

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 5481 measured reflections
 5011 independent reflections
 2984 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.010$
 $\theta_{\text{max}} = 29.97^\circ$
 $h = -16 \rightarrow 16$
 $k = 0 \rightarrow 11$
 $l = -25 \rightarrow 17$
 2 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.090$
 $S = 1.194$
 5011 reflections
 217 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.6101P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.486 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.360 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å , $^\circ$)

Ni—O	1.830 (2)	N3—C1	1.332 (3)
Ni—N3	1.831 (2)	N2—C1	1.300 (3)
Ni—N1	1.847 (2)	C1—S	1.765 (2)
Ni—N4	1.916 (2)	C3—C5	1.413 (3)
N1—C3	1.321 (3)	S—C2	1.782 (3)
N1—N2	1.405 (2)	C6—C5	1.365 (3)
O—C6	1.308 (2)		
O—Ni—N3	177.85 (7)	O—Ni—N4	88.62 (7)
O—Ni—N1	96.10 (7)	N3—Ni—N4	93.01 (8)
N3—Ni—N1	82.28 (8)	N1—Ni—N4	175.28 (7)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local modification of *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1411). Services for accessing these data are described at the back of the journal.

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Dichloro[(cyclopentadienyl)tris(dimethylphosphito-*P*)cobalt(III)-*O, O', O''*]oxomolybdenum(V)†

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Abstract

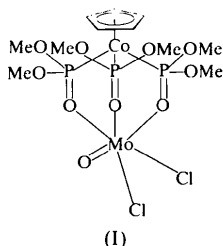
In the title compound, [(C₅H₅)Co{P(O)(OCH₃)₂}₃MoOCl₂], an oxomolybdenum(V) unit binds to two chloro ligands and one tripodal oxygen-donating ligand. The coordination geometry around the Mo atom is a distorted octahedron.

Comment

The oxochloromolybdenum complex [(C₅H₅)MoOCl₂] (Cousins & Green, 1964) was obtained from [(C₅H₅)MoCl₄(thf)] (thf is tetrahydrofuran) and its structure was suggested on the basis of infrared spectroscopy. [HB(pyrazol-1-yl)₃MoOCl₂] (Lincoln & Koch, 1986) was produced by the reaction of [HB(pyrazol-1-yl)₃MoCl₃] with O₂ in dry CH₂Cl₂ and fully characterized by X-ray diffraction analysis. [HB(3,5-dimethylpyrazol-1-yl)₃MoCl₂] (Cleland *et al.*, 1987) was also isolated but was not fully characterized. More recently, [CpCo{P(O)(OMe)₂}₃]WObBr₂ (Kläui *et al.*, 1995) was identified

† Systematic name: dichloro-1 κ^2 -Cl-[2(η^5)-cyclopentadienyl]tris[μ -dimethoxyoxophosphato(1-)-1:2 κ^2 O:P](oxo-1 κ O)cobalt(III)-molybdenum(V).

by elemental analysis and infrared spectroscopy. $[\text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]\text{MoOCl}_2$ (Kläui *et al.*, 1987) and $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]\text{MoOCl}_2$ (Kläui & Hardt, 1996) have been reported, but have not been fully characterized. We obtained the title compound, $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]\text{MoOCl}_2$, (I), from a wet dichloromethane solution of the product afforded from the reaction of $\text{MoCl}_4(\text{thf})_2$ with $\text{Na}[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]$ in dry tetrahydrofuran.



The coordination geometry around the Mo atom is a distorted octahedron, consisting of O1, O2 and O3 from the $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]$ ligand, and two Cl atoms and one terminal O atom. The bond angles between the *cis*-position atoms are in the range $81.2(1)$ – $97.8(1)^\circ$ and those between the *trans*-position atoms are in the range $166.73(9)$ – $172.5(1)^\circ$. The Mo—O distance is $1.734(3)$ Å, which is longer than that in $[\text{HB}(\text{pyrazol-1-yl})_3]\text{MoOCl}_2$ [$1.670(4)$ and $1.671(4)$ Å; Lincoln & Koch, 1986]. This implies that the $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]$ ligand is a stronger electron donor than the $[\text{HB}(\text{pyrazol-1-yl})_3]$ ligand. The Mo—O3 dis-

tance is $2.171(3)$ Å, which is longer than the Mo—O1 and Mo—O2 distances [$2.054(3)$ and $2.042(3)$ Å, respectively], showing the strong *trans*-influence of the oxo group. The Mo—Cl1 and Mo—Cl2 bond lengths [both $2.3384(12)$ Å] are similar to those in $[\text{HB}(\text{pyrazol-1-yl})_3]\text{MoOCl}_2$ [$2.346(2)$ and $2.364(2)$ Å; Lincoln & Koch, 1986]. Other numerical parameters of the $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]$ ligand are comparable with those in $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]_2\text{La}(\text{OH}_2)_2\text{Cl}_2$ (Cho *et al.*, 1995), $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]\text{Y}(\text{acetate})$ (Kim *et al.*, 1996) or $[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]\text{Y}(\text{acetylacetonate})$ (Kim *et al.*, 1997).

Experimental

Dry tetrahydrofuran (40 ml) was introduced into a mixture of $[\text{MoCl}_4(\text{thf})_2]$ (0.244 g, 0.640 mmol) and $\text{Na}[\text{CpCo}\{\text{P}(\text{O})(\text{OMe})_2\}_3]$ (0.303 g, 0.640 mmol), both prepared according to literature methods (Dilworth & Richards, 1980; Kläui, 1979). The yellow–brown suspension was stirred for 5 d at ambient temperature. The resulting solution was evaporated *in vacuo* and the residue was extracted with wet dichloromethane. The solution was evaporated slowly to afford green crystals of (I) (0.217 g, 59% yield based on Mo). This compound is stable in air. An NMR study was not carried out due to the paramagnetism of (I). Analysis calculated for $\text{C}_{11}\text{H}_{23}\text{Cl}_2\text{CoMoO}_{10}\text{P}_3$: C 20.83, H 3.65%; found: C 20.87, H 3.60%; IR (KBr, pellet): 3099 (*m*), 2995 (*m*), 2949 (*s*), 2899 (*m, sh*), 2814 (*m*), 2441 (*m*), 1791 (*w*), 1614 (*w*), 1456 (*w*), 1429 (*w*), 1338 (*w*), 1263 (*w*), 1263 (*w*), 1176 (*m, sh*), 1078 (*vs, sh*), 1035 (*vs*), 956 (*s*), 842 (*w*), 794 (*s*), 742 (*s*), 657 (*w*), 638 (*w*), 594 (*m*), 468 (*m*) cm^{-1} .

Crystal data

$[\text{CoMo}(\text{C}_5\text{H}_5)(\text{C}_2\text{H}_6\text{O}_3\text{P})_3\text{Cl}_2\text{O}]$
 $M_r = 633.97$
 Monoclinic
 $P2_1/n$
 $a = 9.7378(5)$ Å
 $b = 14.9883(7)$ Å
 $c = 15.4828(10)$ Å
 $\beta = 100.244(5)^\circ$
 $V = 2223.7(2)$ Å³
 $Z = 4$
 $D_x = 1.894$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10$ – 15°
 $\mu = 1.810$ mm⁻¹
 $T = 293(2)$ K
 Rectangular block
 $0.6 \times 0.6 \times 0.2$ mm
 Green

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scan
 Absorption correction: ψ scan (Fair, 1990)
 $T_{\min} = 0.353$, $T_{\max} = 0.690$
 3999 measured reflections
 3858 independent reflections
 3466 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.011$
 $\theta_{\text{max}} = 25.51^\circ$
 $h = -11 \rightarrow 11$
 $k = 0 \rightarrow 18$
 $l = 0 \rightarrow 18$
 2 standard reflections
 frequency: 60 min
 intensity decay: 0.01%

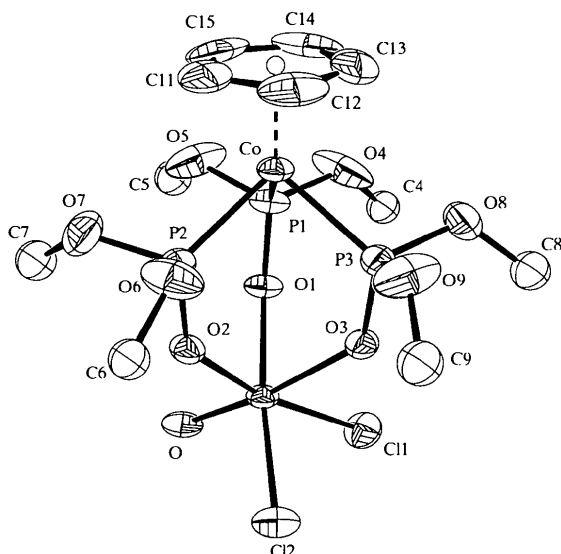


Fig. 1. The molecular structure of (I) showing 40% probability displacement ellipsoids. H atoms have been omitted for clarity. The methoxy groups have their C atoms disordered over two sites and, for clarity, only one of these positions is shown.

Refinement

Refinement on F^2 $R = 0.039$ $wR = 0.108$ $S = 1.080$

3858 reflections

247 parameters

H atoms constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0601P)^2]$ $+ 4.7336P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.900 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -1.122 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Mo—O	1.734 (3)	Co—P1	2.1473 (13)
Mo—O2	2.042 (3)	Co—P3	2.1519 (13)
Mo—O1	2.054 (3)	Co—P2	2.1555 (13)
Mo—O3	2.171 (3)	P1—O1	1.525 (3)
Mo—Cl1	2.3384 (12)	P2—O2	1.521 (3)
Mo—Cl2	2.3384 (12)	P3—O3	1.514 (3)
O—Mo—O2	93.71 (14)	O3—Mo—Cl1	85.74 (9)
O—Mo—O1	92.96 (14)	O—Mo—Cl2	97.77 (12)
O2—Mo—O1	85.88 (12)	O2—Mo—Cl2	89.12 (9)
O—Mo—O3	172.54 (13)	O1—Mo—Cl2	168.44 (9)
O2—Mo—O3	81.16 (12)	O3—Mo—Cl2	87.62 (9)
O1—Mo—O3	81.32 (12)	Cl1—Mo—Cl2	92.46 (5)
O—Mo—Cl1	99.12 (12)	P1—Co—P3	89.40 (5)
O2—Mo—Cl1	166.73 (9)	P1—Co—P2	92.44 (5)
O1—Mo—Cl1	90.08 (9)	P3—Co—P2	90.33 (5)

All phosphite methyl groups were disordered and their C atoms were refined on U_{iso} and with an occupancy factor of 0.5. No disorder was resolved for the Cp ring atoms, but they display large torsional displacements. The largest difference map features lie close to Mo. H atoms were constrained with a riding model and with $U(\text{H})$ fixed at 1.5 (Me) or 1.2 (Cp) times U_{eq} of the parent atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (McArdle, 1995). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1313). Services for accessing these data are described at the back of the journal.

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Trimethylgermylethyl *p*-nitrobenzoate†

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Abstract

The structure of the title compound, C₁₂H₁₇GeNO₄ or [Ge(CH₃)₃(C₉H₈NO₄)], was determined as part of ongoing studies of the properties of esters substituted in the β position with group IV metal atoms. The conformation of the Ge—C—C—O moiety is *gauche*, the CH₂—O distance is 1.463 (3) Å, the average Ge—Me distance is 1.944 (3) Å and the Ge—CH₂ distance is 1.966 (3) Å.

Comment

As part of our general interest in the structural consequences of the σ — σ^* interaction between the high-lying C—M σ -bonding orbital ($M = \text{Si, Ge, Sn}$) and the low-lying C—O σ^* -antibonding orbital in esters, ethers and alcohols substituted in the β position with group IV metal atoms (White, 1995; White & Robertson 1992; Green *et al.*, 1995; Chan *et al.*, 1996), the structure of trimethylgermylethyl *p*-nitrobenzoate, (I), was deter-

† Metal–organic name: trimethyl(*p*-nitrobenzoyloxyethyl)germanium(IV).