$2\theta/\omega$ scans
Absorption correction:
  ψ scan (North *et al.*,
  1968)
  $T_{min} = 0.749$, $T_{max} = 0.833$
3618 measured reflections
3618 independent reflections

$\theta_{max} = 26.47°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 11$
3 standard reflections
  every 100 reflections
  intensity decay: $<1\%$

Refinement

Refinement on F
$R = 0.056$
$wR = 0.070$
$S = 1.433$
3180 reflections
192 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + 0.005F^2]$
$(\Delta/\sigma)_{max} = 0.0029$
$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction correction: none

Scattering factors from
  International Tables for
  Crystallography (Vol. C)
Absolute structure: all
  Bijvoet pairs of reflections
  were measured and used
  for determination of the
  absolute structure; the
  final absolute structure is
  the one which converged
  the Rogers parameter, η,
  to 1.01 (6)

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Table 1. *Selected geometric parameters (Å, °)*

Co1—O1	1.910 (3)	C2—C3	1.408 (6)
Co1—N11	1.976 (4)	C3—C4	1.401 (6)
Co1—N14	1.953 (4)	C3—O2	1.337 (6)
O1—N1	1.365 (4)	C4—C5	1.364 (6)
N1—C1	1.342 (5)	O2—C6	1.456 (7)
N1—C5	1.361 (5)	N11—C12	1.492 (7)
C1—C1^i	1.478 (5)	C12—C13	1.461 (8)
C1—C2	1.381 (6)	C13—N14	1.484 (7)
O1—Co1—O1^i	91.3 (2)	N1—C1—C2	120.8 (4)
O1—Co1—N11	177.1 (2)	C1^i—C1—C2	120.3 (4)
O1—Co1—N11^i	85.8 (2)	C1—C2—C3	118.5 (4)
O1—Co1—N14	94.6 (2)	C2—C3—C4	119.4 (4)
O1—Co1—N14^i	87.6 (2)	C2—C3—O2	124.0 (4)
N11—Co1—N11^i	97.1 (2)	C4—C3—O2	116.7 (4)
N11—Co1—N14	85.6 (2)	C3—C4—C5	119.3 (4)
N11—Co1—N14^i	92.3 (2)	N1—C5—C4	120.5 (4)
N14—Co1—N14^i	176.9 (2)	C3—O2—C6	118.3 (4)
Co1—O1—N1	115.8 (3)	Co1—N11—C12	107.6 (3)
O1—N1—C1	119.6 (3)	N11—C12—C13	106.3 (5)
O1—N1—C5	118.8 (3)	C12—C13—N14	107.9 (5)
C1—N1—C5	121.4 (4)	Co1—N14—C13	108.1 (3)
N1—C1—C1^i	118.9 (4)		

Symmetry code: (i) $x, -y, -z$.

The title structure was solved by direct methods and refined by full-matrix least-squares calculations using *CRYSTAN-GM* (Gilmore & Brown, 1988). H atoms were placed in geometrically idealized positions, with distances of 0.96 Å, and the equivalent isotropic displacement parameters were fixed at 0.06 Å^{-2}.

Data collection: *MXC Operation Manual* (MacScience Co. Ltd, 1989). Cell refinement: *MXC Operation Manual.* Data reduction: *CRYSTAN-GM.* Program(s) used to solve structure: *CRYSTAN-GM.* Program(s) used to refine structure: *CRYSTAN-GM.* Molecular graphics: *CRYSTAN-GM.* Software used to prepare material for publication: *CRYSTAN-GM.*

Carbonyl(1,3-diphenyl-1,3-propanedionato-*O,O'*)(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-*P*)rhodium(I)

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Abstract

The bicyclic phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane reacts in a 1:1 molar ratio with dicarbonyl(1,3-diphenyl-1,3-propanedionato-*O,O'*)-rhodium(I) to yield the title compound, [Rh(C$_{15}$H$_{11}$O$_2$)-(C$_5$H$_9$O$_3$P)(CO)], with square-planar geometry about the Rh atom. The Rh—P bond distance is 2.1690 (11) Å.

Comment

The syntheses, structure and reactivity of complexes of the type [Rh(β-diketonato)(CO)(*P*)], where *P* = phosphine and/or phosphite, form part of a study mainly focused upon relating the chemical and electrochemical oxidation behaviour of the rhodium centre. In order to manipulate the Lewis basicity of the rhodium centre

in [Rh(DBM)(CO)(PPh₃)] (DBM is the 1,3-diphenyl-1,3-propanedionate ion), the title compound [Rh(DBM)-(CO){P(OCH₂)₃CCH₃}], (I), was prepared by introducing the bicyclic phosphite ester as a strong π-acceptor ligand.
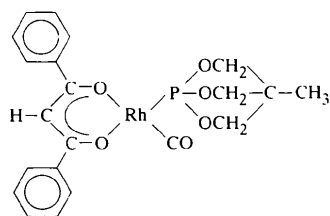
(I)

The structure of (I) is shown in Fig. 1. The compound exhibits square-planar geometry about the Rh atom. The carbonyl ligand is considered to be linear, with an Rh—C16—O3 angle of 179.4 (5)°. The larger *trans* influence of the phosphite ligand in comparison with the carbonyl ligand is illustrated in the difference of 0.028 Å between Rh—O2 [2.059 (3) Å] and Rh—O1 [2.031 (3) Å]. This tendency has been observed previously in the triphenylphosphine analogue [Rh(DBM)(CO)(PPh₃)] (Lamprecht *et al.*, 1997), as well as in the acetylacetonate (ACAC) complex [Rh(ACAC)-(CO)(PPh₃)] (Leipoldt *et al.*, 1978). The enhanced π-accepting ability of the bicyclic phosphite ligand compared with triphenylphosphine is clearly demonstrated in the difference of 0.072 Å between the Rh—P bond distances in the title compound [2.1690 (11) Å] and in [Rh(DBM)(CO)(PPh₃)] [2.241 (5) Å, representing the average distance in two crystallographically independent molecules; Lamprecht *et al.*, 1997].
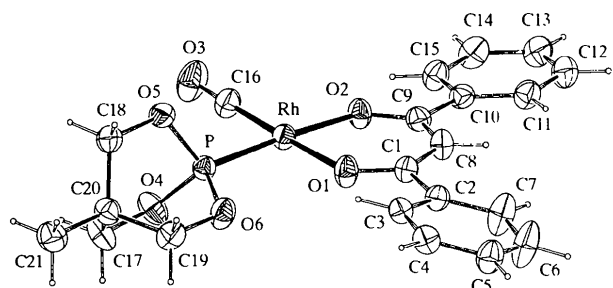

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atom-numbering scheme. Displacement ellipsoids correspond to the 30% probability level.

Back donation to the phosphite ligand tends to reduce electron density on the central metal atom to a larger extent compared with PPh₃, leading to a weakened ability to reduce the carbonyl bond order in the case of the title compound. This is demonstrated by comparing the carbonyl stretching frequency (ν_{CO} = 1992 cm⁻¹) with those observed in the case of the triphenylphosphine analogue (ν_{CO} = 1972 and 1982 cm⁻¹ representing the two molecules in the asymmetric unit).

The small Tolman (1977) cone angle of the caged phosphite (101°) compared with PPh₃ (145°) suggests reduced steric interaction in the case of the title compound compared with the PPh₃ analogue. Very slight rotation about the C1—C2 bond does occur, minimizing steric interaction between the phenyl group and the *cis*-located phosphite; the dihedral angle between the best plane through atoms O1, C1, C8, C9 and O2, and that through C1–C7 is 14.7 (3)°.

Experimental

The title compound was prepared by reacting a well stirred solution of dicarbonyl(1,3-diphenyl-1,3-propanedionato)-rhodium(I) (62 mg, 0.162 mmol; Lamprecht *et al.*, 1984) in 5 ml of a 6:4 mixture of ethanol and acetone with exactly one equivalent of solid resublimed 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (26 mg, 0.176 mmol; Heitsch & Verkade, 1962) at room temperature. Vigorous evolution of carbon monoxide gas indicated substitution of the carbonyl ligand. The bright yellow precipitate which separated after a few minutes was redissolved by heating the stirred solution to *ca* 323 K. Hot filtration through a short Celite column yielded a dark-yellow concentrated solution which was covered and left to cool down to room temperature. Light-yellow prismatic crystals suitable for X-ray analysis separated after *ca* 4 h (51 mg, *ca* 63% yield). ¹H NMR (acetone-*d₆*): δ 0.93 (*s*, 3H, CH₃), 7.11 (*s*, 1H, CH). ³¹P NMR (acetone): δ 114.51 (*d*, 1P, ¹J_{Rh-P} = 282.03 Hz).

Crystal data

[Rh(C₁₅H₁₁O₂)(C₅H₉O₃P)-(CO)]	Mo *K*α radiation
M_r = 502.26	λ = 0.7107 Å
Monoclinic	Cell parameters from 24
$P2_1/a$	reflections
a = 11.715 (2) Å	θ = 19.9–20.0°
b = 11.385 (5) Å	μ = 0.933 mm⁻¹
c = 16.071 (3) Å	T = 298.2 K
β = 104.57 (1)°	Prismatic
V = 2074.6 (10) Å³	0.37 × 0.37 × 0.20 mm
Z = 4	Light yellow
D_x = 1.608 Mg m⁻³	
D_m = 1.605 Mg m⁻³	
D_m measured by flotation in NaI/H₂O solution	

Data collection

Rigaku AFC-7*R* diffractometer	3720 reflections with
ω–2θ scans	$I > 2\sigma(I)$
Absorption correction:	R_{int} = 0.038
ψ scan (North *et al.*, 1968)	θ_{max} = 27.50°
	h = −14 → 15
	k = 0 → 14
T_{min} = 0.550, T_{max} = 0.830	l = −20 → 0
5179 measured reflections	3 standard reflections
4764 independent reflections	every 150 reflections
	intensity decay: 0.76%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.187$
$S = 1.175$
4764 reflections
264 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1279P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.924$ e Å^{-3}
$\Delta\rho_{min} = -1.865$ e Å^{-3}
Extinction correction:
  SHELXL97
Extinction coefficient:
  0.0054 (13)
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Rh—P	2.1690 (11)	O1—C1	1.270 (5)
Rh—O1	2.031 (3)	O2—C9	1.281 (6)
Rh—O2	2.059 (3)	O3—C16	1.139 (6)
Rh—C16	1.803 (5)	C1—C2	1.496 (6)
P—O4	1.587 (4)	C9—C10	1.492 (6)
P—O5	1.588 (3)	C20—C21	1.544 (6)
P—O6	1.582 (3)		
O1—Rh—P	91.57 (10)	C16—Rh—O2	92.78 (19)
O2—Rh—P	176.07 (11)	O4—P—Rh	114.78 (14)
O1—Rh—O2	88.06 (14)	O5—P—Rh	118.03 (13)
C16—Rh—P	87.75 (17)	O6—P—Rh	114.36 (13)
C16—Rh—O1	177.4 (2)	O3—C16—Rh	179.4 (5)

H atoms were allowed for as riding atoms with C—H = 0.93–0.97 Å. The H atoms on the methyl C21 atom were allowed to rotate but not tip around the C20—C21 bond. The largest positive maximum (0.924 e Å^{-3}) in the final difference map was at 1.42 Å from the Rh atom and the largest negative minimum (−1.865 e Å^{-3}) was at 0.73 Å from the Rh atom.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1995). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1997). Software used to prepare material for publication: *TEXSAN* and *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1391). Services for accessing these data are described at the back of the journal.

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Iodo(1,10-phenanthroline-N,N')(triphenylphosphine)copper(I)

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Abstract

In the title complex, [CuI(C$_{12}$H$_8$N$_2$)(C$_{18}$H$_{15}$P)], phenanthroline acts as a bidentate ligand coordinating via two N atoms to copper. The coordination polyhedron around the Cu atom is a distorted tetrahedron, with a Cu—P distance of 2.1977 (9) Å, Cu—N distances of 2.111 (3) and 2.071 (3) Å, and a Cu—I distance of 2.6157 (6) Å.

Comment

In the course of our work on the synthesis of Mo(W)–Cu–S clusters containing large N-donor ligands, the title complex, (I), was prepared and used as one of the reactants.
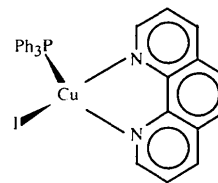
(I)

The [Cu(phen)(PPh$_3$)]$^+$ cation of the title complex (where phen is 1,10-phenanthroline) can be regarded as being analogous to the [Cu(phen)(PPh$_3$)$_2$]$^{2+}$ cation of [Cu(phen)(PPh$_3$)$_2$]NO$_3$.1.5EtOH, (II) (Kirchhoff et