

**Tetracarbonyldi- $\mu$ -iodo- $\mu$ -{[tetracarbonyl(triphenylphosphine)rhenio(0)]gallio(III)}-bis(triphenylphosphine)dirhenium(0)(Re–Re)**

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**Abstract.**  $[\text{Re}_2\text{I}_2\{\text{Ga}[\text{Re}\{\text{P}(\text{C}_6\text{H}_5)_3\}(\text{CO})_4]\}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\text{CO})_4]$ ,  $M_r = 1893.1$ , triclinic,  $P\bar{1}$ ,  $a = 12.857(6)$ ,  $b = 13.119(6)$ ,  $c = 20.160(6)$  Å,  $\alpha = 78.03(3)$ ,  $\beta = 87.92(3)$ ,  $\gamma = 69.68(6)^\circ$ ,  $U = 3117(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.016$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 7.045$  mm<sup>-1</sup>,  $F(000) = 1776$ ,  $T = 294(1)$  K, final  $R = 0.049$  for 6698 unique reflexions. The molecular structure of  $\text{C}_{62}\text{H}_{45}\text{GaI}_2\text{O}_8\text{P}_3\text{Re}_3$  contains an inner  $\text{GaI}_2\text{Re}_2$  molecular fragment with an Re–Re bond. This transition-metal–transition-metal bond is bridged by two iodine atoms and one trivalent Ga atom possessing a terminal  $\text{Re}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$  group. The two Re atoms are central atoms from a pair of distorted octahedra sharing a face with the three bridge atoms. Each of these Re atoms has two CO and one  $\text{P}(\text{C}_6\text{H}_5)_3$  as terminal ligands. Their two CO ligands are *trans* to the iodine atoms and the two phosphines *trans* to the Ga atom. The Re atom of the terminal  $\text{Re}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$  group has a distorted octahedral ligand arrangement with the Ga and P atoms in axial and the four CO ligands in equatorial positions.

**Introduction.** The influence of different metal atoms on the geometry of four-membered rings in clusters of the type  $M_2(\text{CO})_8[\mu\text{-}M'\text{M}(\text{CO})_5]_2$  with a transannular metal–metal bond ( $M\text{--}M$ ) (Haupt, Flörke & Preut, 1986) and without such a bond (Preut & Haupt, 1979) ( $M$  = transition metal,  $M'$  = main-group metal) has been the subject of several studies. The present structural determination of the title substance has continued this investigation on heteronuclear metal-atom clusters with the new core  $M_2M'X_2$  containing an  $M\text{--}M$  bond triple bridged by one  $M' = \text{Ga}^{\text{III}}$  atom and two  $X = \text{I}$  atoms. The structure of the title substance can be related to those of the class of  $A_2X_9$  molecules ( $A$  = metal atom,  $X$  = ligand) (Wells, 1984).

**Experimental.** Yellow crystals of title compound prepared with stoichiometric amounts of  $\text{GaI}_3$  and *trans*- $\text{Re}_2(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_3]_2$  in a boiling xylene solution. Yellow crystal,  $0.10 \times 0.20 \times 0.25$  mm; Enraf–Nonius CAD-4 diffractometer,  $\theta/2\theta$  scan; lattice parameters refined from 25 reflections with  $8 \leq \theta \leq 13^\circ$ ; 11 285 reflections measured,  $2 \leq \theta \leq 25^\circ$ ,  $-15 \leq h \leq 15$ ,

$-15 \leq k \leq 15$ ,  $0 \leq l \leq 24$ ; 2 standard reflections every 200 reflections, only random deviations;  $L_p$  correction, empirical absorption correction from  $\psi$  scans, min. correction 0.95, max. 1.00; after merging ( $R_{\text{int}} = 0.016$ ) 6698 unique reflections with  $I > 2.5 \sigma(I)$ ; structure solved by Patterson and  $\Delta F$  syntheses; H atoms located from geometrical considerations; full-matrix least-squares refinement on  $F$ ; 225 parameters; phenyl groups treated as rigid bodies (C–C 1.395, C–H 0.98 Å); Re, I, Ga and P anisotropically refined; unit weights, final  $R = 0.049$ ; max.  $(\Delta/\sigma) = 0.02$ ; max. heights in final  $\Delta F$  synthesis  $+1.5/-0.4$  e Å<sup>-3</sup> near heavy-atom position; scattering factors and  $f'$ ,  $f''$  values from Cromer & Mann (1968) and Cromer & Liberman (1970). Programs used: *SHELX76* (Sheldrick, 1976) and *PLUTO* (Motherwell, 1978) on a Prime 750 computer.

**Discussion.** The structure of the title compound is shown in Fig. 1 (*PLUTO*) and in a stereoscopic view in Fig. 2. Atomic parameters are given in Table 1,\* bond lengths and angles in Table 2.

The arrangement of the  $\text{GaI}_2\text{P}_3\text{Re}_3$  atoms resides on two intersecting perpendicular non-crystallographic local mirror planes with the  $\text{GaI}_2\text{Re}_2$  group as the central molecule fragment. This nucleus exhibits an Re(1)–Re(2) bond, which accounts for the diamagnetism and gives each of these Re atoms the Rn closed-shell electron configuration. Each of these Re atoms (oxidation number 0) occupies the interstices of a pair of octahedra sharing a face with one trivalent Ga atom and the two iodine atoms at the corners. The homonuclear metal–metal bond corresponds to the normal to this plane. The Re atoms are in strongly distorted octahedral surroundings caused by the different kinds of ligands. Furthermore, the bond angle enclosed at both iodine bridge atoms is about  $8^\circ$  smaller than the value of  $70.5^\circ$  for regular octahedra

\* Lists of structure factors, anisotropic temperature factors and a complete list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42606 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sharing a face. The analogous Re(1)—Ga—Re(2) bond angle is close to this value (70.8°). This bond angle is also reduced by about 3.5 (1)° compared with the corresponding bond angle in the three-membered GaRe<sub>2</sub> rings of Re<sub>2</sub>(CO)<sub>8</sub>[μ-GaRe(CO)<sub>5</sub>]<sub>2</sub> (Haupt, Flörke & Preut, 1986). This decrease is accompanied by a shortening of the Re—Re bond by about 0.214 (1) Å and can be explained by a reinforcement of these bonds. The observed Re(1)—Re(2) bond length of the title substance is also about 0.116 (1) Å shorter than the covalent single bond in Re<sub>2</sub>(CO)<sub>10</sub> (Churchill, Amoh & Wasserman, 1981). With regard to the terminal ligands at the Re(1) and Re(2) atoms, the two CO ligands, as stronger π-acceptor ligands, are *trans* to the Re—I bonds and the weaker P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> ligand is *trans* to the Re—Ga bond. From the viewpoint of an optimal minimization of non-bonding repulsive forces

Table 1. Fractional atomic coordinates and isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U <sub>eq</sub> /U <sub>iso</sub>
Re(1)	0.0849 (1)	0.2359 (1)	0.2788 (1)	28 (1)*
Re(2)	0.1221 (1)	0.5859 (1)	-0.2938 (1)	29 (1)*
Re(3)	0.1803 (1)	-0.2526 (1)	-0.1130 (1)	45 (1)*
I(1)	0.0127 (1)	-0.2440 (1)	-0.4049 (1)	53 (1)*
I(2)	-0.0803 (1)	0.5517 (1)	-0.2911 (1)	38 (1)*
Ga	0.0909 (1)	-0.2961 (1)	-0.2061 (1)	35 (1)*
P(1)	-0.2716 (3)	-0.1333 (3)	-0.3246 (2)	32 (2)*
P(2)	0.2247 (3)	0.4467 (3)	-0.3557 (2)	35 (2)*
P(3)	0.2706 (4)	-0.1997 (4)	-0.0284 (2)	57 (3)*
C(1)	-0.068 (1)	0.897 (2)	-0.2714 (9)	57 (5)
O(1)	-0.057 (1)	0.981 (1)	-0.2665 (7)	71 (4)
C(2)	-0.135 (2)	0.736 (2)	-0.192 (1)	66 (5)
O(2)	-0.163 (1)	0.722 (1)	-0.1360 (8)	84 (4)
C(3)	0.176 (1)	0.485 (1)	-0.2141 (9)	54 (4)
O(3)	0.207 (1)	0.419 (1)	-0.1614 (7)	79 (4)
C(4)	0.239 (1)	0.641 (1)	-0.3051 (9)	51 (4)
O(4)	0.310 (1)	0.677 (1)	-0.3123 (7)	79 (4)
C(5)	0.032 (2)	0.852 (2)	-0.104 (1)	62 (5)
O(5)	-0.062 (1)	0.902 (1)	-0.1016 (8)	92 (5)
C(6)	0.319 (2)	0.634 (2)	-0.132 (1)	61 (5)
O(6)	0.397 (1)	0.570 (1)	-0.1483 (8)	86 (4)
C(7)	0.139 (2)	0.634 (2)	-0.050 (1)	73 (6)
O(7)	0.110 (1)	0.567 (2)	-0.0172 (9)	108 (5)
C(8)	0.209 (2)	-0.143 (2)	-0.183 (1)	69 (5)
O(8)	0.231 (1)	0.915 (1)	-0.2273 (9)	104 (5)
C(21)	-0.288 (1)	0.9712 (9)	-0.4038 (5)	51 (4)
C(22)	-0.207 (1)	1.0193 (9)	-0.4189 (5)	67 (5)
C(23)	-0.219 (1)	1.1019 (9)	-0.4772 (5)	90 (7)
C(24)	-0.313 (1)	1.1363 (9)	-0.5204 (5)	93 (7)
C(25)	-0.394 (1)	1.0882 (9)	-0.5052 (5)	106 (8)
C(26)	-0.382 (1)	1.0056 (9)	-0.4469 (5)	94 (7)
C(31)	-0.3381 (9)	0.7733 (8)	-0.3430 (6)	44 (4)
C(32)	-0.3915 (9)	0.7236 (8)	-0.2918 (6)	67 (5)
C(33)	-0.4309 (9)	0.6417 (8)	-0.3029 (6)	74 (6)
C(34)	-0.4168 (9)	0.6095 (8)	-0.3653 (6)	75 (6)
C(35)	-0.3634 (9)	0.6592 (8)	-0.4166 (6)	72 (6)
C(36)	-0.3240 (9)	0.7411 (8)	-0.4055 (6)	59 (5)
C(41)	-0.3724 (9)	0.947 (1)	-0.2698 (6)	53 (4)
C(42)	-0.4861 (9)	0.980 (1)	-0.2841 (6)	86 (7)
C(43)	-0.5618 (9)	1.043 (1)	-0.2441 (6)	89 (7)
C(44)	-0.5238 (9)	1.073 (1)	-0.1898 (6)	83 (6)
C(45)	-0.4101 (9)	1.040 (1)	-0.1755 (6)	74 (6)
C(46)	-0.3344 (9)	0.977 (1)	-0.2155 (6)	61 (5)
C(51)	0.3730 (7)	0.3743 (9)	-0.3293 (6)	45 (4)
C(52)	0.4375 (7)	0.2977 (9)	-0.3665 (6)	66 (5)
C(53)	0.5501 (7)	0.2419 (9)	-0.3494 (6)	69 (5)
C(54)	0.5982 (7)	0.2627 (9)	-0.2951 (6)	63 (5)
C(55)	0.5338 (7)	0.3393 (9)	-0.2579 (6)	66 (5)
C(56)	0.4212 (7)	0.3951 (9)	-0.2750 (6)	59 (5)
C(61)	0.1791 (9)	0.3287 (8)	-0.3558 (6)	48 (4)
C(62)	0.1366 (9)	0.2847 (8)	-0.2965 (6)	58 (5)
C(63)	0.1039 (9)	0.1931 (8)	-0.2940 (6)	70 (5)
C(64)	0.1138 (9)	0.1455 (8)	-0.3508 (6)	78 (6)
C(65)	0.1563 (9)	0.1895 (8)	-0.4101 (6)	84 (6)
C(66)	0.1890 (9)	0.2811 (8)	-0.4126 (6)	75 (6)
C(71)	0.2287 (9)	0.5102 (9)	0.5555 (4)	49 (4)
C(72)	0.3167 (9)	0.5460 (9)	0.5332 (4)	56 (4)
C(73)	0.3141 (9)	0.6056 (9)	0.4670 (4)	67 (5)
C(74)	0.2234 (9)	0.6295 (9)	0.4231 (4)	81 (6)
C(75)	0.1354 (9)	0.5938 (9)	0.4454 (4)	73 (6)
C(76)	0.1380 (9)	0.5342 (9)	0.5116 (4)	62 (5)
C(81)	0.245 (1)	0.9485 (9)	-0.0379 (7)	56 (4)
C(82)	0.144 (1)	1.0261 (9)	-0.0672 (7)	90 (7)
C(83)	0.123 (1)	1.1394 (9)	-0.0729 (7)	117 (9)
C(84)	0.203 (1)	1.1750 (9)	-0.0493 (7)	107 (8)
C(85)	0.303 (1)	1.0973 (9)	-0.0201 (7)	102 (8)
C(86)	0.324 (1)	0.9841 (9)	-0.0144 (7)	80 (6)
C(91)	0.236 (1)	0.758 (1)	0.0584 (5)	52 (4)
C(92)	0.190 (1)	0.835 (1)	0.0993 (5)	67 (5)
C(93)	0.162 (1)	0.799 (1)	0.1656 (5)	73 (6)
C(94)	0.182 (1)	0.686 (1)	0.1908 (5)	76 (6)
C(95)	0.229 (1)	0.609 (1)	0.1499 (5)	84 (6)
C(96)	0.256 (1)	0.645 (1)	0.0837 (5)	69 (5)
C(101)	0.4227 (7)	0.746 (1)	-0.0288 (6)	56 (4)
C(102)	0.4724 (7)	0.766 (1)	-0.0904 (6)	77 (6)
C(103)	0.5878 (7)	0.728 (1)	-0.0934 (6)	91 (7)
C(104)	0.6534 (7)	0.668 (1)	-0.0349 (6)	83 (6)
C(105)	0.6037 (7)	0.647 (1)	0.0266 (6)	83 (6)
C(106)	0.4883 (7)	0.686 (1)	0.0297 (6)	74 (6)

\* Atoms refined anisotropically.

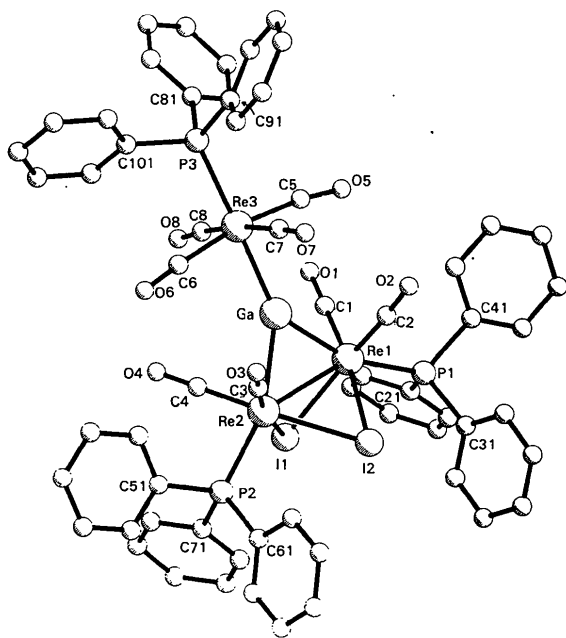


Fig. 1. General view of the title molecule.

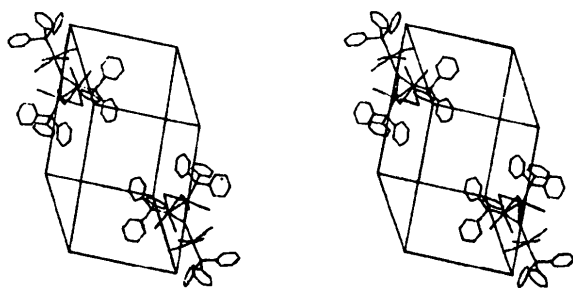


Fig. 2. Packing of the molecules.

between the ligands of the  $\text{GaI}_2\text{Re}_2$  nucleus, including the four equatorial CO ligands of the Re(3) atom, there exists for the phosphines [P(1) and P(2)] no alternative position in the polyhedra of the Re(1) and Re(2) central atoms. This can be proved by mutually exchanging the positions of the phosphine and CO ligands in a structure model of the title substance, where the phosphine phenyl groups become interlocked with the equatorial CO groups and free rotation of the phosphine ligands around their Re—P axis is prevented. Therefore, one factor with influence on the observed eclipsed arrangement of the CO ligand pairs around the Re(1)—Re(2) bond may be of steric origin.

A view around the Ga—Re(3) bond direction shows that the four CO ligands are staggered with respect to the positions of the four equatorial CO ligands of the Re(3) octahedron. The Ga atom with its three Re ligand atoms is situated at the centre of the eight CO ligands. This accumulation of atoms around the Lewis acid  $\text{Ga}^{\text{III}}$  has a screening effect and prevents a solvated species of the title substance from a typical addition reaction for a trivalent Ga atom with a Lewis base as has been proved with different halide ions.

Intermolecular distances do not indicate interactions exceeding van der Waals forces.

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Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Re(1)—Re(2)	2.925 (1)	Mean values	
—I(1)	2.800 (1)	Re(1)—C	1.85 (2)
—I(2)	2.829 (2)	Re(2)—C	1.85 (2)
—Ga	2.531 (3)	Re(3)—C	1.94 (3)
—P1	2.414 (6)	P(1)—C	1.83 (2)
Re(2)—I(1)	2.820 (1)	P(2)—C	1.83 (1)
—I(2)	2.788 (2)	P(3)—C	1.82 (2)
—Ga	2.516 (2)	C—O	1.16 (3)
—P(2)	2.406 (5)		
Re(3)—Ga	2.494 (2)		
—P(3)	2.437 (6)		
Re(1)—I(1)—Re(2)	62.71 (3)	Ga—Re(1)—Re(2)	54.36 (5)
Re(1)—I(2)—Re(2)	62.76 (4)	Ga—Re(2)—I(1)	97.86 (6)
Re(1)—Ga—Re(2)	70.83 (6)	Ga—Re(2)—I(2)	99.91 (7)
Re(3)—Ga—Re(1)	144.1 (1)	Ga—Re(2)—Re(1)	54.81 (6)
Re(3)—Ga—Re(2)	144.8 (1)	P(1)—Re(1)—Re(2)	144.7 (1)
Ga—Re(1)—I(1)	98.04 (7)	P(2)—Re(2)—Re(1)	148.2 (1)
Ga—Re(1)—I(2)	98.48 (6)	P(3)—Re(3)—Ga	175.8 (1)

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## Structures of Diguanidinium Tetrachloropalladate(II) and Guanidinium Tetrachloroaurate(III)

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**Abstract.**  $2\text{CH}_6\text{N}_3^+.\text{PdCl}_4^{2-}$  (1),  $M_r = 368.40$ , tetragonal,  $P4_2/n$ ,  $a = 10.755$  (1),  $c = 11.006$  (1) Å,  $V = 1273.0$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.93$ ,  $D_x = 1.94$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 2.24$  mm<sup>-1</sup>,  $F(000) = 720$ ,  $T = 296$  K, final  $R = 0.056$  for 1083 observed reflections.  $\text{CH}_6\text{N}_3^+.\text{AuCl}_4^-$  (2),  $M_r = 398.87$ , monoclinic,  $P2_1/c$ ,  $a = 15.235$  (4),  $b = 3.944$  (1),  $c = 14.688$  (3) Å,  $\beta = 94.60$  (2)°,  $V = 879.7$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 3.00$ ,  $D_x = 3.01$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 18.23$  mm<sup>-1</sup>,  $F(000) = 720$ ,  $T = 296$  K, final  $R = 0.056$  for 1161 observed

reflections. In (1) two planar guanidinium ions related by the center of symmetry lie close together with a C...C distance of 3.32 (1) Å. Such paired cations and square-planar  $\text{PdCl}_4^{2-}$  anions are in the alternate arrangement analogous to the NaCl structure, more adequately described by the (anti)pyrite  $\text{FeS}_2$ -*p* structure. In (2) square-planar  $\text{AuCl}_4^-$  anions, like  $\text{PdCl}_4^{2-}$  in (1), construct the pseudo face-centered lattice, but the anion and cation are arranged in such a unique way that each cation is surrounded by four anions in a nearly square coordination and *vice versa*. In both structures all H atoms participate in N—H...Cl hydrogen bonding to form three-dimensional hydrogen-bonded frameworks.

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