that the complex has a *trans* stereochemistry and the observed splitting is, therefore, due to the solid-state correlation effect. We would hence like to emphasize that assignments of configuration solely on the basis of the number of ν^{M-Cl} bands could be erroneous in the absence of X-ray or other confirmatory evidence. The Pd—N and Pd—Cl distances are close to those published in the literature for related complexes (Navarro-Ranninger, Martínez-Carrera & García-Blanco, 1985). The aromatic ring of p-FA has C_{2v} (mm) symmetry. The deviations of the ring C atoms are hardly significant. However, they suggest a minor deformation of the ring towards a twist-boat model. The ring angles at the C atoms to which the substituents are attached are considerably larger than 120°. These results are in agreement with those in p-fluoroaniline hydrochloride (Colapietro, Domenicano, Marciante & Portalone, 1981). The bond distances C(2)—C(3), C(5)—C(6) and C(6)—C(1) are considerably longer than the other three C—C distances of the ring. The deviations of the atoms from planarity are: C(1) −0·010 (8), C(2) 0·006 (6), C(3) 0·001 (6), C(4) −0·004 (7), C(5) 0·000 (6), C(6) 0·007 (7), N 0·011 (7) and F −0·008 (8) Å. The ring torsion angles

are shown in Fig. 1. The least-squares plane of the benzene ring makes an angle of 73·2 (9)° with the metal coordination plane. The C(4)—F distance 1·36 (1) Å is the same as in p-fluoroaniline hydrochloride (Colapietro *et al.*, 1981); the minor axis of the thermal ellipsoid of the F atom is collinear with the C(4)—F bond.

There are no intermolecular contacts less than the van der Waals distance.

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Heptacarbonyl-μ-(2-formyl-3-diphenylphosphinophenylido-O,P,C^{α},C^{1})-(triphenylphosphine)dirhenium(I), [Re$_2${P(C$_6$H$_5$)$_2$(C$_7$H$_3$O)}(CO)$_7${P(C$_6$H$_5$)$_3$}]

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Abstract. (C$_6$H$_5$)$_2$P[C$_6$H$_3$(CO)Re(CO)$_4$][Re(CO)$_3$-P(C$_6$H$_3$)$_3$], $M_r = 1119\cdot05$, monoclinic, $P2_1/n$, $a = 15\cdot265$ (2), $b = 13\cdot506$ (5), $c = 19\cdot869$ (2) Å, $\beta = 93\cdot54$ (9)°, $U = 4089$ (2) Å^3, $Z = 4$, $D_x = 1\cdot817$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 58\cdot07$ cm^{-1}, $F(000) = 2144$, $T = 294$ (1) K, final $R = 0\cdot064$ for 3629 unique reflexions. The molecular structure of C$_{44}$H$_{28}$O$_8$P$_2$Re$_2$ contains two rhenium atoms each with an essentially octahedral arrangement of ligands. One rhenium atom is coordinated to four carbonyl groups while each of the three CO ligands on the other rhenium atom is *trans* to a different atom. The two rhenium atoms are bridged by a quadridentate ligand that is bidentate to each metal atom. The molecule has an extended planar tricyclic ring system that includes two five-membered heterocyclic rings and one homonuclear ring.

Introduction. A complex decomposition process of the substance Re$_2$(CO)$_8$[P(C$_6$H$_5$)$_3$]$_2$ in the presence of Ga$_2$I$_3$ leads to the previously unknown heterocyclic title compound, which can exist in several isomeric molecular formulas. ^{1}H NMR and IR spectroscopic measurements of C$_{44}$H$_{28}$O$_8$P$_2$Re$_2$ gave no indication which isomer was present; therefore, the molecular structure has been elucidated.

Experimental. Dark-yellow crystals prepared in a one-pot process with Re$_2$(CO)$_8$[P(C$_6$H$_5$)$_3$]$_2$ in the presence of Ga$_2$I$_3$ at 423 K. $\omega/2\theta$ scan, scan width 1·45°, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, crystal size 0·1 × 0·1 × 0·4 mm, lattice parameters refined from 25 reflections $5 \leq \theta \leq 10°$; 4 standard reflections recorded every 680 reflections showed only random deviations; $1 \leq \theta \leq 22°$,

$-16 \leq h \leq 16$, $0 \leq k \leq 14$, $0 \leq l \leq 20$; after averaging ($R_{int} = 0.018$) 3629 observed reflections with $F_o > 3\sigma(F_o)$, Lp correction, absorption correction via φ scans, max., min. correction 1·00, 0·95; systematic absences: $h0l$, $h+l = 2n+1$, $0k0$, $k = 2n+1$; structure solution by Patterson and direct methods, ΔF syntheses, H atoms located from geometrical considerations with common temperature factors $U = 0.05$ Å^2, phenyl groups treated as rigid bodies, C—C = 1·395 Å, C—H = 0·98 Å; blocked full-matrix least-squares refinement with anisotropic temperature factors for Re and P, based on F^2 and 170 refined parameters, $R = 0.064$, unit weights, $(\Delta/\sigma)_{max} = 0.01$, no significant features in final ΔF synthesis; complex neutral-atom scattering factors from Cromer & Mann (1968) and Cromer & Liberman (1970); programs (Prime 750 computer): *SHELX76* (Sheldrick, 1976), *PLUTO* (Motherwell, 1978).

Discussion. The molecular structure of the title compound is shown in Fig. 1; a stereoview of the four molecules in the unit cell is given in Fig. 2. The final

Fig. 1. General view of the molecule.

Fig. 2. Stereoscopic view of the packing.

atomic coordinates, bond distances and angles are given in Tables 1* and 2.

Of special interest in the molecule are the two heterocyclic five-membered rings containing Re(1), O(8), C(8), C(62), C(63) and Re(2), P(2), C(61), C(62), C(8) and the position of the P(C$_6$H$_5$)$_3$ ligand attached to Re(1). Apart from the angle O(8)—Re(1)—C(63), the bond angles between the so-called Re(1) ring

* Lists of structure factors, anisotropic thermal parameters and a complete list of bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42238 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U
Re(1)	7483 (1)	4348 (1)	729 (1)	40 (1)
Re(2)	9214 (1)	7363 (1)	21 (1)	43 (1)
P(1)	6966 (3)	5321 (4)	1682 (2)	42 (3)
P(2)	8043 (3)	7759 (4)	−826 (2)	44 (3)
C(1)	8181 (14)	3545 (17)	1328 (11)	49 (5)
O(1)	8647 (12)	2992 (14)	1667 (9)	79 (5)
C(2)	6567 (15)	3479 (18)	675 (11)	56 (6)
O(2)	5945 (10)	2940 (12)	620 (8)	62 (4)
C(3)	7893 (15)	3642 (18)	21 (12)	55 (6)
O(3)	8110 (12)	3168 (14)	−459 (9)	82 (5)
C(4)	9924 (15)	6941 (17)	786 (12)	53 (6)
O(4)	312 (11)	6636 (13)	1281 (9)	77 (5)
C(5)	8703 (15)	8406 (18)	584 (12)	59 (6)
O(5)	8434 (11)	8985 (14)	932 (9)	78 (5)
C(6)	35 (20)	8301 (23)	−300 (15)	85 (8)
O(6)	524 (15)	8849 (18)	−519 (11)	111 (7)
C(7)	9681 (16)	6277 (19)	−465 (13)	65 (7)
O(7)	9905 (12)	5622 (15)	−811 (10)	91 (5)
C(8)	8281 (14)	6269 (16)	240 (11)	48 (5)
O(8)	8413 (8)	5559 (10)	671 (6)	41 (3)
C(11)	6077 (8)	3758 (9)	2244 (7)	44 (5)
C(12)	5412 (8)	3322 (9)	2594 (7)	68 (7)
C(13)	4747 (8)	3907 (9)	2836 (7)	70 (7)
C(14)	4747 (8)	4928 (9)	2728 (7)	79 (8)
C(15)	5412 (8)	5363 (9)	2378 (7)	59 (6)
C(16)	6077 (8)	4778 (9)	2136 (7)	48 (5)
C(21)	8696 (9)	5483 (12)	2246 (6)	65 (6)
C(22)	9324 (9)	5706 (12)	2764 (6)	81 (8)
C(23)	9061 (9)	5989 (12)	3396 (6)	78 (8)
C(24)	8171 (9)	6048 (12)	3511 (6)	73 (7)
C(25)	7542 (9)	5825 (12)	2993 (6)	54 (6)
C(26)	7805 (9)	5542 (12)	2361 (6)	58 (6)
C(31)	5795 (9)	6582 (8)	1003 (7)	55 (6)
C(32)	5444 (9)	7500 (8)	810 (7)	60 (6)
C(33)	5828 (9)	8368 (8)	1070 (7)	60 (6)
C(34)	6563 (9)	8318 (8)	1522 (7)	60 (6)
C(35)	6913 (9)	7399 (8)	1715 (7)	59 (6)
C(36)	6530 (9)	6532 (8)	1455 (7)	43 (5)
C(41)	6651 (9)	9030 (9)	−500 (7)	87 (8)
C(42)	6307 (9)	9971 (9)	−396 (7)	85 (8)
C(43)	6818 (9)	809 (9)	−494 (7)	101 (10)
C(44)	7673 (9)	706 (9)	−695 (7)	101 (10)
C(45)	8016 (9)	9765 (9)	−799 (7)	82 (8)
C(46)	7505 (9)	8927 (9)	−701 (7)	43 (5)
C(51)	8948 (9)	7352 (12)	−1983 (7)	62 (6)
C(52)	9055 (9)	7373 (12)	−2675 (7)	88 (8)
C(53)	8423 (9)	7826 (12)	−3109 (7)	106 (10)
C(54)	7684 (9)	8257 (12)	−2852 (7)	80 (8)
C(55)	7577 (9)	8235 (12)	−2160 (7)	100 (10)
C(56)	8209 (9)	7783 (12)	−1725 (7)	55 (6)
C(61)	7253 (8)	6786 (8)	−685 (6)	52 (5)
C(62)	7462 (8)	6127 (8)	−159 (6)	34 (4)
C(63)	6897 (8)	5345 (8)	−35 (6)	43 (5)
C(64)	6123 (8)	5222 (8)	−438 (6)	49 (5)
C(65)	5915 (8)	5880 (8)	−965 (6)	56 (6)
C(66)	6480 (8)	6663 (8)	−1088 (6)	64 (6)
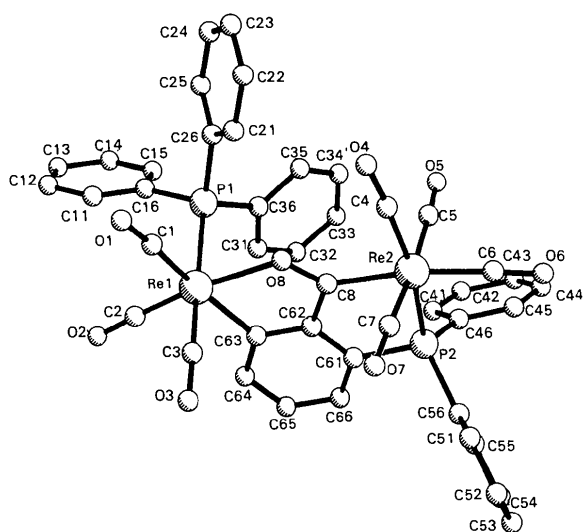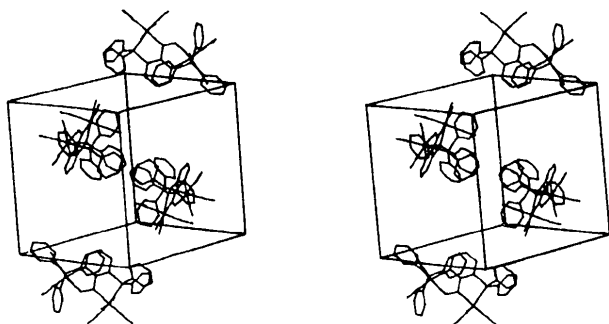
Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Re(1)—P(1)	2·474 (5)	C(1)—O(1)	1·208 (28)
—O(8)	2·173 (13)	C(2)—O(2)	1·196 (28)
—C(1)	1·889 (21)	C(3)—O(3)	1·211 (30)
—C(2)	1·823 (23)	C(4)—O(4)	1·189 (28)
—C(3)	1·841 (24)	C(5)—O(5)	1·137 (30)
—C(63)	2·179 (11)	C(6)—O(6)	1·155 (29)
		C(7)—O(7)	1·183 (32)
Re(2)—P(2)	2·437 (5)	C(8)—O(8)	1·293 (25)
—C(4)	1·899 (23)	C(8)—C(62)	1·451 (24)
—C(5)	1·988 (24)		
—C(6)	1·918 (31)	O(8)—Re(1)—C(63)	74·9 (4)
—C(7)	1·917 (25)	Re(1)—O(8)—C(8)	121·2 (12)
—C(8)	2·116 (22)	O(8)—C(8)—C(62)	110·9 (16)
		C(8)—C(62)—C(63)	121·6 (13)
P(1)—C(16)	1·828 (14)	C(62)—C(63)—Re(1)	111·0 (8)
—C(26)	1·826 (13)		
—C(36)	1·812 (12)	C(8)—Re(2)—P(2)	79·7 (6)
		Re(2)—P(2)—C(61)	101·6 (4)
P(2)—C(46)	1·803 (13)	P(2)—C(61)—C(62)	117·0 (9)
—C(56)	1·819 (14)	C(61)—C(62)—C(8)	118·3 (13)
—C(61)	1·817 (12)	C(62)—C(8)—Re(2)	123·2 (13)

and the analogous Re—O—C—C—C ring in [C₆H₅CO(o-C₆H₄)Re(CO)₃{P(C₆H₅)₃}] [C—Re—O 74·4 (4), Re—O—C 117·7 (9), O—C—C 119·1 (12), C—C—C 115·7 (10), C—C—Re 112·6 (7)°] (Preut & Haupt, 1980) are different. These variations of the internal bond angles at the non-metal ring atoms are connected with the change in substituent attached to the benzoylic C(8) atom, from Re(CO)₄ to a phenyl group. The Re(1) ring, like the corresponding ring of the above-mentioned metalation product of benzophenone, is planar. This ring property and the comparable bond lengths {[Re(C₁₃H₉O)(C₁₈H₁₅P)(CO)₃]: Re—O 2·174 (9), Re—C 2·199 (10), C—O 1·240 (17) and C—C 1·427 (17) Å} seem to be compatible with delocalized π electrons in such heterocyclic rings, as was suggested for an analogous Mn ring in [CH₃CO(o-C₆H₄)Mn(CO)₄] (Knobler, Crawford & Kaesz 1975).

The Re(1) ring of the title compound is one part of an extended planar tricyclic ring system that includes the bridging benzoyl ligand and the Re(1) and Re(2) atoms. This indicates that the Re(2) ring also has π-electron delocalization. The structural parameters of the Re(2) ring support this proposal. For example the Re(2)—P(2) bond shows a significant shortening compared with the Re(1)—P(1) bond. This may be ascribed to a stronger σ, π bond between the Re(2)—P(2) ring atoms.

The coordination around both Re atoms is distorted octahedral. Each of the three CO ligands at the Re(1) atom is *trans* to a different atom. Two of the four carbonyl ligands at the Re(2) atom are arranged *trans* to the ring atoms and the remaining two in apical positions. The two rhenium atoms are bridged by the quadridentate ligand, which is bidentate to each Re atom.

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

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Structure of Tetracarbonyl(phenanthroline)molybdenum(0), [Mo(CO)₄(C₁₂H₈N₂)], at 185 K

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Abstract. $M_r = 388 \cdot 2$, monoclinic, $C2/m$, $a = 15 \cdot 482$ (5), $b = 11 \cdot 980$ (3), $c = 8 \cdot 177$ (3) Å, $\beta = 106 \cdot 58$ (3)°, $V = 1453 \cdot 6$ Å³, $Z = 4$, $D_x = 1 \cdot 77$ Mg m⁻³, $\lambda(\text{Mo } K\bar{\alpha}) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 869$ mm⁻¹, $F(000) = 768$, $T = 185$ K. $R = 0 \cdot 0183$ for 923 unique observed reflections. The molecule possesses crystallographically imposed C_s symmetry, with the mirror plane bisecting the N—Mo—N angle. The geometry at Mo is distorted

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