Cl1—Ti—Cl2	92.8 (1)	89.6 (1)
Cl1—Ti—Cl3	96.2 (1)	98.0 (2)
Cl2—Ti—Cl3	102.3 (1)	99.3 (1)
C4—O1—Cl	108.8 (2)	109.5 (2)
C4—O1—Ti	124.8 (2)	126.9 (2)
Cl—O1—Ti	126.4 (2)	121.7 (1)
C5—O2—Ti	116.3 (2)	124.2 (2)
C9—O3—C6	110.1 (2)	111.2 (2)
C9—O3—Ti	131.0 (2)	134.4 (1)
C6—O3—Ti	117.7 (2)	113.8 (2)
O1—C1—C2	105.0 (2)	104.9 (2)
C1—C2—C3	104.2 (3)	103.1 (2)
C4—C3—C2	102.0 (3)	101.9 (2)
O1—C4—C3	104.8 (2)	104.9 (2)
O2—C5—C6	105.6 (3)	106.0 (2)
O3—C6—C7	106.0 (3)	103.7 (3)
O3—C6—C5	105.3 (2)	103.5 (2)
C7—C6—C5	117.0 (4)	119.5 (3)
C6—C7—C8	103.7 (4)	103.8 (4)
C9—C8—C7	104.2 (3)	103.1 (2)
O3—C9—C8	104.3 (2)	104.4 (2)
O3—Ti—O2—C5	17.2 (3)	16.1 (2)
O2—Ti—O3—C9	−153.1 (2)	−158.7 (2)
O2—Ti—O3—C6	12.8 (2)	11.3 (1)
Ti—O2—C5—C6	−41.9 (4)	−38.2 (3)
C9—O3—C6—C7	6.1 (4)	15.4 (3)
Ti—O3—C6—C7	−162.5 (4)	−156.9 (3)
C9—O3—C6—C5	130.7 (3)	140.9 (2)
Ti—O3—C6—C5	−38.0 (3)	−31.5 (2)
O2—C5—C6—O3	48.0 (4)	40.0 (3)
O2—C5—C6—C7	165.4 (4)	154.5 (3)
O3—C6—C7—C8	−25.0 (6)	−32.3 (5)
C5—C6—C7—C8	−142.0 (4)	−146.7 (3)
C6—C7—C8—C9	34.3 (6)	37.2 (4)
C6—O3—C9—C8	15.4 (2)	7.8 (2)
Ti—O3—C9—C8	−177.9 (2)	178.0 (1)
C7—C8—C9—O3	−30.6 (4)	−27.5 (3)

During the measurements the crystals were kept in a stream of cooled nitrogen. Refinement of the ordered model of both structures gave a final R of 0.0306 for (I) and 0.0307 for (II). In both cases, however, residual electron densities on the different Fourier maps (ca 1–2 e Å⁻³) in the vicinity of the chiral C6 atom were found. This may be explained by the assumption that enantiomers of the chelating ligand occupy the same crystallographic position. We refined a model in which only atoms C5, C6 and C7 (and attached H atoms) of both enantiomers had the different positions; the remaining atoms of ligands were assumed to overlap. Bonds for the disordered part of ligand enantiomers were restrained to be equal within 0.03 Å. The refined site-occupation factors for the major component were 0.84 for (I) and 0.83 for (II). Non-H atoms of the minor component were allowed isotropic motion; all other non-H atoms were refined anisotropically. H atoms were refined except for those attached to the disordered atoms, for which a riding model (with U_{iso} refined for the major component and fixed for the minor component) was used. For (II), an alternative cell (P2₁/n) with c = 11.862 Å and β = 95.83° was generated by the matrix 100/010/101.

For both compounds, data collection: KM4 Software (Kuma, 1989); program(s) used to solve structures: SHELXS86 (Sheldrick, 1985); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: ORTEPII (Johnson, 1976).

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). Acc. Chem. Res. 16, 146–153.
Furberg, S. & Jensen, L. H. (1968). J. Am. Chem. Soc. 90, 470–474.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Karol, F. J., Kao, S. C. & Cann, K. J. (1993). J. Polym. Sci. Part A, 31, 2541–2553.
Kuma (1989). Kuma KM4 Software. User's Guide. Version 4.00. Kuma Diffraction, Wrocław, Poland.
Kunz, R. W., Pregosin, P. S., Camalli, M., Caruso, F. & Zambonelli, L. (1983). Helv. Chim. Acta, 66, 1661–1671.
Manzer, L. E. (1982). Inorg. Synth. 21, 137.
Sheldrick, G. M. (1985). SHELXS86. Program for the Solution of Crystal Structures. University of Göttingen, Germany.
Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
Winter, C. H., Sheridon, P. H. & Hegg, J. (1991). Inorg. Chem. 30, 1962–1964.

[Bis(diphenylphosphino)amine-P,P']bromotricarbonylrhenium(I), [ReBr(CO)₃{NH(PPh₂)₂}]

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Abstract

The structure of [ReBr(CO)₃(C₂₄H₂₁NP₂)] consists of discrete molecules in which the Re ion has a six-coordinate octahedral environment with the three carbonyl groups in facial positions.

Comment

The attention received by Tc compounds in view of the applications of new ⁹⁹ᵐTc radiopharmaceuticals is well known (Deutsch, Libson, Jurisson & Linday, 1983). As a result of the very similar chemical behaviour of the third-row Re congener, synthetic routes tested with Re may be usefully transferred to the preparation of analogous radioactive ⁹⁹Tc or ⁹⁹ᵐTc compounds. In addition, complexes of Re and Tc are often isomorphous (Rossi et al., 1989). This study is a continuation of a series of investigations of Re and Tc complexes. Crystals of [ReBr(CO)₃{NH(PPh₂)₂}], (I), were kindly supplied by the late Professor Magon.

The structure consists of discrete molecules in which the Re atom has a six-coordinate octahedral environ-

(I)
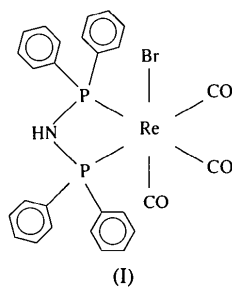
ment with the CO groups in facial positions. Deviations from the idealized geometry are essentially due to the constraints imposed by the bidentate ligand, which subtends an angle of only 66.8 (1)° at the metal ion. Re—P bond lengths compare well with the values found in similar compounds; the Re—Br distance of 2.644 (2) Å is rather long if compared with the sum of the covalent (2.42 Å) or of the atomic radii (2.50 Å). The formal P—N single bonds [1.70 (1) and 1.682 (8) Å] agree with the sum of the atomic radii (1.65 Å) and can be compared with those of 1.67 (4) Å found in $Cl_2P(O)NMe_2$ (Vilkov & Khaikin, 1975), 1.681 (6) Å in $Ph_2P(O)NMe_2$ (Ul-Haque & Caughlan, 1976) and 1.62–1.69 Å in dimethylaminophosphazenes (e.g. Bullen & Dann, 1974). Shorter P—N distances [1.539 (2) Å] are found in the symmetrical cation $[Ph_3P—N—PPh_3]^+$ where the P—N bonds have partial double-bond character (e.g. Wilson & Bau, 1974).

The Re—P—N angles [mean 93.7 (3)°] and the Re—P—C angles [mean 122.2 (3)°] are clearly determined by coordination requirements. It is noteworthy that the four C—P—N angles, which range between 107.0 (4) and 108.3 (4)°, are significantly larger than the C—P—C angles (~101.8°).
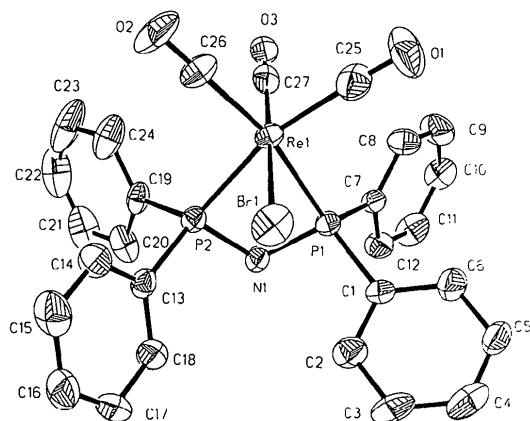

Fig. 1. The crystal structure of $[ReBr(CO)_3\{NH(PPh_2)_2\}]$. Ellipsoids are drawn at the 50% probability level.

Experimental

Crystal data

$[ReBr(CO)_3(C_{24}H_{21}NP_2)]$
$M_r = 735.5$

Monoclinic
$P2_1/n$
$a = 11.388 (4)$ Å
$b = 19.834 (6)$ Å
$c = 13.009 (5)$ Å
$\beta = 112.18 (3)°$
$V = 2721 (2)$ Å^3
$Z = 4$
$D_x = 1.79$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–12°$
$\mu = 6.0$ mm^{-1}
$T = 293$ K
Prism
$0.4 \times 0.3 \times 0.2$ mm
Red–orange

Data collection

Philips PW1100 four-circle (FEBO system) diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Matthews, 1968)
$T_{min} = 0.85$, $T_{max} = 0.98$
5070 measured reflections
4690 independent reflections

3223 observed reflections
$[I > 3\sigma(I)]$
$R_{int} = 0.012$
$\theta_{max} = 25°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 14$
2 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.042$
$S = 3.69$
3223 reflections
262 parameters
H atoms: see below
Unit weights applied

$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 1.2$ e Å^{-3}
$\Delta\rho_{min} = -0.8$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

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(1)	0.19445 (4)	0.13229 (2)	0.41476 (3)	0.0382 (1)
Br(1)	0.2849 (1)	0.25636 (7)	0.4572 (1)	0.0723 (6)
P(1)	−0.0140 (2)	0.1799 (1)	0.3083 (2)	0.0366 (9)
P(2)	0.1602 (2)	0.1532 (1)	0.2203 (2)	0.0381 (9)
N(1)	0.0102 (8)	0.1799 (4)	0.1874 (7)	0.045 (3)
C(2)	−0.0129 (7)	0.3194 (4)	0.2866 (6)	0.060 (6)
C(3)	−0.0401 (7)	0.3852 (4)	0.3086 (6)	0.073 (6)
C(4)	−0.1112 (7)	0.3965 (4)	0.3739 (6)	0.073 (6)
C(5)	−0.1549 (7)	0.3420 (4)	0.4173 (6)	0.065 (6)
C(6)	−0.1277 (7)	0.2762 (4)	0.3954 (6)	0.062 (5)
C(1)	−0.0566 (7)	0.2649 (4)	0.3300 (6)	0.044 (4)
C(8)	−0.1654 (6)	0.0886 (4)	0.3656 (5)	0.054 (5)
C(9)	−0.2796 (6)	0.0564 (4)	0.3508 (5)	0.079 (7)
C(10)	−0.3877 (6)	0.0702 (4)	0.2570 (5)	0.071 (6)
C(11)	−0.3818 (6)	0.1162 (4)	0.1780 (5)	0.072 (6)
C(12)	−0.2676 (6)	0.1484 (4)	0.1928 (5)	0.056 (5)
C(7)	−0.1594 (6)	0.1346 (4)	0.2866 (5)	0.040 (4)
C(14)	0.3791 (6)	0.2191 (4)	0.2363 (7)	0.059 (5)
C(15)	0.4498 (6)	0.2718 (4)	0.2175 (7)	0.084 (8)
C(16)	0.3884 (6)	0.3253 (4)	0.1486 (7)	0.084 (8)
C(17)	0.2564 (6)	0.3262 (4)	0.0984 (7)	0.092 (9)
C(18)	0.1857 (6)	0.2735 (4)	0.1171 (7)	0.067 (6)
C(13)	0.2471 (6)	0.2200 (4)	0.1861 (7)	0.044 (4)
C(20)	0.0859 (8)	0.0999 (4)	0.0076 (6)	0.068 (6)
C(21)	0.0865 (8)	0.0522 (4)	−0.0710 (6)	0.091 (8)
C(22)	0.1576 (8)	−0.0067 (4)	−0.0372 (6)	0.101 (9)
C(23)	0.2281 (8)	−0.0179 (4)	0.0752 (6)	0.11 (1)
C(24)	0.2275 (8)	0.0298 (4)	0.1538 (6)	0.082 (7)
C(19)	0.1563 (8)	0.0887 (4)	0.1200 (6)	0.046 (4)

C(25)	0.177 (1)	0.1280 (6)	0.560 (1)	0.066 (5)
C(26)	0.370 (1)	0.0974 (6)	0.473 (1)	0.060 (5)
C(27)	0.125 (1)	0.0415 (8)	0.378 (1)	0.13 (1)
O(1)	0.1584 (9)	0.1267 (8)	0.6376 (8)	0.110 (6)
O(2)	0.4687 (8)	0.0781 (5)	0.505 (1)	0.098 (5)
O(3)	0.074 (1)	−0.0063 (9)	0.361 (1)	0.110 (7)

Table 2. Selected geometric parameters (Å, °)

Re(1)—P(1)	2.442 (2)	Re(1)—Br(1)	2.644 (2)
Re(1)—P(2)	2.445 (3)	Re(1)—C(25)	1.97 (1)
P(1)—C(1)	1.806 (8)	Re(1)—C(26)	1.98 (1)
P(1)—C(7)	1.811 (8)	Re(1)—C(27)	1.95 (1)
P(1)—N(1)	1.70 (1)	C(25)—O(1)	1.11 (2)
P(2)—C(13)	1.807 (9)	C(26)—O(2)	1.11 (1)
P(2)—C(19)	1.816 (9)	C(27)—O(3)	1.09 (2)
P(2)—N(1)	1.682 (8)		
Br(1)—Re(1)—C(27)	178.22 (6)	Re(1)—C(25)—O(1)	175 (1)
C(25)—Re(1)—C(26)	94.2 (5)	Re(1)—C(26)—O(2)	180 (1)
P(1)—Re(1)—P(2)	66.8 (1)	Re(1)—C(27)—O(3)	171 (1)
Re(1)—P(1)—C(1)	122.3 (3)	Re(1)—P(2)—C(13)	119.4 (3)
Re(1)—P(1)—C(7)	122.2 (2)	Re(1)—P(2)—C(19)	125.1 (3)
Re(1)—P(1)—N(1)	93.6 (3)	Re(1)—P(2)—N(1)	93.8 (3)
C(1)—P(1)—N(1)	107.0 (4)	C(13)—P(2)—N(1)	107.7 (4)
C(7)—P(1)—N(1)	108.3 (4)	C(19)—P(2)—N(1)	107.0 (4)
C(1)—P(1)—C(7)	101.8 (4)	C(13)—P(2)—C(19)	101.9 (4)
P(1)—N(1)—P(2)	105.6 (5)		

Intensities were corrected for Lorentz and polarization factors and for absorption. The structure was solved by the heavy-atom method and final scale factor, atomic coordinates and displacement parameters were obtained by full-matrix least-squares refinement. Phenyl groups were refined as rigid bodies (C—C = 1.395 Å) and H atoms (apart from that bonded to N, which was not considered in the calculations) introduced in calculated positions (C—H = 1.08 Å) with a fixed displacement parameter (U_{iso} = 0.08 Å²). All calculations were performed on a MicroVAX computer.

Data collection: Philips diffractometer software. Cell refinement: Philips diffractometer software. Data reduction: local program. Program(s) used to solve structure: SHELX76 (Sheldrick, 1976). Program(s) used to refine structure: SHELX76. Molecular graphics: ORTEPII (Johnson, 1976).

References

Bullen, G. J. & Dann, P. E. (1974). J. Chem. Soc. Dalton Trans. pp. 705–709.
Deutsch, E., Libson, K., Jurisson, S. & Linday, F. (1983). Prog. Inorg. Chem. 30, 75–139.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). Acta Cryst. A24, 351–359.
Rossi, R., Marchi, A., Magon, L., Duatti, A., Casellato, U. & Graziani, R. (1989). Inorg. Chim. Acta, pp. 23–28.
Sheldrick, G. M. (1976). SHELX76. Program for Crystal Structure Determination. University of Cambridge, England.
Ul-Haque, M. & Caughlan, C. N. (1976). J. Chem. Soc. Perkin Trans. 2, pp. 1101–1104.
Vilkov, L. & Khaikin, L. S. (1975). Top. Curr. Chem. 53, 25–70.
Wilson, R. D. & Bau, R. (1974). J. Am. Chem. Soc. 96, 7601–7602.

1-Carbonyl-2,2-cis-dicarbonyl-μ-formato-1C:2O,O'-1-nitrosyl-1-(η⁵-pentamethylcyclopentadienyl)-2,2-trans-bis(triphenylphosphine)dirhenium

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Abstract

The title compound {systematic name: tricarbonyl-$1\kappa C, 2\kappa^2 C$-μ-formato-$(2-)$-$1\kappa C:2\kappa^2 O, O'$-nitrosyl-$1\kappa N$-[1(η⁵)-pentamethylcyclopentadienyl]bis(triphenylphosphine)-$2\kappa^2 P$-dirhenium}, [Re₂(CO₂)(NO)(C₁₀H₁₅)-(C₁₈H₁₅P)₂(CO)₃], has a carbon dioxide ligand bridged between two octahedral rhenium centers. The presence of two triphenylphosphine ligands, which are trans to each other on Re(2), alters the orientation of the bridging CO₂ ligand relative to ligands bound to Re(1) in this compound as compared with the analog having a single triphenylphosphine ligand on Re(2).

Comment

As part of a general study of the properties of compounds having CO₂ bridged between two metal centers (Gibson et al., 1995), we prepared the title compound, (I), in order to compare its spectral and structural properties with the analog having a single triphenylphosphine ligand on Re(2), CpRe(CO)(NO)–(CO₂)–Re(CO)₃(PPh₃), (II), (Gibson, Mehta, Ye, Richardson & Mashuta, 1994).

(I)
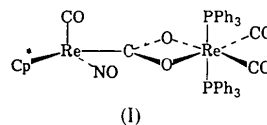
The principal structural difference between (I) and (II) is the orientation of the plane containing the bridging CO₂ group relative to ligands bound to the face-capped Re(1) center. In (I) the CO₂ plane is almost perpendicular to the N(1)—Re(1)—C(4) plane, whereas in (II) the CO₂ plane is almost coincident with the Re(1)—N(1)—O(4) plane. The CO₂ O—Re(2) bond lengths are increased slightly in (I) [2.178 (5) and 2.215 (5) Å] as compared with those in (II) [2.165 (4) and 2.175 (3) Å], due to increased crowding around this rhenium center in (I). The CO₂ C—Re(1) bond length is also consistent with an increased bond length