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Structure of Trimethylplatinum(IV) with a Tripod Ligand

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Abstract. [1(η^5 -Cyclopentadienyl)-tris- μ -(dimethylphosphito-1 κ P:2 κ O)(trimethyl-2 κ^3 C)cobaltplatinum, [CoPt(C₂H₆O₃P)₃(C₅H₅)(CH₃)₃], M_r = 691.35, triclinic, $P\bar{1}$, a = 9.106 (3), b = 14.803 (3), c = 15.147 (3) Å, α = 112.95 (2), β = 103.68 (2), γ = 95.10 (2)°, V = 1788.9 (9) Å³, Z = 3, D_x = 1.93 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, μ = 68.69 cm⁻¹, $F(000)$ = 1014, room temperature, R = 0.038 for 4620 reflections with $F_o^2 > 3\sigma(F_o^2)$. The trimethylplatinum(IV) completes octahedral coordination by bonding to three O atoms of the tripod-shaped methoxy Kläui ligand. There are two independent molecules in the cell, one disordered about a center of symmetry. The ordered molecule has normal bond distances and angles; Pt—C = 2.001 (11) and Pt—O = 2.173 (5) Å. Many distances in the disordered molecule are uncertain, particularly in the areas of the Cp C atoms and the CH₃ groups, which overlap in the two orientations.

Introduction. Interest in the activation and functionalization of saturated hydrocarbons by aqueous platinum chloride solutions (Shilov, 1984, 1989;

Labinger, Herring & Bercaw, 1990*a,b*) has led to our synthesizing model Pt complexes containing 'hard' ligands (Herring, Henling, Labinger & Bercaw, 1991). Model complexes analogous to the putative Pt(R)Cl₄(H₂O)⁻ species that have been proposed as intermediates in the activation/functionalization of alkanes by Pt (Shul'pin, Shilov, Kitaigorodskii & Zeile Krevor, 1980; Shibaera, Rozenberg, Lobkovskaya, Shilov & Shul'pin, 1981; Shul'pin, Nizova & Nikitaev, 1984; Khrushch, Laurushki, Misharin, Moravsky & Shilov, 1983) are thus attractive targets, but few examples of structurally well characterized complexes are available. The tripod ligand (η^5 -C₅H₅)Co[P(O)(OR)₂]₃⁻ (henceforth abbreviated to L_{OR}) behaves as a hard ligand, with field strengths approximately equal to that of three F⁻ ligands (Kläui, 1990). Recently the synthesis of Pt(CH₃)₃ L_{OR} , where R = Me and Et, as well as the crystal and molecular structure of the latter, have been reported (Nettle, Valderrama, Contreras, Scotti, Peters, von Schnering & Werner, 1988). In the course of preparing these complexes for study of their chemical behavior, we obtained crystals of Pt(CH₃)₃ L_{OMe} , and decided to determine its structure for purposes of comparison. Formation of methanol

* Contribution No. 8533.

Table 1. Final refined positional parameters ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) or isotropic displacement parameters (\AA^2) for Pt(CH₃)₃L_{OMe}

Atoms O10–O18 were refined with isotropic displacement parameters, *B*. Other atoms were refined with anisotropic displacement parameters; $U_{\text{eq}} = (4/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B/U</i> _{eq}
Pt1	2511 (.4)	83 (.2)	2764 (.3)	480 (1)
Co1	1646 (1)	2860 (1)	3835 (1)	461 (2)
P1	1247 (3)	1786 (2)	4439 (2)	562 (5)
P2	3894 (3)	2538 (2)	3770 (2)	637 (6)
P3	563 (3)	1736 (2)	2313 (2)	637 (6)
O1	1582 (7)	757 (4)	4009 (4)	660 (15)
O2	4151 (6)	1493 (4)	3355 (5)	768 (19)
O3	893 (7)	700 (4)	1966 (4)	757 (19)
C1	3991 (12)	-443 (7)	3551 (8)	958 (34)
C2	988 (11)	-1194 (6)	2237 (8)	853 (33)
C3	3368 (12)	-498 (7)	1599 (8)	913 (31)
O4	-508 (8)	1675 (6)	4439 (7)	1252 (26)
O5	2122 (10)	2288 (5)	5607 (5)	1122 (29)
O6	5049 (7)	3125 (5)	4892 (6)	1172 (29)
O7	4580 (11)	3103 (6)	3232 (8)	1516 (31)
O8	918 (11)	2203 (5)	1579 (5)	1254 (31)
O9	-1258 (8)	1631 (5)	2068 (6)	1168 (29)
Cp1	7 (14)	3730 (8)	3829 (18)	1157 (53)
Cp2	1163 (32)	4061 (11)	3524 (10)	1188 (51)
Cp3	2464 (17)	4364 (8)	4272 (19)	1140 (52)
Cp4	2172 (24)	4224 (9)	5059 (10)	1102 (52)
Cp5	615 (27)	3823 (10)	4782 (17)	1122 (46)
C4	-1368 (17)	858 (12)	4427 (16)	1977 (70)
C5	2962 (16)	1859 (9)	6117 (9)	1295 (48)
C6	6446 (14)	2898 (10)	5192 (9)	1239 (45)
C7	5176 (21)	2723 (13)	2487 (14)	1764 (61)
C8	841 (19)	1643 (10)	591 (9)	1464 (55)
C9	-2308 (16)	774 (11)	1611 (14)	1742 (69)
Pt2	6392 (1)	4794 (1)	-1149 (1)	432 (2)
Co2	4044 (4)	5141 (3)	853 (3)	496 (7)
P4	4576 (5)	6252 (3)	315 (3)	500 (10)
P5	3303 (5)	3954 (3)	-666 (4)	628 (12)
P6	6382 (5)	4890 (4)	1072 (3)	586 (11)
O10	5174 (12)	6014 (7)	-570 (8)	4.4 (2)
O11	7285 (12)	4954 (8)	383 (8)	4.5 (2)
O12	4351 (12)	3774 (8)	-1325 (8)	4.8 (2)
O13	5742 (15)	7213 (10)	1257 (10)	6.6 (3)
O14	2668 (16)	2880 (11)	-738 (11)	7.8 (3)
O15	1678 (16)	4155 (11)	-1246 (11)	7.7 (3)
O16	7445 (18)	5615 (11)	2199 (11)	8.1 (4)
O17	6316 (17)	3796 (11)	1048 (11)	8.1 (4)
O18	3124 (16)	6774 (10)	94 (11)	7.6 (3)
C13	6636 (12)	7956 (7)	1095 (9)	995 (34)
C14	8953 (13)	6202 (9)	2375 (8)	1157 (43)
C15	7574 (12)	3243 (9)	834 (9)	1049 (34)

during aqueous decomposition of Pt(CH₃)₃L_{OR} will be reported elsewhere.

Experimental. A truncated bipyramid crystal, $0.34 \times 0.30 \times 0.30$ mm, was used for data collection on a CAD-4 diffractometer with θ - 2θ scans. 25 reflections with $36 < 2\theta < 38^\circ$ were used to determine cell dimensions. Data were not corrected for absorption effects (φ scans showed relative transmissions of 0.97 to 1.03, and the uncorrected data merged with a goodness of fit of 1.04). Data were collected to $(\sin\theta/\lambda)_{\text{max}} = 0.60 \text{ \AA}^{-1}$; *h* from -10 to 10, *k* from -17 to 17, *l* from -18 to 18. Three standard reflections ($\bar{1}24$, $\bar{3}31$ and $0\bar{1}4$) showed a slight isotropic decay, for which a correction was made. 12652 reflections were measured, of which 6284 were independent ($R_{\text{int}} = 0.030$ for 5449 reflections with exactly two observations). All reflections were used

Table 2. Selected distances (\AA) and angles ($^\circ$) for Pt(CH₃)₃L_{OMe}

Pt1—O1	2.168 (6)	P2—O2	1.489 (7)
Pt1—O2	2.178 (6)	P2—O6	1.609 (8)
Pt1—O3	2.174 (6)	P2—O7	1.560 (11)
Pt1—C1	1.998 (11)	P3—O3	1.498 (7)
Pt1—C2	1.991 (10)	P3—O8	1.596 (9)
Pt1—C3	2.013 (11)	P3—O9	1.591 (8)
Co1—P1	2.166 (3)	O4—C4	1.37 (2)
Co1—P2	2.159 (3)	O5—C5	1.331 (16)
Co1—P3	2.168 (3)	O6—C6	1.365 (15)
Co1—Cp1	2.057 (17)	O7—C7	1.32 (2)
Co1—Cp2	2.07 (2)	O8—C8	1.380 (18)
Co1—Cp3	2.066 (19)	O9—C9	1.337 (19)
Co1—Cp4	2.057 (17)	Cp1—Cp2	1.37 (3)
Co1—Cp5	2.06 (2)	Cp1—Cp5	1.37 (3)
P1—O1	1.497 (6)	Cp2—Cp3	1.33 (3)
P1—O4	1.592 (9)	Cp3—Cp4	1.37 (3)
P1—O5	1.587 (8)	Cp4—Cp5	1.38 (3)
O2—Pt1—O1	88.1 (2)	O6—P2—Co1	106.9 (3)
O3—Pt1—O1	86.5 (2)	O7—P2—Co1	109.5 (4)
C1—Pt1—O1	91.3 (4)	O6—P2—O2	108.0 (4)
C2—Pt1—O1	91.0 (3)	O7—P2—O2	107.9 (5)
C3—Pt1—O1	177.9 (4)	O7—P2—O6	100.4 (5)
O3—Pt1—O2	87.8 (2)	O3—P3—Co1	121.6 (3)
C1—Pt1—O2	91.3 (4)	O8—P3—Co1	107.1 (3)
C2—Pt1—O2	179.0 (3)	O9—P3—Co1	108.9 (3)
C3—Pt1—O2	90.6 (4)	O8—P3—O3	108.5 (4)
C1—Pt1—O3	177.7 (4)	O9—P3—O3	107.6 (4)
C2—Pt1—O3	91.8 (3)	O9—P3—O8	101.3 (4)
C3—Pt1—O3	91.9 (4)	P1—O1—Pt1	128.9 (4)
C2—Pt1—C1	89.1 (4)	P2—O2—Pt1	129.4 (4)
C3—Pt1—C1	90.3 (4)	P3—O3—Pt1	129.3 (4)
C3—Pt1—C2	90.3 (4)	C4—O4—P1	125.2 (10)
P2—Co1—P1	91.7 (1)	C5—O5—P1	126.1 (8)
P3—Co1—P1	91.4 (1)	C6—O6—P2	123.0 (8)
P3—Co1—P2	91.7 (1)	C7—O7—P2	127.1 (11)
O1—P1—Co1	122.2 (3)	C8—O8—P3	124.1 (9)
O4—P1—Co1	107.1 (3)	C9—O9—P3	126.2 (9)
O5—P1—Co1	108.6 (3)	Cp5—Cp1—Cp2	108.8 (17)
O4—P1—O1	108.0 (4)	Cp3—Cp2—Cp1	108.0 (18)
O5—P1—O1	107.6 (4)	Cp4—Cp3—Cp2	109.2 (17)
O5—P1—O4	101.3 (5)	Cp5—Cp4—Cp3	107.7 (16)
O2—P2—Co1	122.0 (3)	Cp4—Cp5—Cp1	106.3 (18)

in solution and refinement of the structure. Pt and Co atom locations were deduced from a Patterson map; the locations of the remaining heavy atoms were found from successive structure factor–Fourier calculations. F^2 values were used in the refinement. H atoms on the ordered molecule were placed by calculation (C—H 0.95 \AA) assuming staggered geometry; H-atom parameters were not refined, but were included as constant contributions to the structure factors; H atoms were not introduced on the disordered molecule. Coordinates and anisotropic displacement parameters of all heavy atoms of the ordered molecule, a scale factor and a secondary-extinction parameter (Larson, 1967) were refined. In the disordered molecule the Co and Pt atoms, which are separated by 0.65 \AA , were refined satisfactorily as half-weight anisotropic atoms. The three P atoms were also refined as half-weight anisotropic atoms, and the nine O atoms as half-weight isotropic atoms. On the other hand, the six C atoms of the methoxy groups appeared to be closely overlapped in the two orientations, and were refined as three full-weight anisotropic atoms. Overlap of the five atoms of the Cp ring with the three Pt-coordinated methyl groups was complicated; these atoms were placed in idea-

lized half-populated sites with isotropic B values and not refined. The final difference map clearly showed that the modeling in this area was incomplete, presumably because of the neglect of the large anisotropies in the U_{ij} values expected for such atoms. For all 5754 reflections with $F_o^2 > 0$, final R (on F) = 0.051, wR (on F^2) = 0.008; $S = 1.81$. Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term,

$(0.014I)^2$, variances of the merged data by propagation of e.s.d. plus another additional term, $(0.014I)^2$. The ratio of maximum shift to standard deviation in the final cycle was 0.03; maximum and minimum peaks in the final difference map were 1.33 (near the Cp ring on the disordered molecule – the five largest peaks are in this region) and $-1.01 \text{ e } \text{Å}^{-3}$ (0.7 Å from P3); the secondary-extinction parameter refined to $0.94(3) \times 10^{-6}$. Atomic scattering factors were taken from Cromer & Waber (1974) and dispersion corrections from Cromer (1974). Programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEPII* (Johnson, 1976). Final refined parameters are listed in Table 1 with selected distances and angles in Table 2. The two independent molecules are shown in Figs. 1 and 2; Fig. 3 shows the packing.*

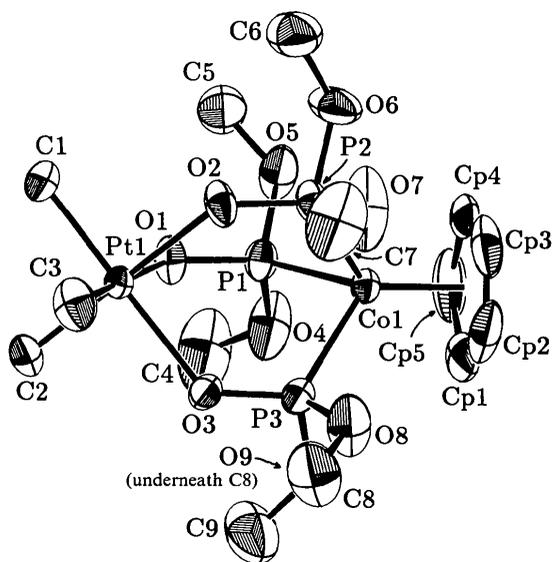


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the ordered cation with 50% probability ellipsoids showing the numbering system. H atoms are not shown.

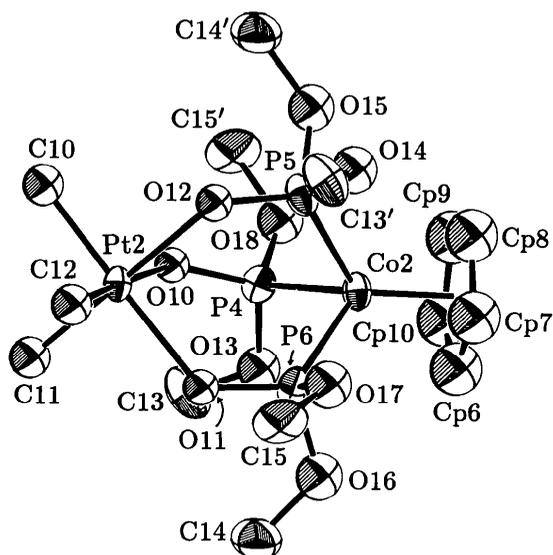


Fig. 2. An *ORTEPII* (Johnson, 1976) drawing of the disordered cation with 50% probability ellipsoids showing the numbering system. Primed atoms are related to unprimed atoms by a center of symmetry.

Discussion. The molecular structure of $\text{Pt}(\text{CH}_3)_3\text{LOMe}$ is quite similar to that previously reported for the ethyl analog, which in turn displays structural parameters closely resembling those of other complexes containing the LOR tripod ligand as well as those with the PtMe_3 moiety (Nettle *et al.*, 1988).

* Lists of assigned H-atom parameters, anisotropic displacement parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55138 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0605]

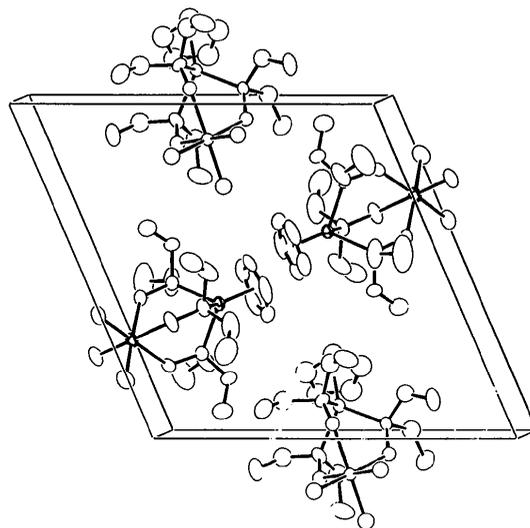


Fig. 3. An *ORTEPII* (Johnson, 1976) packing drawing projected approximately down a showing the contents of a unit cell, with the unit cell outlined. The c axis is horizontal. Atoms are shown as 50% probability ellipsoids, with Co and Pt atoms of the ordered cation shaded; H atoms are not shown. Only one orientation of the disordered cation is shown.

Comparing bond distances and angles between the two Pt(CH₃)₃L_{OR} structures, nearly all agree to within experimental uncertainty. The only apparently significant differences are found in the P=O—Pt linkages: the average values for Pt—O, O—P and Pt—O—P are 2.196 (1), 1.507 (8) Å and 125.1 (9)° for Pt(CH₃)₃L_{OEt}, and 2.173 (5), 1.492 (6) Å and 129.2 (3)° for the ordered molecule of Pt(CH₃)₃L_{OMe}, respectively. (Values for the disordered molecule are intermediate, but the uncertainties in these parameters are considerably larger and their significance is dubious.) Increased steric crowding around the set of P=O ligands could result in a greater separation between the tripod ligand and the Pt center and the observed increase in bond lengths for Pt(CH₃)₃L_{OEt}, but this interpretation predicts an increase in Pt—O—P angles, whereas a decrease is found.

The crystal structure of Pt(CH₃)₃L_{OMe} exhibits an interesting feature: of the two independent molecules in the unit cell, one is disordered about a center of symmetry (Fig. 2). It may be noteworthy that each of the six C atoms of the methoxy groups virtually overlaps its partner in the other orientation of the disordered molecule; perhaps the breaking of this pseudo-symmetry element by additional substitution is responsible for the fact no such disorder was found for the ethyl analog.

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Structures of the Nickel(II) and Copper(II) Complexes of 3-Hydroxy-6-methylpyridine-2-thione

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Abstract. (I) Bis(6-methylpyridine-2-thion-3-olato)-nickel(II) bis(dimethylformamide), Ni(C₆H₆NOS)₂·2C₃H₇NO, *M*_r = 485.28, monoclinic, *P*2₁/*c*, *a* = 8.518 (2), *b* = 13.545 (2), *c* = 9.340 (1) Å, *β* =

94.19 (2)°, *V* (241 K) = 1074.7 (4) Å³, *Z* = 2, *D*_m(295 K) = 1.53 (1), *D*_x(295 K); *V* = 1086.4 (3) Å³ = 1.48 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 31.47 cm⁻¹, *F*(000) = 508, *T* = 241 (1) K, *R* = 0.0500 for 1240 observed reflections. The complex is planar with the Ni ion at the origin of the unit cell. A hydrogen bond exists between the N—H of the ligand and the carbonyl O atom of the

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