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# New Rh derivatives of *s*-indacene active in dehydrogenative silylation of styrene

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#### Abstract

The mono- and bimetallic complexes [(2,6-diethyl-4,8-dimethyl-s-indacenide){Rh(COD)}] (1), anti-[(2,6-diethyl-4,8-dimethyl-s-indacenediide){Rh(COD)}\_2] (2a), syn-[(2,6-diethyl-4,8-dimethyl-s-indacenediide){Rh(COD)}\_2] (2b) were synthesized and characterized spectroscopically and in the case of complex 2b, by means of X-ray diffraction. The <sup>13</sup>C and <sup>103</sup>Rh NMR studies suggest that the bonding mode of the indacenediide ligand can be described as intermediate between  $\eta^3$ - and  $\eta^5$ -coordination. This result was confirmed by the crystal structure of 2b as evidenced by the slippage of the rhodium atom towards the periphery of the ligand. Cyclic voltammetry studies revealed a strong intermetallic communication through the fused ring ligand. This property was further illustrated by higher activity and selectivity of binuclear complexes 2 for the catalytic dehydrogenative silylation of styrene.

Keywords: Rhodium complex; s-indacene; Silylation

### 1. Introduction

Electronic communication between metals in polynuclear complexes has focused considerable attention [1]. This interest has been stimulated by the dramatic modifications of the physical and chemical properties of complexes compared to those of mononuclear species [2]. This process, which is termed "cooperative effect", has found significant implications for the design of materials exhibiting nonlinear optical activity or unusual electrochemical properties [3]. In this context, it is evident, that these properties are profoundly affected by the link which mediates electron interaction between metals. Depending on the flexibility and on the delocalization along this ligand, the degree of metalto-metal communication may vary to a large extend. Among the multiple candidates, fulvalene-derived ligands and fused delocalized polycyclic arenes have been shown to be notably efficient for allowing electronic interaction between two metals [4]. For instance, homo- and heterobimetallic complexes incorporating pentalene and s-indacene as bridging ligand, possess the highest electronic interaction between two metals, as in systems such as [Mn(CO)<sub>3</sub>]<sub>2</sub>(µ- $\eta^5, \eta^3-C_8H_6$  (C<sub>8</sub>H<sub>6</sub> = pentalenediide) or [Cp\*M-Spacer- $M'Cp^*$ ] (Spacer = pentalenediide, *s*-indacenediide; M, M' = Fe, Ru, Ni, Co) [5]. Thus, their potential of application for electronic devices is wide and attracting. However, the relevance of cooperative effect goes well beyond the field of material chemistry since electron transfer is a fundamental process which is involved in the chemical reactivity of molecules [6]. The presence of two metals in close proximity potentially may lead to cooperative interactions which can facilitate transformations that cannot occur for the monometallic species. Additionally, an expanded range of oxidation states is accessible to dinuclear complexes as a result of

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stabilizing metal-metal interactions. These characteristics offer significant opportunities in the field of metal-mediated reactions for the design of new and efficient catalytic systems.

Extensive works have been focused on complexes incorporating Cp or Cp-derived ligands. Indeed, cyclopentadienyl ligand is ubiquitous in organometallic chemistry since it can bind to a large number of metals with different oxidation states. However, in contrast to the well-documented chemistry of fulvalene and fulvalene-like bridged binuclear complexes [4,7], chemical reactivity of dimetallic fused rings systems has been much less developed. These rare investigations were focused on ligand mobility and substitutional lability, steps which are fundamental for the development of potential catalyst. Indeed, comparison of the reactivity of the ancillary NBD or COD ligands (NBD = norbornadiene; COD = 1,5-cyclooctadiene) with carbon monoxide has been used as a criterion for evaluating influence of "indenvl effect" in several indenvl and indacene anions derived mono- and bimetallic complexes.

However, to the best of our knowledge, extension of the scope of this stoichiometric reaction to a catalytic process has been successfully realized only in two cases.  $[(CO)_3Cr(\mu-\eta^6,\eta^3-Ind)Rh(COD)]$  (Ind = heptamethylinde-nyl) catalyzes the trimerization of various alkynes, the presence of  $(CO)_3Cr$  being responsible of an increase of efficiency (factor of 10<sup>3</sup>). This behaviour was mainly attributed to an enhanced coordinative insaturation at rhodium, an effect dubbed "extra indenyl effect" [8]. In the second example, we successfully employed the pentalene complex  $[Cp^*Ru(\mu-\eta^5,\eta^3-C_8H_6)Rh(COD)]$  ( $C_8H_6$  = pentalenediide) for the highly effective and selective dehydrogenative silylation of styrene with triethylsilane [9]. Its selectivity and activity were found to be similar to those of the most efficient rhodium catalysts reported  $[Rh(COD)_2]BF_4/PPh_3$ 

[10]. Cooperative effect was proposed to be involved, however, dihydropentalenes are known to oligomerize readily and are reacted in situ at low temperature to form pentalenyl complexes [11]. Thus, the employment of alternative ligand is highly desirable.

Following our interest in the synthesis and the study of the physical and chemical properties of binuclear complexes bridged by fused ring systems, we have recently developed a new effective and selective route to polyalkylated s-indacenes. These compounds are obtained in high yields and are easy to handle and to convert to the corresponding mono- or dianions [12]. In this context, s-indacene presents an attractive alternative as a bridging ligand. This work describes the synthesis and characterization of the monometallic [(2,6-diethyl-4,8-dimethyl-s-indacenide)Rh(COD)], and of the bimetallic anti-[(2,6-diethyl-4,8-dimethyl-s-indacenediide) $\{Rh(COD)\}_2$  and syn-[(2,6-diethyl-4,8-dimethyls-indacenediide){Rh(COD)} complexes. As part of our effort to add to our understanding of the influence of metal-metal interaction, the spectroscopic, electrochemical and catalytic properties of mono- and bimetallic have been investigated in details. The particular physical and chemical characteristics of the binuclear compounds are strongly influenced by the presence of the second metal centers and will be rationalized in terms of cooperative effect.

#### 2. Results and discussion

#### 2.1. Synthesis

The Rh(I) homobimetallic complexes of the substituted *s*-indacenediide were prepared by two paths as shown in Scheme 1. In the two steps process (path I), the addition of one equivalent of *n*-BuLi to a THF solution of the 2,6-diethyl-4,8-dimethyl-*s*-indacene ligand at -80 °C



Scheme 1.

affords the transient monolithiated compound which in turn reacts with [{Rh( $\mu$ -Cl)( $\eta^4$ -COD)}]<sub>2</sub>]. The mono-rhodium compound 1 was isolated as a vellow solid in an almost quantitative yield. No trace of homobimetallic complex was observed. Subsequent metallation of 1 by *n*-BuLi and reaction with one equivalent of  $[{Rh(\mu-Cl)(\eta^4-$ COD [2] gives the homobimetallic complexes 2 as orange solids in good yield (65%). Compounds 2 can be also prepared in a one-step bis-metallation reaction (path II) by addition of two equivalents of *n*-BuLi to the starting sindacene followed by reaction with rhodium chloride dimer in a comparable yield. In both cases, a mixture of svn and anti isomers was obtained in the same ratio (syn/anti, 2:1) determined by <sup>1</sup>H NMR. A lot of hypotheses have been already proposed to explain the different syn/anti ratio in related homo- and heterobinuclear complexes. Among them, we can cite: the structures and the relative stabilities of both the lithiated intermediates and the metal dimers, the steric hindrance, the solvent effect (THF), the influence of the ancillary ligand of rhodium (COD vs. CO). Ceccon et al. [13] who studied in more details this aspect, concluded that the role of ligand seems preponderant: a large preference for the syn isomer was observed with ancillary ligands as COD or NBD and for the anti form with CO. In our case where two different pathways were used, implying various reactional intermediates but the same deprotonation/metallation procedures, it seems reasonable to envisage that the same hypothesis (dominant influence of the COD ligand) could explain the identical ratio obtained for the two paths. Meanwhile, this chelating olefin affords a smaller excess of the syn isomer than that obtained for sindacenediide spacer (90%) [13]. This presumably results from the slightly higher hindrance of the alkylated s-indacene compared to that of the unsubstituted analogue. Fractional precipitation using benzene as solvent allows us to separate these isomers, the syn form 2b precipitates whereas the anti form 2a remains in the benzenic solution.

#### 2.2. X-ray and NMR structural analysis

X-ray quality single crystals of **2b** were grown from benzenic solution: the solid state structure of **2b** is depicted in Fig. 1 and confirms the synfacial coordination of the Rh(COD) moieties on the polycyclic ligand. Relevant bond distances



Fig. 1. Crystal structure of  $\mathbf{2b}$  at the 50% probability level for the thermal ellipsoids.

are listed in Table 1. The homobinuclear complex *syn*- $[(2,6-diethyl-4,8-dimethyl-s-indacenediide){Rh(COD)}_2]$ , presented an apparent symmetrical structure, slightly curved on the tips, with a molecular angle distortion of 6.89°. Consequently, the *s*-indacenediide loses its aromaticity as evidenced by the noticeable deviation from planarity of the five membered rings.

The puckering of the five membered ring of s-indacene has already been noted for homobinuclear s-indacene  $[Cp^*M(s-indacenediide)MCp^*]^{n+}$  (M = Fe and n = 0, 1; M = Co and n = 0. 2: M = Ni and n = 0. 1) [5a]. As a matter of fact, the complex 2b displays Rh-C (of the ring junction) (Rh–C: 2.407(3)–2.479(3)Å) bonds significantly longer than those involving the periphery carbon atoms (Rh–C: 2.169(3)–2.226(3) Å). The extend of the differences between these distances is larger than those found for analogues in the literature. Indeed, this effect is emphasized when comparing  $\Delta$ (M–C) [14–16] values of **2b** ( $\Delta$ (Rh1– C) = 0.25 Å and  $\Delta$ (Rh2–C) = 0.24 Å) with those for [(hydro-s-indacenide)Rh(COD)] ( $\Delta$ (Rh–C) = 0.15 Å) [17], [(5-hydro-2,6-dimethyl-s-indacenide)Rh(COD)]  $(\Delta(Rh-$ C = 0.16 Å [18], [(6-hydro-2,7-dimethyl-as-indacenide)] Rh(COD)],  $(\Delta(Rh-C) = 0.14 \text{ Å})$  [18], or *syn*-[(2,7-dimethylas-indacenediide){Rh(COD)}<sub>2</sub>] ( $\Delta$ (Rh1–C) = 0.07 Å and  $\Delta$ (Rh2–C) = 0.19 Å) [13], anti-[(2,7-dimethyl-as-indacenediide){Rh(COD)}<sub>2</sub>] ( $\Delta$ (Rh1–C) = 0.00 Å and  $\Delta$ (Rh2– C = 0.01 Å [13].

The COD ligands assume the usual conformation: the two olefin double bonds of each COD lie in a plane almost parallel to the indacenediide ligand and are oriented in a direction almost perpendicular to the ring junction bonds (C4a–C7a and C3a–C8a). This orientation allows the absence of short intramolecular distances between COD (shortest non-bonded C...C: 3.94 Å). In contrast, in the related *syn*-[(2,7-dimethyl-*as*-indacenediide){Rh(COD)}<sub>2</sub>], the proximity of the olefinic ligand (C...C: 3.47 Å) results in the change of conformation of one COD and in the emergence of intramolecular  $\pi$ -hydrogen bonds between indacenediide and COD ligand [13]. In **2b**, the COD

Table 1 Selected bond distances (Å) for complex **2b** 

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Rh(1)–C(8a)	2.419(3)	Rh(1)-C(3a)	2.479(3)
Rh(1)-C(3)	2.226(3)	Rh(1)-C(2)	2.218(3)
Rh(1)-C(1)	2.169(3)	Rh(2)-C(4a)	2.407(3)
Rh(2)-C(7a)	2.441(3)	Rh(2)–C(7)	2.202(3)
Rh(2)-C(6)	2.223(3)	Rh(2)-C(5)	2.178(3)
C(3a)–C(8a)	1.448(3)	C(4a)–C(7a)	1.448(3)
C(1)–C(8a)	1.463(4)	C(3)–C(3a)	1.460(4)
C(1)-C(2)	1.426(4)	C(2)–C(3)	1.420(4)
C(4a)-C(5)	1.468(4)	C(5)–C(6)	1.427(4)
C(6)–C(7)	1.423(4)	C(7)–C(7a)	1.448(4)
Rh(1)-C(15)	2.123(3)	Rh(1)-C(16)	2.114(3)
Rh(1)-C(19)	2.122(3)	Rh(1)-C(20)	2.150(3)
Rh(2)-C(23)	2.110(3)	Rh(2)-C(24)	2.133(3)
Rh(2)-C(27)	2.127(3)	Rh(2)-C(28)	2.130(3)
C(15)-C(16)	1.407(4)	C(19)-C(20)	1.404(4)
C(23)-C(24)	1.393(4)	C(27)-C(28)	1.388(5)

ligands are far enough to allow typical COD conformation. Thus, steric repulsions do not seem to be the sole factor responsible for the larger shift of Rh(COD) fragments toward the periphery of the indacenediide ligand.

<sup>103</sup>Rh NMR has also been shown to be an effective tool for the determination of cyclopentadienyl analogues hapticity in organometallic complexes [16]. Chemical shifts of 1-2 have been determined by using HMBC between the olefinic protons of the COD ligand and the <sup>103</sup>Rh atom  $(J_{\rm H-Rh} = 2 \text{ Hz})$  and are reported in Table 2. The <sup>103</sup>Rh NMR spectra of complexes 1-2 display signal with chemical shifts similar to those found for the related indenvl- and (indenyl)Rh(COD) complexes (-278)alkylated to -519 ppm) [19]. The bonding mode has been described as intermediate between  $\eta^3$ - and  $\eta^5$ -coordination (i.e.,  $\eta^2 + \eta^3$ ). The situation in *s*-indacene complexes is comparable since chemical shifts of 1-2 are in-between that of true  $\eta^3$ -bonding mode in  $[(\eta^3$ -cyclooctenyl)Rh(COD)] (-9 ppm) and that of  $[(\eta^5-\text{Cp})\text{Rh}(\text{COD})]$  which exhibits a quasi-perfect  $\eta^5$ -hapticity (-777 ppm).

As previously shown in related *as*-indacenediide complexes, <sup>103</sup>Rh NMR chemical shift can be used as a good indicator to evaluate the relative Rh centers slippage.  $\delta(^{103}$ Rh) of *syn* complex **2b** is shifted about 70 ppm down-field compared to that of *anti* analogue **2a**. This difference may reflect a slightly more pronounced  $\eta^3$ -character in the *syn* complex, presumably to possible higher steric repulsion of Rh(COD) fragments in **2a** which, then, slips away.

<sup>13</sup>C NMR spectra are also of diagnostic importance in the determination of the hapticity of Cp-derived ligand. Indeed, in the case of indenyl, it can be deduced by comparing the NMR chemical shifts of the five-membered ring carbon atoms in the complex with those of indenyl sodium ( $\Delta \delta^{13}$ C). For  $\eta^3$ -indenyl ligand, periphery carbon atoms are shielded while ring-junction ones are not. The closer to a  $\eta^5$ -bonding mode, the more shielded the ringjunction carbons signal ( $\Delta \delta^{13}C = -20$  to -40 ppm in true  $\eta^5$ -coordination) [20]. Same considerations can also be done in s-indacene complexes. Significant shielding (-20 to -35 ppm in 1 and 2) clearly shows the presence of interaction between ring-junction carbon atoms and the rhodium center and confirms  $\eta^2 + \eta^3$  coordination mode for the indacene ligand. However, no detailed study correlating chemical shift differences and hapticity are currently available, and thus this prevents further analysis of these values.

Table 2

Experimental chemical shifts,  $\delta(^{103}Rh)$  of the studied mono- and bimetallic rhodium complexes 1, 2a and 2b

Complex	δ
	(ppm)
[(2,6-Diethyl-4,8-dimethyl-s-indacenide){Rh(COD)}] (1)	-486
anti-[(2,6-Diethyl-4,8-dimethyl-s-indacenediide){Rh(COD)}2] (2a)	-334
<i>syn</i> -[(2,6-Diethyl-4,8-dimethyl- <i>s</i> -indacenediide){Rh(COD)} <sub>2</sub> ] ( <b>2b</b> )	-261

#### 2.3. Cyclic voltammetry studies

The resulting cyclic voltammograms of all products present cathodic and anodic processes that are summarized in Table 3. This tool has been previously used as an indicator for the interaction between two metallic centers bonded by a bridging ligand, even if quantification remains difficult [21]. Complex 1 can be used as a reference compound, in order to evidence the effect of the second metal listed as  $\Delta Ep$ .

All complexes, presented a one electron oxidation of the Rh center. Complex 1 owned a very positive potential, indicative of the low electronic density the mononuclear complex may have had in order to stabilize higher oxidation states. Comparing complex 1 with its binuclear analogues these presented over 950 mV shift into less positive potentials. This large shift was due to electronic factors given by a ligand which was then more negatively charged. The values of  $I_a/I_c$  listed in Table 3 are higher than unity for complexes 1 and 2b, suggesting the presence of a coupled irreversible chemical reaction while 2a has quasi-reversible electrochemistry. This result could be indicative of a cooperative effect between both metallic centers, absent in isomer 2b, possibly related to a spatial interaction between both Rh atoms, yielding a decomposition of the oxidized specie, consistent with its electrochemical irreversibility.

#### 2.4. Catalysis

Spectroscopic and CV studies have underlined that the presence of a second metal center dramatically affects the physical and chemical properties of Rh(COD) entities. Similar phenomena associated to the electronic communication between two metal centers have been shown to have implications in stoichiometric reaction such substitution reactions in the related bimetallic complexes *syn-* and *anti-*[(*as-*indacenediide){Rh(COD)}<sub>2</sub>]: the substitution by carbonyl ligands of the first COD is much faster than that of the second one [13]. However, definitive proofs for the involvement of cooperative effect in catalytic processes remain very rare [4].

Table 3 Cyclic voltammetry results

Cycle voltaininetry results						
Complex <sup>a</sup>	$E_{a}^{b}$	$\Delta E^{c}$	$I_{\rm a}/I_{\rm c}$	$\Delta E_2^{d}$		
1	1.42	0.14	1.6	0.00		
2a	0.46	0.17	1.0	0.96		
2b	0.37	0.09	1.8	1.05		

<sup>a</sup> Conditions: solvent CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [NBu<sub>4</sub>][BF<sub>4</sub>] as supporting electrolyte, using Pt as working electrode, a Pt wire as an auxiliary electrode, and SCE as the reference electrode. All complexes had a working concentration of  $5 \times 10^{-4}$  M. All potential values listed in volts.

<sup>b</sup> Potential value for the respective anodic peak.

<sup>c</sup> Difference between respective anodic and cathodic peak.

<sup>d</sup> Difference between anodic peak of reference complex **1** and that of listed compound.

We have recently reported that the related heterobimetallic pentalenediide complex  $Cp^*Ru(\mu-\eta^5,\eta^3-pentalenedi$ ide)Rh(COD) was one of the most active rhodium catalysts reported to date for dehydrogenative silvlation [9]. This prompted us to test the activity of 2 for this reaction. In addition, the availability of mono- and bimetallic complexes 1-2 offers a unique opportunity to study potential involvement of a cooperative effect. The reaction of triethylsilane (1.5 mmol) with styrene (4.5 mmol) in the presence of catalytic amount of complexes 1-2 (0.030 mmol of Rh) at 80 °C gave a mixture of (E)-1-phenyl-2-(triethylsilvl)ethene (3, dehydrogenative silvlation product), 1-phenyl-2-(triethylsilyl)ethane (4) 1-phenyl-1-(triethylsilyl)-ethane (5) (4 and 5: hydrosilylation products) (Eq. (1)). Along with these products, ethylbenzene was obtained in an equal amount to that of 3, and this result clearly showed that styrene acted also as hydrogen acceptor. The reaction conditions and the product distribution of the different catalytic tests are summarized in Table 4



Comparison between catalytic results of runs with mono- and binuclear complexes show that in the latter case, the second metallic center created a remarkable effect, the most pronounced consequence being on the activity of the catalyst. Indeed, concentration of Rh was kept constant for all catalytic tests and, this allowed direct assessment of relative activity. Mononuclear complexes presented a reaction time of 450 min (see Table 4), while complete silane consumption is observed within 35 and 180 min, for 2a and 2b, respectively. The strong electronic interaction between both metals channeled through the bridging ligand can be invoked to account for the higher activities of dinuclear complexes. The differences of efficiency between 2a and 2b, can be rationalized in terms of steric hindrance due to the proximity of the two Rh(COD) entities in the syn isomer. Similarly, different behaviours between syn and anti isomers of bimetallic compounds have been already reported and identified by different chemical reactivity or physicochemical properties [4]. The selectivity was also found to depend on the nature (mono- vs. bimetallic) of the catalyst. Indeed, homobinuclear compounds

Table 4

Effect	of	complexes	on	dehydro	ogenative	silvlation	of	styrene <sup>a</sup>

Entry	Complex	HSiEt3 <sup>b</sup>	Time (min)	Product distribution <sup>c</sup> 3:4:5
1	1	100	450	75:14:11
2	2a	100	35	88:12:0
3	2b	100	180	85:11:4

<sup>a</sup> A mixture of styrene (4.5 mmol), HSiEt<sub>3</sub> (1.5 mmol), **1** (0.030 mmol), **2a** and **2b** (0.015 mmol) and toluene (5 mL) was stirred under argon at 80 °C.

<sup>b</sup> Silane consumed %.

<sup>c</sup> Determined by GC.

leads to similar product distribution, i.e., 85-88% of **3** and 12-15% of hydrosilylation products **4** and **5**. In contrast, the selectivity of the reaction in the presence of mononuclear complex **1a** drops to 75\%. However, these differences remain weak and hazardous to rationalize.

Thus, the difference of activity provides direct evidence for the involvement of cooperative effect between both metal centers during the catalysis. Dehydrogenative silylation and hydrosilylation products result from two competitive catalytic cycles and electronic communication may have stabilized intermediaries, which may have not taken place with mononuclear complexes. Detailed mechanism remain to be clarified and in particular, the precise role of the electronic communication during the reaction. Further exploration in this direction is currently in progress.

# 3. Conclusions

We have synthesized and fully characterized new bimetallic rhodium complexes incorporating the fused delocalized ligand (2,6-diethyl-4,8-dimethyl-s-indacenediide). X-ray diffraction analysis of the syn isomer clearly shows that, in the solid state, the rhodium moieties were closer to a  $\eta^3$ bonding than those previously in related complexes. In addition, the preparation of the mononuclear compound allowed a relevant comparison of the influence of electronic communication on physical and chemical properties. Cyclic voltammetry studies together with catalytic properties of **2** for the dehydrogenative silylation of styrene insinuate a cooperative effect between both metallic centers. In order to verify this, EPR experiments of these complexes and their oxidized derivatives are being carried out for a future article.

#### 4. Experimental

#### 4.1. General considerations

All manipulations were carried out under pure dinitrogen atmosphere using a vacuum atmosphere drybox equipped with a Model HE 493 Dri-Train purifier or a vacuum line using standard Schlenk-tube techniques. Reagent grade solvents were distilled under dinitrogen from sodium benzophenone ketyl (tetrahydrofuran, toluene, petroleum ether). [{Rh( $\mu$ -Cl)( $\eta^4$ -COD)}] was prepared by the literature procedures [22]. 2,6-Diethyl-4,8-dimethyl-s-indacene was prepared as previously described [12]. Styrene and triethylsilane were purchased from Aldrich and were degassed before use. n-Butyllithium (1.6 M in hexane) was purchased from Aldrich. <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR spectra were recorded on Bruker Avance 400 MHz. All <sup>103</sup>Rh NMR spectra were performed on a Bruker AMX-400 spectrometer. The  $\delta(^{103}Rh)$  values were calculated by determining the absolute frequency of the cross-peak (HMBC experiments) relating it to the reference frequency of 12.64 MHz  $(\Xi = 3.16 \text{ MHz} \text{ at } 100 \text{ MHz})$ . GC and GC-MS spectra (EI, 70 eV) were recorded on HP 5890 series II and HP 5889 A spectrometers. Elemental analyses (C and H) were

made with a Fisons EA 1108 microanalyzer. Cyclic voltammetry experiments were performed in an airtight three-electrode cell connected to an argon line. The reference electrode was an SCE. The counter electrode was a platinum wire, and the working electrode was a platine disc of ca. 3 mm in diameter. The currents and potentials were recorded on a Pentium II 350 MHz processor, with a BAS CV-50 Voltammetric Analyzer Potentiometer. Each experiment employed CH<sub>2</sub>Cl<sub>2</sub> refluxed over phosphorous pentoxide and [NBu<sub>4</sub>]BF<sub>4</sub>, was dried prior use.

## *4.2.* [(2,6-Diethyl-4,8-dimethyl-s-indacenide) {*R*h(*COD*)}] (1)

A solution of *n*-butyllithium (2.52 mmol) in hexane (1.6 M) was added to a solution of 2,6-diethyl-4,8dimethyl-s-indacene (0.60 g, 2.52 mmol) in THF (25 mL) at -80 °C. The solution was allowed to reach room temperature and stirred for 1.5 h. Then, the resulting mixture was cooled to  $-80 \,^{\circ}\text{C}$  and a solution of  $[\{\text{Rh}(\mu\text{-Cl})(\eta^4 - \eta^4)\}]$ COD}<sub>2</sub> (0.62 g, 1.26 mmol) in THF (20 mL) was added via syringe. The temperature was raised to room temperature, and the mixture was stirred for 2 h. The solvents were removed under reduced pressure. To the remaining solid, 10 mL of pentane was added and the insoluble lithium chloride was removed by filtration. The solution was concentrated giving a yellow solid of 1 (Yield: 1.07 g, 95%) <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.08 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 3H, C<sub>6</sub>–CH<sub>2</sub>–CH<sub>3</sub>), 1.38 (t,  ${}^{3}J_{HH} = 7.5$  Hz, 3H, C<sub>2</sub>–CH<sub>2</sub>– CH<sub>3</sub>), 1.73 and 1.88 (m, 8H, COD-CH<sub>2</sub>), 2.21 (s, 3H,  $CH_3-C_8$ ), 2.28 (q,  ${}^3J_{HH} = 7.5$  Hz, 2H,  $C_2-CH_2-CH_3$ ), 2.34 (s, 3H,  $CH_3-C_4$ ), 2.59 (q,  ${}^3J_{HH} = 7.5$  Hz, 2H,  $C_6 CH_2$ -CH<sub>3</sub>), 2.99 (br s, 2H,  $C_5$ -H<sub>2</sub>), 4.10 (m, 4H,  ${}^{2}J_{\text{HRh}} = 2$  Hz, COD–CH), 4.98 and 5.00 (d,  ${}^{4}J_{\text{HH}} = 1.6$  Hz, 2H,  $C_{1,3}$ -H), 6.67 (m, 1H,  $C_7$ -H). <sup>13</sup>C{<sup>1</sup>H} (100 MHz, C<sub>6</sub>D<sub>6</sub>), 13.92 (C<sub>6</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 15.32 (CH<sub>3</sub>-C<sub>4</sub>), 15.51 (CH<sub>3</sub>-C<sub>8</sub>), 16.00 (C<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 23.09 (C<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 25.00  $(C_6-CH_2-CH_3)$ , 31.12 and 31.67  $(COD-CH_2)$ , 39.61 (C<sub>5</sub>), 66.38 and 66.63 (d,  ${}^{1}J_{CRh} = 2$  Hz, CH–COD), 75.33 and 75.62 (d,  ${}^{1}J_{CRh} = 4.3$  Hz, C<sub>1,3</sub>), 110.86 and 113.10 (d,  ${}^{1}J_{CRh} = 2.5$  Hz,  $C_{3a,8a}$ ), 114.93 (d,  ${}^{1}J_{CRh} = 5$  Hz, C<sub>2</sub>), 115.37 (C<sub>4a</sub>), 119.56 (C<sub>7a</sub>), 124.84 (C<sub>7</sub>), 136.23 (C<sub>8</sub>), 139.57 (C<sub>4</sub>), 149.12 (C<sub>6</sub>). Anal. Found: C, 69.59; H, 7.40. C<sub>26</sub>H<sub>33</sub>Rh: Calc.: C, 69.64; H, 7.37.

# 4.3. Anti-[(2,6-diethyl-4,8-dimethyl-s-indacenediide)-{Rh(COD)}<sub>2</sub>] (2a) and syn (2b)

Stepwise synthesis (Path Ib): A solution of *n*-butyllithium (0.49 mmol) in hexane (1.6 M) was added to a solution of **1** (0.22 g, 0.49 mmol) in THF (15 mL) at -80 °C. The temperature was raised to room temperature and the mixture was stirred for 1.5 h. The solution was cooled to -80 °C and a solution of [{Rh( $\mu$ -Cl)( $\eta^4$ -COD)}<sub>2</sub>] (0.12 g, 0.25 mmol) in THF (10 mL) was added. After stirring for 2 h, the solvents were removed under reduced pressure. To the remaining solid, 15 mL of toluene is added and the insoluble lithium chloride is removed by filtration. The solution was concentrated giving an orange solid made up of an *anti/syn* isomer mixture in a 1:2 ratio, respectively (Yield: 0.21 g, 65%).

Direct synthesis (Path II): A solution of n-butyllithium (5.88 mmol) in hexane (1.6 M) was added to a solution of 2,6-diethyl-4,8-dimethyl-s-indacene (0.70 g, 2.94 mmol) in THF (25 mL) at -80 °C. The reaction mixture was allowed to reach room temperature and stirred for 1.5 h, followed by stirring at 50 °C for another 2 h. The solution was cooled to  $-80 \,^{\circ}\text{C}$  and  $[\{\text{Rh}(\mu\text{-Cl})(\eta^4\text{-COD})\}_2]$  (1.44 g, 2.94 mmol) in THF (30 mL) was slowly added via syringe. The mixture was allowed to reach room temperature and stirred for 2 h. The solvents were evaporated under reduced pressure. To the remaining solid, 15 mL of toluene is added and the insoluble lithium chloride is removed by filtration. This solution was concentrated giving an orange solid consisting of an *anti/syn* isomer mixture in a 1:2 ratio (Yield: 1.20 g, 62%). Fractional precipitation using benzene as solvent allows us to separate these isomers: the syn form 2b precipitates (Yield: 0.72 g, 37% – related to s-indacene) giving suitable crystals for X-ray study whereas the anti form 2a remains in the benzenic solution (Yield: 0.43 g, 22% related to s-indacene).

Anti-[(2,6-diethyl-4,8-dimethyl-s-indacenediide) {Rh- $(COD)_{2}$  (2a): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.31 (t,  ${}^{3}J_{\rm HH} = 7.5$  Hz, 6H, C<sub>2,6</sub>–CH<sub>2</sub>–CH<sub>3</sub>), 1.68 and 1.78 (m, 16H, COD-CH<sub>2</sub>), 2.29 (s, 6H, C<sub>4,8</sub>-CH<sub>3</sub>), 2.52 (q.d,  ${}^{3}J_{\text{HH}} = 7.5 \text{ Hz}, {}^{3}J_{\text{HRh}} = 1.4 \text{ Hz}, 4\text{H}, \text{ C}_{2,6}\text{--}\text{CH}_{2}\text{--}\text{CH}_{3}), 4.16$ (br.s, 8H, COD–CH), 5.00 (s, 4H,  $C_{1,3,5,7}$ –H). <sup>13</sup>C{<sup>1</sup>H} (100 MHz, C<sub>6</sub>D<sub>6</sub>), 15.21 (C<sub>2,6</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 15.59 (C<sub>4,8</sub>-CH<sub>3</sub>), 23.55 (C<sub>2,6</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 32.12 (COD-CH<sub>2</sub>), 68.56 (d,  ${}^{1}J_{CRh} = 13$  Hz, CH–COD), 73.75 (d,  ${}^{1}J_{CRh} = 5$  Hz, (d,  $J_{CRh}$  10 Hz, CH COL),  $H_{CRh}$  (c,  $I_{CRh}$  = 1.6 Hz,  $C_{3a,4a,7a,8a}$ ), 117.50 (d,  $I_{CRh}$  = 6 Hz,  $C_{2, 6}$ ). Anal. Found: C, 61.95; H, 6.74. C<sub>34</sub>H<sub>44</sub>Rh<sub>2</sub>: Calc.: C, 62.01; H, 6.69. Syn-[(2,6-diethyl-4,8-dimethyl-s-indacenediide)  $\{Rh(COD)\}_2$ , isomer, (2b): <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.31 (t,  ${}^{3}J_{\text{HH}} = 7.5 \text{ Hz}$ , 6H, C<sub>2,6</sub>–CH<sub>2</sub>–CH<sub>3</sub>), 1.69 and 2.10 (m, 16H, COD-CH<sub>2</sub>), 2.20 (s, 6H, C<sub>4,8</sub>-CH<sub>3</sub>), 2.56  $(q.d, {}^{3}J_{HH} = 7.5 \text{ Hz}, {}^{3}J_{HRh} = 1.5 \text{ Hz}. 4\text{H}, C_{2.6}-CH_{2}-$ CH<sub>3</sub>), 4.33 (br.s, 8H, COD-CH), 4.93 (br.s, 4H, C<sub>1,3,5,7</sub>-*H*).  $^{13}C{^{1}H}$  (100 MHz, C<sub>6</sub>D<sub>6</sub>), 15.22 (C<sub>2,6</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 15.08 (C<sub>4,8</sub>-CH<sub>3</sub>), 23.78 (C<sub>2,6</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 32.19 (COD-CH<sub>2</sub>), 68.33 (d,  ${}^{1}J_{CRh} = 13$  Hz, CH-COD), 73.69 (d,  ${}^{1}J_{\text{CRh}} = 4.5 \text{ Hz}, \text{ C}_{1,3,5,7}$ , 112.13 (C<sub>4, 8</sub>), 115.92 (d,  ${}^{1}J_{\text{CRh}} =$ 1.2 Hz,  $C_{3a,4a,7a,8a}$ ), 117.18 (d,  ${}^{1}J_{CRh} = 6$  Hz,  $C_{2,6}$ ). Mass spectra: m/z [M, %]: 658 [M<sup>+</sup>, 100], 447 [M - Rh(COD), 44]. Anal. Found: C, 61.98; H, 6.73. C<sub>34</sub>H<sub>44</sub>Rh<sub>2</sub>: Calc.: C, 62.01; H, 6.69.

#### 4.4. Crystallography

*Crystal data for* (2b):  $C_{34}H_{44}Rh_2$ , M = 658.51, orthorhombic, *Pbca*, a = 13.809(5) Å, b = 13.909(5) Å, c = 29.277(10) Å, V = 5623(3) Å<sup>3</sup>, Z = 8, T = 193(2) K. 30,597 reflections (5717 independent,  $R_{int} = 0.0365$ ) were

collected. Largest electron density residue: 0.514 e Å<sup>-3</sup>,  $R_1$ (for  $I > 2\sigma(I)$ ) = 0.0259 and  $wR_2$  = 0.0629 (all data) with  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$  and  $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{0.5}$ . The data for **2b** were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods [23] and all non-hydrogen atoms were refined anisotropically using the least-squares method on  $F^2$  [24].

# 4.5. General procedure for the dehydrogenative silylation of styrene

A two-necked flask equipped with a magnetic bar was charged with the complex (0.030 mmol for 1 and 0.015 mmol for 2). The reactor was evacuated and filled with argon. Styrene (0.52 mL, 4.5 mmol) and toluene (5 mL) were added, and the mixture was stirred for 5 min. Then Et<sub>3</sub>SiH (0.24 mL, 1.5 mmol) was added. The reaction flask was immersed in an 80 °C thermo-stabilized bath. The progress of the reaction was monitored by GC (disappearance of Et<sub>3</sub>SiH). The products were identified by <sup>1</sup>H NMR, by GC–MS, and by comparison with the literature data [10].

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#### Appendix A. Supplementary material

CCDC 295720 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.009.

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