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Heterobinuclear *s*-Indacene Rhodium Complexes: Synthesis and Characterization

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The monometallic complexes [Cp*M(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] [M = Fe (**1**), Ru (**2**), Co (**3**)] and the bimetallic species *anti*-[Cp*M(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] [M = Fe (**4a**), Ru (**5a**), Co (**6a**)] together with *syn*-[Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**5b**) were synthesized and characterized spectroscopically and in the case of complexes **1** and **5b** by X-ray diffraction. ^{13}C and ^{103}Rh NMR spectroscopic studies suggest that the bonding mode of the rhodium center to the *s*-indacenediide ligand can be described as an intermediate between η^3- and η^5-coordination, but closer to an η^3 bonding mode when compared to indenyl–Rh complexes. This result was confirmed by the crystal structure of **5b**, as evidenced by the slippage of the rhodium atom towards the periphery of the ligand. Cyclic voltammetry studies revealed intermetallic communication through the fused-ring ligand exclusively in the cases of **5a** and **6a**.

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Introduction

Since the seminal work of Creutz and Taube,[1] the synthesis and study of the properties of bimetallic complexes have become topics of great interest. This attention has been stimulated by the dramatic modifications of the chemical and physical behaviors of binuclear complexes relative to those of their mononuclear counterparts.[2] This phenomenon associated with the communication between the metal centers has relevance in many fields ranging from magnetic materials, molecular wires, and nonlinear optic devices to catalysis.[2,3] In this context, the choice of the bridging ligand that spans the corresponding transition-metal atoms is critical for the efficiency of electronic delocalization. Among the multiple candidates, fused delocalized polycyclic arenes (pentalenediide, *s*- and *as*-indacenediide, and indenyl) have been identified as very promising candidates,[2a,2f] as they display a planar backbone with a high delocalizability of their electron-rich π system. In addition, the rigidity of these spacers offers the unique opportunity to provide exact knowledge of the intermetallic distance, which is of critical importance for analyzing electron-transfer phenomena[4] and which is often lacking in the well-documented bimetallic complexes involving flexible chains within the spacer framework.[2g]

In fused aromatic ring bridged bimetallic systems, indenyl-based complexes are the most documented ones. Structural properties together with stoichiometric reactivity and catalytic activity have been examined over the last 20 years.[5] In contrast, the coordination chemistry of the *s*- and *as*-indacenyl dianion has been much less developed since the first synthesis of their homobinuclear half-sandwich iron complexes,[6,7] despite their conspicuousness fueled by the formal analogy existing with the ubiquitous cyclopentadienyl ligand known for its potential for binding and stabilizing a large number of metals with different oxidation states. The interest paid to these species has also been reinforced by their potential application as electronic devices exemplified by the high electronic communication interaction between the two metals {as in [(*s*-indacenediide)(MCp*)$_2$] systems with M = Fe, Co, Ni}[7] or for designing efficient and selective catalysts (dehydrogenative silylation of styrene catalyzed by [(2,6-diethyl-4,8-dimethyl-*s*-indacenediide){Rh(η^4-cod)}$_2$]).[8] Nevertheless, studies reported in the literature concern quasi-exclusively homobi-

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metallic *s*-indacenediide derived complexes, and the extension to their heterobimetallic counterparts still remains a vexing issue. Indeed, to the best of our knowledge, the sole example of heterobimetallic species described up to now is an *as*-indacenediide-based complex {[CpFe(μ-η^5:η^5-*as*-indacenediide)RhL$_2$] with L$_2$ = cod, nbd (norbornadiene), (ethylene)$_2$}, which could be only characterized by spectroscopic methods.[9] This preparation was achieved through the deprotonation of [CpFe(η^5-*as*-hydroindacenide)] and subsequent reaction with a rhodium source. However, the instability of the related CpFe(η^5-*s*-hydroindacenediide) precluded the preparation of the *s*-indacenediide analogue.

Following our interest in the synthesis and study of the physical and chemical properties of binuclear complexes bridged by fused-ring systems, we recently developed a new, effective, and selective route to polyalkylated *s*-indacenes. In contrast to the 1,5-dihydro-*s*-indacene, these compounds are obtained in high yields and are easy to handle and to convert selectively into the corresponding mono- or dianions.[10] In this context, these polyalkylated *s*-indacene offer a unique opportunity for the synthesis of heterobimetallic complexes by stepwise introduction of different metal fragments.

This contribution describes the general approach for the successful preparation of the first series of *s*-indacenediide-derived heterobimetallic complexes [Cp*M(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (M = Fe, Ru, Co). These species (or the corresponding cation in the case of the paramagnetic cobalt complexes) were fully characterized by spectroscopic methods and cyclic voltammetry. The X-ray structure analysis of [Cp*Fe(η^5-2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] and that of *syn*-[Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] are also presented herein.

Results and Discussion

Syntheses of the Complexes

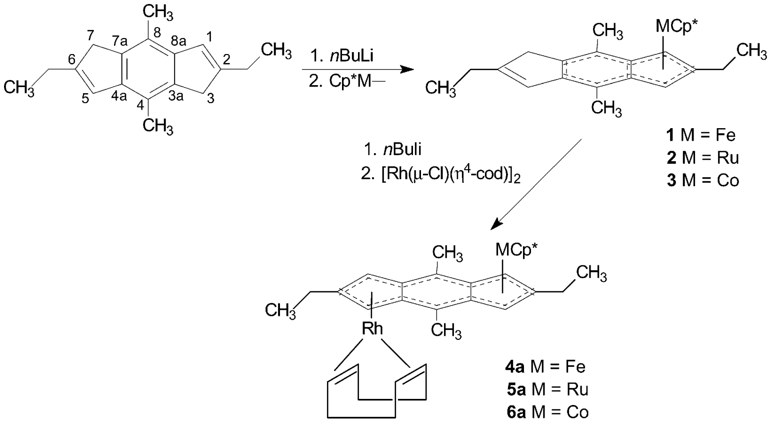
The Rh^I heterobimetallic complexes of substituted 2,6-diethyl-4,8-dimethyl-*s*-indacenediide were prepared using by two pathways as shown in Schemes 1 and 2.

Firstly, the addition of one equivalent of *n*-butyllithium to a thf solution of 2,6-diethyl-4,8-dimethyl-*s*-indacene gives the monolithiated intermediate, which in turn reacts with one equivalent of a suitable metallic center such as [Cp*Fe(acac)], [Cp*Ru(μ-Cl)]$_4$, or [Cp*Co(acac)] to yield the respective compounds [Cp*Fe(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] (**1**), [Cp*Ru(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] (**2**), or [Cp*Co(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] (**3**) (Scheme 1). These monometallic complexes were isolated as very air-sensitive, colored powders in high yields (89–97%). Then, subsequent deprotonation with *n*BuLi followed by the addition of [Rh(μ-Cl)(η^4-cod)]$_2$ led to the sole formation of one isomeric form of the bimetallic complexes [Cp*Fe(μ-2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**4a**), [Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**5a**), and [Cp*Co(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**6a**) as shown by NMR spectroscopic analyses.

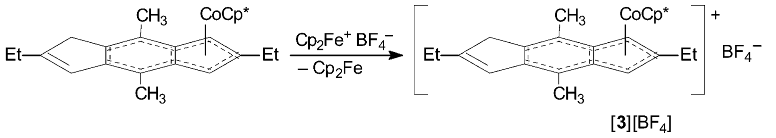
In the case of paramagnetic cobalt complexes **3** and **6a**, NMR spectroscopic characterizations were carried out on the respective diamagnetic oxidized products **3**[BF$_4$] and **6a**[BF$_4$]. The synthesis of **3**[BF$_4$] consists of the oxidation of **3** with ferrocenium tetrafluoroborate [Equation (1)]. This air-stable complex was isolated as a red-brownish powder, which is readily soluble in polar solvents such as acetone, acetonitrile, and thf.

Similarly, the oxidation reaction was performed with **6** to give the corresponding diamagnetic species **6a**[BF$_4$].

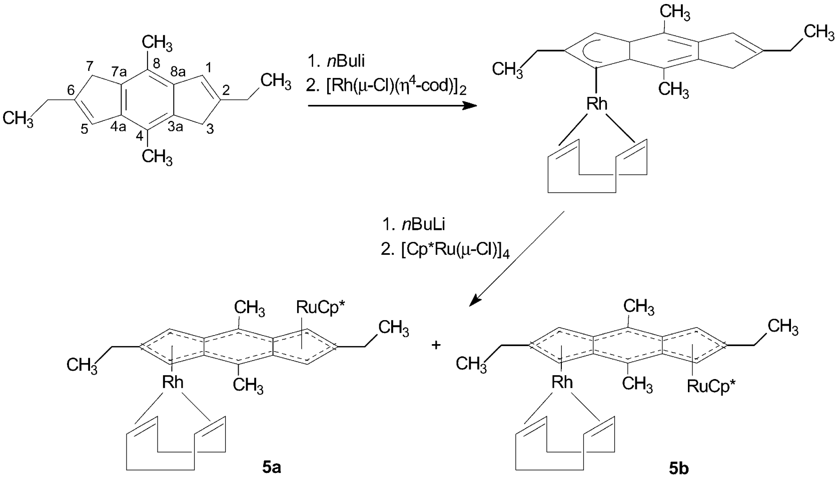
An alternative route to yield **4**–**6** is the coordination in a first step of the fragment Rh(η^4-cod) onto the alkylated *s*-indacene ligand, as described previously {deprotonation of 2,6-diethyl-4,8-dimethyl-*s*-indacene with 1 equiv. of *n*BuLi followed by the addition of [Rh(μ-Cl)(η^4-cod)]$_2$}.[8] The subsequent reaction of [Cp*Ru(μ-Cl)]$_4$ with deprotonated species Li[Rh(η^4-cod)(η^3-2,6-diethyl-4,8-dimethyl-*s*-indacenediide)] gives a mixture of *anti*/*syn* isomers (**5a** and **5b**) in a ca. 1:1 ratio (Scheme 2). Surprisingly, no considerable product formation occurs with the iron or cobalt sources, [Cp*Fe(acac)] or [Cp*Co(acac)]. As a result of the low quantities used in each synthetic step and the low respective yields, this reaction was not further attempted.



Scheme 1.



(1)



Scheme 2.

Separation of these isomers was performed by fractional crystallization with the use of benzene. The less-soluble isomer crystallized and was identified as the *syn* isomer, as evidenced by its X-ray structure analysis. This also allowed us to assign unambiguously the ^{1}H NMR signals of both isomers, confirming that previously obtained complex **5a** was the *anti* isomer. Consistently, previous articles have reported that the use of the frequently adopted deprotonation/metalation procedure involving CpM or Cp*M fragments yielded exclusively the *anti* isomers presumably because of steric hindrance factors.[2g,7,11] For complexes **4a** and **6a**, it seems reasonable to assume that the complexes obtained by the first step (Scheme 1) are the *anti* isomers.

Previous studies have shown that the isomer ratio depends on a combination of several factors including steric hindrance, temperature and solvent effects, nature of the ancillary ligand, and symmetry of the indacene ligand.[12] Ceccon and al., who studied this aspect in more detail for rhodium and iridium homobinuclear complexes incorporating *s*- and *as*-indacene ligands {[(μ-η^3:η^3-indacenediide)(RhL$_2$)$_2$] with L$_2$ = cod, nbd, (CO)$_2$}, concluded that the role of the ancillary ligands L seems preponderant: a large preference for the *syn* species is obtained with the cod or nbd ligand, whereas the *anti* isomer is favored with the CO ligand.[12,13] We recently obtained comparable results with Rh derivatives of *s*-indacene.[8]

In our case, the *anti*/*syn* ratio is dependent on the sequence of addition of the metallic fragments. A possible explanation could lie in the nature of the metallic fragments. The rigid and bulky Cp*M metallic moieties attached to *s*-indacene, as in **1**, **2**, and **3**, may indeed hinder entry on the same side of the second fragment such as Rh(η^4-cod) and thus yield selectively the *anti* isomer. In contrast, the cod ligand in Rh(η^4-cod) is known as a versatile ligand that is able to adopt various conformations according to steric constraints or weak attractive interactions.[14] Thus, such behavior may allow the ligation of Cp*M on the same side and may account for a mixture of the *anti*/*syn* isomers.

Another possible explanation for the variable *anti*/*syn* ratio could lie in the stability of the intermediates. Amongst several others, one of the crucial factors may lie in the most stable *anti* or *syn* isomer, depending on the nature of the metallic fragment M in the lithiated metallic complex Li[M(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)]. Nevertheless, a kinetic effect could also be responsible for the different product stereoselectivities, depending on the chosen synthetic approach, where one of the isomers of the lithiated metallic complexes may be more reactive than the other, which possibly may explain the formation of both isomers as a final product.

At this stage, all possible explanations are highly speculative; however, in order to further clarify the factors that affect the *anti*/*syn* ratio, theoretical studies of the reagents and products, as well as the degree of basicity or nucleophilicity of the intermediate species, could provide some answers, elucidating which interactions are responsible for the product formation.

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NMR Spectroscopic Study of the Complexes

In the ^{1}H NMR spectra of monometallic complexes **1**, **2**, and **3**[BF$_4$], the most notable features are the differences induced by the metal effect on the closest protons, that is, on the protons of the coordinated five-membered ring of the *s*-indacenide ligand. For instance, these protons have largely different values directly related to the effect on the electropositivity (or electronegativity) of each metal. As complex **3**[BF$_4$] has a metallic fragment with a Co^{III} center, this strongly deshields these protons to a value of 5.46 ppm, whereas a less-electronegative fragment, as Fe^{II} in complex **1**, shifts these same protons to 4.02 ppm. A comparable effect was observed between heterobimetallic complexes **4a** and **6a**[BF$_4$]. Concerning the *anti* and *syn* isomers, **5a** and **5b**, whereas fairly discrete chemical shift value differences have been observed for the protons of the *s*-indacene ligand, the Cp* protons of the *syn* isomer (1.80 ppm) are shifted downfield relative to those of the *anti* isomer (1.53 ppm). The relative deshielding of the *syn* isomer is probably due to the presence of the secondary metallic fragment on the same side of the *s*-indacene ligand. Similar effects were obtained by ^{13}C NMR spectroscopy.

Moreover, the ^{13}C NMR spectra can also provide some information about the hapticity of the Cp-derived ligand.[15] In the case of indenyl, it can be deduced from the variation of the chemical shifts of the ring-junction carbon atoms of the five-membered rings. On the basis of this correlation, we recently evidenced, in mono- and bimetallic *s*-indacene-derived complexes, the presence of an interaction between the ring-junction carbon atoms and the rhodium center, and thus, this led us to propose a $\eta^2 + \eta^3$ coordination mode.[8] As the values of the chemical shifts of the ring-junction carbon atoms (117.84 and 116.00 ppm for **4a** and **5a**, respectively) are very close to those obtained for the homobinuclear rhodium complex (114.28 and 117.18 ppm for the *anti* and *syn* isomers, respectively), a similar hapticity, for example, $\eta^2 + \eta^3$, is expected for the rhodium atom in complexes **4a**–**6a**.

^{103}Rh NMR has also been shown to be an effective tool for the determination of the hapticity of cyclopentadienyl analogues in organometallic complexes.[16] Chemical shifts of **4a**–**6a** were determined by using HMBC, a 2D experiment that allows a ^{103}Rh NMR spectrum to be quickly obtained. In this case, this tool can be used because of the presence of a scalar coupling between the olefinic protons of the cod ligand and the ^{103}Rh nucleus ($J_{H,Rh}$ = 2 Hz). The ^{103}Rh NMR spectra of complexes **4a**–**6a** display a signal ranging from –281 to –245 ppm with chemical shifts closer to η^3 than those found for the related indenyl- and alkylated (indenyl)Rh(cod) complexes.[17] These results show a bonding mode that can be described as intermediate between η^3- and η^5-coordination (i.e., $\eta^2 + \eta^3$) but with a much more pronounced η^3 bonding mode, as the chemical shifts of **4a**–**6a** have a downfield shift of approximately 240 ppm relative to those of indenyl–Rh(cod) (–486 ppm).

The chemical shift value for ^{103}Rh of *syn* complex **5b** is shifted approximately 40 ppm downfield relative to that of *anti* analogue **5a**. This difference may reflect a slightly more-pronounced η^3-character in the *syn* complex, presumably due to higher steric repulsion of the Rh(cod) fragments in **5b**.

X-ray Analyses

Crystallographic studies of compounds **1** and **5b** were established. In the structure of **1** (see Figure 1), the coordination of the Cp*Fe fragment by the *s*-indacene system shows a slight distortion of a η^5 mode, but the Fe–C(*s*-indacene) distances [2.041(3)–2.095(2) Å] are very close to the values observed for the Fe–C(Cp*) distances [2.033(3)–2.050(3) Å]. In the *s*-indacene system, the coordination of the iron fragment introduces aromatization of the corresponding five-membered ring, which leads to partial localization of the double bonds in the C6–C7 and C11–12 bonds.

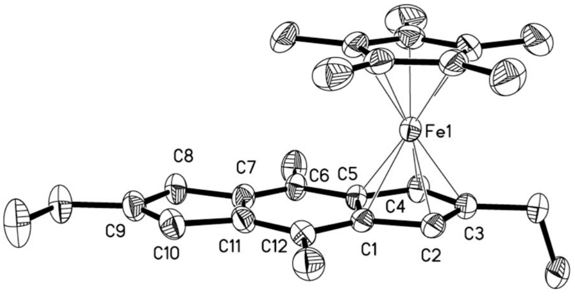

Figure 1. Molecular structure of **1** (50 % probability level). Selected bond lengths [Å]: C1–C2 1.431(3), C2–C3 1.426(4), C3–C4 1.420(4), C4–C5 1.431(3), C1–C5 1.439(4), C1–C12 1.440(4), C5–C6 1.444(3), C6–C7 1.353(4), C7–C11 1.441(4), C11–C12 1.378(4), C7–C8 1.513(3), C8–C9 1.500(4), C9–C10 1.347(4), C10–C11 1.465(4).

In the case of **5b** (see Figure 2), the two metal atoms are not coordinated in the same manner by the bridging *s*-indacene system. The coordination of the Ru fragment is nearly perfect η^5, whereas the coordination of the Rh atom could be seen as something in between η^3 and η^5. The *s*-indacene centroid distances to the metals are 2.006 and 1.843 Å for rhodium and ruthenium, respectively. Furthermore, the distance between the Ru and Cp* centers is 1.775 Å, which provides evidence that ruthenium has a stronger coordination to Cp* than to the *s*-indacene system. The steric hindrance of the two metal fragments, which are located on the same side of the *s*-indacene ligand, provokes a distortion of 14° (torsion angle C3–C1A–C8A–C7) of the ligand system as well as a hinge angle of 15.9°[18] and a ring slippage value of 0.41 for Rh. Moreover, the different coordination modes for the metals leads to a stronger localization of the double bonds in the C1–C1A and C4A–C5 positions, as observed in **1**, which results in a hinge angle of 1.75° and a ring slippage value for the Fe atom of 0.048; this indicates that the iron atom is located near the center of the respective *s*-indacene five-membered ring.

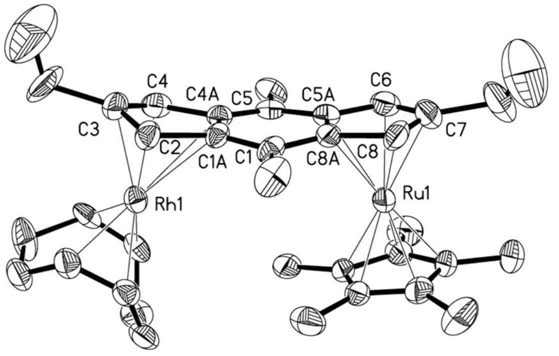

Figure 2. Molecular structure of **5b** (30% probability level). Selected bond lengths [Å]: Rh1–C1A 2.59(1), Rh1–C2 2.19(2), Rh1–C3 2.16(1), Rh1–C4 2.18(1), Rh1–C4A 2.60(1), Ru1–C5A 2.25(1), Ru1–C6 2.19(1), Ru1–C7 2.16(1), Ru1–C8 2.16(1), Ru1–C8A 2.26(1), C1A–C2 1.50(1), C2–C3 1.42(2), C3–C4 1.40(2), C4–C4A 1.49(2), C1A–C4A 1.41(1), C1–C1A 1.35(1), C5–C4A 1.35(1), C5–C5A 1.45(2), C5A–C8A 1.44(2), C1–C8A 1.41(1), C5A–C6 1.41(2), C6–C7 1.43(2), C7–C8 1.39(2), C8–C8A 1.46(2).

Cyclic Voltammetry Studies

Our heterobinuclear complexes present no redox potential waves for rhodium, possibly explained to the high oxidation energy needed, which is most likely beyond the solvent positive limit. Therefore, rather than performing a comparison with the difference of the first minus the second oxidation value, a comparison of each binuclear complex was carried out with its respective mononuclear complex, as already reported.[8] The fourth column in Table 1 is the difference between the potentials of the mononuclear complex and its binuclear analogue (ΔE), allowing us to establish comparisons between the complexes reported here. In the case of binuclear complexes, large ΔE values are expected, characteristic of strong electronic interaction between both metals. Our heterobinuclear complexes present values ranging mostly between 336–628 mV (see Table 1) with the exception of complex **4a** (58 mV). Complex **4a** presents a minimal interaction once Rh(cod) is bonded to *s*-indacene in **1**, showing a reversible wave at 35 mV (I_a/I_c = 1.0), evidencing the ferrocene-like behavior of this compound. When a second metal is bonded to the system, this wave is almost in the same position (E_{ox} = –23 mV, I_a/I_c = 1.0; see Table 1). In complex **4a**, both metallic fragments show different behaviors, as one is more electropositive than the other and more prone to oxidation, it is almost unaffected by the rhodium atom. In contrast, the oxidation process for **2** occurs at 438 mV (I_a/I_c = 0.9), and binuclear complexes **5a** and **5b** have this peak shifted to 79 and 102 mV (I_a/I_c = 1.0), respectively, indicating an intermediate degree of communication in comparison to that of homobinuclear complexes previously reported.[19]

Complex **2** presents an unusual redox wave, with a small value of I_a/I_c. This may be indicative of nonfaradaic processes, such as the oxidative adsorption on the electrode surface of the metallic complex. Previous reports have stated that ruthenocenium cations are known for their low stability, unlike that of ferrocenium salts,[20] possibly decomposing and presenting an adsorption current due to chemical fragments formed because of the possible decomposition of **2**.

The differences between the *anti* and *syn* isomers may be viewed as negligible. In both cases, the oxidation of the ruthenium moiety takes place almost at the same potential (see Table 1). In previous works,[21] the oxidation of a binuclear *s*-indacene *syn* isomer owning two $Fe(CO)_3$ groups led to the shortening of the distance between both metallic atoms as a result of the bridging capacity the carbonyl ligand, which reduced the Fe–Fe distance by ca. 0.4 Å. This interaction would surely present a difference in the value for the first oxidation wave as a result of the stabilizing effect of a “double” bridge for the Fe atoms, but in our case, the two bulky Cp* and cod ligands would prevent this, and as they also lack bridging capacity, the resulting differences would therefore be minimal.

In the case of complex **6a**, the redox couple was very near the reduction limit that dichloromethane presents under these conditions, which made the determination of a clear reduction peak impossible. Despite this, some information may be gathered: complex **6a** encloses a cobaltocene moiety behaving similarly to a 19-electron metallocene, which is easily oxidized; hence, the low oxidation value. Comparing complexes **3** and **6a**, a notorious redox potential shift takes place, which indicates that a secondary metallic fragment plus a doubly negatively charged ligand make the Co center a stronger reducing agent.

Table 1. Potentials listed (vs. SCE) at 100 mV s^{-1}.

Complexes	$E_{1/2}$[a] [mV]	ΔE[b] [mV]	I_a/I_c	ΔE[e] [mV]
[Cp*Fe(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] (**1**)	35	75	1.0	–
[Cp*Ru(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] (**2**)	438	169	0.9	–
[Cp*Co(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] (**3**)	–865	154	1.0	–
[(2,6-Diethyl-4,8-dimethyl-1-hydroindacenide)Rh(η^4-cod)][c]	1348	140	1.6	–
anti-[Cp*Fe(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**4a**)	–23	125	1.0	58 (**1**)
anti-[Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**5a**)	79	178	1.0	359 (**2**)
syn-[Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**5b**)	102	210	1.0	336 (**2**)
anti-[Cp*Co(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (**6a**)	–1493	[d]	[d]	628 (**3**)

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$. [b] Difference between respective anodic and cathodic peak potential value. [c] Results taken from ref.[8] [d] Cathodic peak was unclear due to an overlapping with the working solvent window. [e] Difference between the potential values of the mononuclear complex and its binuclear analogue [$E_{1/2(\text{mononuclear})} - E_{1/2(\text{binuclear})}$].

Conclusions

This work describes the isolation and full characterization including X-ray structural analysis of the first series of heterobimetallic complexes incorporating an *s*-indacene-derived ligand: [Cp*M(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (M = Fe, Ru, Co). A two-step procedure involving coordination of the Cp*M fragments before introduction of the Rh(η^4-cod) moiety allows the sole formation of the *anti* isomer of the heterobimetallic complexes. In contrast, inversion of the addition order of the metallic fragments yielded, in the case of the RuRh species, a mixture of the *syn* and *anti* isomers.

X-ray diffraction analysis of the [Cp*Fe(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)] and *syn*-[Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] complexes clearly shows that, in the solid state, the Fe and Ru atoms are bonded in a quasiperfect pentahapto bonding mode toward the *s*-indacene-derived ligand. The rhodium moiety is closer to η^3 bonding than those previously reported in related mono- and binuclear rhodium complexes. Cyclic voltammetry studies of [Cp*M(2,6-diethyl-4,8-dimethyl-*s*-indacenediide)Rh(η^4-cod)] (M = Fe) show no significant difference with its mononuclear counterpart [Cp*Fe(2,6-diethyl-4,8-dimethyl-1-hydroindacenide)], whereas in the case of M = Co and Ru, electronic communication was evidenced. Theoretical tools for these molecular systems would be most suitable to further characterize these heterobinuclear complexes.

Experimental Section

General: All manipulations were carried out under a pure dinitrogen atmosphere by using a vacuum atmosphere dry box equipped with a Model HE 493 Dri-Train purifier or with the use of a vacuum line by using standard Schlenk tube techniques. Reagent grade solvents were distilled under an atmosphere of dinitrogen from sodium benzophenone ketyl (tetrahydrofuran, toluene, petroleum ether). The starting compounds 2,6-diethyl-4,8-dimethyl-*s*-indacene,[10] [Cp*Ru(μ-Cl)]$_4$,[22] [Rh(μ-Cl)(η^4-cod)]$_2$[23] (cod = 1,5-cyclooctadiene), [Cp*Fe(acac)] and [Cp*Co(acac)][24] (Cp* = pentamethylcyclopentadienyl, acac = $C_5H_7O_2$) were prepared according to published methods. *n*-Butyllithium (1.6 M in hexane) was purchased from Aldrich. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker Avance 400 MHz instrument by using C_6D_6 for solvent (with the exception of [**3**][BF$_4$] and [**6a**][BF$_4$], which were measured in CD$_3$CN), at 25 °C by using TMS for reference sample. All ^{103}Rh NMR spectra were performed with a Bruker AMX-400 spectrometer (CDCl$_3$, T = 298 K) operating at 400.13 MHz by using a 5 mm inverse low-frequency probe head with a *z*-gradient coil. The $\delta(^{103}\text{Rh})$ values were calculated by determining the absolute frequency of the cross-peak (HMBC experiments) relating it to the arbitrary reference frequency of 3.16 MHz (value at 100 MHz) scaled to the resonance frequency of TMS at 12.64 MHz. The HMBC experiments were determined by using the already published pulse sequence.[27] Acquisition time = 13 h. The concentration of each sample was approximately 0.05 M. Mass spectra were measured with a Hewlett–Packard HP 5989A in the electron impact mode (70 eV). 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 (saturated calomel electrode). The counter electrode was a platinum wire, and the working electrode was a platinum disc with diameter of ca. 3 mm. The currents and potentials were recorded with a Pentium II 350 MHz processor, with a BAS CV-50 Voltammetric Analyzer Potentiometer. Each electrochemical experiment employed the first fraction of distilled CH$_2$Cl$_2$, which was collected over phosphorus pentoxide and heated at reflux once again. The supporting electrolyte, [NBu$_4$]BF$_4$, was dried under vacuum and with heating (60 °C) for 3 h prior use.

Cp*Fe(2,6-diethyl-4,8-dimethyl-1-hydro-*s*-indacene) (1): *n*-Butyllithium (1.6 M in hexanes, 1.3 mL, 2.10 mmol) was slowly added to a solution of 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (0.5 g, 2.10 mmol) in thf (20 mL) at –80 °C. The mixture was stirred for 1 h at room temperature to yield the monolithiated ligand. The solution was cooled to –80 °C and dropwise added to an in situ prepared solution of Cp*Fe(acac) (0.61 g, 2.10 mmol) in thf (30 mL). This mixture was allowed to reach room temperature and then stirred for 2 h. Then, the solvent was removed, and the raw product was washed with pentane and filtered to remove the insoluble Li(acac). Bright red-colored crystals unstable to air were obtained. Yield: 0.79 g (89%). $C_{28}H_{36}Fe$ (428.44): calcd. C 78.53, H 8.41; found C 78.32, H 8.56. ^{1}H NMR (C_6D_6): δ = 1.08 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C_2-CH$_2$-*CH*$_3$), 1.10 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C_6-CH$_2$-*CH*$_3$), 1.54 (s, 15 H, *CH*$_3$-Cp), 2.19 (s, 3 H, C_8-*CH*$_3$), 2.22 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, C_2-*CH*$_2$-CH$_3$), 2.27 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, C_6-*CH*$_2$-CH$_3$), 2.32 (s, 3 H, C_4-*CH*$_3$), 3.04 [s, 2 H, $C_{(7)}H_2$], 4.02 [br. s, 2 H, $C_{(1,3)}H$], 6.60 [s, 1 H, $C_{(5)}H$] ppm. ^{13}C NMR (C_6D_6): δ = 9.69 (Cp-*CH*$_3$), 13.13 (C_2-CH$_2$-*CH*$_3$), 14.94 (C_8-*CH*$_3$), 15.18 (C_6-CH$_2$-*CH*$_3$), 15.34 (C_4-*CH*$_3$), 22.59 (C_6-*CH*$_2$-CH$_3$), 25.14 (C_2-*CH*$_2$-CH$_3$), 39.09 [$C_{(7)}H_2$], 66.59 [$C_{(1)}H$], 66.91 [$C_{(3)}H$], 77.24 (*Cp*-CH$_3$), 93.47 (C_{8a}), 95.06 (C_{3a}), 96.00 (C_2), 119.78 (C_4), 123.52 (C_8) 124.38 (C_5), 134.13 (C_{7a}), 138.27 (C_{4a}), 148.82 (C_6) ppm. MS (EI): *m*/*z* (%) = 428 (100) [M]$^+$, 293 (26.9) [Fe – Ic]$^+$, 192 (44.2) [Cp*FeH]$^+$.

Cp*Ru(2,6-diethyl-4,8-dimethyl-1-hydro-*s*-indacene) (2): Complex **2** was prepared by using the same procedure as that used for the preparation of **1** by using *n*-butyllithium (1.6 M in hexane, 1.3 mL, 2.1 mmol), 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (0.5 g, 2.1 mmol), and [Cp*Ru-Cl]$_4$ (0.57 g, 0.5 mmol). In this case, LiCl was eliminated through filtration with pentane. A yellow-greenish crystalline solid unstable to air was obtained. Yield: 0.96 g (97%). ^{1}H NMR (C_6D_6): δ = 1.11 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C_2-CH$_2$-*CH*$_3$), 1.18 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C_6-CH$_2$-*CH*$_3$), 1.59 (s, 15 H, *CH*$_3$-Cp), 2.14 (s, 3 H, C_8-*CH*$_3$), 2.27 (s, 3 H, C_4-*CH*$_3$), 2.37 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, C_2-*CH*$_2$-CH$_3$), 2.41 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, C_6-*CH*$_2$-CH$_3$), 3.04 [s, 2 H, $C_{(7)}H_2$], 4.67 [br. s, 2 H, $C_{(1,3)}H$], 6.24 [s, 1 H, $C_{(5)}H$] ppm. ^{13}C NMR (C_6D_6): δ = 10.80 (Cp-*CH*$_3$), 12.70 (C_6-CH$_2$-*CH*$_3$), 15.68 (C_8-*CH*$_3$), 16.46 (C_2-CH$_2$-*CH*$_3$), 15.43 (C_4-*CH*$_3$), 22.03 (C_2-*CH*$_2$-CH$_3$), 24.81 (C_6-*CH*$_2$-CH$_3$), 38.84 [$C_{(7)}H_2$], 62.90 [$C_{(1,3)}H$], 82.21 (*Cp*-CH$_3$), 88.40 (C_{8a}), 90.48 (C_{3a}), 92.70 (C_2), 119.60 (C_4), 124.19 [$C_{(5)}H$], 125.39 (C_{7a}), 135.20 (C_6), 139.36 (C_{4a}), 143.52 (C_8) ppm. MS (EI): *m*/*z* (%) = 474 (100) [M]$^+$, 339 (31.0) [Ru – Ic]$^+$, 238 (58.7) [Cp*RuH]$^+$.

Cp*Co(2,6-diethyl-4,8-dimethyl-1-hydro-*s*-indacene) (3): Complex **3** was obtained by using the same procedure as that used for the preparation of **1** by using *n*BuLi (1.6 M in hexanes, 1.3 mL, 2.1 mmol), 2,6-diethyl-4,8-dimethyl-1,5-dihydro-*s*-indacene (0.5 g, 2.1 mmol), and Cp*Co(acac) (0.62 g, 2.1 mmol). Yield: 0.81 g (89%). Given this is a paramagnetic compound, only mass spectrometry and elemental analysis were carried out. $C_{28}H_{36}Co$ (431.53): calcd. C 77.93, H 8.41; found C 74.31, H 8.96. MS (EI): *m*/*z* (%) = 431 (32), 339 (100) [Cp*Co].

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[Cp*Co(2,6-diethyl-4,8-dimethyl-1-hydro-*s*-indacene)][BF$_4$] ([3][BF$_4$]): In a 50-mL round-bottomed flask, provided with a nitrogen inlet, cobalt complex **3** (0.3 g, 0.69 mmol) was mixed with ferrocenium tetrafluoroborate (0.15 g, 0.55 mmol). Later, to this flask, was added thf (30 mL) to allow the solids to dissolve and react with vigorous stirring. After 1 h, thf was evaporated, and the remaining solid was washed with pentane (30 mL) to afford the insoluble red-brownish product. Yield: 0.26 g (92%). ^{1}H NMR (CD$_3$CN): δ = 1.15 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, C$_2$-CH$_2$-*CH$_3$*), 1.26 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, C$_6$-CH$_2$-*CH$_3$*), 1.58 (s, 15 H, *CH$_3$*-Cp), 2.28 (q, $^3J_{H,H}$ = 6.7 Hz, 2 H, C$_2$-*CH$_2$*-CH$_3$), 2.34 (s, 3 H, C$_8$-*CH$_3$*), 2.39 (s, 3 H, C$_4$-*CH$_3$*), 2.52 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, C$_6$-*CH$_2$*-CH$_3$), 3.40 [br. s, 2 H, C$_{(7)}$H$_2$], 5.46 [br. s, 2 H, C$_{(1,3)}$H], 6.74 [s, 1 H, C$_{(5)}$H] ppm. ^{13}C NMR (CD$_3$CN): δ = 8.75 (*CH$_3$*-Cp), 12.70 (C$_6$-CH$_2$-*CH$_3$*), 15.08 (C$_4$-*CH$_3$*), 15.31 (C$_8$-*CH$_3$*), 15.69 (C$_2$-CH$_2$-*CH$_3$*), 20.43 (C$_2$-*CH$_2$*-CH$_3$), 25.36 (C$_6$-*CH$_2$*-CH$_3$), 40.09 (C$_7$), 75.11 (C$_1$), 75.20 (C$_3$), 95.23 (*Cp*-CH$_3$), 106.20 (C$_2$), 117.45 (C$_4$), 123.95 (C$_{8a}$), 124.14 (C$_{3a}$), 144.62 (C$_{7a}$), 145.38 (C$_5$), 148.39 (C$_8$), 148.54 (C$_{4a}$), 157.90 (C$_6$) ppm.

Cp*Fe(2,6-diethyl-4,8-dimethyl-*s*-indacene)Rh(η^4-cod) (4a): *n*-Butyllithium (1.6 M in hexanes, 1.1 mL, 1.7 mmol) was added dropwise to a solution of **1** (0.7 g, 1.63 mmol) in thf (30 mL) at –80 °C. The resulting mixture was vigorously stirred for 1 h at room temperature. Then, a solution of [(cod)RhCl]$_2$ (0.40 g, 0.81 mmol) in thf (20 mL) was added to the mixture of lithiated **1** at –80 °C, and the mixture was vigorously stirred for 2 h at room temperature. Then, the solvent was removed, and the resulting product was washed with hexane and filtered to remove the insoluble LiCl. A black-greenish dust unstable to air was obtained. Yield: 0.89 g (85%). C$_{36}$H$_{47}$FeRh (638.52): calcd. C 67.72, H 7.42; found C 67.61, H 7.76. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.03 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, C$_2$-CH$_2$-C*H$_3$*), 1.32 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, C$_6$-CH$_2$-C*H$_3$*), 1.53 (s, 15 H, CH$_3$-Cp), 1.69 (br. s, 8 H, cod-CH$_2$), 2.25 (q, $^3J_{H,H}$ = 7.5 Hz, 2 H, C$_2$-C*H$_2$*-CH$_3$), 2.38 (s, 6 H, CH$_3$-C$_{4,8}$), 2.53 (qd, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,Rh}$ = 1.7 Hz, 2 H, C$_6$-C*H$_2$*-CH$_3$), 4.20 [s, 2 H, C$_{(1,3)}$H], 4.32 (s, 4 H, cod-C=*CH*), 5.04 [s, 2 H, C$_{(5,7)}$H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 10.15 (Cp-*CH$_3$*), 14.85 (C$_6$-CH$_2$-*CH$_3$*), 16.24 (C$_{4,8}$-*CH$_3$*), 16.55 (C$_2$-CH$_2$-*CH$_3$*), 22.55 (C$_2$-*CH$_2$*-CH$_3$), 24.05 (C$_6$-*CH$_2$*-CH$_3$), 31.88 (cod- *CH$_2$*), 61.54 (C$_{1,3}$), 70.60 (d, $^1J_{C,Rh}$ = 13.0 Hz, cod-*C*=*C*), 71.81 (d, $^1J_{C,Rh}$ = 4.9 Hz, C$_{5,7}$), 77.01 (*Cp*-CH$_3$), 92.98 (C$_{4,8}$), 94.34 (C$_2$), 117.62 (C$_{3a,8a}$), 117.84 (d, $^1J_{C,Rh}$ = 1.3 Hz, C$_{4a,7a}$), 121.03 (d, $^1J_{C,Rh}$ = 6.7 Hz, C$_6$) ppm. ^{103}Rh NMR (14 MHz, C$_6$D$_6$): δ = –275 ppm. MS (EI): *m*/*z* (%) = 638 (62.5) [M]$^+$, 428 (100.0) [M – Rh(cod)]H$^+$, 211 (37.5) [Rh(cod)]$^+$, 108 (10.4) [cod]$^+$.

***anti*-Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacene)Rh(η^4-cod) (5a):** Complex **5a** was obtained by using the same procedure as that use for the preparation of **4a** by using *n*-butyllithium (1.6 M in hexanes, 1.0 mL, 1.6 mmol), **2** (0.7 g, 1.48 mmol), and [(cod)RhCl]$_2$ (0.37 g, 0.75 mmol). A black-greenish dust unstable to air was obtained. Yield: 0.86 g (85%). C$_{36}$H$_{47}$RhRu (683.74): calcd. C 63.24, H 6.93; found C 62.91, H 7.01. ^{1}H NMR (C$_6$D$_6$): δ = 1.11 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C$_2$-CH$_2$-*CH$_3$*), 1.30 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C$_6$-CH$_2$-*CH$_3$*), 1.53 (s, 15 H, Cp-*CH$_3$*), 1.77 (m, 8 H, cod-CH$_2$), 2.21 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, C$_2$-*CH$_2$*-CH$_3$), 2.27 (s, 6 H, C$_{4,8}$-*CH$_3$*), 2.53 (qd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,Rh}$ = 1.6 Hz, 2 H, C$_6$-*CH$_2$*-CH$_3$), 4.34 (s, 4 H, cod-C=*CH*), 4.74 [s, 2 H, C$_{(1,3)}$H], 5.00 [s, 2 H, C$_{(5,7)}$H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 10.79 (Cp-*CH$_3$*), 15.10 (C$_6$-CH$_2$-*CH$_3$*), 15.20 (C$_2$-CH$_2$-*CH$_3$*), 15.29 (C$_{4,8}$-*CH$_3$*), 22.74 (C$_2$-*CH$_2$*-CH$_3$), 25.25 (C$_6$-*CH$_2$*-CH$_3$), 31.68 (cod-*CH$_2$*), 65.69 (C$_{1,3}$), 70.44 (d, $^1J_{C,Rh}$ = 13.1 Hz, cod-*C*=*C*), 71.73 (d, $^1J_{C,Rh}$ = 4.5 Hz, C$_{5,7}$), 81.71 (*Cp*-CH$_3$), 95.78 (C$_2$), 96.59 (C$_{4,8}$), 96.62 (C$_{3a,8a}$), 116.00 (d, $^1J_{C,Rh}$ = 1.4 Hz, C$_{4a,7a}$), 120.55 (d, $^1J_{C,Rh}$ = 6.5 Hz, C$_6$) ppm. ^{103}Rh NMR (14 MHz, C$_6$D$_6$): δ = –281 ppm. MS (EI): *m*/*z* (%) = 684 (55.5) [M]$^+$, 474 (100.0) [M – Rh(cod)]H$^+$, 211 (44.1) [Rh(cod)]$^+$, 108 (8.4) [cod]$^+$.

Preparation of *syn*/*anti* Isomeric Mixture of Cp*Ru(2,6-diethyl-4,8-dimethyl-*s*-indacene)Rh(η^4-cod) (5a and 5b): *n*-Butyllithium (1.6 M in hexane, 1.48 mL, 2.4 mmol) was slowly added to a –80 °C solution of the previously prepared compound 1-hydro-2,6-diethyl-4,8-dimethyl-*s*-indacene-Rh(cod)[8] (0.95 g, 2.1 mmol) in thf (30 mL). The mixture was stirred for 1 h at room temperature to yield the monolithiated anionic complex. In a second flask with a side exit, [Cp*Ru-Cl]$_4$ (0.57 g, 0.5 mmol) was dissolved in thf (30 mL). This latter solution was dropwise added to the lithiated 1-hydro-2,6-diethyl-4,8-dimethyl-*s*-indacene–Rh(cod) solution. This mixture was stirred for 2 h at room temperature. Then, the solvent was removed, and the raw product was washed with pentane and filtered to eliminate the insoluble LiCl. A dark orange dust unstable to air was obtained. Yield: 1.33 g (92%). NMR revealed the formation of both isomers: *syn*/*anti*, 53:47. Data for the *syn* isomer (**5b**): ^{1}H NMR (C$_6$D$_6$): δ = 1.13 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C$_2$-CH$_2$-*CH$_3$*), 1.22 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C$_6$-CH$_2$-*CH$_3$*), 1.73 (m, 8 H, cod-*CH$_2$*), 1.80 (s, 15 H, Cp-*CH$_3$*), 2.06 (s, 6 H, C$_{4,8}$-*CH$_3$*), 2.19 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, C$_2$-*CH$_2$*-CH$_3$), 2.52 (qd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,Rh}$ = 1.5 Hz, 2 H, C$_6$-*CH$_2$*-CH$_3$), 4.28 (s, 4 H, cod-C=*CH*), 4.61 [s, 2 H, C$_{(1,3)}$H], 4.90 [s, 2 H, C$_{(5,7)}$H] ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 11.34 (Cp-*CH$_3$*), 14.73 (C$_{4,8}$-*CH$_3$*), 14.97 (C$_6$-CH$_2$-*CH$_3$*), 15.35 (C$_2$-CH$_2$-*CH$_3$*), 22.76 (C$_2$-*CH$_2$*-CH$_3$), 24.00 (C$_6$-*CH$_2$*-CH$_3$), 31.32 (cod-*CH$_2$*), 65.97 (C$_{1,3}$), 70.77 (d, $^1J_{C,Rh}$ = 10.3 Hz, cod-*C*=*C*), 72.71 (d, $^1J_{C,Rh}$ = 5.1 Hz, C$_{5,7}$), 81.55 (*Cp*-CH$_3$), 95.71 (C$_{4,8}$), 95.83 (C$_2$), 97.28 (C$_{3a,8a}$), 116.48 (d, $^1J_{C,Rh}$ = 1.1 Hz, C$_{4a,7a}$), 120.41 (d, $^1J_{C,Rh}$ = 7.8 Hz, C$_6$) ppm. ^{103}Rh NMR (14 MHz, C$_6$D$_6$): δ = –245 ppm. MS (EI): *m*/*z* (%) = 684 (43.4) [M]$^+$, 474 (100.0) [M – Rh(cod)]H$^+$, 211 (65.3) [Rh(cod)]$^+$, 108 (11.2) [cod]$^+$.

Procedure for the Separation of Isomeric Complexes 5a and 5b: The isomeric mixture of **5a**/**5b** was separated through fractional precipitation by using hexane as solvent. The *syn* isomer crystallized, whereas the *anti* isomer remained dissolved.

***anti*-[Cp*Co(2,6-diethyl-4,8-dimethyl-*s*-indacene)Rh(η^4-cod)] (6a):** Complex **6a** was prepared by using the same procedure as that used for the preparation of complexes **4a** and **5a** by using *n*BuLi (1.6 M in hexanes, 1.1 mL, 1.7 mmol), **2** (0.71 g, 1.65 mmol), and [(cod)-RhCl]$_2$ (0.40 g, 0.81 mmol). A black dust very unstable to air was obtained. Yield: 0.62 g (58%). C$_{36}$H$_{47}$CoRh (641.61): calcd. C 77.93, H 8.41; found C 78.01, H 8.76. MS (EI): *m*/*z* (%) = 641 (19) [M$^{\cdot}$]$^+$, 430 (100) [Rh(cod)H], 211 (56) [Rh(cod)$^{\cdot}$]$^+$.

***anti*-[Cp*Co(2,6-diethyl-4,8-dimethyl-*s*-indacene)Rh(η^4-cod)][BF$_4$] ([6a][BF$_4$]):** Complex [**6a**][BF$_4$] was prepared by using the same procedure as that used for the preparation of [**3**][BF$_4$] by using **6a** (0.30 g, 0.47 mmol) and ferrocenium tetrafluoroborate (0.10 g, 0.37 mmol). An insoluble black dust was formed. Yield: 0.30 g (89%). ^{1}H NMR (CD$_3$CN): δ = 1.18 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C$_2$-CH$_2$-*CH$_3$*), 1.39 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, C$_6$-CH$_2$-*CH$_3$*), 1.55 (s, 15 H, Cp-*CH$_3$*), 1.93 (s, 8 H, cod-*CH$_2$*), 2.52 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, C$_2$-*CH$_2$*-CH$_3$), 2.32 (s, 6 H, C$_{4,8}$-*CH$_3$*), 2.69 (qd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{Rh,H}$ = 1.2 Hz, 2 H, C$_6$-*CH$_2$*-CH$_3$), 4.46 (s, 4 H, cod-C=*CH*), 5.38 [s, 2 H, C$_{(1,3)}$H], 5.53 [s, 2 H, C$_{(5,7)}$H] ppm. ^{13}C NMR (CD$_3$CN): δ = 14.13 (C$_2$-CH$_2$-*CH$_3$*), 14.28 (C$_6$-CH$_2$-*CH$_3$*), 14.81 (C$_{4,8}$-*CH$_3$*), 15.03 (Cp-*CH$_3$*), 19.97 (C$_2$-*CH$_2$*-CH$_3$), 20.17 (C$_6$-*CH$_2$*-CH$_3$), 30.30 (cod- *CH$_2$*), 69.68 (C$_{5,7}$), 74.51 (d, $^1J_{Rh,C}$ = 12.8 Hz, cod-*C*=*C*), 75.02 (C$_{1,3}$), 93.01 (*Cp*-CH$_3$), 99.75 (C$_{4a,7a}$), 106.00 (C$_2$), 112.95 (C$_{4,8}$), 121.54 (C$_{3a,8a}$), 126.77 (d, $^1J_{Rh,C}$ = 5.0 Hz, C$_6$) ppm. ^{103}Rh NMR (14 MHz, C$_6$D$_6$): δ = –271 ppm.

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X-ray Structural Determination: All data for both structures represented in this paper were collected with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods[25] and all non-hydrogen atoms were refined anisotropically by using the least-squares method on F^2.[26] Data for **1**: $C_{28}H_{36}Fe$, M = 428.42, triclinic, a = 8.902(1) Å, b = 10.696(1) Å, c = 13.584(2) Å, α = 76.112(2)°, β = 77.359(2)°, γ = 69.346(3)°, V = 1162.0(2) Å^3, T = 193(2) K, space group $P\bar{1}$, Z = 2, μ = 0.666 mm^{-1}, 6877 reflections measured, (4679 independent, R_{int} = 0.0326) were collected. Largest diff. peak and hole: 0.406 and –0.249 e Å^{-3}. R_1 [$I > 2\sigma(I)$] = 0.0488 and wR_2 = 0.1180 (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. Data for **5b**: $C_{36}H_{47}RhRu$, M = 683.72, tetragonal, a = b = 14.481 Å, c = 30.053 Å, V = 6302.1 Å^3, T = 294(2) K, space group $P4_12_12$, Z = 8, μ = 1.025 mm^{-1}, 13488 reflections measured, (6397 independent, R_{int} = 0.1961) were collected. Largest diff. peak and hole: 0.722 and –1.250 e Å^{-3}. R_1 [$I > 2\sigma(I)$] = 0.0528 and wR_2 = 0.1478 (all data).

CCDC-703446 (for **1**) and -703447 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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