

Mo2—O14	1.871 (4)	Mo9—O35	1.825 (4)
Mo2—O15	1.876 (3)	Mo9—O36	1.890 (4)
Mo2—O7	1.960 (3)	Mo9—O13	1.969 (3)
Mo2—O5	1.984 (3)	Mo9—O31	2.020 (3)
Mo3—O5	1.814 (3)	Mo10—O18	1.887 (3)
Mo3—O12	1.832 (4)	Mo10—O23	1.896 (3)
Mo3—O21	2.016 (4)	Mo10—O36	1.950 (4)
Mo3—O22	2.074 (4)	Mo10—O10	1.956 (4)
Mo4—O29	1.836 (4)	Mo11—O19	1.837 (4)
Mo4—O6	1.865 (4)	Mo11—O10	1.857 (4)
Mo4—O19	1.985 (4)	Mo11—O9	1.964 (4)
Mo4—O35	2.001 (4)	Mo11—O11	2.037 (4)
Mo5—O31	1.845 (3)	Mo12—O21	1.841 (4)
Mo5—O7	1.861 (3)	Mo12—O16	1.863 (4)
Mo5—O18	1.979 (4)	Mo12—O17	1.955 (4)
Mo5—O12	2.037 (3)	Mo12—O26	2.017 (4)
Mo6—O11	1.796 (4)	P1—O1A	1.467 (4)
Mo6—O17	1.879 (4)	P1—N1A	1.595 (5)
Mo6—O23	1.947 (3)	P1—N2A	1.610 (5)
Mo6—O22	2.112 (3)	P1—N3A	1.806 (5)
Mo7—O4	1.881 (4)	P2—O1B	1.495 (5)
Mo7—O20	1.910 (4)	P3—O1C	1.497 (5)
Mo7—O16	1.949 (4)	P4—O1D	1.501 (5)
Mo7—O14	1.995 (4)	P5—O1E	1.524 (4)
C6A—N3A—C5A	108.7 (5)	C5A—N3A—P1	118.7 (4)
C6A—N3A—P1	109.5 (4)		

The Mo atoms were first located by direct methods and successive full-matrix least-squares refinements revealed the complete structure. 23 H atoms were located from successive difference Fourier maps and were refined isotropically. A further 69 H atoms were positioned geometrically and were then allowed to ride on their parent C atoms. One of the water molecules (O2W) is disordered and its H atoms were not located, and neither were the four attached to the molybdosilicate residue. The two highest peaks in the difference Fourier map lie close to Mo5 (0.731 Å) and Mo9 (0.738 Å).

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Geometrical calculations: PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1354). Services for accessing these data are described at the back of the journal.

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1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2- $[\mu$ -bis(diphenylphosphino)methane- P' , P'']-3-(trimethylphosphite- P)-triangulotruthenium(0)†

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Abstract

In $[\text{Ru}_3(\text{C}_3\text{H}_9\text{O}_3\text{P})(\text{C}_{25}\text{H}_{22}\text{P}_2)(\text{CO})_9]$, one Ru—Ru bond is slightly longer than the other two and axial Ru—CO bonds are longer than corresponding equatorial bonds. The bridging bis(diphenylphosphino)methane (dppm) forms longer P—Ru distances than the equatorial trimethylphosphite ligand.

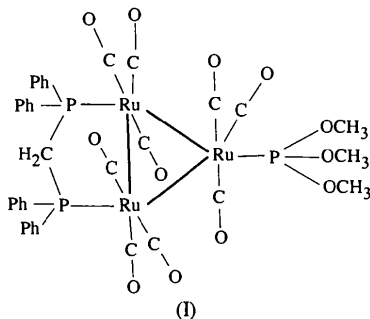
Comment

Extensive synthetic studies have been performed on mixed-ligand triruthenium cluster carbonyls (Bruce, Liddel, Hughes *et al.*, 1988; Bruce, Kehoe *et al.*, 1982; Bruce, Nicholson *et al.*, 1983; Bruce, Matison *et al.*, 1982; Bruce, Liddel, Shawkataly *et al.*, 1988). In particular, mixed-ligand cluster carbonyls with group 15

† Alternative name: μ -bis(diphenylphosphino)methane- $1\kappa^3P:2\kappa^3P$ -nonacarbonyl- $1\kappa^3C,2\kappa^3C,3\kappa^3C$ -trimethylphosphite- $3\kappa^3P$ -triangulo-triruthenium(0)(3 Ru—Ru).

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donor-atom ligands are of special interest because of their catalytic activity. Furthermore, the group 15 ligands allow a degree of tuning of the reactivity of the clusters (Bruce, Matison *et al.*, 1983). However, structural reports on complexes [Ru₃(CO)₉(dppm)(L)] (where dppm is Ph₂PCH₂PPh₂ and L is PR₃) are sparse (Adams *et al.*, 1994). The crystal structure of [Ru₃(CO)₉(dppm){P(OCH₃)₃}] (I), is reported in this paper.



Two of the Ru—Ru distances are almost equal [2.8515(4) and 2.8473(4) Å], whereas the third bond is somewhat longer [2.8760(3) Å]. A similar variation is observed in the parent compound (Churchill *et al.*, 1977). The axial Ru—CO bond lengths [1.910(3)–1.944(3) Å] are longer than the equatorial bonds [1.879(3)–1.890(4) Å], as observed in [Ru₃(CO)₁₂] and [Ru₃(CO)₁₀(dppm)] (Churchill *et al.*, 1977; Coleman *et al.*, 1984). Ru—P bond distances involving the chelating dppm are similar [2.325(1) and 2.324(1) Å], but the equatorial Ru3—P3 bond distance [2.264(1) Å] is significantly shorter, being close to the value observed in [Ru₃(C)₁₁{P(OMe)₃}] by Shawkataly *et al.* (1991). Other distances and angles in (I) are unexceptional.

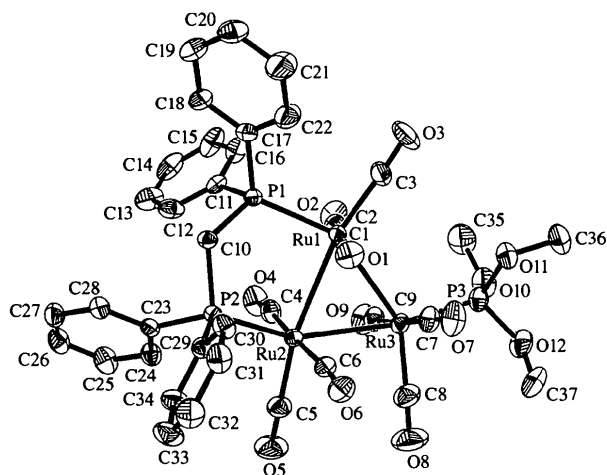


Fig. 1. A view of (I) showing 30% probability ellipsoids. H atoms have been omitted for clarity.

Experimental

A mixture of [Ru₃(CO)₁₀(dppm)] and P(OCH₃)₃ in dry THF (1:1 ratio) under nitrogen was treated with diphenylketyl radical and the product separated by thin-layer chromatography and recrystallized from CH₂Cl₂ and CH₃OH.

Crystal data

[Ru₃(C₃H₉O₃P)(C₂₅H₂₂P₂)-
(CO)₉]
M_r = 1063.74
Monoclinic
P2₁/n
a = 17.491 (2) Å
b = 12.428 (1) Å
c = 19.081 (2) Å
β = 96.18 (1)°
V = 4123.7 (7) Å³
Z = 4
D_x = 1.713 Mg m⁻³
D_m not measured

Mo Kα radiation
λ = 0.71073 Å
Cell parameters from 51 reflections
θ = 2.00–12.52°
μ = 1.260 mm⁻¹
T = 293 (2) K
Prismatic
0.96 × 0.88 × 0.72 mm
Red brown

Data collection

Siemens P4 diffractometer
θ/2θ scans
Absorption correction:
empirical ψ scans
(XSCANS; Siemens, 1994)
T_{min} = 0.705, T_{max} = 0.787
11 264 measured reflections
9407 independent reflections
8100 reflections with
I > 2σ(I)

R_{int} = 0.015
θ_{max} = 27.50°
h = -1 → 22
k = -1 → 16
l = -24 → 24
3 standard reflections
every 97 reflections
intensity decay: <3%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.027
wR(F²) = 0.075
S = 1.029
9407 reflections
496 parameters
H atoms riding on parent C
atom

w = 1/[σ²(F_o²) + (0.0383P)²
+ 1.0529P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.004
Δρ_{max} = 0.407 e Å⁻³
Δρ_{min} = -0.557 e Å⁻³
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ru1—P1	2.3251 (7)	P2—C29	1.833 (2)
Ru1—Ru2	2.8515 (4)	P2—C23	1.833 (2)
Ru1—Ru3	2.8760 (3)	P2—C10	1.853 (2)
Ru2—P2	2.3242 (7)	P3—O11	1.590 (2)
Ru2—Ru3	2.8473 (4)	P3—O10	1.591 (2)
Ru3—P3	2.2642 (8)	P3—O12	1.606 (2)
P1—C11	1.822 (3)	O10—C35	1.403 (5)
P1—C17	1.838 (2)	O11—C36	1.453 (4)
P1—C10	1.842 (2)	O12—C37	1.432 (5)
C3—Ru1—Ru2	166.99 (9)	C5—Ru2—Ru1	162.28 (11)
C1—Ru1—Ru2	80.50 (8)	C4—Ru2—Ru1	80.68 (9)
C2—Ru1—Ru2	96.69 (9)	C6—Ru2—Ru1	97.22 (8)

P1—Ru1—Ru2	90.03 (2)	P2—Ru2—Ru1	94.28 (2)
C3—Ru1—Ru3	109.18 (10)	Ru3—Ru2—Ru1	60.618 (7)
C1—Ru1—Ru3	90.82 (8)	C8—Ru3—Ru2	88.70 (12)
C2—Ru1—Ru3	83.26 (9)	C7—Ru3—Ru2	94.86 (9)
P1—Ru1—Ru3	148.94 (2)	C9—Ru3—Ru2	86.35 (10)
Ru2—Ru1—Ru3	59.619 (9)	P3—Ru3—Ru2	170.91 (2)
C5—Ru2—P2	102.19 (11)	C8—Ru3—Ru1	148.07 (12)
C4—Ru2—P2	94.06 (9)	C7—Ru3—Ru1	82.59 (9)
C6—Ru2—P2	91.38 (8)	C9—Ru3—Ru1	92.52 (10)
C5—Ru2—Ru3	104.27 (11)	P3—Ru3—Ru1	111.76 (2)
C4—Ru2—Ru3	92.80 (9)	Ru2—Ru3—Ru1	59.762 (9)
C6—Ru2—Ru3	81.57 (8)	P1—C10—P2	115.25 (12)
P2—Ru2—Ru3	152.44 (2)		

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*. Program used for geometric calculations: *PARST* (Nardelli, 1983).

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A Novel Cyclotriphosphazene Complex with a Short Transannular P...P Contact

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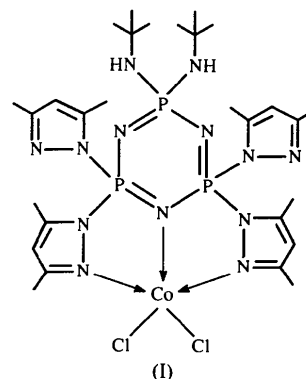
(Received 11 April 1997; accepted 3 November 1997)

Abstract

The structure of dichloro[2,2-di-*tert*-butylamino-4,4,6,6-tetrakis(3,5-dimethylpyrazolyl)cyclotriphosphazene]cobalt(II), [CoCl₂(C₂₈H₄₈N₁₃P₃)], exhibits an unusual transannular P...P interaction.

Comment

Interest in heterocycles such as cyclotriphosphazenes results from their novel reactivity towards various organometallic reagents and transition metal ions, and their industrial applications (Allcock *et al.*, 1987; Chandrasekhar & Thomas, 1993). Pyrazolyl-substituted cyclotriphosphazenes have been shown to possess interesting coordination chemistry (Thomas *et al.*, 1993, 1994; Chandrasekaran *et al.*, 1994; Byun *et al.*, 1996). In an attempt to study the electronic and steric effect exerted by the substituents on the coordination behaviour of the cyclotriphosphazene moiety, we have synthesized the title compound, (I), which includes two bulky *tert*-butylamino groups.



In (I), the Co^{II} atom assumes a distorted trigonal-bipyramidal geometry comprising of two pyrazolyl N atoms, a cyclophosphazene N atom and two Cl[−] ions. The trigonal plane contains two Cl[−] ions and a cyclophosphazene N atom. The Co—Cl distances are simi-

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