mentation Center, Bose Institute, Calcutta, for providing the diffractometer data. NPN thanks the University Grants Commission, India, for a research fellowship and NRC thanks The Council of Scientific & Industrial Research, New Delhi, for a grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1171). Services for accessing these data are described at the back of the journal.

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The Racemic C_3-Symmetrical Propeller Structure of Chlorotris(1,3-diphenyl-1,3-propanedionato-*O*,*O*′)zirconium(IV)

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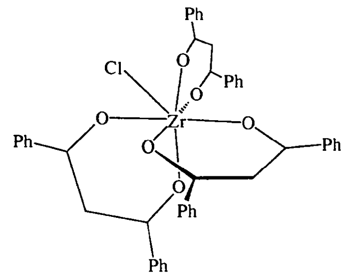
Abstract

The title compound, [ZrCl(C$_{15}$H$_{11}$O$_2$)$_3$], contains three 1,3-diphenyl-1,3-propanedionato (or dibenzoylmethanate) ligands arranged as propeller blades around the C_3 Zr—Cl axis to give a chiral molecule. The centrosymmetric space group contains a racemic mixture of left- and right-handed propellers. The coordination geometry around the seven-coordinate Zr metal atom is a capped octahedron.

Comment

Zirconium β-diketonate complexes have recently been described in combination with methylalumoxane as single-site catalysts for the polymerization of ethene (Janiak *et al.*, 1994; Ueki *et al.*, 1992) and styrene (Longo *et al.*, 1994). The use of these chelate ligands or complexes in catalysis was based on the idea that bis- or tris-chelate complexes can assume chiral Δ and Λ forms. Chiral catalytic centres are a prerequisite for the tailored stereoregular coordination polymerization of prochiral α-olefins. To verify this formation of enantiomeric forms in the pre-catalytic chelate complexes, the molecular and crystal structures of the title compound, (I), were determined.



(I)

The molecular structure is shown in Fig. 1 and illustrates the C_3-symmetrical propeller arrangement of the diphenylpropanedionato ligands. A left- or right-handed position of the propeller 'blades' gives rise to the two enantiomeric forms. In the centrosymmetric space group $R\bar{3}$, the crystal comprises a racemic mixture. The crystal packing is based on the π-stacking of the phenyl groups. The parallel orientation of the phenyl π systems contrary to the geared or orthogonal stacking

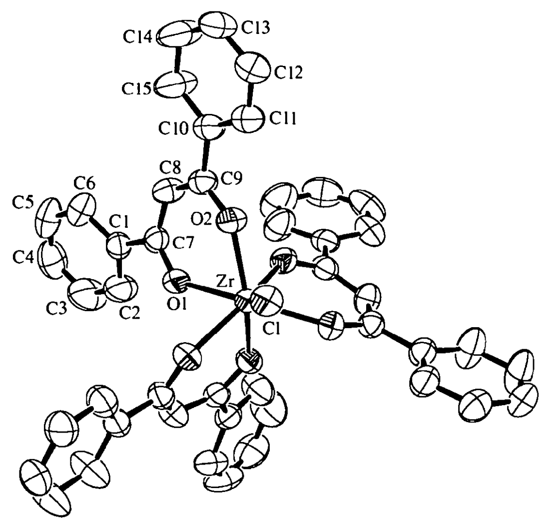


Fig. 1. The molecular structure of (I) viewed at an angle of 10° to the C_3 Cl—Zr axis; displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

observed in the crystal structure of benzene (Cox *et al.*, 1958; Piermarini *et al.*, 1969) or other aromatic hydrocarbons (Goddard *et al.*, 1995) may be explained by the relative electron deficiency of the former due to the neighbouring carbonyl function (Hunter, 1993). The zirconium coordination sphere can be described as a distorted capped octahedron with a slight envelope conformation of the six-membered chelate rings [Zr—O—C—C torsion angles 7.0 (3) and 18.0 (2)°]. Each ring is slightly tilted with respect to the C—C═O moiety of the central propanedionato unit to which it is bonded; the dihedral angle between the mean planes defined by atoms C1–C6 and by C8—C7—O1 is 21.9 (2)°, and that between C10–C15 and C8—C9—O2 is 8.1 (3)°.

A comparison of the structure of (I) with the structure of chlorotris(1,3-propanedionato)zirconium(IV) (VonDreele *et al.*, 1971) illustrates the influence of the ligand size on the molecular geometry. The coordination polyhedron of the 1,3-propanedionato complex is a distorted pentagonal bipyramid, with the Cl atom and one O atom occupying the axial positions. The other known zirconium structure with the 1,3-diphenyl-1,3-propanedionato ligand is that of the tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV) complex with a square antiprismatic arrangement of the eight O atoms around the metal centre (Chun *et al.*, 1979). The Zr—O distances in (I) are unremarkable with respect to Zr—O distances typically observed in acetylacetonato complexes (Orpen *et al.*, 1989; Silverton & Hoard, 1963; Stezowski & Eick, 1965; VonDreele *et al.*, 1971; Muller *et al.*, 1975; Chun *et al.*, 1979). For a seven-coordinate complex, the Zr—Cl bond in (I) appears to be unusually long (Orpen *et al.*, 1989). The comparative value for chlorotris(acetylacetonato)zirconium(IV) is 2.472 (6) Å (VonDreele *et al.*, 1971).

Experimental

The commercially available chemicals were used as received. The synthesis of the title compound was carried out with a modification of the literature method (Cox *et al.*, 1964; Wolf & Tröltzsch, 1962) with diethyl ether as solvent instead of benzene, in the following way. A solution of dibenzoylmethane (10.56 g, 47.1 mmol) in diethyl ether (60 ml) was slowly added to a slurry of zirconium tetrachloride (1.94 g, 8.3 mmol) in diethyl ether (20 ml). The mixture was refluxed for 14 h, then the yellow–green precipitate was separated by filtration and washed with diethyl ether (10 ml) and hexane (10 ml) to give 6.29 g (95%) of the product which was already pure enough for further reactions. Yellow single crystals were obtained by overlayering a toluene solution of the compound with hexane; m.p. 553–555 K. Analysis calculated for $C_{45}H_{33}ClO_6Zr$: C 67.87, H 4.18%: found: C 67.52, H 4.11%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.25 (*s*, 1H, CH), 7.46 (*tt*, 4H, *m*-C_6H_5), 7.56 (*tt*, 2H, *p*-C_6H_5), 8.15 (*td*, 4H, *o*-C_6H_5), J = 7 and 2 Hz (Note that the splitting pattern and coupling constants given here describe the superficial appearance. The hindered rotation of the phenyl rings actually gives rise to an $AA'BB'C$ coupling system.) ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 97.44 (CH), 128.46, 128.95, 132.91 (*o*-, *m*-, *p*-C_6H_5), 137.31 (*ipso*-C_6H_5), 184.41 (CO); MS (EI, 573 K): *m*/*z* (%) = 759 [M − Cl]$^+$ (100), 571 [M − $(C_6H_5CO)_2CH$]$^+$ (90), 267 [$(C_6H_5CO)_2CH + C_2H_4O$]$^+$ (25), 224 [$(C_6H_5CO)_2CH_2$]$^+$ (39), 147 [$C_6H_5COCH_2CO$]$^+$ (15), 105 [C_6H_5CO]$^+$ (100).

Crystal data

$[ZrCl(C_{15}H_{11}O_2)_3]$	Mo $K\alpha$ radiation
M_r = 796.43	λ = 0.71069 Å
Trigonal	Cell parameters from 25 reflections
$R\bar{3}$	θ = 10.0–12.5°
a = 14.818 (2) Å	μ = 0.410 mm^{-1}
c = 29.903 (6) Å	T = 293 (2) K
V = 5686.1 (16) Å^3	Rhombus
Z = 6	1.00 × 0.50 × 0.25 mm
D_x = 1.395 Mg m^{-3}	Yellow
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.023
ω–2θ scans	θ_{max} = 24.88°
Absorption correction: none	h = 0 → 15
5648 measured reflections	k = 0 → 15
2186 independent reflections	l = −35 → 35
2116 reflections with $I > 2\sigma(I)$	3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.024	$\Delta\rho_{max}$ = 0.217 e Å^{-3}
$wR(F^2)$ = 0.066	$\Delta\rho_{min}$ = −0.141 e Å^{-3}
S = 1.085	Extinction correction: none
2186 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
204 parameters	
All H atoms refined	
$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 3.5609P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zr	2/3	1/3	0.130449 (8)	0.03907 (11)
Cl	2/3	1/3	0.04522 (2)	0.0538 (2)
O1	0.70624 (8)	0.45448 (9)	0.17870 (4)	0.0509 (3)
O2	0.82401 (8)	0.44170 (9)	0.11578 (4)	0.0499 (3)
C1	0.78164 (13)	0.57417 (13)	0.23741 (6)	0.0506 (4)
C2	0.6933 (2)	0.5212 (2)	0.26307 (8)	0.0774 (6)
C3	0.6808 (2)	0.5640 (3)	0.30208 (10)	0.0996 (9)
C4	0.7559 (2)	0.6606 (2)	0.31532 (9)	0.0865 (7)
C5	0.8428 (3)	0.7148 (2)	0.29028 (8)	0.0795 (7)
C6	0.8572 (2)	0.67228 (15)	0.25151 (7)	0.0633 (5)
C7	0.79142 (13)	0.52565 (12)	0.19560 (5)	0.0466 (4)
C8	0.88774 (14)	0.55795 (15)	0.17618 (6)	0.0554 (4)
C9	0.90006 (12)	0.51922 (13)	0.13587 (5)	0.0483 (4)
C10	1.00171 (12)	0.56671 (14)	0.11228 (6)	0.0525 (4)
C11	1.0111 (2)	0.5220 (2)	0.07321 (7)	0.0622 (5)
C12	1.1021 (2)	0.5684 (2)	0.04875 (8)	0.0712 (5)
C13	1.1852 (2)	0.6595 (2)	0.06261 (8)	0.0736 (6)
C14	1.1788 (2)	0.7041 (2)	0.10161 (10)	0.0971 (9)
C15	1.0874 (2)	0.6591 (2)	0.12627 (9)	0.0848 (7)

Table 2. *Selected geometric parameters (Å, °)*

Zr—O2	2.1126 (11)	C1—C7	1.485 (2)
Zr—O1	2.1436 (11)	C7—C8	1.386 (2)
Zr—Cl	2.5484 (9)	C8—C9	1.386 (3)
O1—C7	1.277 (2)	C9—C10	1.484 (2)
O2—C9	1.287 (2)		
O2—Zr—O2^{i}	115.81 (2)	O2—Zr—Cl	78.02 (3)
O2—Zr—O1^{i}	149.67 (5)	O1—Zr—Cl	132.30 (3)
O2—Zr—O1	76.55 (4)	C7—O1—Zr	134.57 (10)
O2^{i}—Zr—O1	77.80 (4)	C9—O2—Zr	136.28 (10)
O1^{i}—Zr—O1	79.66 (5)		

Symmetry code: (i) $1 - y, x - y, z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*3 for *Windows* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1194). Services for accessing these data are described at the back of the journal.

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(9,10-Dioxo-9,10-dihydro-1-anthrylaminato-*N*)(triphenylphosphine-*P*)gold

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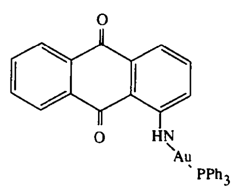
Abstract

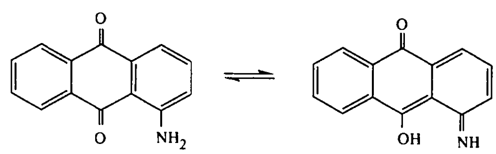
In the title compound, [Au(C$_{14}$H$_8$NO$_2$)(C$_{18}$H$_{15}$P)], the AuPPh$_3$ group is located at the amino group. The Au—N and Au—P distances are 2.019 (3) and 2.2420 (8) Å, respectively. The amino group H atom is involved in an intramolecular hydrogen bond with a carbonyl O atom. The bond-length distribution in the aminoanthraquinone ligand is slightly different from that in the free ligand, manifesting itself as a more pronounced contribution from the quinoid structure.

Comment

The title compound, (1), is a (triphenylphosphine)gold derivative of 1-aminoanthracene-9,10-dione, (2). The initial photochromic organic compound (2) can exist in two tautomeric forms, amino and imino (see scheme below).



(1)



(2)

In the imino form, two types of imino group configuration, resulting in different kinds of hydrogen bonds, may be proposed. Based on X-ray structural investiga-

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