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Indenyl and indacenyl ligands in homo and heterobimetallic complexes

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Abstract

Metal atoms that are held in close proximity exhibit unique properties and many ligands have been tested for their ability to coordinate two or more transition metals in an effort to search for new chemical and physical properties. During the last decade, extensive studies have been conducted on a series of heterobimetallic indenyl complexes of Cr(0) and Rh(I). The mutual effect of the two metal units, viz. $Cr(CO)_3$ and RhL_2 [L_2 = COD, NBD, $(CO)_2$], *anti* coordinated to the same planar bridging ligand influences both the reactivity and the catalytic activity of the two metals. Some insight into the dependence of the mutual effects on the stereochemistry of the bimetallic complexes may be provided by the availability of pairs of pure *syn* and *anti* bimetallic stereoisomers of rigid bridging ligands. Reported here are the preliminary results concerning the synthesis of *syn* and *anti* homobimetallic *s*-indacene-diide-$[RhL_2]_2$ complexes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chromium; Rhodium; Indenyl; Indacenyl; *Syn* and *anti* structures

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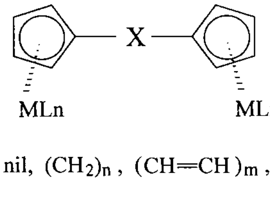
1. Introduction

One of the rationales for the great interest in homo and heterobimetallic organometallic complexes is the expectation that their chemical behavior both in stoichiometric and catalytic reactions may differ significantly from that of the analogous mononuclear complexes [1]. A common assumption is that cooperative interaction between the two metal centers might cause significant increase in the reaction rates or lead to transformations which do not occur when monometallic complexes are involved.

In order to demonstrate unambiguously the validity of this hypothesis, one should compare strictly correlated mono and dinuclear complexes and, to this purpose, there have been few systems suitable for such a comparison. A vexing question in the building of a bimetallic compound is: how to anchor two metals in close proximity? In principle, ligands could be designed that control the distance and orientation between two metal centers. Depending on the electronic and steric properties of the ligand and the relative disposition of the two metals, cooperative effects may arise because of a strong through-bond interaction facilitated by the bridging ligand and of a direct metal–metal interaction.

Perhaps, the most investigated class of bimetallic complexes is that in which two cyclopentadienyl rings are directly connected by a single bond (*fulvalene*



Scheme 1.

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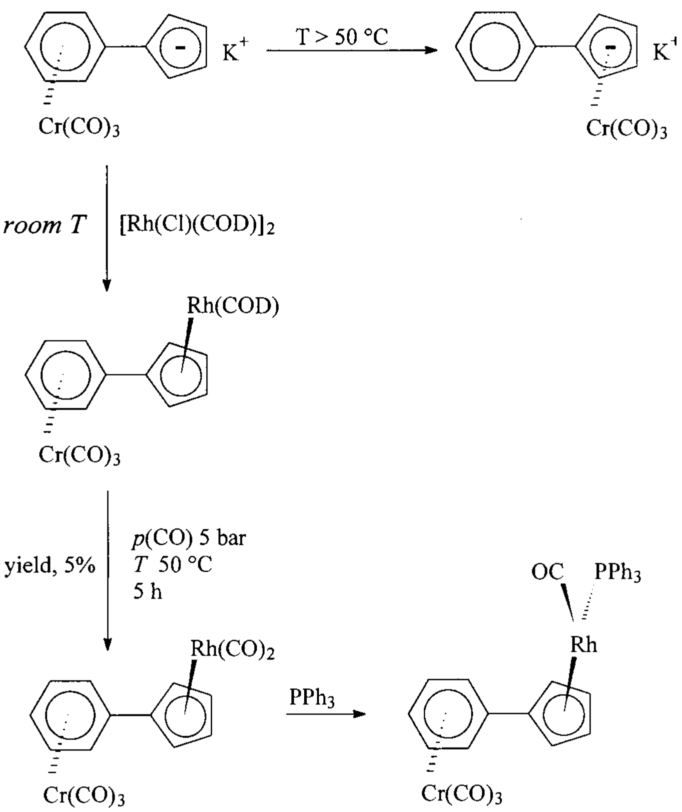


Scheme 2. Heterobimetallic complexes of the phenylcyclopentadienyl ligand.

derivatives) or by a saturated or unsaturated chain [2], as shown in Scheme 1.

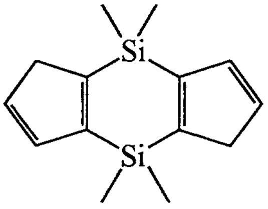
Generally in this class of compounds orientation and distance between the two metal groups are not certain and the organometallic fragments may adopt a transoid or a cisoid conformation. In the last case, strong metal–metal interactions may intervene although, owing to steric repulsion, *syn* complexes seem to be generally disfavored with respect to the *anti* isomers. Unlike the fulvalene bimetallic complexes, the coordination of two Cp rings in bis(cyclopentadienyl)methane or similar ligands where the linkage is assured by one chain does not introduce significant strain into the ring portion of the molecule and metal–metal bonds are formed between the two well-positioned metals.

An isoelectronic ligand of the fulvalene dianion is the phenyl-cyclopentadienyl anion. In the course of our investigation on heterobimetallic complexes of Cr(0) and Rh(I), we were able to synthesize the monometallic [$Cr(CO)_3$-phenyl]cyclopentadiene complex [3]. Deprotonation by KH in THF gave the η^6-$Cr(CO)_3$-phenyl-cyclopentadienyl anion [4] which reacted with $[Rh(Cl)COD]_2$ to give the complex [$Cr(CO)_3$-phenyl]CpRh(COD), as shown in Scheme 2.

An evaluation of the effect of the presence of the second metal moiety, viz. $Cr(CO)_3$, may be inferred from the change of reactivity at the rhodium center and, in particular, from the ease of substitution of the ancillary COD. In fact, substitution of COD by CO is not strongly influenced by $Cr(CO)_3$ neither is the substitution of one carbonyl with triphenylphosphine [5]. Thus, the coordination of the second metal to the η^6-$Cr(CO)_3$-phenyl-cyclopentadienyl anion does not seem to influence much the reactivity at rhodium. Similarly, the mobility of the $Cr(CO)_3$ group in the same bimetallic complex does not differ much from that shown by the monometallic phenyl-substituted $Cr(CO)_3$ complexes in the exchange reactions with other arene or olefin ligands [5].

Another possibility to bridge two Cp ligands which allows a more controlled separation between the metal sites is branching the two Cp rings by two alkyl or silyl linkages ([6]a), as shown in Scheme 3.

Here a minimum of orientational freedom for the Cp–metal fragments can be achieved and the interaction in the dinuclear metal derivatives can be predetermined since different dispositions of the two metals in *syn* or *anti* conformations are definitively certain. Deprotonation with *n*-BuLi of the ligand 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene, **A**,

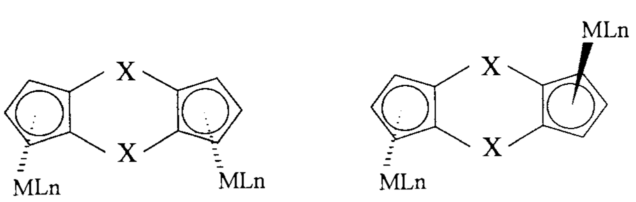


A

for example, produces the dilithium salt for which an *anti* arrangement is expected from the electrostatic interaction of the charges ([6]b), and *anti* bimetallic complexes should also be formed by reaction with transition metal compounds.

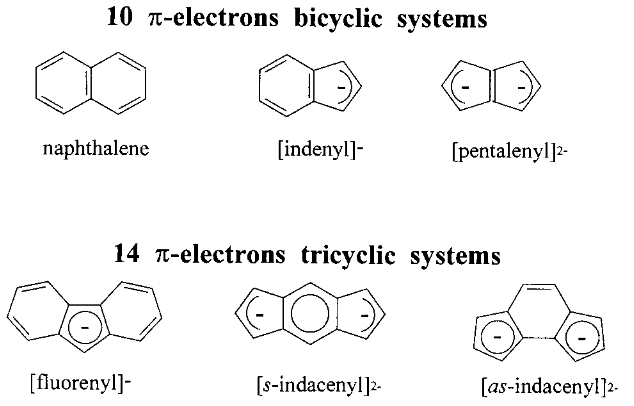
Bimetallic complexes of fused aromatic bicyclic or tricyclic ligands have attracted much attention in the last decade since these ligands have the potential to bridge two or more metal moieties in both their reduced or oxidized forms. Some of the most common 10π and 14π electron ligands are shown in Scheme 4.

Unlike the fulvalene-type dianions, the rigid ligands shown in Scheme 4 allow two metal groups to bond



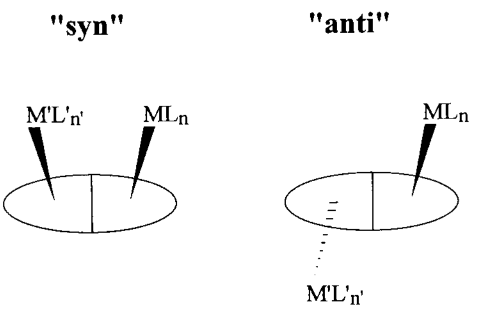
X = alkyl, alkenyl, SiR_2, ...

Scheme 3.

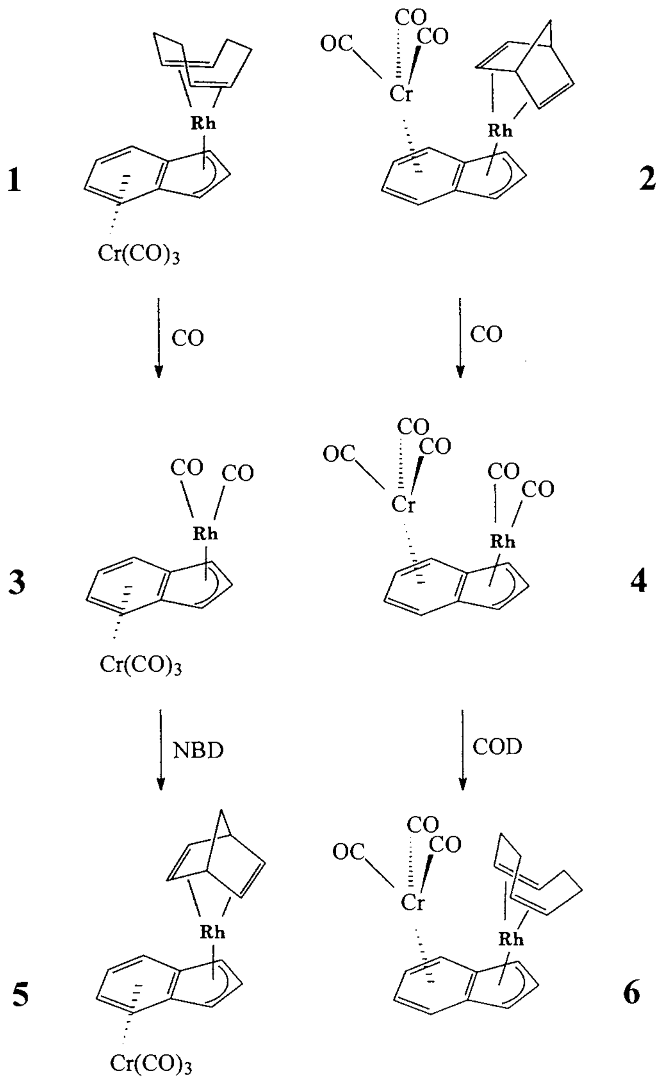


Scheme 4.

either in *syn* or *anti* disposition with respect to the plane of the ligands so that orientation and distance between the two metals are certain as sketched in Scheme 5 and an efficient transmission of the electronic effects is assured. These can be separated from the through-distance metal–metal interactions if couples of *syn*/*anti* isomers can be prepared and their chemical behavior compared. To the best of our knowledge only one report on the formation of a *syn*/*anti* couple has been reported so far [7], and many important questions remain unanswered: of the two isomers, which is the more stable? does isomerization occur? how does the mutual disposition of the two metals affect the reactivity in stoichiometric and catalytic reactions?



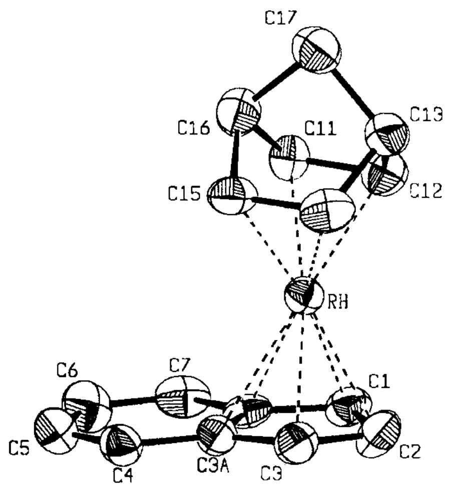
Scheme 5.



Scheme 6. *Anti* and *syn* isomeric couples of some $Cr(CO)_3$-indenyl-RhL_2 complexes.

Bimetallic complexes of naphthalene were prepared and to all but very few cases an *anti* disposition of the two metal groups has been assigned from X-ray structures or by analogy with similar complexes. The *anti*-naphthalene-$(FeCp)_2$ ([8]a), $(Cr\text{-arene})_2$ ([8]b) and $(RuCOD)_2$ ([8]c) complexes can be classified as 'slipped triple decker' complexes where coordination of both metals to the two six-membered rings is characterized by the shift of the metals towards the periphery carbons of the ligand naphthalene (distorted η^6 hapticity). The $(RuCOD)_2$-μ-naphthalene complex has been shown to act as a source of the very reactive 12-electron fragment $Ru(C_8H_{12})$ differently from the monometallic complex which is more stable. The planarity of the bridging naphthalene is generally modified depending on the nature of the bound metal groups, the magnitude of the fold angle varying from 14° for the bis-(FeCp) complex to 30–40° for an heterobimetallic Cr–Co complex ([8]a). The homobimetallic $[Mn(CO)_3]_2$ and the heterobimetallic $[Mn(CO)_3][Fe(CO)_2]$-μ-naphthalene complexes with *syn*-facially bound metal atoms have recently been reported and their structure was confirmed by single crystal X-ray structure analysis. The synthetic procedure in this case consists in a facile $Mn(CO)_3$ transfer to form bis-complexes which, in the absence of steric constraints, adopt a *syn*-facial structure ([8]d).

Binuclear metallocenes with pentalenyl anion as bridging ligand have been known since the early 1970's. Ni–allyl, or Fe–Cp, Co–Cp, Ni–Cp and Ru–Cp (or –Cp*) fragments coordinated to the two fused cyclopentadienyl rings in an antarafacial arrangement



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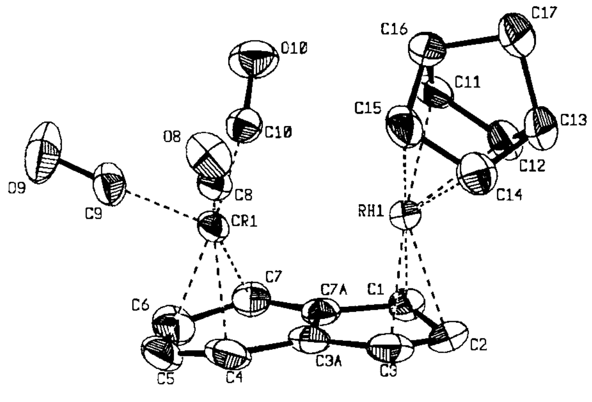

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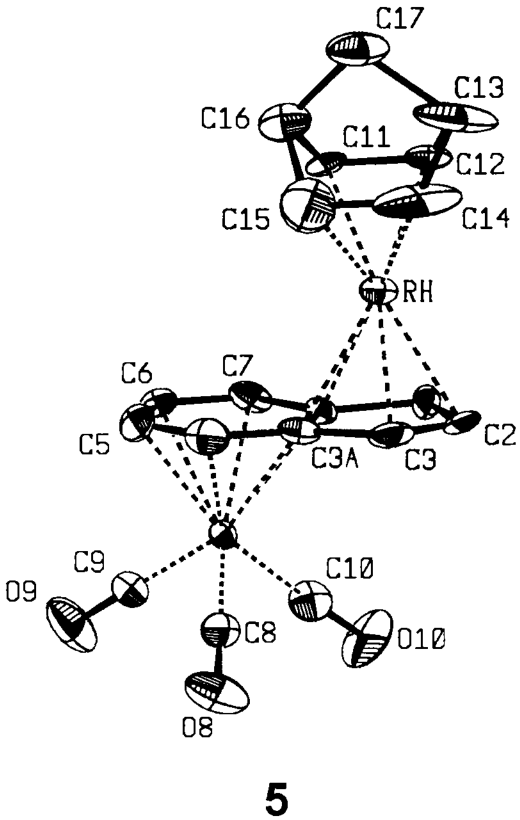

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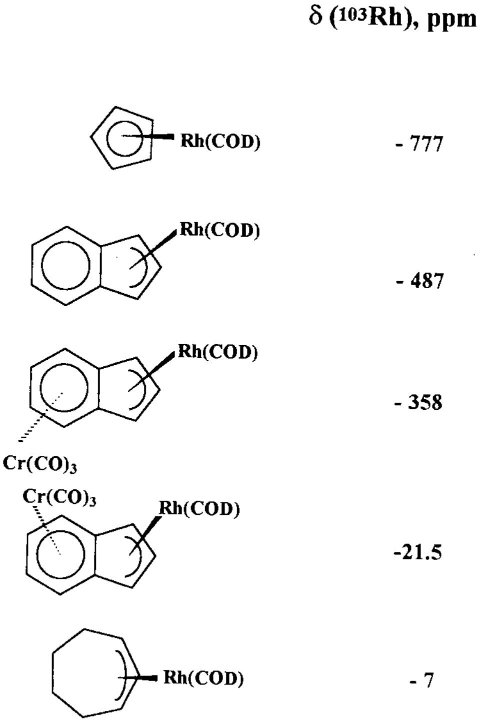
Fig. 1. A perspective view of the molecules of indenyl-Rh(NBD), **7**, *syn*-[Cr(CO)$_3$-indenyl-Rh(NBD)], **2**, and *anti*-[Cr(CO)$_3$-indenyl-Rh(NBD)], **5**.

were readily prepared from LiCp (or LiCp*) and Li$_2$(pentalene-diide) in good yields [9]. The preference for an *anti* disposition of the metals was attributed to the dominance of steric effects and in this conformation the complexes generally exhibit a behavior consistent with significant electronic interactions between the metal centers including large potential separations between successive one-electron redox events ([9]c).

2. Heterobimetallic indenyl complexes

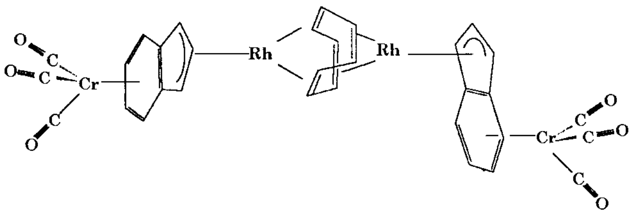
Monometallic transition metal complexes of the indenyl ligand have been object of extensive studies since when it was found that their reactivity and catalytic activity are significantly greater than those of the analogous cyclopentadienyl complexes (the ‘indenyl effect’) [10]. Our original thoughts in starting work with bimetallic indenyl complexes were that we might be able to increase the enhanced reactivity of the monometallic indenyl complexes by coordinating a second metal group to the free six-membered ring of the ligand. The success in the synthesis of bimetallic indenyl complexes was based on our previous results obtained in the kinetic study of the $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement of the η^6-Cr(CO)$_3$-indenyl anion [11]. Quantitative metallation by KH in THF of indene-Cr(CO)$_3$ produces the η^6 anion which is stable at − 30°C leaving the cyclopentadienyl ring available to the attack of a second metal. The quenching of the η^6 anion was carried out separately by two different rhodium dimers as electrophiles, viz. [Rh(μ-Cl)(COD)]$_2$ [12] and [Rh(μ-Cl)(NBD)]$_2$ [13] under identical conditions. Two bimetallic complexes were isolated after the work up of the respective reaction solutions; the corresponding ^{1}H-NMR spectra displayed the pattern characteristic of an indenyl ligand coordinated to rhodium, although very different trends of the chemical shift values were observed suggesting that the two complexes are isomers (except for the nature of the olefin ligand at rhodium). The mutual disposition of the two metal fragments in the two complexes *anti*-[Cr(CO)$_3$-indenyl-Rh(COD)], **1**, and *syn*-[Cr(CO)$_3$-indenyl-Rh(NBD)], **2**, was established by X-ray structural determinations.



Scheme 7. Some ^{103}Rh-NMR data on mono- and heterobimetallic complexes.

The availability of the two stable complexes **1** and **2** of different stereochemistry allowed the easy preparation of other Cr(CO)$_3$-indenyl-RhL$_2$ complexes by an L exchange reaction which takes place by retention of the original molecular geometry. Thus, quantitative formation of the fully carbonylated bimetallic isomers *anti*-[Cr(CO)$_3$-indenyl-Rh(CO)$_2$], **3**, [14] and *syn*-[Cr(CO)$_3$-indenyl-Rh(CO)$_2$], **4**, [13] was obtained by bubbling CO through a CH$_2$Cl$_2$ solution of **1** and **2**, respectively. The easy substitution of carbonyls at rhodium with COD or NBD afforded *anti*-[Cr(CO)$_3$-indenyl-Rh (NBD)], **5**, [15] (i.e. the isomer of **2**) and *syn*-[Cr(CO)$_3$-indenyl-Rh(COD)], **6** [16] (i.e. the isomer of **1**), as shown in Scheme 6.

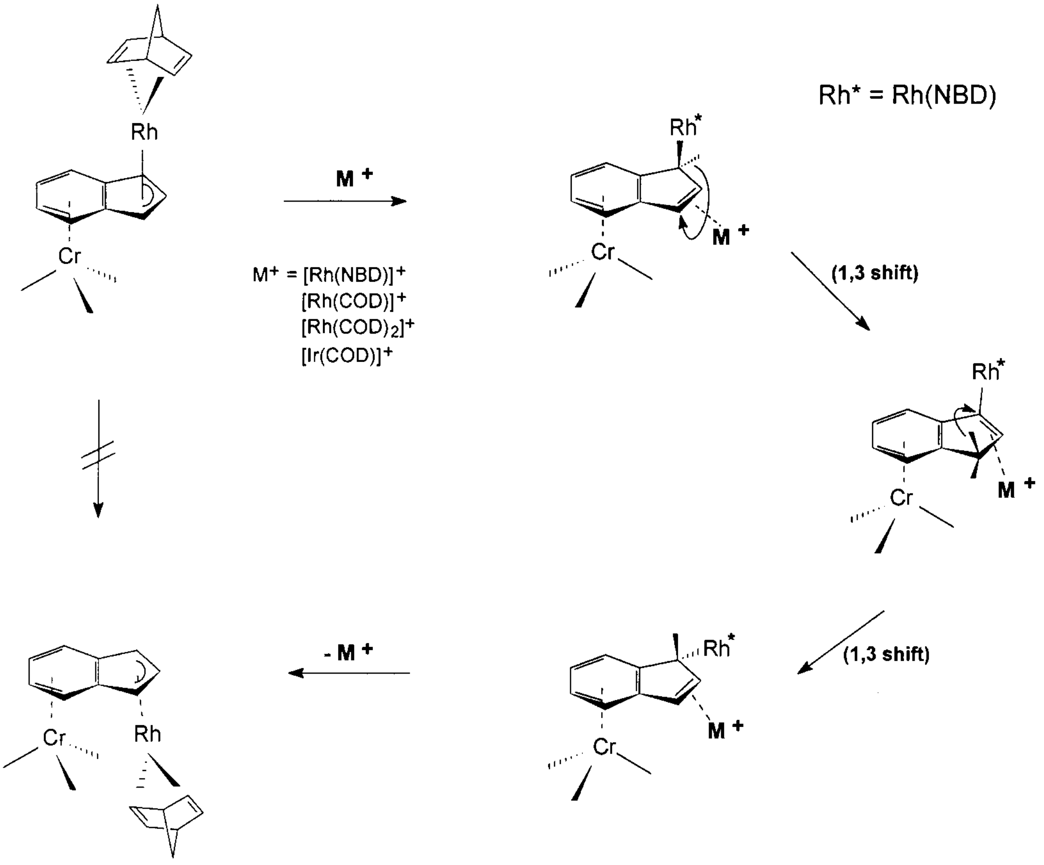
The high mobility of carbonyls coordinated to the rhodium in complex **3** was confirmed by the results obtained with cyclooctatetraene, COT. The slipped triple-decker complex *anti*-[Cr(CO)$_3$-indenyl-Rh(COT)], formed from **3** by exchanging COT for CO’s, reacts further with the precursor to afford the slipped *pseudo*-pentadecker *anti,anti*-[Cr(CO)$_3$-indenyl-Rh-μ-COT-μ-Rh-indenyl-Cr(CO)$_3$] complex [17]:



Thus, the ancillary carbonyls at rhodium appear quite labile at least in the *anti* bimetallic indenyl complex **3**. This behavior was substantiated by the results obtained for the reactivity and the catalytic activity of **3** when compared with those of the mononuclear indenyl-Rh(CO)$_2$ complex (see below).

X-ray structural data were obtained for the bimetallic complexes **1**, **2**, and **4**–**6**. In contrast to **4**, compound **3** is stable in solution only at low temperatures and for a short time.

The comparison between the structural characteristics of the *syn* and *anti* isomers is instructive. From the values of the selected bond distances and angles obtained for **2** and **5** and those for the monometallic indenyl-Rh(NBD) complex, **7**, (the structures are shown in Fig. 1) is was clear that (i) the slippage of rhodium and chromium from the centroid of the coordinated rings towards the periphery carbon atoms (C$_2$, and C$_{5,6}$, respectively) is more pronounced when the two metals are coordinated to the same side of the ligand. Conversely, the structural parameters of the CpRh(NBD)

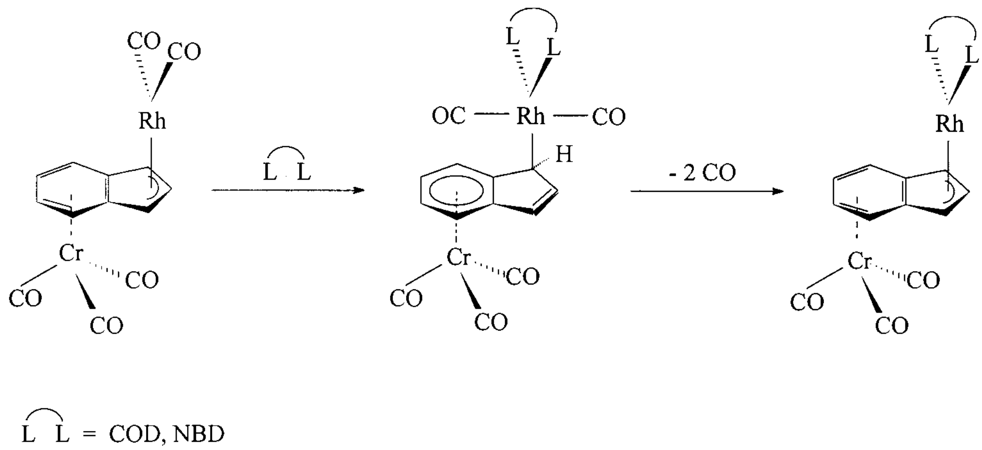


Scheme 8. Proposed mechanism of *anti*-**5**→*syn*-**2** isomerization (Rh*≡Rh(NBD)).

subunit in the *anti* isomer are not significantly different from those observed for the monometallic indenyl-Rh(NBD); (ii) the distortion of the coordination of NBD about rhodium is much more pronounced in **2** than in **5** and **7**; (iii) the coordination with $Cr(CO)_3$ causes the puckering of the benzene ring which is markedly higher in the *syn* complex than in the *anti* one. Very similar findings were obtained by comparing the isomeric COD complexes **1** and **6**.

In conclusion, the molecular distortions in the *syn* isomers are substantially greater than in the *anti* isomers indicating a pronounced shift of rhodium from the ideal η^5 towards an η^3 hapticity and of chromium from the ideal η^6 towards an η^4 hapticity.

The differences between the structural features of *syn* and *anti* isomers also persist in solution as shown by the ^1H and ^{13}C-NMR results. A detailed spectroscopic study for a series of indenyl- and $Cr(CO)_3$-indenyl-RhL_2 has been reported [18]. Only the ^{103}Rh data illustrated in Scheme 7 will be discussed. The ligand hapticity and the electron density at the metal markedly affects the ^{103}Rh chemical shift values [19]. In the monometallic (η-indenyl)Rh(COD) complex, the ^{103}Rh nucleus resonates at δ −487 ppm, an intermediate value between those of the Cp (η^5 hapticity, δ −777 ppm) and cyclooctenyl (η^3 hapticity, δ −7 ppm) derivatives. Thus, the situation in indenyl complexes may be described as a distorted η^5 coordination. The complexation of the benzene ring with $Cr(CO)_3$ induces a downfield shift of the ^{103}Rh resonance (δ −358 ppm) which cannot be justified by the electron-withdrawing properties of $Cr(CO)_3$ alone, but a different rhodium–indenyl bonding mode in bimetallic with respect to the monometallic species must be invoked. In particular, in the *anti* derivative, the rhodium adopts an even more distorted η^5 bonding mode. Conversely, in the *syn* derivative **6**, the rhodium resonates at δ −21.5 ppm [17], a value very close to that of cyclooctenyl-Rh(COD), suggesting that rhodium coordinates the Cp ring in an η^3 allyl mode. A very similar trend was observed in the series indenyl-Rh(NBD), ($\delta(^{103}Rh) =$ −520 ppm), *anti*-[$Cr(CO)_3$-indenyl-Rh(NBD)], ($\delta(^{103}Rh) =$ −433 ppm) and *syn*-[$Cr(CO)_3$-indenyl-Rh(NBD)], ($\delta(^{103}Rh) =$ −45 ppm) [17]. Therefore, the changes of the spectral parameters following the introduction of the $Cr(CO)_3$ unit suggest significant modifications on the electronic distribution in the indenyl moiety in the ground state.



Scheme 9. Proposed η^1-intermediate in the exchange reaction of CO's by diolefins in *anti*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$], **3**.

2.1. Reactivity of $Cr(CO)_3$-indenyl-RhL_2 complexes and syn/anti isomerization

The availability of pure samples of *syn* and *anti* isomer pairs allowed us to investigate about the possibility of an isomerization process in which one metal goup moves through the Cp or benzo plane of the indenyl ligand. As far as we are aware, this kind of isomerization is unprecedented.

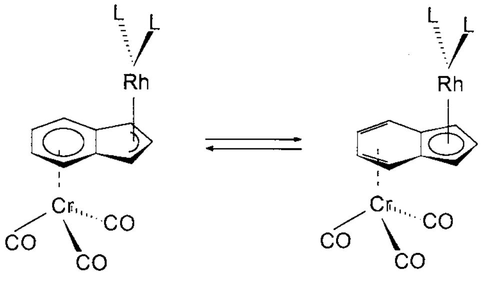
Attempts to accomplish the *anti*→*syn* isomerization starting from complex **1** or **5** when dissolved in pure THF failed. As a matter of fact, it was found that **5** isomerizes to **2** at room temperature in THF in the presence of salts such as $[Rh(NBD)]^+BF_4^-$, $[Rh(COD)]^+BF_4^-$, $[Rh(COD)_2]^+BF_4^-$, $[Ir(COD)]^+BF_4^-$ [15].

The process exhibits a relatively low activation enthalpy and a negative activation entropy, and its mechanism was shown to be an intramolecular one assisted by the ML_2 cation, as shown in Scheme 8. It was suggested that the conversion of the *anti* isomer to the more stable *syn* isomer occurs through the formation of an (η^1-indenyl)-Rh species in which the two metal groups are still in the *anti* conformation. A *syn* stereochemistry can be achieved through two fast [1,3]-hydrogen shifts (probably promoted by the catalyst salt) necessary to invert the configuration at the indene carbon atom σ-bonded to Rh(NBD).

Therefore, in contrast to what could be anticipated on the basis of structural evidence, the *syn* isomer **2** is thermodynamically more stable that the *anti* isomer **6**. This result caused us to re-examine the reaction between the η^6-indenyl-$Cr(CO)_3$ potassium salt and $[Rh(\mu\text{-}Cl)(NBD)]_2$ in THF. At −30°C, the reaction afforded quantitatively the *anti* isomer **5** (the kinetic product) which is stable only below −30°C. At higher temperatures, **5**, isomerizes quantitatively to the *syn* isomer **2** (the thermodynamic product), the unexpected stability of which seems to trace to some Cr–Rh bond interaction and stabilizing effects between suitably-oriented olefin hydrogens of NBD and the facing carbonyl groups [13]. *Anti*→*syn* isomerization of **1** carried out under similar conditions did not take place, the *anti* isomer being stable up to the working-up temperature. A descriptive MO picture of cofacial and antarafacial indenyl bimetallic isomers has been reported together with the implications for the indenyl effect [20].

It is commonly accepted that nucleophilic attack by olefins and alkynes at transition metal centers represents the crucial step in many isomerization and polymerization processes. We are aware of the accurate kinetic studies carried out by Basolo et al. on the substitution of carbon monoxide by phosphorus-donor molecules ([10]f,g)[21]. Evidence for an associative pathway was demonstrated for many cyclopentadienyl– and indenyl–ML_n compounds. Conversely, we are not aware of any report dealing with the kinetics of attack of olefins to transition metal complexes of the same structure.

Measurements of the rate constants for the substitution reaction of CO's by COD or NBD were carried out for three indenyl complexes, viz. Indenyl-$Rh(CO)_2$, 5-NO_2-indenyl-$Rh(CO)_2$ and *anti*-[$Cr(CO)_3$-indenyl-$Rh(CO)_2$] [14,22]. For each substrate the pseudo first-



I **II**

Scheme 10.

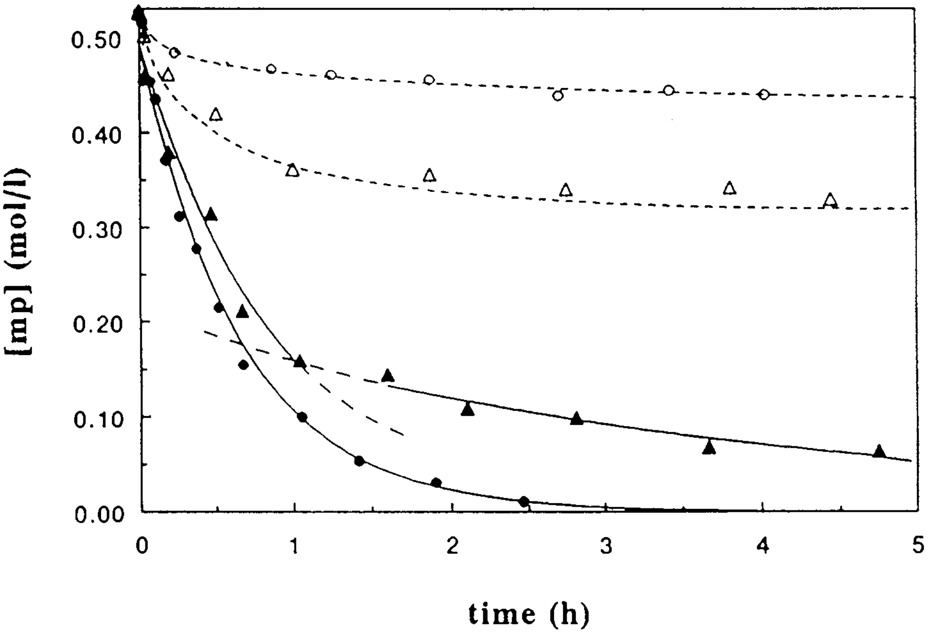


Fig. 2. ○, Monomer disappearance in the methyl propiolate cyclotrimerization reaction catalized by Ind*-Rh(COD); △, Ind*-Rh(CO)$_2$; ●, *anti*-[Cr(CO)$_3$-Ind*-Rh(COD)] and ▲, *anti*-[Cr(CO)$_3$-Ind*-Rh(CO)$_2$].

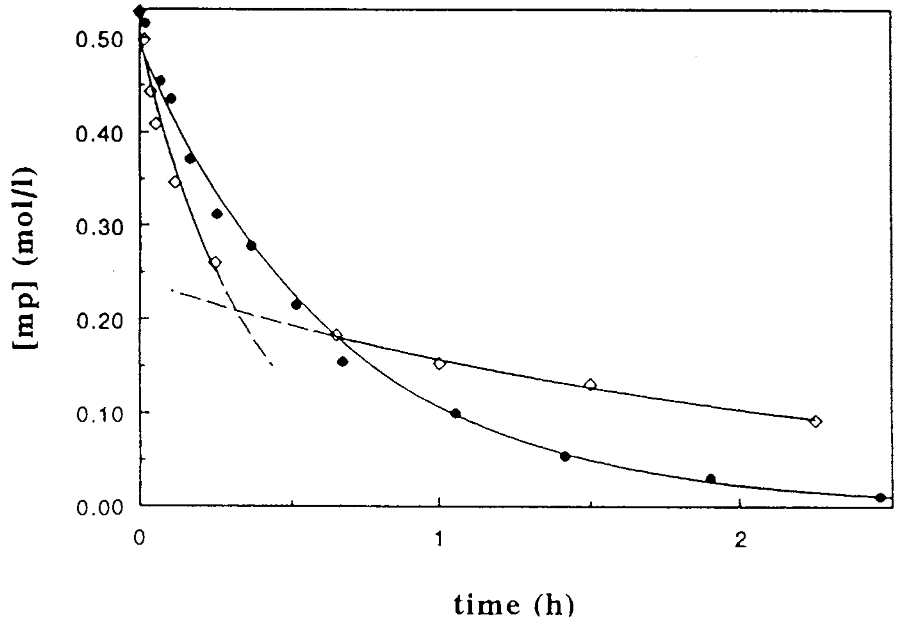
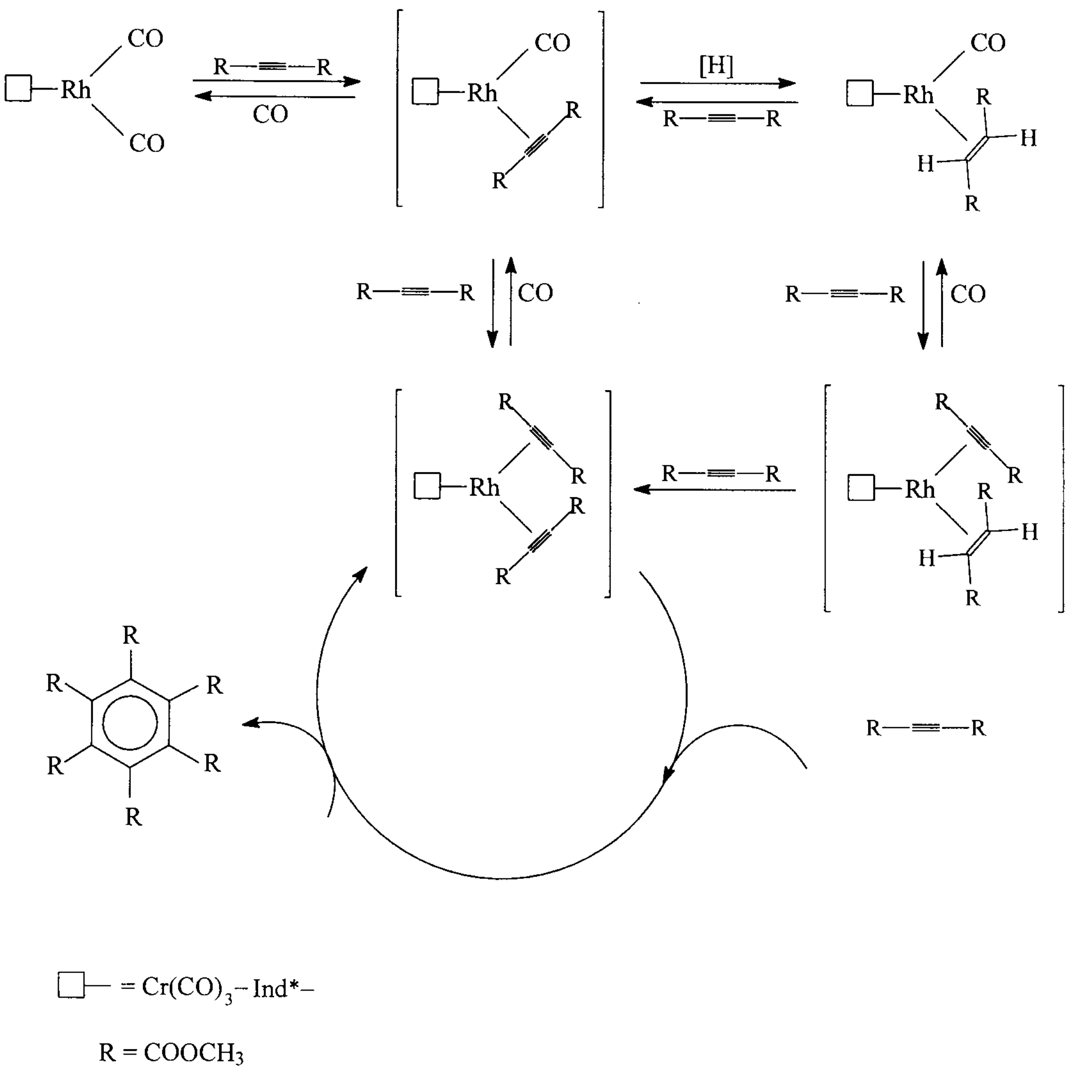


Fig. 3. ●, Monomer disappearance in the methyl propiolate cyclotrimerization reaction catalyzed by *anti*-[Cr(CO)$_3$-Ind*-Rh(COD)] and ◇, *anti*-[Cr(CO)$_3$-Ind-Rh(COD)].

order rate constant depends linearly on the concentration of olefin. Thus, the overall substitution is a bimolecular associative process represented by the second order rate constant, k_2. The nitro group bonded to the six-membered ring increases the k_2 value of the unsubstituted indenyl complex ca. five times, whereas an effect of ca. 2000 times is produced by the *anti*-Cr(CO)$_3$ group. This huge increase in rate ('extra-indenyl effect') can be only to a little extent attributed to the electron-withdrawing power of the Cr(CO)$_3$ group comparable to that of NO$_2$ [23]; it was ascribed, instead, to the simultaneous *anti* coordination of two inorganic 12-electron units to the same 10π electron ligand which sets up an electronic structure where both metals exhibit an overall coordinative unsaturation.

From the comparison of the activation parameters of the substitution reactions by the two olefins, it was suggested that a plausible mechanism is the rate-determining step addition of the bidentate olefin to produce an η^1 species (as shown in Scheme 9), from which the



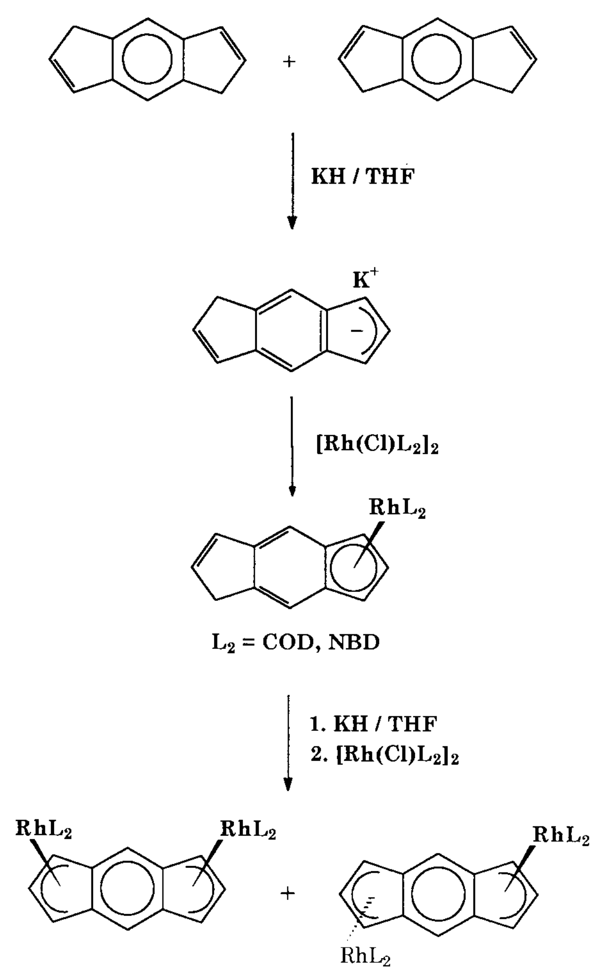
Scheme 11. Proposed mechanism for the cyclotrimerization reaction of dimethyl acetylenedicarboxylate catalyzed by *anti*-[Cr(CO)$_3$-Ind*-Rh(CO)$_2$].

loss of two CO's to restore the η^5 coordination occurs in a subsequent fast step.

Besides the reactivity of the ancillary ligands at rhodium, also the mobility of Cr(CO)$_3$ is influenced by the presence of the RhL$_2$ unit. To this purpose, we investigated the exchange of Cr(CO)$_3$ between the complexes *anti*-[Cr(CO)$_3$-indenyl-RhL$_2$ (L$_2$ = COD, (CO)$_2$) and suitable acceptors, viz. hexamethylbenzene and cycloheptatriene [22]. The results were compared with those obtained for the monometallic indene-Cr(CO)$_3$ and naphthalene-Cr(CO)$_3$. The lability of the Cr(CO)$_3$–arene bond decreases in the order indene $\ll$ naphthalene $<$ bimetallic complexes. The qualitative trend was confirmed by kinetic measurements carried out in CH$_2$Cl$_2$ by allowing cycloheptatriene to react with the complex *anti*-[Cr(CO)$_3$-indenyl-Rh(COD)] and with naphthalene-Cr(CO)$_3$. From the second order rate constant values, k_2, it was shown that the bimetallic complex exchanges Cr(CO)$_3$ ca. 50 times faster than naphthalene-Cr(CO)$_3$. The increase in rate was attributed to the facile $\eta^6 \rightarrow \eta^4$ metal slippage induced by the incoming ligand that is energetically favored by the aromatization of the fused CpRhL$_2$ ring, as well as a similar η^4-Cr(CO)$_3$ intermediate is favored by the aromatization of the fused free ring in the naphthalene-Cr(CO)$_3$ exchange reactions [24].

A model which explains the kinetic results obtained for substitution and exchange reactions in *anti*-bimetallic indenyl complexes requires the existence in the ground state of the haptomeric equilibrium between **I** and **II** shown in Scheme 10 which represents a suitable description of the coordinative unsaturation which justifies the increased reactivity of the metal centers.

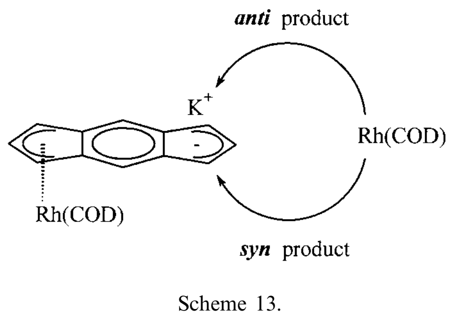
The enhanced rate of exchange of the ancillary ligands in the *anti* bimetallic complexes in comparison with the monometallic analogues parallels with the significant increase of their activity as catalysts. A huge increase of the rate of the cyclotrimerization reaction of



Scheme 12. Two-step synthesis of homobimetallic complexes of the *s*-indacene-diide ligand.

the alkyne esters, viz. methylpropiolate, **MP**, and dimethylacetylenedicarboxylate, **DMAD**, in cyclohexane, is in fact obtained when bimetallic *anti*-(Cr,Rh)indenyl species are used as catalysts [25], as depicted in Fig. 2. Moreover, the permethylation of the indenyl framework noticeably increases the stability of the catalyst without an appreciable decrease of the rate (see Fig. 3) [26].

The *anti*-[Cr(CO)$_3$-Ind*-Rh(CO)$_2$] (or Rh(COD)) species therefore appears the most appropriate complex for a detailed study of the mechanism of alkyne cyclotrimerization. The easy spectroscopic recognition of the precursor complex (or its derivatives) by ^{1}H-NMR spectroscopy makes it possible to follow its fate during the reaction. The most relevant results of this study are: (i) both the CO's are displaced by alkyne molecules, the substitution of the second one being the slow step of the reaction: (ii) the precursor is reformed, in part, at the end of the catalytic cycle; (iii) a chiral complex, viz. *anti*-[Cr(CO)$_3$-Ind*-Rh(CO)(FADE)] (FADE, fumaric acid dimethyl ester) is the main component of the organometallic residue isolated at the end of the catalytic cycle. The FADE ligand must originate from the *trans*-hydrogenation of the alkyne diester, **DMAD,** and we suggested an intermolecular C–H bond activation of cyclohexane as a source of hydrogen. A detailed representation of the catalytic cycle is shown in Scheme 11.

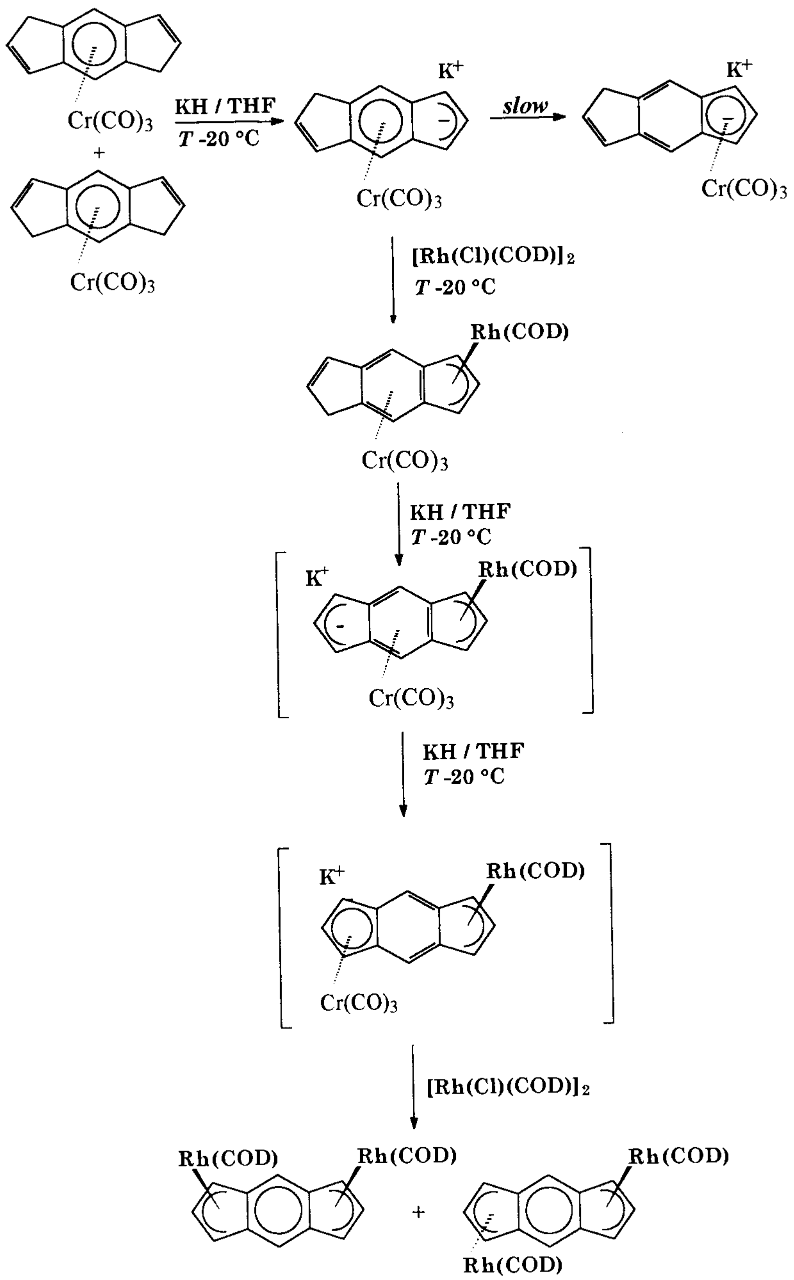


Scheme 13.

The presence in the precursor of very labile ancillary CO's is the decisive factor for the thermal formation of the unsaturated fragment necessary for accomodation of the C–H bond electrons together with an accessible $n+2$ oxidation state of rhodium. The thermal C–H bond activation of alkanes by rhodium indenyl complexes under mild conditions is not unprecedented [27] on condition that the structure of the catalyst precursor is characterized by the presence of the coordinatively flexible indenyl ligand and of easily displaceable ancillary ligands, e.g. ethylene. It seems, therefore, that complexes of general structure *anti*-[Cr(CO)$_3$-Ind*-ML$_2$] (M = Rh, Ir) are promising systems for the activation of alkane C–H bonds under very mild thermal conditions, and our experimental investigation is now directed in that direction.

3. Homobimetallic *s*- and *as*-indacene-diide complexes

The coordination with FeCp of the two terminal cyclopentadienyls of the *as*-indacene-diide was already described since the late 1970's [28]. A series of binuclear MCp* (M = Fe, Ru, Co, Ni) complexes of the same ligand was obtained by one-pot syntheses; in all complexes the two inorganic fragments reside on opposite faces of the fused μ-bridging ring system ([9]c). Metal carbonyl homodinuclear complexes of manganese [29] and molybdenum [7] of *s*- and *as*-indacene-diide have been described and only for the Mn(CO)$_3$ complexes a mixture of *anti* and *syn* isomers was identified spectroscopically, the *anti* being the major component. Perhaps, a rationale for the almost exclusive formation of the *anti* isomer is the *anti* arrangement of contact ion pairs of the dilithium salt of indacene-diide. In fact, an *anti* arrangement of the two Li$^+$ cations has been found experimentally in the solid state for the Li derivatives of naphthalene ([30]a) and anthracene ([30]b), as well as for the dilithium 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene-diide salt



Scheme 14.

([6]b). Thus, the reaction of these Li salts with suitable transition metal compounds should yield *anti* bimetallic complexes. Any factor which reduces the stability of the contact ion pairs should favor the formation of *syn* derivatives shifting the *anti*/*syn* ratio to lower values, unless big steric congestion of the two metal fragments in the *syn* arrangement makes the *syn* route less favorable. As part of our effort to add to our understanding of chemistry of bimetallic complexes with a bi- or poly-cyclic bridging ligand in a *syn* or *anti* stereochemistry, we started an investigation to establish the experimental conditions for a stereocontrolled synthesis of the two metal isomers.

The synthetic route for the synthesis of Rh(I) homobimetallic complexes of the *s*-indacene-diide was the two-step synthesis shown in Scheme 12.

The isolation of the mono-complex 5-hydro-indacenide-Rh(COD) and its subsequent metallation and reaction with [Rh-(μ-Cl)(COD]$_2$ affords different ratios of the *syn*/*anti* isomers (as shown by IR and NMR spectra) depending on the concentration of the 5-hydro-*s*-indacenide potassium salt and on the presence of 18-crown-6 ether in the solution. The *anti* isomer is practically the unique product (99%) in presence of crown ether, i.e. when the reactant rhodium-complexed salt is present as free ion or as a solvent-separated ion pair. This stereocontrol is probably due to steric reasons, and a difference of $\Delta G^{\neq}$ ca. 3 Kcal mol^{-1} can be estimated between the two competitive pathways. On the other hand, at relatively high concentration of the potassium salt (ca. 0.01 M) the *syn*/*anti* ratio raises to ca. three and it is further increased to 15 at higher reactant concentrations (ca. 0.03 M). A likely explanation of these results is offered by the scheme depicted in Scheme 13.

In the hypothesis that the potassium salt is present as a contact ion pair in THF, its probable structure places the K^+ cation on the opposite site of the Rh(COD) group (structures of contact ion pair of $Cr(CO)_3$-indenyl potassium salts have been shown to utilize an *anti* configuration [11,31]). When contact ion pairs prevail in solution, attack of the rhodium dimer from the *anti* side is more difficult than from the *syn* side by steric and electrostatic repulsions (an overall energy value of 3.5–4.0 Kcal mol^{-1} for these interactions which accounts also for the solvation energy of the K^+ cation can be estimated at a 0.03 M salt concentration) and the *syn* product will prevail. On the other hand, a solvent-separated ion pair or a free anion such as in the presence of the 18-crown-ether makes the *anti* attack almost exclusive. Spectroscopic and chemical properties of these bimetallic isomers are now under investigation.

An attempted synthesis of a trimetallic *s*-indacene-diide complex containing two Rh(COD) units and one $Cr(CO)_3$ unit is shown in Scheme 14. Deprotonation of an 1,5-dihydro- and 1,7-dihydro-$Cr(CO)_3$-*s*-indacene isomeric mixture gives the η^6-$Cr(CO)_3$-5-hydro-*s*-indacenyl anion which is stable up to -20°C; at higher temperatures it isomerizes to the corresponding η^5 hapto isomer. Quenching with $[Rh(\mu\text{-}Cl)(COD)]_2$ affords the $Cr(CO)_3$-5-hydro-*s*-indacenyl-Rh(COD) complex which, on the basis of its spectroscopic data, has the two metal fragments bound to the opposite sites of the ligand [32]. Subsequent ionization carried out at -20°C (at lower temperatures the metallation is not efficient) produces instantaneously the η^5-$Cr(CO)_3$-*s*-indacene-diide-Rh(COD) potassium salt as evidenced by IR measurements. Thus, the presence of the Rh(COD) unit accelerates enormously the $\eta^6 \rightarrow \eta^5$ haptotropic shift of $Cr(CO)_3$ with respect to that observed in the η^6-$Cr(CO)_3$-indenyl anion monitored under the same conditions [11]. The successive treatment with $[Rh(\mu\text{-}Cl)(COD)]_2$ gives a mixture of the *syn* and *anti* homobimetallic indacene-diide-$[Rh(COD)]_2$ isomers meaning that substitution of $Cr(CO)_3$ by Rh(COD) has occurred. This behavior differs from that we observed for the η^5-$Cr(CO)_3$-indenyl anion whose quenching with $[Rh(\mu\text{-}Cl)(COD)]_2$ afforded the bimetallic *anti*-$[Cr(CO)_3$-indenyl-Rh(COD)] complex [12]. From these results we conclude that the reverse $\eta^5 \rightarrow \eta^6$ rearrangement is not feasible in the indacene-diide species if the second cyclopentadienyl ring is coordinated with Rh(COD).

In order to achieve the purpose of obtaining trimetallic complexes, the rate of the $\eta^6 \rightarrow \eta^5$ rearrangement in the etherobimetallic *s*-indacene-diide should be decreased. We have shown that modifications to the $\eta^6 \rightleftharpoons \eta^5$ equilibrium ratios follow the order of increased electron density at the metal [33] and that the η^6 species is stabilized as more electron density at chromium is assured by ligands [31]. Therefore, our current synthetic strategies are being revised and pursued in the synthesis of trimetallic complexes of methylated *s*- and *as*-indacene ligands; the complexes of 1,5-dihydro-1,2,3,4,5,6,7,8-octamethyl-soindacene with $Cr(CO)_3$, RhCp* and $Mn(CO)_3$ have been very recently reported [34].

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