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Article

Synthesis, Characterization, and Reactivity Studies of (Cyclohexenyl)nickel(II) Complexes†

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The synthesis and characterization of the complexes [(cyclohexenyl)Ni(NCMe)$_2$][B(Ar$_F$)$_4$] (**1**) and [(cyclohexenyl)Ni(mesitylene)][B(Ar$_F$)$_4$] (**2**) are reported. Abstraction of the nitrile ligands in **1** with B(C$_6$F$_5$)$_3$ yields a "ligand-free" [(cyclohexenyl)Ni^{II}]$^+$ species which coordinates 1,3-dienes, including butadiene (BD), isoprene (IP), 1,3-cyclohexadiene (1,3-CHD), 1,4-cyclohexadiene (1,4-CHD), and 2,3-dimethyl-1,3-butadiene (DMBD) at low temperatures. Diene insertion is observed at temperatures above ca. −20 °C. An *s-trans* diene complex is formed upon coordination of DMBD. Hydrogen transfer is observed when complex **2** is exposed to 1-hexene or cyclopentadiene to generate new allyl nickel complexes and 1 equiv of cyclohexene. Polymerization of 1,3-CHD and DMBD with **2** is described, and a coupling product formed between DMBD and **2** is observed and characterized.

Introduction

(Allyl)nickel(II) complexes are important catalysts and intermediates in organometallic chemistry.[1] A variety of neutral (allyl)nickel(II) complexes as well as [(allyl)NiL$_2$]$^+$ complexes containing labile ligands have been synthesized and characterized.[2−21] These Ni complexes serve as precursors to highly reactive Ni(II) species shown to be active for polymerization and oligomerization reactions.[5−13,19] In early work Tkatchenko showed that [(2-R-allyl)Ni(L)$_n$]$^+$ complexes, where L = 1,5-cyclooctadiene (COD), acetonitrile (CH$_3$CN), tetrahydrofuran (THF), or benzonitrile, are active catalysts for ethylene oligomerization.[14] Extensive pioneering work from the groups of Taube,[5−11] Porri,[12,13] and Teyssié[19] explored the behavior and mechanistic details of butadiene polymerization catalyzed by numerous (allyl)nickel species. Additionally, Goodall[16−18] and Cámpora[20,21] have shown that cationic (allyl)nickel complexes bearing labile ligands are efficient initiators for norbornene and 1,3-diene polymerizations. We recently investigated the use of [(2-R-allyl)M(L)$_n$]$^+$ (M = Ni, Pd; L = mesitylene (mes), CH$_3$CN; R = H, Me) for diene and norbornene insertion polymerization.[3,4,15,22]

Much less is known about the cyclohexenyl analogues of the acyclic (allyl)nickel(II) cations. Wilke was the first to report the synthesis of (cyclohexenyl)$_2$Ni and [(cyclohexenyl)-NiBr]$_2$ dimers.[2] More recently, Hartwig identified (cyclohexenyl)nickel(II) and -palladium(II) phosphine complexes as intermediates in the hydroamination of 1,3-dienes by alkylamines.[23,24] Additionally, we previously have observed

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hydrogen atom transfer from cyclohexene to the (allyl)Ni(mes)$^+$ complex to generate (cyclohexenyl)Ni(mes)$^+$ in situ.[25]

(Cyclohexenyl)palladium(II) species are more common in the literature, as they have been identified as intermediates in asymmetric allylic alkylation reactions.[26] Additionally, cyclic dienes or olefins have been shown to react with group 10 metals to generate cyclic enyl metal complexes. Maitilis[27–29] and co-workers observed the hydropalladation of 1,3-cyclohexadiene to generate the (cyclohexenyl)Pd(dppe)$^+$ complex. This hydropalladation reaction was applied to 1,3-cyclopentadiene and 1,3- or 1,4-cyclooctadiene to generate (cyclopentenyl)- and (cyclooctenyl)palladium complexes, respectively.[27,28] We recently reported hydrogen atom transfer from cyclohexene to the (allyl)Ni(mes)$^+$ complex to generate (cyclohexenyl)Ni(mes)$^+$ and 1 equiv of propene.[25]

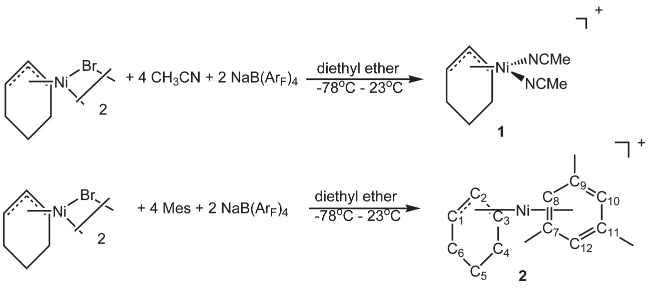
Previously, we showed that the nitrile complexes [(2-R-allyl)Ni(NCMe)$_2$][B(Ar$_F$)$_4$] (R = H, Me; Ar$_F$ = (C$_6$H$_3$)-(CF$_3$)$_2$) serve as precursors to "naked" nickel allyl cations by treatment with B(C$_6$F$_5$)$_3$. In the presence of 1 equiv of butadiene (BD) and 2 equiv of B(C$_6$F$_5$)$_3$, η^4 coordination of BD occurs at low temperatures and the (2-R-allyl)Ni-(η^4-butadiene)$^+$ complexes can be observed. However, upon exposure to excess butadiene rapid insertion of 3 equiv of BD occurs to yield wrap-around complexes.[15] Additionally, we have shown that [(2-R-allyl)Ni(mes)][B(Ar$_F$)$_4$] (R = H, CH$_3$) complexes exhibit interesting reactivity with olefins[25] and are highly active catalysts for polymerization of 1,3-dienes and styrene.[22]

We report here the synthesis of [(cyclohexenyl)Ni-(NCMe)$_2$][B(Ar$_F$)$_4$] (**1**) and [(cyclohexenyl)Ni(mes)][B(Ar$_F$)$_4$] (**2**) and an investigation of the reactivity of these complexes with 1,3-dienes and α-olefins. Similar to previous experiments using acyclic allyl complexes, a cationic ligand-free (cyclohexenyl)nickel(II) complex, in which a single Ar$_F$ ring is coordinated to nickel, can be observed at low temperature. Interestingly, in contrast to the acyclic allyl complexes, the (cyclohexenyl)Ni(η^4-diene)$^+$ complexes react with dienes only at temperatures above ca. −20 °C in the presence of excess diene. The reactions of **2** with olefins and 1,3-dienes and intramolecular hydrogen atom transfer are discussed. Additionally, we describe here the first observation of Ni(II) binding a 1,3-diene in an *s-trans* conformation.

Results and Discussion

Catalyst Synthesis and Structure. The synthesis of [(cyclohexenyl)Ni(NCMe)$_2$][B(Ar$_F$)$_4$] (**1**) and [(cyclohexenyl)-Ni(mes)][B(Ar$_F$)$_4$] (**2**) was achieved using methods similar to those previously described for the preparation of the analogous acyclic allyl compounds.[15,25] Salt metathesis of [(cyclohexenyl)-NiBr]$_2$ (readily synthesized via literature methods)[2] with 2 equiv of NaB(Ar$_F$)$_4$ in diethyl ether in the presence of either mesitylene or acetonitrile generates compounds **1** and **2** in good yields (Scheme 1). Characterization of the compounds was achieved using ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

Scheme 1. Synthesis of Cationic (Cyclohexenyl)nickel(II) Complexes



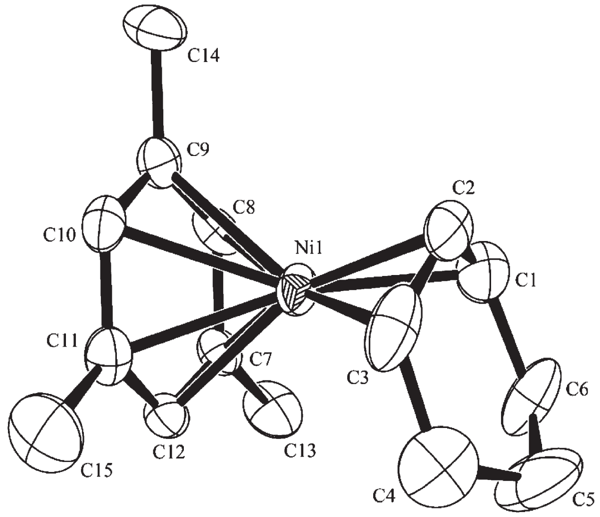


Figure 1. Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and [B(Ar$_F$)$_4$]$^-$ are omitted for clarity. Selected bond lengths (Å): Ni(1)−C(2) = 1.934(5), Ni(1)−C(3) = 2.015(5), Ni(1)−C(1) = 2.063(6), Ni(1)−C(8) = 2.149(5), Ni(1)−C(12) = 2.154(4), Ni(1)−C(11) = 2.157(5), Ni(1)−C(7) = 2.159(4), Ni(1)−C(10) = 2.193(5), Ni(1)−C(9) = 2.224(5).

The solid-state structure of **2** was established using X-ray crystallography (Figure 1).[30] The mesitylene ligand of **2** exhibits no puckering or bending upon coordination. The C$_5$ methylene group of the cyclohexenyl ligand is bent out of the plane and points away from the mesitylene ring. The Ni−C$_1$, Ni−C$_2$, and Ni−C$_3$ bond lengths of the allyl moiety are nearly identical, consistent with similar bond distances observed for the [(allyl)Ni(mes)][B(Ar$_F$)$_4$] complex.[25] Interestingly, this structure shows variation in the Ni−C bond lengths of the arene. Ni−C$_{11}$, Ni−C$_{12}$, Ni−C$_7$, and Ni−C$_8$ exhibit bond lengths in the range 2.15−2.16 Å, while the Ni−C$_{10}$ and Ni−C$_9$ bond lengths are elongated to 2.19 and 2.22 Å, respectively. The significant differences in the bond lengths suggest a ring slippage away from an ideal η^6-binding mode and a stronger interaction of Ni with the C$_8$−C$_7$−C$_{11}$−C$_{12}$ diene unit relative to the C$_{10}$−C$_9$ olefinic unit.

Ligand Exchange Reactions. The lability of the mesitylene group coordinated to the (cyclohexenyl)nickel(II) fragment was probed through the addition of various ligands. Addition of 5 equiv of mesitylene-d_{12} to complex **2** at room temperature generates a resonance for free mesitylene at δ 6.79 and indicates exchange of free and bound mesitylene.

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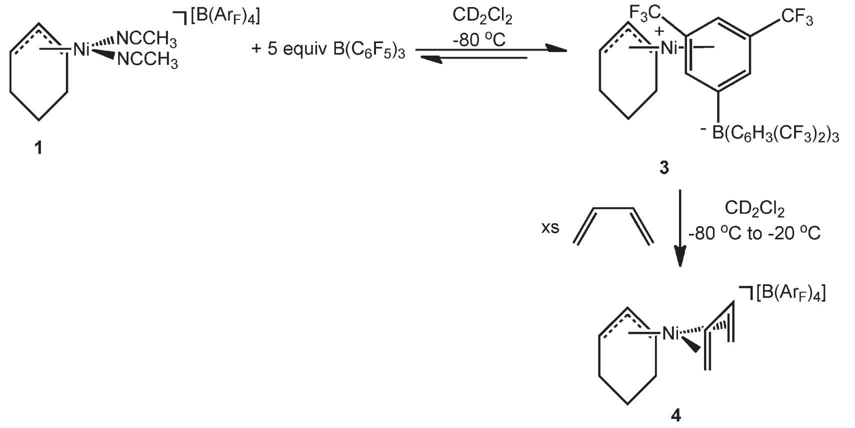
(30) See the Supporting Information for X-ray structure data.

Scheme 2. Generation of [(cyclohexenyl)Ni][B(Ar_F)$_4$] (3) and [(cyclohexenyl)Ni(η^4-butadiene)][B(Ar_F)$_4$] (4) at Low Temperatures

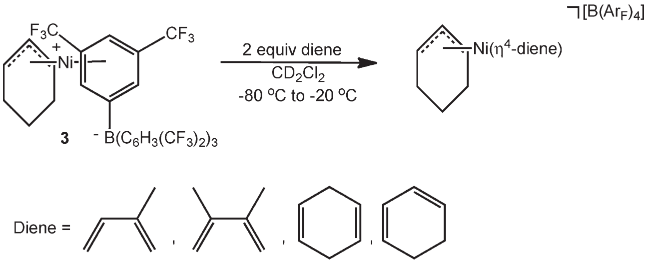


Equilibrium is reached within 4 h. The ratio of coordinated: free mesitylene is 3:7 approximately 10 min after mixing complex **2** with mesitylene-d_{12}. After 4 h, the ratio of coordinated to free mesitylene changes to 1:6 and remains constant. No line broadening is observed in the ^{1}H NMR spectrum when protio mesitylene is added to complex **2**, indicating arene exchange is slow on the NMR time scale, consistent with exchange on the time scale of minutes at 23 °C. Complete displacement of the mesitylene by 5.5 equiv of hexamethylbenzene (hmb) occurs to form [(cyclohexenyl)-Ni(hmb)]$^+$ within 4 h at room temperature. The ratio of **2**:[(cyclohexenyl)Ni(hmb)]$^+$ was 1:9 within 10 min of adding hmb to compound **2**. Complete conversion to the hexamethylbenzene complex is achieved within 1 h and is much slower than the analogous exchange reaction reported for the [(allyl)Ni(mes)]$^+$ analogue.[25] Exposure of **2** to 9 equiv of diethyl ether results in very minor displacement of mesitylene after 1 day, indicating that diethyl ether does not effectively compete with mesitylene for binding to Ni.

Reactions with 1,3-Dienes. The reaction of **1** in the presence of 5 equiv of B(C_6F_5)$_3$ generates [(cyclohexenyl)Ni][B(Ar_F)$_4$] (**3**) at low temperatures (Scheme 2). This species was identified by ^{1}H and ^{19}F NMR spectroscopy and shows the presence of four new resonances in the ^{1}H spectrum for the coordinated [B(Ar_F)$_4$]$^-$ anion. The ratio of the new proton signals in the ^{1}H NMR spectrum is 1:6:3:2. In the ^{19}F NMR spectrum there are two signals for coordinated [B(Ar_F)$_4$]$^-$ in a 1:3 ratio, corresponding to the coordinated and uncoordinated Ar_F rings, respectively. This pattern indicates one Ar_F ring is bound to nickel, while the remaining three aryl rings are unbound, as previously observed for [(allyl)Ni][B(Ar_F)$_4$] and [(2-methallyl)Ni][B(Ar_F)$_4$].[15]

Intramolecular exchange is observed for the Ar_F rings at −40 °C through broadening of the coordinated Ar_F resonances.[15] ^{1}H variable-temperature NMR experiments between −70 and −35 °C showed the barrier to intramolecular Ni migration among the rings to be $\Delta G^\ddagger = 11.9$ kcal/mol. Intermolecular exchange of coordinated [B(Ar_F)]$_4^-$ with free [B(Ar_F)$_4$]$^-$ occurs on the NMR time scale at temperatures above 0 °C. Details of this dynamic process are described in the Experimental Section. Species **3** is in equilibrium with starting complex **1**, and the equilibrium is temperature-dependent, shifting toward species **3** at higher temperatures. At −20 °C, the ratio of **3**:**1** is 4:1.

Scheme 3. Coordination of 1,3-Dienes to Ligand-Free 3 at Low Temperatures



Species **3** rapidly coordinates butadiene at −80 °C to form the η^4-diene adduct [(cyclohexenyl)Ni(η^4-butadiene)]-[B(Ar_F)$_4$] (**4**) (Scheme 2). Only one isomer, the *s-cis* η^4-diene complex **4**, is observed in the ^{1}H NMR spectrum and this *cis* η^4 species is the most stable structure predicted by DFT calculations.[31] At temperatures below −20 °C, insertion reactions do not take place in the presence of excess butadiene. This is in contrast with our previous result using [(allyl)Ni][B(Ar_F)$_4$], which rapidly inserts 3 equiv of butadiene to form stable wrap-around complexes below −110 °C.[15] The cyclohexenyl insertion product formed at −20 °C has a characteristic ^{1}H NMR spectrum for a wrap-around complex, but the spectrum is too complex to assign all resonances.

Addition of 2 equiv of isoprene (IP), 1,3-cyclohexadiene (1,3-CHD), and 1,4-cyclohexadiene (1,4-CHD) to ligand-free species **3** at −80 °C yields [(cyclohexenyl)Ni(η^4-IP)]-[B(Ar_F)$_4$] (**5**), [(cyclohexenyl)Ni(η^4-1,3-CHD)][B(Ar_F)$_4$] (**6**), and [(cyclohexenyl)Ni(η^4-1,4-CHD)][B(Ar_F)$_4$] (**7**), respectively (Scheme 3). Complexes **5** and **6** undergo insertion of diene at −20 °C, while **7** is stable at room temperature. Each of the CH_2 groups of the cyclohexenyl ring is diastereotopic when diene or arene is coordinated, facilitating their assignment in the ^{1}H NMR spectrum (see the Experimental Section and the Supporting Information for spectral characterizations).

To compare the stability of the cyclohexenyl derivatives to that of the (allyl)nickel(II) complexes, we generated the (2-methallyl)Ni(η^4-1,3-cyclohexadiene)$^+$ complex in situ. Exposure of 1 equiv of 1,3-CHD to the ligand-free species [(2-methallyl)Ni]$^+$ at −80 °C produces [(2-methallyl)Ni-(η^4-1,3-cyclohexadiene)][B(Ar_F)$_4$] (**Me-6**) (Scheme 4). The ^{1}H NMR spectrum at −70 °C exhibits two broad singlets at 6.31 (2H) and 6.11 (2H) ppm corresponding to the vinylic hydrogens of the coordinated cyclohexadiene. There are three

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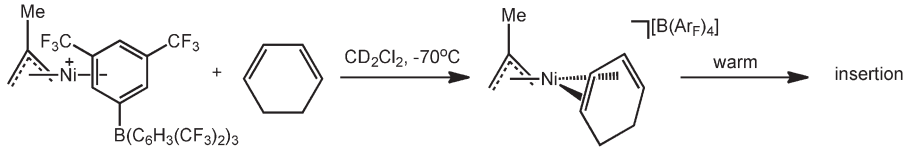
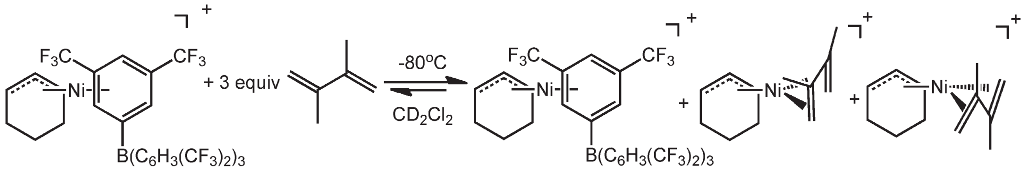
[31] Tobisch, S.; Bögel, H.; Taube, R. *Organometallics* **1996**, *15*, 3563–3571.

Scheme 4. Reaction of Cyclohexadiene with [(2-methallyl)Ni][B(Ar$_F$)$_4$]



Me-6

Scheme 5. Reaction of 3 with 2,3-Dimethyl-1,3-butadiene



3 **3** **8** **9**

singlets at 5.14 (2H), 2.59 (2H), and 2.15 (3H) ppm that are assigned to the syn, anti, and CH_3 protons of the allyl ligand, respectively. The final resonance is a roofed multiplet at 1.77 ppm assigned to the diastereotopic methylene hydrogens. At temperatures above −30 °C, insertion of CHD into the allyl group is observed. Thus, the allyl η^4-diene complexes insert diene at lower temperatures than do the cyclohexenyl derivatives.

When complex **3** is exposed to DMBD, an unusual result is obtained. Two isomers of an η^4-diene species, one major and one minor, in addition to the ligand-free complex **3** are observed at −80 °C, and upon warming to −20 °C, there is no spectral evidence for **3** in solution. Through spectroscopic data provided from $^1H-^1H$-COSY NMR experiments, the identities of the two isomers were established as [(cyclohexenyl)Ni(η^4-*s-cis*-DMB)]$^+$ (**8**), the major isomer, and [(cyclohexenyl)Ni(η^4-*s-trans*-DMB)]$^+$ (**9**), the minor isomer (Scheme 5). This is the first observation of an η^4-*s-trans*-coordinated nickel(II) diene complex. In the ^{1}H NMR spectrum at −20 °C, *s-trans* complex **9** exhibits four signals (each integrating for 1H) that appear in the region for coordinated olefin (δ 5.19, 5.04, 4.46, and 4.30) as well as two methyl resonances (δ 1.94, 1.50), each correlating to a different set of olefinic signals. These ^{1}H NMR characteristics point to an η^4-diene complex in which the DMBD moiety is in the *s-trans* geometry. Additionally, for the minor isomer, separate terminal allyl proton resonances (each integrating for 1H) appear at 6.32 (H_1) and 6.30 ($H_{1'}$) while the central allyl proton (H_2) appears at 5.32 ppm. The ^{1}H NMR spectrum for the *s-cis* coordinated diene fragment of species **8** exhibits two olefinic signals at δ 4.97 (2H) and 2.93 (2H) and a single 6H methyl resonance (δ 2.21). The ratio of the two isomers (cis:trans) is 4:1 at −20 °C. This ratio does not change over time, suggesting this is the thermodynamic ratio.

The identification of an η^4-*trans* diene coordinated to Ni may have implications concerning the mechanism for *trans*-1,4-enchainment of polybutadiene. DFT calculations by Tobisch and Taube indicate that the barrier to coupling of a π-allyl unit with an η^4-*s-trans*-butadiene is substantially higher than coupling with an η^4-*s-cis*-butadiene and that *trans*-enchained 1,4-polybutadiene is unlikely to result from insertion of η^4-*s-trans*-butadiene.[32] Indeed, there is good theoretical and experimental evidence that under conditions where high fractions of 1,4-*trans*-enchained polybutadiene are formed (coordinating anions or ligands present) *trans* enchainment results from insertion of *s-cis*-butadiene to yield an *anti*-allyl species followed by anti to syn isomerization prior to the next diene insertion.[11,13,32−36] Under ligand-free conditions using noncoordinating counteranions very low fractions of *trans* enchainment (ca. 2%) are always observed.[5,8,9,15,22] While the observed equilibrium between an η^4-*s-trans*-1,3-diene complex, **9**, and the *s-cis* form, **8**, certainly does not imply an *s-trans*-butadiene Ni complex is involved in chain growth, it is worth careful consideration as to whether a high energy insertion pathway via the *s-trans* isomer may be responsible for the small fraction of *trans*-enchainment under ligand-free conditions.

Qualitative experiments were performed to assess the binding strengths of 1,3-dienes to the (cyclohexenyl)nickel(II) fragment. Exposing a solution of η^4-butadiene species **4** at −60 °C to 2 equiv of IP leads to a 3:1 ratio of complexes **5** and **4**, indicating a slight preference for binding the more electron-rich IP to the nickel center. We have observed a similar trend for preferential coordination of more electron-rich arenes to cationic (allyl)nickel(II) and (allyl)palladium(II) fragments.[25] No insertion of BD or IP is observed at this temperature. When the temperature is raised, the resonances for the η^4-BD coordinated species **4** broaden, while those for the η^4-IP species remain fairly sharp. At −10 °C, the resonances for **4** are broadened into the baseline, and at 0 °C both species exhibit broad resonances, indicating exchange of dienes on the NMR time scale.

An interesting reaction is observed upon the addition of cyclopentadiene to ligand-free **3** or mesitylene complex **2**. Exposure of species **3** to 2 equiv of cyclopentadiene at −80 °C results in a rapid color change from yellow-brown to green-yellow. The ^{1}H NMR spectrum indicates the formation of [(cyclopentadienyl)Ni(η^4-cyclopentadiene)][B(Ar$_F$)$_4$] (**10**), which was independently synthesized through protonation of Cp_2Ni with [H(OEt$_2$)][B(Ar$_F$)$_4$]. [(cyclopentadienyl)Ni(η^4-cyclopentadiene)]$^+$ with BF_4^-[37] or OTf$^-$[38] as counteranions

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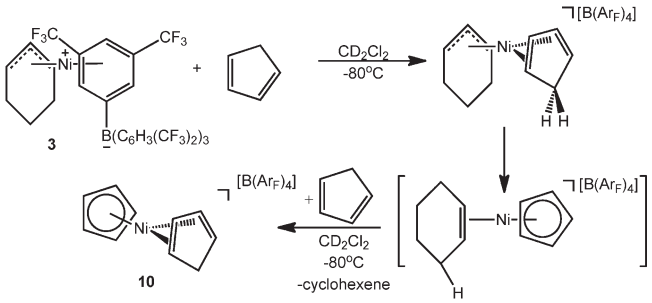
Scheme 6. Addition of Cyclopentadiene to Ligand-Free Species 3 at −80 °C



has previously been reported. This species is quite robust and is not active for butadiene polymerization. Similarly, exposure of complex **2** to 3 equiv of cyclopentadiene at 0 °C leads to the direct formation of species **10** and 1 equiv of cyclohexene. This product forms via hydrogen atom transfer from cyclopentadiene to the cyclohexenyl group. In the ^{1}H NMR spectrum, all mestiylene is now uncoordinated, as indicated by a downfield shift of the aryl singlet resonance to 6.79 ppm. We propose this reaction occurs through a mechanism similar to that observed for the hydrogen transfer reactions when 1-hexene is exposed to [(2-R-allyl)Ni(mes)]$^{+}$[25] (Scheme 6). Coordination of η^4-cyclopentadiene likely occurs prior to hydrogen atom transfer. This speculation is supported by observation of a minor amount of a transient complex tentatively assigned as [(cyclohexenyl)Ni(η^4-cyclopentadiene)]$^{+}$ in the ^{1}H NMR spectrum at −80 °C.

Polymerization Screening. [(cyclohexenyl)Ni(mes)][B(Ar_F)$_4$] (**2**) is active for the polymerization of 1,3-dienes. The polymerization of 850 equiv of 1,3-CHD is achieved within 1 h at room temperature in methylene chloride. Upon monomer addition, the solution changes color from red-orange to yellow. The reaction is highly exothermic, and within 2 min the solution temperature has risen substantially. The polymer produced is insoluble in CH_2Cl_2 and precipitates as a white powder (85% isolated). Additionally, catalyst **2** is active for DMBD polymerization at room temperature in CH_2Cl_2. Within 6 h, 32% conversion is achieved using **2** as the initiator. The polymer produced is also insoluble in CH_2Cl_2 and precipitates from solution. Within 6 h catalyst decomposition has occurred, as evidenced by a colorless solution. The mesitylene catalyst is not active for polymerization of 1,3-CHD or DMBD at temperatures much below 0 °C. Efforts to further characterize the highly insoluble polymers were unsuccessful. Details of these polymerizations can be found in the Supporting Information.

Reaction with Olefins. Reaction of mesitylene complex **2** with olefins leads to hydrogen atom transfer products, analogous to the findings reported for the [(2-R-allyl)-Ni(mes)][B(Ar_F)$_4$] complexes (R = H, Me).[25] Exposure of 4−5 equiv of 1-hexene to species **2** at room temperature generates 1 equiv of cyclohexene and a new allyl complex, [(2-hexenyl)Ni(mes)][B(Ar_F)$_4$] (**11**), after 24 h (Scheme 7). Rapid isomerization of 1-hexene to the internal 2- and 3-isomers is observed within 10 min of olefin addition, and only minor formation of the new allyl species occurs at 10 min. After 2.5 h, the ^{1}H spectrum shows a signal for the olefinic hydrogens of cyclohexene at 5.66 ppm and a new allyl resonance integrating for 2H at 3.11 ppm, with complex **2** still present in solution. We previously reported the characterization of species **11**.[25] This intramolecular hydrogen atom transfer reaction in the cyclohexenyl system is much slower in comparison to the case for the [(allyl)Ni(mes)]$^{+}$ system. Similar to previous experiments, the addition of ethylene produced ethylene oligomers.[25]

The mechanism to form complex **11** involves intramolecular hydrogen atom transfer from hexene to the cyclohexenyl moiety. ^{1}H NMR studies show that rapid isomerization of 1-hexene to the 2- and 3-hexene isomers occurs prior to hydrogen atom transfer; however, the details of the isomerization mechanism are still unclear. We know from previous experiments that the internal *cis*-2-hexene and *trans*-2-hexene isomers also undergo hydrogen atom transfer reactions with (allyl)Ni(mes)$^{+}$.[25] It is uncertain as to which isomer or isomers of hexene are needed to generate complex **11**. Following isomerization, hydrogen atom transfer from hexene generates 1 equiv of cyclohexene and complex **11** after trapping with mesitylene.

Reaction of 2 with DMBD. When complex **2** is treated with DMBD, a new (allyl)nickel(II) product which results from carbon−carbon coupling is formed. The reaction of 40 equiv of DMBD with **2** was monitored at −20 °C using ^{1}H NMR spectroscopy. A new allyl species displaying two allyl resonances, a *syn* resonance at 3.38 ppm (s, 1H) and an *anti* resonance at 2.65 ppm (s, 1H), is formed. This species also exhibits two broad olefinic triplets characteristic of an unsymmetrically substituted cyclohexene at 5.43 and 5.66 ppm. Structure **12** is consistent with these NMR data. There is no evidence of cyclohexene (δ 5.66, 1.61, 1.26) in the ^{1}H NMR spectrum, as would be expected if hydrogen atom transfer to the cyclohexenyl ligand occurred. The expected upfield resonances for species **12** are masked by excess DMBD and oligomers present in solution; therefore, the structure assignment is not fully confirmed.

Scheme 8 shows a plausible sequence to form presumed **12**. η^4 coordination of DMBD occurs first, and this species then undergoes C−C coupling followed by trapping with mesitylene. Although the formation of η^4-diene complexes has never been observed at low temperature by ^{1}H NMR when **2** is exposed to 1,3-dienes, we believe DMBD likely coordinates in an η^4 fashion to facilitate C−C coupling. This new allyl species, **12**, is similar to the previously reported assignment of the coupling product of an allyl moiety and DMBD formed in the reaction of [(allyl)Ni(mes)][B(Ar_F)$_4$] with 40 equiv of DMBD.[22] The strong similarity of these reactions supports the structural assignment of **12**.

The above experiments support the hypothesis that chain transfer in 1,3-diene polymerization probably occurs through intramolecular hydrogen atom transfer in which a discrete Ni−H intermediate is unlikely.[25,39] Observation of intramolecular hydrogen atom transfer from added olefin to the cyclohexenyl fragment supports a mechanism in which chain transfer in Ni(II) butadiene polymerizations occurs via a hydrogen atom transfer, adding experimental credence to Tobisch's DFT calculations.[40]

Summary

The reactions of cationic (cyclohexenyl)nickel(II) complexes with olefins and 1,3-dienes were investigated. Exposure

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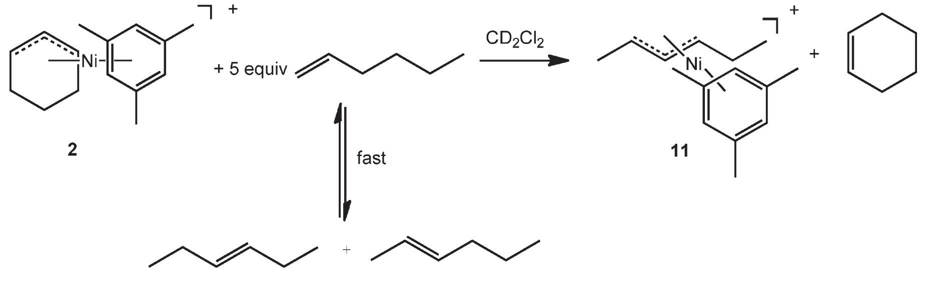
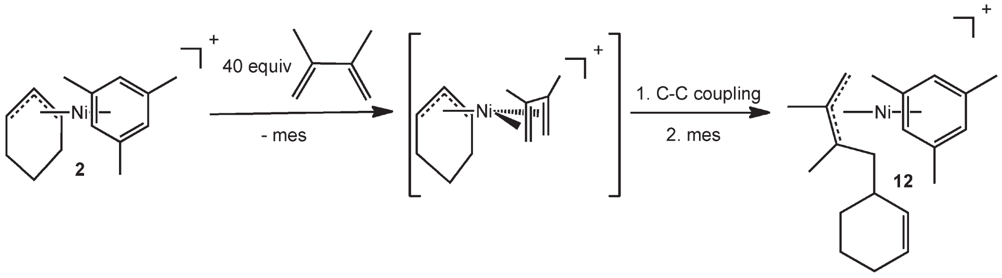
(39) Taube, R.; Wache, S.; Langlotz, J. Mol Mass Regulation in the Allyl Nickel Complex Catalyzed 1,4-*cis* Polymerization of Butadiene. In *Catalyst Design for Tailor-Made Polyolefins. Studies in Surface Science and Catalysis*; Soga, K., Terano, M., Eds.; Elsevier: Tokyo, 1994; pp 315−325.

(40) Tobisch, S. *Macromolecules* **2003**, *36*, 6235–6244.

Scheme 7. Reaction of 1-Hexene with Complex 2 at Room Temperature



Scheme 8. C−C Coupling of Complex 2 with DMBD



of [(cyclohexenyl)Ni(NCMe)$_2$][B(Ar$_F$)$_4$] to 2 equiv of B(C$_6$F$_5$)$_3$ generated the ligand-free species [(cyclohexenyl)-Ni][B(Ar$_F$)$_4$] (**3**) at low temperatures. Stable (η^4-diene)-Ni(cyclohexenyl)$^+$ complexes (diene = BD, IP, DMBD, 1,3-CHD, and 1,4-CHD) have been observed for the first time by reaction of **3** with dienes. These (cyclohexenyl)nickel(II) 1,3-diene complexes are more thermally stable than their acyclic analogues. The mesitylene complex **2** serves as an initiator for polymerization of 1,3-CHD and DMBD. Significantly, the first example of an η^4-*s-trans* 1,3-diene coordinated to a Ni(II) center has been observed.[41] Additionally, we have observed intramolecular hydrogen atom transfer reactions from olefin to the cyclohexenyl moiety when [(cyclohexenyl)Ni(mes)][B(Ar$_F$)$_4$] was treated with 1-hexene and η^4-cyclopentadiene. Such hydrogen transfer reactions are likely closely related to chain transfer reactions in Ni(II)-catalyzed diene polymerizations.

Experimental Section

General Considerations. All reactions, unless otherwise stated, were conducted under an atmosphere of dry, oxygen-free argon using standard high-vacuum, Schlenk, or drybox techniques. Argon was purified by passage through BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. All nickel catalysts were stored under argon in an M. Braun glovebox at −35 °C. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DRX 500 MHz, a Bruker DRX 400 MHz, or a Bruker 300 MHz spectrometer. Chemical shifts are referenced relative to residual CHCl$_3$ (δ 7.24 for ^{1}H), CH(D)Cl$_2$ (δ 5.32 for ^{1}H), ^{13}CD$_2$Cl$_2$ (δ 53.8 for ^{13}C), ^{13}CDCl$_3$ (δ 77.0 for ^{13}C). Elemental analyses were performed by Robertson Microlit Laboratories of Madison, NJ.

Materials. All solvents were deoxygenated and dried by passage over columns of activated alumina.[42] CD$_2$Cl$_2$, purchased from Cambridge Laboratories, Inc., was dried over CaH$_2$, vacuum-transferred to a Teflon-sealable Schlenk flask containing 4 Å molecular sieves, and degassed via three freeze−pump−thaw cycles. Butadiene and isoprene were purchased from Aldrich and purified by vacuum transfer through a column of 4 Å molecular sieves and stored under argon at −35 °C. 1,3-Cyclohexadiene was purified by drying over NaBH$_4$ overnight, vacuum-transferred to a Teflon-sealable flask, and degassed via three freeze−pump−thaw cycles. 2,3-Dimethyl-1,3-butadiene and 1,4-cyclohexadiene were purified by degassing using three freeze−pump−thaw cycles. Ni[COD]$_2$ and B(C$_6$F$_5$)$_3$ were purchased from Strem. NaB(Ar$_F$)$_4$ (Ar$_F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$),[43] nickelocene (Cp$_2$Ni),[44] and [H(OEt$_2$)][B(Ar$_F$)$_4$][45] were synthesized according to literature methods. Cyclopentadiene was distilled fresh prior to use through cracking of dicyclopentadiene purchased from Aldrich and stored cold. 1-Hexene was purchased from Aldrich, dried over CaH$_2$, and vacuum-transferred to a sealable flask. Acetonitrile, mesitylene (mes), hexamethylbenzene (hmb), mesitylene-d_{12}, and 3-bromocyclohexene were purchased from Aldrich or Acros and used without further purification. [(cyclohexenyl)NiBr]$_2$ was synthesized according to literature methods.[2]

Spectral Data for [B(Ar$_F$)$_4$]$^-$. The ^{1}H and ^{13}C spectral data for the B(Ar$_F$)$_4$$^-$ counteranion were unchanged for all Ni(II) cationic complexes and are not included in the characterization unless otherwise stated. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 20 °C): δ 7.72 (s, 8H, Ar$_F$ H$_o$), 7.57 (s, 4H, Ar$_F$ H$_p$). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, 20 °C): δ 162.1 (q, $^1J_{C-B}$ = 49.8 Hz, Ar$_F$ C$_{ipso}$), 135.2 (s, Ar$_F$ C$_o$), 129.2 (qq, $^3J_{C-B}$ = 3.0 Hz, $^2J_{C-F}$ = 34.4 Hz, Ar$_F$ CF$_3$), 122.3 (q, $^1J_{C-F}$ = 273.2 Hz, Ar$_F$ CF$_3$), 117.8 (bt, Ar$_F$ C$_p$).

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[41] For examples of mononuclear *s-trans*-butadiene complexes of early metals see: (a) Strauch, H. C.; Wibbeling, B.; Fröhlich, R.; Erker, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 3082–3812. (b) Strauch, J. W.; Fauré, J.-L.; Bredeau, S.; Wang, C.; Kehr, G.; Fröhlich, R.; Luftmann, H.; Erker, G. *J. Am. Chem. Soc.* **2004**, *126*, 2089–2104. (c) Wang, L.; Fettinger, J. C.; Poli, R.; Meunier-Prest, R. *Organometallics* **1998**, *17*, 2692–2701.

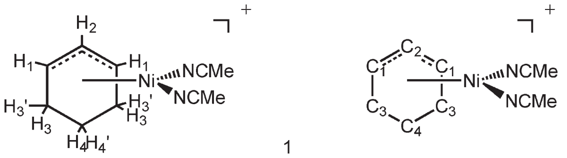
[42] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[43] Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579–3581.

[44] Wilkinson, G.; Pauson, P. L.; Cotton, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 1970–1974.

[45] Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3290–3922.

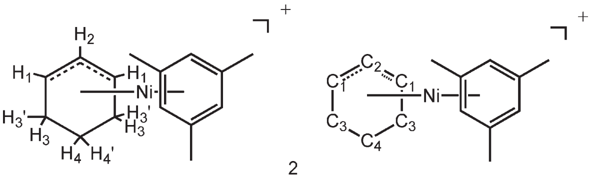
Synthesis of (Cyclohexenyl)nickel(II) Complexes. [(Cyclohexenyl)Ni(NCMe)$_2$][B(Ar$_F$)$_4$] (1).



1

A flame-dried Schlenk tube was charged with [(cyclohexenyl)NiBr]$_2$ dimer (0.070 g, 0.159 mmol) and NaB(Ar$_F$)$_4$ (0.282 g, 0.318 mmol) and cooled to −78 °C. The solids were dissolved in diethyl ether (10.0 mL) to yield an orange solution with a fine precipitate. Acetonitrile (33.2 μL, 0.636 mmol) was added, and the solution turned yellow. The reaction mixture was then warmed to room temperature and stirred for 1 h. The solution was filtered via cannula filter, and the volatiles were removed in vacuo to yield a yellow oily product. The oil was washed with pentane (6.0 mL) and stirred vigorously for 30 min. At this point a yellow powder was allowed to settle and the liquid layer was decanted. The powder was dried in vacuo. Excess NaB(Ar$_F$)$_4$ was removed through an additional filtration step in which the yellow powder was dissolved in CH$_2$Cl$_2$ (5.0 mL) and the solution filtered through a Celite pad. The volatiles were removed in vacuo to yield a yellow oil. Pentane (5.0 mL) was added, and the product was again stirred until a yellow powder formed. The pentane layer was decanted, and the yellow powder was dried in vacuo overnight to yield 56% of **1** (0.190 g, 0.175 mmol). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C): δ 5.70 (t, $^{3}J_{H-H}$ = 6.5 Hz, 1H, H$_2$), 5.86 (t, $^{3}J_{H-H}$ = 6.5 Hz, 2H, H$_1$), 2.23 (s, 6H, CNCH$_3$), 1.71 (br. m, 2H, H$_3$), 1.61 (m, 1H, H$_4$), 1.41 (m, 2H, H$_{3'}$), 0.78 (m, 1H, H$_{4'}$). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): δ 107.6 (s, C$_2$), 77.6 (s, C$_1$), 29.1 (s, C$_3$), 17.6 (s, C4), 3.5 (br. s, NC*C*H$_3$). The nitrile carbon could not be located. Anal. Calcd for C$_{42}$H$_{27}$N$_2$BNi: C, 46.49; N, 2.58; H, 2.47. Found: C, 46.40; N, 2.41; H, 2.34.

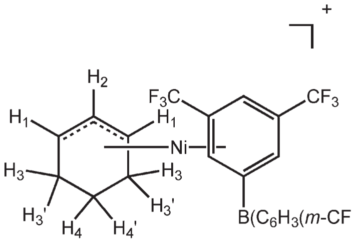
[(Cyclohexenyl)Ni(mes)][B(Ar$_F$)$_4$] (2).



2

A flame-dried Schlenk flask was charged with [(cyclohexenyl)NiBr]$_2$ dimer (0.150 g, 0.314 mmol) and NaB(Ar$_F$)$_4$ (0.604 g, 0.682 mmol) and cooled to −78 °C in a dry ice–isopropyl alcohol bath. Dry diethyl ether (10.0 mL) was added, yielding an orange solution with a fine brown precipitate. After approximately 5 min of stirring, mesitylene (190 μL, 1.36 mmol) was added dropwise via syringe. The solution was warmed to 0 °C and stirred for 1 h. The solution was filtered via cannula filter, and the solvent was removed in vacuo to yield a red powder. The solid was purified by dissolving in a minimal amount of methylene chloride and filtering through Celite. The volatiles were then removed in vacuo to give **2** in 65% yield (0.491 g, 0.437 mmol). Brick red X-ray-quality crystals of the complex were obtained by dissolving complex **2** in CH$_2$Cl$_2$ (2.0 mL), layering with pentane (6.0 mL), and storing in a freezer at −35 °C for 4 days. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): δ 6.52 (s, 3H, mes$_{CH}$), 5.86 (t, $^{3}J_{H-H}$ = 6.3 Hz, 1H, H$_2$), 4.81 (td, $^{3}J_{H-H}$ = 6.3 Hz, $^{3}J_{H-H}$ = 1.8 Hz, 2H, H$_1$), 2.34 (s, 9H, mes$_{CH_3}$), 1.57−1.17 (m, 6H, H$_3$, H$_{3'}$, H$_4$, H$_{4'}$). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): 123.9 (s, mesC$_{Ar}$), 109.7 (s, mesC$_{ArCH_3}$), 100.4 (s, C$_2$), 78.4 (s, C$_1$), 28.5 (s, C$_3$), 20.2 (s, C$_4$), 20.2 (s, mes*C*H$_3$, overlapping with C$_4$). Anal. Calcd for C$_{47}$H$_{33}$F$_{24}$BNi: C, 50.26; H, 2.97. Found: C, 49.04; H, 2.97.

In Situ Generation of [(cyclohexenyl)Ni(η^4-diene)][B(Ar$_F$)$_4$] Complexes. [(Cyclohexenyl)Ni(B(Ar$_F$)$_4$] (3).

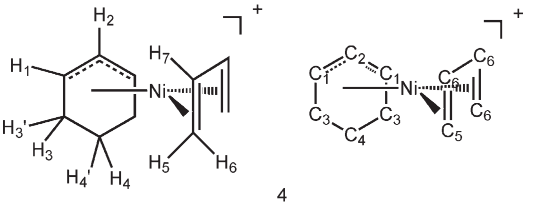


3

A screw-top NMR tube was charged with **1** (0.010 g, 0.009 mmol) and B(C$_6$F$_5$)$_3$ (0.024 g, 0.047 mmol). The NMR tube was cooled to −80 °C in a dry ice−acetone bath. The tube was placed under an argon stream, and the two solids were dissolved in CD$_2$Cl$_2$. The NMR tube was quickly inverted to allow for mixing and placed again in the cold bath. The solution turned from bright yellow to yellowish brown, which is indicative of ligand-free complex formation. The tube was placed into a precooled NMR probe, and the reaction was monitored by ^{1}H NMR spectroscopy. An equilibrium exists between starting complex **1** and species **3**. The ratio of **1**:**3** is 1:4 at −20 °C. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, −60 °C): δ 8.04 (s, 1H, Ar$_{Fp}$ coordinated), 7.74 (s, 6H, Ar$_{Fm}$), 7.66 (s, 3H, Ar$_{Fp}$), 7.22 (s, 2H, Ar$_{Fm}$ coordinated), 4.60 (br s, 2H, H$_1$), 4.00 (br t, 1H, H$_2$), 2.70 (s, borane adduct of CH$_3$CN), 2.32 (s, 2H, H$_3$), 1.10 (br. s, 4H, H$_{3'}$, H$_4$, H$_{4'}$). ^{19}F NMR (471 MHz, CD$_2$Cl$_2$, −40 °C): δ −62.7 (s, 6F), −62.9 (s, 18F).

^{1}H NMR Line-Broadening Experiments To Determine Barrier to Ni Migration among the Ar$_F$ Rings of [B(Ar$_F$)$_4$]$^-$ in Species 3. A solution of **3** was prepared in CD$_2$Cl$_2$ as described above. Broadening of the coordinated Ar$_F$ ^{1}H resonance, corresponding to Ar$_F$ H$_p$ (8.04 ppm), was monitored between −70 and −35 °C. The initial half-height line width was 10 Hz at −70 °C, 12 Hz at −56 °C, 15 Hz at −46 °C, and 23 Hz at −35 °C. The rate constants, calculated from the slow exchange approximation ($k_{ex} = \pi\Delta\omega$) at the temperatures listed above, are k_{ex} = 6.3, 15.7, 40.8 s^{-1}, where $\Delta\omega$ = 2, 5, 13 Hz, respectively ($\Delta G^{\ddagger}_{avg}$ = 11.9 kcal/mol, average of three values).

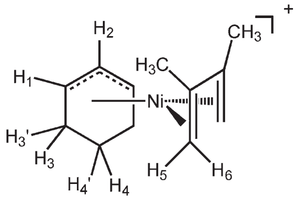
[(Cyclohexenyl)Ni(η^4-butadiene)][B(Ar$_F$)$_4$] (4).



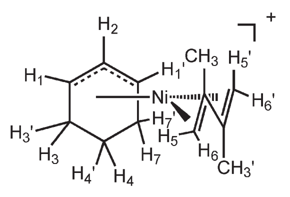
4

A dry screw-top NMR tube was charged with **1** (0.010 g, 0.009 mmol) and B(C$_6$F$_5$)$_3$ (0.009 g, 0.018 mmol) and cooled to −78 °C. The tube was placed under argon, and the solids were dissolved in CD$_2$Cl$_2$ and quickly mixed by inversion of the tube. Two equivalents of butadiene (0.37 M in CD$_2$Cl$_2$; 50 μL, 0.019 mmol) was added via syringe, and the NMR tube was quickly inverted to allow for mixing as previously described.[15] The NMR tube was placed in a precooled probe and monitored by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, −53 °C): δ 6.77 (t, $^{3}J_{H-H}$ = 6.5 Hz, 2H, H$_1$), 6.25 (m, 2H, H$_7$), 5.91 (t, $^{3}J_{H-H}$ = 6.5 Hz, 1H, H$_2$), 5.20 (d, $^{3}J_{H-H}$ = 7.0 Hz, 2H, H$_5$), 3.26 (dd, $^{3}J_{H-H}$ = 14.0 Hz, $^{2}J_{H-H}$ = 1.5 Hz, 2H, H$_6$), 2.09 (br m, 2H, H$_3$), 1.21 (m, 1H, H$_4$), 0.73 (m, 1H, H$_{4'}$), 0.59 (m, 2H, H$_{3'}$). ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, −53 °C): δ 111.4 (s, C$_2$), 109.2 (s, C$_6$), 90.4 (s, C$_1$), 83.0 (s, C$_5$), 28.8 (s, C$_3$), 14.3 (s, C$_4$). The solution remained yellow until insertion occurred, and then the solution turned orange (∼ −20 °C).

[(Cyclohexenyl)Ni(η^4-s-*cis*-2,3-dimethyl-1,3-butadiene)][B(Ar$_F$)$_4$] (8) and [(cyclohexenyl)Ni(η^4-s-*trans*-2,3-dimethyl-1,3-butadiene)]-[B(Ar$_F$)$_4$] (9).



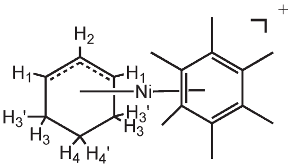
8



9

This experiment was conducted using the procedure described above for the formation of complex **5**. Complex **1** (0.010 g, 0.009 mmol) and B(C$_6$F$_5$)$_3$ (0.009 g, 0.018 mmol) were dissolved in CD$_2$Cl$_2$ (600 μL), and 2,3-dimethyl-1,3-butadiene (1.1 μL, 0.010 mmol) was added. Species **9** is observed in solution along with **3** and **8** at −80 °C. At −20 °C only **8** and **9** are observed in solution. The ratio **8**:**9** in solution at −20 °C is 4:1. Complex **8**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, −80 °C) δ 6.54 (t, $^3J_{H-H}$ = 6.8 Hz, 2H, H$_1$), 5.77 (t, $^3J_{H-H}$ = 6.5 Hz, 1H, H$_2$), 4.97 (s, 2H, H$_5$), 2.93 (s, 2H, H$_6$), 2.21 (s, 6H, CH$_3$), 2.18 (br m, 2H, H$_3$), 1.27 (br s, 1H, H$_4$), 0.85−0.48 (br m, 3H, H$_{4'}$, H$_{3'}$). Complex **9**: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, −20 °C) δ 6.32 (br m, 1H, H$_1$), 6.30 (br m, 1H, H$_{1'}$), 5.33 (t, 1H, H$_2$, under CDHCl$_2$), 5.19 (s, 1H, H$_5$), 5.04 (s, 1H, H$_{5'}$, under free DMBD), 4.46 (s, 1H, H$_6$), 4.30 (s, 1H, H$_{6'}$), 1.94 (s, 3H, CH$_{3'}$), 1.50 (s, 3H, CH$_3$), CH$_2$ groups masked by *cis* isomer and oligomers of DMBD. Insertion of DMBD occurs upon warming to −10 °C.

Assessment of the Lability of Coordinated Mesitylene in Complex 2. Reaction of Complex 2 with Hexamethylbenzene (hmb).

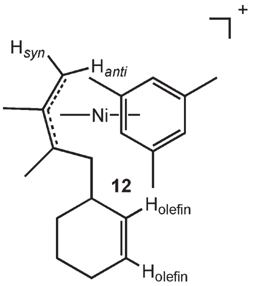


A screw-top NMR tube was charged with **2** (0.005 g, 0.004 mmol) and hmb (0.004 g, 0.022 mmol), and these compounds were dissolved at room temperature in CD$_2$Cl$_2$ (500 μL). The NMR tube was shaken to allow for mixing. Within 10 min of addition of CD$_2$Cl$_2$ to the tube, the ^{1}H NMR spectrum was recorded for this reaction. The reaction was then monitored by ^{1}H NMR spectroscopy every 1 h until complete conversion. After 10 min, the ratio **2**:[(cyclohexenyl)Ni(hmb)]$^+$ was 1:9, and after 1 h complete conversion to the hmb complex was achieved. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): δ 5.68 (t, $^3J_{H-H}$ = 6.6 Hz, 1H, H$_2$), 4.26 (br t, 2H, H$_1$), 2.28 (s, 18H, CH$_3$), 1.47−1.37 (m, 3H, H$_3$, H$_4$), 1.11−0.99 (m, 3H, H$_{3'}$, H$_{4'}$).

Reaction of 2 with Mesitylene-*d*$_{12}$. A screw-cap NMR tube was charged with **2** (0.005 g, 0.004 mmol), and the compound was dissolved in CD$_2$Cl$_2$ (500 μL) in the glovebox. Mesitylene-*d*$_{12}$ (3.1 μL, 0.022 mmol) was then introduced via syringe. The reaction was monitored at room temperature by ^{1}H NMR spectroscopy. The first spectrum was recorded 10 min after the addition of mesitylene-*d*$_{12}$, and at this point the ratio **2**:**2**-*d*$_{12}$ was 3:7, as determined from integrating free (δ 6.79) vs bound mesitylene (δ 6.55). After 4 h, the ratio changed to 1:6, and this value did not change overnight.

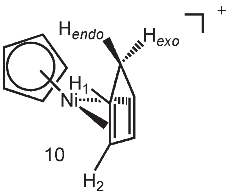
In Situ Observation of [(2-hexenyl)Ni(mes)][B(Ar$_F$)$_4$] (11). A J. Young tube was charged with complex **2** (0.010 g, 0.009 mmol), and the compound was dissolved in 500 μL of CD$_2$Cl$_2$. 1-Hexene (5.0 μL, 0.040 mmol) was then added, and the tube was inverted to allow for mixing. The reaction was monitored by ^{1}H NMR spectroscopy. Only the observable resonances for complex **11**, which are not masked by excess hexene, are reported. Formation of cyclohexene is also observed in the ^{1}H NMR spectrum. Characteristic resonances: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C) δ 6.44 (s, 3H, mesAr$_H$), 5.66 (br s, free cyclohexene), 3.11 (m, 2H, H$_{anti}$), 2.32 (s, 9H, mesCH$_3$).[25]

In Situ Generation of Coupling Product 12.



Complex **2** (0.010 g, 0.009 mmol) was added to a screw-cap NMR tube, and the compound was dissolved in CD$_2$Cl$_2$ (600 μL). The NMR tube was cooled to −80 °C and then charged with 2,3-dimethyl-1,3-butadiene (60.4 μL, 0.534 mmol) and quickly mixed by inversion of the tube. The solution remained deep red. The reaction was monitored at low temperatures using ^{1}H NMR spectroscopy. Polymerization of DMBD occurred upon warming to 10 °C, with polyDMBD precipitating out of solution. Formation of **12**, the C−C coupling product of DMBD and complex **2**, is observed at 10 °C. Complete identification of all resonances for **12** could not be established, due to the presence of excess DMBD, which masks many of the signals. Here we report the observable characteristic peaks assigned to complex **12**.[25] ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 10 °C): δ 6.42 (s, 3H, mesAr$_H$), 5.66 (br t, 1H, H$_{olefin}$), 5.43 (t, 1H, $^3J_{H-H}$ = 8.5 Hz, H$_{olefin}$), 3.38 (s, 1H, H$_{syn}$), 2.65 (s, 1H, H$_{anti}$), 2.31 (s, 9H, mesCH$_3$), 0.89 (s, 3H, CH$_3$). The resonances for the methyl and methylene groups are masked by excess DMBD and oligomers in solution.

Reaction of 3 with Cyclopentadiene To Form [(cyclopentadienyl)Ni(η^4-cyclopentadiene)][B(Ar$_F$)$_4$] (10).



10

Complex **2** or **3** (0.010 g) was added to a screw-cap NMR tube and cooled to −80 °C in a cold bath. The complex was dissolved in 600 μL of CD$_2$Cl$_2$ and mixed. Cyclopentadiene (2−3 equiv) was added, and the reaction mixture was quickly mixed again. The solution remained red until the temperature rose to 0 °C. At temperatures above 0 °C, the solution turned yellow-green and complex **10** was formed. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): δ 7.09 (br s, 2H, H$_2$), 6.79 (s, free mesitylene), 5.78 (s, 5H, Cp$_H$), 5.66 (s, free cyclohexene), 5.41 (t, 2H, $^3J_{H-H}$ = 2.4 Hz, H$_1$), 3.30 (roofed dt, 1H, $^2J_{H-H}$ = 22.0 Hz, $^3J_{H-H}$ = 2.4 Hz, H$_{endo}$), 3.03 (roofed d, 1H, $^2J_{H-H}$ = 22.0 Hz, H$_{exo}$), 1.61 (bs, free cyclohexene), 1.26 (bs, free cyclohexene). These data match literature values[37,38] and those of an independently generated sample (see the Supporting Information).

Crystallographic Information. The molecular structure for complex **2** was determined using a Bruker APEX II diffractometer at −173 °C equipped with Mo radiation. All necessary information regarding the crystal structure data can be found in the Supporting Information and Figure 1.

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Supporting Information Available: Text, tables, figures, and a CIF file giving experimental details and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.