

Dichlorobis(triphenylphosphine oxide)magnesium

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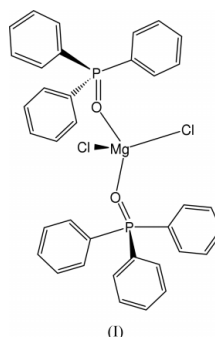
Key indicators

Single-crystal X-ray study
 $T = 90$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.023
 wR factor = 0.061
Data-to-parameter ratio = 24.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The compound $[\text{MgCl}_2(\text{C}_{18}\text{H}_{15}\text{OP})_2]$ was inadvertently crystallized during a reaction involving magnesium germanide. It is isostructural to the Mn, Co, Cu and Zn analogs. Since four-coordinate Mg is rare, its structure is reported here. The Mg atom lies on a twofold axis and is surrounded by two O atoms and two Cl atoms in a distorted tetrahedral coordination geometry.

Comment

Dichlorobis(triphenylphosphine oxide)magnesium, (I), was prepared serendipitously from the reaction of germanium tetrachloride, triphenylphosphine and magnesium germanide in 2-methoxyethyl ether. We were interested in trapping intermediates formed during the preparation of germanium nanoclusters (Taylor *et al.*, 1999) with triphenylphosphine and obtained colorless parallelepiped crystals of (I).



Crystals of (I) are orthorhombic and crystallize in space group $Fdd2$, as do its analogs where magnesium is replaced by zinc (Rose *et al.*, 1980; Kosky *et al.*, 1982), copper (Bertrand & Kalyanaraman, 1971; Weinberger *et al.*, 1997), cobalt (Cotton *et al.*, 2002), and manganese (Tomita, 1985). The only notable difference is that (I) has a more idealized tetrahedral coordination, with bond angles about the metal atom ranging from $101.44(5)$ to $113.54(3)^\circ$. The Mg atom lies on a twofold axis. Table 1 compares various geometric parameters of the M^{II} isomorphs. The dihedral angle between the $\text{O}-\text{M}-\text{O}'$ and $\text{Cl}-\text{M}-\text{Cl}'$ planes is another measure of distortion from idealized tetrahedral geometry, since an angle of 90° would correspond to tetrahedral and 0° would correspond to square planar. This angle is similar in all of the complexes except in the Cu complex. It shows considerable flattening of the tetrahedral geometry, as has been previously noted (Rose *et al.*, 1980; Kosky *et al.*, 1982; Weinberger *et al.*, 1997). Compound (I) is soluble in polar organic solvents, such as chloroform and dichloromethane, supporting the use of phosphine oxides as extraction agents for alkaline earth metals (Arnaud-Neu *et al.*, 1999).

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Experimental

2-Methoxyethyl ether was distilled twice under argon from sodium and benzophenone prior to use. A degassed solution of triphenylphosphine (0.345 g, 1.32 mmol), germanium tetrachloride (0.15 ml, 0.282 g, 1.32 mmol) and 20 ml of 2-methoxyethyl ether was added to a 250 ml Schlenk flask containing magnesium germanide (53 mg, 0.437 mmol) and 2-methoxyethyl ether (20 ml). The resultant mixture was refluxed for 18 h and cooled. Volatiles were removed *in vacuo*. Solids were dissolved in 10 ml of dried, degassed dichloromethane and separated from a small amount of solids *via* a cannula. Over the period of several months crystals of (I) formed from this solution.

Crystal data

[MgCl₂(C₁₈H₁₅OP)₂]
M_r = 651.75
 Orthorhombic, *Fdd*2
a = 20.786 (2) Å
b = 32.459 (3) Å
c = 9.7270 (11) Å
V = 6562.8 (12) Å³
Z = 8
D_x = 1.319 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 718 reflections
 $\theta = 2.3\text{--}30.5^\circ$
 $\mu = 0.35\text{ mm}^{-1}$
T = 90 (2) K
 Parallelepiped, colorless
 0.43 × 0.23 × 0.13 mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.865, *T_{max}* = 0.956
 21340 measured reflections

4774 independent reflections
 4691 reflections with *I* > 2σ(*I*)
R_{int} = 0.020
 $\theta_{\text{max}} = 30.0^\circ$
h = -26 → 26
k = -45 → 45
l = -13 → 13

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.023
wR (*F*²) = 0.061
S = 1.07
 4774 reflections
 196 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 2.5125P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.32\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.16\text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 2262 Friedel pairs
 Flack parameter = 0.03 (3)

Table 1

Comparison of geometric parameters (Å, °) for MCl₂(OPPh₃)₂ (*M* = Mg, Mn, Cu, Co, Zn).

<i>M</i> ^{II}	<i>M</i> —O	<i>M</i> —Cl	<i>M</i> —O—P	Dihedral	Range of angles at <i>M</i> ^{II}
Mg ^a	1.9401 (8)	2.2889 (4)	157.64 (6)	88.0	101.4–113.5
Mn ^b	2.069 (6)	2.294 (3)	156.0 (4)	87.5	98.6–115.7
Co ^c	1.971 (2)	2.2269 (10)	153.5 (2)	87.8	97.9–112.8
Cu ^d	2.011 (3)	2.132 (2)	148.5 (2)	71.4	89.7–127.8
Zn ^e	1.974 (5)	2.204 (2)	153.4 (3)	87.7	96.8–116.3
Zn ^f	1.967 (5)	2.187 (3)	154.1 (3)	87.8	97.0–117.2

References: (a) this work; (b) Tomita, 1985; (c) Cotton *et al.* (2002); (d) Weinberger *et al.* (1997); (e) Rose *et al.* (1980); (f) Kosky *et al.* (1982).

Phenyl H atoms were placed at idealized positions and refined using a model whereby the H atom was riding on the bonded carbon at a distance of 0.95 Å and with an isotropic *U* value equal to 1.2 times the equivalent isotropic *U* of the bonded carbon.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve

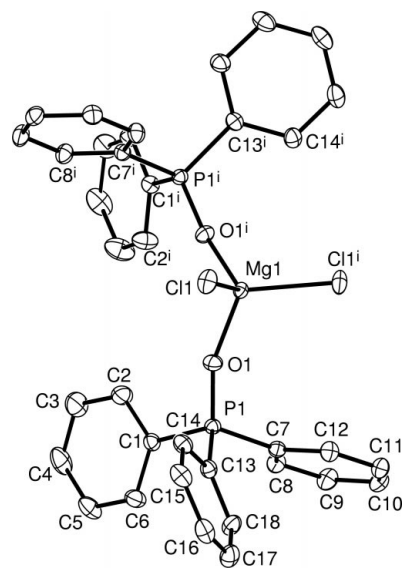


Figure 1

View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, z$.]

structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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