Organometallics **1994**, *13*, 2066-2074

Synthesis of Allylnickel Aryloxides and Arenethiolates: Study of Their Dynamic Isomerization and 1,3-Diene Polymerization Activity

Philip D. Hampton,* Si Wu, and Todd M. Alam

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Jerome P. Claverie

Division of Chemistry and Chemical Engineering, 164-30, California Institute of Technology, Pasadena, California 91125

Received November 1, 1993[⊗]

A new family of allylnickel(II) complexes, $[Ni(\eta^3\text{-allyl})(\mu\text{-X})]_2$ (X = ArO, ArS), have been synthesized by anion metathesis of the sodium or lithium salts of aryloxides or arenethiolates with $[Ni(\eta^3\text{-allyl})(\mu\text{-Br})]_2$. The complexes are proposed to be dimeric and to consist of a mixture of cis and trans isomers. A dynamic process rapidly equilibrates the cis and trans isomers of the pentafluorophenoxide, 2,6-difluorophenoxide, and 3,5-bis(trifluoromethyl)phenoxide complexes on the ^1H NMR time scale. The 2,6-dimethylphenoxide, 2,6-diisopropylphenoxide, 2,4,6-tris(trifluoromethyl)phenoxide, and pentafluorothiophenoxide complexes are static at room temperature. A variable-temperature NMR study of the 3,5-bis(trifluoromethyl)phenoxide complex provided activation enthalpy and entropy values of 12.9 kcal/mol and −6.6 cal/(K mol), respectively. Allyl rotation or cleavage of one of the μ-X bridges is proposed as the mechanism for the isomerization. The pentafluorophenoxide, 3,5-bis(trifluoromethyl)phenoxide, and 2,4,6-tris(trifluoromethyl)phenoxide complexes initiate the rapid polymerization of 1,3-cyclohexadiene and 1,3-butadiene to form high-molecular weight, 1,4-linked polymers.

Introduction

Allylnickel complexes have received considerable attention for their ability to initiate the polymerization of 1,3-dienes.[1-4] The poly(1,3-dienes) produced by transition-metal initiators can possess either a 1,2- or a 1,4-linked structure, and the alkene units in the 1,4-linked polymer backbone can be cis or trans. Since the activity, regiospecificity, and stereospecificity of 1,3-diene polymerization is observed to depend strongly on the nature of the initiator, there is great interest in the design of new allylnickel initiators that allow for greater control of polymer structure and molecular weight.

Three general routes have been reported for the synthesis of allylnickel complexes: (1) oxidative addition of allyl–X (X = Cl, Br, I, O_2CCF_3) to either $Ni(CO)_4$ or bis(cycloocta-1,5-diene)nickel ($[Ni(COD)_2]$), (2) anion metathesis with $[Ni(\eta^3\text{-allyl})(\mu\text{-Br})]_2$, and (3) protonation of diallylnickel complexes. Teyssié and co-workers have reported the synthesis of $[Ni(\eta^3\text{-allyl})(\mu\text{-}O_2CCX_3)]_2$ complexes (X = F, Cl, Br) by either route 1 or 3 and have examined the 1,3-diene polymerization activity of the complexes.[2] The trifluoroacetate complex (X = F) is reported to be a "living" initiator for the 1,4-polymerization of 1,3-butadiene in the presence of additives (triphenyl phosphite, *o*-chloranil) and exhibits a dynamic isomerization on the NMR time scale.[2e,f] Taube and co-workers have prepared $[(\eta^3{:}\eta^2{:}\eta^2\text{-dodecatrienyl})nickel]X$ complexes (X = PF_6^-, SbF_6^-, BF_4^-) by protonation of the diallyl complex $[(\eta^3{:}\eta^2{:}\eta^3\text{-dodeca-2}(Z),6(E),10(Z)\text{-triene-1,12-diyl})nickel(II)]$.[3] The activity of these allylnickel complexes and the stereoselectivity of the resulting polymers are observed to depend on the electronegativity of the X anion, where initiators that possess electron-withdrawing X exhibit higher activities and higher cis content for the 1,4-linked polymer.[2b,d,3]

Despite the ease of variation of the steric and electronic properties of alkoxide and aryloxide ligands, there have been only a few reports of the synthesis of allylnickel alkoxides and aryloxides and no reports of their ability to polymerize dienes. Bönnemann and co-workers have reported the synthesis of $[Ni(\eta^3\text{-allyl})(\mu\text{-OR})]_2$ (R = Me, Et, Ph) by anion metathesis and have observed the complexes to catalyze the dimerization of alkenes.[5] Yamamoto and co-workers have reported the synthesis of $[Ni(\eta^3\text{-allyl})(OPh)(PPh_3)]$ by the oxidative addition of allyl phenyl ether to $Ni(COD)_2$.[6]

This paper describes the synthesis of a new family of allylnickel(II) complexes, $[Ni(\eta^3\text{-allyl})(\mu\text{-X})]_2$, where X is

---

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

[1] (a) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235 and references therein. (b) Wilke, G.; Bogdanović, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151 and references therein. (c) Porri, L.; Aglietto, M. *Makromol. Chem.* **1976**, *177*, 1465.

[2] (a) Julémont, M.; Walckiers, E.; Warin, R.; Teyssié, P. *Makromol. Chem.* **1974**, *175*, 1673. (b) Dawans, F.; Teyssié, P. *Polym. Lett.* **1969**, *7*, 111. (c) Dawans, F.; Marechal, J. C.; Teyssié, P. *J. Organomet. Chem.* **1970**, *21*, 259. (d) Durand, J. P.; Dawans, F.; Teyssié, P. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 979. (e) Hadjiandreou, P.; Julémont, M.; Teyssié, P. *Macromolecules* **1984**, *17*, 2455. (f) Warin, R.; Julémont, M.; Teyssié, P. *J. Organomet. Chem.* **1980**, *185*, 413.

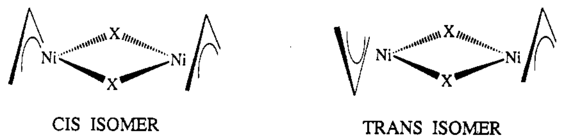
[3] Taube, R.; Schmidt, U.; Gehrke, J.-P.; Böhme, P.; Langlotz, J.; Wache, S. *Makromol. Chem., Makromol. Symp.* **1993**, *66*, 245 and references therein.

[4] Dolgoplosk, B. A.; Beilin, S. I.; Korshak, Y. V.; Chernenko, G. M.; Vardanyan, L. M.; Teterina, M. P. *Eur. Polym. J.* **1973**, *9*, 895.

[5] (a) Bönnemann, H. Ph.D. Thesis, Aachen, Germany, 1966. (b) Birkenstock, U.; Bönnemann, H.; Bogdanović, B.; Walter, D.; Wilke, G. In *Homogeneous Catalysis*; Gould, R. F., Ed.; Advances in Chemistry 70; American Chemical Society: Washington, DC, 1968; pp 251–265. (c) Bönnemann, H.; Jentsch, J.-D. *Appl. Organomet. Chem.* **1993**, *7*, 553.

[6] Yamamoto, T.; Ishizu, J.; Yamamoto, A. *Chem. Lett.* **1979**, 1385.

0276-7333/94/2313-2066$04.50/0



1: X= 2,6-dimethylphenoxide
2: X= 2,6-diisopropylphenoxide
3: X= 2,6-dichlorophenoxide
4: X= 2,6-difluorophenoxide
5: X= pentafluorophenoxide
6: X= 3,5-bis(trifluoromethyl)phenoxide
7: X= 2,4,6-tris(trifluoromethyl)phenoxide
8: X= pentafluorothiophenoxide

Figure 1. Proposed cis and trans isomer structures for complexes 1–8.

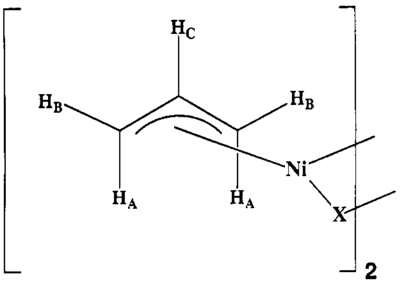


Figure 2. Allyl proton assignments for complexes 1–8.

an aryloxide or an arenethiolate ligand (Figure 1), that are well-defined initiators for the polymerization of 1,3-dienes. The polymerization activity of the complexes can be readily tuned through the steric and electronic properties of the aryloxide ligand. Several of the complexes exhibit a dynamic isomerization on the NMR time scale. The use of one of these catalysts (5; Figure 1) as an initiator for the polymerization of *cis*-5,6-bis(trimethylsiloxy)-1,3-cyclohexadiene has previously been reported in patent literature.[7]

Results and Discussion

Synthesis of Allylnickel Aryloxides and Arenethiolates. The allylnickel aryloxide and arenethiolate complexes 1–8 (Figure 1) have been isolated in high yield (72–99%) by anion exchange of lithium or sodium salts of phenols or thiophenols with $[Ni(\eta^3\text{-allyl})(\mu\text{-Br})]_2$ in diethyl ether. The very low yield (32%) obtained for the pentafluorothiophenoxide complex 8 is unoptimized and is a result of its extreme insolubility, which complicated its isolation.

All of the complexes 1–8 are orange to orange-red powders which are extremely air and moisture sensitive in solution. As solids in air, the complexes exhibit a slow decomposition to form a green product. Glovebox or Schlenk techniques were used in both the synthesis and handling of the compounds. The complexes are observed to decompose gradually above 50 °C in toluene. This thermal sensitivity is consistent with Bönnemann and coworkers' observation that $[Ni(\eta^3\text{-allyl})(\mu\text{-OPh})]_2$ decomposes at 65 °C.[5a] In the presence of a 1,3-diene, complexes 1–8 are more stable and exhibit no significant decomposition over 24 h at 50 °C.

Complexes 1–8 are proposed to be dimeric, as shown in Figure 1, and have been characterized by elemental analysis, FTIR, mass spectroscopy, and ^1H and ^{19}F NMR. The elemental analyses for complexes 2, 3, 5, and 8 were within standard errors, whereas complexes 1, 4, 6, and 7 provided poor elemental analyses. Hydrolysis or reaction with oxygen during the sample preparation is probably responsible for the low carbon and hydrogen contents. Similar poor analyses have been reported for other allylnickel(II) complexes.[2b,c] Low-resolution mass spectral analysis (EI) provided molecular ion peaks at *m/z* 456, 458, and 460 for complex 4 and *m/z* 564 and 568 for complex 5, which are consistent with a dimeric structure and with the natural-abundance isotopes of nickel (^{58}Ni and ^{60}Ni). The inability to observe molecular ions for the other complexes may be due to their low volatility and thermal instability. The proposed dimeric structure in Figure 1 is consistent with reported crystal structures for a number of allylnickel complexes, i.e. $[Ni(\eta^3\text{-}2\text{-}MeC_3H_4)(\mu\text{-}OCH_3)]_2$,[8] $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}SCH_3)]_2$,[8] $[Ni(\eta^3\text{-}2\text{-}EtOC(O)C_3H_4)(\mu\text{-}Br)]_2$,[9] and $[Ni(\eta^3\text{-}syn,syn\text{-}1,3\text{-}Me_2C_3H_3)(\mu\text{-}CH_3)]_2$.[8b,10] Many attempts have been made to prepare single crystals of complexes 1–8 to confirm their dimeric structure; however, the isolated crystals lost solvent and fractured.

Characterization of Nickel Complexes 1–8 by ^1H NMR. The dimeric complexes are proposed to consist of a mixture of cis and trans isomers as shown in Figure 1. As a result of their symmetry, the top and bottom faces are equivalent in the trans isomer and inequivalent in the cis isomer. The presence of cis and trans isomers is confirmed by ^1H NMR spectra of the complexes. The assignments of the H_A and H_B protons on the allyl ligand (Figure 2) were based upon their coupling with H_C, since the anti-periplanar H_A should have a larger coupling constant (11–13 Hz) than the syn-periplanar H_B proton (6–8 Hz). No geminal coupling between H_A and H_B is observed at either 250- or 400-MHz resonant frequencies; thus, this coupling constant must be small (<1 Hz). Small geminal coupling constants have been reported for other allylnickel complexes.[2f]

The ^1H NMR spectra for the 2,6-dimethylphenoxide (1), 2,6-diisopropylphenoxide (2), and pentafluorothiophenoxide (8) complexes are consistent with a static mixture of cis and trans isomers. For each of these complexes, the H_A and H_B allyl protons appear as two sets of doublets in the ^1H NMR spectrum. Complexes 1 and 2 each exhibit a total of three doublets for the meta protons in the 2,6-dimethylphenoxide and 2,6-diisopropylphenoxide ligands; two doublets are for the cis isomer, and the third doublet is for the trans isomer. The para protons in complexes 1 and 2 appear to be insensitive to the mixture of isomers, since only one triplet is observed. The isopropyl methyl groups in 2 appear as four doublets, which is also consistent with a mixture of cis and trans isomers. These observations indicate that rotation about the O–Ar bond in complexes 1 and 2 is slow on the NMR time scale.

The ratio of the cis and trans isomers can be determined on the basis of the resonances for the aryloxide ortho substituents in complexes 1 and 2. The upfield and downfield singlets for the methyl resonances in 1 are proposed to be the inequivalent methyl groups of the cis isomer, and the third singlet is the trans isomer. Since these singlets are in a 1:2:1 integral ratio, in order of decreasing chemical shift, the cis and trans isomers of complex 1 are present in a statistical (1:1) ratio. For complex 2, a total of three isopropyl methine multiplets

---

[7] Grubbs, R. H.; Gin, D. L.; Conticello, V. P.; Hampton, P. D.; Wheeler, D. R. U.S. Patent 5 128 418, 1992.

[8] (a) Gerding, B. Ph.D. Dissertation, Universität Essen, 1979. (b) Goddard, R.; Krüger, C. unpublished results, 1979. (c) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., Vol. 6, Chapter 37, 1982; pp 161–162.

[9] Churchill, M. R.; O'Brien, T. A. *Inorg. Chem.* **1967**, *6*, 1386.

[10] Krüger, C.; Sekutowski, J. C.; Berke, H.; Hoffmann, R. *Z. Naturforsch.*, *B* **1978**, *33*, 1110.

Table 1. Activation Parameters for the Cis–Trans Isomerization of Complexes 4–6 and Literature Activation Parameters for Allyl Isomerization

compd	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/(K mol))	$\Delta G^{\ddagger}$ (kcal/mol)
4/$CDCl_3$			~13^{a} (260 K)
5/$CDCl_3$			~13^{a} (249 K)
5/toluene-d_8			~11^{a} (219 K)
6/$CDCl_3$	12.9	−6.6	14.7^{a} (290 K)
$(\eta^5\text{-Cp})Mo(CO)_2(\eta^3\text{-allyl})_2^{b}$	11.7^{c}	-6.1^{c}	
$(\eta^5\text{-Cp})Mo(CO)_2\text{-}(\eta^3\text{-2-methylallyl})_2^{b}$	16.2^{c}	2.9^{c}	
$(\eta^3\text{-allyl})Fe(CO)_3I^{d}$			17.4 (298 K)
$(\eta^3\text{-allyl})_3Rh^{e}$	8.8^{c}		
$(\eta^3\text{-allyl})_2Fe(CO)_2^{f}$			4.6

[a] The free energy of activation was calculated at the indicated coalescence temperature using the equation $\Delta G^{\ddagger} = RT_c[22.96 + \ln(T_c/\delta)]$, where T_c is the coalescence temperature in K and δ is the chemical shift difference in the absence of exchange.[11] [b] Reference 16a. [c] Calculated at 298 K using activation energy values found in the literature references. [d] Reference 16b. [e] Reference 16c. [f] References 16d,e.

are observed in the ^1H NMR spectrum, two for the cis isomer and one for the trans isomer; integration of the signals results in a 1:1 ratio of isomers.

In contrast to the static ^1H NMR spectra for complexes **1**, **2**, and **8**, the 2,6-difluorophenoxide (**4**), pentafluorophenoxide (**5**), and 3,5-bis(trifluoromethyl)phenoxide (**6**) complexes exhibit only a pair of broadened doublets for protons H_A and H_B. This observation is consistent with a rapid exchange between the cis and trans isomers on the NMR time scale at room temperature. For complexes **4** and **5**, the room-temperature doublets gradually broadened as the temperature was lowered; at low temperatures, −63 °C in $CDCl_3$ or −89 °C in toluene-d_8, protons H_A and H_B were both a pair of doublets. The spectra for these complexes were still in the process of resolving at the freezing points of the solvents, which indicates that exchange between the cis and trans isomers is still rapid at this low temperature. Free energies of activation have been calculated for complexes **4** and **5** at their coalescence temperatures and are listed in Table 1.[11] The chemical shift separations in the absence of exchange (17–23 Hz) were estimated on the basis of the low-temperature spectra.

The 3,5-bis(trifluoromethyl)phenoxide complex **6** is near coalescence at room temperature. At −62 °C in $CDCl_3$, the complex is a static mixture of cis and trans isomers, since a pair of doublets is observed for both the H_A and H_B protons. The spectra on the left side of Figure 3 indicate the changes in the spectrum of proton H_A as a function of temperature. A similar series of spectra were obtained for proton H_B with a smaller splitting of the doublets. The chemical shift separations in the absence of exchange and the coalescence temperatures were unaffected when the concentration of complex **6** was increased by a factor of 2.7.

Computer modeling of the experimental spectra provided the series of simulated spectra on the right side of Figure 3. The experimental and computer-simulated spectra are nearly identical. Calculated exchange rate constants at each temperature are listed beside the simulated spectra in Figure 3. An Arrhenius plot of these rate constants is shown in Figure 4, and the calculated activation parameters for the isomerization are listed in Table 1.

The NMR spectra for the 2,6-dichlorophenoxide (**3**) and 2,4,6-tris(trifluoromethyl)phenoxide (**7**) complexes indicate a more complicated mixture of isomers, and several of the signals in the NMR spectra of the complexes are broad. The relative integral ratios of the broadened signals to the narrow-line signals varied for different preparations of the complexes. The narrow-line component of complex **3** had only one doublet for each of the H_A and H_B protons; this suggests that the cis and trans isomers of the complex are rapidly interconverting on the NMR time scale. This behavior is similar to that of the 2,6-difluorophenoxide complex **4**. The ^1H NMR spectrum of complex **7** consists of a pair of doublets for the H_B proton and a doublet and a broadened multiplet for the H_A proton; this spectrum is consistent with a static mixture of isomers, where one of the isomers possesses inequivalent allyl ligands.

One explanation for the complexity of the spectra of complexes **3** and **7** could be that the $Ni_2(\mu\text{-}X)_2$ ring is puckered in these complexes. Such puckering would be expected to result in the loss of the 2-fold rotational symmetry for the trans isomer, and the allyl groups would no longer be equivalent. The aryl groups could also occupy either pseudoaxial or pseudoequatorial positions in the puckered complex, which could further complicate the system. The simple ^1H NMR spectra for complexes **1**, **2**, **4**–**6**, and **8** could be due to a planar structure for these complexes or to a rapid inversion of the puckered $Ni_2(\mu\text{-}X)_2$ ring. The crystal structures of $[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}SCH_3)]_2$ and $[Ni(\eta^3\text{-}syn,syn\text{-}1,3\text{-}Me_2C_3H_3)(\mu\text{-}CH_3)]_2$ indicate a puckered structure.[8,10]

The broad signals in the ^1H NMR spectra of complexes **3** and **7** could be due to the presence of a paramagnetic nickel complex. Two possible paramagnetic species include a five-coordinate nickel complex, resulting from coordination of one of the *o*-CF_3 or *o*-Cl groups to the nickel center, or a tetrahedral nickel center, resulting from rotation of one of the allyl groups with respect to the $Ni_2(\mu\text{-}X)_2$ plane (**V**; Figure 5). Richardson and co-workers have reported that crystal structures of nickel(II) complexes of 2,6-dichlorophenoxide exhibit coordination of an *o*-chlorine to the nickel center.[12]

Characterization of the Nickel Complexes by ^{19}F NMR. The 2,6-difluorophenoxide (**4**), pentafluorophenoxide (**5**), and 3,5-bis(trifluoromethyl)phenoxide (**6**) complexes show no evidence for the presence of cis and trans isomers in their ^{19}F NMR spectra, since there is only one resonance in the spectra of complexes **4** and **6** and there are three fluorine resonances for complex **5**. Rapid cis–trans isomerization and rotation about the Ar–O bond are probably responsible for the simple spectra. The ^{19}F NMR spectrum for complex **5** is an AA′MM′X pattern consisting of an apparent doublet, triplet, and triplet of triplets for the ortho (A, A′), meta (M, M′), and para (X) fluorine signals, in order of decreasing chemical shift, respectively. Coupling constants were determined by a computer simulation of the spectra.

The ^{19}F NMR spectrum of complex **8** is also an AA′MM′X pattern consisting of an apparent doublet of doublets, a triplet, and a multiplet for the ortho (A, A′), para (X), and meta (M, M′) fluorine signals, in order of decreasing chemical shift, respectively. This order is different than that of complex **5** (ortho > meta > para).

---

(11) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; p 79.

(12) Richardson, M. F.; Wulfsberg, G.; Marlow, R.; Zaghonni, S.; McCorkle, D.; Shadid, K.; Gagliardi, J., Jr.; Farris, B. *Inorg. Chem.* **1993**, *32*, 1913.

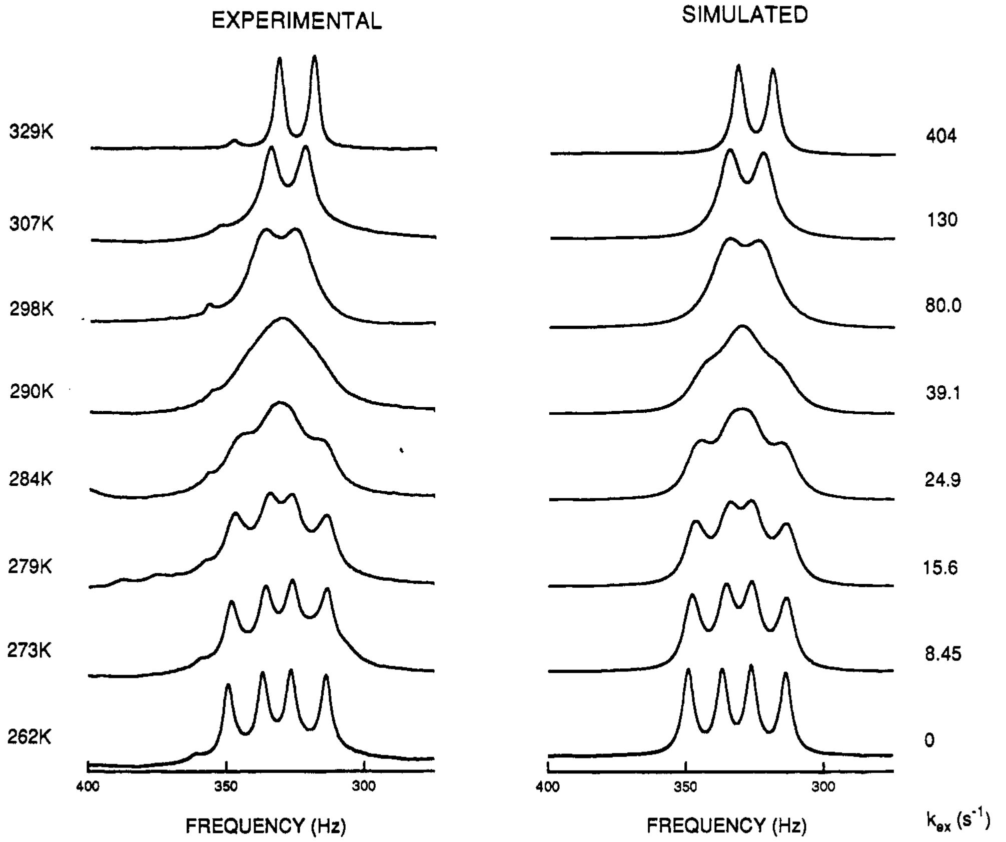


Figure 3. Variable-temperature ^{1}H NMR spectra of the H_A proton in complex **6**: (left) experimental spectra; (right) computer-simulated spectra and exchange rate constants.

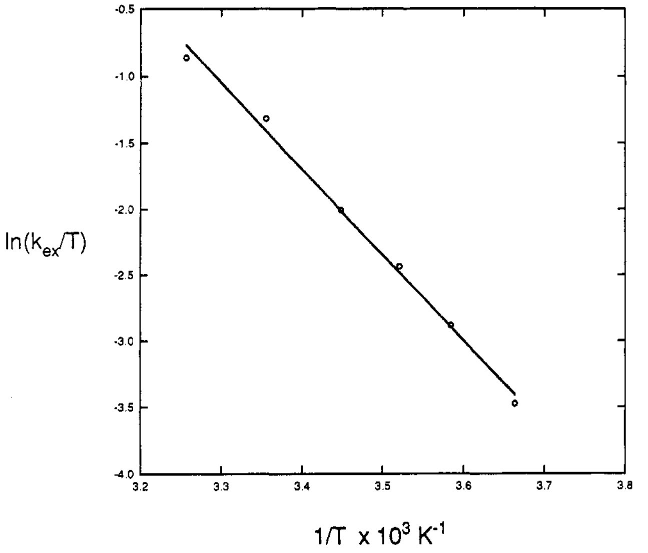


Figure 4. Arrhenius plot for rate constants obtained from computer simulation of variable-temperature ^{1}H NMR spectra of complex **6**.

The simplicity of the ^{19}F NMR spectrum for complex **8** is inconsistent with the presence of a static mixture of cis and trans isomers as observed by ^{1}H NMR, since a total of eight signals are predicted. An insensitivity of the aryl fluorine chemical shifts to the orientation of the allyl ligand in the cis and trans isomers and rapid rotation about the S–Ar bond may explain the conflicting ^{1}H and ^{19}F NMR data.

The ^{19}F NMR spectra for complex **7** indicated a greater complexity than anticipated. At room temperature, a total of six trifluoromethyl signals are observed for this complex in a nonstoichiometric ratio. This spectrum is inconsistent with a static 1:1 mixture of planar cis and trans isomers, since a total of five signals in a 2:1:1:1:1 relative integral ratio would be expected as a result of the equivalence of the *o*-trifluoromethyl groups in the trans isomer. Puckering of the $Ni_2(\mu\text{-}X)_2$ ring may explain the observed six signals in the room-temperature ^{19}F NMR spectrum for complex **7**, since the top and bottom faces of a trans isomer would no longer be equivalent. As the temperature is raised to 59 °C, two of the six signals appear to be moving toward coalescence. This could indicate a more rapid inversion of the puckered ring at higher temperatures.

At low temperatures (−61 °C) a total of nine signals are observed for complex **7**, with five as major signals (1:1: 1:1:1 intensity ratio) and four as minor signals (10–20% of the intensity of the major signals). This complex spectrum could be due to the presence of isomers where the aryl rings occupy pseudoaxial or pseudoequatorial positions in the puckered dimer. Alternatively, coordination of one of the CF_3 groups to a nickel center could also explain the large number of ^{19}F NMR signals for this complex.

Proposed Mechanism for the Dynamic Isomerization of Complexes 4–6. Figure 5 diagrams five mechanisms which we have considered for the isomerization of the cis and trans isomers of complexes **4**–**6**.[13] The possible mechanisms include η^3-allyl to η^1-allyl isomerization,[14] dimer–monomer equilibria,[2f,15] intermolecular exchange between dimers,[2f,15] μ-X bond cleavage,[2f,15b] and allyl rotation.[1b,15b,c,16] Four pieces of evidence lead us to con-

---

(13) For general reviews of allyl isomerization mechanisms: (a) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; pp 441–487. (b) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., Vol. 3, Chapter 20, 1982; pp 110–111, and references therein.

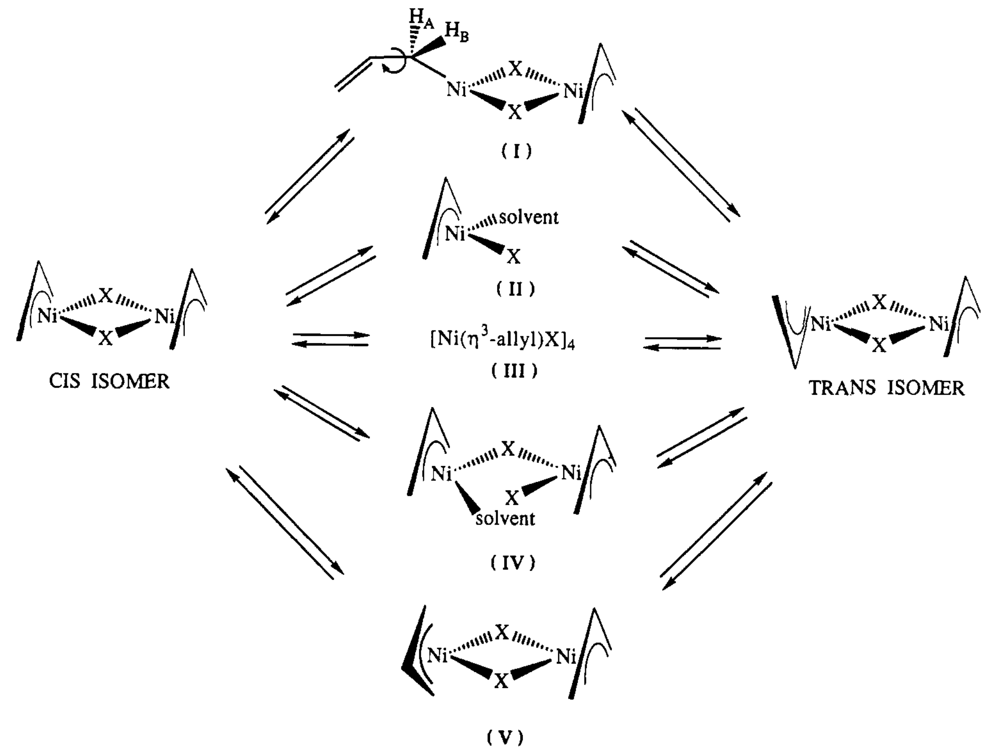


Figure 5. Mechanisms for the dynamic isomerization of complexes 1–8.

clude that either μ-X bond cleavage or allyl rotation is the most likely mechanism for the interconversion: (1) the allyl protons H_A and H_B are inequivalent over a wide temperature range, (2) the rate of isomerization is observed to be independent of the concentration of the complexes, (3) the variable-temperature studies on complex **6** in $CDCl_3$ indicate an activation enthalpy of 12.9 kcal/mol and an activation entropy of –6.6 cal/(K mol), and (4) the rate of isomerization is observed to be faster for complexes possessing electronegative aryloxide ligands.

Conversion of an η^3-allyl to an η^1-allyl group (**I**; Figure 5) has been reported for a number of transition-metal allyl complexes.[14] Allylpalladium complexes, for example, have been proposed to isomerize by this mechanism in the presence of a phosphine ligand.[14b] Rotation about the C–C single bond in the η^1-allyl intermediate **I** not only interconverts the isomers but also causes the H_A and H_B protons to become equivalent. The observation that the H_A and H_B allyl protons are inequivalent over the temperature range where complexes **4**–**6** exhibit dynamic behavior indicates that conversion of an η^3-allyl to an η^1-allyl group is not responsible for the isomerization.

Teyssié and Powell and their co-workers have suggested that dissociation of a dimeric complex to monomers **II** (Figure 5) or intermolecular exchange between dimers via the tetrameric intermediate **III** may be responsible for the dynamic interconversion exhibited by $[Ni(\eta^3\text{-allyl})(\mu\text{-}O_2CCF_3)]_2$ and $[Pd(\eta^3\text{-allyl})(\mu\text{-}O_2CCH_3)]_2$.[2f,15a] The very small and negative activation entropy obtained for complex **6** is inconsistent with a dissociative process unless the solvent coordinates to the monomeric intermediate **II**. Such participation would not be expected to be significant in $CDCl_3$. The observation that the coalescence temperatures and chemical shift separations in the absence of exchange are independent of the concentration of complex **6** indicates that an intermolecular exchange is not responsible for the cis–trans isomerization. Crossover experiments performed on complexes **4**–**6** were not conclusive as a probe of the mechanism, since the ^1H NMR spectra of the H_A, H_B, and H_C protons in complexes **4**–**6** were all too similar. Mass spectral analysis of complexes **4** and **5** mixed as solids indicated the mixed dimer was present; as a result, no attempt was made to determine whether mixtures of **4** and **5** prepared in solution exhibited crossover. The apparent crossover in the solid phase may be due to the high temperatures needed to volatilize the complexes (120 °C).

Ring opening of the $Ni_2(\mu\text{-}X)_2$ core through cleavage of a Ni–(μ-X) bond to form intermediate **IV** (Figure 5) has been proposed as a mechanism for the isomerization of $[Pd(\eta^3\text{-allyl})(\mu\text{-}O_2CCH_3)]_2$ and for the polymerization of dienes by $[Ni(\eta^3\text{-allyl})(\mu\text{-}O_2CCF_3)]_2$.[2f,15b] For this mechanism to result in a cis–trans isomerization, the ring-opened intermediate **IV** must undergo a coordination sphere rearrangement that results in a racemization of one of the nickel centers in the dimer. Solvent coordination could favor this mechanism by stabilizing the 14-electron, ring-opened intermediate.

This mechanism is consistent with each of the experimental observations, since the process would be intramo-

---

[14] For discussions of the η^3-allyl to η^1-allyl isomerization mechanism, see: (a) Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *105*, 101. (b) Cotton, F. A.; Faller, J. W.; Musco, A. *Inorg. Chem.* **1967**, *6*, 179. (c) Becconsall, J. K.; Job, B. E.; O'Brien, S. *J. Chem. Soc. A* **1967**, 423. (d) Becconsall, J. K.; O'Brien, S. *Chem. Commun.* **1966**, 302. (e) Krieger, J. K.; Deutsch, J. M.; Whitesides, G. M. *Inorg. Chem.* **1973**, *12*, 1535.

[15] For discussions of intermolecular exchange and monomer–dimer equilibria mechanisms, see: (a) Powell, J. *J. Am. Chem. Soc.* **1969**, *91*, 4311. (b) Faller, J. W.; Incorvia, M. J.; Thompsen, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 518. (c) Ramey, K. C.; Lini, D. C.; Wise, W. B. *J. Am. Chem. Soc.* **1968**, *90*, 4275. (d) Tibbetts, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1969**, *91*, 1108.

[16] For discussions of the allyl rotation mechanism, see: (a) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840. (b) Faller, J. W.; Adams, M. A. *J. Organomet. Chem.* **1979**, *170*, 71. (c) Becconsall, J. K.; O'Brien, S. *Chem. Commun.* **1966**, 720. (d) Nesmeyanov, A. N.; Ustynyuk, Y. A.; Kritskaya, I. I.; Shchembelov, G. A. *J. Organomet. Chem.* **1968**, *14*, 395. (e) Nesmeyanov, A. N.; Kritskaya, I. I. *J. Organomet. Chem.* **1968**, *14*, 387. (f) Holloway, C. E.; Kelly, J. D.; Stiddard, M. H. B. *J. Chem. Soc. A* **1969**, 931. (g) Trofimenko, S. *J. Am. Chem. Soc.* **1968**, *90*, 4754.

Table 2. Yields and Properties of Poly(1,3-dienes) Obtained from Complexes 5–7

initiator	X	[initiator] (mM)	[diene] (M)	T, (°C)	yield[a] (%)	M_n	% cis
5	F_5PhO	17.8	CHD, 3.0	20	100	*b*	100[c]
6	3,5-$(CF_3)_2PhO$	15.1	CHD, 2.3	20	97	*b*	100[c]
7	2,4,6-$(CF_3)_3PhO$	8.6	CHD, 1.8	20	8.1	*b*	100[c]
7	2,4,6-$(CF_3)_3PhO$	8.6	CHD, 1.8	50	100	*b*	100[c]
5	F_5PhO	8.5	BD, 5.1	50	66[d]	25 200[e]	45.5[f]
6	3,5-$(CF_3)_2PhO$	7.0	BD, 5.1	50	43[d]	14 300[e]	37.2[f]

[a] Yields were obtained after a 24-h reaction time in chlorobenzene. [b] Determination of the molecular weight of poly(CHD) was not possible, owing to its extreme insolubility. [c] Only the cis polymer is possible. [d] Yields are low due to loss of polymer during its isolation. [e] Molecular weights are relative to polystyrene. [f] Determined by ^{13}C NMR.[20]

lecular with only a slight increase in entropy in the transition state. The modest activation enthalpy observed for the interconversion of complex **6** could reflect the energy needed to cleave the Ni–(μ-X) bond. The observation that complexes which possess electronegative aryloxides (**4**–**6**) exhibit faster isomerization compared to complexes with more electropositive aryloxides (**1** and **2**) is consistent with the decreased ability of the electron-poor aryloxides to bridge a pair of metal atoms.[17,18] The static behavior of complex **7** is inconsistent with this mechanism, since the steric bulk and electronegativity of the 2,4,6-tris(trifluoromethyl)phenoxide ligand should favor Ni–(μ-X) bond cleavage.

Rotation of an allyl ligand has also been proposed as a mechanism for the isomerization of a number of transition-metal allyl complexes.[15b,c,16] For complexes **4**–**6** the mechanism involves a 90° rotation of the allyl ligand in its plane about an axis containing the nickel centers. The intermediate **V** in the interconversion would be a dimer that possesses both a square-planar and a tetrahedral nickel center, and as a result of the paramagnetism of tetrahedral Ni(II) complexes, the intermediate may not be observable by NMR.

Since π donation and strong-field ligands are known to stabilize a square-planar geometry, X ligands that are weak-field ligands and poor π donors would be anticipated to allow for a more facile rotation of the allyl ligand. Complexes **4**–**6**, with their weak-field aryloxide ligands, would be expected to exhibit fast isomerization by this mechanism, as we have observed. The static behavior for the 2,6-dialkylphenoxide complexes **1** and **2** and the sulfur-bridged complex **8** is consistent with a greater stability of the square-planar geometry due to the good π-donor ligands. The observed static behavior for complex **7** is consistent with the allyl rotation mechanism, since molecular models indicate increased steric interactions between the H_A and H_B allyl protons and the bulky *o*-trifluoromethyl groups in the tetrahedral intermediate **V**.

The activation free energies, enthalpies, and entropies for complexes **4**–**6** resemble values obtained from studies of other transition-metal allyl complexes where allyl rotation has been proposed as the mechanism (Table 1).[16] The small activation entropy obtained for complex **6** is consistent with the allyl rotation mechanism, since the difference in entropy between a square-planar and a tetrahedral nickel center would be expected to be small. The activation enthalpy could reflect the relative instability of the tetrahedral intermediate compared to the square-planar complexes.

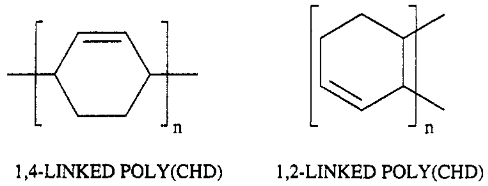


Figure 6. Structures for 1,4- and 1,2-linked poly(CHD).

In summary, we believe that either the allyl rotation or the Ni–(μ-X) bond cleavage mechanism is consistent with the experimental results; however, we cannot exclude a monomer–dimer equilibrium.

Diene Polymerization Activity of the Complexes. The ability of complexes **1**–**8** to initiate the polymerization of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene was examined in several solvents and at several temperatures. Of the five dienes and eight complexes that were examined, only 1,3-butadiene (BD) and 1,3-cyclohexadiene (CHD) were polymerized, and only complexes **5**–**7** initiated the polymerization of these dienes.

The poly(CHD) produced by complexes **5**–**7** was completely insoluble in organic solvents; as a result, only the relative reactivity of the initiators could be determined, **5** > **6** ≫ **7**. Complexes **5** and **6** quantitatively polymerized CHD in 5 min and 1 h, respectively, at room temperature, whereas only an 8% yield of poly(CHD) was obtained for complex **7** after 24 h. At 50 °C all three initiators provided quantitative yields of the insoluble polymer (Table 2). Solid-state CPMAS ^{13}C NMR spectra of the insoluble poly(CHD) are consistent with >95% 1,4-linked poly(CHD) for each of the initiators, since there are only three types of carbon atoms in the NMR spectrum (Figure 6). The 1,2-linked poly(CHD) would possess six different types of carbon atoms. Grubbs and Claverie have determined that the poly(CHD) obtained from initiator **5** is thermally stable and highly crystalline.[19] The yields of poly(CHD) obtained using initiator **5** were higher in aromatic solvents, i.e. chlorobenzene (100%), *o*-dichlorobenzene (99%), and toluene (91%), and lower in heptane (38%). The stereochemistry of polymerization is proposed to be syn addition to 1,3-cyclohexadiene, resulting in the formation of *cis*-

---

(17) The electronegativity of the ligands has been estimated on the basis of the pK_a of the corresponding phenol or thiophenol.[18] The electronegativities of the X anion decrease roughly in the following order: pentafluorothiophenol > pentafluorophenol > 2,6-dichlorophenol > 2,6-difluorophenol > 3,5-bis(trifluoromethyl)phenol > 2,6-dimethylphenol ≈ 2,6-diisopropylphenol.

(18) (a) 2,6-Me_2PhOH, p$K_a(H_2O)$ = 10.62: Zwierzchowska-Nowakowska, Z. *Pol. J. Chem.* **1986**, *60*, 909. (b) 2,6-Cl_2PhOH, p$K_a(H_2O)$ = 6.79: Bosch, E.; Rafols, C.; Roses, M. *Talanta* **1989**, *36*, 1227. (c) 2,6-F_2PhOH, p$K_a(H_2O)$ = 7.30: Donarski, W. J.; Dumas, D. P.; Heitmeyer, D. P.; Lewis, V. E.; Rauschel, F. M. *Biochemistry* **1989**, *28*, 4650. (d) F_5PhOH, p$K_a(H_2O)$ = 5.52 and 2,6-(*i*-Pr)$_2$PhOH, p$K_a(H_2O)$ = 11.08: Kuopio, R. *Acta Chem. Scand.* **1977**, *A31*, 369. (e) 3,5-$(CF_3)_2PhOH$, p$K_a(H_2O)$ = 7.88: Reyntjens, D.; Zeegers-Huyskens, T. *Spectrosc. Lett.* **1976**, *9*, 765. (f) F_5PhSH, p$K_a(H_2O)$ = 2.75: Wilson, J. M.; Bayer, R. J.; Hupe, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 7922.

(19) Poly(CHD) obtained from initiator **5** exhibited *d* spacings at 5.29, 4.51, and 3.91 Å by X-ray powder diffraction and by thermogravimetric analysis was stable up to 340 °C in air or argon: Grubbs, R. H.; Claverie, J. P. Personal communication, 1993.

disubstituted cyclohexene units in the polymer backbone. This mode of polymerization of 1,3-dienes has been proposed by Porri and co-workers.[1c]

Complexes **5** and **6** were observed to polymerize 1,3-butadiene in fair yield, and the isolated poly(BD) was characterized by solution ^{1}H and ^{13}C NMR and by gel permeation chromatography. Poly(BD) was >95% 1,4-linked, as determined by ^{1}H and ^{13}C NMR; no 1,2-linked polymer was detected. The *cis*- and *trans*-diene content of the polymers was determined using solution ^{13}C NMR.[20] The yields, molecular weights (relative to polystyrene), polydispersities, and *cis*-alkene content of the poly(BD) obtained from initiators **5** and **6** are listed in Table 2.

Poly(BD) and poly(CHD) produced using initiators **5–7** are similar to polymers reported for other nickel-based initiator systems; however, the *cis*-1,4-poly(BD) contents are lower for complexes **5** and **6**. Teyssié and co-workers have reported that $[Ni(\eta^3\text{-allyl})(\mu\text{-}O_2CCF_3)]_2$ yields a 65% yield of poly(BD) at 25 °C in toluene. Poly(BD) produced by this initiator is reported to be >95% 1,4-linked with a number-average molecular weight of 16 000 and has 59% *cis*-alkene content.[2e] Dolgoplosk and co-workers have reported that mixtures of $[Ni(\eta^3\text{-allyl})(\mu\text{-}Cl)]_2$ and electron acceptors $[Ni(CCl_3CO_2)_2$ or *o*-chloranil] polymerize 1,3-cyclohexadiene to form 1,4-linked poly(CHD) in low yield (12–40%) which exhibited fair solubility in organic solvents.[4]

The molecular weights and cis stereoselectivity of poly(BD) are only slightly affected by the electronegativity of the X ligand, since the initiator **5**, which possesses a more electronegative aryloxide ligand than **6**, produces poly(BD) with only slightly higher molecular weights and *cis*-alkene contents. Teyssié and Taube and their co-workers report a similar increase in the cis content of 1,4-linked poly(BD) with increasing electronegativity of ligands on the allylnickel complex.[2b,d,3]

Proposed Mechanisms for 1,3-Diene Polymerization. We believe that the observed polymerization activity of the allylnickel complexes **1–8** depends on their ability to generate an open coordination site and on the electrophilicity of the nickel center. Since the diene ligand is a four-electron donor, and since the nickel centers in the $[Ni(\eta^3\text{-allyl})(\mu\text{-}X)]_2$ complexes are 16-electron species, polymerization activity may proceed via a 14-electron intermediate formed from the starting complex. Such a coordinatively unsaturated complex could result from the formation of the η^1-allyl intermediate **I**, dissociation of the dimer into two 14-electron monomers **II**, or cleavage of only one of the Ni–(μ-X) bridges to form the ring-opened intermediate **IV** (Figure 5). Each of these processes could be assisted by coordination of the diene to the dimer. Although η^3-allyl to η^1-allyl isomerization has been excluded as a mechanism for the cis–trans isomerization, it is a viable mechanism in the presence of a coordinating ligand, for example, a 1,3-diene.

It is surprising that there appears to be no direct correlation of the activity of the complexes as diene polymerization initiators with the electronegativity of the bridging ligand. Teyssié and co-workers have reported that the polymerization activity of $[Ni(\eta^3\text{-allyl})(\mu\text{-}O_2CCX_3)]_2$ increases with increasing electronegativity of the carboxylate ligand (X = F > Cl > Br).[2b,d] The relative rates of reactivity would be expected to be **8** > **5** > **3** > **4** > **1** ≈ **2**, if the electronegativity of the X ligand determined the polymerization activity.[17,18] The observed order, **5** > **6** > **7** with **1–4** and **8** inactive as polymerization initiators, indicates that although an electron-deficient X ligand is necessary, it is not a sufficient condition for $[Ni(\eta^3\text{-allyl})(\mu\text{-}X)]_2$ complexes to exhibit polymerization activity.

The inability of complexes **3**, **4**, and **8** to generate an open coordination site may explain their inactivity as polymerization initiators. For complexes **3** and **4**, the inactivity could be due to coordination of the *o*-chlorine or -fluorine atoms to the nickel center, which would reduce the coordinate unsaturation of the initiator. The intermolecular coordination of a diene to the nickel center would have to compete with the intramolecular chelation of the X ligand. The inactivity of complex **8** compared to complex **5** could be due to the better π-donor ability of arenethiolates which could stabilize the dimeric structure and reduce the coordinate unsaturation of the nickel centers.

Finally, there appears to be no direct relationship between isomerization and polymerization activity. Although complexes **5** and **6** both exhibit dynamic behavior and polymerization activity, the 2,6-dichlorophenoxide (**3**) and 2,6-difluorophenoxide (**4**) complexes exhibit dynamic behavior but are inactive as polymerization initiators. In contrast, the 2,4,6-tris(trifluoromethyl)phenoxide complex exhibits no cis–trans isomerization, yet it polymerizes 1,3-cyclohexadiene at room temperature. These observations are consistent with isomerization proceeding via an allyl rotation, since no open coordination site is generated during the isomerization.

Summary

A new family of allylnickel complexes have been prepared that initiate the rapid and high-yield 1,4-polymerization of 1,3-dienes. Due to the ease of variation of the steric and electronic properties of the bridging aryloxide or arenethiolate ligand, it has been possible to tune the properties of the complexes to design new initiators for 1,3-diene polymerization and to obtain information about the mechanisms of isomerization and diene polymerization.

Experimental Section

General Comments. Reagents were obtained from commercial suppliers and purified to remove oxygen and water. Pentane was made olefin-free by stirring with sulfuric acid. All solvents were dried using either calcium hydride or sodium–benzophenone ketyl and degassed. Allyl bromide was distilled, dried over calcium hydride, degassed, and passed through alumina immediately prior to use. The synthesis of $[Ni(\eta^3\text{-allyl})(\mu\text{-}Br)]_2$ was accomplished using the procedure of Wilke.[21] Literature procedures were used to synthesize 2,4,6-tris(trifluoromethyl)phenol.[22] Substituted phenols were dried over molecular sieves (4 Å) and converted to the corresponding sodium or lithium salts using excess sodium hydride or *n*-butyllithium. Diene monomers were purified by distillation, dried over either calcium hydride or sodium metal, degassed, and passed through alumina immediately prior to use.

Solution NMR spectra were recorded on a Bruker AC250 (observed frequencies: ^{1}H, 250 MHz; ^{13}C, 62.9 MHz; ^{19}F, 235.2 MHz). ^{1}H NMR spectra were referenced to tetramethylsilane or to protio solvent impurity. ^{13}C NMR spectra were referenced to natural-abundance ^{13}C in the solvent. ^{19}F NMR spectra were referenced to internal $CFCl_3$. Solid-state NMR spectra were run

---

[20] Wang, H.; Bethea, T. W.; Harwood, J. H. *Macromolecules* **1993**, *26*, 715.

[21] Wilke, G. Belgian Patent 651595, 1965.

[22] Roesky, H. W.; Scholz, M.; Noltemeyer, M.; Edelmann, F. T. *Inorg. Chem.* **1989**, *28*, 3829.

on an AMX400 (observed frequency for ^{13}C 100.6 MHz) at Sandia National Laboratories and were referenced to adamantane.

General Procedure for the Synthesis of $[Ni(\eta^3\text{-allyl})(\mu\text{-}X)]_2$ Complexes (1–8). Solid $[Ni(\eta^3\text{-allyl})(\mu\text{-}Br)]_2$ and a slight excess of the lithium or sodium salt of the aryloxide or arenethiolate (2.2 equiv per $[Ni(\eta^3\text{-allyl})Br]_2$) were weighed as solids into a Schlenk tube inside an inert-atmosphere glovebox. The solids were dissolved in ether and stirred at room temperature for 1 h. The color of the reaction mixture rapidly changed from red to orange, and a white precipitate (lithium or sodium bromide) formed. The solvent was removed and the orange solid was dissolved in methylene chloride and filtered through Celite under an inert atmosphere. Removal of the solvent yielded a powder which was recrystallized from methylene chloride/pentane. The product was dried at room temperature *in vacuo*. The sodium salts were used for the preparation of each of the complexes, except 7 and 8.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}O\text{-}2,6\text{-}(CH_3)_2Ph)]_2$ (1): yield 72%; ^1H NMR ($CDCl_3$) δ 6.92 (d, J = 7.1 Hz, 2H, 3,5-aryl protons on cis isomer), 6.86 (d, J = 7.3 Hz, 4H, 3,5-aryl protons on trans isomer), 6.80 (d, J = 7.1 Hz, 2H, 3,5-aryl protons on cis isomer), 6.56 (t, J = 7.3 Hz, 4H, 4-aryl protons on both isomers), 5.49 and 5.40 (overlapping multiplets, 4H, H_C), 3.18 (s, 6H, CH_3 on cis isomer), 2.87 (s, 12H, CH_3 on trans isomer), 2.55 (s, 6H, CH_3 on cis isomer), 1.53 (d, J = 6.8 Hz, 4H, H_B on cis or trans isomer), 1.50 (d, J = 6.6 Hz, 4H, H_B on cis or trans isomer), 1.20 (d, J = 12.5 Hz, 4H, H_A on cis or trans isomer), 1.14 (d, J = 12.5 Hz, 4H, H_A on cis or trans isomer) (note: cis and trans isomers are present in a 1:1 ratio); IR (KBr) ν 3017, 2965, 2918, 1589, 1464, 1424, 1267, 1223, 908, 764 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_2Ni_2$: C, 59.80; H, 6.39. Found: C, 55.43; H, 5.96.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}O\text{-}2,6\text{-}(i\text{-}Pr)_2Ph]_2$ (2): yield 99%; ^1H NMR ($CDCl_3$) δ 6.98 (d of d, J = 1.6 and 7.5 Hz, 3- or 5-aryl proton on cis isomer), 6.93 (d, J = 7.5 Hz, 3,5-aryl protons on trans isomer), and 6.88 (d of d, J = 1.7 and 7.6 Hz, 3- or 5-aryl proton on cis isomer) (these three signals were overlapping, 8H total integral), 6.73 (t, J = 7.5 Hz, 4H, 4-aryl of cis and trans isomers), 5.2–5.7 (three overlapping multiplets, total integral 6H, $(CH_3)_2CH$ of cis isomer and H_C on both cis and trans isomers), 4.92 (m, 4H, $(CH_3)_2CH$ on trans isomer), 4.42 (m, 2H, $(CH_3)_2CH$ on cis isomer), 1.69, 1.60, 1.54, and 1.45 (four major d overlapping a pair of minor d, J = 6.9 Hz for the major d, J values for the minor d were not resolved, 56H total, $(CH_3)_2CH$ and the H_B allyl protons of the cis and trans isomers), 1.20 (d, J = 12.6 Hz, 4H, H_A allyl protons on cis or trans isomer), 1.13 (d, J = 12.6 Hz, 4H, H_A allyl protons on cis or trans isomer) (note: cis and trans isomers are present in a 1:1 ratio); FTIR (KBr) ν 3059, 2960, 2879, 1586, 1429, 1323, 1254, 1200, 1111, 911, 847, 766 cm^{-1}. Anal. Calcd for $C_{30}H_{44}O_2Ni_2$: C, 65.03; H, 8.01. Found: C, 65.15; H, 8.12.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}O\text{-}2,6\text{-}Cl_2Ph)]_2$ (3): yield 76%; ^1H NMR ($CDCl_3$) δ 7.13 (broad, ~4H, 3,5-aryl protons), 6.80 (d, J = 7.8 Hz, ~0.3H, 3,5-aryl protons), 6.57 (t, J = 7.9 Hz, ~2H, 4-aryl protons), 6.18 (t, J = 7.8 Hz, ~0.14H, 4-aryl protons), 5.59 and 5.46 (broad peak overlapping m, ~2H, H_C), 1.75 (broad, ~4H, H_B), 1.44, 1.28, and 1.25 (pair of d at 1.44 and 1.25, overlapping major broad peak at 1.28, J = 6.6 and 12.5 Hz, respectively, ~4H, H_B and H_A) (note: different batches provided varying integral ratios of the narrow to broad resonances); IR (KBr) ν 2926, 1449, 1285, 1072, 775, 737 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2Cl_4Ni_2$: C, 41.29; H, 3.08. Found: C, 40.86; H, 3.04.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}O\text{-}2,6\text{-}F_2Ph)]_2$ (4): yield 97%; ^1H NMR ($CDCl_3$) δ 6.71 (broad, 4H, 3-aryl protons), 6.53 (br, 2H, 4-aryl protons), 5.67 (broad, 2H, H_C allyl), 1.94 (d, J = 6.3 Hz, 4H, H_B allyl), 1.48 (d, J = 12.3 Hz, 4H, H_A allyl); ^{19}F NMR ($CDCl_3$) δ −129.5 (s); FTIR (KBr) ν 3063, 2992, 2922, 1580, 1495, 1292, 1233, 995, 727 cm^{-1}; MS (EI, 70-eV ionization energy) m/z calcd for $C_{18}H_{16}O_2F_4Ni_2$ (M^+) 456 ($^{58}Ni/^{58}Ni$), 458 ($^{60}Ni/^{58}Ni$), and 460 ($^{60}Ni/^{60}Ni$), obsd 456, 458, and 460 (M^+). Anal. Calcd for $C_{18}H_{16}O_2F_4Ni_2$: C, 47.23; H, 3.52. Found: C, 45.58; H, 3.57.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}OF_5Ph)]_2$ (5): yield 88%; ^1H NMR ($CDCl_3$) δ 5.71 (broad, 2H, H_C), 2.01 (d, J = 6.1 Hz, 4H, H_B), 1.52 (d, J = 12.5 Hz, 4H, H_A); ^{19}F NMR ($CDCl_3$) δ −160 (d, J_{AM} = −25.0, $J_{AM'}$ = 5.5, $J_{AA'}$ = 4.0, and J_{AX} = 6.0 Hz, 4F, 2,6-aryl), −166 (br t, J_{AM} = −25.0, $J_{AM'}$ = 5.5, $J_{MM'}$ = 13.5, and J_{MX} = −22.5 Hz, 2F, 3,5-aryl), −171 (t of t, J_{AX} = 6.0 and J_{MX} = −22.5 Hz, 4F, 4-aryl); IR (KBr) ν 2976, 2934, 1508, 1470, 1308, 1157, 1017, 991 cm^{-1}; MS (EI, 70-eV ionization energy) m/z calcd for $C_{18}H_{10}O_2F_{10}Ni_2$ (M^+) 564 ($^{58}Ni/^{58}Ni$) and 566 ($^{60}Ni/^{58}Ni$), obsd 564 and 566. Anal. Calcd for $C_{18}H_{10}O_2F_{10}Ni_2$: C, 38.22; H, 1.78. Found: C, 38.00; H, 1.73.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}O\text{-}3,5\text{-}(CF_3)_2Ph)]_2$ (6): yield 94%; ^1H NMR ($CDCl_3$) δ 7.27 (s, 4H, 2,6-aryl protons), 7.20 (s, 2H, 4-aryl protons), 5.63 (broad, 2H, H_C), 2.05 (d, J = 6.7 Hz, 4H, H_B), 1.62 (d, J = 12.3 Hz, 4H, H_A); ^{19}F NMR ($CDCl_3$) −63.5 (s); IR (KBr) ν 2932, 1603, 1464, 1375, 1279, 1167, 1128, 953 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_2F_{12}Ni_2$: C, 40.17; H, 2.45. Found: C, 38.69; H, 2.35.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}O\text{-}2,4,6\text{-}(CF_3)_3Ph)]_2$ (7): yield 89%; ^1H NMR ($CDCl_3$) δ 7.89 and 7.85 (pair of s overlapping a broad signal at ~7.9, ~4.2H, 3,5-aryl protons), 7.63 (s, ~1H, 3,5-aryl protons), 5.69 and 5.58 (m overlapping a broad signal, 2H, H_C), 1.88 and 1.85 (pair of overlapping doublets, J = ~7 and 6.9 Hz, ~4H, H_B), 1.47 (d, J = 12.9 Hz, ~1.4H, H_A), 1.25 (broadened d, J = ~10 Hz, 3.3H, H_A) (note: different batches provided varying integral ratios for the broad and narrow resonances); ^{19}F NMR ($CDCl_3$, 298 K) δ −61.6 (s, 1F), −62.4 (s, 1.6F), −62.5 (s, 1.5F), −62.8 (s, 1.4F), −63.5 (s, 1.3F), −64.9 (s, 1.5F); ^{19}F NMR ($CDCl_3$, 247 K) δ −61.1 (s, 1F), −61.7 (s, 0.04F), −61.9 (s, 2F), −62.1 (s, 0.23F), −62.2 (s, 0.18F), −62.7 (s, 0.07F), −62.8 (s, 2F), −63.63 (s, 2F), −64.83 (s, 2F); IR (KBr) ν 2932, 2963, 1630, 1591, 1481, 1379, 1300, 1273, 1206, 1136, 918, 804, 667 cm^{-1}. Anal. Calcd for $C_{24}H_{14}O_2F_{18}Ni_2$: C, 36.32; H, 1.78. Found: C, 34.53; H, 1.31.

$[Ni(\eta^3\text{-}C_3H_5)(\mu\text{-}S\text{-}F_5Ph)]_2$ (8): yield 32%; ^1H NMR ($CDCl_3$) δ 5.5 (broad, 2H, H_C), 2.88 and 2.81 (pair of d, J = 6.8 and 6.6 Hz, 4H, H_B), 2.29 and 2.17 (pair of d, J = 13.9 and 12.7 Hz, 4H, H_A); ^{19}F NMR ($CDCl_3$) δ −131.0 (d of d, J_{AM} = −24.8, $J_{AM'}$ = 7.1, $J_{AA'}$ = 0.8, and J_{AX} = 1.0 Hz, 4F, 2,6-aryl), −157.1 (t, J_{AX} = 1.0 and J_{MX} = −21.0 Hz, 2F, 4-aryl), −162.2 (m, J_{AM} = −24.8, $J_{AM'}$ = 7.1, $J_{MM'}$ = 1.4, and J_{MX} = −21.0 Hz, 4F, 3,5-aryl); IR (KBr) ν 2924, 1510, 1481, 1084, 972, 855 cm^{-1}. Anal. Calcd for $C_{18}H_{10}O_2F_{10}Ni_2$: C, 36.17; H, 1.69. Found: C, 36.51; H, 1.77.

Simulation of NMR Spectra. For simulation of NMR line shapes, experimental spectra were transferred to a PC using ZZNET.[23] Dynamic NMR simulations were obtained using a modified version of DNMR5.[24] Simulation of the ^{19}F NMR spectra were obtained from iterative fitting of experimental spectra using the Fortran program PCNMR developed in our laboratory. The cis–trans isomerization was treated as an equally populated, two-site process with the exchange rate constant k_{ex}. The temperature dependence of the chemical shift (ν) and relaxation time (T_2) of the H_A protons on the cis and trans isomers of 6 were found to be linear: $\nu(H_A) = T(-0.03636) + 329.4$, $\nu(H_{A'}) = T(-0.07855) + 363.6$, and $T_2 = T(4.662 \times 10^{-4}) - 5.681 \times 10^{-2}$ (for both H_A and $H_{A'}$), where H_A and $H_{A'}$ are the upfield and downfield doublets, respectively, and T is the temperature in K. The coupling constants were found to be invariant with changes of temperature.

General Procedure for Polymerization of 1,3-Dienes. Approximately 10–20 mg of an allylnickel complex was weighed in a glovebox into a small Schlenk tube and was dissolved in 5 mL of a dry, degassed solvent (chlorobenzene, dichlorobenzene, toluene, or heptane). For 1,3-cyclohexadiene, the polymerization was initiated by the addition of the diene to the solution of the nickel complex. For polymerizations of 1,3-butadiene, the Schlenk tube containing the solvent and initiator was placed in liquid nitrogen and evacuated, and approximately 5 mL of dry, degassed 1,3-butadiene was transferred in the gas phase to the Schlenk tube.

The polymerizations were carried out at 50 °C for 24 h and then quenched by the addition of methanol (30 mL) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, 10–20 mg). The result-

---

[23] Zolani, Z.; Westler, W. M.; Ulrich, E. L.; Markley, J. L. *J. Magn. Reson.* **1990**, *88*, 511.

[24] Stephenson, D. S.; Binsch, G. DNMR5; Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405, 1978; Program 365.

ing polymer slurry was decanted, centrifuged (at −50 °C for poly(BD)), and washed twice with methanol. The isolated poly(CHD) was insoluble even in hot chlorobenzene. For poly(BD), the polymer was redissolved in a minimum of methylene chloride containing BHT, precipitated by the addition of methanol, centrifuged at −50 °C, and washed twice with methanol. The polymers were dried *in vacuo* at room temperature and weighed. Gel permeation chromatography of poly(BD) was performed in THF, and the reported molecular weights are relative to polystyrene standards. The solution ^{1}H and ^{13}C NMR spectra of poly(BD) prepared using initiators **5** and **6** were identical, as were the solid-state CPMAS ^{13}C NMR spectra of poly(CHD) prepared from initiators **5**–**7**.

Poly(1,3-butadiene) Characterization: ^{1}H NMR ($CDCl_3$) δ 5.40 and 5.35 (overlapping br s, 2H, $=\mathrm{C}H\mathrm{CH}_2$ for *trans*- and *cis*-alkene linkages), 2.05 and 2.02 (overlapping br s, 4H, $=\mathrm{CHC}H_2$ for *trans*- and *cis*-alkene linkages); ^{13}C NMR ($CDCl_3$, inverse gate) δ 130.1 and 130.0 (1.25C, $=CHCH_2$ *trans*-1,4-poly(BD)), 129.6 and 129.4 (1C, $=CHCH_2$ *cis*-1,4-poly(BD)), 32.7 (s, 1.25 C, $=\mathrm{CH}CH_2$ *trans*-1,4-poly(BD)), 27.4 (s, 1C, $=\mathrm{CH}CH_2$ *cis*-1,4-poly(BD)) (note: the above ^{13}C integral ratios (1.25:1 trans/cis) are for poly(BD) obtained from initiator **5**).

Poly(1,3-cyclohexadiene) Characterization: solid-state ^{13}C NMR spectra (CPMAS, spinning speed 6.2 KHz, 5-mm rotor) δ 131.60, spinning sidebands at 255.13, 193.10, 70.10, and 8.29 (2C total, olefinic), 40.62 (2C, allylic methine), 24.87 (2C, methylene).

Acknowledgment. We gratefully acknowledge Prof. Robert H. Grubbs for many helpful discussions. The Air Force Office of Scientific Research is acknowledged for providing financial assistance to J.P.C. We thank Dr. Roger Assink and Ralph H. Hunkins at Sandia National Laboratories for providing ^{13}C-CPMAS NMR spectra of poly(CHD). We acknowledge the NSF Chemical Instrumentation Program for providing a low-field NMR spectrometer.

Supplementary Material Available: ^{19}F NMR spectra for complexes **5** and **8** along with the computer-simulated spectra, a table of ^{19}F coupling constants for these complexes, and a solid-state ^{13}C-CPMAS NMR spectrum of poly(CHD) obtained from initiator **5** (4 pages). Ordering information is given on any current masthead page.

OM9307444