected atomic parameters of (I)–(IV) are given in Table 1 and selected bond lengths and angles in Table 2.*

The diamagnetic rhenium clusters (I)–(IV) have a phosphido-bridged planar Re₃(μ -P)₃ core as a central molecular fragment. This edge-bridged triangular arrangement of Re atoms is capped by two triply bridging hydrides in (I) and one triply bridging

* Lists of structure factors, anisotropic temperature factors, complete list of atomic coordinates, bond lengths and angles, and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54252 (132 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hydrido and one μ_3 -phosphorus atom in (II)–(III). In (IV) the core is unbridged. The non-crystallographic local geometry of the coordinated six or the five non-metal ligand atoms at each Re atom is of idealized C_{2v} symmetry in (I) or (IV). For the six ligand atoms in (II) and (III), this geometry is of idealized C_s symmetry. In general, the coordination sphere of an Re atom with six ligand atoms is that of a distorted octahedron in (I)–(III). If the organic groups at the μ -P atoms are considered, a lack of symmetry (C_1) in (I)–(IV) appears. (III) can form six geometrical isomers of which the one with two Ph groups and one Me residue near to the μ_3 -P atom, and the remaining Ph and Me groups on the μ_3 -H side of Re ring, was obtained

The changes of multiply-bridged Re—Re bond lengths are of special interest. They stand in connection with different substitution patterns for a distinct VE number and allow a study of the effectiveness of different VE counts. The multiple-bond character of

a 44 VE Re_3 ring is characterized by the average Re—Re bond length by 2.730 (1) Å in $Re_3(CO)_6(\mu_3-H)_2(\mu-PPh_2)_3$ (Haupt, Flörke & Balsaa, 1988a). The exchange of Ph vs Cy groups in (I) enlarges the Re—Re bond lengths by about 0.026 (2) Å. The observed bond length increase comprises not only the Re—Re but also the Re—P bonds in the common $Re_3(\mu-P)_3$ plane with a π delocalization effect and is originated by the electronic properties of Ph and Cy residues. On going from (I) to (II), exchanging μ_3 -H for μ -P leads to an average Re—Re bond lengthening of 0.053 (1) Å in the 46 VE cluster (II). Such an Re—Re bond elongation increases in the following sequence from 44 VE in $Re_3(CO)_6(\mu_3-H)_2(\mu-PPh_2)_3$ [av. Re—Re 2.730 (1) Å] to 46 VE clusters. Such couples have values of 0.074 (2) with (III), of 0.078 (1) with $Re_3(CO)_6(\mu_3-H)(\mu_3-Cl)(\mu-PPh_2)_3$ (Haupt, Woyciechowski & Flörke, 1991) and of 0.096 (1) Å with $Re_3(CO)_5(\mu_3-H)(\mu-I)(\mu-PPh_2)_3(PPh_3)$ (Flörke & Haupt, 1990).

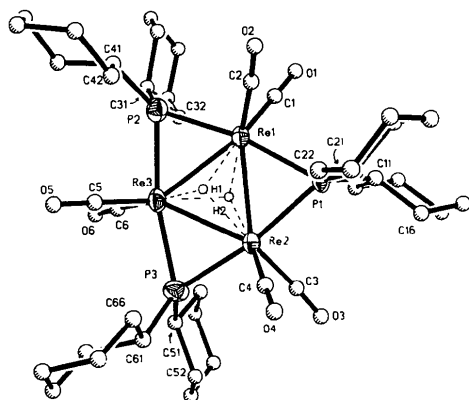


Fig. 1. General view of the molecule (I) with atom numbering.

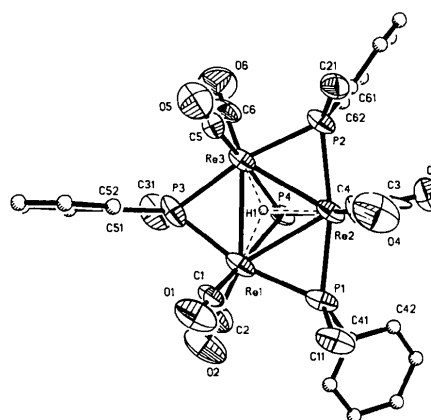


Fig. 3. General view of the molecule (III) with atom numbering.

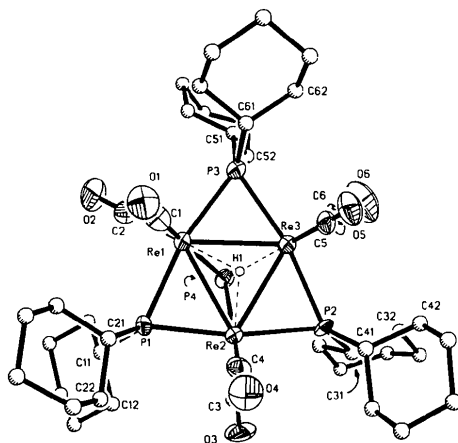


Fig. 2. General view of the molecule (II) with atom numbering.

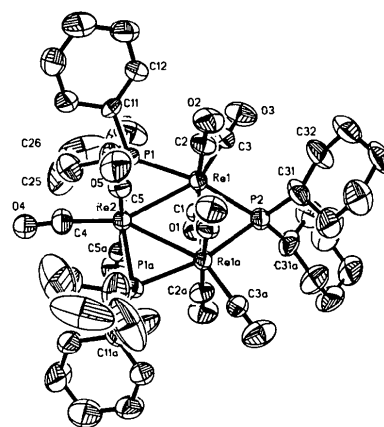


Fig. 4. General view of the molecule (IV) with atom numbering.

Table 1. Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
(I)				
Re(1)	3776 (1)	6957 (1)	-62 (1)	30 (1)
Re(2)	4466 (1)	8298 (1)	-176 (1)	32 (1)
Re(3)	3421 (1)	7597 (1)	-1111 (1)	33 (1)
P(1)	4704 (6)	7650 (3)	689 (3)	30 (4)
P(2)	2814 (6)	6458 (3)	-914 (3)	37 (4)
P(3)	3951 (6)	8775 (3)	-1098 (3)	41 (4)
C(1)	2592 (29)	6594 (15)	432 (14)	73 (9)
O(1)	1857 (18)	6363 (9)	741 (9)	73 (6)
C(2)	4820 (25)	6213 (13)	143 (12)	52 (8)
O(2)	5517 (19)	5758 (9)	232 (9)	72 (6)
C(3)	3927 (24)	9077 (13)	238 (12)	50 (7)
O(3)	3614 (17)	9564 (9)	464 (8)	66 (6)
C(4)	6167 (29)	8658 (14)	-141 (13)	66 (9)
O(4)	7240 (18)	8853 (9)	-114 (8)	71 (6)
C(5)	4222 (26)	7387 (13)	-1773 (13)	55 (8)
O(5)	4817 (19)	7257 (9)	-2188 (10)	82 (7)
C(6)	1934 (28)	7740 (13)	-1595 (13)	64 (9)
O(6)	975 (20)	7848 (9)	-1891 (9)	83 (7)
(II)				
Re(1)	4187 (1)	998 (1)	3156 (1)	42 (1)
Re(2)	3601 (1)	-41 (1)	1648 (1)	43 (1)
Re(3)	3489 (1)	2159 (1)	1692 (1)	42 (1)
P(1)	4195 (4)	-876 (8)	2940 (4)	48 (5)
P(2)	3128 (4)	1125 (8)	496 (3)	49 (4)
P(3)	3916 (5)	2884 (7)	3013 (4)	54 (5)
P(4)	2436 (4)	906 (6)	2128 (3)	37 (4)
C(1)	5489 (19)	1082 (25)	3754 (11)	25 (16)
O(1)	6325 (12)	1069 (20)	4064 (10)	72 (14)
C(2)	4021 (18)	894 (28)	4151 (16)	74 (22)
O(2)	3870 (14)	814 (22)	4714 (11)	99 (19)
C(3)	2737 (19)	-1014 (32)	994 (15)	65 (22)
O(3)	2106 (15)	-1600 (17)	556 (13)	80 (17)
C(4)	4589 (19)	-590 (23)	1431 (15)	58 (21)
O(4)	5208 (13)	-895 (21)	1313 (12)	102 (17)
C(5)	4406 (19)	2903 (22)	1467 (15)	51 (19)
O(5)	4972 (13)	3359 (17)	1302 (12)	83 (16)
C(6)	2478 (21)	3163 (28)	1138 (16)	66 (24)
O(6)	1853 (16)	3725 (21)	819 (15)	107 (21)
(III)				
Re(1)	489 (1)	2168 (1)	7984 (1)	27 (1)
Re(2)	28 (1)	1919 (1)	6728 (1)	25 (1)
Re(3)	-1015 (1)	1103 (1)	7510 (1)	27 (1)
P(1)	1276 (5)	2798 (2)	7215 (2)	28 (3)
P(2)	-1297 (5)	989 (2)	6431 (2)	23 (3)
P(3)	-500 (5)	1401 (2)	8561 (2)	31 (3)
P(4)	1580 (5)	1227 (2)	7530 (2)	27 (3)
C(1)	-529 (19)	2830 (9)	8208 (10)	38 (13)
O(1)	-1246 (14)	3230 (7)	8316 (8)	59 (11)
C(2)	1952 (22)	2387 (9)	8627 (10)	38 (13)
O(2)	2797 (15)	2526 (8)	9011 (8)	65 (12)
C(3)	966 (18)	1788 (9)	6074 (10)	32 (13)
O(3)	1457 (17)	1684 (7)	5660 (7)	61 (12)
C(4)	-1191 (22)	2453 (10)	6282 (11)	49 (15)
O(4)	-2033 (16)	2774 (7)	5964 (8)	64 (12)
C(5)	-2865 (21)	1198 (8)	7474 (9)	34 (13)
O(5)	-4012 (15)	1280 (7)	7455 (8)	53 (11)
C(6)	-1114 (22)	211 (9)	7651 (11)	45 (15)
O(6)	-1199 (20)	-307 (7)	7774 (10)	90 (17)
(IV)				
Re(1)	620 (1)	2344 (1)	1791 (1)	42 (1)
Re(2)	0	3392 (1)	2500	42 (1)
P(1)	1016 (3)	3271 (2)	1340 (3)	49 (3)
P(2)	0	1546 (2)	2500	48 (3)
C(1)	-820 (12)	2327 (7)	1232 (9)	51 (10)
O(1)	-1634 (9)	2306 (5)	898 (6)	72 (8)
C(2)	2107 (12)	2317 (7)	2297 (8)	52 (10)
O(2)	2997 (9)	2277 (5)	2569 (6)	74 (8)
C(3)	1302 (13)	1938 (7)	962 (10)	57 (11)
O(3)	1701 (10)	1695 (6)	472 (7)	88 (10)
C(4)	0	4184 (9)	2500	58 (15)
O(4)	-4 (27)	4671 (7)	2665 (13)	60 (6)*
C(5)	1448 (12)	3423 (6)	3049 (8)	46 (9)
O(5)	2290 (10)	3478 (5)	3359 (7)	81 (9)

* Disordered around twofold axis, s.o.f. = 0.5.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

(I)				
Re(1)—Re(2)	2.757 (1)	Re(1)—Re(3)	2.756 (1)	
Re(1)—P(1)	2.383 (6)	Re(1)—P(2)	2.388 (7)	
Re(2)—Re(3)	2.753 (1)	Re(2)—P(1)	2.387 (6)	
Re(2)—P(3)	2.377 (7)	Re(3)—P(2)	2.386 (6)	
Re(3)—P(3)	2.387 (7)			
P(1)—Re(1)—P(2)	169.2 (2)	Re(2)—Re(1)—Re(3)	59.9 (1)	
P(1)—Re(2)—P(3)	169.0 (2)	Re(1)—Re(2)—Re(3)	60.0 (1)	
P(2)—Re(3)—P(3)	167.9 (2)	Re(1)—Re(3)—Re(2)	60.0 (1)	
Re(1)—P(2)—Re(3)	70.5 (2)	Re(1)—P(1)—Re(2)	70.6 (2)	
		Re(2)—P(3)—Re(3)	70.6 (2)	
(II)				
Re(1)—Re(2)	2.819 (2)	Re(1)—Re(3)	2.823 (2)	
Re(1)—P(1)	2.385 (10)	Re(1)—P(3)	2.400 (9)	
Re(2)—P(4)	2.585 (4)	Re(2)—Re(3)	2.770 (2)	
Re(2)—P(1)	2.377 (7)	Re(2)—P(2)	2.403 (7)	
Re(2)—P(4)	2.588 (5)	Re(3)—P(2)	2.386 (7)	
Re(3)—P(3)	2.386 (7)	Re(3)—P(4)	2.610 (6)	
Re(2)—Re(1)—Re(3)	58.8 (1)	P(1)—Re(1)—P(3)	165.4 (2)	
P(1)—Re(1)—P(4)	85.0 (2)	P(3)—Re(1)—P(4)	83.2 (2)	
Re(1)—Re(2)—Re(3)	60.7 (1)	P(1)—Re(2)—P(2)	168.4 (3)	
P(1)—Re(2)—P(4)	85.1 (2)	P(2)—Re(2)—P(4)	90.3 (2)	
Re(1)—Re(3)—Re(2)	60.5 (1)	P(2)—Re(3)—P(3)	169.4 (3)	
P(2)—Re(3)—P(4)	90.2 (2)	P(3)—Re(3)—P(4)	82.9 (2)	
Re(1)—P(1)—Re(2)	72.6 (3)	Re(2)—P(2)—Re(3)	70.7 (2)	
Re(1)—P(3)—Re(3)	72.3 (2)	Re(1)—P(4)—Re(2)	66.0 (1)	
Re(1)—P(4)—Re(3)	65.8 (1)	Re(2)—P(4)—Re(3)	64.4 (1)	
(III)				
Re(1)—Re(2)	2.824 (1)	Re(1)—Re(3)	2.819 (1)	
Re(1)—P(1)	2.427 (5)	Re(1)—P(3)	2.406 (5)	
Re(1)—P(4)	2.577 (5)	Re(2)—Re(3)	2.803 (1)	
Re(2)—P(1)	2.400 (5)	Re(2)—P(2)	2.408 (5)	
Re(2)—P(4)	2.612 (5)	Re(3)—P(2)	2.400 (5)	
Re(3)—P(3)	2.405 (5)	Re(3)—P(4)	2.622 (4)	
Re(2)—Re(1)—Re(3)	59.5 (1)	P(1)—Re(1)—P(3)	167.4 (2)	
P(1)—Re(1)—P(4)	85.8 (2)	P(3)—Re(1)—P(4)	86.4 (2)	
Re(1)—Re(2)—Re(3)	60.1 (1)	P(1)—Re(2)—P(2)	169.0 (2)	
P(1)—Re(2)—P(4)	85.6 (2)	P(2)—Re(2)—P(4)	87.9 (2)	
Re(1)—Re(3)—Re(2)	60.3 (1)	P(2)—Re(3)—P(3)	168.9 (2)	
P(2)—Re(3)—P(4)	87.8 (2)	P(3)—Re(3)—P(4)	85.4 (2)	
Re(1)—P(1)—Re(2)	71.6 (1)	Re(2)—P(2)—Re(3)	71.3 (1)	
Re(1)—P(3)—Re(3)	71.8 (2)	Re(1)—P(4)—Re(2)	65.9 (1)	
Re(1)—P(4)—Re(3)	65.7 (1)	Re(2)—P(4)—Re(3)	64.8 (1)	
(IV)				
Re(1)—Re(1a)	2.920 (1)	Re(1)—Re(2)	2.909 (1)	
Re(1)—P(1)	2.412 (4)	Re(1)—P(2)	2.409 (4)	
Re(2)—P(1)	2.408 (4)			
P(1)—Re(1)—P(2)	165.4 (1)	Re(1a)—Re(1)—Re(2)	59.9 (1)	
P(1)—Re(2)—P(1a)	166.1 (1)	Re(1)—Re(2)—Re(1a)	60.3 (1)	
Re(1)—P(2)—Re(1a)	74.6 (2)	Re(1)—P(1)—Re(2)	74.3 (1)	

The lack of an unsaturated Re—Re bond character in the Re₃ triangles gives Re—Re bond elongations of 0.160 (2) between (I) and (IV) and of 0.184 (4) \AA in Re₃(CO)₆(μ_3 -H)₂(μ -PPh₂)₃ and Re₃(CO)₉(μ -PPh₂)₃ (Haupt, Flörke & Balsaa, 1988c). Both (IV) and its Ph derivative are not affected by a change from Cy [av. Re—Re 2.916 (2) \AA] to Ph [av. Re—Re 2.914 (4) \AA] residues.

The Re—Re bond alterations in this kind of phosphido-bridged compound let us conclude that a replacement of Ph against Cy groups affects unsaturated 44 VE clusters more than saturated 48 VE clusters. Furthermore, each exchange of μ_3 -H in 44 VE clusters of the type Re₃(CO)₆(μ_3 -H)₂(μ -PR₂)₃

against μ_3 -P, μ_3 -Cl and μ_3 -I atoms, which is accompanied by a conversion of 44 VE to 46 VE cluster species, reveals Re—Re bond elongation in the 46 VE species of about 0.053 (1)–0.094 (1) Å. The electronic structure of the μ_3 -X ligands seems to be a factor of greater influence than the atomic size of X, because in the series of substances of type $\text{Re}_3(\text{CO})_6(\mu_3\text{-H})(\mu_3\text{-X})(\mu\text{-PPh}_2)_3$ [X: Cl > Br > I, Re—Re 2.808 (1) > 2.809 (2) > 2.820 (1) Å], such a steric factor can almost be neglected. In general, the rather rigid phosphido-bridged Re—Re triangles do not show extensive geometrical changes.

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Structure of *trans*-Aquanitrido(1,4,8,11-tetraazacyclotetradecan-5-onato-*N,N',N'',N'''*)technetium(V) Chloride Dihydrate

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Abstract. $[\text{TcN}(\text{C}_{10}\text{H}_{21}\text{N}_4\text{O})(\text{H}_2\text{O})]^+ \cdot \text{Cl}^- \cdot 2\text{H}_2\text{O}$, $M_r = 415.81$, monoclinic, $P2_1/c$, $a = 7.609$ (1), $b = 16.405$ (3), $c = 13.642$ (3) Å, $\beta = 99.57$ (1)°, $V = 1679.2$ (5) Å³, $Z = 4$, $D_x = 1.64$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 1.018$ mm⁻¹, $F(000) = 856$, $T = 298$ K, $R = 0.021$ for 3262 observed reflections. The complex cation displays a distorted octahedral structure, with a water molecule in the *trans* position with respect to the $\text{Tc}\equiv\text{N}$ group and the four N atoms of the ligand in the equatorial position. The degree of pyramidalization of the coordination polyhedron is important [average $\text{N}\equiv\text{Tc}-\text{N}$ angle of 101 (3)°] and the $\text{Tc}-\text{OH}_2$ bond distance is abnormally long (2.560 Å), as a consequence of the strong *trans* influence exerted by the nitrido group. These facts are consistent with an incipient transition from a square pyramidal to octahedral geometry of the coordination polyhedron caused by the incoming water molecule.

Introduction. The application of complexes of metastable technetium-99m in diagnostic nuclear medicine

has stimulated a major development of technetium chemistry.

The chemistry of technetium(V) is largely dominated by $[\text{Tc}\equiv\text{O}]^{3+}$ and *trans*-dioxo $[\text{O}=\text{Tc}=\text{O}]^+$ cores. Throughout this paper the form $[\text{Tc}\equiv\text{O}]^{3+}$ is used to describe the Tc—oxo multiple bond according to the well known bond situation in oxo complexes where the $M-\text{O}$ bond has three components (one σ and two π), out of which two are covalent and one is donor–acceptor ($\text{Tc}\equiv\text{O}$) (Shustorovich, Porai-Koshits & Buslaev, 1975). This formalism is useful to distinguish the bond situation in oxo $[\text{Tc}\equiv\text{O}]^{3+}$ complexes, where Tc—O distances fall in the range 1.61–1.68 Å with stretching frequencies in the range 920–1020 cm⁻¹, from that in dioxo $[\text{O}=\text{Tc}=\text{O}]^+$ complexes where the distances and stretching frequencies occur in the ranges 1.74–1.75 Å and 790–880 cm⁻¹ respectively (Zuckman, Freeman, Troutner, Volkert, Holmes, Van Derveer & Kent Barefield, 1981; Kastner, Lindsay & Clarke, 1982; Jurisson, Aston, Fair, Schlemper, Sharp & Troutner, 1987).

Lipophilic square-pyramidal complexes containing the $[\text{Tc}\equiv\text{O}]^{3+}$ moiety as $[\text{TcO}(L)]$ ($L = \text{diamino-}$

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