Co(2)—Ru(1)—Co(3)	54.4 (1)	Ru(1)—Co(3)—C(13)	85.8 (3)
Co(3)—Ru(1)—Co(1)	54.5 (1)	Co(1)—Co(3)—C(13)	49.6 (3)
Co(3)—Ru(1)—P(1)	117.8 (1)	C(9)—Co(3)—C(13)	94.5 (5)
Co(2)—Ru(1)—C(3)	99.7 (4)	Au—Co(1)—Ru(1)	115.0 (1)
Co(1)—Ru(1)—C(3)	94.8 (4)	Ru(1)—Co(1)—Co(2)	61.7 (1)
Co(2)—Ru(1)—C(1)	145.5 (4)	Ru(1)—Co(1)—Co(3)	61.6 (1)
Co(1)—Ru(1)—C(1)	92.9 (4)	Au—Co(1)—C(5)	72.3 (4)
C(3)—Ru(1)—C(1)	94.0 (5)	Co(2)—Co(1)—C(5)	126.3 (4)
Co(3)—Ru(1)—C(6)	87.9 (3)	Au—Co(1)—C(4)	165.3 (4)
P(1)—Ru(1)—C(6)	83.2 (3)	Co(2)—Co(1)—C(4)	128.7 (4)
C(1)—Ru(1)—C(6)	172.9 (4)	C(5)—Co(1)—C(4)	93.3 (5)
Co(3)—Ru(1)—C(8)	40.5 (3)	Ru(1)—Co(1)—C(12)	83.1 (3)
P(1)—Ru(1)—C(8)	83.2 (3)	Co(3)—Co(1)—C(12)	108.0 (3)
C(1)—Ru(1)—C(8)	81.4 (4)	C(4)—Co(1)—C(12)	97.2 (5)
Au—Co(2)—Ru(1)	117.3 (1)	Ru(1)—Co(1)—C(13)	84.4 (3)
Ru(1)—Co(2)—Co(3)	62.7 (1)	Co(3)—Co(1)—C(13)	49.8 (3)
Ru(1)—Co(2)—Co(1)	63.6 (1)	C(4)—Co(1)—C(13)	98.5 (5)
Au—Co(2)—C(6)	176.9 (4)	Ru(1)—C(6)—Co(2)	77.8 (5)
Co(3)—Co(2)—C(6)	113.8 (4)	Co(2)—C(23)—Co(3)	79.1 (5)
Au—Co(2)—C(7)	82.8 (4)	Co(3)—C(13)—Co(1)	80.7 (4)
Co(2)—Au—Co(1)	55.4 (1)	Co(1)—Co(2)—C(7)	132.6 (4)
Co(2)—Au—P(4)	149.0 (1)	Au—Co(2)—C(23)	79.5 (4)
Co(1)—Au—P(4)	151.7 (1)	Co(3)—Co(2)—C(23)	50.0 (4)
Co(2)—Ru(1)—Co(1)	54.7 (1)	C(6)—Co(2)—C(23)	97.4 (5)
Co(2)—Ru(1)—P(1)	116.9 (1)	Au—Co(2)—C(12)	85.2 (3)
Co(1)—Ru(1)—P(1)	170.5 (1)	Co(3)—Co(2)—C(12)	111.7 (3)
Co(3)—Ru(1)—C(3)	146.9 (4)	C(6)—Co(2)—C(12)	97.8 (5)
P(1)—Ru(1)—C(3)	91.1 (4)	C(23)—Co(2)—C(12)	160.2 (5)
Co(3)—Ru(1)—C(1)	99.1 (3)	Au—Co(3)—Co(2)	61.8 (1)
P(1)—Ru(1)—C(1)	94.1 (4)	Au—Co(3)—Co(1)	62.1 (1)
Co(2)—Ru(1)—C(6)	40.0 (3)	Co(2)—Co(3)—Co(1)	60.6 (1)
Co(1)—Ru(1)—C(6)	90.6 (3)	Ru(1)—Co(3)—C(8)	58.7 (3)
C(3)—Ru(1)—C(6)	79.6 (5)	Co(1)—Co(3)—C(8)	116.7 (3)
Co(2)—Ru(1)—C(8)	87.5 (3)	Ru(1)—Co(3)—C(9)	154.8 (4)
Co(1)—Ru(1)—C(8)	91.6 (3)	Co(1)—Co(3)—C(9)	133.1 (4)
C(3)—Ru(1)—C(8)	172.3 (4)	Au—Co(3)—C(23)	78.4 (3)
C(6)—Ru(1)—C(8)	104.7 (4)	Co(2)—Co(3)—C(23)	50.9 (3)
Au—Co(2)—Co(3)	64.1 (1)	C(8)—Co(3)—C(23)	94.7 (5)
Au—Co(2)—Co(1)	62.7 (1)	Au—Co(3)—C(13)	84.5 (3)
Co(3)—Co(2)—Co(1)	60.2 (1)	Co(2)—Co(3)—C(13)	110.2 (3)
Ru(1)—Co(2)—C(6)	62.2 (4)	C(8)—Co(3)—C(13)	101.1 (5)
Co(1)—Co(2)—C(6)	118.5 (4)	C(23)—Co(3)—C(13)	159.1 (5)
Ru(1)—Co(2)—C(7)	159.9 (4)	Au—Co(1)—Co(2)	61.9 (1)
Co(3)—Co(2)—C(7)	132.8 (4)	Au—Co(1)—Co(3)	63.4 (1)
C(6)—Co(2)—C(7)	97.7 (6)	Co(2)—Co(1)—Co(3)	59.1 (1)
Ru(1)—Co(2)—C(23)	90.2 (3)	Ru(1)—Co(1)—C(5)	171.9 (4)
Co(1)—Co(2)—C(23)	109.7 (4)	Co(3)—Co(1)—C(5)	122.1 (4)
C(7)—Co(2)—C(23)	93.4 (5)	Ru(1)—Co(1)—C(4)	79.5 (4)
Ru(1)—Co(2)—C(12)	85.8 (3)	Co(3)—Co(1)—C(4)	129.5 (4)
Co(1)—Co(2)—C(12)	51.5 (3)	Au—Co(1)—C(12)	83.2 (3)
C(7)—Co(2)—C(12)	97.0 (5)	Co(2)—Co(1)—C(12)	48.8 (3)
Au—Co(3)—Ru(1)	115.7 (1)	C(5)—Co(1)—C(12)	101.6 (5)
Ru(1)—Co(3)—Co(2)	63.0 (1)	Au—Co(1)—C(13)	85.5 (3)
Ru(1)—Co(3)—Co(1)	63.8 (1)	Co(2)—Co(1)—C(13)	108.9 (4)
Au—Co(3)—C(8)	171.4 (4)	C(5)—Co(1)—C(13)	93.2 (5)
Co(2)—Co(3)—C(8)	109.8 (4)	C(12)—Co(1)—C(13)	157.7 (5)
Au—Co(3)—C(9)	89.3 (4)	Ru(1)—C(8)—Co(3)	80.8 (4)
Co(2)—Co(3)—C(9)	138.6 (4)	Co(2)—C(12)—Co(1)	79.7 (4)
C(8)—Co(3)—C(9)	96.8 (5)		

All crystallographic calculations were performed using the *SHELXTL-Plus* program package (Sheldrick, 1987). The structure was determined by direct methods and subsequent ΔS calculations. Metal, P and O atoms were refined anisotropically as were C atoms in the methyl groups, C(111) and C(112), and in the carbonyl groups. Phenyl rings were refined as rigid groups with anisotropic displacement parameters. H atoms were placed in calculated positions (C—H = 0.96 Å, U_{iso} = 0.09 Å^2).

References

Hidai, M., Orisaku, M., Ue, M., Koyasu, Y., Kodama, T. & Uchida, Y. (1983). *Organometallics*, **2**, 292–298.

Pursiainen, J., Ahlgrèn, M., Pakkanen, T. A. & Valkonen, J. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1147–1153.

Pursiainen, J., Hirva, P. & Pakkanen, T. A. (1991). *J. Organomet. Chem.* **419**, 193–203.

Pursiainen, J. & Pakkanen, T. A. (1989). *Acta Chem. Scand.* **43**, 463–470.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet *R3m/V* crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

A New Phase of Bis[2-(Diphenylphosphino-κP)phenylazanido-κN](ethanolato)(oxo)-rhenium(V)

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Abstract

The title compound, $[Re(C_{18}H_{15}NP)_2(C_2H_5O)O]$, was synthesized by the oxidation–substitution reaction of $[Re^{III}(PNH)_2(PNH_2)]Cl$, where PNH_2 is 2-(diphenylphosphino)phenylamine, with NEt_3 in EtOH. The X-ray diffraction study of this new triclinic phase, designated β, confirms the molecular structural details for the monoclinic α isomer, which crystallized in space group $P2_1/c$ with $a = 12.056$ (3), $b = 26.303$ (6), $c = 11.005$ (3) Å, $\beta = 102.32$ (2)° [Refosco, Tisato, Bandoli, Bolzati, Dolmella, Moresco & Nicolini (1993). *J. Chem. Soc. Dalton Trans.* pp. 605–618].

Comment

The structure contains discrete monomeric neutral units (I), with the coordination geometry around the Re atom being highly distorted octahedral. The fitted

(I)
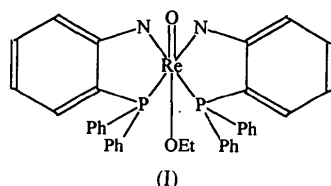
octahedron atoms of the α and β phases, overlapped using the BMFIT program (Nyburg, 1974), show a weighted root-mean-square deviation of only 0.05 Å. In fact, in the $P_2N_2O_2$ coordination polyhedron of the β phase the Re atom is 1.13 (1) Å from the plane formed by the atoms N(1), N(2) and O(2), and -1.10 (1) Å from the plane formed by atoms P(1), P(2) and O(1), the angle between the two triangles being 13.8 (1)°; the corresponding values in the α phase are 1.17 (1), -1.09 (1) Å and 14.6 (1)°. The two PCCN coordinating rings are bent away from the oxo group and make dihedral angles of 12.5 (3) and 2.9 (3)° with the P_2N_2 mean equatorial plane; the corresponding values are 23.6 (4) and 9.8 (4)° in the α isomer. However, the two isomers differ significantly in the periphery, in particular in the orientation of the phenyl rings, as evidenced by the pertinent torsion angles, i.e. Re—P(1)—C(13)—C(14), Re—P(1)—C(19)—C(20), Re—P(2)—C(25)—C(26) and Re—P(2)—C(31)—C(32) which have values of -61.6 (2), -18.6 (2), 50.0 (2) and -107.5 (2)°, respectively, in the α isomer, and -56.6 (2), -55.6 (2), -60.9 (2) and 146.5 (2)°, respectively, in the β isomer. It should be noted also that the closely related chlorooxobis[(o-amido-phenyl)diphenylphosphine]rhenium(V) complex presents two different phases in the solid state (Refosco et al., 1993).

IR spectra of the title compound and its α phase in KBr pellets show two major differences; in the β phase the band at 1098 cm^{-1} becomes very strong and a new absorption appears at 625 cm^{-1}. On the other hand, the stretching vibration associated with the N—H group (3300 cm^{-1}) remains unchanged and only a minor shift (from 887 to 883 cm^{-1}) is observed for $\nu_{Re=O}$. A detailed analysis of the structural data reveals that the α and β phases show slight but significant differences for the rhenium–donor distances; these differences could arise from the different packing of the two phases. In fact, in the β isomer, the intermolecular contact (via hydrogen bonding) between the O(1) and HN(1a) atoms (2.41 Å) weakens both the Re=O(1) [from 1.692 (7) to 1.717 (8) Å] and Re—N(1) bonds [from 1.990 (8) to 2.033 (7) Å]; such a lengthening is accompanied, within the same coordinated ligand, by a shortening of the Re—P(1) bond [from 2.495 (2) to 2.467 (2) Å]. In contrast, the other PNH$^-$ chelate is coordinated to the metal by a weakened Re—P(2) bond [from 2.493 (3) to 2.535 (3) Å] and a reinforced Re—N(2)

bond [from 2.003 (7) to 1.959 (7) Å]. A similar interaction between the oxo O atom and the H atom bonded to an amino N atom of the ligand skeleton of a neighbouring unit has been described for a neutral rhenium diaminooxodithiolato complex (Jackson, Kojima & Lambrecht, 1992). In spite of the different nature of the N_2S_2 and bis-NP backbones, as well as the coordinating geometry of the resulting complexes (square pyramidal versus distorted octahedral), the relevant spectroscopic data for [ReO(te)], where te is 3,10-diethyl-5,8-diaza-3,10-dodecanedithiolate, follow the trend of those of the title compound. In particular, the Re=O bond length is 1.709 Å and $\nu_{Re=O}$ is 920 cm^{-1}, showing a slight bathochromic shift with respect to the analogous complex syn-[ReO(nmtm)], where nmtm is 2,4,9-trimethyl-4,7-diaza-2,9-decanedithiolate (Mahmood, Baidoo & Lever, 1990).

The β-[ReO(OEt)(PNH)$_2$] complex can also be described as a syn species, the O(1)$\cdots$(H1a)—N(1a) and O(1a)$\cdots$H(1)—N(1) angles being approximately 160°. When dissolved in CHCl$_3$ solution, the ethoxo group in β-[ReO(OEt)(PNH)$_2$] is easily exchanged with water, the complex rearranging to the hydroxo derivative [ReO(OH)(PNH)$_2$]; both α- and β-isomers of [ReO(OEt)(PNH)$_2$] are still present in solution as traces.
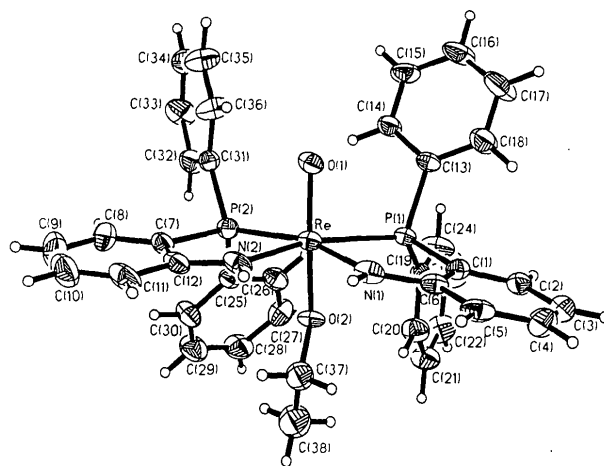

Fig. 1. ORTEP (Johnson, 1965) view of the title complex showing the atom-labelling scheme with atom contours at the 50% probability level.

Experimental

Crystal data

[Re(C$_{18}$H$_{15}$NP)$_2$(C$_2$H$_5$O)O]	D_x = 1.56 Mg m^{-3}
M_r = 799.8	D_m = 1.55 Mg m^{-3}

Triclinic
$P\bar{1}$
$a = 11.335$ (3) Å
$b = 13.208$ (3) Å
$c = 13.288$ (4) Å
$\alpha = 61.06$ (2)°
$\beta = 79.11$ (2)°
$\gamma = 80.71$ (2)°
$V = 1703.9$ (9) Å^3
$Z = 2$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50
  reflections
$\theta = 9\text{--}13°$
$\mu = 3.7$ mm^{-1}
$T = 296$ K
Prismatic
$0.20 \times 0.15 \times 0.10$ mm
Brown

Data collection

Nicolet Siemens $R3m/V$
  diffractometer
$\omega\text{--}2\theta$ scans (2.5-14.5°
  min^{-1} in ω, range 1.35°)
Absorption correction:
  empirical
  $T_{min} = 0.73$, $T_{max} = 0.98$
4714 measured reflections
4447 independent reflections
3393 observed reflections
  $[|F_o| > 3\sigma(F_o)]$

$R_{int} = 0.022$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$
2 standard reflections
  monitored every 100
  reflections
  intensity variation: ±2.1%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.044$
$S = 0.76$
3393 reflections
397 parameters
Only H-atom U's refined
$w = [\sigma^2(F) + 0.02F^2]^{-1}$
$(\Delta/\sigma)_{max} = 0.16$

$\Delta\rho_{max} = 1.1$
  (0.95 Å from Re)
$\Delta\rho_{min} = -1.3$ e Å^{-3}
Atomic scattering factors
  from *International Tables*
  for X-ray Crystallography
  (1974, Vol. IV), inlaid in
  SHELXTL-Plus (Sheldrick,
  1987)

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}
Re	0.3573 (1)	0.0750 (1)	0.1188 (1)	0.034 (1)
P(1)	0.3203 (2)	−0.0790 (2)	0.3209 (2)	0.031 (1)
P(2)	0.1882 (2)	0.2357 (2)	0.0735 (2)	0.038 (1)
O(1)	0.2800 (6)	0.0058 (5)	0.0737 (5)	0.042 (3)
O(2)	0.3946 (5)	0.1529 (5)	0.2046 (5)	0.038 (3)
N(1)	0.5192 (7)	−0.0198 (7)	0.1434 (7)	0.042 (4)
N(2)	0.4265 (7)	0.1948 (7)	−0.0306 (7)	0.046 (4)
C(1)	0.4703 (8)	−0.1549 (8)	0.3434 (8)	0.036 (5)
C(2)	0.5082 (9)	−0.2467 (8)	0.4489 (9)	0.047 (5)
C(3)	0.6242 (10)	−0.3039 (9)	0.4576 (10)	0.057 (6)
C(4)	0.7043 (9)	−0.2673 (10)	0.3612 (11)	0.061 (7)
C(5)	0.6730 (9)	−0.1742 (10)	0.2562 (11)	0.053 (6)
C(6)	0.5555 (8)	−0.1152 (8)	0.2466 (8)	0.038 (5)
C(7)	0.2490 (9)	0.3407 (8)	−0.0678 (8)	0.045 (5)
C(8)	0.1881 (11)	0.4440 (10)	−0.1431 (8)	0.062 (6)
C(9)	0.2422 (15)	0.5188 (12)	−0.2474 (11)	0.089 (8)
C(10)	0.3598 (15)	0.4837 (12)	−0.2761 (11)	0.086 (8)
C(11)	0.4250 (12)	0.3801 (10)	−0.2068 (9)	0.068 (6)
C(12)	0.3692 (10)	0.3039 (9)	−0.0989 (8)	0.047 (5)
C(13)	0.2224 (8)	−0.1809 (8)	0.3354 (8)	0.037 (5)
C(14)	0.1081 (8)	−0.1370 (8)	0.2976 (9)	0.049 (5)
C(15)	0.0288 (10)	−0.2105 (10)	0.3112 (10)	0.059 (6)
C(16)	0.0628 (10)	−0.3262 (10)	0.3600 (11)	0.070 (7)
C(17)	0.1757 (11)	−0.3736 (10)	0.3989 (13)	0.086 (9)
C(18)	0.2552 (10)	−0.2991 (9)	0.3840 (11)	0.066 (6)
C(19)	0.2743 (7)	−0.0576 (7)	0.4485 (7)	0.033 (4)
C(20)	0.3398 (10)	0.0034 (9)	0.4737 (8)	0.058 (6)
C(21)	0.3104 (10)	0.0240 (9)	0.5684 (9)	0.058 (6)
C(22)	0.2133 (11)	−0.0192 (11)	0.6395 (9)	0.067 (6)
C(23)	0.1463 (11)	−0.0806 (12)	0.6181 (10)	0.085 (8)
C(24)	0.1756 (10)	−0.1001 (10)	0.5249 (9)	0.066 (7)
C(25)	0.1610 (8)	0.3031 (8)	0.1678 (8)	0.039 (5)
C(26)	0.1283 (9)	0.2335 (9)	0.2842 (9)	0.052 (5)
C(27)	0.1059 (10)	0.2746 (10)	0.3639 (9)	0.060 (6)
C(28)	0.0112 (11)	0.3927 (10)	0.3254 (11)	0.071 (7)
C(29)	0.1426 (11)	0.4625 (10)	0.2102 (11)	0.073 (7)
C(30)	0.1686 (10)	0.4166 (8)	0.1320 (9)	0.058 (6)
C(31)	0.0365 (8)	0.2251 (8)	0.0501 (7)	0.039 (4)
C(32)	−0.0659 (9)	0.2817 (9)	0.0834 (10)	0.057 (6)
C(33)	−0.1781 (9)	0.2677 (10)	0.0659 (11)	0.069 (7)
C(34)	−0.1907 (11)	0.2013 (10)	0.0149 (10)	0.065 (6)
C(35)	−0.0900 (11)	0.1477 (12)	−0.0144 (11)	0.076 (8)
C(36)	0.0237 (10)	0.1594 (11)	−0.0012 (10)	0.067 (7)
C(37)	0.4976 (10)	0.2090 (9)	0.1806 (9)	0.057 (3)
C(38)	0.4874 (12)	0.2740 (11)	0.2467 (11)	0.082 (4)

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

Re—P(1)	2.467 (2)	Re—P(2)	2.535 (3)
Re—O(1)	1.717 (8)	Re—O(2)	1.997 (8)
Re—N(1)	2.033 (7)	Re—N(2)	1.959 (7)
P(1)—C(1)	1.827 (9)	P(2)—C(7)	1.795 (8)
N(1)—C(6)	1.42 (1)	N(2)—C(12)	1.41 (1)
O(1)—Re—N(1)	103.2 (4)	O(1)—Re—N(2)	100.7 (4)
P(1)—Re—N(1)	77.4 (2)	P(2)—Re—N(2)	78.9 (2)
P(1)—Re—O(1)	90.4 (2)	P(2)—Re—O(1)	89.3 (2)
P(1)—Re—O(2)	79.2 (2)	P(2)—Re—O(2)	79.5 (2)
P(1)—Re—P(2)	110.8 (1)	N(1)—Re—N(2)	90.9 (3)
P(1)—Re—N(2)	165.6 (3)	P(2)—Re—N(1)	165.2 (3)
O(1)—Re—O(2)	160.8 (3)	Re—O(2)—C(37)	125.6 (7)
Re—P(1)—C(1)	101.2 (3)	Re—P(2)—C(7)	100.5 (3)
Re—N(1)—C(6)	128.5 (6)	Re—N(2)—C(12)	126.0 (6)

Integrated intensities were corrected for Lorentz and polarization effects. The structure was solved by the heavy-atom method and the H atoms were included in calculated positions with a common variable isotropic displacement parameter. Refinement was by full-matrix least squares with anistropic displacement parameters for non-H atoms. Structure determination and refinement were performed with the *SHELXTL-Plus* program system (Sheldrick, 1987).

References

Jackson, T., Kojima, M. & Lambrecht, R. (1992). *Abstracts IXth Int. Symp. Radiopharm. Chem. Paris*, pp. 424–425.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Mahmood, A., Baidoo, K. E. & Lever, S. Z. (1990). *Technetium and Rhenium in Chemistry and Nuclear Medicine* 3, edited by M. Nicolini, G. Bandoli & U. Mazzi, pp. 117–124. New York: Raven Press.

Nyburg, S. C. (1974). *Acta Cryst.* B30, 251–253.

Refosco, F., Tisato, F., Bandoli, G., Bolzati, C., Dolmella, A., Moresco, A. & Nicolini, M. (1993). *J. Chem. Soc. Dalton Trans.* pp. 605–618.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet *R3m/V* crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.