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Ring Closure of 1,4-Pentadiene to Cyclopentene by a Zwitterionic Nickel Catalyst

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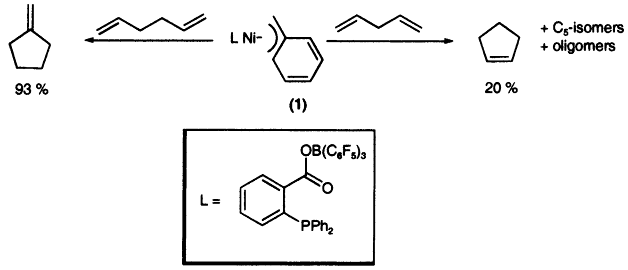
Summary: Ring closing of 1,5-hexadiene with $[(C_6H_5)_2PC_6H_4C(O-B(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2C_6H_5)$ *gives methylenecyclopentane. The reaction with 1,4-pentadiene provides 20% cyclopentene.*

Transition-metal-mediated ring-closing reactions have become an important tool for organic chemists.[1,2] An excellent example is the ring-closing olefin metathesis (RCM) of α,ω-dienes to cyclic structures with internal olefins, which takes advantage of ruthenium or molybdenum catalysts.[3] Early-transition-metal catalysts can also react with α,ω-dienes; however, this occurs via olefin insertion into a metal alkyl fragment, followed by elimination, to yield cyclic products different from those obtained by RCM. For example, 1,6- and 1,7-dienes undergo titanium-catalyzed ring closure to yield *exo*-methylenecycloalkanes, including heterocyclic compounds.[4] Competing reactions include oligomerization and olefin migration. Other metals have also been used to obtain different cyclization products.[2,5]

Despite their high reactivity toward olefins, the electrophilic nature of high-oxidation-state early transition metals makes their application in ring-closing reactions difficult when functionalized substrates are envisioned.[6] It was therefore of interest to examine the reactivity of α,ω-dienes with zwitterionic nickel complexes, such as $[(C_6H_5)_2PC_6H_4C(O-B(C_6F_5)_3)O\text{-}\kappa^2P,O]$-$Ni(\eta^3\text{-}CH_2C_6H_5)$[7] (**1**), for several reasons. First, activation occurs by Lewis acid attachment at a site removed from the substrate trajectory. Second, the partial positive charge at the metal center is less pronounced than in related cationic counterparts.[8] Third, a variety of Lewis acids can be used, including BF_3,[9] to modulate the steric encumbrance around the active site and the electron density at Ni. Finally, compound **1** shows a very high activity toward ethylene; however, it is possible to tune the reaction conditions so that the majority of the product is 1-butene.[7] Therefore, oligomerization reactions that diminish cyclization yields, or force the use of dilute concentrations, should be less significant. In this contribution we report on the reactivity of **1** with 1,5-hexadiene and on the unexpected ring closure of 1,4-pentadiene to cyclopentene.

^1H NMR spectroscopy of a solution with **1** (8 mM) and 1,5-hexadiene (0.8 M) in benzene shows quantitative formation of *exo*-methylenecyclopentane[10] over a period of 6 h (Scheme 1). No formation of the thermodynamically stable internal olefins was detected after a period of 43 h. This result was confirmed further by GC and GC/MS experiments. The *exo*-methylenecyclopentane is the expected product from 1,2-insertion followed by cyclization, as shown by previous reports.[6,11]

Scheme 1



The analogous reaction between **1** and 30 equiv of 1,4-pentadiene is more complex, is considerably slower, and does not reach completion. After 95 h, the main product is cyclopentene (20%, relative to 1,4-pentadiene, 6 turnovers per nickel site; Scheme 1), together with small amounts of *cis*- and *trans*-1,3-pentadiene (<5%) and oligomers (∼1%). Analysis of larger scale reactions under more dilute conditions ([Ni] = 1.2 mM, $[C_5H_8]$ =

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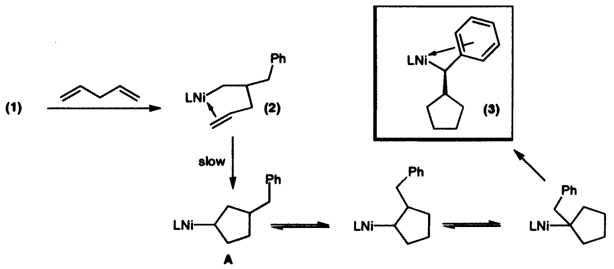
36 mM, toluene) using an internal standard with GC and GC/MS provides similar results, except that the oligomer fraction is lower.

To gain insight into this unprecedented metal-mediated conversion to cyclopentene, we examined the stoichiometric reaction between **1** (0.05 M) and 1,4-pentadiene (0.05 M) by NMR spectroscopy in C_6D_6 at room temperature. After 260 min, the ^{1}H NMR spectrum shows that 50% of **1** (relative to toluene as an internal standard) has been consumed to yield a new organometallic species (**2**), characterized by diastereotopic Ni−CH_2 signals (0.66 and 0.1 ppm) and a coordinated olefin (6.33, 4.85, and 4.78 ppm). While the ^{31}P NMR spectrum of **1** shows a signal at 25 ppm, **2** displays a peak at 15 ppm. On the basis of this information, we propose that this species is the olefin adduct **2** in Scheme 2, which forms upon direct insertion into **1**, followed by olefin coordination to the vacant metal site. Compound **2** is an intermediate, since its concentration reaches a maximum at approximately 340 min, while a second organometallic product begins to grow at the expense of **2**. This new compound (**3**) has no olefinic signals. The C−*H* adjacent to the carboxylic group resonates at 8.4 ppm. Additionally, there are aliphatic signals in the 1.7−0.6 ppm range and a single benzylic signal at 0.2 ppm. The ^{31}P NMR spectrum displays a signal at 21 ppm for **3**. However, NMR data could not be used for unambiguous characterization.

Scheme 2



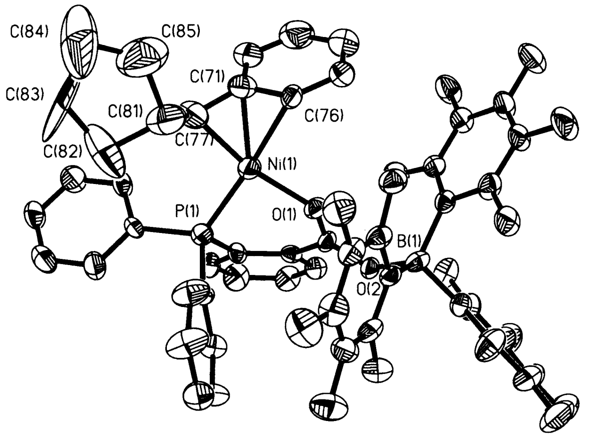
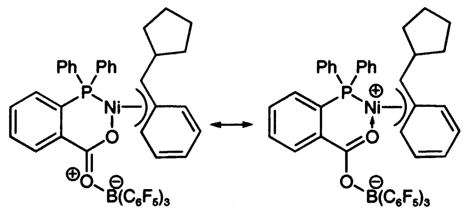


Figure 1. ORTEP drawing of [2-(diphenylphosphino)benzoate tris(pentafluorophenyl)borate-κ^2P,O](α-cyclopentylbenzyl)nickel(II) (**3**). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Pentane was layered on a C_6D_6 solution from NMR experiments, and the mixture was allowed to stand overnight. Red single crystals suitable for an X-ray structure determination were obtained, and the results of this study are shown in Figure 1.[12] Compound **3** is [2-(diphenylphosphino)benzoate tris(pentafluorophenyl)borate-κ^2P,O](η^3-α-cyclopentylbenzyl)nickel, with a pseudo-square-planar arrangement around the Ni(II) atom. The ancillary P−O ligand is essentially unperturbed, relative to **1**.[7] The most striking structural detail is the η^3-α-cyclopentylbenzyl ligand, which is derived from 1 equiv of 1,4-pentadiene and the η^3-benzyl fragment in **1**. The fragment chooses to bind so that the cyclopentane substituent is pseudo-trans to the aryl ring. The C−ONi (**3**; 1.203(9) Å) and C−OB (**3**; 1.259(8) Å) distances are intermediate between single and double C−O bond character, which requires participation of the two resonance structures



A plausible mechanism for the formation of **3** is shown in Scheme 2. Insertion of 1,4-pentadiene into **1** forms the olefin adduct **2**. Since four-membered-ring products are not obtained, 1,2-insertion of the olefin into the Ni−C$_\alpha$ bond (as is the case for the transformation of 1,5-hexadiene to methylenecyclopentane) does not take place. Instead, we propose 2,1-insertion regiochemistry to yield a Ni−cyclopentane intermediate (**A**) with benzyl substitution at the γ site. From this point the nickel may bind to the different carbons on the cyclopentane framework by β-H elimination and reinsertion reactions similar to those described for the formation of branched polyethylene from ethylene (i.e. “chain walking”) by cationic (α-diimine)nickel(II) complexes.[8,13] From the situation where Ni is bound to the tertiary carbon, β-elimination and reinsertion yields the Ni−(η^3-α-cyclopentylbenzyl) species.[14] It should be noted that addition of 1,4-pentadiene to **3** gives rise to a product distribution similar to that obtained using **1**. Thus, both compounds can initiate the cyclization reaction. We note the observation of (cyclopentylidene)methylbenzene by GC/MS in the product distribution when 5 equiv of 1,4-pentadiene is used, consistent with the presence of **3** during the catalytic reactions.

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(12) Crystal data for **3**: $C_{51.5}H_{35}BF_{15}NiO_2P$, M_r = 1071.29, crystal dimensions 0.27 × 0.20 × 0.03 mm, a = 16.46(2) Å, b = 12.489(12) Å, c = 23.97(2) Å, α = 90°, β = 104.42(2)°, γ = 90°, V = 4771(8) Å^3, monoclinic, $P2_1/c$, Z = 4, ρ_{calcd} = 1.492 g cm^{-3}, F(000) = 2172, μ = 0.540 mm^{-1}, 19 426 reflections measured, 6243 independent reflections, 6236 observed reflections ($I > 2\sigma(I)$), R1(observed data) = 0.0752, wR2(all data) = 0.2009, Siemens Smart CCD diffractometer, Mo Kα radiation (λ = 0.710 73 Å), graphite monochromator, T = 200 K. All calculations were completed using SHELXTL, including successive difference Fourier methods for refinement; final full-matrix refinements were against F^2. The file CCDC 233823 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts.retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, U.K., fax (+44)1223-336-033, or deposit@ccdc.cam.ac.uk).

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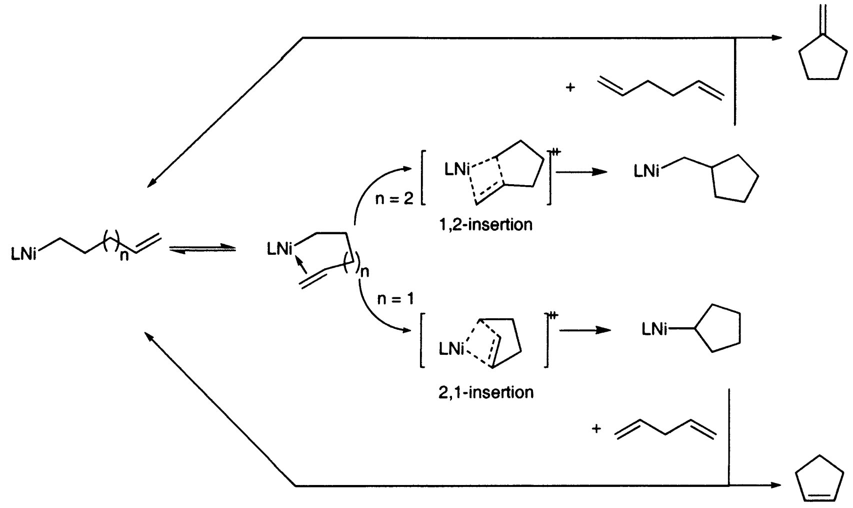
Scheme 3



The mechanism for the formation of **3** can also be used to understand the generation of cyclopentene from 1,4-pentadiene. Reaction of 1,4-pentadiene by the formal insertion into Ni−H yields an intermediate similar to **2**, with H in place of the benzyl substituent. Cyclization by 2,1-insertion provides a structural analogue of **A**, again with H instead of benzyl: i.e., a Ni−cyclopentyl intermediate. "Walking" of nickel around the five-membered ring only produces degenerate structures. Subsequent reaction with 1,4-pentadiene regenerates the olefin adduct analogue of **2** and produces 1 equiv of cyclopentene. There are two plausible mechanisms for the initial insertion of the substrate. The first involves a β-H elimination step that yields the product and a Ni−H species which quickly inserts one of the olefin functionalities to yield the Ni−alkyl species. The second possibility is a β-H transfer step induced by the substrate. While we favor the second option on the basis of theoretical examination of analogous nickel systems,[15] the exact mechanism has not been determined at this stage.

The cyclization step (**2** → **A** in Scheme 2) is slow, probably because of the twisted nature and high ring strain of the transition step required for 2,1-insertion (Scheme 3). With 1,5-hexadiene, the longer tether allows for 1,2-insertion and concomitant formation of methylenecyclopentane. During catalytic action chain walking from the olefin adduct with H (instead of benzyl) becomes a statistical probability. Once the nickel reaches the inner carbon of the chain, allyl formation takes place (Figure 2), which has a considerably slower reaction rate toward olefins with respect to the η^3-benzyl group. No further reaction takes place at this point.[7]

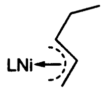


Figure 2. Catalytic deactivation by formation of η^3-pentyl species.

In summary, we have shown that it is possible to form cyclopentene from 1,4-pentadiene by using **1** as the initiator. The observation of **2** and the isolation of **3** from the stoichiometric reaction support a mechanism which involves 2,1-insertion from the olefin adduct **A**. Product selectivity of 1,4-pentadiene and 1,5-hexadiene is determined by the strain of the transition state leading to olefin insertion. The trimethylene chain leads to a prohibitively high ring strain for the case of 1,2-insertion but allows for the 2,1-insertion geometry. No such restrictions are evident for a tetramethylene chain, and one obtains the expected methylenecyclopentane product.

Experimental Section. Procedure for NMR-Scale Reactions. An NMR tube was charged with approximately 2.5−15 mg (3−16 μmol) of **1** and 500 μL of C_6D_6. 1,5-Pentadiene was added in a 30-fold excess; 1,5-hexadiene was added in a 100-fold excess. The tube was capped, sealed with Parafilm, and shaken to mix the reagents. Whenever possible, the spectra of the products were confirmed by comparison with those of authentic samples.

Observation of 2 and Characterization of 3. A resealable NMR tube was charged with 29 mg (30 μmol) of **1**, 600 μL of C_6D_6, and 2 mg (30 μmol) of 1,4-pentadiene. ^{1}H and ^{31}P NMR spectra were used to monitor the consumption of **1** and showed new signals for **2**. Broad signals precluded calculation of most coupling constants, and the presence of some impurities obscured complete assignment of NMR resonances. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.63 (m, 1 H, ortho to carboxylate), 7.2−6.4 (m, 18 H, aromatic), 6.33 (m, 1H, $CH_2C\mathit{H}{=}CH_2$), 4.85 (d, 1 H, J_{HH} = 8 Hz, cis-terminal olefinic), 4.78 (d, 1 H, J_{HH} = 16 Hz, trans-terminal olefinic), 2.7−1.3 (m, 3 H, methylene + methine), 0.9 (d, 2 H, J_{HH} = 4 Hz, $C\mathit{H}_2Ph$), 0.6 (m, 1 H, $-C\mathit{H}_2Ni$), 0.1 (m, 1 H, $-C\mathit{H}_2Ni$). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 15 (br).

The solution was allowed to stand for 5 days, during which time the color of the solution changed from orange to red. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.4 (ddd, 1 H, J_{HH} = 8 Hz, J_{HP} = 4 Hz, J_{HH} = 1 Hz, *o*- to carboxylate), 7.3−6.5 (m, 18 H, aromatic), 1.7−0.6 (m, 9 H, cyclopentyl methylene + methine), 0.2 (m, 1 H, benzylic). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 21. X-ray-quality crystals were obtained by pentane diffusion into a solution of **3** in benzene.

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General Procedure for Cyclization Reactions. A 20 mL vial was charged with **1**, 5 mL of toluene, and the appropriate diolefin. The reaction mixture was stirred rapidly, and 0.3 mL aliquots were taken periodically for analysis by GC and GC/MS. Each aliquot was diluted with 0.5 mL of 1-chlorohexadecane and filtered through a plug of alumina. Yield determination was carried out by GC, while GC/MS was used for structural assignment. The results from the NMR scale reactions were also used as an aid in identifying products. Whenever possible, retention times and fragmentation patterns were compared with authentic samples.

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, and all bond lengths and angles for **3**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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