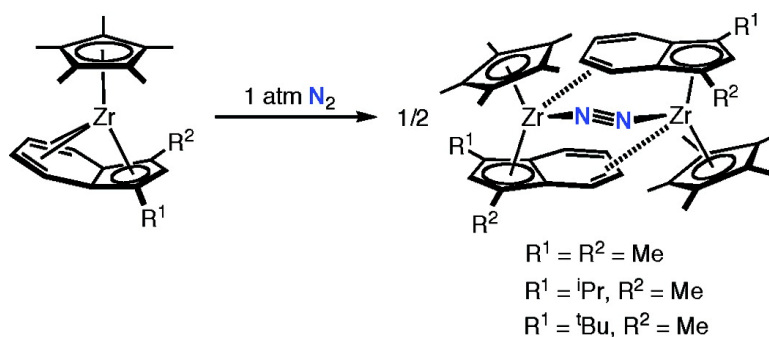


Indenyl Zirconium Dinitrogen Chemistry: N Coordination to an Isolated Zirconium Sandwich and Synthesis of Side-on, End-on Dinitrogen Compounds

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Indenyl Zirconium Dinitrogen Chemistry: N₂ Coordination to an Isolated Zirconium Sandwich and Synthesis of Side-on, End-on Dinitrogen Compounds

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Abstract: Exposure of the isolable zirconocene sandwich compounds, (η^5 -C₅Me₅)(η^5 -C₉H₅-1-R¹-3-R²)Zr (R¹ = Me, ⁱPr, ^tBu; R² = Me) to one atmosphere of dinitrogen resulted in N₂ coordination. X-ray diffraction and NMR spectroscopy establish that the resulting dimeric dinitrogen compounds contain an unusual μ_2, η^2 -bridging indenyl ring and a weakly activated N₂ ligand. N₂ coordination from the isolable zirconium sandwich compounds is extremely sensitive to the number and size of the indenyl substituents. Compounds bearing two [ⁱPr] or three methyl substituents are stable as η^9 sandwich compounds for weeks under dinitrogen likely due to the inability to dimerize through a two-atom N₂ bridge. Performing the reduction of (η^5 -C₅Me₅)(η^5 -C₉H₅-1-R¹-3-R²)ZrCl₂ (R¹ = ⁱPr, ^tBu; R² = Me; R¹ = R² = SiMe₃) under an N₂ atmosphere produced a different outcome; rare examples of side-on, end-on zirconium dinitrogen compounds were isolated and in one case, crystallographically characterized. Protonolysis studies with weak Brønsted acids were used to evaluate the relative activation of the bridging dinitrogen ligands.

Introduction

Dinitrogen complexes of the group 4 transition metals, while now known for over three decades, have received renewed interest due, in part, to the number of transformations available for elaboration of the N–N bond.^{1–4} The majority of isolable compounds are dimeric and contain a bridging dinitrogen ligand in one of two limiting hapticities (Figure 1). Seminal examples relied on sterically crowded cyclopentadienyl ligands (e.g., Cp* = η^5 -C₅Me₅) for stabilization and contained weakly activated μ_2, η^1, η^1 (“end-on”) dinitrogen ligands.^{5–7} Since that time, the other limiting hapticity, μ_2, η^2, η^2 (“side-on”) has emerged as the dominant coordination mode¹ and remains a prominent synthetic target due to the prevalence of 4-electron-reduced bridging N₂ ligands with elongated N–N bonds.⁸ A third possibility, μ_2, η^2, η^1 (“side-on, end-on”), is a combination of these two extremes. To date, the only example of this hapticity in group 4 transition

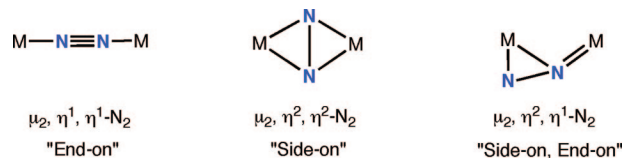


Figure 1. N₂ hapticity in dimeric group 4 transition metal dinitrogen compounds.

metal dinitrogen chemistry is an unusual titanocene cluster.⁹ Expanding the number of compounds with this hapticity into zirconium and hafnium N₂ chemistry and understanding the principles underlying its formation may ultimately lead to new reactions for elaboration of the N–N bond.

One notable example of side-on, end-on dinitrogen coordination is Fryzuk’s ditantalum dihydride compound bearing a tridentate phosphine diamido supporting ligand.^{10,11} In addition to the unusual N₂ hapticity, this compound is remarkable both for how it is synthesized and for its rich dinitrogen functionalization chemistry.^{12–17} Most early transition metal dinitrogen

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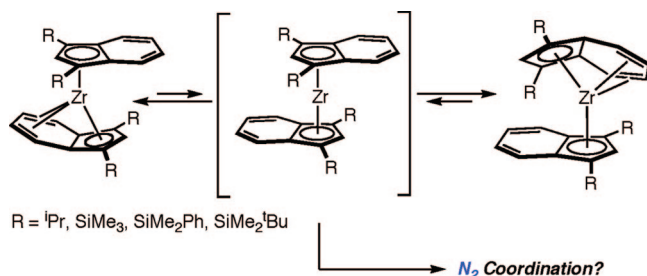


Figure 2. η^9, η^5 -Bis(indenyl)zirconium sandwich complexes.

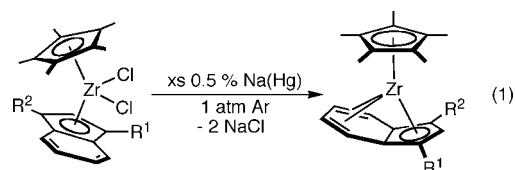
compounds with strongly activated N_2 ligands are prepared by alkali metal reduction of a dihalide precursor.¹⁸ In contrast, the ditantalum dihydride compound with the side-on, end-on dinitrogen ligand is obtained by H_2 reductive elimination from the corresponding ditantalum tetrahydride.¹⁰ Alkali metal-free preparative routes for activated dinitrogen compounds may ultimately prove important in the development of catalytically compatible N_2 functionalization schemes.

Our laboratory has been actively exploring the hydrogenation and related chemistry of zirconium dinitrogen complexes with side-on bound, 4-electron reduced N_2 ligands.² One aspect of this program has been focused on developing new methods for the synthesis of group 4 metallocene dinitrogen compounds that do not rely on alkali metal reduction for the N_2 coordination step. One approach, similar to the Fryzuk tantalum chemistry, is the reductive elimination of H_2 from a metallocene mono-^{19,20} or dihydride, and examples are known in both titanocene²⁰ and zirconocene chemistry.^{21,22} An alternative strategy is direct N_2 coordination to an isolated, divalent metallocene sandwich.^{23,24} While such compounds are now well-precedented for titanium,^{24–26} η^5, η^5 -bis(cyclopentadienyl)zirconium and hafnium examples have not been prepared. Masked forms of zirconocene have been synthesized by replacing the cyclopentadienyl rings with 1,3-disubstituted indenyl ligands²⁷ where coordination of the benzo ring to the metal center has resulted in isolation of unusual η^9, η^5 -bis(indenyl) metal sandwich compounds (Figure 2).²⁸

NMR spectroscopic studies²⁸ augmented by computational results²⁹ support rapid interconversion of the η^9 and η^5 -bound rings in solution and the intermediacy of an η^5, η^5 -zirconocene complex (Figure 2). The observed dynamic behavior raised the question as to whether the putative η^5, η^5 -intermediate could be trapped with N_2 to form rare examples of indenyl zirconium dinitrogen compounds. Previous studies from our group³⁰ and from Veiros³¹ have demonstrated the influence of the 1,3-indenyl substituents on the stability of the η^9 interaction. While 1,3-disilylsubstituted zirconocenes undergo rapid haptotropic rearrangement upon addition of THF and 1,2-dimethoxyethane, the corresponding alkylated compounds are unreactive.³⁰ In this contribution, we explore the effect of introducing smaller 1,3-dialkyl substituents with the goal of trapping an indenyl dinitrogen complex with η^5, η^5 ring coordination through dimerization. These studies have resulted in the first example of dinitrogen coordination by an isolated zirconium sandwich as well as yielded rare examples of side-on, end-on N_2 compounds of zirconium. Both of these classes of compounds exploit the haptotropic flexibility of the indenyl ring for stabilization.

Results and Discussion

Dinitrogen Activation by Mixed-Ring Zirconium Sandwich Complexes. To systematically explore the stability of the η^9 interaction relative to dinitrogen coordination in bis(indenyl) zirconium sandwich compounds, sodium amalgam reduction of a family of mixed ring, pentamethylcyclopentadienyl-indenyl zirconocene dihalide complexes was explored (eq 1).



Initial studies focused on compounds with 1,3-disubstituted indenyl rings as these are known to form isolable η^9 sandwich compounds.²⁸ While [iPr] and [SiMe₃] substituted compounds were prepared for comparison, particular attention was devoted to smaller alkyl substituents with the goal of trapping dinitrogen compounds through dimerization. Each zirconium sandwich compound prepared in this study is presented in Figure 3 along with its shorthand designation.

Our studies commenced with the previously reported isopropyl-substituted compound, **1**.³² Both the reduction of the dihalide and the isolated sandwich are not sensitive to dinitrogen, suggesting that this indenyl substitution pattern is sufficiently large to inhibit dimerization. During the course of our investigations, we obtained X-ray quality crystals of **1** and a depiction of the solid state structure is presented in Figure 4. Selected metrical parameters and a comparison to the previously reported bis(indenyl) zirconium sandwich compound are reported in Table 1. The X-ray structure of **1** confirms the zirconocene sandwich structure and the η^9 hapticity of the indenyl ligand, which was previously assigned by NMR spectroscopy.³² As is typical for this coordination environment, the indenyl ring is bent with a fold angle of 37.0°, similar to the value found in

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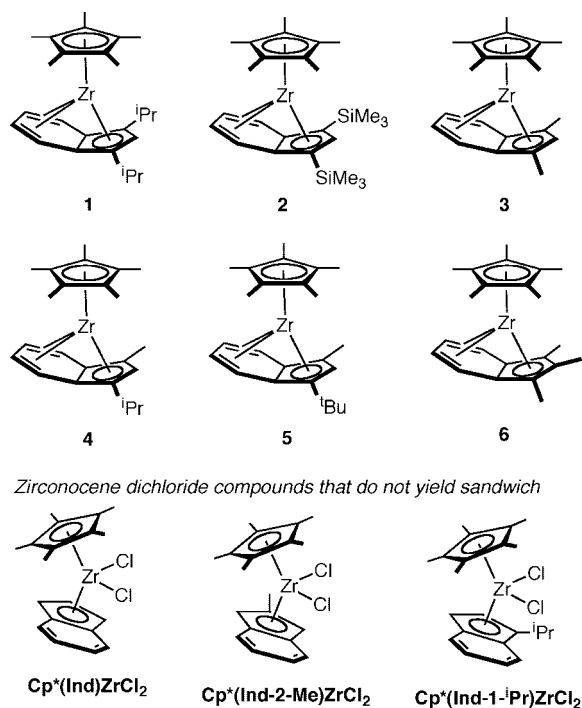


Figure 3. Zirconocene compounds prepared in this study.

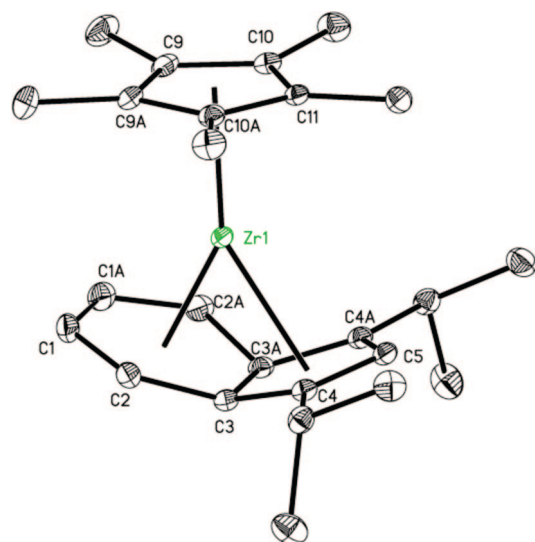


Figure 4. Molecular structure of **1** at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

the corresponding bis(indenyl)sandwich.²⁸ Accordingly, the carbon–carbon bond distances in the coordinated benzo ring are elongated to 1.390(3) and 1.423(2) Å, consistent with reduction by the formally low-valent zirconium center. Thus, replacing the indenyl ligand with a permethylcyclopentadienyl ring has little impact on the metrical parameters of the η^9 indenyl (Table 1).

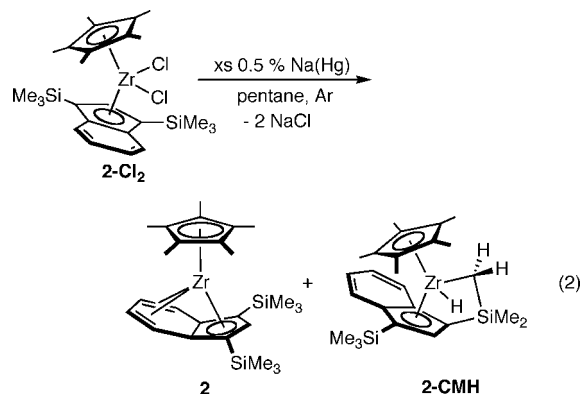
The [SiMe₃]-substituted zirconium sandwich, **2**, was also prepared by reduction of the corresponding dihalide, **2-Cl₂**, under an argon atmosphere (Figure 3). This compound has proven challenging to obtain in pure form due to competing formation of the zirconocene cyclometalated hydride, **2-CMH** (eq 5). At shorter reaction times small amounts (~10%) of **2-CMH** were observed by ¹H NMR spectroscopy; allowing

Table 1. Selected Bond Distances and Angles for **1** and (η^9 -C₉H₅-1,3-(CHMe₂)₂)(η^5 -C₉H₅-1,3-(CHMe₂)₂)Zr²⁸

	1	(η^9 -C ₉ H ₅ -1,3-(CHMe ₂) ₂)(η^5 -C ₉ H ₅ -1,3-(CHMe ₂) ₂)Zr
C(1)–C(2) Å	1.423(2)	1.418(3)
C(1)–C(1a) Å	1.390(3)	1.395(3)
C(1a)–C(2a) Å	1.423(2)	1.426(2)
η^9 fold angle (deg) ^a	37.0	37.6
buckle (deg) ^b	8.2	6.3

^a Defined as the angle between the planes formed by the five-membered cyclopentadienyl and the six-membered benzo rings of the indenyl. ^b Defined as the deviation from planarity of the benzo ring, which is the angle between the planes formed by C(2)–C(1)–C(1a)–C(2a) and C(2)–C(3)–C(3a)–C(2a). Indenyl labeling scheme based on the structure in Figure 4.

benzene-*d*₆ solutions of **2** to stand at 23 °C increased the amount of cyclometalation. Only one diastereomer of **2-CMH** has been detected by ¹H and ¹³C NMR spectroscopy and has been assigned by NOESY NMR experiments as the isomer depicted in equation 2. This diastereomer is likely preferred because of the sterically demanding [SiMe₃] substituent in the more open lateral position of the metallocene wedge unlike the alternative where this group would be in the narrow, “back” portion of the molecule.



Each of the new zirconium sandwich compounds, **2–6** (Figure 3), was characterized by ¹H and ¹³C NMR spectroscopy. Upfield-shifted benzo resonances were observed in the benzene-*d*₆ ¹H and ¹³C NMR spectra, diagnostic of η^9 coordination.²⁸ The dimethyl-substituted compound, **3**, has proven challenging to synthesize, and the standard sodium amalgam reduction method used to prepare related compounds²⁸ has been irreproducible as oftentimes no clean product was obtained. Nevertheless, the compound was obtained and observed by ¹H NMR spectroscopy. Attempts to prepare sandwich compounds bearing less substituted indenyl ligands were unsuccessful (Figure 3). Sodium amalgam reduction of Cp*(Ind)ZrCl₂, Cp*(Ind-2-Me)ZrCl₂, and Cp*(Ind-1-Pr)ZrCl₂, produced unidentified products. However, magnesium or sodium amalgam reduction under a CO atmosphere yielded the corresponding zirconocene dicarbonyl compounds, suggesting that the presence of strong field ligands facilitates reduction and stabilizes the formally low-

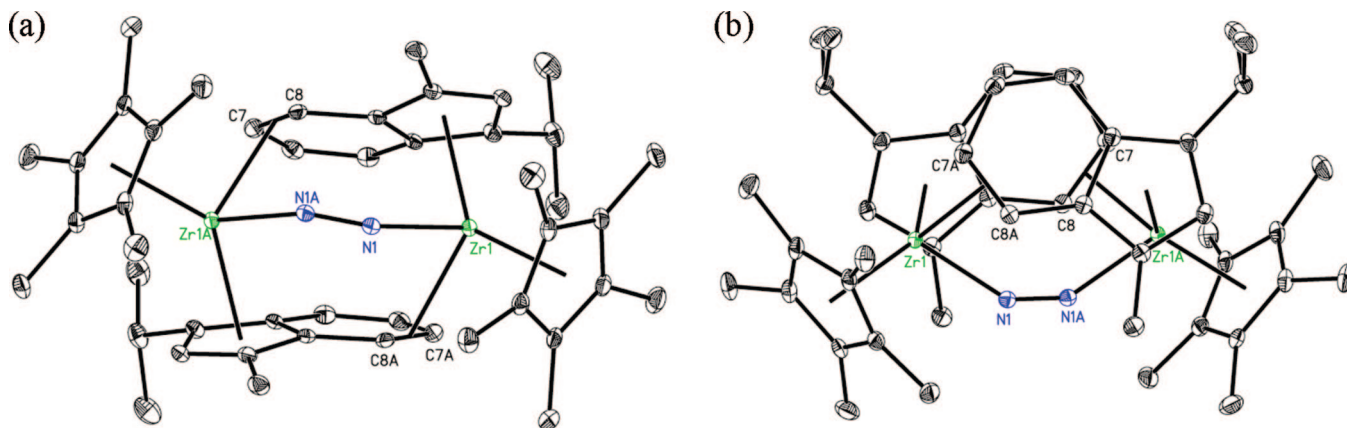
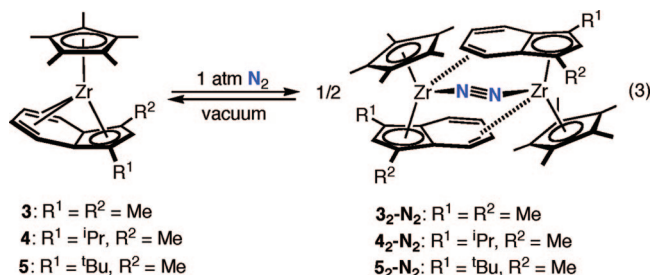


Figure 5. Molecular structure of 4_2-N_2 (a) side view and (b) top view at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

valent species.³³ Complete experimental details and spectroscopic characterization of all of the zirconocene dicarbonyl compounds prepared in this work are reported in the Supporting Information.

Mixed-ring sandwich compounds **1**, **2**, and **4** were treated with large excesses of THF to explore the possibility of ligand-induced haptotropic rearrangement.³⁰ No evidence for THF coordination or indenyl migration was obtained by ^1H NMR spectroscopy. This lack of reactivity is likely due to the presence of the electron-donating pentamethylcyclopentadienyl rings. Both experimental³⁰ and computational³¹ studies have established that electron-releasing indenyl (or in this case cyclopentadienyl rings) disfavor ligand induced haptotropic rearrangement.

Allowing benzene- d_6 or pentane solutions of **3**, **4**, or **5** to stand under 1 atm of N_2 at 23 or -35 °C, resulted in color changes from burgundy to deep purple, signaling formation of new zirconocene dinitrogen compounds (eq 3). For **4**, N_2 coordination at 23 °C occurred over the course of 7 days; conversion of **3** and **5** took place over one month. Exposure of the dinitrogen compounds to vacuum and heating to 45 °C resulted in N_2 dissociation and reformation of the sandwich. However, repeated cycles of heating the samples induced decomposition to unidentified zirconium compounds. Introduction of a third indenyl methyl substituent inhibited N_2 coordination, as no change was observed upon letting solutions of **6** stand for 7 months under a dinitrogen atmosphere. For both 4_2-N_2 and 5_2-N_2 , only one isomer was observed by NMR spectroscopy. Because the resulting N_2 compounds are similar in each case, only the chemistry and spectroscopic characterization of 4_2-N_2 will be described in detail. Complete characterization data for the other compounds are reported in experimental details contained in the Supporting Information.



Monitoring the conversion of **4** to 4_2-N_2 in benzene- d_6 by ^1H NMR spectroscopy revealed smooth disappearance of the

η^9 benzo resonances at 5.13, 5.02, 3.84, and 3.68 ppm to new upfield peaks at 6.41, 6.33, 3.30, and 2.63 ppm, signaling a change in indenyl hapticity. The chemical shift range of the new peaks indicates that coordination to the zirconium is maintained. This spectral change occurred over the course of seven days and was only observed under N_2 ; no change was observed under vacuum. The ^{15}N NMR spectrum of $4_2\text{-}^{15}\text{N}_2$, prepared by addition of $^{15}\text{N}_2$ gas to a benzene- d_6 solution of 4_2-N_2 , exhibits a single resonance centered at 598.7 ppm, indicating formation of a single isomer with equivalent nitrogen atoms. A medium intensity pentane solution IR band was observed at 1563 cm^{-1} . These data are consistent with a weakly activated, $\mu_2, \eta^1, \eta^1\text{-N}_2$ ligand.³⁴

Allowing pentane solutions of **4** to stand at -35 °C under a dinitrogen atmosphere deposited crystals of 4_2-N_2 . The solid-state structure of 4_2-N_2 was determined by X-ray diffraction and confirms the formation of an end-on dinitrogen complex with μ_2, η^2 -bridging indenyl ligands (Figure 5).³⁵ Consistent with benzene- d_6 solution NOESY NMR data, the observed isomer is the one in which the indenyl rings are *trans* across the dimer with the isopropyl groups in a *syn* arrangement. The bridging, end-on dinitrogen ligand is weakly activated with an $\text{N}\equiv\text{N}$ bond distance of $1.197(3)\text{ \AA}$, in agreement with the frequency of the band observed by IR spectroscopy. The bond distances ($d(\text{C}(7)\text{--C}(8), \text{C}(7\text{a})\text{--C}(8\text{a})) = 1.429(3)\text{ \AA}$) for the μ_2, η^2 -indenyl fragment are consistent with 2-electron reduction and significant dialkyl character in the zirconium carbon bonds. This interaction is also the origin of the upfield chemical shifts observed in the ^1H NMR spectrum and is also likely responsible for the weak activation of the bridging N_2 ligand. Thus, these complexes are conceptually similar to Bercaw's $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{-Zr}(\text{N}_2)]_2(\mu_2, \eta^1, \eta^1\text{-N}_2)$,³⁴ where the presence of additional π -acids results in weak activation of the bridging dinitrogen ligand. Accordingly, each metal in the indenyl zirconium dinitrogen complexes is best described as a coordinatively saturated, 18-electron $\text{Zr}(\text{IV})$ center with a 2-electron-reduced η^2 alkene and an $[\text{N}_2]^0$ ligand completing the coordination sphere. An alterna-

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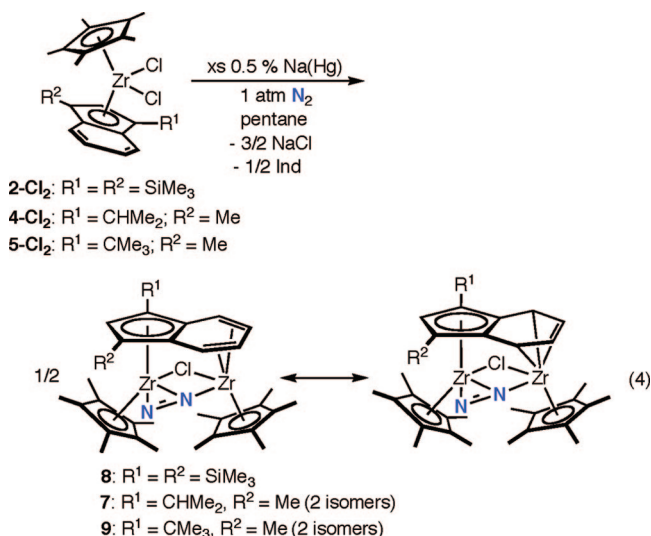
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tive description would be an $[\text{N}_2]^{4-}$ hydrazido complex with neutral η^2 -alkene ligands, although this view is inconsistent with the metrical parameters.

Notably the transformations of the isolable zirconium sandwich compounds, **3–5**, to the corresponding dinitrogen complexes are rare examples of N_2 coordination from isolated zirconium sandwich complexes. Typically, to obtain these compounds, a group 4 transition metal dihalide complex is treated with a strong reducing agent under a dinitrogen atmosphere, and the outcome of these reactions is often complex.³⁶ In addition, these results clearly demonstrate the importance of indenyl steric effects in dinitrogen complex formation. The presence of two large 1,3 substituents (e.g., the size of isopropyl or larger) inhibits dimerization through a μ_2, η^1, η^1 - N_2 ligand. Likewise, three methyl groups produce the same outcome. One methyl substituent and a second methyl, isopropyl, or *tert*-butyl group allows dimerization, and hence, isolable dinitrogen complexes are obtained. The 1,3-indenyl disubstitution pattern appears essential as reduction of complexes bearing only one substituent did not provide identifiable sandwich or dinitrogen compounds. Once again, these results highlight the importance of reversible benzo coordination to allow access to Zr(II) chemistry and provide rare examples of indenyl dinitrogen compounds.

Synthesis of Side-On, End-On Zirconium Dinitrogen Compounds. Attempts to prepare **4** $_2$ - N_2 by direct sodium amalgam reduction of **4-Cl** $_2$ under a dinitrogen rather than argon atmosphere produced a different outcome, highlighting the importance of isolating the sandwich for direct N_2 coordination. The product of the reduction reaction was neither **4** nor **4** $_2$ - N_2 but rather a new compound, **7**, identified as a side-on, end-on zirconium complex with a μ_2, η^5, η^4 -indenyl ligand (eq 4).



The benzene- d_6 ^1H NMR spectrum of **7** established a 3:1 mixture of isomeric products, each with two inequivalent Cp* environments and only one indenyl ring *per dimer*.³⁵ Free indene was detected by ^1H NMR spectroscopy and accounts for the ejected ligand. Upfield-shifted benzo resonances are observed between 2 and 5 ppm, diagnostic of coordination to zirconium.²⁸ A medium intensity $\text{N}=\text{N}$ stretch was observed at 1583 cm^{-1} ($\nu_{\text{N}_2} = 1584\text{ cm}^{-1}$ pentane) in the solid state (KBr) IR spectrum,

consistent with a weakly activated dinitrogen ligand. This band shifts to 1533 cm^{-1} (KBr, calculated = 1529 cm^{-1}) for the ^{15}N isotopologue, prepared by reduction of **4-Cl** $_2$ under $^{15}\text{N}_2$ gas. The $\text{N}=\text{N}$ band in the side-on, end-on dinitrogen complex, **7**, appears at much higher frequency than the value of 1165 cm^{-1} reported by Fryzuk and co-workers for the tantalum compound with side-on, end-on N_2 hapticity.³⁷ Two inequivalent nitrogen atoms were also observed by ^{15}N NMR spectroscopy, consistent with side-on, end-on N_2 coordination. For the major isomer, peaks are observed at 490.0 and 599.9 ppm with a $^1J_{\text{N}-\text{N}} = 20\text{ Hz}$. Similar chemical shifts of 494.9 and 610.1 ppm with $^1J_{\text{N}-\text{N}}$ coupling constants of 21 Hz were observed for the minor. These values compare to the ^{15}N NMR shifts of 360.0 and 544.0 ppm ($^1J_{\text{N}-\text{N}} = 21.5\text{ Hz}$) for the ditantalum compound.¹¹ All ^{15}N values are referenced to liquid ammonia.

Two other examples of zirconium side-on, end-on dinitrogen compounds, **8** and **9**, were synthesized by sodium amalgam reduction of **2-Cl** $_2$ and **5-Cl** $_2$ under an N_2 atmosphere, respectively (eq 4). The ^1H NMR spectral features of **8** and **9** are similar to those observed for **7** and clearly establish one indenyl ring per dimer. Again, free indene was observed during each synthesis and accounts for the ejected ligand during the reduction. For **9**, a 1.5:1 ratio of two isomers was observed by NMR spectroscopy. Obtaining silylated dinitrogen complex, **8**, in pure form proved challenging. Approximately 10–15% of the material was a bridging dichloride complex with a bridging indenyl ligand. Halide contamination is frequently observed during reductions of silyl-substituted zirconocenes as the electron-withdrawing properties of the ligand render reduction to low oxidation states more challenging.²¹ Attempts to prepare **7** in higher yield by reduction of **4-Cl** $_2$ in the presence of (η^2 - C_5Me_5) ZrCl_3 were unsuccessful as the latter compound was completely consumed prior to reaction of **4-Cl** $_2$ with Na(Hg).

X-ray diffraction studies on single crystals of **7** (Figure 6) contained both isomers of the product in the unit cell and established the identity of the molecule as the “side-on, end-on” zirconium dinitrogen compound with bridging chloride and indenyl ligands. The difference between the two isomers is the relative orientation of the isopropyl (or methyl) indenyl substituent relative to the bridging chloride ligand. The major isomer has these two ligands *syn*, while the minor isomer has the opposite configuration (Figure 6). Consistent with the solution NMR data, there is only one indenyl ring per two zirconium atoms. The N–N bond distances of 1.196(4) (major) and 1.220(10) (minor) Å are indicative of weak to modest activation and are significantly shorter than the value of 1.319(4) Å reported by Fryzuk and co-workers for the tantalum N_2 compound with a similar hapticity.¹¹

The bond lengths and angles of the benzo portion of the μ_2, η^4 -bridging indenyl ligand are also consistent with 2-electron reduction (Table 2).³⁸ In the major isomer, elongated C(5)–C(6) and C(7)–C(8) distances of 1.418(3) and 1.402(4) Å, respectively, are observed with concomitant contraction of the C(6)–C(7) distance to 1.390(3) Å. Likewise, the benzo portion of the ring is buckled by 23.2° also consistent with dialkyl character and reduction of the six-membered ring. Thus, the Zr(II) metallocene can be described as an 18-electron compound

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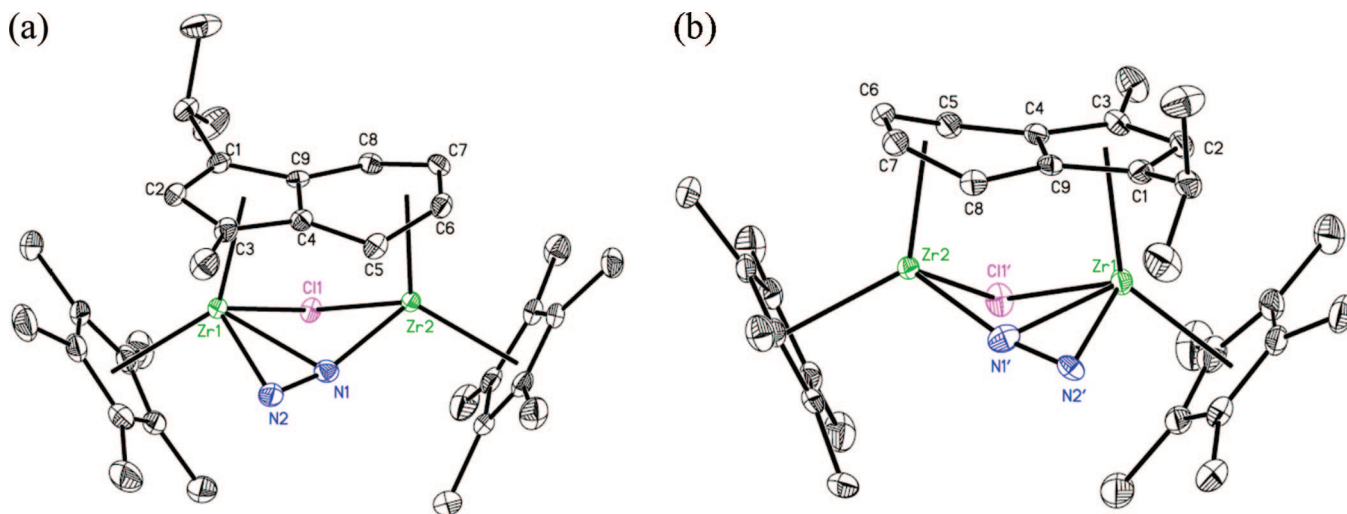


Figure 6. Molecular structure of the (a) major and (b) minor isomers of **7** at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **4₂-N₂** and the Isomers of **7**

	4₂-N₂	7
C(4)–C(5) (Å)	1.435(3)	1.445(3)
C(5)–C(6) (Å)	1.350(3)	1.418(3)
C(6)–C(7) (Å)	1.433(3)	1.390(3)
C(7)–C(8) (Å)	1.429(3)	1.402(4)
C(8)–C(9) (Å)	1.435(3)	1.458(3)
η^9 fold angle (deg)	10.2	1.6
buckle	1.0	23.2
dihedral angle (deg)	57.9	1.2

with a side-on bound $[N_2]^{2-}$ ligand completing the coordination sphere. In this view, the other zirconium, Zr(2), is a formally 16-electron metal center with a dative bond to the end-on coordinated N_2 ligand and a 2-electron reduced, “butadiene-like” η^4 benzo ring.

For the tantalum compound, Fryzuk and co-workers have provided compelling evidence that the bridging hydrides force the two metal centers so close together that alternative N_2 hapticities become disfavored.¹¹ To determine whether the μ_2, η^4 -hapticity of the indenyl ligand was responsible for the observation of side-on, end-on N_2 coordination in **7–9**, a related zirconium tetrahydroindenyl diiodide complex was prepared and reduced under dinitrogen (Figure 7).

Exposure of benzene- d_6 or toluene solution of **4** to 4 atm of dihydrogen resulted in rapid formation of the corresponding zirconocene dihydride, **4-H₂**, where the indenyl ring remains intact. Prolonged exposure to H_2 gas resulted in complete hydrogenation of the benzo ring to the tetrahydroindenyl derivative, **4-THI-H₂**.^{39,40} Treatment of the dihydride complex

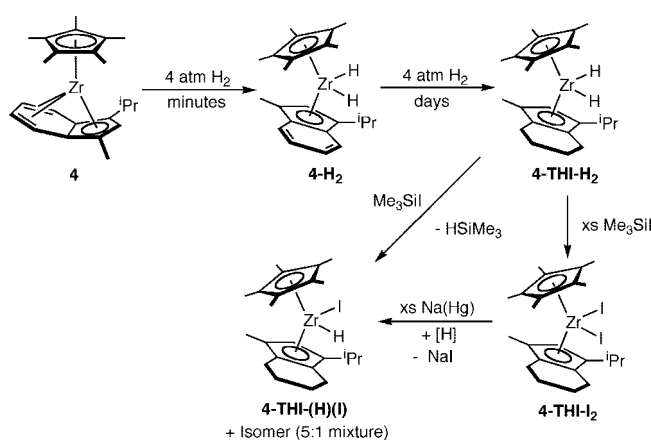


Figure 7. Preparation and attempted alkali metal reduction of **4-THI-I₂**.

with excess Me_3SiI resulted in smooth conversion to the desired zirconocene diiodide. All of the compounds in this sequence were readily identified by routine NMR spectroscopic experiments and by comparison to related compounds.³⁹

Sodium amalgam reduction of **4-THI-I₂** yielded a 5:1 mixture of two zirconocene compounds, identified as two isomers of the zirconocene hydrido iodide. It is likely that the major isomer is the one where the hydride is *syn* to the isopropyl group and the minor the one where it is *anti*. Diagnostic, downfield hydride peaks are observed in the benzene- d_6 1H NMR spectrum at 7.96 (major) and 8.08 (minor) ppm. The source of the hydrogen atom during the reduction is unknown, but minor amounts of a cyclometalated zirconocene iodide were also observed, suggesting a ligand C–H bond activation is likely. It should also be noted that hydrido chloride compounds are frequently observed as byproducts in the reductions of zirconocene and hafnocene dihalide compounds with sodium amalgam.^{41,45} Notably, no dinitrogen compound was observed from these experiments.

Protonolysis Studies. With new structural types of zirconocene dinitrogen compounds in hand, the activation of the dinitrogen

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Table 3. Protonolysis of Indenyl-Substituted Zirconium Dinitrogen Compounds to Hydrazine; Protonolysis of $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$ Included for Comparison

protonolysis reaction	% N ₂ H ₄
4 ₂ -N ₂ + xs HCl	45
4 ₂ -N ₂ + xs H ₂ O	0
5 ₂ -N ₂ + xs HCl	70
7 + xs HCl	57
7 + xs H ₂ O	73
7 + xs EtOH	66
8 + xs HCl	66
$[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$ + HCl	>95
$[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$ + H ₂ O	84

ligand observed in the ground-state was probed by a series of protonolysis experiments. Previous work from Bercaw's laboratory⁴² and our research group⁴³ has established that zirconocene dinitrogen complexes bearing weakly activated, [N₂]⁰-type ligands undergo loss of dinitrogen when hydrolyzed with EtOH or water, whereas strongly activated, side-on bound haptomers with [N₂]⁴⁻ yield hydrazine.⁴⁴ Both structural types yield hydrazine upon treatment with mineral acids such as HCl.^{34,45}

The results of the protonolysis of several of the new indenyl ligated zirconium dinitrogen compounds are summarized in Table 3. Previous work with the side-on bound bis(cyclopentadienyl)zirconocene dinitrogen compound is also reported for comparison. The indenyl zirconium dinitrogen compound bearing the weakly activated, end-on coordinated N₂ ligand, 4₂-N₂, produced no N₂H₄ upon treatment with water. As anticipated, all of the end-on dinitrogen compounds produce a modest to good yield of hydrazine upon addition of excess gaseous HCl. The stronger activation observed in the ground state of the side-on, end-on dinitrogen compound translates on its protonolysis chemistry. Unlike the end-on compounds, addition of water or ethanol to 7 produced 73 and 66% of the expected amount of hydrazine, respectively.

Concluding Remarks

New indenyl-ligated zirconocene dinitrogen complexes have been synthesized that exploit the haptropic flexibility of the indenyl ligand and as a result, add to the structural diversity of known group 4 transition metal N₂ complexes. Isolated sandwich compounds bearing one methyl and one other (R = Me, ⁱPr, ^tBu) indenyl substituent reversibly coordinate dinitrogen following dissociation of the benzo ring of the η⁹ indenyl ligand. The resulting dinitrogen complexes contain an end-on bound N₂ ligand and exhibit a μ₂, η² indenyl interaction. Related compounds bearing larger 1,3 indenyl substituents do not form isolable dinitrogen complexes likely due to the inability to dimerize through a two atom, N₂ bridge. Performing the reductions of the zirconocene dichloride complexes directly under an N₂ atmosphere produced rare examples of side-on, end-on dinitrogen compounds, where one indenyl ligand has been ejected and the remaining ring bridges two zirconium centers. This μ₂, η⁵, η⁴-interaction likely brings the two metal centers in proximity and favors side-on, end-on coordination. The stronger activation of the dinitrogen ligand in this class of compounds is translated onto N₂ functionalization by weak Brønsted acids such as ethanol and water. In contrast, the weakly

activated end-on compounds only yield hydrazine when treated with mineral acid.

Experimental Section⁴⁶

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_9\text{H}_5\text{-1-(ⁱPr)-3-(Me))ZrCl_2$ (4-Cl₂). A 500 mL round-bottom flask was charged with 2.21 g (6.64 mmol) of $(\eta^5\text{-C}_5\text{Me}_5)ZrCl_3$ and approximately 100 mL of diethyl ether was added. The pale yellow solution was chilled in a liquid nitrogen cooled cold well for 20 min and 1.18 g (6.64 mmol) of Li[C₉H₅-1-(ⁱPr)-3-(Me)] was added to the solution and the resulting mixture stirred for two days. The solvent was removed *in vacuo* and the yellow solid washed with pentane and subsequently extracted into toluene and filtered through Celite. Removal of the toluene *in vacuo* yielded 2.56 g (82%) of 4-Cl₂ as a yellow powder. Anal. Calcd for C₂₃H₃₀ZrCl₂: C, 58.95; H, 6.45. Found: C, 57.93; H, 6.34. ¹H NMR (benzene-*d*₆): δ = 1.21 (d, 9.2 Hz, 3H, CHMe₂), 1.28 (d, 9.2 Hz, 3H, CHMe₂), 1.79 (s, 15H, Cp* Me), 2.12 (s, 3H, Me), 3.26 (m, 1H, CHMe₂), 5.77 (s, 1H, CpH), 7.05 (m, 2H, Benzo), 7.49 (d, 8.4 Hz, 1H, Benzo), 7.67 (d, 8.4 Hz, 1H, Benzo). ¹³C {¹H} NMR (benzene-*d*₆): δ = 12.42, 12.44 (Cp* Me/Ind Me), 23.47, 24.00, 28.69 (CHMe₂), 119.13, 124.40, 124.73, 125.00, 125.14, 125.35 (Cp/Benzo).

Preparation of $(\eta^5\text{-C}_5\text{Me}_5)(\eta^9\text{-C}_9\text{H}_5\text{-1-(ⁱPr)-3-(Me))Zr$ (4). A 100 mL round-bottom flask was charged with 8.84 g (44.05 mmol) of mercury and approximately 10 mL of pentane in a nitrogen drybox. With stirring, 0.044 g (1.91 mmol) of sodium metal was added and the resulting amalgam was stirred for 20 min. A pentane slurry containing 0.150 g (0.32 mmol) of 4-Cl₂ was added. The resulting reaction mixture was stirred vigorously for 24 h under argon and the burgundy solution was decanted from the amalgam and filtered through Celite in a nitrogen filled drybox. Removal of the pentane *in vacuo* yielded 0.126 g (99%) of 4 as a burgundy oil. ¹H NMR (benzene-*d*₆): δ = 1.10 (d, 6.8 Hz, 3H, CHMe₂), 1.12 (d, 6.8 Hz, 3H, CHMe₂), 1.78 (s, 15H, Cp* Me), 2.05 (s, 3H, Ind Me), 3.24 (m, 1H, CHMe₂), 3.68 (m, 1H, η⁹-Benzo), 3.84 (m, 1H, η⁹-Benzo), 5.02 (d, 6 Hz, 1H, η⁹-Benzo), 5.13 (d, 6 Hz, 1H, η⁹-Benzo), 5.56 (s, 1H, CpH). ¹³C {¹H} NMR (benzene-*d*₆): δ = 11.49, 12.06 (Me), 22.13, 27.05, 28.94 (CHMe), 65.47, 66.45, 94.03, 96.19 (η⁹-Benzo), 112.08, 113.90, 118.51 (Cp). Three Cp resonances not located.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)Zr]_2[\mu_2\text{-}\eta^2, \eta^2\text{-}\{4,5\text{-}(\eta^5\text{-C}_9\text{H}_5\text{-1-(ⁱPr)-3-(Me))\}_2(\mu_2\text{-}\eta^1, \eta^1\text{-N}_2)$ (4₂-N₂). A 20 mL scintillation vial was charged with 0.116 g of 4 and approximately 3 mL pentane. The resulting solution was chilled at -35 °C for one week, producing a purple solution with precipitate. The brown precipitate was isolated and yielded 20 mg (17%) of a brown solid identified as 4₂-N₂. Anal. Calcd for C₄₆H₆₀Zr₂N₂: C, 67.10; H, 7.34; N, 3.40. Found: C, 67.25; H, 7.31; N, 3.03. ¹H NMR (benzene-*d*₆): δ = 1.34 (d, 6.5 Hz, 6H, CHMe₂), 1.42 (d, 6.5 Hz, 6H, CHMe₂), 1.80 (s, 30H, Cp* Me), 2.25 (s, 6H, Ind Me), 2.63 (m, 4H, CHMe₂, η²-Benzo), 3.30 (m, 2H, η²-Benzo), 5.64 (s, 2H, CpH), 6.33 (m, 2H, Benzo), 6.41 (d, 8 Hz, 2H, Benzo). ¹³C {¹H} NMR (benzene-*d*₆): δ = 12.06 (Cp* Me), 13.51 (Ind Me), 24.82, 25.45 (CHMe), 29.56 (CHMe), 66.03, 77.68 (η²-Benzo), 103.97 (Cp), 109.63 (Ind CpH), 112.09 (Cp), 112.54 (Benzo), 124.16 (Cp), 126.05 (Benzo). Two Cp/Benzo resonances not located. ¹⁵N {¹H} NMR (benzene-*d*₆): δ = 598.69. IR (pentane): ν(NN) = 1563 cm⁻¹.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)Zr]_2[\mu_2\text{-}\eta^5, \eta^4\text{-}(\eta^5\text{-C}_9\text{H}_5\text{-1-(ⁱPr)-3-(Me))\}_2(\mu_2\text{-}\eta^2, \eta^1\text{-N}_2)(\mu_2\text{-}\eta^1, \eta^1\text{-Cl})$ (7). This compound was prepared in a similar manner to 4 using 8.84 g (44.05 mmol) of mercury, 0.044 g (1.91 mmol) of sodium metal and 0.150 g (0.32 mmol) of 4-Cl₂. Stirring the reaction mixture for 2 days and subsequent workup in a nitrogen drybox afforded a brown oil. Recrystallization from pentane afforded 0.079 g (72%) of a brown solid identified as two isomers of 7 in a 3:1 ratio. Anal. Calcd for C₃₃H₄₅Zr₂N₂Cl: C, 57.64; H, 6.60; N, 4.07. Found: C, 57.61; H, 6.47; N, 3.87. ¹H

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(46) Representative procedures for one specific class of compounds are reported. Full details on all of the remaining compounds, including general considerations, are described in the Supporting Information.

NMR (benzene- d_6): δ = 0.58 (d, 8 Hz, 3H, minor CHMe₂), 0.63 (d, 8 Hz, 3H, major CHMe₂), 0.74 (s, 3H, major Ind Me), 0.91 (d, 8 Hz, 3H, minor CHMe₂), 1.04 (s, 3H, minor Ind Me), 1.11 (d, 8 Hz, 3H, major CHMe₂), 1.90 (s, 15H, major Cp* Me), 1.91 (s, 15H, minor Cp* Me), 1.94 (s, 15H, major Cp* Me), 1.95 (s, 15H, minor Cp* Me), 1.96 (m, 2H, major/minor CHMe₂), 2.22 (dd, 8 Hz, 4 Hz, 1H, major Benzo), 2.66 (dd, 8 Hz, 4 Hz, 1H, minor Benzo), 3.49 (m, 1H, minor Benzo), 3.83 (dd, 8 Hz, 4 Hz, 1H, major Benzo), 4.34 (s, 1H, major CpH), 4.42 (s, 1H, minor CpH), 4.73 (m, 1H, major Benzo), 4.85 (d, 8 Hz, 1H, minor Benzo). ¹³C{¹H} NMR (benzene- d_6): δ = 9.15 (major Ind Me), 11.86, (major Cp* Me), 11.96 (minor Cp* Me), 11.98 (major Cp* Me), 12.06 (minor Cp* Me), 22.56 (major CHMe₂), 22.90 (minor CHMe₂), 24.81 (major CHMe₂), 25.07, 27.14 (minor CHMe₂), 27.87 (major CHMe₂), 68.24, 68.45, 83.19, 84.08, 87.52, 93.11, 93.79, 94.39, 95.72, 95.88, 100.81, 106.36, 114.95, 115.25, 115.97, 116.02, 116.39, 118.29, 119.15, 119.90, 120.58, 121.87 (Cp/Benzo). Minor Ind Me reso-

nance not located. ¹⁵N {¹H} NMR (benzene- d_6): δ = 490.0 (d, 20 Hz, major), 494.9 (d, 21 Hz, minor), 599.9 (d, 20 Hz, major), 610.1 (d, 21 Hz, minor). IR(pentane): ν (NN) = 1584 cm⁻¹.

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Supporting Information Available: Experimental procedures and crystallographic data for **1**, **4₂-N₂**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>

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