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 ($U_{\rm iso}$ = 0.08 Å^2). 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).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1196). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Carbonyl-2,2-*cis*-dicarbonyl-μ-formato-1*C*:2*O*,*O*′-1-nitrosyl-1-(η^5-pentamethylcyclopentadienyl)-2,2-*trans*-bis(triphenylphosphine)dirhenium

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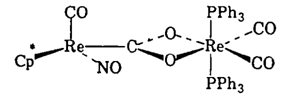
Abstract

The title compound {systematic name: tricarbonyl-1κC,2$\kappa^2 C$-μ-formato(2−)-1κC:2$\kappa^2 O$,O'-nitrosyl-1κN-[1(η^5)-pentamethylcyclopentadienyl]bis(triphenylphosphine)-2$\kappa^2 P$-dirhenium}, [Re$_2$(CO$_2$)(NO)(C$_{10}$H$_{15}$)(C$_{18}$H$_{15}$P)$_2$(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 CO$_2$ 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 CO$_2$ 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)–(CO$_2$)–Re(CO)$_3$(PPh$_3$), (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 CO$_2$ group relative to ligands bound to the face-capped Re(1) center. In (I) the CO$_2$ plane is almost perpendicular to the N(1)—Re(1)—C(4) plane, whereas in (II) the CO$_2$ plane is almost coincident with the Re(1)—N(1)—O(4) plane. The CO$_2$ 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 CO$_2$ C—Re(1) bond length is also consistent with an increased bond length

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[2.104 (8) in (I), 2.089 (6) Å in (II)], possibly because of the change in orientation of the CO_2 group at Re(1) in (I). However, the change in orientation of the CO_2 group relative to the ligands bound to Re(1) and the slight changes in the O—Re bond lengths have little effect on the IR-stretching frequencies of the bridging CO_2 ligand as evidenced in DRIFTS spectra (Griffiths & de Haseth, 1986); the ν_{OCO} bands in (I) are at 1435 and 1279 cm^{-1}, while those in (II) are at 1437 and 1282 cm^{-1} (Gibson *et al.*, 1994).

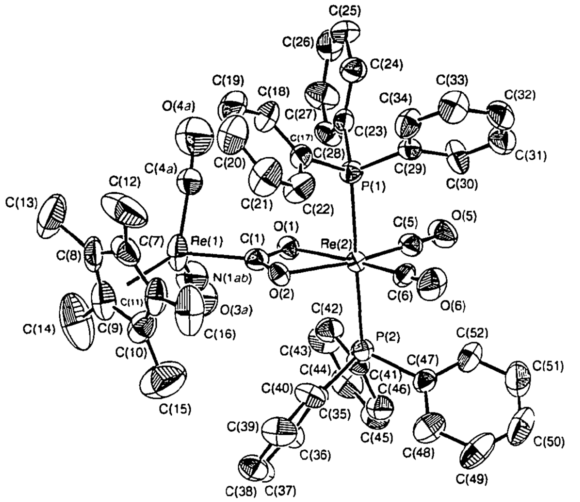

Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title complex showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Synthesis was carried out by the reaction of *mer,trans*-$Re(CO)_3(PPh_3)_2(O_2CCF_3)$ with excess $Cp^*Re(CO)(NO)COOH$ in toluene solution at 358 K in the presence of Na_2CO_3 (1:4:4 molar ratio) over 16 h. The product was purified by recrystallization from CH_2Cl_2/hexane.

Crystal data

$[Re_2(CO_2)(NO)(C_{10}H_{15})(C_{18}H_{15}P)_2(CO)_3]$
$M_r = 1190.27$
Monoclinic
$P2_1/n$
$a = 13.236\,(3)$ Å
$b = 17.146\,(5)$ Å
$c = 20.781\,(6)$ Å
$\beta = 103.04\,(2)°$
$V = 4595\,(2)$ Å^3
$Z = 4$
$D_x = 1.721$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–18°$
$\mu = 5.39$ mm^{-1}
$T = 296$ K
Block
0.33 × 0.20 × 0.14 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.218$, $T_{max} = 0.340$
8766 measured reflections
8559 independent reflections
5546 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = -15 \rightarrow 0$
$k = 0 \rightarrow 20$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: 3.6%

Refinement

Refinement on F
$R = 0.034$
$wR = 0.034$
$S = 1.59$
5545 reflections
543 parameters
H-atom parameters not refined, located from Δ maps
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.03$

$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -1.03$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 2.68×10^{-11}
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)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Re(1)	−0.28756 (3)	0.08073 (2)	0.17380 (2)	4.60 (1)
Re(2)	0.04831 (2)	0.17480 (2)	0.17337 (1)	2.378 (7)
P(1)	0.1056 (2)	0.1078 (1)	0.27784 (10)	2.74 (5)
P(2)	−0.0058 (2)	0.2415 (1)	0.06848 (9)	2.75 (5)
O(1)	−0.1045 (4)	0.1853 (3)	0.1954 (2)	2.9 (1)
O(2)	−0.0716 (4)	0.0837 (3)	0.1428 (2)	2.9 (1)
O(3*a*)†	−0.3574 (9)	0.2486 (7)	0.1409 (6)	6.9 (3)
O(3*b*)†	−0.350 (2)	0.244 (2)	0.186 (1)	9.5 (8)
O(4*a*)†	−0.212 (1)	0.0741 (8)	0.3221 (7)	8.3 (4)
O(4*b*)†	−0.252 (2)	0.103 (1)	0.314 (1)	5.7 (5)
O(5)	0.1547 (5)	0.3230 (4)	0.2336 (3)	4.9 (2)
O(6)	0.2406 (5)	0.1187 (4)	0.1306 (3)	5.4 (2)
N(1*ab*)	−0.3268 (8)	0.1821 (7)	0.1637 (5)	8.6 (3)
C(1)	−0.1382 (6)	0.1187 (5)	0.1690 (4)	3.0 (2)
C(4*b*)†	−0.273 (2)	0.102 (2)	0.252 (1)	3.8 (6)
C(4*a*)†	−0.239 (1)	0.0791 (9)	0.2654 (7)	3.6 (3)
C(5)	0.1172 (6)	0.2646 (5)	0.2095 (4)	3.2 (2)
C(6)	0.1684 (6)	0.1427 (5)	0.1479 (4)	3.4 (2)
C(7)	−0.3203 (8)	−0.0503 (5)	0.1543 (5)	4.9 (3)
C(8)	−0.4150 (8)	−0.0138 (7)	0.1575 (5)	5.6 (3)
C(9)	−0.4401 (7)	0.0406 (6)	0.1060 (6)	5.8 (3)
C(10)	−0.3611 (9)	0.0367 (6)	0.0696 (5)	5.2 (3)
C(11)	−0.2867 (7)	−0.0201 (6)	0.0988 (5)	4.8 (3)
C(12)	−0.271 (1)	−0.1162 (7)	0.1960 (6)	9.6 (4)
C(13)	−0.483 (1)	−0.0338 (8)	0.2039 (6)	10.0 (5)
C(14)	−0.5359 (9)	0.0912 (8)	0.0882 (8)	10.6 (5)
C(15)	−0.358 (1)	0.0816 (8)	0.0078 (6)	10.3 (5)
C(16)	−0.1995 (8)	−0.0501 (7)	0.0731 (6)	7.9 (4)
C(17)	0.0589 (6)	0.0078 (4)	0.2807 (4)	3.1 (2)
C(18)	0.0130 (7)	−0.0207 (5)	0.3290 (4)	4.4 (2)
C(19)	−0.0125 (9)	−0.0995 (6)	0.3279 (5)	5.8 (3)
C(20)	0.0104 (9)	−0.1500 (5)	0.2823 (6)	6.2 (3)
C(21)	0.0527 (9)	−0.1204 (6)	0.2330 (5)	6.1 (3)
C(22)	0.0770 (8)	−0.0423 (5)	0.2320 (5)	5.0 (3)
C(23)	0.0765 (6)	0.1534 (4)	0.3514 (4)	3.1 (2)
C(24)	0.1273 (6)	0.1296 (5)	0.4142 (4)	3.8 (2)
C(25)	0.1021 (7)	0.1606 (6)	0.4697 (4)	4.5 (2)
C(26)	0.0292 (7)	0.2181 (6)	0.4633 (4)	4.9 (3)
C(27)	−0.0197 (7)	0.2433 (6)	0.4016 (4)	5.1 (3)
C(28)	0.0024 (6)	0.2112 (5)	0.3459 (4)	3.7 (2)
C(29)	0.2476 (6)	0.0951 (5)	0.3025 (3)	3.0 (2)

C(30)	0.3102 (6)	0.1592 (5)	0.3025 (4)	4.4 (2)
C(31)	0.4170 (7)	0.1541 (5)	0.3224 (4)	4.8 (2)
C(32)	0.4639 (7)	0.0837 (6)	0.3415 (4)	4.7 (2)
C(33)	0.4028 (7)	0.0196 (5)	0.3419 (5)	4.8 (3)
C(34)	0.2952 (7)	0.0248 (5)	0.3230 (4)	4.3 (2)
C(35)	−0.0871 (6)	0.1873 (5)	−0.0003 (3)	2.9 (2)
C(36)	−0.1748 (6)	0.2186 (5)	−0.0419 (4)	3.5 (2)
C(37)	−0.2297 (7)	0.1741 (6)	−0.0942 (4)	4.6 (2)
C(38)	−0.1978 (7)	0.1009 (5)	−0.1063 (4)	4.3 (2)
C(39)	−0.1103 (8)	0.0700 (5)	−0.0649 (4)	4.9 (2)
C(40)	−0.0561 (7)	0.1128 (5)	−0.0119 (4)	3.9 (2)
C(41)	−0.0758 (6)	0.3336 (4)	0.0684 (3)	2.8 (2)
C(42)	−0.1354 (7)	0.3454 (5)	0.1150 (4)	3.9 (2)
C(43)	−0.1914 (7)	0.4136 (5)	0.1148 (4)	4.5 (2)
C(44)	−0.1883 (7)	0.4698 (5)	0.0682 (5)	4.6 (2)
C(45)	−0.1312 (7)	0.4593 (5)	0.0219 (4)	3.9 (2)
C(46)	−0.0764 (6)	0.3916 (5)	0.0210 (4)	3.6 (2)
C(47)	0.1021 (6)	0.2725 (5)	0.0325 (4)	3.2 (2)
C(48)	0.1067 (7)	0.2567 (6)	−0.0315 (4)	4.9 (3)
C(49)	0.1887 (9)	0.2840 (7)	−0.0582 (5)	6.3 (3)
C(50)	0.2658 (8)	0.3261 (7)	−0.0205 (6)	6.1 (3)
C(51)	0.2636 (8)	0.3427 (7)	0.0439 (6)	7.2 (3)
C(52)	0.1806 (8)	0.3161 (7)	0.0692 (5)	6.0 (3)

† Partial occupancy (see below).

Table 2. *Selected geometric parameters (Å)*

Re(1)—N(1*ab*)	1.81 (1)	Re(1)—C(1)	2.105 (8)
Re(1)—C(4*b*)	1.64 (3)	Re(1)—C(4*a*)	1.87 (1)
Re(1)—C(7)	2.306 (9)	Re(1)—C(8)	2.309 (9)
Re(1)—C(9)	2.290 (10)	Re(1)—C(10)	2.290 (9)
Re(1)—C(11)	2.328 (9)	Re(2)—P(1)	2.423 (2)
Re(2)—P(2)	2.423 (2)	Re(2)—O(1)	2.180 (5)
Re(2)—O(2)	2.215 (5)	Re(2)—C(5)	1.859 (8)
Re(2)—C(6)	1.868 (8)	P(1)—C(17)	1.829 (8)
P(1)—C(23)	1.832 (8)	P(1)—C(29)	1.847 (8)
P(2)—C(35)	1.834 (7)	P(2)—C(41)	1.831 (8)
P(2)—C(47)	1.835 (8)	O(1)—C(1)	1.302 (8)
O(2)—C(1)	1.285 (8)	O(3*b*)—N(1*ab*)	1.23 (3)
O(3*a*)—N(1*ab*)	1.27 (1)	O(4*b*)—C(4*b*)	1.25 (3)
O(4*a*)—C(4*a*)	1.16 (2)	O(5)—C(5)	1.177 (9)
O(6)—C(6)	1.168 (9)		

Range for phenyl C—C bond distances is 1.35–1.41 Å [average 1.38 (1) Å]. Range for internal Cp* C—C bond distances is 1.40–1.42 Å [average 1.41 (1) Å]. Range for *ipso*-C to Cp* C—C bond distances is 1.47–1.51 Å [average 1.50 (1) Å].

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); corrections for anomalous-dispersion effects were made. The structure was solved using heavy-atom Patterson methods (*SAPI*91; Fan, 1991) and expanded using Fourier techniques. All non-H atoms (not involved in the carbonyl or nitrosyl disorder) were refined anisotropically. H atoms were located by Δ maps but were not refined. The carbonyl disorder was modeled with C—O groups of occupancies 2/3 (C4*a*, O4*a*) and 1/3 (C4*b*, O4*b*). The nitrosyl was modeled with a common N atom (N1*ab*) and two O atoms having occupancies of 2/3 (O3*a*) and 1/3 (O3*b*). All computations were performed using the *TEXSAN* package (Molecular Structure Corporation, 1994).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a figure showing the disorder in the molecule, have been deposited with the IUCr (Reference: BK1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two ‘Ruthenium-Blue’ Precursors: Tri-μ-chloro-hexakis(dimethylphenylarsine)-diruthenium(II) Trifluoromethanesulfonate and Tri-μ-bromo-hexakis(trimethylarsine)-diruthenium(II) Trifluoromethanesulfonate

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Abstract

Confacial bi-octahedral $[Ru_2(\mu\text{-}Cl)_3(AsMe_2Ph)_6]CF_3SO_3$, (1), and $[Ru_2(\mu\text{-}Br)_3(AsMe_3)_6]CF_3SO_3$, (2), are the first tertiary-arsine-capped systems within the wider class of redox-active $[L_3Ru(\mu\text{-}X)_3RuL_3]^{+/2+}$ complexes (L = NR_3, PR_3 or AsR_3; X = Cl or Br) to be structurally characterized. Compounds (1) and (2) have measured internuclear separations and mean bridgehead angles (Ru$^{II}\cdots$Ru^{II}/Ru—X—Ru) of 3.275 (2)/83.5 and 3.413 (1) Å/81.8°, respectively.

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