

The crystal structure of 5-hydro- and 7-hydro-*s*-indacenide-Rh(COD). A comparison with similar complexes

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Abstract

The monometallic complex with Rh(COD) of 5-hydro and 7-hydro-*s*-indacenide has been synthesized and structurally characterized. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.513(2)$, $b = 15.902(2)$, $c = 8.423(1)$ Å, $\alpha = 97.0(1)$, $\beta = 91.4(1)$, $\gamma = 111.7(1)^\circ$. The geometry of the ligand was revealed to be substantially different from that of its 2,6-dimethylated homologues. An explanation for this behaviour is given in terms of electronic and mesomeric effects. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Mononuclear Rh and Ir complexes of 2,6-dimethyl-*s*- and 2,7-dimethyl-*as*-hydroindacenide ligands have been the subject of a recent report where physico-chemical properties and crystal structures have been widely described [1]. Mononuclear complexes of non-methylated *s*- and *as*-hydroindacenide ligands of different transition metals have also been reported in the last few years [2]. A quite interesting behaviour among these complexes deals with the mononuclear derivatives of the *s*-indacene ligand. Inspection of the reported data reveals that while the chemical properties of homologous compounds, methylated or non-methylated, are virtually the same, the structure of the indacenyl ligand does substantially change. On the contrary, the molecular structure of the ligand seems to be unaffected by varying the coordinating metal [2]. These properties could be evidenced from a structural comparison of the 5-hydro and 7-hydro-*s*-indacenide-Rh(COD) reported here, with its 2,6-dimethylated homologues and with the

analogous complex hydro-*s*-indacenide-Mn(CO)₃. We will give an explanation for these findings in terms of electronic and mesomeric effects. The description of the chemical properties and reactivity of the examined complex is omitted here, being almost unchanged with respect to those of similar or homologous complexes already examined [1].

2. Results and discussion

The structure of the two molecular subunits 7-hydro-*s*-indacenide-Rh(COD) (**A**) and 5-hydro-*s*-indacenide-Rh(COD) (**B**) forming the asymmetric structural unit is shown in Fig. 1, together with the atom numbering scheme. Some relevant geometrical parameters are given in Table 1.

At first sight, the two molecules **A** and **B** seem to be related by a glide plane parallel to *ac*. However, this pseudo symmetry is absolutely unmatched with the crystal lattice geometry (see Fig. 2), which removes any possible structural misinterpretation. The two subunits turn out to be enantiomorphous isoclined [3] with respect to the direction *c*, as it arises from the unambiguous location of the methylene groups and, corre-

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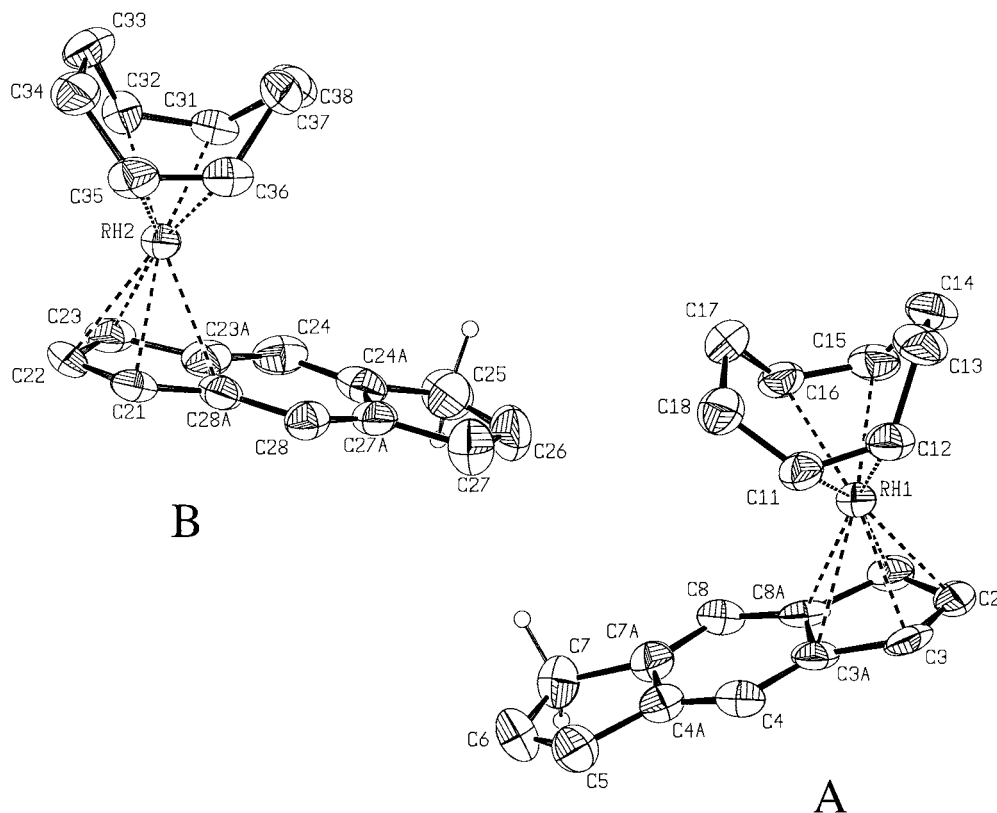


Fig. 1. ORTEP view of 7-hydro-*s*-indacene-Rh(COD) (**A**) and 5-hydro-*s*-indacene-Rh(COD) (**B**) forming the independent structural unit.

spondingly, of the olefin double bond in the uncomplexed five-membered rings. The pattern of bond lengths in the indacene ligand indicates well-localized double bonds between C(4)–C(4A) (1.38(1) Å), C(7A)–C(8) (1.36(1) Å) and C(5)–C(6) (1.37(1) Å) in **A** and C(24)–C(24A) (1.36(1) Å), C(28)–C(27A) (1.35(1) Å) and C(26)–C(27) (1.33(1) Å) in **B**, respectively. The emerging electronic structure of this ligand is quite different from that of the homologous 2,6-dimethyl derivative [1], where for the indenyl residue (including the coordinated five-membered ring and the adjacent benzene ring) a definite resonant structure with delocalized electrons was observed (see Scheme 2). In the parent non-methylated complex, the electronic structure of the indacene ligand showing clearly localized single and double bonds seems to be assisted and stabilized by the olefin double bond present in the uncomplexed five-membered ring, which in fact would induce a favourable conjugated system according to Scheme 1 [4].

The same structure was also found in the case of the complex hydro-*s*-indacene-Mn(CO)₃ [2], confirming our results and showing that this feature does not depend on the nature of the metal.

This behaviour likely opposes the presence of a CH₃ group bonded to C(6) in the methylated derivative

through a conjecturable hyperconjugative effect [5] according to Scheme 2, which leads to the structure labelled with (*) as actually observed.

Table 1
Some relevant geometrical parameters for **A** and **B**

	A	B
Rh–C(1)	2.210(9)	2.210(9)
Rh–C(2)	2.229(8)	2.239(9)
Rh–C(3)	2.205(9)	2.229(9)
Rh–C(3A)	2.372(9)	2.365(8)
Rh–C(8A)	2.360(8)	2.379(8)
C(1)–C(2)	1.42(1)	1.40(1)
C(2)–C(3)	1.41(1)	1.41(1)
C(3)–C(3A)	1.45(1)	1.45(1)
C(3A)–C(8A)	1.44(2)	1.43(1)
C(1)–C(8A)	1.44(1)	1.45(1)
C(3A)–C(4)	1.42(1)	1.43(1)
C(4)–C(4A)	1.38(1)	1.36(1)
C(4A)–C(7A)	1.42(2)	1.44(1)
C(4A)–C(5)	1.48(1)	1.47(1)
C(5)–C(6)	1.37(1)	1.45(1)
C(6)–C(7)	1.45(2)	1.33(1)
C(7)–C(7A)	1.52(1)	1.49(1)
C(7A)–C(8)	1.36(1)	1.35(1)
C(8)–C(8A)	1.43(1)	1.42(1)
Δ(M–C) (Å)	0.15	0.15
HA (°)	4	5

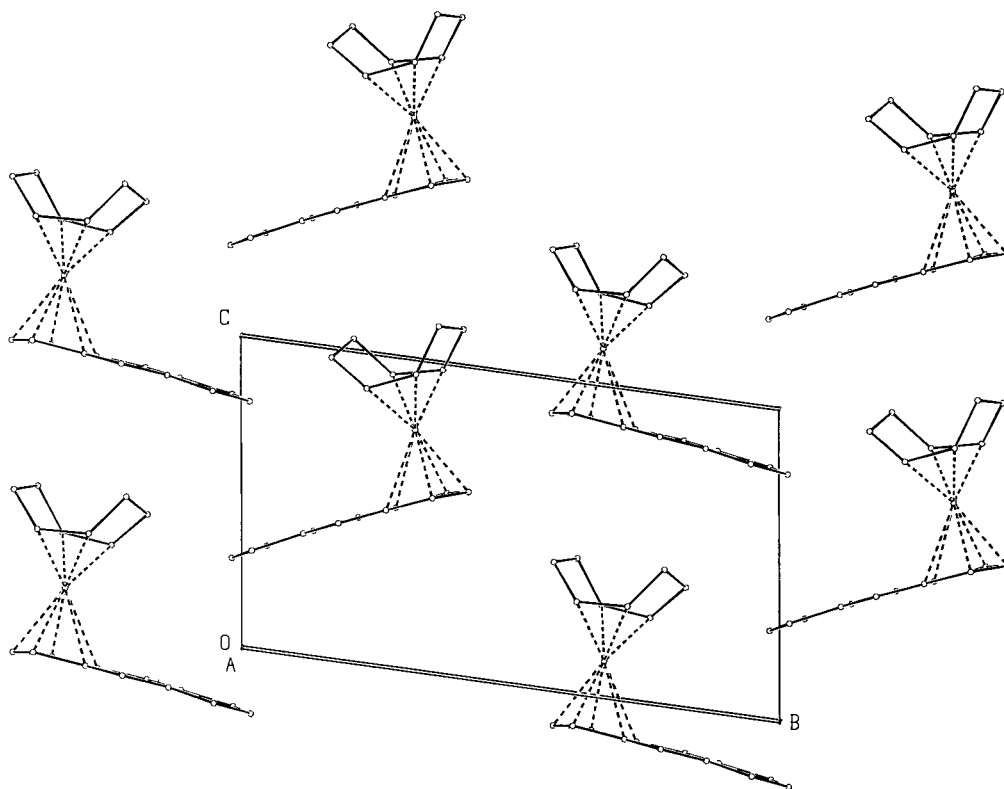


Fig. 2. Mode of packing of the title compounds as viewed along *a*. The stacking-like disposition of the indacenide rings is evidenced.

In this way also the acidic character of the cyclopentene ring is expected to be rather different in these two homologous compounds [6] (although not observed in the chemical behaviour we have investigated).

The COD ring assumes, in both the two subunits **A** and **B**, an identical orientation with its double bonds in a direction orthogonal to the C(8A)–C(3A) ring junction bond. This fact is certainly not casual and indicates that such a conformation, which is identical to that found in all the symmetric indenyl derivatives, is not affected by the asymmetric nature of the indacene ligand, as has been exhaustively explained and predicted elsewhere [7,8].

The packing in the direction *c* is characterized by an insertion of the indacenide rings into the hollows opened between indacenide and COD rings of adjacent molecules (see Fig. 2) with the shortest C...C intermolecular contact distances in the range 3.6–3.8 Å. This optimal close-packing arrangement could not be achievable in the case of 2,6-dimethyl-*s*-hydro-indacenide-Rh(COD), for which a completely different structure was found [1]. As a matter of fact, in this last complex the packing is mainly controlled by the protruding CH₃ groups, which would inhibit the particular assembly of molecular units stacked in the direction *c*, as here observed (see Fig. 2).

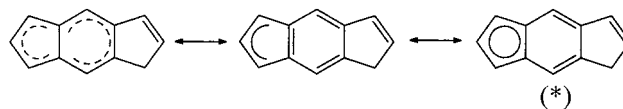
3. Experimental

3.1. Synthesis

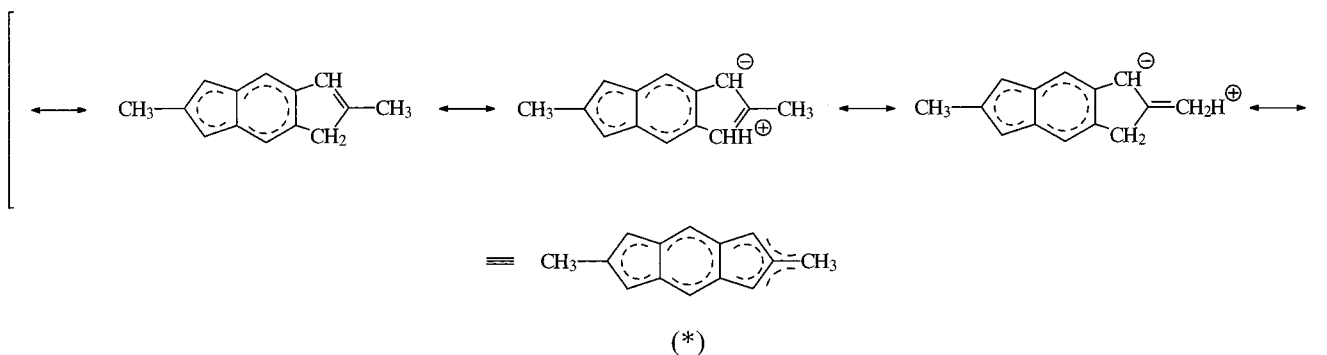
The synthesis of complex 5-hydro and 7-hydro-*s*-indacenide-Rh(COD) has been previously reported [1].

3.2. X-ray diffraction

Suitable crystals of the title compound, grown from THF–hexane solutions, were mounted on a Philips PW-100 computer-controlled four-circle diffractometer with graphite monochromator (Mo–K_α radiation). Indexing of 25 high-angle reflections, followed by short preliminary data collection, led to the assignment of a triclinic unit cell for which the space group $P\bar{1}$ was initially assigned and later confirmed by a well-behaved refinement process. The initial Patterson map was solved for Rh positions; subsequent least-squares differ-



Scheme 1. Limit forms predictable for the ligand in the title compound. The label (*) indicates the structure as determined in the present investigation.



Scheme 2. Resonance equilibrium for the 2,6-dimethyl-*s*-indacene ligand in its complex with Rh(COD) in terms of hyperconjugative effects. The label (*) indicates the average structure as found and described in Ref. [1].

Table 2
Summary of the crystal data and intensity data collection for *s*-indacene-Rh(COD)

Formula	C ₂₀ H ₂₁ Rh
<i>M</i>	384.29
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.513(2)
<i>b</i> (Å)	15.902(2)
<i>c</i> (Å)	8.423(1)
α (°)	97.0(1)
β (°)	91.4(1)
γ (°)	111.7(1)
<i>V</i> (Å ³)	1541.2
<i>Z</i>	4
Crystal dimensions (mm)	0.30 × 0.25 × 0.20
<i>D</i> _{calc} (g cm ⁻³)	1.57
μ (cm ⁻¹)	9.85
<i>T</i> (K)	298
Radiation	Mo-K α (λ = 0.7107 Å)
Take off angle (°)	3
Scan speed (°·min ⁻¹)	2.0 in the 2 θ scan mode
2 θ range (°)	3.0 ≤ 2 θ ≤ 45
Observed reflections with $F_o^2 > 3\sigma(F_o^2)$	3995
<i>R</i> (on <i>F_o</i>)	0.056
<i>R_w</i>	0.054
Highest map residue (e Å ⁻³)	0.60
Goodness-of-fit	0.95

ence Fourier cycles revealed all the non-hydrogen atoms. The independent structural unit appeared to consist of two molecular units **A** and **B**. Most of the hydrogen atoms were located from the final difference Fourier synthesis, yet they were geometrically recalculated, included isotropically in the final calculations but not refined. Particular care was taken for the 7-hydro and 5-hydro ends of the ligand in the subunits **A** and **B**, respectively, where the methylene carbon atoms were unambiguously identified before including the hydrogen atoms for them and their immediate neighbours. The thermal parameters for all the non-hydrogen atoms were treated anisotropically. The model converged to give weighted and unweighted *R* factors of 0.054 and

0.056, respectively. In the final difference map the largest residual peak was less than 0.60 e Å⁻³. The intensities were corrected for Lorentz and polarization effects, but not for absorption (μ = 9.85 cm⁻¹). Crystal data and intensity collection data are reported in Table 2.

4. Supplementary material

Final positional and thermal parameters and a complete list of the geometrical parameters are available as supplementary material upon request from the authors.

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