Crystal structures and Hirshfeld surface analysis of [κ²-P,N-{(C₆H₅)₂(C₅H₅N)P}Re(CO)₃Br]·2CHCl₃ and the product of its reaction with piperidine, [P-{(C₆H₅)₂(C₅H₅N)P}(C₅H₁₁N)Re(CO)₃Br]

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The coordination of the ligands with respect to the central atom in the complex bromidotricarbonyl[diphenyl(pyridin-2-yl)phosphane-κ²N,P]rhenium(I) chloroform disolvate, [ReBr(C₁₇H₁₄NP)(CO)₃]·2CHCl₃ or [κ²-P,N-{(C₆H₅)₂(C₅H₅N)P}Re(CO)₃Br]·2CHCl₃, (**I**·2CHCl₃), is best described as a distorted octahedron with three carbonyls in a facial conformation, a bromide atom, and a biting P,N-diphenylpyridylphosphine ligand. Hirshfeld surface analysis shows that C—Cl···H interactions contribute 26%, the distance of these interactions are between 2.895 and 3.213 Å. The reaction between **I** and piperidine (C₅H₁₁N) at 313 K in dichloromethane leads to the partial decoordination of the pyridylphosphine ligand, whose pyridyl group is replaced by a piperidine molecule, and the complex bromidotricarbonyl[diphenyl-(pyridin-2-yl)phosphane-κP](piperidine-κN)rhenium(I), [ReBr(C₅H₁₁N)-(C₁₇H₁₄NP)(CO)₃] or [P-{(C₆H₅)₂(C₅H₅N)P}(C₅H₁₁N)Re(CO)₃Br] (**II**). The molecule has an intramolecular N—H···N hydrogen bond between the non-coordinated pyridyl nitrogen atom and the amine hydrogen atom from piperidine with D···A = 2.992 (9) Å. Thermogravimetry shows that **I**·2CHCl₃ losses 28% of its mass in a narrow range between 318 and 333 K, which is completely consistent with two solvating chloroform molecules very weakly bonded to **I**. The remaining **I** is stable at least to 573 K. In contrast, **II** seems to lose solvent and piperidine (12% of mass) between 427 and 463 K, while the additional 33% loss from this last temperature to 573 K corresponds to the release of 2-pyridylphosphine. The contribution to the scattering from highly disordered solvent molecules in **II** was removed with the SQUEEZE routine [Spek (2015). Acta Cryst. C71, 9-18] in PLATON. The stated crystal data for M_r, μ etc. do not take this solvent into account.
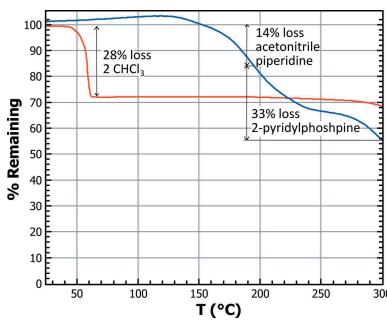
1. Chemical context

Phosphine-type ligands having a second type of atom or coordinating function have been of great interest in many areas of chemistry. The existence of a second coordination atom with different properties, coordination capability or *trans* effect adds possibilities during a catalytic cycle (Guiry & Saunders, 2004). In particular, much attention has been paid to one of the simplest molecules of this kind, diphenylpyridyl-phosphine P(C₆H₅)₂(C₅H₅N) (PPh₂Py). The molecule is a rigid bidentate ligand (Abram *et al.*, 1999; Knebel & Angelici, 1973).

The reaction of the diphenylpyridylphosphine ligand with the rhenium dimer (Re(CO)₃(OC₄H₈)Br)₂ in chloroform as

solvent leads to the complex P,N-{$(C_6H_5)_2(C_5H_5N)P$}Re-$(CO)_3Br$]·2CHCl$_3$ (I·2CHCl$_3$). It presents a similar structure to the widely studied [(N,N)Re(CO)$_3(L)$] complexes, which have interesting photophysical and photochemical properties (Cannizzo et al., 2008). Complex **I** has been shown to be a dual emitter (Pizarro et al., 2015). It is also interesting to note that the PPh$_2$Py ligand can be partially decoordinated by reaction of the complex with a monodentate ligand, like piperidine ($C_5H_{11}N$), leading to the complex [P-{$(C_6H_5)_2(C_5H_5N)P$}-$(C_5H_{11}N)$Re(CO)$_3Br$] (**II**).

Table 1
Selected geometric parameters (Å, °) for **I**·2CHCl$_3$.

Re1—C2	1.892 (6)	Re1—N1	2.173 (4)
Re1—C1	1.914 (5)	Re1—P1	2.4687 (13)
Re1—C3	1.943 (5)	Re1—Br1	2.6066 (8)
C2—Re1—C1	90.2 (2)	C3—Re1—P1	163.62 (15)
C2—Re1—C3	88.3 (2)	N1—Re1—P1	65.39 (9)
C1—Re1—C3	93.39 (19)	C2—Re1—Br1	176.20 (14)
C2—Re1—N1	93.39 (17)	C1—Re1—Br1	92.84 (14)
C1—Re1—N1	167.89 (15)	C3—Re1—Br1	89.22 (15)
C3—Re1—N1	98.27 (17)	N1—Re1—Br1	84.11 (10)
C2—Re1—P1	93.56 (13)	P1—Re1—Br1	88.01 (3)
C1—Re1—P1	102.86 (12)		

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

Re1—C1	1.870 (8)	Re1—N2	2.246 (6)
Re1—C2	1.918 (7)	Re1—P1	2.4915 (18)
Re1—C3	1.932 (8)	Re1—Br1	2.6430 (9)
C1—Re1—C2	90.1 (3)	C3—Re1—P1	89.0 (2)
C1—Re1—C3	89.4 (3)	N2—Re1—P1	93.28 (16)
C2—Re1—C3	88.0 (3)	C1—Re1—Br1	175.3 (2)
C1—Re1—N2	92.3 (3)	C2—Re1—Br1	92.1 (2)
C2—Re1—N2	89.6 (3)	C3—Re1—Br1	94.9 (2)
C3—Re1—N2	177.1 (3)	N2—Re1—Br1	83.53 (17)
C1—Re1—P1	91.6 (2)	P1—Re1—Br1	86.44 (5)
C2—Re1—P1	176.6 (2)		

2. Structural commentary

The mononuclear Re^I complex **I** with a bidentate P,N (chelating) ligand crystallized from a chloroform solution in the monoclinic space $P2_1/c$. Selected geometrical data are summarized in Table 1, and the molecular structure of complex **I**·2CHCl$_3$ is given in Fig. 1. The coordination environment of the central rhenium atom is defined for phosphorus

and nitrogen atoms from PPh$_2$Py, a bromide atom in an apical position and three carbonyl carbon atoms in a *fac* correlation, generating a distorted octahedral environment. Additionally, two chloroform molecules crystallize together with the complex molecule.

The mononuclear Re^I complex **II**, crystallized from a CH$_2$Cl$_2$/CH$_3$CN (2:1) solution in the triclinic space group $P\bar{1}$. Selected geometrical data are given in Table 2, and the molecular structure of the complex is illustrated in Fig. 2. The

Figure 1
Molecular view of complex **I**·2CHCl$_3$, showing the numbering scheme. Displacement ellipsoids are shown at the 33% probability level. For clarity, the C-bound H atoms of **I** have been omitted.
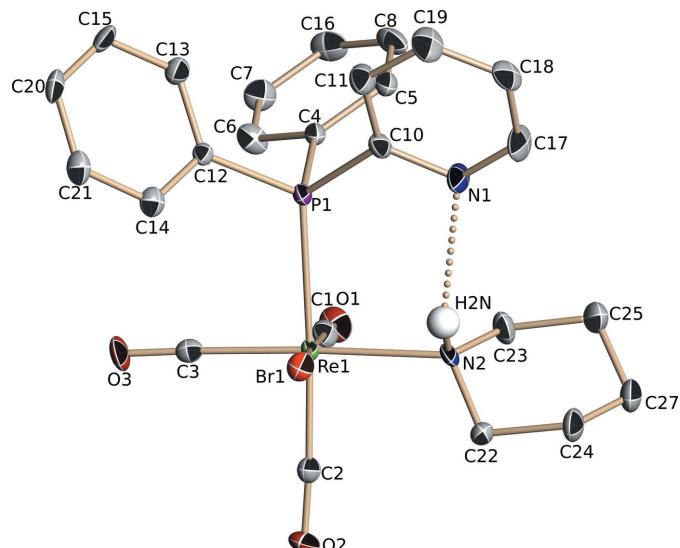

Figure 2
Molecular view of complex **II** showing the numbering scheme. Displacement ellipsoids are shown at the 33% probability level. For clarity, the C-bound H atoms have been omitted.

Table 3
Hydrogen-bond geometry (Å, °) for **I**·2CHCl$_3$.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C21—H21···Br1^i	0.98	2.66	3.490 (5)	143
C4—H4···Br1^{ii}	0.93	2.80	3.552 (5)	139

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z$.

Table 4
Hydrogen-bond geometry (Å, °) for **II**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N···N1	0.82	2.34	2.992 (9)	138
C14—H14···Br1	0.93	2.78	3.586 (8)	146
C22—H22B···Br1	0.97	2.83	3.499 (7)	127

central rhenium atom displays a non-regular octahedral coordination geometry, with three facial carbonyl groups, a monodentate PPh$_2$Py ligand, a piperidine C$_5$H$_{11}$N molecule and a bromide anion. The piperidine ring displays a chair-like conformation. An intramolecular hydrogen bond is defined between the non-coordinated pyridyl nitrogen atom and the amine hydrogen atom from piperidine, N2—H2N···N1, with $D\cdots A$ = 2.992 (9) Å (Table 4). There are also two C—H···Br intramolecular contacts present involving atom Br1 and a phenyl H atom (H14) and a methylene H atom (H22B) of the pypridine ring (Table 4).

3. Supramolecular features

In the crystal of **I**·2CHCl$_3$, the lattice has two solvating molecules of chloroform per complex molecule. The cell has a larger volume than for the unsolvated one [2836.7 (15) vs 2119.2 (3) Å^3 (Venegas $et~al.$, 2011)] whose geometrical parameters are very similar to those of complex **I**. In the crystal, the chloroform solvent molecules are involved in weak C—H···Br hydrogen bonds and they link the complex molecules to form layers lying parallel to the bc plane (Fig. 3 and Table 3).

In the crystal of **II**, a region of highly disordered electron density was equated to the present of a disordered acetonitrile molecule. The contribution to the scattering was removed with the SQUEEZE routine in $PLATON$ (Spek, 2015). A view of the crystal packing, showing the regions, or voids, occupied by this disordered solvent in given in Fig. 4.
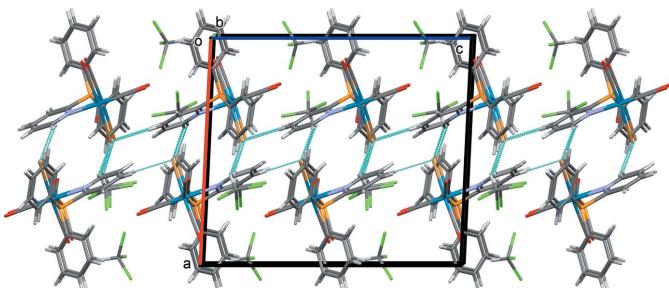

Figure 3
A view along the b axis of the crystal packing of complex **I**·2CHCl$_3$. The hydrogen bonds are shown as dashed lines (see Table 3).
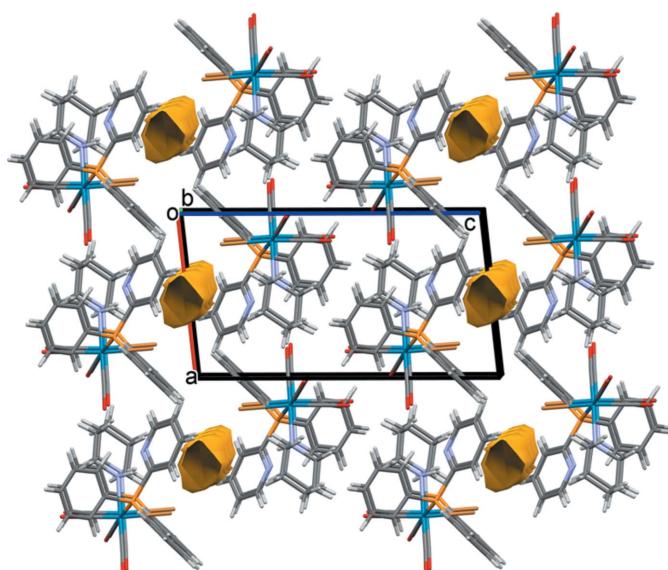
Figure 4
A view along the b axis of the crystal packing of complex **II**. The voids occupied by the disordered solvent molecules are shown in yellow–brown (calculated using $Mercury$; Macrae $et~al.$, 2008).

4. Hirshfeld surface analysis of complex I·2CHCl$_3$

In order to visualize and quantify the intermolecular interactions in the crystal packing of complex **I**·2CHCl$_3$, in particular those involving the chloroform solvent molecules, an Hirshfeld surface analysis was performed and two-dimensional fingerprint plots generated. The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon $et~al.$, 2007) were performed with $CrystalExplorer17$ (Turner $et~al.$, 2017). The Hirshfeld surface mapped over $d_{norm} = d_e + d_i$, is given in Fig. 5a (d_e represents the distance from the surface to the nearest nucleus external to the surface, and d_i is the distance from the surface to the nearest nucleus internal to the surface). In this d_{norm} view (Fig. 5a), blue represents the longest distances while the shortest distances are depicted as red spots (Dalal $et~al.$, 2015).

The two-dimensional fingerprint plot for the whole complex is given in Fig. 5b. Apart from the H···H intermolecular
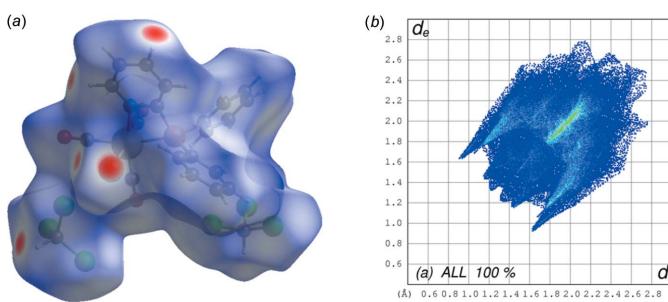
Figure 5
(a) The Hirshfeld surface of complex **I**·2CHCl$_3$, mapped over d_{norm} in the range -0.2767 to $+1.3337$ arbitrary units. (b) The two-dimensional fingerprint plot of complex **I**·2CHCl$_3$.
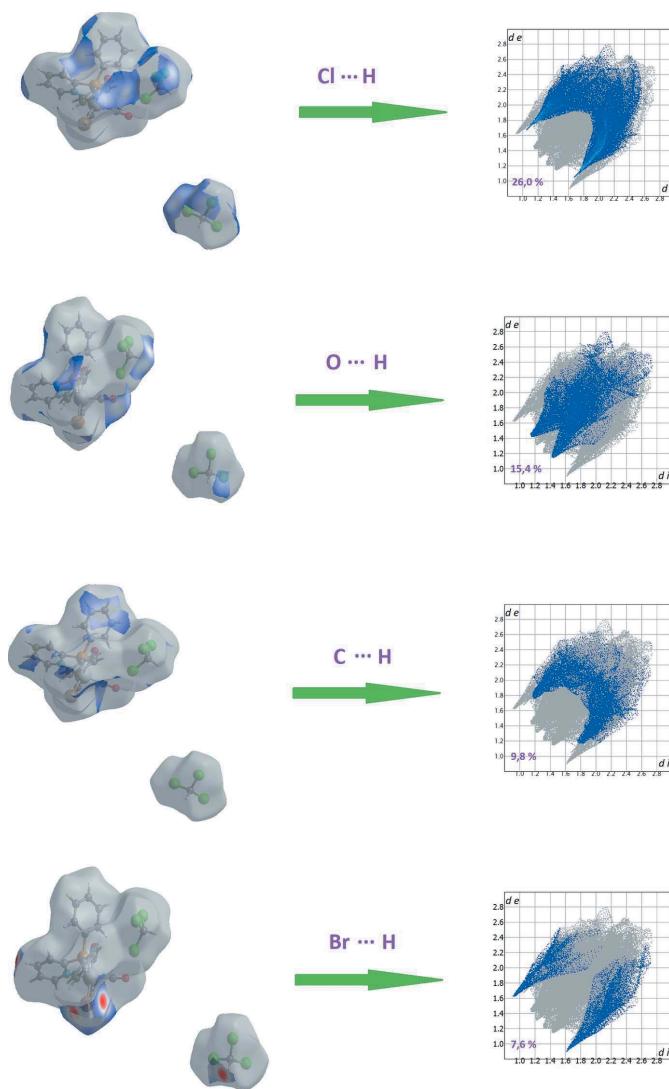
Figure 6
Two-dimensional fingerprint plots with a d_{norm} view of the Cl$\cdots$H/H$\cdots$Cl (26.0%), O$\cdots$H/H$\cdots$O (15.4%), C$\cdots$H/H$\cdots$C (9.8%) and Br$\cdots$H/H$\cdots$Br (7.6%) contacts in the coordination complex I·2CHCl$_3$.

contacts that contribute *ca* 15% the other most relevant intermolecular interactions, as determined from the Hirshfeld surface analysis of complex I·2CHCl$_3$, are shown in Fig. 6. The Cl$\cdots$H/H$\cdots$Cl, O$\cdots$H/H$\cdots$O and C$\cdots$H/H$\cdots$C interactions contribute 26.0, 15.4 and 9.8%, respectively, to the Hirshfeld surface. Some distances for these interactions are Cl1$\cdots$H19 = 2.90 Å, H22$\cdots$O2 = 2.69 Å and H21$\cdots$Br1 = 2.66 Å.

5. Thermogravimetric analysis

Thermogravimetric analyses from 25 to 300°C were performed for both compounds under an N$_2$ flux at a heating rate of 1°C min^{-1} (see Fig. 7). Thermogravimetric analysis for compound I·2CHCl$_3$ (Fig. 7, red line), shows that it loses 28% of its mass in a narrow range, between 45 and 60°C. This mass loss is completely consistent with the two solvating chloroform molecules detected by the crystal structure analysis. The boiling point of chloroform, 61°C, is almost identical to the

temperature where the mass loss stops, suggesting that the chloroform molecules are weakly bonded to the rhenium ones in the solid. From 60 to 300°C the remaining matrix is completely stable.

Compound II loses 12% of its initial mass between 154 and 190°C (Fig. 7, blue line). This loss of mass can be associated with the release of the acetonitrile and piperidine molecules (14.7%). The relatively high temperature at which decomposition begins compared to the piperidine boiling point, 105°C, suggest that it is strongly bonded to II. From 190 to 300°C, another 33% of mass loss is registered, which can be associated with the release of the PPh$_2$Py (36.6%, b.p.163°C).

6. Database survey

The diphenylpyridylphosphine ligand has been extensively studied and used as a monodentate and bidentate ligand with different metals, including Ru^{II} (Ooyama & Sato, 2004) where the CO$_2$-reducing properties of the complex were studied. Another Ru^{II} complex with PPh$_2$Py (Kumar *et al.*, 2011) has been studied as an inhibitor of DNA-topoisomerases of the filarial parasite *S. cervi*. Re^I–nitrosil complexes with PPh$_2$Py have been studied structurally and photophysically (Machura & Kruszynski, 2006).

Piperidine is a ligand that has been widely used with various transition metals. It has been used as a ligand with tungsten and molybdenum to study the *cis–trans* effect by using larger ligands and increasing the steric hindrance (Darensbourg *et al.*, 2007).

7. Synthesis and crystallization

The reagents, (Re(CO)$_3$(OC$_4$H$_8$)Br)$_2$ and (C$_6$H$_5$)$_2$(C$_5$H$_5$N)P were used as provided from supplier (Aldrich), with no purification before use. Seccosolv^{TM} solvents were used without
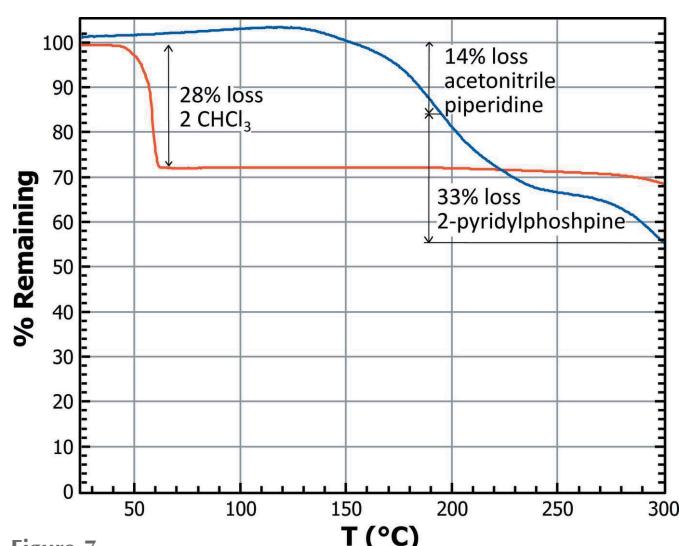

Figure 7
Weight loss for I·2CHCl$_3$ (red line) and II (blue line) between room temperature and 300°C.

Table 5
Experimental details.

	I·2CHCl₃	II
Crystal data		
Chemical formula	[ReBr(C$_{17}$H$_{14}$NP)(CO)$_3$]·2CHCl$_3$	[ReBr(C$_5$H$_{11}$N)(C$_{17}$H$_{14}$NP)(CO)$_3$]
M_r	852.14	698.55
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	150	150
a, b, c (Å)	14.194 (4), 12.314 (4), 16.249 (5)	9.1384 (17), 9.8348 (18), 15.671 (3)
α, β, γ (°)	90, 92.701 (4), 90	82.956 (2), 82.047 (2), 69.765 (2)
V (Å^3)	2836.7 (15)	1304.5 (4)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	6.34	6.28
Crystal size (mm)	0.16 × 0.13 × 0.05	0.07 × 0.04 × 0.03
Data collection		
Diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)	Numerical (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.386, 0.746	0.560, 0.858
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19979, 5550, 4526	10214, 5113, 4493
R_{int}	0.048	0.042
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.617
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.065, 0.99	0.042, 0.082, 1.11
No. of reflections	5550	5113
No. of parameters	317	303
No. of restraints	0	1
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.39, −0.35	1.96, −1.79

Computer programs: *SMART* and *SAINT* (Bruker, 2012), *SHELXS* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

any further purification. Standard Schlenck techniques under argon atmosphere were used for all manipulations.

Synthesis of I. 500 mg of (Re(CO)$_3$(OC$_4$H$_8$)Br)$_2$ (0.590 mmol) were dissolved in 5 ml of chloroform. 312 mg of diphenyl-2-pyridylphosphine (1.18 mmol) was dissolved in 10 ml of chloroform. The two solutions were mixed, changing from colourless to a translucent yellow after 10 minutes of reaction. The reaction was left to continue for a further 2 h. Addition of 2 ml of pentane to the mixture and standing by one day lead to yellow diffraction-quality crystals of I·2CHCl$_3$ (601 mg, 82.8% yield).
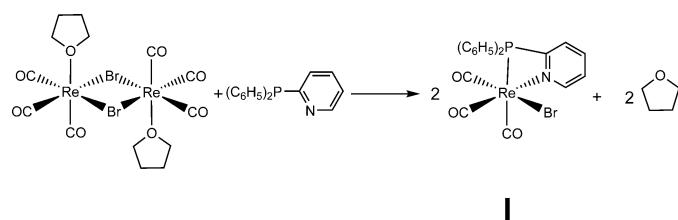
Synthesis of II. The compound was prepared by direct reaction between **I** and an excess of piperidine (C$_5$H$_{11}$N) at 313 K in CH$_2$Cl$_2$. 50.0 mg of [P,N-{(C$_6$H$_5$)$_2$(C$_5$H$_5$N)P}Re-(CO)$_3$Br] (0.082 mmol) were dissolved in 10 ml of CH$_2$Cl$_2$ giving rise to a yellow solution. Then, 40 µL of piperidine (0.51 mmol) was slowly added. The reaction was allowed to continue for six days with constant agitation at 313 K. After cooling, the reaction mixture was layered with acetonitrile.

Small orange–yellow diffraction-quality crystals were obtained after one week.
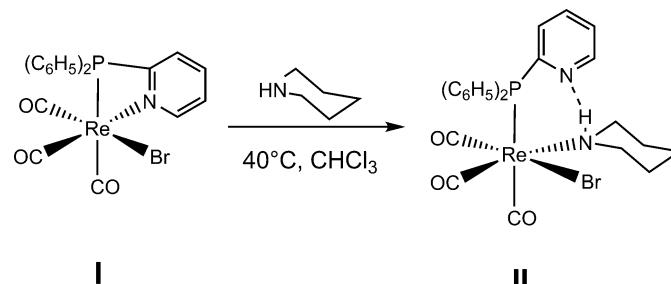
8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. For both compounds, the hydrogen atoms were positioned geometrically and refined using a riding model: C—H = 0.93-0.97 Å with U_{iso}(H) = 1.2U_{eq}(C). For **II**, the amine hydrogen atom of the piperidine ring was located in a Fourier-difference map and then subsequently refined with a distant constraint of 0.82 Å. During the last stages of the refinement of **II**, a region of highly disordered electron density was detected within the crystal structure. As no meaningful model could be achieved, SQUEEZE (Spek, 2015) was used to model the unresolved electron density resulting from the disordered solvent. 25 electrons per cell suggest, in addition to thermogravimetry, a half acetonitrile

molecule per complex molecule of **II**. The contribution of this solvent was not included in the crystal data.

References

Abram, U., Alberto, R., Dilworth, J. R., Zheng, Y. & Ortner, K. (1999). *Polyhedron*, **18**, 2995–3003.

Bruker (2012). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cannizzo, A., Blanco-Rodríguez, A. M., El Nahhas, A., Šebera, J., Záliš, S., Vlček, A. Jr & Chergui, M. (2008). *J. Am. Chem. Soc.* **130**, 8967–8974.

Dalal, J., Sinha, N., Yadav, H. & Kumar, B. (2015). *RSC Adv.* **5**, 57735–57748.

Darensbourg, D. J., Andreatta, J. R., Stranahan, S. M. & Reibenspies, J. H. (2007). *Organometallics*, **26**, 6832–6838.

Guiry, P. J. & Saunders, C. P. (2004). *Adv. Synth. Catal.* **346**, 497–537.

Knebel, W. J. & Angelici, R. J. (1973). *Inorg. Chim. Acta*, **7**, 713–716.

Kumar, P., Singh, A. K., Pandey, R. & Pandey, D. S. (2011). *J. Organomet. Chem.* **696**, 3454–3464.

Machura, B. & Kruszynski, R. (2006). *Polyhedron*, **25**, 1985–1993.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

Ooyama, D. & Sato, M. (2004). *Appl. Organomet. Chem.* **18**, 380–381.

Pizarro, N., Duque, M., Chamorro, E., Nonell, S., Manzur, J., de la Fuente, J. R., Günther, G., Cepeda-Plaza, M. & Vega, A. (2015). *J. Phys. Chem. A*, **119**, 3929–3935.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Spek, A. L. (2015). *Acta Cryst.* C**71**, 9–18.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. http://hirshfeldsurface.net

Venegas, F., Pizarro, N. & Vega, A. (2011). *J. Chil. Chem. Soc.* **56**, 823–826.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Crystal structures and Hirshfeld surface analysis of [κ^2-*P*,*N*-{(C$_6$H$_5$)$_2$(C$_5$H$_5$N)P}Re(CO)$_3$Br]·2CHCl$_3$ and the product of its reaction with piperidine, [*P*-{(C$_6$H$_5$)$_2$(C$_5$H$_5$N)P}(C$_5$H$_{11}$N)Re(CO)$_3$Br]

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Computing details

For both structures, data collection: *SMART* (Bruker, 2012); cell refinement: *SMART* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Bromidotricarbonyl[diphenyl(pyridin-2-yl)phosphane-κ^2*N*,*P*]rhenium(I) chloroform disolvate, [ReBr(C$_{17}$H$_{14}$NP)(CO)$_3$]·2CHCl$_3$ (I-2CHCl3)

Crystal data

[ReBr(C$_{17}$H$_{14}$NP)(CO)$_3$]·2CHCl$_3$	$F(000) = 1624$
$M_r = 852.14$	$D_x = 1.995$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 14.194$ (4) Å	Cell parameters from 6313 reflections
$b = 12.314$ (4) Å	$\theta = 2.5$–28.5°
$c = 16.249$ (5) Å	$\mu = 6.34$ mm^{-1}
$\beta = 92.701$ (4)°	$T = 150$ K
$V = 2836.7$ (15) Å^3	Block, yellow
$Z = 4$	$0.16 \times 0.13 \times 0.05$ mm

Data collection

Bruker SMART CCD area detector diffractometer	5550 independent reflections
	4526 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.048$
phi and ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$h = -17 \rightarrow 17$
	$k = -15 \rightarrow 15$
$T_{min} = 0.386$, $T_{max} = 0.746$	$l = -19 \rightarrow 20$
19979 measured reflections	

Refinement

Refinement on F^2	5550 reflections
Least-squares matrix: full	317 parameters
$R[F^2 > 2\sigma(F^2)] = 0.026$	0 restraints
$wR(F^2) = 0.065$	Primary atom site location: structure-invariant
$S = 0.99$	direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00027 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Re1	0.29082 (2)	0.42455 (2)	0.08046 (2)	0.06954 (7)
Br1	0.45807 (3)	0.36073 (4)	0.13313 (3)	0.07781 (13)
P1	0.25501 (8)	0.23375 (8)	0.04434 (7)	0.0705 (3)
N1	0.3373 (3)	0.3742 (3)	−0.0392 (2)	0.0722 (9)
C1	0.2470 (3)	0.4367 (3)	0.1897 (3)	0.0742 (11)
O1	0.2190 (3)	0.4391 (3)	0.2547 (2)	0.0860 (9)
C2	0.1733 (4)	0.4761 (3)	0.0367 (3)	0.0779 (11)
O2	0.1045 (3)	0.5103 (3)	0.0100 (2)	0.0879 (9)
C3	0.3368 (4)	0.5732 (4)	0.0793 (3)	0.0792 (11)
O3	0.3635 (3)	0.6583 (3)	0.0772 (2)	0.0949 (10)
C4	0.3826 (3)	0.4234 (4)	−0.0986 (3)	0.0783 (11)
H4	0.3974	0.4967	−0.0932	0.094*
C5	0.4076 (4)	0.3694 (4)	−0.1669 (3)	0.0861 (13)
H5	0.4382	0.4061	−0.2079	0.103*
C6	0.3879 (4)	0.2598 (4)	−0.1759 (3)	0.0855 (13)
H6	0.4053	0.2222	−0.2224	0.103*
C7	0.3422 (3)	0.2081 (4)	−0.1148 (3)	0.0792 (11)
H7	0.3283	0.1344	−0.1189	0.095*
C8	0.3171 (3)	0.2667 (3)	−0.0476 (3)	0.0701 (10)
C9	0.3085 (3)	0.1116 (3)	0.0857 (3)	0.0735 (11)
C10	0.4032 (4)	0.0890 (3)	0.0778 (3)	0.0788 (12)
H10	0.4404	0.1362	0.0486	0.095*
C11	0.4429 (4)	−0.0041 (4)	0.1134 (3)	0.0860 (13)
H11	0.5066	−0.0187	0.1080	0.103*
C12	0.3890 (4)	−0.0741 (4)	0.1561 (3)	0.0896 (14)
H12	0.4161	−0.1365	0.1793	0.108*
C13	0.2950 (4)	−0.0530 (4)	0.1651 (3)	0.0873 (14)
H13	0.2586	−0.1006	0.1946	0.105*
C14	0.2549 (4)	0.0392 (4)	0.1300 (3)	0.0812 (12)
H14	0.1912	0.0532	0.1360	0.097*
C15	0.1366 (3)	0.1951 (3)	0.0108 (3)	0.0723 (10)
C16	0.1182 (4)	0.1207 (4)	−0.0506 (3)	0.0830 (12)

H16	0.1680	0.0861	−0.0750	0.100*
C17	0.0272 (4)	0.0967 (4)	−0.0765 (3)	0.0912 (14)
H17	0.0156	0.0465	−0.1185	0.109*
C18	−0.0466 (4)	0.1470 (4)	−0.0402 (4)	0.0987 (16)
H18	−0.1084	0.1319	−0.0583	0.118*
C19	−0.0293 (4)	0.2190 (4)	0.0223 (4)	0.1030 (17)
H19	−0.0794	0.2512	0.0480	0.124*
C20	0.0622 (4)	0.2446 (4)	0.0478 (4)	0.0910 (14)
H20	0.0736	0.2950	0.0897	0.109*
C21	0.3309 (4)	0.7174 (4)	0.3787 (3)	0.0853 (13)
H21	0.3903	0.7468	0.4026	0.102*
Cl1	0.24667 (11)	0.82254 (11)	0.37214 (10)	0.1001 (4)
Cl2	0.29219 (12)	0.61431 (11)	0.44304 (10)	0.1061 (4)
Cl3	0.35045 (12)	0.66739 (12)	0.28107 (9)	0.1034 (4)
C22	0.0251 (4)	0.0957 (4)	0.3284 (4)	0.0959 (15)
H22	0.0155	0.1018	0.3876	0.115*
Cl4	0.02810 (13)	−0.04155 (12)	0.30240 (11)	0.1102 (4)
Cl5	0.13277 (12)	0.15706 (16)	0.30768 (12)	0.1288 (6)
Cl6	−0.06727 (13)	0.16078 (13)	0.27497 (13)	0.1261 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re1	0.06848 (12)	0.06853 (9)	0.07162 (11)	0.00019 (7)	0.00347 (7)	0.00016 (7)
Br1	0.0707 (3)	0.0804 (2)	0.0822 (3)	−0.00035 (19)	0.0024 (2)	0.0055 (2)
P1	0.0706 (7)	0.0695 (5)	0.0717 (7)	0.0009 (5)	0.0046 (5)	−0.0012 (5)
N1	0.069 (2)	0.0740 (18)	0.074 (2)	0.0018 (16)	0.0066 (17)	0.0004 (16)
C1	0.071 (3)	0.071 (2)	0.079 (3)	−0.0012 (19)	−0.005 (2)	0.000 (2)
O1	0.088 (2)	0.097 (2)	0.074 (2)	0.0047 (17)	0.0056 (17)	−0.0020 (16)
C2	0.088 (3)	0.070 (2)	0.077 (3)	0.000 (2)	0.012 (2)	−0.003 (2)
O2	0.078 (2)	0.092 (2)	0.092 (2)	0.0048 (17)	−0.0031 (18)	0.0046 (17)
C3	0.083 (3)	0.079 (2)	0.074 (3)	0.005 (2)	−0.006 (2)	−0.005 (2)
O3	0.111 (3)	0.0759 (18)	0.097 (3)	−0.0122 (18)	0.000 (2)	0.0000 (16)
C4	0.073 (3)	0.080 (2)	0.083 (3)	0.002 (2)	0.009 (2)	0.008 (2)
C5	0.076 (3)	0.099 (3)	0.083 (3)	0.002 (2)	0.013 (2)	0.010 (2)
C6	0.080 (3)	0.100 (3)	0.077 (3)	0.005 (2)	0.007 (2)	−0.002 (2)
C7	0.074 (3)	0.083 (2)	0.081 (3)	−0.001 (2)	0.002 (2)	−0.006 (2)
C8	0.064 (3)	0.071 (2)	0.074 (3)	0.0006 (17)	0.001 (2)	0.0005 (18)
C9	0.080 (3)	0.071 (2)	0.069 (3)	−0.0015 (19)	0.002 (2)	−0.0065 (18)
C10	0.080 (3)	0.071 (2)	0.085 (3)	0.001 (2)	−0.003 (2)	−0.003 (2)
C11	0.083 (3)	0.079 (2)	0.095 (4)	0.011 (2)	−0.005 (3)	−0.004 (2)
C12	0.101 (4)	0.076 (2)	0.090 (3)	0.006 (3)	−0.010 (3)	−0.002 (2)
C13	0.104 (4)	0.077 (2)	0.079 (3)	−0.003 (2)	−0.005 (3)	0.008 (2)
C14	0.081 (3)	0.081 (2)	0.082 (3)	0.003 (2)	0.003 (2)	−0.001 (2)
C15	0.072 (3)	0.0675 (19)	0.078 (3)	−0.0029 (18)	0.004 (2)	0.0041 (18)
C16	0.080 (3)	0.087 (3)	0.083 (3)	−0.010 (2)	0.006 (2)	0.000 (2)
C17	0.087 (4)	0.100 (3)	0.087 (4)	−0.015 (3)	0.001 (3)	0.000 (3)
C18	0.078 (4)	0.093 (3)	0.123 (5)	−0.014 (3)	−0.009 (3)	0.010 (3)

C19	0.073 (4)	0.090 (3)	0.146 (5)	−0.003 (3)	0.014 (3)	−0.006 (3)
C20	0.079 (3)	0.081 (3)	0.115 (4)	−0.003 (2)	0.018 (3)	−0.013 (3)
C21	0.085 (3)	0.088 (3)	0.084 (3)	−0.008 (2)	0.007 (3)	0.006 (2)
Cl1	0.1005 (10)	0.0898 (7)	0.1106 (10)	0.0026 (6)	0.0119 (8)	0.0115 (7)
Cl2	0.1271 (13)	0.0897 (7)	0.1023 (10)	−0.0028 (7)	0.0146 (9)	0.0158 (7)
Cl3	0.1147 (11)	0.1028 (8)	0.0938 (9)	−0.0140 (8)	0.0153 (8)	−0.0114 (7)
C22	0.087 (4)	0.108 (3)	0.092 (4)	−0.008 (3)	−0.001 (3)	−0.006 (3)
Cl4	0.1192 (12)	0.1039 (8)	0.1067 (11)	0.0020 (8)	−0.0035 (9)	0.0022 (8)
Cl5	0.1014 (12)	0.1516 (14)	0.1350 (14)	−0.0353 (10)	0.0217 (10)	−0.0418 (11)
Cl6	0.1167 (13)	0.1064 (9)	0.1519 (16)	−0.0004 (9)	−0.0286 (11)	0.0013 (9)

Geometric parameters (Å, º)

Re1—C2	1.892 (6)	C11—C12	1.364 (7)
Re1—C1	1.914 (5)	C11—H11	0.9300
Re1—C3	1.943 (5)	C12—C13	1.373 (8)
Re1—N1	2.173 (4)	C12—H12	0.9300
Re1—P1	2.4687 (13)	C13—C14	1.382 (6)
Re1—Br1	2.6066 (8)	C13—H13	0.9300
P1—C9	1.800 (5)	C14—H14	0.9300
P1—C15	1.806 (5)	C15—C16	1.370 (6)
P1—C8	1.815 (5)	C15—C20	1.382 (6)
N1—C4	1.330 (5)	C16—C17	1.371 (7)
N1—C8	1.360 (5)	C16—H16	0.9300
C1—O1	1.147 (5)	C17—C18	1.374 (8)
C2—O2	1.131 (6)	C17—H17	0.9300
C3—O3	1.116 (5)	C18—C19	1.362 (8)
C4—C5	1.355 (7)	C18—H18	0.9300
C4—H4	0.9300	C19—C20	1.381 (8)
C5—C6	1.384 (7)	C19—H19	0.9300
C5—H5	0.9300	C20—H20	0.9300
C6—C7	1.368 (7)	C21—Cl3	1.737 (5)
C6—H6	0.9300	C21—Cl2	1.749 (5)
C7—C8	1.370 (6)	C21—Cl1	1.762 (5)
C7—H7	0.9300	C21—H21	0.9800
C9—C10	1.385 (6)	C22—Cl6	1.735 (6)
C9—C14	1.394 (6)	C22—Cl4	1.743 (6)
C10—C11	1.392 (6)	C22—Cl5	1.751 (6)
C10—H10	0.9300	C22—H22	0.9800
C2—Re1—C1	90.2 (2)	C9—C10—C11	120.2 (5)
C2—Re1—C3	88.3 (2)	C9—C10—H10	119.9
C1—Re1—C3	93.39 (19)	C11—C10—H10	119.9
C2—Re1—N1	93.39 (17)	C12—C11—C10	120.5 (5)
C1—Re1—N1	167.89 (15)	C12—C11—H11	119.8
C3—Re1—N1	98.27 (17)	C10—C11—H11	119.8
C2—Re1—P1	93.56 (13)	C11—C12—C13	120.3 (5)
C1—Re1—P1	102.86 (12)	C11—C12—H12	119.9

C3—Re1—P1	163.62 (15)	C13—C12—H12	119.9
N1—Re1—P1	65.39 (9)	C12—C13—C14	119.8 (5)
C2—Re1—Br1	176.20 (14)	C12—C13—H13	120.1
C1—Re1—Br1	92.84 (14)	C14—C13—H13	120.1
C3—Re1—Br1	89.22 (15)	C13—C14—C9	120.9 (5)
N1—Re1—Br1	84.11 (10)	C13—C14—H14	119.5
P1—Re1—Br1	88.01 (3)	C9—C14—H14	119.5
C9—P1—C15	105.2 (2)	C16—C15—C20	119.2 (5)
C9—P1—C8	106.3 (2)	C16—C15—P1	122.6 (4)
C15—P1—C8	106.9 (2)	C20—C15—P1	118.2 (4)
C9—P1—Re1	128.88 (16)	C15—C16—C17	120.8 (5)
C15—P1—Re1	120.04 (14)	C15—C16—H16	119.6
C8—P1—Re1	83.14 (13)	C17—C16—H16	119.6
C4—N1—C8	118.5 (4)	C16—C17—C18	119.8 (5)
C4—N1—Re1	134.2 (3)	C16—C17—H17	120.1
C8—N1—Re1	107.2 (3)	C18—C17—H17	120.1
O1—C1—Re1	176.7 (4)	C19—C18—C17	119.9 (5)
O2—C2—Re1	177.7 (4)	C19—C18—H18	120.1
O3—C3—Re1	178.8 (5)	C17—C18—H18	120.1
N1—C4—C5	121.7 (4)	C18—C19—C20	120.5 (5)
N1—C4—H4	119.2	C18—C19—H19	119.8
C5—C4—H4	119.2	C20—C19—H19	119.8
C4—C5—C6	120.3 (5)	C19—C20—C15	119.7 (5)
C4—C5—H5	119.8	C19—C20—H20	120.1
C6—C5—H5	119.8	C15—C20—H20	120.1
C7—C6—C5	118.6 (5)	Cl3—C21—Cl2	110.9 (3)
C7—C6—H6	120.7	Cl3—C21—Cl1	110.0 (3)
C5—C6—H6	120.7	Cl2—C21—Cl1	109.8 (3)
C6—C7—C8	118.9 (4)	Cl3—C21—H21	108.7
C6—C7—H7	120.6	Cl2—C21—H21	108.7
C8—C7—H7	120.6	Cl1—C21—H21	108.7
N1—C8—C7	122.0 (4)	Cl6—C22—Cl4	110.7 (3)
N1—C8—P1	104.1 (3)	Cl6—C22—Cl5	110.5 (3)
C7—C8—P1	133.9 (3)	Cl4—C22—Cl5	109.9 (3)
C10—C9—C14	118.4 (4)	Cl6—C22—H22	108.6
C10—C9—P1	121.8 (3)	Cl4—C22—H22	108.6
C14—C9—P1	119.7 (4)	Cl5—C22—H22	108.6
C8—N1—C4—C5	0.8 (7)	C14—C9—C10—C11	0.1 (7)
Re1—N1—C4—C5	176.3 (4)	P1—C9—C10—C11	177.4 (4)
N1—C4—C5—C6	−1.2 (8)	C9—C10—C11—C12	0.2 (8)
C4—C5—C6—C7	0.5 (8)	C10—C11—C12—C13	−0.5 (8)
C5—C6—C7—C8	0.4 (7)	C11—C12—C13—C14	0.5 (8)
C4—N1—C8—C7	0.2 (7)	C12—C13—C14—C9	−0.2 (8)
Re1—N1—C8—C7	−176.4 (4)	C10—C9—C14—C13	−0.1 (7)
C4—N1—C8—P1	−179.2 (3)	P1—C9—C14—C13	−177.5 (4)
Re1—N1—C8—P1	4.2 (3)	C9—P1—C15—C16	−63.3 (4)
C6—C7—C8—N1	−0.8 (7)	C8—P1—C15—C16	49.5 (4)

C6—C7—C8—P1	178.3 (4)	Re1—P1—C15—C16	141.4 (3)
C9—P1—C8—N1	−132.1 (3)	C9—P1—C15—C20	118.0 (4)
C15—P1—C8—N1	115.8 (3)	C8—P1—C15—C20	−129.2 (4)
Re1—P1—C8—N1	−3.5 (3)	Re1—P1—C15—C20	−37.3 (4)
C9—P1—C8—C7	48.6 (5)	C20—C15—C16—C17	1.3 (7)
C15—P1—C8—C7	−63.4 (5)	P1—C15—C16—C17	−177.4 (4)
Re1—P1—C8—C7	177.2 (5)	C15—C16—C17—C18	−0.5 (8)
C15—P1—C9—C10	145.3 (4)	C16—C17—C18—C19	−1.2 (9)
C8—P1—C9—C10	32.1 (4)	C17—C18—C19—C20	2.1 (9)
Re1—P1—C9—C10	−62.3 (4)	C18—C19—C20—C15	−1.3 (9)
C15—P1—C9—C14	−37.4 (4)	C16—C15—C20—C19	−0.3 (8)
C8—P1—C9—C14	−150.6 (4)	P1—C15—C20—C19	178.4 (4)
Re1—P1—C9—C14	115.0 (4)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C21—H21···Br1[i]	0.98	2.66	3.490 (5)	143
C4—H4···Br1[ii]	0.93	2.80	3.552 (5)	139

Symmetry codes: (i) −x+1, y+1/2, −z+1/2; (ii) −x+1, −y+1, −z.

Bromidotricarbonyl[diphenyl(pyridin-2-yl)phosphane-κP](piperidine-κN)rhenium(I) (II)

Crystal data

[ReBr(C$_5$H$_{11}$N)(C$_{17}$H$_{14}$NP)(CO)$_3$]·[+solvent]	$Z = 2$
$M_r = 698.55$	$F(000) = 676.0$
Triclinic, $P\overline{1}$	$D_x = 1.778$ Mg m^{-3}
$a = 9.1384$ (17) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.8348$ (18) Å	Cell parameters from 4721 reflections
$c = 15.671$ (3) Å	$\theta = 2.4–22.8°$
$\alpha = 82.956$ (2)°	$\mu = 6.28$ mm^{-1}
$\beta = 82.047$ (2)°	$T = 150$ K
$\gamma = 69.765$ (2)°	Stick, orange
$V = 1304.5$ (4) Å^3	$0.07 \times 0.04 \times 0.03$ mm

Data collection

Bruker SMART CCD area detector diffractometer	5113 independent reflections
Radiation source: sealed tube	4493 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.042$
Absorption correction: numerical (SADABS; Bruker, 2012)	$\theta_{max} = 26.0°$, $\theta_{min} = 2.2°$
$T_{min} = 0.560$, $T_{max} = 0.858$	$h = -11 \rightarrow 11$
10214 measured reflections	$k = -12 \rightarrow 12$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	303 parameters
Least-squares matrix: full	1 restraint
$R[F^2 > 2\sigma(F^2)] = 0.042$	Primary atom site location: structure-invariant direct methods
$wR(F^2) = 0.082$	
$S = 1.11$	Secondary atom site location: difference Fourier map
5113 reflections	

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 9.4699P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.96$ e Å^{-3}

$\Delta\rho_{min} = -1.79$ e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00125 (18)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Re1	0.83162 (3)	0.70525 (3)	0.70289 (2)	0.01774 (10)
Br1	0.80946 (9)	0.74617 (8)	0.86842 (5)	0.03004 (19)
P1	0.7341 (2)	0.49823 (19)	0.75160 (12)	0.0202 (4)
O1	0.8277 (7)	0.6670 (7)	0.5117 (4)	0.0422 (15)
O3	1.1681 (6)	0.4948 (6)	0.6944 (4)	0.0390 (14)
C1	0.8293 (9)	0.6804 (8)	0.5867 (5)	0.0311 (18)
C3	1.0438 (9)	0.5701 (8)	0.6993 (5)	0.0262 (17)
O2	0.9776 (6)	0.9453 (6)	0.6454 (4)	0.0403 (14)
C2	0.9177 (8)	0.8584 (8)	0.6688 (5)	0.0272 (17)
N1	0.4375 (7)	0.6604 (7)	0.8008 (5)	0.0404 (18)
C10	0.5477 (8)	0.5329 (8)	0.8209 (5)	0.0258 (16)
C12	0.8652 (8)	0.3427 (7)	0.8099 (4)	0.0212 (15)
C4	0.7011 (8)	0.4161 (7)	0.6619 (5)	0.0226 (15)
C13	0.8598 (9)	0.2025 (8)	0.8069 (5)	0.0294 (17)
H13	0.7924	0.1883	0.7722	0.035*
C5	0.5513 (8)	0.4262 (8)	0.6451 (5)	0.0271 (17)
H5	0.4635	0.4741	0.6812	0.032*
C6	0.8295 (9)	0.3428 (9)	0.6070 (5)	0.0329 (19)
H6	0.9298	0.3356	0.6175	0.039*
C14	0.9678 (8)	0.3586 (8)	0.8629 (5)	0.0288 (17)
H14	0.9738	0.4502	0.8667	0.035*
C15	0.9527 (9)	0.0861 (8)	0.8545 (5)	0.035 (2)
H15	0.9469	−0.0058	0.8516	0.042*
C11	0.5179 (9)	0.4359 (9)	0.8863 (5)	0.037 (2)
H11	0.5958	0.3487	0.9002	0.044*
C7	0.8101 (10)	0.2809 (9)	0.5372 (5)	0.038 (2)
H7	0.8971	0.2322	0.5009	0.045*
C8	0.5355 (10)	0.3635 (9)	0.5731 (5)	0.038 (2)
H8	0.4361	0.3716	0.5607	0.046*
N2	0.5893 (6)	0.8705 (7)	0.7094 (4)	0.0267 (14)
C20	1.0531 (8)	0.1025 (8)	0.9058 (5)	0.0312 (19)
H20	1.1158	0.0226	0.9375	0.037*

C22	0.5748 (8)	1.0155 (7)	0.7304 (5)	0.0265 (17)
H22A	0.6209	1.0630	0.6815	0.032*
H22B	0.6333	1.0066	0.7791	0.032*
C21	1.0610 (9)	0.2390 (9)	0.9101 (5)	0.0330 (19)
H21	1.1293	0.2509	0.9451	0.040*
C16	0.6639 (11)	0.2905 (10)	0.5211 (6)	0.042 (2)
H16	0.6518	0.2470	0.4743	0.050*
C18	0.2572 (9)	0.5974 (9)	0.9089 (5)	0.038 (2)
H18	0.1558	0.6203	0.9366	0.046*
C17	0.2958 (9)	0.6904 (10)	0.8455 (7)	0.052 (3)
H17	0.2198	0.7794	0.8325	0.063*
C23	0.4992 (9)	0.8828 (9)	0.6357 (6)	0.038 (2)
H23A	0.5059	0.7862	0.6237	0.045*
H23B	0.5463	0.9251	0.5848	0.045*
C19	0.3699 (10)	0.4708 (10)	0.9308 (6)	0.046 (2)
H19	0.3477	0.4074	0.9756	0.056*
C24	0.4037 (9)	1.1105 (9)	0.7526 (6)	0.037 (2)
H24A	0.3600	1.0682	0.8047	0.045*
H24B	0.3999	1.2067	0.7637	0.045*
C25	0.3279 (9)	0.9750 (9)	0.6520 (6)	0.043 (2)
H25A	0.2777	0.9872	0.5996	0.052*
H25B	0.2763	0.9245	0.6966	0.052*
C27	0.3068 (9)	1.1232 (9)	0.6799 (6)	0.042 (2)
H3A	0.3377	1.1818	0.6312	0.051*
H3B	0.1971	1.1717	0.6986	0.051*
H2N	0.567 (8)	0.828 (5)	0.755 (2)	0.08 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re1	0.01153 (15)	0.01837 (15)	0.02204 (17)	−0.00440 (10)	−0.00090 (10)	0.00044 (10)
Br1	0.0329 (4)	0.0300 (4)	0.0260 (4)	−0.0077 (3)	−0.0048 (3)	−0.0040 (3)
P1	0.0141 (9)	0.0199 (9)	0.0252 (10)	−0.0052 (7)	−0.0009 (7)	0.0008 (8)
O1	0.042 (4)	0.057 (4)	0.028 (3)	−0.018 (3)	−0.009 (3)	0.004 (3)
O3	0.013 (3)	0.045 (3)	0.051 (4)	−0.001 (3)	0.000 (2)	−0.005 (3)
C1	0.023 (4)	0.034 (4)	0.033 (5)	−0.009 (3)	0.003 (3)	0.001 (4)
C3	0.031 (4)	0.025 (4)	0.025 (4)	−0.012 (4)	−0.003 (3)	−0.002 (3)
O2	0.031 (3)	0.035 (3)	0.061 (4)	−0.022 (3)	0.001 (3)	−0.001 (3)
C2	0.023 (4)	0.024 (4)	0.032 (4)	−0.005 (3)	0.000 (3)	−0.004 (3)
N1	0.018 (3)	0.031 (4)	0.060 (5)	−0.002 (3)	0.013 (3)	0.009 (3)
C10	0.018 (4)	0.028 (4)	0.030 (4)	−0.008 (3)	0.002 (3)	−0.006 (3)
C12	0.017 (3)	0.021 (4)	0.023 (4)	−0.005 (3)	0.002 (3)	0.001 (3)
C4	0.019 (4)	0.021 (4)	0.028 (4)	−0.006 (3)	−0.005 (3)	0.002 (3)
C13	0.027 (4)	0.026 (4)	0.032 (4)	−0.006 (3)	−0.002 (3)	−0.001 (3)
C5	0.023 (4)	0.025 (4)	0.032 (4)	−0.008 (3)	−0.006 (3)	0.003 (3)
C6	0.032 (4)	0.047 (5)	0.023 (4)	−0.016 (4)	0.003 (3)	−0.011 (4)
C14	0.026 (4)	0.031 (4)	0.025 (4)	−0.005 (3)	0.001 (3)	−0.005 (3)
C15	0.030 (4)	0.014 (4)	0.050 (5)	0.001 (3)	0.002 (4)	0.004 (3)

C11	0.026 (4)	0.038 (5)	0.040 (5)	−0.007 (4)	0.006 (4)	0.002 (4)
C7	0.042 (5)	0.039 (5)	0.032 (5)	−0.012 (4)	0.002 (4)	−0.013 (4)
C8	0.037 (5)	0.048 (5)	0.039 (5)	−0.025 (4)	−0.018 (4)	0.010 (4)
N2	0.011 (3)	0.028 (3)	0.039 (4)	−0.008 (3)	−0.002 (3)	0.007 (3)
C20	0.021 (4)	0.028 (4)	0.029 (4)	0.006 (3)	0.002 (3)	0.005 (3)
C22	0.024 (4)	0.020 (4)	0.036 (4)	−0.007 (3)	−0.006 (3)	−0.002 (3)
C21	0.027 (4)	0.040 (5)	0.026 (4)	−0.002 (4)	−0.005 (3)	−0.001 (4)
C16	0.058 (6)	0.048 (5)	0.031 (5)	−0.029 (5)	−0.021 (4)	0.000 (4)
C18	0.024 (4)	0.046 (5)	0.043 (5)	−0.014 (4)	0.014 (4)	−0.012 (4)
C17	0.021 (4)	0.039 (5)	0.076 (7)	0.005 (4)	0.019 (4)	−0.001 (5)
C23	0.022 (4)	0.040 (5)	0.051 (6)	−0.004 (4)	−0.014 (4)	−0.010 (4)
C19	0.033 (5)	0.055 (6)	0.042 (5)	−0.014 (4)	0.013 (4)	0.006 (4)
C24	0.022 (4)	0.032 (4)	0.048 (5)	0.003 (3)	−0.001 (4)	−0.003 (4)
C25	0.032 (5)	0.035 (5)	0.063 (6)	−0.007 (4)	−0.021 (4)	0.004 (4)
C27	0.023 (4)	0.034 (5)	0.061 (6)	0.000 (4)	−0.008 (4)	0.003 (4)

Geometric parameters (Å, º)

Re1—C1	1.870 (8)	C7—C16	1.363 (11)
Re1—C2	1.918 (7)	C7—H7	0.9300
Re1—C3	1.932 (8)	C8—C16	1.361 (12)
Re1—N2	2.246 (6)	C8—H8	0.9300
Re1—P1	2.4915 (18)	N2—C22	1.460 (9)
Re1—Br1	2.6430 (9)	N2—C23	1.479 (10)
P1—C4	1.812 (7)	N2—H2N	0.8200 (10)
P1—C12	1.817 (7)	C20—C21	1.379 (11)
P1—C10	1.837 (7)	C20—H20	0.9300
O1—C1	1.202 (9)	C22—C24	1.536 (10)
O3—C3	1.120 (8)	C22—H22A	0.9700
O2—C2	1.164 (8)	C22—H22B	0.9700
N1—C17	1.338 (9)	C21—H21	0.9300
N1—C10	1.343 (9)	C16—H16	0.9300
C10—C11	1.377 (10)	C18—C19	1.354 (11)
C12—C14	1.394 (10)	C18—C17	1.361 (12)
C12—C13	1.404 (10)	C18—H18	0.9300
C4—C6	1.387 (10)	C17—H17	0.9300
C4—C5	1.398 (9)	C23—C25	1.517 (10)
C13—C15	1.371 (10)	C23—H23A	0.9700
C13—H13	0.9300	C23—H23B	0.9700
C5—C8	1.396 (11)	C19—H19	0.9300
C5—H5	0.9300	C24—C27	1.505 (12)
C6—C7	1.375 (10)	C24—H24A	0.9700
C6—H6	0.9300	C24—H24B	0.9700
C14—C21	1.387 (10)	C25—C27	1.514 (11)
C14—H14	0.9300	C25—H25A	0.9700
C15—C20	1.362 (11)	C25—H25B	0.9700
C15—H15	0.9300	C27—H3A	0.9700
C11—C19	1.382 (10)	C27—H3B	0.9700

C11—H11	0.9300		
C1—Re1—C2	90.1 (3)	C16—C8—H8	119.6
C1—Re1—C3	89.4 (3)	C5—C8—H8	119.6
C2—Re1—C3	88.0 (3)	C22—N2—C23	109.6 (6)
C1—Re1—N2	92.3 (3)	C22—N2—Re1	116.4 (4)
C2—Re1—N2	89.6 (3)	C23—N2—Re1	116.1 (5)
C3—Re1—N2	177.1 (3)	C22—N2—H2N	106 (4)
C1—Re1—P1	91.6 (2)	C23—N2—H2N	118 (5)
C2—Re1—P1	176.6 (2)	Re1—N2—H2N	89 (5)
C3—Re1—P1	89.0 (2)	C15—C20—C21	119.3 (7)
N2—Re1—P1	93.28 (16)	C15—C20—H20	120.4
C1—Re1—Br1	175.3 (2)	C21—C20—H20	120.4
C2—Re1—Br1	92.1 (2)	N2—C22—C24	112.6 (6)
C3—Re1—Br1	94.9 (2)	N2—C22—H22A	109.1
N2—Re1—Br1	83.53 (17)	C24—C22—H22A	109.1
P1—Re1—Br1	86.44 (5)	N2—C22—H22B	109.1
C4—P1—C12	102.0 (3)	C24—C22—H22B	109.1
C4—P1—C10	102.6 (3)	H22A—C22—H22B	107.8
C12—P1—C10	102.6 (3)	C20—C21—C14	120.6 (8)
C4—P1—Re1	112.4 (2)	C20—C21—H21	119.7
C12—P1—Re1	116.4 (2)	C14—C21—H21	119.7
C10—P1—Re1	118.7 (2)	C8—C16—C7	120.3 (8)
O1—C1—Re1	178.8 (7)	C8—C16—H16	119.8
O3—C3—Re1	177.3 (7)	C7—C16—H16	119.8
O2—C2—Re1	175.9 (6)	C19—C18—C17	118.4 (7)
C17—N1—C10	118.0 (7)	C19—C18—H18	120.8
N1—C10—C11	121.6 (7)	C17—C18—H18	120.8
N1—C10—P1	114.4 (5)	N1—C17—C18	123.4 (8)
C11—C10—P1	124.0 (6)	N1—C17—H17	118.3
C14—C12—C13	117.5 (7)	C18—C17—H17	118.3
C14—C12—P1	121.7 (5)	N2—C23—C25	113.0 (7)
C13—C12—P1	120.7 (5)	N2—C23—H23A	109.0
C6—C4—C5	118.9 (7)	C25—C23—H23A	109.0
C6—C4—P1	118.6 (5)	N2—C23—H23B	109.0
C5—C4—P1	122.5 (6)	C25—C23—H23B	109.0
C15—C13—C12	120.9 (7)	H23A—C23—H23B	107.8
C15—C13—H13	119.6	C18—C19—C11	119.9 (8)
C12—C13—H13	119.6	C18—C19—H19	120.0
C8—C5—C4	119.0 (7)	C11—C19—H19	120.0
C8—C5—H5	120.5	C27—C24—C22	111.0 (7)
C4—C5—H5	120.5	C27—C24—H24A	109.4
C7—C6—C4	120.7 (7)	C22—C24—H24A	109.4
C7—C6—H6	119.7	C27—C24—H24B	109.4
C4—C6—H6	119.7	C22—C24—H24B	109.4
C21—C14—C12	120.5 (7)	H24A—C24—H24B	108.0
C21—C14—H14	119.7	C27—C25—C23	112.4 (7)
C12—C14—H14	119.7	C27—C25—H25A	109.1

C20—C15—C13	121.2 (8)	C23—C25—H25A	109.1
C20—C15—H15	119.4	C27—C25—H25B	109.1
C13—C15—H15	119.4	C23—C25—H25B	109.1
C10—C11—C19	118.6 (8)	H25A—C25—H25B	107.8
C10—C11—H11	120.7	C24—C27—C25	111.1 (7)
C19—C11—H11	120.7	C24—C27—H3A	109.4
C16—C7—C6	120.3 (8)	C25—C27—H3A	109.4
C16—C7—H7	119.8	C24—C27—H3B	109.4
C6—C7—H7	119.8	C25—C27—H3B	109.4
C16—C8—C5	120.8 (7)	H3A—C27—H3B	108.0
C17—N1—C10—C11	−0.9 (13)	P1—C4—C6—C7	−178.9 (6)
C17—N1—C10—P1	176.7 (7)	C13—C12—C14—C21	0.4 (10)
C4—P1—C10—N1	−86.6 (6)	P1—C12—C14—C21	176.7 (5)
C12—P1—C10—N1	167.9 (6)	C12—C13—C15—C20	−0.2 (12)
Re1—P1—C10—N1	37.9 (7)	N1—C10—C11—C19	1.1 (13)
C4—P1—C10—C11	90.9 (7)	P1—C10—C11—C19	−176.3 (7)
C12—P1—C10—C11	−14.6 (8)	C4—C6—C7—C16	−0.1 (13)
Re1—P1—C10—C11	−144.5 (6)	C4—C5—C8—C16	1.5 (11)
C4—P1—C12—C14	155.1 (6)	C13—C15—C20—C21	0.3 (12)
C10—P1—C12—C14	−98.9 (6)	C23—N2—C22—C24	58.2 (8)
Re1—P1—C12—C14	32.4 (7)	Re1—N2—C22—C24	−167.6 (5)
C4—P1—C12—C13	−28.7 (6)	C15—C20—C21—C14	0.0 (11)
C10—P1—C12—C13	77.3 (6)	C12—C14—C21—C20	−0.3 (11)
Re1—P1—C12—C13	−151.4 (5)	C5—C8—C16—C7	−1.7 (13)
C12—P1—C4—C6	−58.3 (6)	C6—C7—C16—C8	1.0 (13)
C10—P1—C4—C6	−164.3 (6)	C10—N1—C17—C18	−1.2 (15)
Re1—P1—C4—C6	67.1 (6)	C19—C18—C17—N1	3.1 (15)
C12—P1—C4—C5	123.0 (6)	C22—N2—C23—C25	−56.3 (8)
C10—P1—C4—C5	17.0 (7)	Re1—N2—C23—C25	169.3 (5)
Re1—P1—C4—C5	−111.6 (6)	C17—C18—C19—C11	−2.9 (14)
C14—C12—C13—C15	−0.1 (11)	C10—C11—C19—C18	0.8 (14)
P1—C12—C13—C15	−176.5 (6)	N2—C22—C24—C27	−56.7 (9)
C6—C4—C5—C8	−0.5 (11)	N2—C23—C25—C27	53.0 (10)
P1—C4—C5—C8	178.2 (6)	C22—C24—C27—C25	51.0 (9)
C5—C4—C6—C7	−0.2 (11)	C23—C25—C27—C24	−49.9 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···N1	0.82	2.34	2.992 (9)	138
C14—H14···Br1	0.93	2.78	3.586 (8)	146
C22—H22*B*···Br1	0.97	2.83	3.499 (7)	127