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***trans*-Chlorobis(diphenylglyoximato)(tri-*n*-butylphosphine)cobalt(III)**

RICHARD J. BARTON,^a QUINN MAJOR,^b LYNN M. MIHICHUK,^b BEVERLY E. ROBERTSON^a AND CANDACE SEIP^b

^aUniversity of Regina, Department of Physics, Regina, Saskatchewan, Canada S4S 0A2, and ^bUniversity of Regina, Department of Chemistry, Regina, Saskatchewan, Canada S4S 0A2. E-mail: mihichuk@meena.cc.uregina.ca

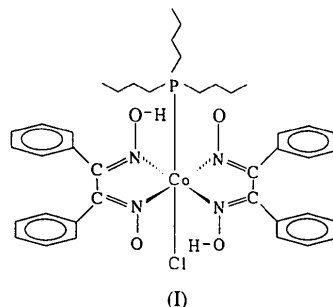
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Abstract

The Co atom in the title cobaloxime, [CoCl(C₁₄H₁₁N₂O₂)₂(C₁₂H₂₇P)], is octahedrally coordinated to the two bidentate diphenylglyoximato ligands, approximating a plane with the Cl and P atoms located above and below the plane. The diphenylglyoximato moieties are themselves bent 6.6(1) and 9.8(1)° from the central plane of the four N atoms by the bulk of the tri-*n*-butylphosphine ligand. The four phenyl rings of the two diphenylglyoximato groups form a propeller geometry with an average rotation from the central plane of 47(5)°.

Comment

This analysis was carried out as part of an ongoing study of the reactions between organohaloarsines and cobaloximes. Specifically, the structure of the title compound, (I), can be used to compare the effects of the in-plane methyl groups with the effects of in-plane phenyl groups on the geometry of the cobaloxime. The atom labelling is shown in Fig. 1. The angles between the phenyl rings and the central plane defined by the four N atoms are 42.6(1), 53.6(1), 45.6(1) and 46.3(1)° for the phenyl rings on atoms C1, C2, C3 and C4, respectively. Short intramolecular hydrogen bonds are formed between atoms O1 and O3 and atoms O2 and O4. The shorter hydrogen bonds are to atoms O2 and O3. The N—C bonds associated with the shorter H bonds are also marginally shorter [0.02(1) Å] than those associated with the longer hydrogen bonds. However, the N—O bond lengths do not show a consistent pattern.



Relative to an arsine derivative (Mihichuk, Mombourquette, Einstein & Willis, 1982) and phosphine and phosphite derivatives (Bresciani-Pahor, Calligaris & Randaccio, 1980) of a bis(dimethylglyoximate)-cobaloxime, the C—methyl distances average 0.04(4) Å longer than the C—phenyl distances reported here. The

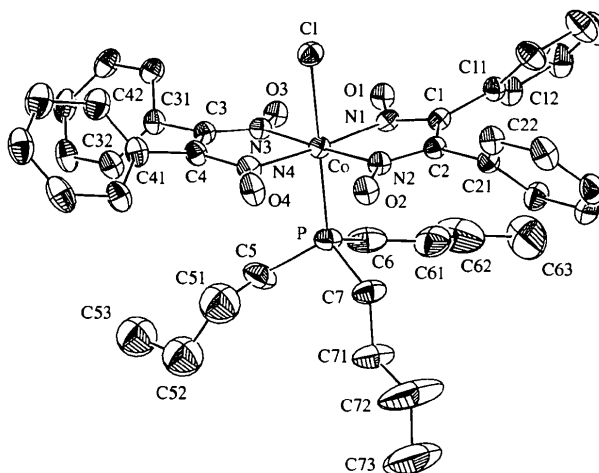


Fig. 1. ORTEP (Johnson, 1976) diagram of the molecule showing the labelling of the non-H atoms with 30% probability displacement ellipsoids. The ring C atoms are labelled Cij, where *i* = 1–4 and *j* = 1–6.

Co atom is displaced 0.058 (1) Å toward the P atom from the aforementioned plane of the four N atoms, compared with an average of 0.03 (2) Å for the methyl derivatives.

Experimental

Cobalt acetate tetrahydrate (1.29 g, 5.18 mmol) dissolved in 25 ml of hot 95% ethanol, was added to diphenylglyoxime (2.40 g, 10.0 mmol) also dissolved in 25 ml of hot ethanol. The dark brown solution was boiled for 2 min, after which a 2 ml aqueous sodium chloride solution (0.44 g, 7.5 mmol) was added. After boiling for 2 min, tri-*n*-butylphosphine (1.98 g, 7.54 mmol) was added and the solution was boiled for an additional 5 min with the addition of ethanol to offset evaporation. The solution was left at 298 K for 2 d, resulting in the formation of red-brown crystals of the title compound, which were filtered, washed with water, ethanol and ether, and dried under vacuum. Yield: 3.0 g (70%).

Crystal data

[CoCl(C ₁₄ H ₁₁ N ₂ O ₂) ₂ · (C ₁₂ H ₂₇ P)]	Mo K α radiation
$M_r = 775.22$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 34 reflections
$P2_1/c$	$\theta = 18-21^\circ$
$a = 12.030$ (1) Å	$\mu = 0.588$ mm ⁻¹
$b = 19.854$ (2) Å	$T = 293$ K
$c = 17.091$ (2) Å	Plate
$\beta = 97.21$ (1)°	$0.45 \times 0.28 \times 0.10$ mm
$V = 4049.8$ (7) Å ³	Red-brown
$Z = 4$	
$D_x = 1.271$ Mg m ⁻³	
D_m not measured	

Data collection

Picker FACS-I diffractometer	8367 reflections with $I_{\text{net}} > 0$
$\theta/2\theta$ scans	$R_{\text{int}} = 0.121$
Absorption correction:	$\theta_{\text{max}} = 27.5^\circ$
Gaussian by integration	$h = -15 \rightarrow 15$
(<i>Xtal3.2</i> ; Hall, Flack & Stewart, 1992)	$k = 0 \rightarrow 25$
$T_{\text{min}} = 0.762$, $T_{\text{max}} = 0.840$	$l = 0 \rightarrow 22$
9308 measured reflections	3 standard reflections
9301 independent reflections	every 47 reflections
	intensity decay: 1%

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.002$
$R = 0.085$	$\Delta\rho_{\text{max}} = 0.716$ e Å ⁻³
$wR = 0.043$	$\Delta\rho_{\text{min}} = -0.466$ e Å ⁻³
$S = 1.352$	Extinction correction: none
8367 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
528 parameters	
All H atoms refined	

Table 1. Selected bond lengths (Å)

N1—O1	1.335 (3)	N4—O4	1.342 (3)
N1—C1	1.318 (3)	N4—C4	1.318 (3)
N2—O2	1.328 (3)	C1—C11	1.480 (4)

N2—C2	1.302 (3)	C2—C21	1.478 (3)
N3—O3	1.339 (3)	C3—C31	1.491 (4)
N3—C3	1.288 (3)	C4—C41	1.472 (4)

Table 2. Hydrogen-bonding geometry (Å, °)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2 $\cdots$ O4	1.19 (4)	1.28 (4)	2.468 (3)	178 (4)
O3—H1 $\cdots$ O1	1.15 (4)	1.32 (4)	2.464 (3)	172 (3)

During the initial refinement the *n*-butyl groups showed large displacement parameters. Furthermore, the bond lengths of the *n*-butyl group involving C5 were not reasonable. This group is clearly disordered. A rigid body was constructed for atoms C51, C52 and C53. The C51—C52 and C52—C53 distances and the C51—C52—C53 angle were taken as the average of values obtained from the two other *n*-butyl groups of this structure and from three other structures containing the P(*n*-butyl)₃ group (Adams & Lenhert, 1973; Marzilli, Epps, Sorrell & Kistenmacher, 1975; Bresciani-Pahor, Calligaris & Randaccio, 1980). These values were 1.54, 1.50 Å and 112°, respectively. The atoms of the rigid group were placed into the structure and refinement proceeded. The high residual density is a consequence of the disorder. The positions of the H atoms on atoms C5, C51, C52, C53, C6, C61, C62, C63, C7, C71, C72 and C73 were not found or calculated and they were not included in the refinement. All other H atoms, including those on the glyoximate groups, were found and refined. The original refinement was a conventional refinement and used only data with $I > 2\sigma(I)$. There is no theoretical justification for the exclusion of weak data (Schwarzenbach *et al.*, 1989). Therefore, a second refinement was carried out with all data for which $I > 0.0$. This refinement produced standard uncertainties roughly 10% lower than the previous values. The REGWT procedure (*Xtal3.2*; Hall, Flack & Stewart, 1992), designed to modify the weighting scheme in order to make optimum use of the available data, was applied to the refinement. Thus, the weights used were calculated as $(\sigma_c^2 + \sigma_m^2)^{-1}$, where σ_c is calculated from the counting statistics of the individual reflection and from the excess scatter in the intensities of the standard reflections, and σ_m is a correction determined by the REGWT procedure. Specifically, $\sigma_m^2 = 7.18 \times 10^{16} - 9.86 \times 10^4 (\sin\theta/\lambda) - 1.85 \times 10^{22} (F \sin\theta/\lambda) + 209(\sin\theta/\lambda)^2$. This procedure further lowered the s.u.'s to roughly half of the original values. The large difference between R and wR is an anticipated consequence of weight modification.

Data collection: *NRCC Diffractometer Control System* (Gabe, Larson, Lee & Wang, 1979). Cell refinement: *NRCC Diffractometer Control System*. Data reduction: *Xtal3.2*. Program(s) used to solve structure: *Xtal3.2*. Program(s) used to refine structure: *Xtal3.2 CRYLSQ REGWT*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *Xtal3.2*. Software used to prepare material for publication: *Xtal3.2 BONDLA CIFIO*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1214). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-[7,8-Bis(diphenylphosphino)-7,8-dicarba-nido-undecaborato-*P,P'*]dichloro-gold(III) Chloroform Solvate

PETER G. JONES,^a M. DOLORES VILLACAMPA,^a OLGA CRESPO,^b M. CONCEPCIÓN GIMENO^b AND ANTONIO LAGUNA^b

^aInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and ^bDepartamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain.
 E-mail: jones@xray36.anchem.nat.tu-bs.de

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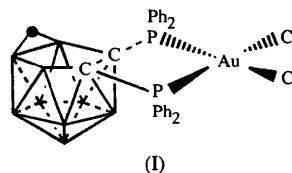
Abstract

The title compound, [AuCl₂{C₂B₉H₁₀(Ph₂P)₂}]·CHCl₃, contains the expected *cis* square-planar gold(III) units, with Au—P 2.306 and 2.296 (2), and Au—Cl 2.335 and 2.326 (2) Å. The dicarbaundecaborate anion acts as a *P,P'*-bidentate ligand. The open B₂C₃ face contains one bridging (B—H—B) H atom.

Comment

We have recently started a systematic investigation of metal complexes of the partially degraded 1,2-dicarba-*closo*-dodecaborane derivative, the 7,8-bis(diphenylphosphino)-7,8-dicarba-nido-undecaborate anion {[7,8-(PPh₂)₂-7,8-C₂B₉H₁₀][−], henceforth PP} (Crespo, Gimeno, Jones & Laguna, 1996, and references therein). The anion usually acts as a *P,P'*-bidentate ligand.

We present here the structure of the neutral gold(III) complex [AuCl₂(PP)], (I), which crystallizes as a chloroform solvate. The scheme shows BH groups as vertices, with the bridging H atom as a black dot. The preparation of the title compound and the structure of the analogous bis(diisopropylphosphino) complex have been reported by Teixidor, Viñas, Abad, Kivekäs & Sillanpää (1996).



As expected for Au^{III}, the metal atom displays a square-planar coordination; it lies only 0.068 (1) Å out of the plane of the four donor atoms (mean deviation 0.01 Å). An additional weak axial contact to a solvent Cl atom is observed [Au···Cl4 3.863 (3) Å]. The configuration is necessarily *cis* because of the restricted bite of the PP ligand; P1··P2 3.183 (3) Å and P2—Au—P1 87.53 (7)°. The chelate ring displays an envelope conformation, with the Au atom 0.490 (5) Å out of the plane formed by the C7, C8, P1 and P2 atoms (mean deviation < 0.001 Å). The Au—P [2.306 and 2.296 (2) Å] and Au—Cl [2.335 and 2.326 (2) Å] bond lengths are broadly similar to those given by Teixidor *et al.* (1996); Au—P 2.313 and 2.327 (2) Å (which are, however, significantly longer than those in the title compound), and Au—Cl 2.331 and 2.344 (2) Å. A search of the Cambridge Structural Database (April 1996 version; Allen & Kennard, 1993) revealed, surprisingly, no other example of P₂Cl₂ coordination at Au^{III}, perhaps because most compounds of this type would be

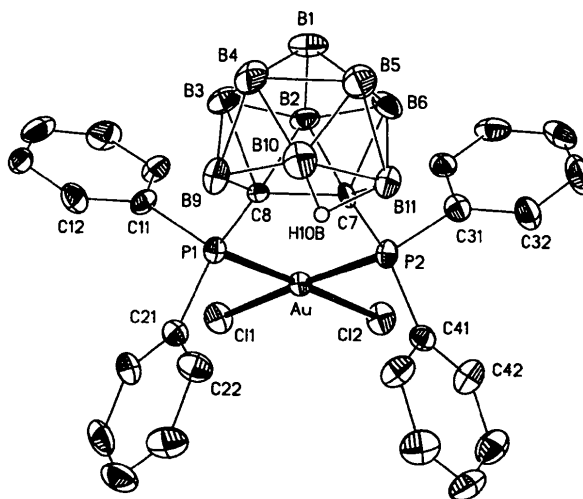


Fig. 1. The molecule of the title compound in the crystal (solvent omitted). Ellipsoids are drawn at the 50% probability level and all H atoms except the bridging open-face H atom have been omitted.