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Unexpected Re_2P_2 Ring Deformation in Bis[μ-cyclohexyl(iodo)phosphido-κP]bis(tetracarbonylrhenium), $[Re_2(C_6H_{11}IP)_2(CO)_8]$

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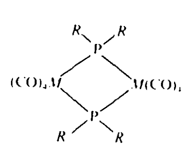
Abstract

The central molecular fragment is a four-membered Re_2P_2 ring, which, in contrast to M_2P_2 rings of related structures, deviates considerably from planarity with a dihedral angle of 15.2°. The cyclohexyl and iodo ligands at the bridging P atoms are in *syn* positions.

Comment

Among the doubly phosphine-bridged binuclear metal carbonyl complexes with an M_2P_2 ring as the common central molecular fragment, the manganese and rhenium compounds have been subject to several investigations. Single-crystal X-ray structure determinations are known for the *R*-substituted compounds $[(CO)_8M_2(\mu\text{-}PR_2)_2]$, with *M* = Mn and *R* = H [(1); Deppisch, Schäfer, Binder & Leske, 1984], *R* = methyl (Me) [(2); Vahrenkamp, 1978], *R* = phenyl (Ph) [(3); Masuda, Taga, Machida & Kawamura, 1987], *R* = cyclohexyl (Cy) [(4); Flörke & Haupt, 1993*a*,*b*], and *M* = Re and *R* = Ph [(5); Flörke, Woyciechowski & Haupt, 1988]. The structures with two different ligands *R* and *R'* are $(CO)_8M_2(\mu\text{-}PRR')_2$, with *M* = Mn and *RR'* = HPh [(6); Brown *et al.*, 1991; Flörke & Haupt, 1993*a*], *RR'* = PhCOMe [(7); Brown *et al.*, 1991], *RR'* = HCy [(8); Flörke & Haupt, 1993*b*] and *M* = Re and *RR'* = MePh [(9); Flörke & Haupt, 1993*c*], *RR'* = EtPh [(10); Flörke & Haupt, 1993*c*], *RR'* = HC [(11); Flörke & Haupt, unpublished], *RR'* = IPh [(12); Flörke & Haupt, 1993*d*], *RR'* = ClPh [(13); Flörke & Haupt, 1993*e*], and *R* = Ph, *R'* = $C_2H_4C_5NH_4$ [(14); Flörke, Haupt & Seshadri, 1993]. A heteronuclear complex with both metals is $[(CO)_8MnRe(\mu\text{-}PHCy)_2]$ [(15); Flörke & Haupt, unpublished].



For the molecules with two different ligands at the P atom, both *syn* and *anti* arrangements of *R* and *R'* are possible, but the *syn* arrangement has been crystallized only for (13) and (15). In the crystals, the geometric centres of all these molecules lie either on special sites, $\bar{1}$ or $2/m$, which force the M_2P_2 rings to be planar, or on general sites. The latter is valid for the *anti* structure (7), the two *syn* structures (13) and (15) and both the diphenylmanganese and rhenium complexes (3) and (5). In these five structures, the M_2P_2 ring deviates slightly from planarity, with dihedral angles ranging from 3.2° for (15) to 4.6° for (5) and (7). Other common structural features for the compounds are the endocyclic *M*—P—*M* ring angles (and the corresponding P—*M*—P angles), which are in the narrow range 101.0 (1)–104.6 (1)° [75.4 (1)–79.0 (1)° for P—*M*—P] and are obviously independent of the metal or *R* ligand (Deppisch *et al.*, 1984). The *M*—P bond distances, on the other hand, reflect the nature of the *R* groups, which has been discussed previously (Flörke & Haupt, 1993*b*).

The title compound is another representative of these phosphine-bridged binuclear metal complexes. The geometric centre lies on a crystallographic twofold axis, which is perpendicular to the ring. Each Re atom reaches distorted octahedral coordination *via* two P atoms and four carbonyl ligands. The axial CO groups possess an almost ecliptic arrangement at both metal centres, tilted only 1.6° on average around the Re···Re vector. The Re—P bond length is 2.485 (2) Å and the mean axial Re—C bonds [average 2.001 (10) Å] tend to be longer than the mean equatorial Re—C bonds [average 1.950 (10) Å], which is a well known effect (Brown *et al.*, 1991). The bond lengths from the P atom to the ligands are 1.864 (10) (P—Cy) and 2.478 (3) Å (P—I). The *R*—P—*R'* angle [102.0 (3)°] is significantly larger than the corresponding angles of most of the other complexes, which have values between 96.5 and 99.1°. This is due to the rather voluminous *R* ligands and it is not surprising that for complex (4), with the most sterically demanding dicyclohexyl group, this Cy—P—Cy angle is increased to 107.3°. The endocyclic ring angles P—Re—P [74.0 (1)°] and Re—P—Re [104.7 (1)°], and the non-bonding Re···Re distance (3.943 Å) correspond well with those for other $[(CO)_8M_2(\mu\text{-}PRR')_2]$ structures. However, the ring shows an unexpectedly large deviation from planarity with a dihedral angle of 15.2°, which may be regarded as a folding of the two ReP_2 halves along the P···P vector. This is accompanied by a large increase in the non-bonding distances of the axial carbonyl ligands on the cyclohexyl side on the one hand (O···O 4.911 Å) and a decrease on the side of the iodo ligands on the other (C···C 3.312, O···O 2.971 Å). Other intramolecular non-bonding contacts, which are also approximately equal to the sum of the corresponding van der Waals radii, are axial-OC···I 3.76, I···H—Cy 3.26 and axial-OC···H—Cy 2.74 Å. An *R*—P—*R'*

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angle of 98° (average value from the other structures) would produce a short I···H—Cy distance (3.09 Å), but the actual angle of 102.0° produces close contacts between the Cy ligand and the carbonyl groups. These OC···H—Cy contacts would then become less than 2.3 Å for a planar Re_2P_2 ring, as was calculated from a planar model. However, the carbonyl groups are able to reduce the repulsion through the folding of the Re_2P_2 ring. For comparison, the most interesting intermolecular distances are axial-CO···H—Cy > 3.7, axial-OC···H—Cy > 3.5 and I···H—Cy > 3.3 Å.

The large deviation from planarity of the ring is thus mainly due to intramolecular repulsion forces rather than packing forces. For the other M_2P_2 complexes, this large folding is either less necessary because of less sterically demanding ligands R and R', or, with equal R groups on both sides of the ring, hardly possible.

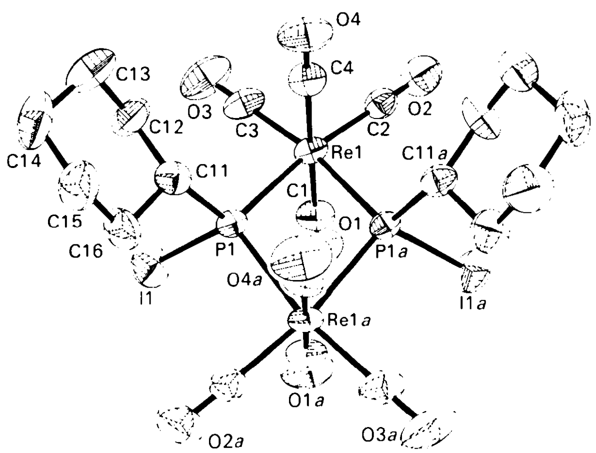

Fig. 1. Molecular structure of the title compound with H atoms omitted.

Experimental

The title compound was obtained from the reaction between $[Re_2(CO)_8(\mu\text{-}PHCy)_2]$ and CI_4 in trichloromethane solution at 293 K.

Crystal data

$[Re_2(C_6H_{11}IP)_2(CO)_8]$
M_r = 1078.5
Monoclinic
$C2/c$
a = 22.156 (6) Å
b = 8.979 (2) Å
c = 15.897 (3) Å
β = 112.52 (2)°
V = 2921.4 (12) Å^3
Z = 4

D_x = 2.4522 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 33 reflections
θ = 6.5-19°
μ = 10.63 mm^{-1}
T = 293 K
Plate
0.62 × 0.56 × 0.11 mm
Yellow

Data collection

Siemens *R3m/V* diffractometer
ω-2θ scans
Absorption correction: empirical, ψ-scans, lamina correction
T_{min} = 0.09, T_{max} = 0.54
3190 measured reflections
3074 independent reflections
2507 observed reflections [$F > 4\sigma(F)$]

R_{int} = 0.028
θ_{max} = 27.5°
h = −28 → 28
k = 0 → 11
l = 0 → 20
3 standard reflections monitored every 400 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.045
wR = 0.041
S = 1.868
2507 reflections
154 parameters
H-atom parameters not refined

Calculated weights $w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.2 e Å^{-3}
$\Delta\rho_{min}$ = −1.3 e Å^{-3}
Atomic scattering factors from *SHELXTL-Plus*88 (Sheldrick, 1988)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Re1	0.4959 (1)	0.2132 (1)	0.1242 (1)	0.034 (1)
I1	0.3394 (1)	0.0521 (1)	0.1719 (1)	0.066 (1)
P1	0.4270 (1)	0.2425 (2)	0.2151 (2)	0.035 (1)
C1	0.4992 (6)	−0.0088 (11)	0.1454 (7)	0.051 (5)
O1	0.5007 (6)	−0.1309 (8)	0.1570 (7)	0.070 (5)
C2	0.5627 (6)	0.1936 (11)	0.0734 (6)	0.045 (5)
O2	0.6023 (5)	0.1863 (10)	0.0439 (6)	0.078 (5)
C3	0.4229 (7)	0.1899 (11)	0.0072 (7)	0.051 (5)
O3	0.3790 (6)	0.1775 (10)	−0.0620 (6)	0.077 (6)
C4	0.4943 (6)	0.4318 (11)	0.1054 (7)	0.047 (5)
O4	0.4933 (5)	0.5557 (7)	0.0922 (6)	0.063 (5)
C11	0.3794 (5)	0.4194 (10)	0.1923 (6)	0.043 (5)
C12	0.3341 (6)	0.4433 (12)	0.0923 (7)	0.059 (6)
C13	0.3069 (8)	0.6010 (13)	0.0794 (9)	0.068 (7)
C14	0.2700 (6)	0.6281 (14)	0.1439 (10)	0.068 (6)
C15	0.3148 (7)	0.6036 (14)	0.2421 (9)	0.069 (6)
C16	0.3424 (6)	0.4446 (12)	0.2556 (9)	0.067 (6)

Table 2. *Selected geometric parameters* (Å, °)

Re1—P1	2.485 (2)	I1—P1	2.478 (3)
Re1—P1a	2.485 (2)		
P1—Re1—P1a	74.0 (1)	Re1—P1—C11	113.9 (3)
Re1—P1—Re1a	104.7 (1)	Re1a—P1—C11	113.9 (3)
Re1—P1—I1	110.9 (1)	I1—P1—C11	102.0 (3)

H-atom parameters were fixed at idealized positions with U_{iso} = 0.08 Å^2. All calculations and structure solution and refinement: *SHELXTL-Plus*88 (Sheldrick 1988). Other programs: *PARST* (Nardelli, 1983), *MISSYM* (Le Page, 1987).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71647 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1036]

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Bis(1,10-phenanthroline)copper(II)-μ-cyano-cyano(1,10-phenanthroline)copper(I) Thiocyanate Dihydrate

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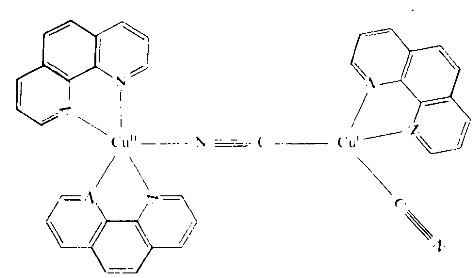
Abstract

By reaction of $Cu(NO_3)_2$, NH_4OH, phen (1,10-phenanthroline), KSCN and KCN in the molar ratio 1:40:2:1:1 in a water–ethanol solution a new mixed-valence complex, μ-cyano-1κN:2κC-cyano-2κN-tris(1,10-phenanthroline)-1$\kappa^4 N,N'$;2$\kappa^2 N,N'$-dicopper-(I,II) thiocyanate dihydrate, $[Cu_2(phen)_3(CN)_2]$-$(SCN).2H_2O$, was prepared. The $[Cu^{II}(phen)_2]^{2+}$ and $[Cu^I(phen)CN]$ moieties are bridged by a CN^- ion giving rise to a binuclear cation with deformed trigonal-bipyramidal and deformed tetrahedral coordination for the divalent and univalent Cu atoms, respectively. SCN^- anions do not enter the inner coordination sphere of the Cu atoms. Uncoordinated H_2O molecules are held together by hydrogen bonds forming a four-membered ring. Two SCN^- anions are bonded, also by hydrogen bonds, to this ring forming a central $[SCN—4(H_2O)—NCS]^{2-}$ grouping. The latter is further attached by two other HOH···NC hydrogen bonds to the binuclear cations forming a centrosymmetric adduct of composition $\{[Cu_2(phen)_3(CN)_2](NCS)(H_2O)_2\}_2$. These adducts are packed by van der Waals forces in the crystal structure.

Comment

As a part of our studies of the synthesis, crystallochemistry and properties of mixed-valence Cu compounds with pseudohalogenide anions, the title compound (I) was prepared by mixing $Cu(NO_3)_2$, NH_4OH, phen (1,10-phenanthroline), KSCN and KCN in the molar ratio 1:40:2:1:1 in a water–ethanol solution. After slow crystallization (for several months) dark green crystals appeared. Details of preparation, identification and properties will be published elsewhere (Dunaj-Jurčo, 1993).



(I)

The crystal structure is formed by discrete binuclear $[Cu^{II}Cu^I(phen)_3(CN)_2]^+$ cations, SCN^- anions and uncoordinated H_2O molecules. These moieties, which associate *via* hydrogen bonds, give a centrosymmetric adduct of composition $\{[Cu_2(phen)_3(CN)_2](NCS).(H_2O)_2\}_2$. Fig. 1 shows one formula unit along with the atomic labelling scheme. The Cu^{II} atom is coordinated by two phen molecules, while the Cu^I atom binds one phen molecule and one terminal CN^- group through the C atom. Coordination geometries around the Cu^{II} and Cu^I atoms are completed to form approximately trigonal-bipyramidal and tetrahedral polyhedra, respectively,