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Cis, Isotactic Selective ROMP of Nobornenes Fused with N-Arylpyrrolidines. Double Stranded Polynorbornene-Based Ladderphanes with Z-Double Bonds

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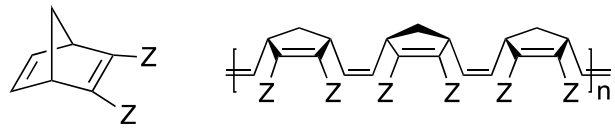
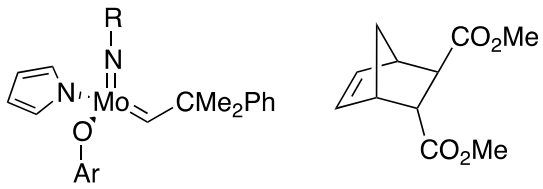
There is an ever burgeoning interest in the stereoselective formation of double bonds by olefin metathesis.[1-6] Various catalysts have recently been developed for Z-selectivity in homocoupling,[2] cross metathesis (CM),[3] ring closing metathesis (RCM),[4,] and ring opening metathesis polymerization (ROMP).[5] The involvement of a bulky or a chelated ligand is crucial to direct the orientation of the incoming olefin that may lead to the stereoselective formation of a metallacyclobutane intermediate.[1-6] Alkyne metathesis followed by partial hydrogenation offers an alternative route for the synthesis of Z-olefins.[7] The nature of olefin substrates may also control the stereochemistry of double bonds in olefin metathesis. For example, the presence of a bulky 2-silyl substituent in terminal olefins furnishes exclusively E-silyl-substituted cycloalkenes which are converted to the corresponding Z-alkenes by desilylation.[8] Certain cycloalkenes also undergo ROMP stereoselectively under various conditions.[5,9– 11] Thus, norbornadiene derivatives **1** give cis, syndiotactic ROMP polymer **2** upon treatment with a Mo-catalyst **3**.[5a,b] Similar reaction with

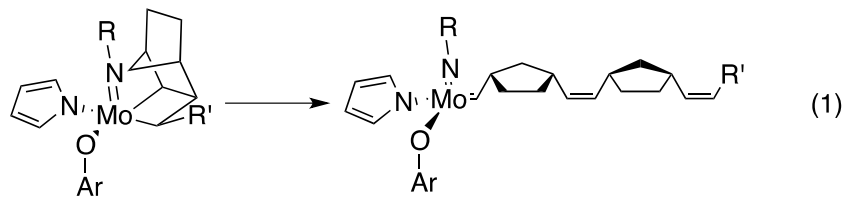
racemic *endo,exo*-5,6-dicarbomethoxynorbornene **4** yields predominantly the corresponding polynorbornene with *cis,syndio,alt* selectivity.[5c] The key to the success relies on the steric differentiation between small imido and bulky aryloxide ligands resulting all substituents on the metallacyclobutane intermediate to have a *syn* relationship. The inversion of metal configuration in each insertion of the monomeric norbornene derivative during the course of polymerization would be responsible for the syndiotactic selectivity (eq 1). A chelated ruthenium catalyst **7** has recently been disclosed to show cis-selectivity in ROMP of norbornene derivatives.[5d]



1 **2**

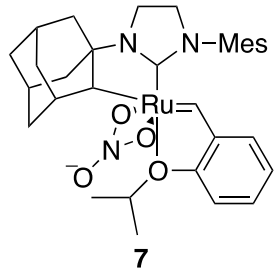


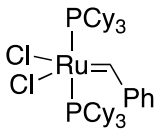
3 **4**



(1)

5 **6**

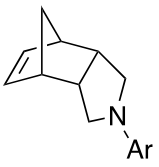




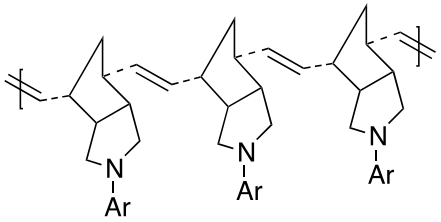
7 **8**

ROMPs of norbornenes fused with *endo*-N-arylpyrrolidine **9** with the first generation Grubbs catalyst **8** yield polynorbornene **10** with isotactic stereochemistry and trans

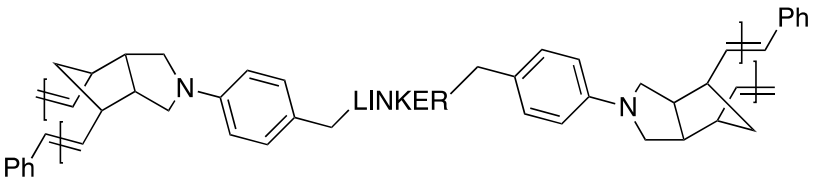
double bonds.[9] This protocol has been employed for the synthesis of a series of double stranded ladderphanes **11**.[11] It is noteworthy that the presence of the N-aryl pendant in **9** is indispensible in these transformations. Unlike **1** and **4**, the endo site of the norbornene moiety in **9** is highly crowded. It is envisaged that, upon treatment with a Mo catalyst like **3**, the mode of interactions between **9** and the molybdenum catalyst could be very different from those shown in eq 1.[5a-c] In particular, when bulky bidentate substituted biaryl-*o,o'*-diphenoxide ligand is used,[12] the front side of the catalyst **12** would be blocked by the biaryl ligand. Accordingly, the double bond of **9** would interact with molybdenum–carbene moiety from the backside. In order to avoid steric interaction between the endo-pyrrolidine group and the imido ligand as in **14**, the orientation of the incoming nobornene moiety **9** would preferentially interact with intermediate **13** via a transition state **15**. Polynorbornene **16** thus obtained may adopt a cis, isotactic stereochemistry. Indeed, when enantiomerically pure **4** is treated with **3**, that a mixture of the corresponding *cis,syndio,alt*- and *cis,iso,sing*-polynorbornenes is obtained can be understood within the framework of the steric interactions between the *endo*-carbomethoxy substituent and ligands in **3**.[5c] The steric hindrance around the *endo* site in **9** would be much larger than that in **4**. It is therefore felt that a much better cis, isotactic selectivity would be obtained upon treatment with an appropriate molybdenum-carbene catalyst. We now wish to report the first cis, isotactic- polynorbornenes from the reactions of **9** and related bisnorbornenes **18** and **20** with **12**.



9 Ar = $C_6H_4CO_2Et$



10 Ar = $C_6H_4CO_2Et$



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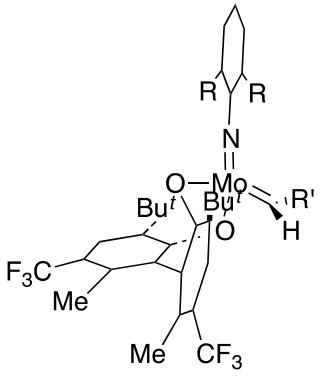
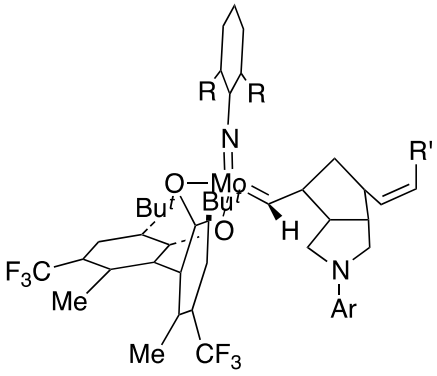
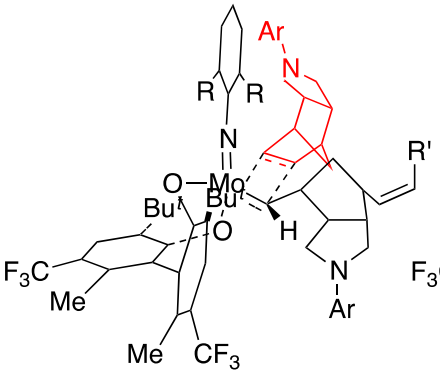
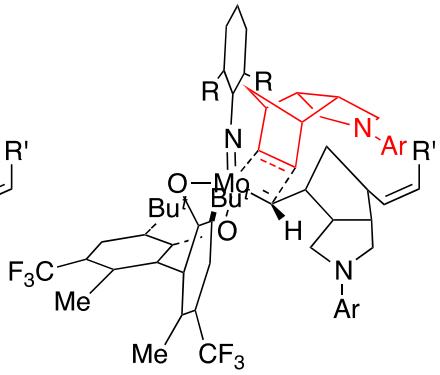




12a R = ^{i}Pr, R' = $PhMe_2C$-
12b R = Me, R' = $PhMe_2C$-

13



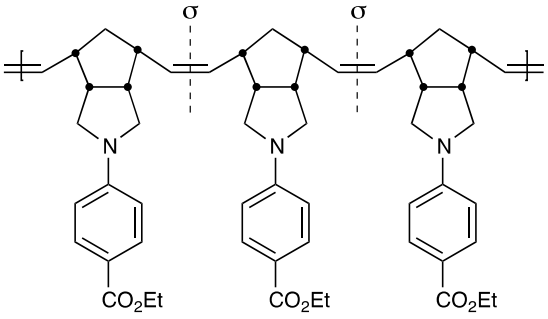


14

15

Treatment of **9** with **12a** in DCM at rt for 2 h followed by quenching with PhCHO afforded **16a** in 68% yield and the results are summarized in Table 1. Similar result was obtained from the reaction of **9** with **12b**. The ^{13}C NMR spectrum of **16a** shows four single peaks at δ 39.2, 40.4, 47.5, and 49.4 attributed to the ring carbons of the

azabicyclooctane skeletons for each of the monomeric unit. These results suggest that there is a symmetry plane between adjacent monomeric units in **16a** and the double bonds should therefore be in cis configuration. This pattern is completely different from those of **10a** having trans double bonds and isotactic structure, which exhibits essentially two sets of ^{13}C signals in the high field region because of the lack of the symmetric plane between adjacent monomeric units.[9] The same hydrogenated product **17** obtained from the diimide reductions of **16a** and of **10a** indicates that both **16** and **10** should have same isotactic stereochemistry.



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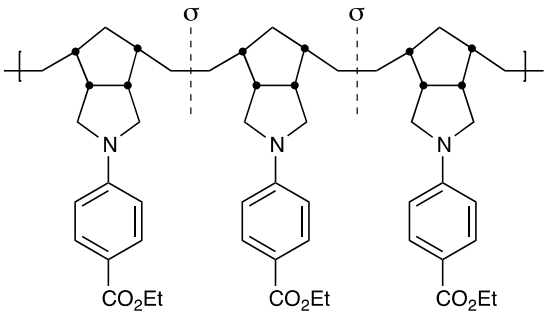


17

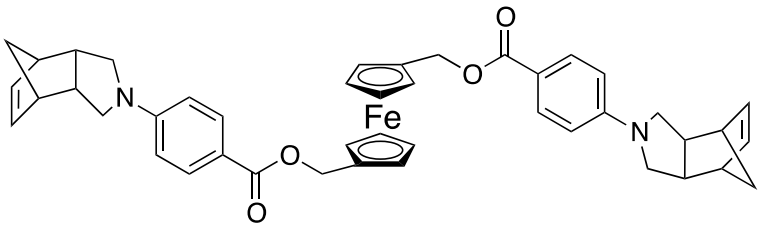
Polynorbornene-based double-stranded and triple stranded ladderphanes have recently been disclosed by **8**-catalyzed ROMP of the corresponding bis- and tris-norbornene monomers.[11] One of the most important criteria for the successful synthesis of these ladderphanes relies on the stereoselective formation of single stranded polynorbornenes. It is therefore believed that the molybdenum-catalyzed stereoselective synthesis of cis, isotactic-**16** mentioned above has paved the way for the access of ladderphanes with Z-double bonds. Thus, reaction of **18** with a catalytic amount of **12a** in DCM afforded ladderphane **19** in 50% yield. The ^{13}C

Table 1. Gel permeation chromatography results of polymers.

Polymer	M_n	M_w	PDI	n[a]
16a	55,300	69,600	1.3	195
17	55,600	69,000	1.2	195
19	11,500	14,600	1.3	16
16b	4,500	5,500	1.2	16
21	14,900	17,200	1.2	24
16c	7,100	8,400	1.2	25
22	12,800	16,900	1.3	18
10b	5,700	7,000	1.2	20
23	9,600	11,200	1.2	16
10c	4,700	5,800	1.2	17

[a]Degree of polymerization.

NMR spectrum of **19** shows characteristic signals at δ 38.8, 40.6, 40.9, and 46.5 attributed to the carbons of the azabicyclooctane moieties with two double bond substituents in cis configuration. Ethanolysis of **19** with NaOEt gave 86% yield of **16b**. In a similar manner, ladderphane **21** was obtained in 56% yield from the **12a**-catalyzed ROMP of **20**. Again, **21** was transformed into **16c** by ethanolysis with NaOEt. Similar degree of polymerization for **19** and **16b** and for **21** and **16c** further support the double stranded nature of **19** and **21**. The corresponding ladderphanes **22** and **23** with all trans double bonds were prepared from **18** and **20** by **8**-catalyzed ROMPs for comparison. Ethanolysis of **22** and **23** gave **10b** and **10c**, respectively having trans, isotactic stereochemistry.



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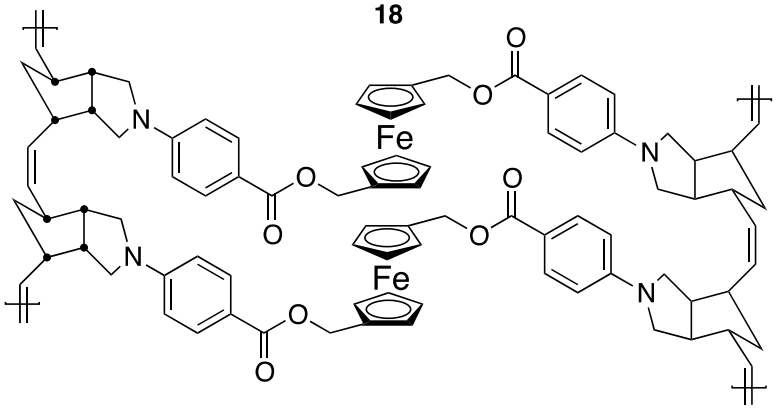

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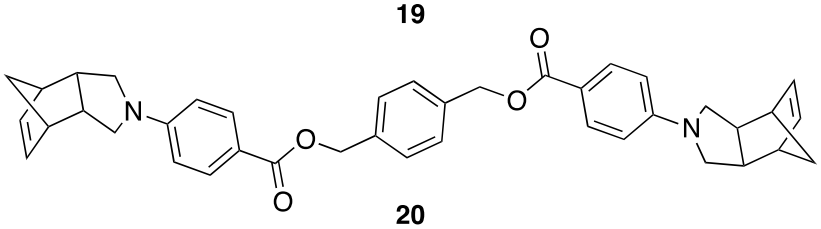

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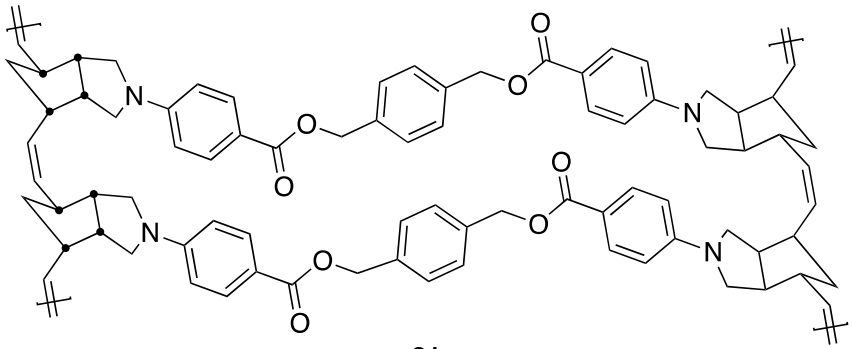

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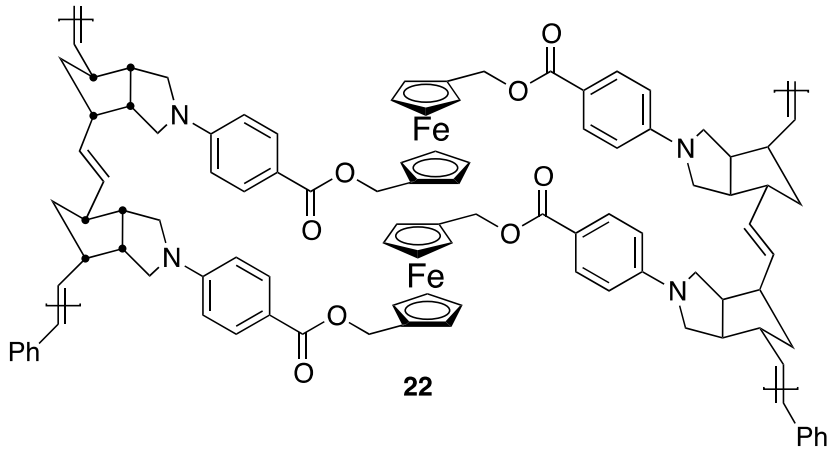

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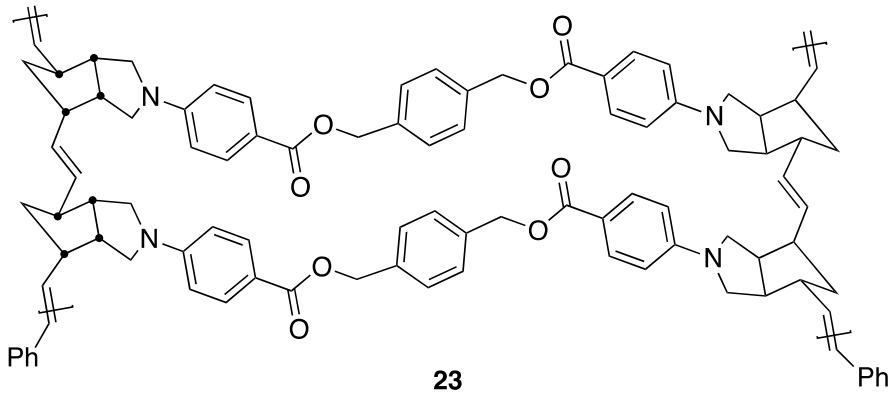

23

It is known that polynorbornene-based double stranded ladderphanes **11** with trans double bonds can form a two-dimensional well-oriented array on highly ordered pyrolytic graphite surface (HOPG) as revealed by scanning tunneling microscopy (STM).[11,13] Stacking interaction between styrene and vinyl end groups along the longitudinal axis of the polymer and van der Waals interaction between polymeric backbones in the second dimension may be responsible for such ordered pattern.[13] Polymers **19** and **21** have similar end groups (styrene and substituted vinyl). It is therefore envisaged that a similar aggregate may also be formed from these ladderphanes with all cis double bonds. Indeed, the STM image of **19** shown in Figure 1 exhibits a nice two-dimensional array. The relatively bright and dark features of the lamellae are ascribed, respectively, to the aromatics and norbornyl moieties based on their tunneling efficiency. High resolution images (Figure 1b) show the nominal width of ~2.5 nm and the spacing of 0.5–0.6 nm between linkers, consistent with the corresponding dimensions of **19**. The stability of the assembly

for **19** appears inferior to that of its trans analogue **22**. After being subjected to STM scanning, the former becomes disordered after a couple of imaging frames while the latter is unaffected.[11,13] The observation suggests weaker interactions of the cis polymer **19** with the substrate and between the terminal groups.

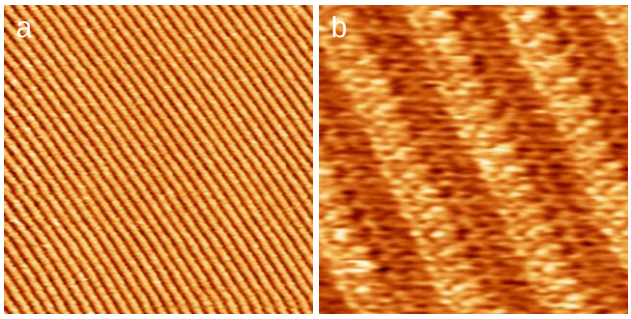

Figure 1. STM images of **19** exhibiting submicron, long-range order array. Image size: (a) 80x80 nm (b) 8x8 nm. Imaging conditions of E_{bias} and $i_{tunneling}$: (a) 0.90 V, 50 pA, (b) 0.90 V, 90 pA. Sample preparation: dropcasting 10-・L **19**-containing phenyloctane on HOPG and subsequently being shear-aligned by removal excess solvent with a piece of tissue.[11,13,14].

In summary, we have described the first synthesis of cis, isotactic polynorbornenes stereoselectively using a molybdenum-carbene catalyst. The presence of *endo*-fused N-arylpyrrolidine moiety in monomeric norbornenes may play a pivotal role to direct the stereoselectivity of the ROMP of these norbornenes catalyzed by **12**. The present results using molybdenum catalyst **12** complement the previous works employing ruthernium catalyst **8** on the ROMP of polynorbornenes fused with endo-N-arylpyrrolidine monomers.[9,11] It is worth noting that morphology of ladderphanes with Z double bonds (e.g. **19** and **21**) on HOPG behave similarly to those with E double bonds.[11]

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