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The first example of a bromo- and phosphido-bridged binuclear rhenium carbonyl complex

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Key indicators

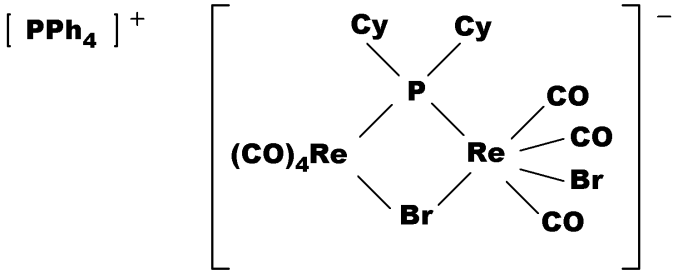
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.037
wR factor = 0.076
Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The ionic crystals of the title complex, tetraphenylphosphonium μ-bromo-bromoheptacarbonyl-μ-dicyclohexylphosphido-dirhenate, $(C_{24}H_{20}P)[Re_2Br_2(C_{12}H_{22}P)(CO)_7]$, are built of tetraphenylphosphonium cations and $(\mu\text{-Br})(\mu\text{-PCy}_2)(CO)_7BrRe_2^-$ anions. The latter is the first example of a bromo- and phosphido-bridged binuclear rhenium carbonyl complex. The Re—Br bond lengths are 2.6786 (7) and 2.6482 (7) Å for the bridging Br atom, and 2.6146 (8) Å for the terminal Br ligand. The Re···Re distance of 3.930 Å is clearly non-bonding which is not unexpected for the 36 valence-electron complex anion.

Comment

The title complex, (I), was synthesized in the course of optimizing reaction paths to the neutral carbonyl complex $(\mu\text{-Br})(\mu\text{-PCy}_2)(CO)_8Re_2$ (Haupt *et al.*, 1994).



(I)

The central fragment of the anion (Fig. 1) is the four-membered $Re_2(\mu\text{-Br})(\mu\text{-P})$ ring which is nearly planar; the maximum deviation from the best plane is 0.061 (2) Å for the P1 atom. Each Re atom is hexacoordinated (three carbonyl groups and one terminal Br ligand at Re1, four terminal carbonyl groups at Re2, and bridging P1 and Br2 at both metal atoms). The resulting octahedral coordination spheres are only slightly distorted and the terminal ligands attached to both Re atoms show an eclipsed arrangement along the Re···Re vector with pseudo-torsion angles L—Re···Re—L', involving pairs of eclipsed ligands L and L', ranging from 0.7 to 4.3°. The phosphido bridge is symmetric with Re—P1 distances of 2.5214 (15) and 2.5381 (14) Å, whereas the two Re—μ-Br2 bond lengths of 2.6482 (7) and 2.6786 (7) Å differ by about 0.030 Å. Other Re compounds with bromo bridges show Re—μ-Br bond lengths varying from 2.515 to 2.679 Å (Filippou *et al.*, 1996; Calderazzo *et al.*, 1978; Atwood *et al.*, 1978). The distance of 2.6146 (8) Å from Re1 to the terminal

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Br1 ligand is somewhat elongated compared to the distance of 2.590 (3) Å in (μ-PCy$_2$)(CO)$_8$BrRe$_2$ (Haupt *et al.*, 1994).

Experimental

(μ-PCy$_2$)(CO)$_8$BrRe$_2$ was refluxed in tetrahydrofuran for 3 h with PPh$_4$Br (molar ratio 1:1). After removal of the solvent *in vacuo*, the residue was recrystallized from CHCl$_3$/pentane to give yellow prismatic crystals of the title compound. A full description of the synthesis is given elsewhere (Petters, 1999).

Crystal data

$(C_{24}H_{20}P)[Re_2Br_2(C_{12}H_{22}P)(CO)_7]$	D_x = 1.883 Mg m^{-3}
M_r = 1264.93	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 24 reflections
a = 18.795 (2) Å	θ = 11.8–14.5°
b = 13.320 (1) Å	μ = 7.33 mm^{-1}
c = 19.579 (2) Å	T = 293 (2) K
β = 114.42 (1)°	Prism, yellow
V = 4463.1 (7) Å^3	0.30 × 0.25 × 0.15 mm
Z = 4	

Data collection

Nonius MACH3 diffractometer	R_{int} = 0.052
ω–2θ scans	θ_{max} = 26.0°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -23 \rightarrow 21$
T_{min} = 0.385, T_{max} = 0.997	$k = -16 \rightarrow 15$
17 450 measured reflections	$l = 0 \rightarrow 24$
8736 independent reflections	3 standard reflections frequency: 60 min
5813 reflections with $I > 2\sigma(I)$	intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$(\Delta/\sigma)_{max}$ = 0.002
$wR(F^2)$ = 0.076	$\Delta\rho_{max}$ = 0.93 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −0.67 e Å^{-3}
8736 reflections	Extinction correction: *SHELXL*97
506 parameters	Extinction coefficient: 0.00045 (4)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Re1—P1	2.5214 (15)	Re2—P1	2.5381 (14)
Re1—Br1	2.6146 (8)	Re2—Br2	2.6482 (7)
Re1—Br2	2.6786 (7)		
C3—Re1—Br1	92.5 (2)	Br1—Re1—Br2	86.73 (2)
C2—Re1—Br1	89.8 (2)	P1—Re2—Br2	81.42 (4)
C1—Re1—Br1	177.9 (2)	Re2—Br2—Re1	95.07 (2)
P1—Re1—Br1	87.67 (4)	Re1—P1—Re2	101.92 (5)
P1—Re1—Br2	81.13 (4)		

H atoms were included in the refinement in the riding model approximation with isotropic displacement parameters U(H) = 1.2U_{eq}(C). Substantial anisotropic displacement parameters of cyclohexyl C atoms C21–C26 indicate some degree of (orientational) disorder which was impossible to resolve. Therefore, the geometric parameters for this cyclohexyl group are less reliable. Cyclohexyl groups C11–C16 and C21–C26 were refined using *SHELXTL SAME* restraints (Bruker, 1998), phenyl groups C31–C36, C41–C46, C51–C56 and C61–C66 were restrained with both *FLAT* and *SAME* instructions.

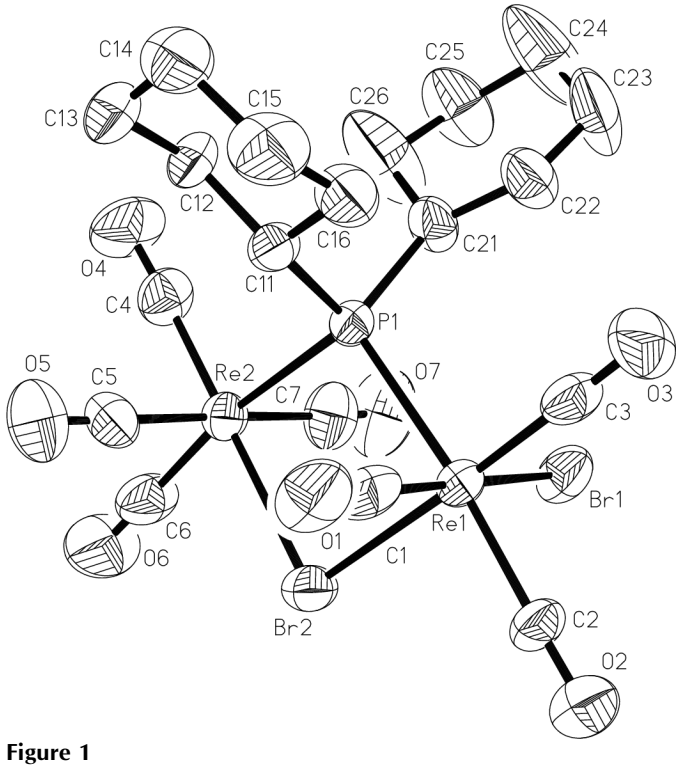

Figure 1
The structure of the title anion showing 50% probability ellipsoids. The H atoms have been omitted for clarity.

Data collection: *MACH3/PC* (Nonius, 1989); cell refinement: *MACH3/PC* (Nonius, 1989); data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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