Data collection

CAD-4 MicroVAX-controlled diffractometer
θ/ω scans
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.62$, $T_{\max} = 0.69$
3006 measured reflections
2849 independent reflections
2497 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.087$
$S = 1.100$
2849 reflections
235 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 2.1859P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.662$ e Å^{-3}
$\Delta\rho_{\min} = -0.641$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cr1—O20	1.959 (2)	Ca1—O23$^{\rm iii}$	2.481 (2)
Cr1—O30	1.960 (2)	Ca1—O32$^{\rm i}$	2.513 (2)
Cr1—O10	1.968 (2)	Ca1—O23$^{\rm ii}$	2.701 (2)
Cr1—O33	1.977 (2)	K1—O5	2.696 (3)
Cr1—O22	1.977 (2)	K1—O4	2.774 (3)
Cr1—O12	1.978 (2)	K1—O2$^{\rm iv}$	2.776 (3)
Ca1—O2	2.445 (2)	K1—O13$^{\rm iv}$	2.944 (2)
Ca1—O31$^{\rm i}$	2.456 (2)	K1—O30$^{\rm v}$	3.043 (2)
Ca1—O1	2.468 (2)	K1—O22$^{\rm v}$	3.301 (2)
Ca1—O21$^{\rm ii}$	2.470 (2)		

Symmetry codes: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x, y - 1, z$; (iii) $-x, 1 - y, -z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

The structure was solved using the *SHELXS*86 (Sheldrick, 1990) Patterson heavy-atom method and refined using *SHELXL*93 (Sheldrick, 1993). H atoms were found in difference maps.

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Molecular graphics: *PLATON*96 (Spek, 1996). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1140). Services for accessing these data are described at the back of the journal.

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[(1,2,5,6-η)-1,5-Cyclooctadiene][(11*R*,12*R*)-9,10-dihydro-9,10-ethanoanthracene-11,12-bis(diphenylphosphino-*P*)]rhodium(I) Tetrafluoroborate

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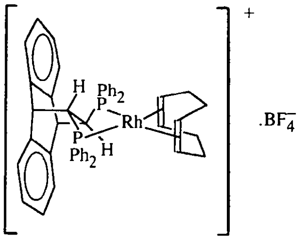
Abstract

The title compound, $[\mathrm{Rh(C_8H_{12})(C_{40}H_{32}P_2)]BF_4}$, which functions as an asymmetric catalyst, contains a five-membered chelate ring, and has molecular geometry and dimensions similar to those in related materials.

Comment

The Rh–anthraphos title complex, (I), was prepared for use as an asymmetric catalyst in hydrogenation reactions (Fu, Liu, Scheffer & Trotter, 1994).



(I)

The cation contains a five-membered chelate ring (Fig. 1) similar to those in the related Rh complexes of norphos (Kyba, Davis, Juri & Shirley, 1981) and chiraphos (Ball & Payne, 1977). The P—C—C—P torsion angle of −60.4 (2)° in the Rh–anthraphos molecule is between those of the other two compounds, 64 and 52°. The Rh—P bond lengths, mean 2.299 (1) Å, are similar to those in the other two compounds, means 2.32 and 2.28 Å; the Rh—P—C angles in the ring, mean 105.5 (1)°, are between those of 103° in Rh–norphos and 110° in Rh–chiraphos.

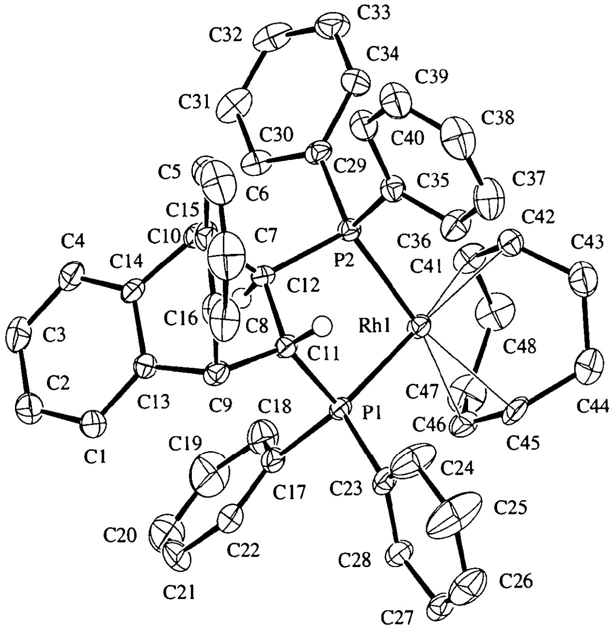


Fig. 1. View of the title molecule (50% ellipsoids). The tetrafluoroborate anion has been omitted.

The chelate ring adopts the λ conformation, and catalytic hydrogenation of (*Z*)-α-acetamidocinnamide gives *N*-acetylphenylalanine of *S* configuration, as predicted (Kagan, 1982), in 90% enantiomeric excess (Fu *et al.*, 1994).

Experimental

The title compound was synthesized *via* an ethanoanthracene-11,12-bis(diphenylphosphine oxide); this material was resolved into optically pure enantiomers. Treatment of the (*R*,*R*)-(−) enantiomer with trichlorosilane afforded (*R*,*R*)-(+)-anthraphos [*trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-bis(diphenylphosphine)]. Reaction of (+)-anthraphos with $[Rh(COD)Cl]_2$, followed by addition of $NaBF_4$, afforded (−)-[Rh(COD)(*R*,*R*-anthraphos)]BF_4. See supplementary data for further details.

Crystal data

$[Rh(C_8H_{12})(C_{40}H_{32}P_2)]BF_4$
$M_r = 872.53$
Tetragonal
$P4_1$
$a = 10.1580(2)$ Å
$c = 39.7543(5)$ Å
$V = 4102.05(11)$ Å^3
$Z = 4$
$D_x = 1.413$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 22 724 reflections
$\theta = 2.0$–$30.1°$
$\mu = 0.545$ mm^{-1}
$T = 180$ K
Prism
0.35 × 0.30 × 0.30 mm
Orange

Data collection

Quantum CCD diffractometer
CCD scans
Absorption correction: semi-empirical, analysis of redundant data using fourth-order spherical harmonics (Molecular Structure Corporation, 1997*b*).
$T_{min} = 0.700$, $T_{max} = 0.849$
37 526 measured reflections

10 690 independent reflections (including 4861 sets of Friedel pairs)
9206 reflections with $I > 3\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 30.12°$
$h = -12 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -41 \rightarrow 54$
Intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.043$
$wR(F^2) = 0.086$
$S = 2.51$
10 690 reflections
504 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.96$ e Å^{-3} (across 4_1 axis from Rh site)
$\Delta\rho_{min} = -2.02$ e Å^{-3} (at Rh site)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Rh1—P1	2.3109 (8)	P1—C11	1.841 (3)
Rh1—P2	2.2873 (7)	P1—C17	1.821 (3)
Rh1—C41	2.260 (3)	P1—C23	1.819 (3)
Rh1—C42	2.257 (3)	P2—C12	1.832 (3)
Rh1—C45	2.248 (3)	P2—C29	1.806 (3)
Rh1—C46	2.236 (3)	P2—C35	1.816 (3)
P1—Rh1—P2	85.23 (3)		

Cell parameters at 294 K are $a = 10.200(7)$ and $c = 39.97(5)$ Å. H atoms were placed in calculated sites, with C—H = 0.98 Å and U(H) = 1.2U(bonded C). The anisotropic displacement parameters of the F atoms (each treated as a single site) are fairly large (as commonly observed for BF_4 groups), corresponding to large thermal motion and/or possible (untreated) disorder. The (*S*,*S*) enantiomer in space group $P4_3$ gave a significantly higher *wR* value (0.088).

Data collection: *DTCOLLECT* (Molecular Structure Corporation, 1997*a*). Cell refinement: *d*TREK* (Molecular Structure Corporation, 1997*b*). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997*c*). Program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1294). Services for accessing these data are described at the back of the journal.

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An η^6-Toluene Complex of Neodymium: [Nd(η^6-$C_6H_5CH_3$)($AlCl_4$)$_3$]

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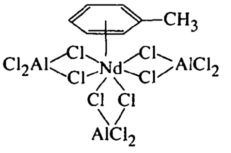
Abstract

The Nd^{III} ion in hexa-μ-chloro-1:2κ^2*Cl*;1:3κ^2*Cl*;1:4κ^2*Cl*-hexachloro-2κ^2*Cl*,3κ^2*Cl*,4κ^2*Cl*-[1(η^6)-toluene]trialuminiumneodymium has distorted pentagonal bipyramidal coordination geometry. Five Cl atoms form the equatorial plane, and the toluene ring and the sixth Cl atom occupy the apical sites. The average Nd—C(η^6) and Nd—Cl distances are 2.926 (5) and 2.857 (1) Å, respectively.

Comment

η^6-Arene–lanthanoid complexes have special catalytic properties (Hu, Tian, Shen & Liang, 1992). We are interested in the chemical behaviour of such complexes when sterically congested ligands are present. During an attempt to synthesize [Nd(η^6-1,3,5-^{t}BuC_6H_3)($AlCl_4$)$_3$] in toluene solution, the title complex, (I), was isolated instead.



(I)

A molecule of (I) (Fig. 1) consists of one Nd atom, one toluene molecule and three aluminium tetrachloride ions. The coordination number of Nd^{III} may be regarded as nine provided that toluene is thought to occupy three vertices of the polyhedron. Alternatively, the coordination polyhedron can be viewed as a distorted pentagonal bipyramid. The equatorial plane comprises five Cl atoms (Cl1, Cl2, Cl3, Cl4 and Cl5), with Cl6 and the centroid of the toluene ring occupying the apical positions. This mode of coordination is similar to those of related Ln^{III} compounds (Cotton & Schwotzer, 1986; Fan, Shen & Lin, 1989*a*; Biagini, Lugli & Millini, 1994) with distorted pentagonal bipyramidal coordination. The equatorial Nd—Cl bond lengths are 2.846 (1)–2.902 (1) Å, rather longer than the apical Nd—Cl6 distance of 2.799 (1) Å. Very similar values have been found for the isomorphous and isostructural Sm compound (Fan, Shen & Lin, 1989*b*).

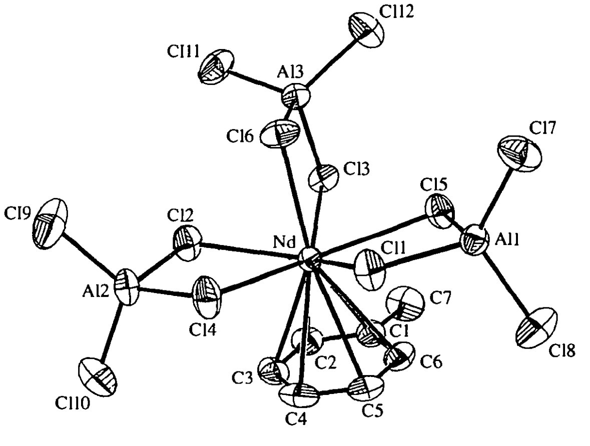


Fig. 1. Molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The synthesis of the title compound was conducted under argon by Schlenk techniques. Crystals were obtained by reac-

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