

Tuning Indenyl Hapticity in Zirconium Bis(indenyl) Complexes with the Nature of Complementary Ligands

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Summary: DFT/B3LYP calculations with a VDZP basis set were used to understand the structural preferences of the bis(indenyl) complexes $[\text{Zr}(\text{Ind})_2\text{L}]$ (Ind = indenyl = C_9H_7^-) as a function of the type of ligand, L. For σ donors, such as THF (OC_4H_8), the formation of adducts with mixed hapticity of the Ind ligands (η^6/η^5) is observed, while for π -acceptors (for example, ethylene) bis(η^5 -Ind) complexes with the coordination geometry of common bent metallocenes are preferred. When both Ind ligands are coordinated in a η^5 mode, the metal valence electrons are fully available for back-donation to L, reinforcing the Zr–L bond and stabilizing the molecule. However, back-donation is a component of the metal–Ind bond when this ligand is η^6 coordinated through the benzene ring. Thus, competition for the metal electrons destabilizes molecules with the simultaneous presence of η^6 -Ind and π acceptors, especially in a d^2 metal such as Zr(II).

Cyclopentadienyl ($\text{Cp} = \text{C}_5\text{H}_5^-$) and indenyl (Ind = C_9H_7^-) are widely used π ligands in organo-transition-metal chemistry¹ that have been historically connected to the development of this field ever since the first preparation of the corresponding sandwich complexes.^{2,3} Although Cp and Ind can be equivalent, in many aspects, especially when they are η^5 coordinated to a metal center,⁴ the long known coordination versatility of indenyl⁵ is the cause of striking reactivity differences between analogous complexes of the two ligands. The well-documented “indenyl effect” is a good example of those differences.⁶

Recently, another remarkable breakthrough in indenyl chemistry was accomplished by Paul Chirik’s group with the isolation⁷ and full structural characterization⁸ of $[\text{Zr}\{\eta^9-(1,3-\text{R}_2\text{Ind})\}\{\eta^5-(1,3-\text{R}_2\text{Ind})\}]$ complexes, revealing a hitherto unknown coordination mode of indenyl (η^9) where all the carbon atoms are engaged in the bonding to zirconium. This structural feature is only matched by the reactivity of those species. The coordination mode of the 1,3- R_2Ind ligands in the product of the reaction of $[\text{Zr}\{\eta^9-(1,3-\text{R}_2\text{Ind})\}\{\eta^5-(1,3-\text{R}_2\text{Ind})\}]$ with a given ligand, L, depends on the nature of this ligand. When L is a σ donor, such as an ether, a chelating ether, or a phosphine,

η^6/η^5 adducts are obtained with one indenyl coordinated by the six-membered ring, in a η^6 fashion:^{7,9} for example, $[\text{Zr}\{\eta^6-(1,3-\text{R}_2\text{Ind})\}\{\eta^5-(1,3-\text{R}_2\text{Ind})\}(\text{THF})]$ (THF = OC_4H_8) for L = THF. On the other hand, when L is a π acceptor such as CO or an unsaturated organic molecule, the products observed have both Ind ligands in the common η^5 coordination mode: $[\text{Zr}\{\eta^5-(1,3-\text{R}_2\text{Ind})\}_2\text{L}]$.^{7,8}

Although $[\text{Zr}\{\eta^9-(1,3-\text{R}_2\text{Ind})\}\{\eta^5-(1,3-\text{R}_2\text{Ind})\}]$ complexes and the η^6/η^5 adducts have been the subject of some experimental^{7–9} and theoretical^{10,11} studies, the reasons underlying the reactivity differences mentioned above were never explicitly addressed. In this work, results of DFT calculations¹² on $[\text{Zr}(\text{Ind})_2\text{L}]$ complexes with both Ind coordination modes, that is, η^6/η^5 and bis- η^5 molecules, are used to establish stability differences as a function of the nature of the ligand L (L = THF, ethylene), allowing the rationalization of the outcome of the reaction between $[\text{Zr}\{\eta^9-(1,3-\text{R}_2\text{Ind})\}\{\eta^5-(1,3-\text{R}_2\text{Ind})\}]$ and L. The calculations were performed on models with unsubstituted indenyl ligands.

The geometries calculated for the $[\text{Zr}(\text{Ind})_2\text{L}]$ complexes are represented in Figure 1. Both Ind coordination modes are considered for each ligand L (THF and ethylene), resulting in a total of four molecules: $[\text{Zr}(\eta^n\text{-Ind})(\eta^5\text{-Ind})\text{L}]$ ($n = 5, 6$ and L = THF, C_2H_4). The THF complexes have been presented before¹⁰ but are repeated here for comparison purposes.

The bis- η^5 complexes (right side of Figure 1) are typical indenyl analogues of bent metallocene complexes⁴ with the two Ind ligands coordinated in a η^5 mode through the C_5 ring and a third coordination position occupied by L, which is THF or ethylene. The geometry optimized for the ethylene complex, $[\text{Zr}(\eta^5\text{-Ind})_2(\text{C}_2\text{H}_4)]$, compares well with the corresponding X-ray structure¹³ with maximum and mean absolute deviations between experimental and calculated Zr–C distances of 0.06 and 0.03 Å, respectively.

The two η^6/η^5 molecules (left side of Figure 1) also have equivalent structures in their general features: two π -coordinated Ind ligands and a third ligand, L. However, in this case one Ind is coordinated by the benzene ring in a η^6 mode, while the other has the common η^5 hapticity, using the C_5 ring to bind the metal. The experimental geometry of the THF adduct, $[\text{Zr}\{\eta^6-(1,3-\text{R}_2\text{Ind})\}\{\eta^5-(1,3-\text{R}_2\text{Ind})\}(\text{THF})]$,⁷ is also well reproduced by the calculations with maximum and mean absolute deviations for the distances around the metal of 0.10 and 0.04 Å, respectively.

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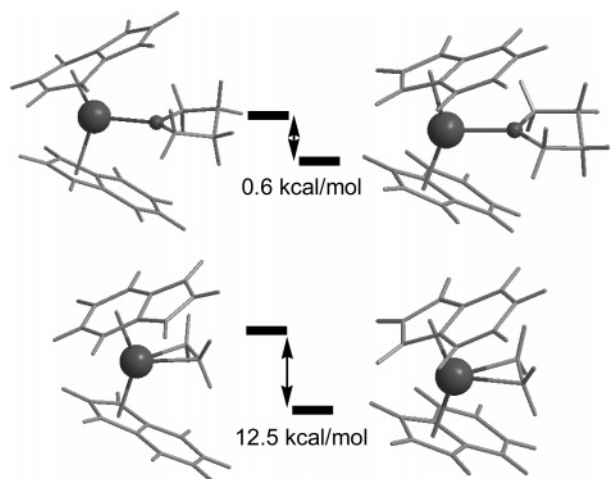


Figure 1. Optimized geometries (B3LYP) for the η^6/η^5 (left) and the bis- η^5 (right) $[\text{Zr}(\text{Ind})_2\text{L}]$ complexes with $\text{L} = \text{THF}$ (top) and ethylene (bottom). The energy differences between isomers with the same L ligand are presented. The Zr and O atoms are highlighted.

It should be noticed that for the ethylene η^6/η^5 molecule there is a significant deviation of this ligand from the metallocene edge, in comparison to the THF complex (see below).

The most important feature of the complexes represented in Figure 1 is the energy difference between isomer pairs. While in the case of THF both species are practically isoenergetic, in the case of ethylene the bis- η^5 molecule is significantly more stable ($12.5 \text{ kcal mol}^{-1}$) than the η^6/η^5 complex. It should be noted that the stability difference between haptomers may depend on the presence of Ind substituents. In fact, the experimental studies^{7–9} were made with 1,3-substituted indenyls and the calculations were performed on models with plain indenyl. It has been shown¹¹ that the presence of indenyl substituents disfavors bis- η^5 species due to stereochemical repulsion between those substituents. However, this corresponds to a fine-tuning of the energy differences and will not affect the semiquantitative discussion intended here. For example, calculations performed on THF complexes with 1,3- Me_2Ind indicate that in this case the bis- η^5 complex, $[\text{Zr}\{\eta^5-(1,3-\text{Me}_2\text{Ind})\}_2(\text{THF})]$, becomes $0.8 \text{ kcal mol}^{-1}$ less stable than its η^6/η^5 haptomer, representing only a variation of $1.4 \text{ kcal mol}^{-1}$ with respect to the stability difference obtained for the models with unsubstituted Ind, shown in Figure 1.

The calculated stability differences support and explain the results experimentally obtained for the reactivity of $[\text{Zr}(\eta^9\text{-Ind})(\eta^5\text{-Ind})]$ with ligands L . Thus, for a π acceptor such as ethylene the great stability of $[\text{Zr}(\eta^5\text{-Ind})_2(\text{C}_2\text{H}_4)]$ over its isomer, $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{C}_2\text{H}_4)]$, justifies the formation of the first as the reaction product. In the case of the σ -donor ($\text{L} = \text{THF}$) there is no such marked thermodynamic stability difference between isomers. Here, the kinetics prevails and the product observed is the one corresponding to the lower activation energy path: $E_a = 8.3 \text{ kcal mol}^{-1}$ for $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{THF})]$ and $E_a = 12.3 \text{ kcal mol}^{-1}$ for $[\text{Zr}(\eta^5\text{-Ind})_2(\text{THF})]$.¹⁰

The energy differences between isomers, as a function of the ligand L , can be understood with a simple orbital analysis of the bonding in each species. The frontier orbitals of the $[\text{Zr}(\text{Ind})_2]$ fragment¹⁴ in both geometries, bis- η^5 and η^6/η^5 , are represented in Figure 2.

The frontier orbitals for the $[\text{Zr}(\text{Ind})_2]$ fragment in both geometries, bis- η^5 and η^6/η^5 , are qualitatively equivalent to the ones belonging to a bent $[\text{MCP}_2]$ moiety (right side of Figure

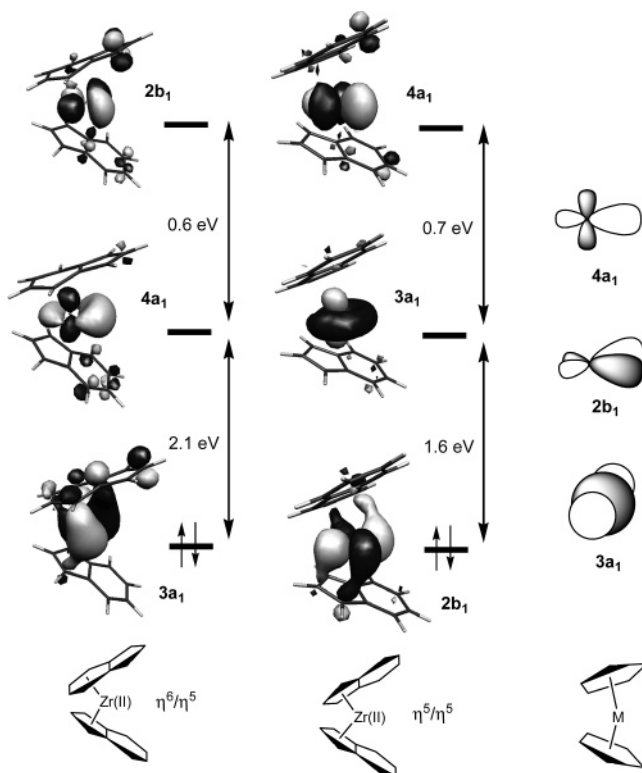


Figure 2. Frontier orbitals and energy splitting calculated for the metallic fragments $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})]$ (left) and $[\text{Zr}(\eta^5\text{-Ind})_2]$ (center) and a schematic representation of the frontier orbitals of the metallic fragment of a bent metallocene, $[\text{MCP}_2]$, with C_{2v} symmetry (right). The electron count corresponds to $\text{Zr}(\text{II})$.

2). These are well-known¹⁵ and correspond to three metal-centered orbitals: $3a_1$, $2b_1$, and $4a_1$.¹⁶ The orbital of choice, in the metallic fragment, to establish a σ bond with L is $4a_1$, and the orbital with the right symmetry to form a π interaction is $2b_1$.¹⁷ This is equally valid for the common bent $[\text{MCP}_2]$ fragment, as for $[\text{Zr}(\text{Ind})_2]$ in the two geometries bis- η^5 and η^6/η^5 . However, there is one major difference between the frontier orbitals of $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})]$ and $[\text{Zr}(\eta^5\text{-Ind})_2]$. While in the case of the bis- η^5 geometry the three fragment orbitals are essentially nonbonding, in the case of the η^6/η^5 $[\text{Zr}(\text{Ind})_2]$ fragment, $3a_1$ is involved in $\text{Zr}-(\eta^6\text{-Ind})$ back-donation with δ symmetry, becoming stabilized with respect to $4a_1$ and $2b_1$ (Figure 2). Thus, in the case of a η^6/η^5 complex with a σ -donor, such as $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{THF})]$, $3a_1$ becomes the HOMO (highest occupied molecular orbital) of the molecule, $4a_1$ being involved in the $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})]-\text{THF}$ σ interaction. This way the coordination of THF only requires the use of $4a_1$, and $3a_1$ is solely involved in back-donation to the Ind coordinated by the benzene ring. The frontier orbitals of the THF adducts in the two geometries bis- η^5 and η^6/η^5 , were published before¹⁰ and are presented as Supporting Information (Figure S2). The HOMO of $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{THF})]$ is repeated in Figure 3, for comparison purposes.

The coordination of a π acceptor, such as ethylene, uses two of the three frontier orbitals of the metallic fragment $[\text{Zr}(\text{Ind})_2]$:

(14) The orbitals in Figure 2 correspond to $[\text{Zr}(\text{Ind})_2]$ fragments with the geometry existing in the THF adducts $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{THF})]$ and $[\text{Zr}(\eta^5\text{-Ind})_2(\text{THF})]$.

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(16) These symmetry labels correspond to a $[\text{MCP}_2]$ with C_{2v} symmetry. Although this is not the symmetry of the $[\text{Zr}(\text{Ind})_2]$ fragments studied here, the same labels will be used throughout the text, for comparison purposes.

(17) A schematic orbital diagram for the $[\text{MCP}_2]-\text{L}$ interaction with σ donors and π acceptors is presented as Supporting Information (Figure S1).

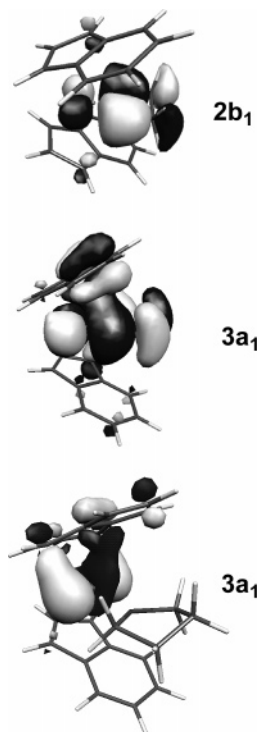


Figure 3. HOMOs of $[\text{Zr}(\eta^5\text{-Ind})_2(\text{C}_2\text{H}_4)]$ (top), $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{C}_2\text{H}_4)]$ (center), and $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{THF})]$ (bottom). The labels identify the metallic fragments involved in each molecular orbital.

$4a_1$ to establish the σ interaction and $2b_1$ for the π component. For a d^2 metal such as Zr(II), the HOMO of the molecule will be the orbital corresponding to metal–L back-donation, derived from $2b_1$ (see Figure S1). The HOMOs of the η^6/η^5 THF adduct and of the two ethylene haptomers are presented in Figure 3.

As expected, the two electrons of Zr(II) are involved in π back-donation to ethylene, in the case of the bis- η^5 complex, by means of orbital $2b_1$, as shown by the corresponding HOMO (top of Figure 3). A similar situation occurs in the η^6/η^5 THF adduct, only in this case there is δ back-donation to the η^6 -coordinated Ind and the metal orbital used is $3a_1$, resulting in the HOMO of $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{THF})]$ (bottom of Figure 3). However, for the ethylene η^6/η^5 complex both ligands compete for the metal electrons: ethylene and η^6 -Ind. The HOMO of this molecule (center of Figure 3) shows simultaneous back-donation for both ligands, meaning that the two electrons in the metal have to be shared by the two ligands. This weakens the two bonds Zr–ethylene and Zr–(η^6 -Ind), destabilizing the molecule and explaining the observed stability difference. This conclusion holds for any π -acceptor as coligand, such as L = CO, for example, since the relevant orbital interactions are qualitatively the same. The bis- η^5 complex with CO, $[\text{Zr}\{\eta^5\text{-(1,3-R}_2\text{Ind)}\}_2(\text{CO})_2]$, was experimentally observed as the reaction product of carbon monoxide with $[\text{Zr}\{\eta^9\text{-(1,3-R}_2\text{Ind)}\}\{\eta^5\text{-(1,3-R}_2\text{Ind)}\}]$.⁷

The Zr–(η^6 -Ind) bond is considerably stronger in the THF adduct than in the ethylene molecule, as shown by a mean Z–C(η^6 -Ind) distance 0.17 Å longer in the latter. The Wiberg indices (WI)¹⁸ also indicate a weaker Zr–(η^6 -Ind) bond in the ethylene η^6/η^5 complex (WI = 0.13–0.22) in comparison with the corresponding THF molecule (WI = 0.21–0.49). The Zr–

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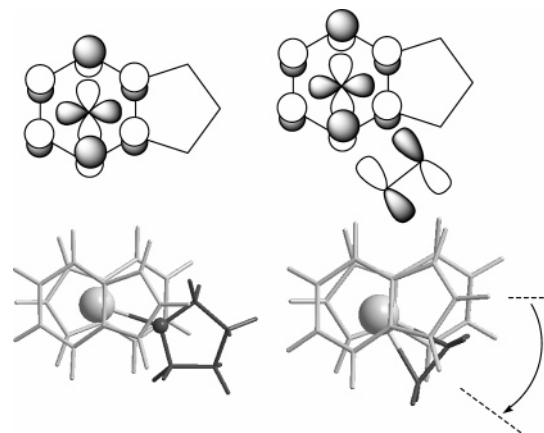


Figure 4. (bottom) Top view of the optimized geometries of the $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})\text{L}]$ complexes for L = THF (left) and C_2H_4 (right) showing the deviation of L (darkened) from the metalocene edge. (top) Schematic representations of the corresponding HOMO.

Table 1. Calculated Charge Distribution (NPA) for the $[\text{Zr}(\eta^5\text{-Ind})_2\text{L}]$ Complexes

complex	Zr	L	η^6 -Ind	η^5 -Ind
$[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{THF})]$	1.33	0.14	−0.95	−0.52
$[\text{Zr}(\eta^5\text{-Ind})_2(\text{THF})]$	1.25	0.11	−0.68	−0.68
$[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{C}_2\text{H}_4)]$	1.49	−0.49	−0.54	−0.46
$[\text{Zr}(\eta^5\text{-Ind})_2(\text{C}_2\text{H}_4)]$	1.61	−0.63	−0.49	−0.49

ethylene bonds in the two isomers also reflect the degree of back-donation, with Zr–C(ethylene) bonds in the bis- η^5 complex ($d_{\text{Zr-C}} = 2.29$ Å, WI = 0.64) shorter and stronger than in the η^6/η^5 isomer ($d_{\text{Zr-C}} = 2.30$ and 2.37 Å, WI = 0.57 and 0.58). The same happens with the C=C bond: the bond in the η^6/η^5 molecule, where there is less back-donation ($d_{\text{Zr-C}} = 1.43$ Å, WI = 1.27), is stronger than in the bis- η^5 species ($d_{\text{Zr-C}} = 1.46$ Å, WI = 1.19).

The charge distribution on the complexes, obtained by means of a natural population analysis (NPA),¹⁹ complements the previous discussion and helps explain the conclusions (Table 1).

The charges in Table 1 confirm the nature of the L ligands. Ethylene is indeed acting as a π acceptor in the molecules, becoming negatively charged in the complexes, and THF, being a σ donor, ends up positive in the complexes. Accordingly, Zr is more positive in ethylene molecules than in THF species, given the presence of a π acceptor in the former. In the η^6/η^5 species η^6 -Ind is always more negative than η^5 -Ind, reflecting the electron density received from the metal. Perhaps more important are the data for $[\text{Zr}(\eta^6\text{-Ind})(\eta^5\text{-Ind})(\text{C}_2\text{H}_4)]$: in this molecule, despite the presence of two ligands competing for the metal electrons, ethylene and η^6 -Ind, the metal is less positive than in $[\text{Zr}(\eta^5\text{-Ind})_2(\text{C}_2\text{H}_4)]$, showing that the efficiency of the metal to ligand back-donation is diminished when such competition occurs and, once again, corroborating the stability differences calculated.

Another interesting aspect is the geometry of the L ligand in the η^6/η^5 complexes, when the THF and the ethylene complexes are compared (Figure 4).

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The deviation of the ligand L from the midpoint of the metallocene edge is considerably larger for ethylene than for THF. In fact, the corresponding angle is 32° wider for ethylene.²⁰ The reason for this distortion is evident from the schematic drawings of the HOMO of each molecule (top of Figure 4). Those orbitals represent metal to ligand back-donation. In the case of the THF adduct there is only back-donation from Zr to the Ind coordinated in a η^6 mode. Thus, the orientation of THF is independent of the HOMO topology. Back-donation occurs between the filled metal d orbital and an empty orbital of Ind, located in the benzene ring, with the right symmetry match for the interaction. However, in the case of the ethylene species there is also Zr–ethylene back-donation. As a consequence, this ligand has to adjust its orientation in order to share the same metal orbital and allow both interactions to occur: Z–ethylene and Zr–(η^6 -Ind) back-donation.

Conclusion

Indenyl hapticity in $[\text{Zr}(\text{Ind})_2\text{L}]$ complexes depends on the characteristics of the ligand L. For σ -donors, η^6/η^5 complexes are favored and the two electrons of Zr(II) are used to stabilize the η^6 -Ind coordination through Zr–Ind back-donation. In the case of π acceptors competition between L and Ind for the metal electrons destabilizes the η^6 coordination of this ligand, and bis- η^5 molecules become the most stable species, the metal d electrons being entirely used for Zr–L back-donation.

Computational Details

All calculations were performed using the Gaussian 98 software package²¹ and the B3LYP hybrid functional, without symmetry constraints. That functional includes a mixture of Hartree–Fock²² exchange with DFT¹² exchange correlation,

(20) This angle can be defined as X–Zr–Y, where X represents the midpoint of the metallocene edge and Y is O for THF and the midpoint of the C=C bond for ethylene.

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given by Becke's three-parameter functional²³ with the Lee, Yang, and Parr correlation functional, which includes both local and nonlocal terms.^{24,25} The LanL2DZ basis set²⁶ augmented with an f-polarization function²⁷ was used for Zr, and a standard 6-31G(d,p)²⁸ basis set was used for the remaining elements. Frequency calculations were performed to confirm the nature of the optimized structures as minima. A natural population analysis (NPA)¹⁹ and the resulting Wiberg indices¹⁸ were used for a detailed study of the electronic structure and bonding of the optimized species. Orbital representations were obtained using the program MOLEKEL 4.0.²⁹

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Supporting Information Available: Figures giving a schematic orbital diagram for the interaction between $[\text{MCp}_2]$ and a σ donor or a π acceptor (Figure S1) and frontier orbitals of the $[\text{Zr}(\text{Ind})_2\text{L}]$ complexes (Figures S2 and S3) and tables giving atomic coordinates for all the optimized species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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