www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 593–594 (2000) 315–324

Journal of Organometallic Chemistry

Synthesis, properties and reactivity of mononuclear Rh(I) and Ir(I) complexes of *s*- and *as*-hydroindacenide ligands

Annalisa Bisello [a], Alberto Ceccon [a,*], Alessandro Gambaro [a], Paolo Ganis [a], Francesco Manoli [b], Saverio Santi [a], Alfonso Venzo [b]

[a] *Dipartimento di Chimica Fisica, Università di Padova, Via Loredan 2, I-35131 Padua, Italy*
[b] *CNR, Centro di Studi sugli Stati Molecolari Radicalici ed Eccitati, Via Loredan 2, I-35131 Padua, Italy*

Received 15 June 1999; accepted 7 September 1999

Dedicated to Professor Fausto Calderazzo on the occasion of his 70th anniversary.

Abstract

The monometallic complexes with Rh(COD) and Ir(COD) of 1,5- and 1,7-dihydro-*s*-indacene, 2,6-dimethyl-1,5-dihydro-*s*-indacene and 2,7-dimethyl-1,6-dihydro-*as*-indacene have been synthesized and characterized spectroscopically and structurally. Deprotonation and further complexation of these compounds afforded mixtures of *syn* and *anti* homobimetallic isomers. The *syn*/*anti* ratio depends on the structure of the ion pairs of the salt and on the *s* or *as* geometry of the bridging ligand. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Monometallic complexes; Hydroindacenide ligands; *s*- and *as*-Indacene; Rhodium complexes; Iridium complexes

1. Introduction

s- and *as*-Indacene–diide ligands have been identified as suitable substrates for bridging two metal atoms in view of the presence of strong electronic interactions between the metal centers which might result in interesting chemical and physical properties [1]. The rigid indacenyl structure allows two metal groups to bond either in the *syn* or *anti* disposition with respect to the plane of the bridge, so that orientation and distance between the two metals are certain. The general synthetic procedure of these bimetallic complexes consists of the reaction of indacene–diide dilithium salts with mononuclear or dinuclear metal reagents. However, the stereochemical control of the reaction is a real dilemma. Groups such as MCp or MCp* ($Cp = C_5H_5$, $Cp^* = C_5Me_5$; M = Fe, Co, Ni) coordinate exclusively *anti* [2]; conversely, a mixture of *syn* and *anti* isomers have been obtained for metal carbonyl complexes of manganese [3]. Finally, recent results by O'Hare [4] on cobalt and iron complexes obtained by reaction of the neutral 1,3,5,7-tetra-*t*-butyl-indacene with dinuclear reagents have only shown the presence of the *syn* isomer. Recently, we have prepared some Rh(I) and Ir(I) bimetallic indacenyl complexes by quenching the dilithium salts of *s*- and *as*-indacene–diides with the opportune metal dimer. The *syn*/*anti* ratio of the isomers in the reaction mixture is in favor of the *syn* isomer; its value, however, depends on the symmetric or asymmetric structure of the indacenyl ligand, and probably on the dimeric or monomeric structure of the metallic reagent [5].

Besides, by a one-step synthesis from dilithium salts bimetallic indacenyl complexes can be obtained from the monometallic complexes of hydroindacenyl ligands by deprotonation and subsequent reaction with metal reagents [6]. Herein we report the synthesis and the structural properties of some monometallic complexes of *s*- and *as*-hydroindacenyl ligands. Their deprotonation and subsequent reaction with rhodium and iridium dimers afforded homo-bimetallic compounds. The *syn*/*anti* ratio of the isomers appears to depend on the structure of the ion pairs of the

---

* Corresponding author. Fax: + 39-049-827-5135.
E-mail address: a.ceccon@chfi.unipd.it (A. Ceccon)

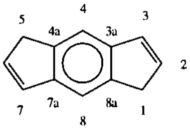
PII: S0022-328X(99)00522-7

[indacene-diide-(M(COD)]$^{-}$K^{+} salt and on the symmetric or asymmetric structure of the bridging ligand.

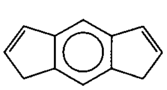
2. Results and discussion

2.1. Synthesis of mononuclear indacenyl complexes

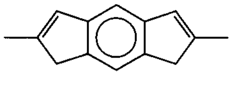
Solutions in anhydrous THF of the three indacene ligands, viz. dihydro-*s*-indacene (obtained as a mixture of the 1,5- and 1,7-isomers, **1** and **1′** [7], 2,6-dimethyl-1,7-dihydro-*s*-indacene (**2**) [3a] and 2,7-dimethyl-1,6-dihydro-*as*-indacene (**3**) [3a], were treated with one equivalent of *t*-BuLi in pentane and then with one equivalent of the [Rh(μ-Cl)(COD)]$_2$ dimer in the interval between −30 and −20°C.



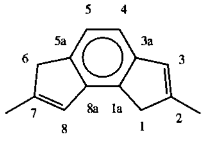
1,5-dihydro-*s*-indacene,
1



1,7-dihydro-*s*-indacene,
1′

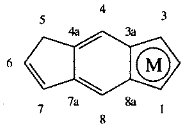


2,6-dimethyl-1,5-dihydro-*s*-indacene,
2

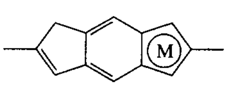


2,7-dimethyl-1,6-dihydro-*as*-indacene,
3

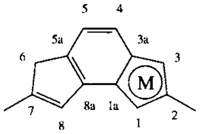
As shown in Table 1, the monometallic derivatives **1-Rh**, **2-Rh**, **3-Rh** and **3a-Rh** were obtained in good to high yields ranging from 70 to 98%.



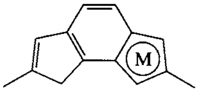
5-hydro-*s*-indacenide-Rh(COD),
1-Rh



2,6-dimethyl-5-hydro-*s*-indacenide-Rh(COD),
2-Rh



2,7-dimethyl-6-hydro-*as*-indacenide-Rh(COD),
3-Rh



2,7-dimethyl-8-hydro-*as*-indacenide-Rh(COD),
3a-Rh

M = Rh(COD)

Comparable yields have been reached in those runs carried out with KH as a base except when **2** is the ligand. The analogous iridium complexes **1-Ir**, **2-Ir**, **3-Ir** and **3a-Ir**, however, were obtained in lower yields (45–60%), as shown in Table 2. The NMR characterization of the complexes is reported below.

From Tables 1 and 2 one can observe that in some runs, besides the monometallic complexes, the homobimetallic complexes, viz. 2,6-dimethyl-*s*-indacene–diide-[Rh(COD)]$_2$ (**2-Rh$_2$**) and 2,7-dimethyl-*as*-indacene–diide-[Rh(COD)]$_2$ (**3-Rh$_2$**) with the inorganic units bound in the *syn* and *anti* arrangement are present

Table 1
Products of the reaction [a] of the hydroindacenide anions with [Rh-(μ-Cl)(COD)]$_2$ [b]

Reagent	[Reagent] (M)	Base [c,d]	Mononuclear product	Yield (%)	Dinuclear product	Yield (%)	*Syn*/*anti* ratio
1		KH [c]	**1-Rh**	70	Not detected	<1	–
1		KH [e]	**1-Rh**	70	Not detected	<1	–
2		KH [c]	**2-Rh**	Low	Not detected	<1	–
2		*t*-BuLi [d]	**2-Rh**	90	**3-Rh$_2$**	ca. 1	Not measured
3		KH [c]	**3-Rh**	98	Not detected	<1	–
3		*t*-BuLi [d]	**3-Rh**	70–80	**3-Rh$_2$**	15–10	1.5:1
3		*n*-BuLi [d]	**3-Rh**	70	**3-Rh$_2$**	15	1.5:1
1-Rh	0.03	KH [c]			**1-Rh$_2$**	≥99	16:1–7:1
1-Rh	0.01	KH [c]			**1-Rh$_2$**	≥99	4:1
1-Rh	0.01	KH/crown [f]			**1-Rh$_2$**	≥99	<0.01
2-Rh		*t*-BuLi			**2-Rh$_2$**	≥99	4.5:1
3-Rh+**3a-Rh** [g]		*t*-BuLi			**3-Rh$_2$**	≥99	1.5:1

[a] Solvent THF, T −20 to −30°C.

[b] One equivalent.

[c] Excess KH was used as a THF slurry.

[d] One equivalent of *n*-BuLi or *t*-BuLi was used.

[e] In this entry one equivalent of [Rh(μ-Cl)(NBD)]$_2$ was used.

[f] Ca. ten equivalents of 18-crown-6 were added.

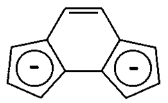
[g] 1:1 mixture.

Table 2
Products of the reaction [a] of the hydroindacenide anions with $[Ir(\mu\text{-}Cl)(COD)]_2$ [b]

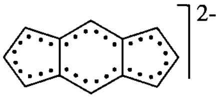
Reagent	Base [c,d]	Mononuclear product	Yield (%)	Dinuclear product	Yield (%)	*Syn*/*anti* ratio
1+**1′** [e]	KH [c]	**1-Ir**	74	Not detected	<1	–
1+**1′** [e]	*t*-BuLi [d]	**1-Ir**	60	Not detected	<1	–
2	KH [c]	**2-Ir**	25	Not detected	<1	–
2	*t*-BuLi [d]	**2-Ir**	45	Not detected	<1	–
3	KH [c]	**3-Ir** [f]	53	**3-Ir$_2$**	24	1:2
3	*n*-BuLi [d]	**3-Ir** [f]	55	**3-Ir$_2$**	22	1:3

[a] Solvent THF, T −20 to −30°C.
[b] One equivalent.
[c] Excess KH was used as a THF slurry.
[d] One equivalent of *n*-BuLi or *t*-BuLi was used.
[e] 1:1 mixture.
[f] 1:1 mixture of 6-hydro-2,7-dimethyl-*as*-indacenide-Ir(COD) (**3-Ir**) and 8-hydro-2,7-dimethyl-*as*-indacenide-Ir(COD) (**3a-Ir**).

among the reaction products; their percentages, however, appear to be significant and comparable with those of the monometallic complexes in the case of the asymmetric indacenyl ligand. Likely, these results can be explained if one considers the electronic structures of the mono- and di-anions of the *s*- and *as*-indacenyl ligands. The *s*- and *as*-monoanions have both a quite stable electronic structure comparable with that of an indenyl anion. This is confirmed by the X-ray analysis of the pattern of bond lengths of the indacenyl skeleton in the crystal structure of the asymmetric mono-complex described below, where the uncoordinated five-membered ring behaves as an unperturbing substituent to the benzene ring and does not affect the electronic structure of the residual resonant 10 π-electron indenyl system. In contrast, the *s*- and *as*-indacene–diides have different electronic structures which are responsible for their different stability and reactivity [8]. From a pictorial point of view, one can envisage a relatively more stable localized electronic structure for the asymmetric dianion where two aromatic cyclopentadienyl rings are connected by a double bond bridge. This is not possible for the symmetric dianion, the more delocalized electronic structure of which makes it an extremely sensitive species at higher energy.

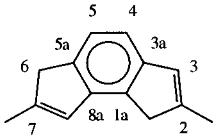


as-indacene-diide



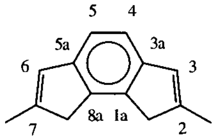
s-indacene-diide

These considerations are of importance when deprotonation of the second cyclopentadienyl ring occurs. It is probable, in fact, that if only one equivalent of *t*-BuLi is used the formation of the bimetallic compounds takes place through deprotonation of the monometallic species as it forms by the ligand monoanion followed by further metal complexation. Support for this is the presence, in percentages comparable with those of the bimetallic derivatives, of all the isomeric forms of the ligand reagent, viz. **3**, **3′**, and **3″**, which indicates that the hydrocarbon underwent a deprotonation–protonation process. Therefore, the deprotonation–complexation process of the asymmetric indacenyl complex must be easier and faster than that of the symmetric complex.



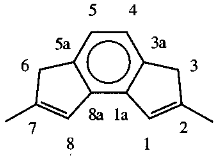
2,7-dimethyl-1,6-dihydro-*as*-indacene

3



2,7-dimethyl-1,8-dihydro-*as*-indacene

3’



2,7-dimethyl-3,6-dihydro-*as*-indacene

3’’

The pure monometallic derivatives have been generally obtained by crystallization of the crude reaction mixture. For the asymmetric iridium complexes the reaction mixture was found by ^{1}H-NMR to be made up of the three isomers **3**, **3′** and **3″** shown above in the statistic ratio of ca. 2:1:1), of two monometallic isomers, viz. **3-Ir** and **3a-Ir** in the 1:1 ratio, and of the two bimetallic isomers **3-Ir$_2$** in a *syn*:*anti* ratio ranging from 1:1 to 3:1. Using medium pressure column chromatography on silica the ligands and the monometallic complexes were eluted as a unique non-resolvable mixture. Of the two bimetallic species only the *anti* isomer was obtained after the elution while the *syn* isomer decomposed in the column. Thus, the *syn* isomer seems to be more reactive than the *anti* isomer, at least in chromatographic conditions. This behavior has been confirmed by a kinetic study carried out on the carbonylation reaction of the two isomeric species of rhodium and iridium complexes [5b].

2.2. NMR characterization of the monocomplexed hydroindacenyl-M(COD) species

The NMR characterization of the mono-complexed indacenyl species was obtained from the variations of the spectra observed on complexing the starting ligands. In fact, the proton spectrum of the 1:1 mixture of the neutral hydrocarbons **1** and **1′** exhibits a large singlet at δ ca. 3.4 ppm due to the methylene protons. The olefin protons $H_{2,6}$ of both isomers are isochronous and resonate at δ 6.9, and the remaining olefin protons are observed at ca. δ 6.5. Conversely, a quite different pattern is exhibited by the aromatic protons H_4 and H_8. In fact, in 1,5-dihydro-*s*-indacene they are equivalent and appear as a singlet at δ 7.49 whereas in 1,7-dihydro-*s*-indacene they are non-equivalent and resonate at δ 7.43 and δ 7.56, respectively. The bonding of one Rh(COD) unit to both **1** and **1′** produces the species **1-Rh**. The complexation causes the disappearance of any molecular symmetry and the signals due to each hydrogen atom are resolved in the ^1H spectrum. In particular, the aromatic protons resonate at δ 7.26 and δ 7.15, i.e. slightly upfield with respect to the corresponding signals of **1** and **1′**, similar to that found for the olefin proton $H_{6,7}$ signals. In analogy with the values found for indenyl–Rh(COD) [9], the resonances of the coordinated cyclopentadienyl ring protons $H_{1,2,3}$ appear strongly shifted upfield by coordination and are observed at δ 5.14, δ 6.04 and δ 5.11, respectively; the triplet due to H_2 is further split by coupling with ^{103}Rh (J 1.95 Hz). The presence of the inorganic unit makes the $H_{5,exo}$ and $H_{5,endo}$ protons non-equivalent and they appear as an AB quartet at δ 3.35–3.39. The COD olefin protons are no more equivalent by the asymmetric nature of the organic ligand and their signals appear as two partially overlapped multiplets at δ 3.94 and 3.91. The ^{13}C-NMR signals have been analyzed in the same way, and the lack of molecular symmetry induces all the 12 carbon nuclei of the hydroindacenide frame to resonate at different frequencies. The olefin and methylene carbon resonances of COD are doubled as well.

The spectrum of **2-Rh** exhibits similar features with the obvious difference that the H_2 and H_6 signals are replaced by those of the methyl groups. The coordination with Rh(COD) causes the splitting of the signal due to 2-CH_3 by coupling with ^{103}Rh (J ca. 1.7 Hz); these methyl protons resonate downfield by ca. 0.2 ppm with respect to those of 7-CH_3. Very similar trends are observed for the spectra of the corresponding iridium derivatives. The spectral parameters are reported in Section 3 and do not require further discussion.

In the case of the 2,7-dimethyl-*as*-indacene derivatives, the synthetic procedure [3a] affords only the isomer **3**. The most evident characteristic of its proton spectrum is the *AB* spin system (δ 7.01 and δ 7.23) due to the non-equivalent aromatic protons H_4 and H_5, respectively. The H_3 and H_8 olefin protons resonate at δ 6.49 and 6.52, the methylene H_1 and H_6 at δ 3.30 and 3.33, and the 2-CH_3 and 7-CH_3 at δ 2.17 and 2.16. The lack of molecular symmetry is evident in the ^{13}C spectrum as well (see Section 3). Coordination of one Rh(COD) unit to a cyclopentadienyl ring affords a 1:1 mixture of the two isomers **3-Rh** and **3a-Rh** whose resonances have been assigned by NOE experiments. For the methylene protons two *AB* spin systems have been observed. The methylene nuclei of **3a-Rh** show the highest chemical shift difference between the *exo* and *endo* positions probably due to its closest proximity to the Rh(COD) unit. In the case of the analogous iridium complex, the spectrum of the crude reaction mixture is much more intriguing, showing the signals of seven species, i.e. the starting **3** together with the isomers **3′** and **3″** in the approximate 2:1:1 ratio, two monometallic isomers, viz. **3-Ir** and **3a-Ir**, in the 1:1 ratio, and two homobimetallic isomers of 2,7-dimethyl-*as*-indacene–diide-$[Ir(COD)]_2$. The relative percentages of free, mono and biscomplexed species are those reported in Table 2. In the aromatic region, we observe the AB quartet due to the starting 1,6-dihydro ligand and two singlets at δ 7.07 and δ 7.10 due to the presence of two symmetric ligand isomers. In the olefinic proton region, two multiplets at δ 6.62 and δ 6.48 are detected whose integrals are half so large as of those measured at δ 7.07 and 7.10, respectively. Finally, new signals appear, i.e. two large singlets at δ 3.32 and 3.31 due to methylene protons and two very close singlets at δ 2.163 and δ 2.166 in the region of the methyl protons. On the basis of the chemical shift values, of the multiplicity of the spin systems and of NOE experiments as well, we attributed these new signals to the plane-symmetric isomers **3″** and **3′**, respectively. As in the case of the *s*-hydroindacenide derivatives, the monometallic iridium complexes have been identified on the basis of the similarity of their spectra with those of the rhodium analogs. The ^1H-NMR parameters are reported in Section 3.

2.3. NMR characterization of the bis-complexed indacene–diide-$[M(COD)]_2$ species

As reported in Tables 1 and 2, when **3** is deprotonated with one equivalent of lithium alkyls and then reacted with one equivalent of the $[Rh(\mu\text{-}Cl)(COD)]_2$ dimer, appreciable amounts (12–30%) of homobimetallic $[Rh(COD)]_2$-indacene–diide complexes are formed. The ^1H-NMR spectrum indicates that two isomeric species are present in the ratio of ca. 1.5:1. These

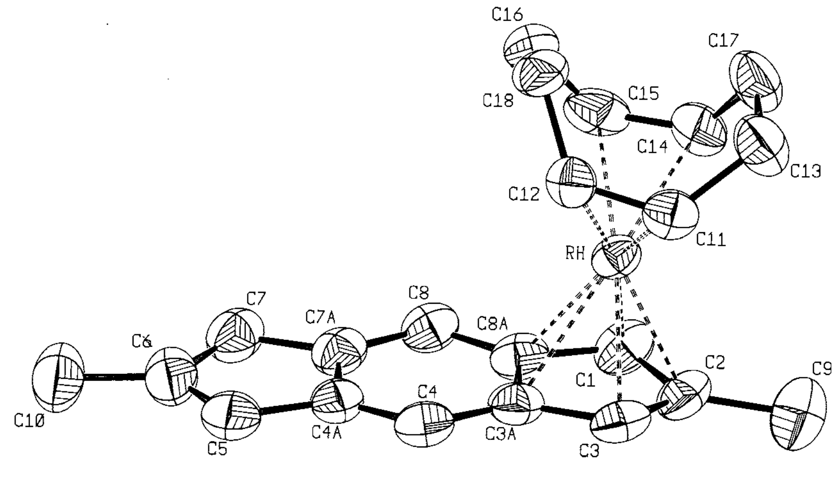


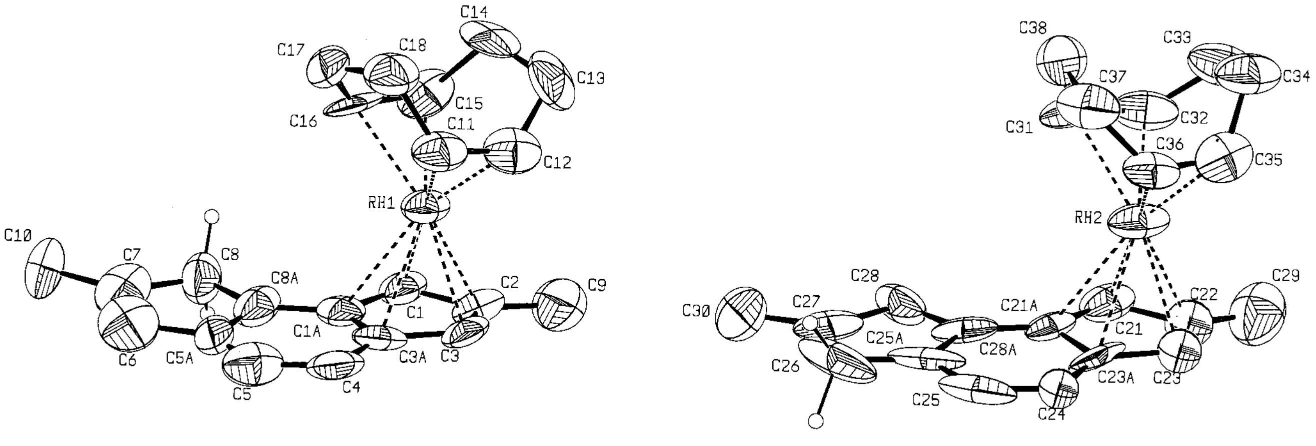
Fig. 1. ORTEP view of 5-hydro-2,6-dimethyl-*s*-indacenide-Rh(COD) (**2-Rh**).

compounds exhibit a very simple spectroscopic pattern owing to their molecular symmetry; only one signal is observed for the aromatic protons, one signal for $H_{3,6}$, one for $H_{1,8}$ and one for the methyls. Again, the signal due to the olefin protons of COD is doubled by the intrinsic asymmetry of the bridging ligand. On the basis of this spectrum, the species present in the minor amount is identified as *anti*-{2,7-dimethyl-*as*-indacene–diide-[Rh(COD)]$_2$} (***anti*-3-Rh$_2$**) as previously reported [5a], the second species as the *syn* isomer, ***syn*-3-Rh$_2$**. A very similar behavior is found in the reaction of dilithium indacene–diide with [Ir(μ-Cl)(COD)]$_2$: the bimetallic species are detected in 22–25% yield, the *syn*/*anti* ratio being ca. 2:1. Surprisingly, the *syn* isomer is formed in higher yield even though steric repulsion between the two COD units located on the same side of the organic ligand are expected to disfavor its formation. More details on the stereoselectivity of the bismetallation reaction as well as on the structure and reactivity of the bimetallic species will be the argument of a forthcoming paper [5b].

In the case of the *s*-indacene derivatives, the bimetallic species are obtained as mixtures of *syn* and *anti* isomers (see Tables 1 and 2) only by deprotonation of pure mono-complexes species and reaction with [M(μ-Cl)(COD)]$_2$ [6]. Even in this case, the characterization was accomplished by NMR spectroscopy, and the

Table 3
Selected bond lengths (Å) and geometrical parameters for the complex 5-hydro-2,6-dimethyl-*s*-indacenide-Rh(COD) (**2-Rh**)

Rh–C(1)	2.187(7)	C(3a)–C(4)	1.39(1)
Rh–C(2)	2.231(9)	C(4)–C(4a)	1.37(1)
Rh–C(3)	2.228(9)	C(4a)–C(7a)	1.44(1)
Rh–C(3a)	2.324(9)	C(7a)–C(8)	1.36(1)
Rh–C(8a)	2.365(8)	C(8)–C(8a)	1.41(1)
C(1)–C(2)	1.41(1)	C(4a)–C(5)	1.47(1)
C(2)–C(3)	1.41(1)	C(5)–C(6)	1.42(1)
C(3)–C(3a)	1.45(1)	C(6)–C(7)	1.43(1)
C(3a)–C(8a)	1.45(1)	C(7)–C(7a)	1.48(1)
Δ(M – C) (Å)	0.164		
HA (°)	9.3		



3a-Rh

3-Rh

Fig. 2. ORTEP view of 6-hydro-2,7-dimethyl-*as*-indacenide-Rh(COD) (**3-Rh**) and 8-hydro-2,7-dimethyl-*as*-indacenide-Rh(COD) (**3a-Rh**).

Table 4
Selected bond lengths (Å) and geometrical parameters for the two structural isomers 6-hydro-2,7-dimethyl-*as*-indacenide-Rh(COD) (**3-Rh**) and 8-hydro-2,7-dimethyl-*as*-indacenide-Rh(COD) (**3a-Rh**)

	3a-Rh		**3-Rh**
Rh–C(1)	2.220(7)	Rh–C(21)	2.220(7)
Rh–C(2)	2.249(7)	Rh–C(22)	2.249(7)
Rh–C(3)	2.224(6)	Rh–C(23)	2.224(6)
Rh–C(3a)	2.375(6)	Rh–C(23a)	2.375(6)
Rh–C(1a)	2.371(6)	Rh–C(21a)	2.371(6)
C(1)–C(2)	1.41(1)	C(21)–C(22)	1.41(1)
C(2)–C(3)	1.41(1)	C(22)–C(23)	1.41(1)
C(3)–C(3a)	1.46(1)	C(23)–C(23a)	1.46(1)
C(1a)–C(1)	1.42(1)	C(21a)–C(21)	1.42(1)
C(3a)–C(4)	1.46(1)	C(23a)–C(24)	1.46(1)
C(4)–C(5)	1.40(1)	C(24)–C(25)	1.40(1)
C(5)–C(5a)	1.39(1)	C(25)–C(25a)	1.39(1)
C(5a)–C(8a)	1.37(1)	C(25a)–C(28a)	1.37(1)
C(8a)–C(1a)	1.40(1)	C(28a)–C(21a)	1.40(1)
C(5a)–C(6)	1.40(1)	C(25a)–C(26)	1.40(1)
C(6)–C(7)	1.48(1)	C(26)–C(27)	1.48(1)
C(7)–C(8)	1.37(1)	C(27)–C(28)	1.37(1)
C(8)–C(8a)	1.48(1)	C(28)–C(28a)	1.48(1)
C(7)–C(8)	1.50(1)	C(27)–C(28)	1.50(1)
Δ(M−C) (Å)	0.14		0.14
HA (°)	6		6

chemical shift values are reported in Section 3. More details on their stability and structure will be published [5b].

2.4. Crystallographic properties of mononuclear indacenyl complexes

The molecular structures of **2-Rh** (the structure of the iridium derivative **2-Ir** is isomorphous and virtually identical) and **3-Rh** are shown in Figs. 1 and 2. Selected geometrical parameters are given in Tables 3 and 4, respectively. Slip distorsions, hinge angles and Rh(Ir)–C bond distances are for both the species in the norm [9]. In the case of **2-Rh**, the pattern of bond lengths in the indacene ligand is consistent with a resonant structure in the indenyl moiety (i.e. the metal coordinated Cp ring and the adjacent benzene ring), and indicates well localized single bonds for C(4a)–C(5) (1.472(6) Å) and C(7a)–C(7) (1.481(5) Å) and values averaged between single and double bond lengths for C(5)–C(6) (1.411(6) Å) and C(6)–C(7) (1.434(8) Å). This reveals the presence of both the predictable isosteric enantiomers in the same site with an estimated statistical weight of 50/50. Thus, the molecule exhibits a pseudo symmetry C_s. The uncoordinated five-membered ring behaves as an unperturbing substituent to benzene and does not affect the electronic structure of the residual resonant indenyl system. We note that this feature is much different from that described in the structure of (5-hydro-*s*-indacenide)−Mn(CO)$_3$ complex, which has been depicted with distinctly localized single and double bonds in the arene ligand [3a].

The pattern of bond lengths in the case of **3-Rh** and **3a-Rh** still indicates a definite resonant structure for the indenyl residue, but in the uncomplexed five-membered ring the single and double bonds are unambiguously identified in both the subunits forming the asymmetric structural unit; C(6)–C(7) (1.372(9) Å) and C(27)–C(28) (1.381(8) Å) are the localized double bonds in the two isomers **3a-Rh** and **3-Rh**, respectively. Thus, both the predictable constitutional isomers **3-Rh** and **3a-Rh** are present in the crystal. Here too, the uncomplexed five-membered ring does not participate to the resonance of the ligand as a whole and leaves the electronic structure of the indenyl residue virtually unperturbed.

A quite interesting feature of all these mononuclear *s*- or *as*-indacenyl-M(COD) complexes deals with the conformation of the COD ring with respect to the whole molecule. In all the previously studied indenyl complexes with M(COD) [9], the COD ring is always oriented with its two olefin double bonds in a direction almost orthogonal to the ring junction bond C(1a)–C(3a), giving rise to a molecular structure having a virtual C_s symmetry. In **2-Rh** and in both the isomers of **3-Rh**, in spite of the disymmetric indacene ligand, the COD ring is still oriented in the same way, revealing that this conformation is likely controlled by the electronic structure of the indenyl residue which maintains the same C_s symmetry. Recently, we have shown that only in the absence of this symmetry we would expect a quite different orientation of the COD ring, such as to allow π-hydrogen bonds of the type C–H···Ar between its CH groups and the central phenyl ring, as found in the corresponding bimetallic compounds [5a]. Thus, the present analysis offers further evidence that symmetry requirements play a substantial leading role in providing conformational stability to a molecule.

2.5. Metallation of the mononuclear indacenyl complexes

The results of the composition of the *syn–anti* bimetallic mixtures obtained from pure monometallic complexes are not of an easy interpretation (see Tables 1 and 2). It can be noted, however, that (i) the *syn*/*anti* ratio of the bimetallic complexes **1-Rh$_2$** is strongly dependent on the concentration of the indacene-diide–Rh(COD) potassium salt, being in favor of the *syn* isomer as the concentration increases; on the other hand, in the presence of 18-crown-ether the isomer *anti* is almost the sole product; (ii) the ratio depends also on the symmetric or asymmetric structure of the ligand bridge, being lower for the asymmetric one. In the likely hypothesis that the potassium (or lithium) salt of the monometallic compounds is present as a contact ion pair in THF, its probable structure places the cation on the opposite side of the RhCOD group. Crystal structure of the alkali metal salts of 1,3,5,7-tetra-*t*-butyl-*s*-indacene–diide showed the two metal atoms to have an *anti* arrangement. This has been attributed to electrostatic repulsion between the cations [4c]; in our opinion, steric effects must also be considered, each metal atom being coordinated to ether molecules. Our preliminary results suggest that, if contact ion pairs prevail in solution, attack of the rhodium or iridium dimer from the *anti* side is more difficult than from the *syn* side and the *syn* product will prevail. On the other hand, when the potassium ion is removed by complexation with the 18-crown-6 ether, between the two free sites of the cyclopentadienyl ring the *anti* face appears strongly favored by steric effects, and the *anti* product is formed almost exclusively. By using the same arguments and taking into account that the distance between the centroids of the two Cp rings is ca. 4 Å in the asymmetric derivatives as against ca. 5 Å in the symmetric analogue [2], one can explain the substantial decrease of the *syn*/*anti* ratio on going from the symmetric to the asymmetric structure of the bridging ligands The *syn* product seems to be less favored in the asymmetric case by steric factors and the ratio *syn*/*anti* decreases. We are now extending our study to complexes with different ancillary ligands at rhodium in order to clarify the importance of the steric and electronic effects of these ligands on the relative yields of the two bimetallic isomers.

3. Experimental

3.1. General

All reactions and complex manipulations were performed in an oxygen and moisture-free atmosphere. The solvents were carefully dried and deoxygenated before use. The complexes appear as microcrystalline air-stable powders, which gave satisfactory elemental analysis. Melting points are uncorrected. Microanalyses were performed at the Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova. The IR spectra were recorded as THF solutions on a Perkin–Elmer 1600 FT-IR spectrometer, and the 70 eV electron impact mass spectra were measured with a VG 16 Micromass spectrometer. The ^{1}H- and ^{13}C-NMR spectra were obtained as $CDCl_3$ or CD_2Cl_2 solutions on a Bruker AM400 spectrometer operating at 400.13 and 100.61 MHz, respectively. The assignments of the proton resonances were performed by standard chemical shift correlation, COSY and NOESY experiments, those of the ^{13}C ones by 2D-heterocorrelated COSY (HMQC with *bird* sequence for the H-bonded carbon atoms, HMBC for the quaternary ones).

3.2. Synthesis of the ligands

The ligands dihydro-*s*-indacene (**1**) (obtained as a mixture of the 1,5- and 1,7-isomers) [7], 2,6-dimethyl-1,7-dihydro-*s*-indacene (**2**) [3a] and 2,7-dimethyl-1,6-dihydro-*as*-indacene (**3**) [3a] were obtained by the quoted methods. The physical properties agree with those reported; conversely, the NMR data differ to some extent from those reported, and the spectral data obtained by 1D and 2D homo and heteronuclear experiments are reported below.

3.3. Isomeric dihydro-*s*-indacenes

^{1}H-NMR ($CDCl_3$, ppm from internal TMS, *T* 298 K).

3.3.1. 1,5 Dihydro-*s*-indacene (*1*)

δ 7.49 (s, 2H, $H_{4,8}$), ca. 6.9 (m, 2H, $H_{2,6}$), ca. 6.5 (m, 2H, $H_{3,7}$), 3.4 (m, 4H, $H_{1,5}$). ^{13}C-NMR ($CDCl_3$, ppm from internal TMS, *T* 298 K): δ 142.23 ($C_{4a,8a}$), 142.07 ($C_{3a,7a}$), 133.11 ($C_{2,6}$), 132.08 ($C_{3,7}$), 116.44 ($C_{4,8}$), 38.59 ($C_{1,5}$).

3.3.2. 1,7-Dihydro-*s*-indacene (*1′*)

δ 7.56 (s, 1H, H_8), 7.43 (s, 1H, H_4), ca. 6.9 (m, 2H, $H_{2,6}$), ca. 6.5 (m, 2H, $H_{3,5}$), 3.4 (m, 4H, $H_{1,7}$). ^{13}C-NMR ($CDCl_3$, ppm from internal TMS, *T* 298 K): δ 143.33 ($C_{3a,4a}$), 140.07 ($C_{7a,8a}$), 133.31 ($C_{2,6}$), 132.10 ($C_{3,7}$), 119.34 (C_8), 113.38 (C_4), 38.58 ($C_{1,5}$).

3.3.3. 2,6-Dimethyl-1,5-dihydro-*s*-indacene (*2*)

δ 7.36 (s, 1H, H_8), 7.13 (s, 1H, H_4), 6.47 (m, 2H, $H_{3,5}$), 3.28 (m, 4H, $H_{1,5}$), 2.16 (s, 6H, 2,6-CH_3). ^{13}C NMR ($CDCl_3$, ppm from internal TMS, *T* 298 K): δ 145.40 (2C, $C_{2,6}$), 144.66 (2C, $C_{3a,4a}$), 139.65 (2C, $C_{7a,8a}$), 127.75 (2C, $C_{3,5}$), 119.24 (1C, C_4), 111.74 (1C, C_8), 42.73 (2C, $C_{1,7}$), 17.23 (2C, 2,6-CH_3).

3.3.4. 2,7-Dimethyl-1,6-dihydro-*as*-indacene (*3*)

δ 7.19 and 6.97 (AB q, J_{AB} 7 Hz, 2H, H_5 and H_4, respectively), 6.53 (m, 1H, H_8), 6.48 (m, 1H, H_3), 3.33 (m, 2H, H_6), 3.30 (m, 1H, H_1), 2.17 (m, 3H, 7-CH_3), 2.15 (m, 3H, 2-CH_3). ^{13}C-NMR ($CDCl_3$, ppm from internal TMS, *T* 298 K): δ 147.318 (1C, C_7), 144.978 (1C, C_2), 144.920 (1C, C_{8a}), 141.119 (1C, C_{4a}), 139.384 (1C, C_{5a}), 134.356 (1C, C_{1a}), 127.908 (1C, C_3), 125.411 (1C, C_8), 121.530 (1C, C_5), 115.538 (1C, C_4), 43.059 (1C, C_6), 41.388 (1C, C_1), 17.397 (1C, 7-CH_3), 12.246 (1C, 2-CH_3).

3.4. Synthesis of the monometallic hydroindacenide complexes

3.4.1. *t*-BuLi as base

To a stirred solution of 1 mmol of the appropriate dihydroindacene in 10 ml of dry THF kept at −30°C under argon, 1 mmol of *t*-BuLi solution in pentane was added slowly by syringe. The indacenide formation is indicated by a change of the solution color from colorless to orange (in the case of **1**), red (in the case of **2**) and yellow (in the case of **3**). After 1 h, the solution is added by a cannula to a cool (−30°C) solution of 0.5 mmol of $[M(\mu\text{-Cl})(COD)]_2$ (M = Rh, Ir) in 15 ml THF obtaining a yellow solution. After 1 h, the temperature is slowly raised to −10°C and the solvents pumped off. The residue was extracted at room temperature with dry CH_2Cl_2 (3 × 10 ml) and purified by flash chromatography (hexane as eluent).

3.4.2. KH as base

To a well-stirred suspension of excess KH (20 mg) in dry THF (10 ml) kept at −20°C under argon 1 mmol of the appropriate dihydroindacene was added as a solid. After 1 h, the excess KH was allowed to settle and the clear solution of $[\text{hydro-indacenide}]^-K^+$ was allowed to react with a cool (−30°C) solution of $[M(\mu\text{-Cl})(COD)]_2$ and worked up as described above.

3.4.3. 5-Hydro-s-indacenide-Rh(COD) (***1-Rh***)

Yield 70%; m.p. 164°C (decomp.). *m*/*z* 364 (M^+). ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 7.26 (m, 1H, H_4), 7.15 (m, 1H, H_8), 6.86 (m, 1H, H_6), 6.47 (m, 1H, H_7), 6.04 (dt, 1H, $^3J(H_1{-}H_2) = {}^3J(H_2{-}H_3)$ 2.8 Hz, $J(^{103}Rh{-}H_2)$ 1.9 Hz, H_2), 5.14 (m, 1H, H_1), 5.11 (m, 1H, H_3), 3.96 (m, 4H, $^3J(^{103}Rh{-}H$ ca. 2 Hz, COD olefin protons) 3.39 and 3.35 (*AB* quartet, J_{AB} −23 Hz, $H_{5,5'}$), 1.9–1.6 (m, 8H, COD methylene protons). ^{13}C-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 141.50 (C_{7a}), 139.41 (C_7). 133.05 (C_6), 132.48 (C_{4a}), 114.25 (C_4), 114.39 and 112.79 ($^1J(^{103}Rh{-}^{13}C)$ 2.0 and 2.3 Hz, respectively, C_{3a} and C_{8a}), 110.49 (C_8), 90.07 ($^1J(^{103}Rh{-}^{13}C)$ 5.2 Hz, C_2), 76.36 and 76.14 ($^1J(^{103}Rh{-}^{13}C)$ 4.0 and 4.4 Hz, respectively, C_1 and C_3, 67.70 and 67.26 (2C each, $^1J(^{103}Rh{-}^{13}C)$ 13.3 and 13.4 Hz, respectively, COD olefin carbons), 32.04 and 31.72 (2C each, COD methylene carbons).

3.4.4. 5-Hydro-s-indacenide-Ir(COD) (***1-Ir***)

Yield 60–74%; m.p 171°C (decomp.). *m*/*z* 453 (M^+). ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 7.29 (m, 1H, H_4), 7.17 (m, 1H, H_8), 6.85 (m, 1H, H_6), 6.50 (m, 1H, H_7), 5.96 (t, 1H, $^3J(H_1{-}H_2) = {}^3J(H_2{-}H_3)$ 2.8 Hz, H_2), 5.29 (m, 1H, H_1), 5.26 (m, 1H, H_3), 3.9-3.8 (m, 4H, COD olefin protons) 3.31 and 3.29 (*AB* quartet, J_{AB} −23 Hz, $H_{5,5'}$), 1.8–1.5 (m, 8H, COD methylene protons). ^{13}C-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 142.69 (C_{7a}), 140.35 (C_{4a}), 134.50 (C_7). 132.62 (C_6), 115.51 (C_4), 110.85 and 109.40 (C_{3a} and C_{8a}), 111.13 (C_8), 83.38 (C_2), 71.60 (C_1), 71.43 (C_3), 50.15 and 49.97 (2C each, COD olefin carbons), 33.61 and 33.15 (2C each, COD methylene carbons).

3.4.5. 5-Hydro-2,6-dimethyl-s-indacenide-Rh(COD) (***2-Rh***)

Yield 90%; m.p. 180°C (decomp.). *m*/*z* 392 (M^+). ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 7.06 (m, 1H, H_8), 6.82 (m, 1H, H_4), 6.43 (m, 1H, H_7), 5.04 (m, 1H, H_3), 5.00 (m, 1H, H_1), 3.94 and 3.91 (2m, 2H each, $^3J(^{103}Rh{-}H$ ca. 2 Hz, COD olefin protons) 3.25 and 3.20 (*AB* quartet, 2H, J_{AB} −23 Hz, $H_{5,5'}$), 2.37 (s, 3H, 2-CH_3), 2.13 (s, 3H, 6-CH_3), 1.84 and 1.72 (2m, 8H overall, COD methylene protons). ^{13}C-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 144.94 (C_6), 142.07 (C_{7a}), 138.78 (C_{4a}), 128.00 (C_7), 113.92 (C_4), 113.53 (C_8), 108.59 and 108.53 ($^1J(^{103}Rh{-}^{13}C)$ 2.0 and 2.3 Hz, respectively, C_{3a} and C_{8a}), 104.70 ($^1J(^{103}Rh{-}^{13}C)$ 2.1, C_2), 78.81 and 78.11 ($^1J(^{103}Rh{-}^{13}C)$ 4.0 and 4.4 Hz, respectively, C_1 and C_3), 67.57 and 67.31 (2C each, $^1J(^{103}Rh{-}^{13}C)$ 13.7 and 13.6 Hz, respectively, COD olefin carbons), 42.24 (C_5), 32.13 and 31.86 (2C each, COD methylene carbons), 17.14 (6-CH_3), 15.41 ($^1J(^{103}Rh{-}^{13}C)$ 1.3 Hz, 2-CH_3).

3.4.6. 5-Hydro-2,6-dimethyl-s-indacenide-Ir(COD) (***2-Ir***)

Yield 25–45%; m.p. 148°C (decomp). *m*/*z* 481 (M^+). ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 7.10 (m, 1H, H_4), 6.90 (m, 1H, H_8), 6.42 (m, 1H, H_7), 5.16 (m, 1H, H_3), 5.20 (m, 1H, H_1), 3.82 and 3.78 (2m, 2H each, COD olefin protons) 3.24 and 3.22 (*AB* q, J_{AB} −22 Hz, 2H, $H_{5exo,5endo}$), 2.36 (s, 3H, 2-CH_3), 2.13 (s, 3H, 6-CH_3), 1.8–1.4 (m, 8H, COD methylene protons). ^{13}C-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 146.17 (C_6), 143.17 (C_{7a}), 139.72 (C_{4a}), 127.74 (C_7), 114.51 (C_4), 110.63 (C_{3a}), 108.12 (C_{8a}), 108.94 (C_8), 100.18 (C_2), 73.65 and 73.46 (C_1 and C_3), 50.02 and 49.84 (2C each, COD olefin carbons), 42.25 (C_2), 33.66 and 33.16 (2C each, COD methylene carbons), 17.12 (2-CH_3), 15.30 (6-CH_3).

3.4.7. 6-Hydro-2,7-dimethyl-as-indacenide-Rh(COD) (***3-Rh***) *and 8-hydro-2,7-dimethyl-as-indacenide-Rh(COD)* (***3a-Rh***) *(50:50 mixture)*

Yield 98% (KH as a base), and 70–80% (alkyl-lithiums as base). *m*/*z* 392 (M^+). 6-hydro-2,7-dimethyl-*as*-indacenide-Rh(COD): ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 7.07 and 6.86 (*AB* quartet, 2H, J_{AB} 8.1 Hz, H_5 and H_4, respectively), 6.50 (m, 1H, H_8), 5.12 (m, 1H, H_1), 5.09 (m, 1H, H_3), 3.92 and 3.86 (2m, 2H each, olefin COD protons), 3.32 and 3.29 (*AB* quartet, 2H, J_{AB} −24 Hz, $H_{6,exo}$ and $H_{6,endo}$, respectively), 2.39 (d, 3H, $J(^{103}Rh{-}H)$ 1.4 Hz, 2-CH_3), 2.20 (s, 3H, 7-CH_3), 1.85–1.65 (m, 8H, COD methylene protons). 8-hydro-2,7-dimethyl-*as*-indacenide-Rh(COD): ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 6.99 and 6.98 (*AB* q, 2H, J_{AB} 8.1 Hz, H_5 and H_4, respectively), 6.47 (m, 1H, H_6), 5.08 (m, 2H, H_1 and

H_3), 4.03 and 3.80 (2m, 2H each, olefin COD protons), 3.22 and 3.10 (*AB* q, 2H, J_{AB} −24 Hz, $H_{8,exo}$ and $H_{8,endo}$, respectively), 2.41 (d, 3H, $J(^{103}Rh–H)$ 1.4 Hz, 2-CH_3), 2.16 (s, 3H, 7-CH_3), 1.85–1.65 (m, 8H, COD methylene protons).

3.4.8. 6-Hydro-2,7-dimethyl-as-indacenide-Ir(COD) (3-Ir) and 8-hydro-2,7-dimethyl-as-indacenide-Rh-(COD) (3a-Ir) (50:50 mixture)

Yield 22% (KH as a base), and 24% (*n*-BuLi as a base). *m*/*z* 481 (M^+). 6-hydro-2,7-dimethyl-*as*-indacenide-Ir(COD): ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 7.12 and 6.90 (*AB* quartet, 2H, J_{AB} 8 Hz, H_5 and H_4, respectively), 6.48 (m, 1H, H_8), 5.29 (m, 1H, H_1), 5.23 (m, 1H, H_3), 3.83 and 3.79 (2m, 2H each, olefin COD protons), 3.31 and 3.28 (*AB* quartet, 2H, J_{AB} −24 Hz, $H_{6,exo}$ and $H_{6,endo}$, respectively), 2.30 (s, 3H, 1.4 Hz, 2-CH_3), 2.22 (s, 3H, 7-CH_3), 1.7–1.5 (m, 8H, COD methylene protons). 8-hydro-2,7-dimethyl-*as*-indacenide-Ir(COD): ^{1}H-NMR (CD_2Cl_2, ppm from internal TMS, *T* 298 K): δ 7.10 and 7.09 (*AB* q, 2H, J_{AB} 8.1 Hz, H_5 and H_4), 6.41 (m, 1H, H_6), 5.22 (m, 2H, H_1), 5.19 (m, 1H, H_3), 3.87 and 3.68 (2m, 2H each, olefin COD protons), 3.26 and 3.19 (*AB* q, 2H, J_{AB} −24 Hz, $H_{8,exo}$ and $H_{8,endo}$, respectively), 2.29 (s, 3H, 2-CH_3), 2.20 (s, 3H, 7-CH_3), 1.7–1.5 (m, 8H, COD methylene protons).

Table 5
Summary of the crystal data and intensity collection for 5-hydro-2,6-dimethyl-*s*-indacenide-Rh(COD) (**2-Rh**) and for the 6(8)hydro-2,7-dimethyl-*as*-indacenide-Rh(COD) (**3-Rh**)

	2-Rh	**3-Rh**
Empirical formula	$C_{22}H_{25}Rh$	$C_{22}H_{25}Rh$
Formula weight	391.33	391.33
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	10.668(2)	18.789(2)
b (Å)	12.539(2)	8.430(1)
c (Å)	7.252(1)	24.455(3)
α (°)	98.2(1)	90
β (°)	94.1(1)	112.0(1)
γ (°)	113.6(1)	90
V (Å^3)	870.22(85)	3591.41(90)
Z	2	8
Crystal dimensions (mm)	0.20 × 0.40 × 0.40	0.30 × 0.30 × 0.60
$D_{calc.}$ (g cm^{-3})	1.49	1.45
μ (cm^{-1})	9.62	8.48
Temperature (K)	297	298
Radiation (Å)	Mo–K_α (λ=0.7107)	
Take-off angle (°)	3	3
Scan speed (° min^{-1})	2.0 in the 2θ mode	
2θ Range (°)	3.0≤2θ≤45	
Unique reflections [$F_o^2 = 2\sigma(F_o^2)$]	3003	1998
Number of refined parameters	220	415
R (on F_o)	0.057	0.064
R_w	0.052	0.057
Highest map residual (e Å^{-3})	0.56	0.43

3.5. Crystallographic studies

Suitable crystals of 2,6-dimethyl-5-hydro-*s*-indacenide-Rh(COD) (**2-Rh**) 2,6-dimethyl-5-hydro-*s*-indacenide-Ir(COD) (**2-Ir**) and 2,7-dimethyl-6(8)-hydro-*as*-indacenide-Rh(COD) (**3-Rh** and **3a-Rh**) (see text), grown from THF/hexane solutions, were mounted on a Philips PW-100 computer-controlled four-circle diffractometer with graphite monochromator (Mo–K_α radiation, λ 0.7107 Å). Indexing of 25 high angle reflections followed by a short preliminary data collection led to the assignment of a triclinic unit cell for **2-Rh**, for which the space group $P\bar{1}$ was initially assigned and later confirmed by a well-behaved refinement process (**2-Ir** was revealed to be isomorphous with **2-Rh**), and the monoclinic $P2_1/c$ space group for the **3-Rh**/**3a-Rh** mixture. The initial Patterson maps were solved for the Rh positions in both cases; subsequent least-squares difference Fourier cycles revealed all the non-hydrogen atoms. Hydrogen atoms were included in calculated positions (C–H = 1.05 Å) and treated isotropically in the final calculations. In the case of the **3-Rh**/**3a-Rh** mixture, special care was taken for the 6-hydro and 8-hydro ends of the ligand were the methylene carbon atoms were unambigously identified before including the hydrogen atoms for them and their immediate neighbors. The thermal parameters for all the non-hydrogen atoms were treated anisotropically. The models converged to give weighted and unweighted *R* factors of 0.062 and 0.057 for **2-Rh** and 0.065 and 0.057 for **3-Rh**/**3a-Rh**, respectively. In the final difference map the largest residual peak was less that 0.56 e Å^{-3}. The intensities were corrected for Lorentz and polarization effects but not for absorption owing to the relatively low values of μ (ca. 8.7 cm^{-1}). Crystal data and intensity data collection are reported in Table 5.

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.

Acknowledgements

This work was supported in part by the CNR (Roma) through its Centro di Studi sugli Stati Molecolari Radicalici ed Eccitati (Padova).

References

[1] (a) S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637. (b) D. Astruc, Acc. Chem. Res. 30 (1997) 383. (c) M.D. Ward, Chem. Soc. Rev. (1997) 12.

[2] J.M. Manriquez, M.D. Ward, W.M. Reiff, J.C. Calabrese, N.L. Jones, P.J. Carroll, E.E. Bunel, J.S. Miller, J. Am. Chem. Soc. 177 (1995) 6182 and Refs. cited therein.

[3] (a) W.A. Bell, C.J. Curtis, C.W. Eigenbrot Jr., C.G. Pierpont, J.L. Robbins, J.C. Smart, Organometallics 6 (1987) 266. (b) W.L. Bell, C.J. Curtis, A. Miedaner, C.W. Eigenbrot Jr., R.C. Haltiwanger, C.G. Pierpont, J.C. Smart, Organometallics 7 (1988) 691.

[4] (a) P. Roussel, M.J. Drewitt, D.R. Cary, C.G. Webster, D. O'Hare, J. Chem. Soc. Chem. Commun. (1998) 2205. (b) D.R. Cary, C.G. Webster, M.J. Drewitt, S. Barlow, J.C. Green, D. O'Hare, J. Chem. Soc. Chem. Commun. (1997) 953. (c) D.R. Cary, J.C. Green, D. O'Hare, Angew. Chem. Int. Ed. Engl. 36 (1997) 2618.

[5] (a) P. Ganis, A. Ceccon, T. Köhler, F. Manoli, S. Santi, A. Venzo, Inorg. Chem. Commun. (1998) 15. (b) A. Bisello, A. Ceccon, P. Ganis, F. Manoli, S. Santi, A. Venzo, Organometallics, submitted for publication.

[6] C. Bonifaci, A. Ceccon, A. Gambaro, F. Manoli, L. Mantovani, P. Ganis, S. Santi, A. Venzo, J. Organomet. Chem. 577 (1998) 97 and Refs. cited therein.

[7] L. Trogen, U. Edlund, Acta Chem. Scand. B 33 (1979) 109.

[8] M.T. Garland, J.-Y. Saillard, I. Chávez, B. Oëlckers, J.-M. Manriquez, J. Mol. Struct. (Theochem. 390 (1997) 199.

[9] (a) P. Cecchetto, A. Ceccon, A. Gambaro, S. Santi, P. Ganis, R. Gobetto, G. Valle, A. Venzo, Organometallics 17 (1998) 752. (b) L. Mantovani, A. Ceccon, A. Gambaro, S. Santi, P. Ganis, A. Venzo, Organometallics 16 (1997) 2682. (c) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, G. Valle, A. Venzo, J. Organomet. Chem. 492 (1995) 35. (d) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, A. Venzo, Organometallics 14 (1995) 2430. (e) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, G. Valle, A. Venzo, J. Organomet. Chem. 492 (1995) 35. (f) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, L. Mantovani, S. Santi, A. Venzo, J. Organomet. Chem. 475 (1994) 267. (g) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, G. Valle, A. Venzo, Organometallics 12 (1993) 4211. (h) A. Ceccon, A. Gambaro, S. Santi, G. Valle, A. Venzo, J. Chem. Soc. Chem. Commun. (1989) 52 and Refs. cited therein.