Nickel(II) and Palladium(II) Complexes with an Alkane-Bridged Macrocyclic Ligand: Synthesis, Characterization, and Polymerization Tests

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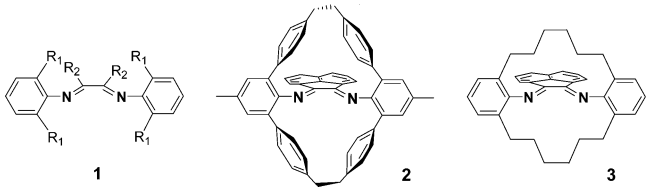
An efficient synthetic route to a novel macrocyclic aryl α-diimine ligand bearing C_6 hydrocarbon bridges connecting the aryl ortho positions is described. Pd(II) and Ni(II) complexes with the new macrocyclic ligand (**10** and **14**) were successfully synthesized and characterized. The X-ray crystal structures of complexes **10** and **14** show that the complexes exhibit coordination geometry similar to that of their acyclic analogues and the alkyl bridges do not introduce significant ring strain into the complexes. The preactivated Pd(II) complex **12** and the allyl nickel complex **14** were tested for ethylene polymerization. Potential reasons for the low catalytic activities are discussed.

Introduction

In polymerization catalyst design both ligand electronics and sterics play important roles in determining the catalyst activity and polymer molecular weight. One remarkable example of ligand steric effects can be found in the development of late transition metal polymerization catalysts. For the Shell higher olefin process (SHOP) catalyst, in which Ni(II) is complexed to a ligand without steric bulk, β-H elimination and chain transfer compete favorably with chain growth and short α-olefins are formed as the major products. The fast chain transfer in late transition metal catalysts is generally believed to be through an associative process, in which olefin monomer associates from the axial direction of the metal center and replaces a terminal polymer olefin formed from β-H elimination. To suppress the facial chain transfer, Brookhart and co-workers developed Ni(II) and Pd(II) complexes with bulky α-diimine ligands that are highly productive for olefin polymerization and form high molar mass polyolefins (**1** in Chart 1).[1−3] Although β-H elimination is still competitive with chain propagation in Brookhart catalysts, as manifested by chain walking to form branched polymers,[1−8] the sterically encumbered α-diimine ligands prevent associative exchange following the formation of olefin-hydride species.[9] A systematic correlation was observed between polymer molecular weight and the ortho-aryl subsituent size in α-diimine ligands, with the more bulky substituent affording higher polymer molecular weight.[10] In other late transition metal polymerization catalysts, ligand sterics are also found to have significant effects on polymer molecular weight.[11]

Chart 1



To completely shut down associative chain transfer from the axial direction for the α-diimine-Ni(II) and -Pd(II) catalysts, our group recently developed a cyclophane-based α-diimine ligand for Ni(II) and Pd(II) complexes for the preparation of highly productive and robust olefin polymerization catalysts (**2** in Chart 1).[12−15] In our cyclophane-based complexes, the metal center is positioned at the core of the ligand so that the macrocycle completely blocks the axial faces of the metal, leaving only two *cis*-coordination sites for monomer entry and polymer growth. The rigid framework of the ligand prohibits free rotation of the aryl−nitrogen bonds, which should allow the catalyst to make high MW polymers at elevated temperature. The lack of rotational flexibility should also prevent C−H activation to the ortho subsitutents, which was proposed to be a

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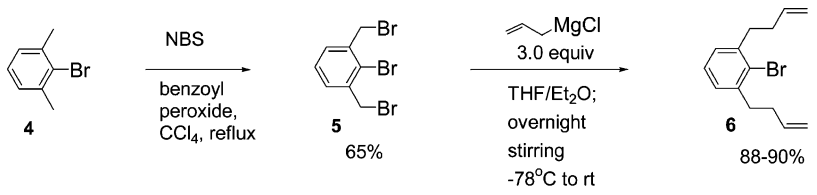
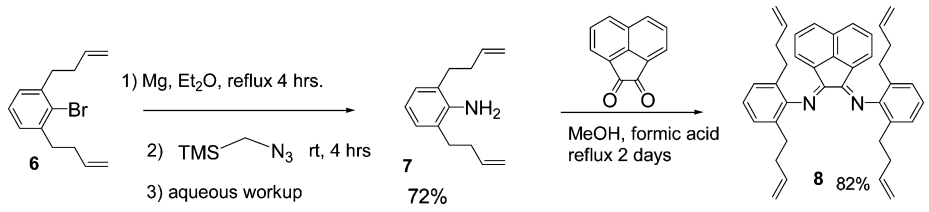
Scheme 1



Scheme 2



potential catalyst deactivation pathway by Brookhart and co-workers.[9] Indeed, we were pleased to observe that our cyclophane-based Ni(II) and Pd(II) catalysts have significantly higher thermal stability than the acyclic analogues.[13] The Ni(II)-cyclophane catalyst was extremely productive for ethylene polymerization to form high molecular weight polyethylene at a range of temperatures.[13] The Ni(II) complex was also able to initiate living polymerization of α-olefins at elevated temperatures.[15] We recently discovered that our cyclophane-based Pd(II) catalyst is much more efficient in incorporating polar olefins such as methyl acrylate.[16]

In our further efforts on investigating macrocyclic ligands for olefin polymerization catalysis, we recently synthesized an alkane-bridged macrocyclic α-diimine ligand **3** (Chart 1). Following a similar concept for our *m*-terphenyl-based cyclophane ligand **2**, ligand **3** is designed to have the two aryl groups being connected by alkyl bridges with the α-diimine moiety situated in the core of the macrocycle. By using alkyl bridges, ligand **3** is viewed as a structurally closer macrocyclic analogue of ligand **1**. The hydrocarbon bridge is envisioned to shield the axial positions of the metal center, which should play an important role in suppressing the associative chain transfer in olefin polymerizations.[17] On the basis of these considerations, we have synthesized the ligand **3** and its corresponding Ni(II) and Pd(II) complexes. Herein we report the synthesis, characterizations, and ethylene polymerization attempts of these complexes.

Results and Discussion

A. Synthesis and Characterization of Alkane-Bridged α-Diimine Ligand. The key step of macrocycle formation in the synthesis of **3** was achieved by ring-closing metathesis (RCM) of an α-diimine precursor containing terminal olefins. This required the preparation of aniline **7**, containing two terminal alkene substituents at ortho positions of the phenyl ring. On the basis of molecular modeling, a six-methylene bridge ($-(CH_2)_6-$) seems to have an ideal fit to the spacing between the two phenyl rings in the α-diimine. Therefore, four-carbon 1-butenyl substituents were first installed onto the ortho positions of aniline **7**. The synthesis started with the α-bromination of the commercially available 2-bromometaxylene **4** to give **5** in good yield.[18] The choice of the bromobenzene **4** as starting material instead of its aniline analogue was to avoid complication with the subsequent Grignard reaction. With the treatment of allylmagnesium chloride, **5** underwent clean substitution at the benzylic positions to give **6** in 90% yield. The bromine at the benzene ring was not affected even with excess allylmagnesium chloride. The next step was a critical transformation in which bromobenzene **6** was converted to aniline **7**. The key to effect this transformation was the choice of trimethylsilylmethyl azide as the aminating agent.[19] Thus, treatment of **6** with Mg gave the corresponding Grignard reagent, which upon addition of trimethylsilylmethyl azide and subsequent aqueous workup afforded aniline **7** in 72% yield.[19,20] The resulting aniline was conveniently converted to α-diimine **8** by condensation with acenaphthenequinone. Initial attempts of cyclization of **8** by ring closing metathesis (RCM) of **8** in dichloromethane using generation 1 or 2 of the Grubbs ruthenium carbene catalysts only afforded a monocyclic product. Computer modeling shows that once the first ring is formed, the opposite side of the aryl opens up, thus making it harder for the remaining olefins to come in proximity, which presumably increases the activation barrier for the second ring-closing reaction. On the basis of this consideration, more forceful conditions were investigated to achieve the double cyclization by RCM. After optimizing reaction conditions, RCM in toluene at 90 °C[21] in combination with slow addition of the Grubbs catalyst with time gave product **9** in 70% yield,[22] which was further hydrogenated to provide the final product, **3**, in 92% yield. The structure of **3** was characterized by ^1H and ^{13}C NMR and combustion analysis.

B. Synthesis and Structural Characterization of Ni(II) and Pd(II) Complexes with the Alkane-Bridged α-Diimine Ligand. Synthesis and Characterization of Pd(II) Complexes. With ligand **3** in

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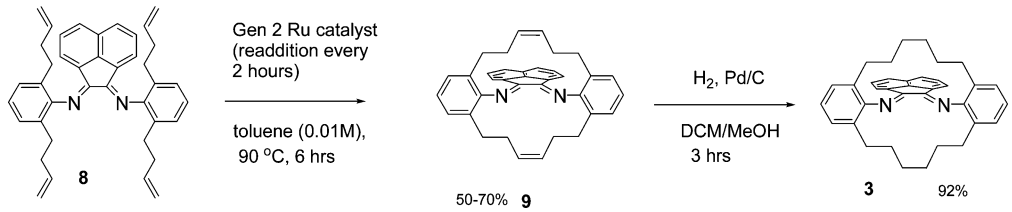
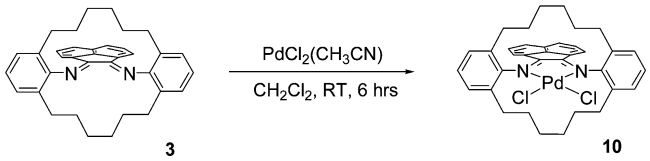
(22) The TLC of the reaction shows three close spots with the same molecular mass, suggestive of cis/trans product ratios. The fractions are combined and used for the hydrogenation step.

Scheme 3



Scheme 4



hand, various Ni(II) and Pd(II) complexes with it were prepared. First, a $PdCl_2$ complex with the new ligand (**3**) was prepared by mixing $PdCl_2(CH_3CN)$ with ligand **3** in dichloromethane. The complexation was evident by a change in color from orange to red-orange. ^{1}H NMR monitoring of the complexation indicated that the reaction was complete within 6 h to give complex **10**. High-quality single crystals suitable for X-ray analysis for the Pd(II) complex **10** were obtained by carefully layering a slightly concentrated dichloromethane solution of **10** with *n*-decane. The X-ray crystal structure of complex **10**[23] (Figure 1) shows a square planar coordination geometry with the Pd(II) center being positioned in the core of the cyclophane ligand. The alkyl bridges lie above and below the coordination plane. The torsion angles between the five-membered palladacyclic coordination plane (Pd1−N1−C1−C11−N2) and the two aryl planes (C13−C18 and C25−C30) are 76.7° and 77.4°, respectively. These are very close to the values for an acyclic Pd(II)-α-diimine complex (78.6° and 79.4°) reported by Brookhart and co-workers,[9] indicating that the alkane bridges do not introduce significant ring strain to the complex. The crystal data and structure refinement parameters and selected bond lengths, angles, and interplanar angles of complex **10** are summarized in Tables 1 and 2, respectively.

Because $PdCl_2$ complexes usually are not good precursors for direct activation by methylaluminoxane (MAO) for olefin polymerization, a preactivated Pd(II) complex was then synthesized for the polymerization test. In the first step, a Pd(Me)Cl complex of ligand **3** was synthesized by following a methodology recently developed in our laboratory.[24] Due to steric encumbrance of the macrocyclic ligand, direction methylation of the $PdCl_2$ complex **10** with various methylation reagents (such as $Sn(CH_3)_4$) was not successful. In our previous studies, we have developed an efficient strategy of synthesizing sterically encumbered LPd(Me)Cl complexes by in situ generation of $(PhCN)_2Pd(Me)Cl$ followed by exchange of the labile benzonitrile (PhCN) ligand with the desired chelating ligand.[24] As shown in Scheme 5, this strategy was successful for the synthesis of the Pd(Me)Cl complex **11** in 80% yield. The complex **11** was subsequently activated by sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (NaBAF) followed by addition of methyl acrylate to give the preactivated Pd(II) catalyst **12** in 95% yield as a brick red solid.

Synthesis and Characterization of Ni(II)-Allyl Complex. Our initial attempts for the preparation of NiX_2 complexes with ligand **3** using $(DME)NiBr_2$, $(DME)NiCl_2$, and NiF_2, respectively, as precursors were not successful. Presumably, the tetrahedral geometry of Ni(II) halide complexes prevents them from coordinating to the macrocyclic ligand due to the sterics imposed by the bridges on both sides of the imine plane. Attempts to make the planar dimethyl complex were also unsuccessful. After many attempts, finally we succeeded in preparing the nickel-allyl complex of ligand **3**. Treating the ligand with π-allyl nickel chloride dimer[25] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAF) afforded the corresponding η^3-allyl(α-diimine)-nickel complex **14** in 67% yield (Scheme 6).

Complex **14** was fully characterized by NMR, high-resolution mass spectroscopy (HRMS), and X-ray crystal analysis. The X-ray crystal structure of complex **14**[26] (Figure 2) shows that the Ni(II) complex has a coordination geometry similar to that of complex **10**. The Ni(II) center is coordinated to the bidentate α-diimine and the π-allyl ligand in a square planar coordination geometry.

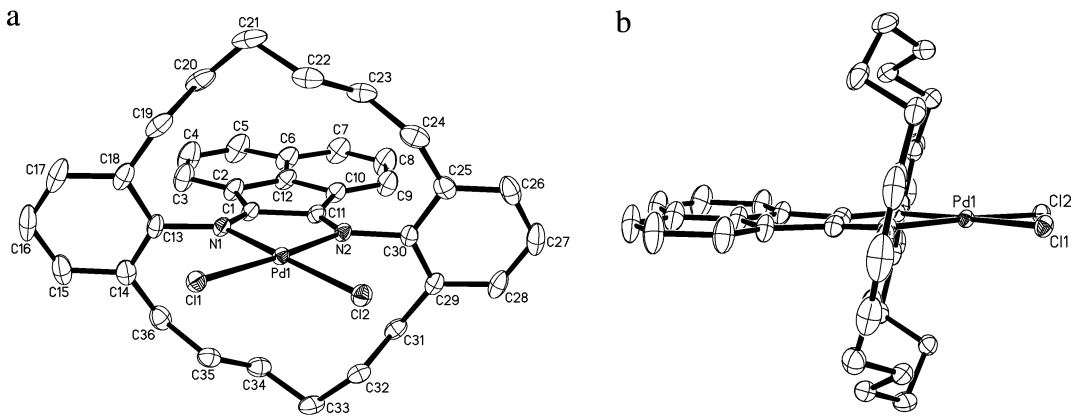


Figure 1. X-ray crystal structure of the $PdCl_2$ complex **10** showing important atoms labeled: (a) front view and (b) side view (*n*-decane solvent molecule was removed for clarity; the atoms were drawn with 50% thermal ellipsoids).

Table 1. Summary of Crystal Data and Structure Refinement Parameters of Complexes 10 and 14

	10	**14**
empirical formula	$C_{36}H_{36}Cl_2N_2Pd\cdot{}^1/_2C_{10}H_{22}$	$C_{71}H_{53}BF_{24}N_2Ni$
fw	745.11	1459.67
cryst color	orange	red
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	12.7132(11)	21.472(2) Å
b (Å)	11.5066(10)	14.6907(15) Å
c (Å)	24.026(2)	21.881(2) Å
α (deg)	90	90
β (deg)	93.064(2)	111.013(2)
γ (deg)	90	90
V (Å^3)	3509.6(5)	6443.0(11)
Z	4	4
density (Mg/m^3)	1.410	1.505
abs coeff (mm^{-1})	0.713	0.416
F(000)	1548	2968
cryst size (mm)	0.34 × 0.32 × 0.22	0.35 × 0.26 × 0.20
scan mode	ω	ω
detector	Bruker-CCD	Bruker-CCD
θ range for data collection (deg)	1.60 to 28.30	1.14 to 24.71
index ranges	$-16 \le h \le 16$, $-15 \le k \le 15$, $-32 \le l \le 31$	$-20 \le h \le 25$, $-16 \le k \le 17$ $-25 \le l \le 25$
no. of reflns collected	35 898	32 601
no. of indep reflns	8470 [R(int) = 0.0205]	10 856 [R(int) = 0.0259]
completeness to $\theta = 28.30°$	97.2%	98.8%
abs corr	semiempirical from equivalents	
max. and min. transmn	0.8589 and 0.7936	0.9214 and 0.8681
refinement method	full-matrix least-squares on F^2	
no. of data/ restraints/ params	8470/6/390	10 856/0/896
goodness-of-fit on F^2	1.067	1.037
final R indices [$I > 2\sigma(I)$]	R1 = 0.0482, wR2 = 0.1475	R1 = 0.0628, wR2 = 0.1600
R indices (all data)	R1 = 0.0531, wR2 = 0.1520	R1 = 0.0772, wR2 = 0.1725
largest diff peak & hole (e·Å^{-3})	3.034 and −0.946	1.504 and −0.646

The alkyl bridges lie above and below the coordination plane. The crystal data of **14** indicate that the allyl C1−C3 unit is slightly disordered. The C2 can occupy two positions: one slightly above the coordination plane and the other slightly below it (see Supporting Information). The torsion angles between the five-membered coordination plane (Ni1−N1−C4−C14−N2) and the two aryl planes (C16−C21 and C28−C33) are 76.7° and 80.0°, respectively. Again, these values are very close to the corresponding torsion angles for the Pd(II) complex **10** and the Brookhart acyclic Pd(II)-α-diimine complex,[9] suggesting that the alkyl bridges do not introduce significant ring strain to the complex. The crystal data and structure refinement parameters and selected bond lengths, angles, and interplanar angles of complex **14** are summarized in Tables 1 and 2, respectively.

C. Ethylene Polymerization Tests and Discussion. Following the synthesis and structural characterization, both the preactivated Pd(II) complex **12** and Ni(II)-allyl complex **14** were tested for ethylene polymerization. To our disappointment, under a variety of ethylene pressures and polymerization temperatures the Pd(II) complex **12** afforded only a trace amount of polyethylene (TON < 10). The Ni(II)-allyl complex **14**, upon activation with tris(pentafluorophenyl)borane, again yielded only a trace amount of polymers. For the Ni(II) complex, we also attempted in situ generation of the **3**−$NiBr_2$ complex, which upon activation by MMAO also gave low activity for ethylene polymerization (TON < 400). The unanticipated low polymerization activity for the Ni(II) and Pd(II) complexes prompted us to reexamine their structures more carefully.

The space-filling representation of the X-ray crystal structures for **10** and **14** are shown in Figure 3. To better view the sterics imposed by the ligand environment to the metal sites, the chloride atoms in **10** and the allyl fragment in **14** are truncated for clarity. It appears that the catalytic sites in both complexes are very crowded because of the alkyl bridges above and below the coordination plane. Compared with the Brookhart acyclic α-diimine complexes and our aromatic cyclophane-based complexes, complexes **10** and **14** are significantly more crowded at the metal centers. Because of the macrocyclic geometry, this high sterics cannot be alleviated by conformational rotation. The high sterics and rigid structure may either prevent the entry of ethylene monomer or significantly increase the insertion activation energy, resulting in reduction of

Table 2. Selected Bond Lengths (Å), Angles (deg), and Interplanar Angles (deg) for 10 and 14

10		**14**	
	Bond Lengths		
Pd(1)−N(2)	2.042(3)	Ni(1)−N(2)	1.936(3)
Pd(1)−N(1)	2.045(3)	Ni(1)−N(1)	1.945(3)
Pd(1)−Cl(2)	2.2800(8)	Ni(1)−C(1)	2.021(4)
Pd(1)−Cl(1)	2.2815(8)	Ni(1)−C(2)	1.975(7)
N(1)−C(1)	1.286(4)	Ni(1)−C(3)	2.016(4)
N(1)−C(13)	1.438(4)	N(1)−C(4)	1.287(4)
C(1)−C(2)	1.460(5)	N(1)−C(16)	1.434(5)
C(1)−C(11)	1.486(5)	C(4)−C(5)	1.459(5)
C(2)−C(12)	1.422(5)	C(4)−C(14)	1.481(5)
		C(5)−C(6)	1.380(5)
	Bond Angles		
N(2)−Pd(1)−N(1)	79.65(11)	N(1)−Ni(1)−N(2)	83.21(12)
N(2)−Pd(1)−Cl(2)	95.12(8)	N(1)−Ni(1)−C(1)	101.44(16)
N(1)−Pd(1)−Cl(2)	174.02(8)	N(1)−Ni(1)−C(3)	174.86(17)
N(2)−Pd(1)−Cl(1)	174.58(8)	N(2)−Ni(1)−C(1)	174.26(16)
N(1)−Pd(1)−Cl(1)	94.95(8)	N(2)−Ni(1)−C(3)	101.73(17)
Cl(2)−Pd(1)−Cl(1)	90.30(3)	C(1)−Ni(1)−C(3)	73.5(2)
(C13−C18)−(Pd1−N1−C1−C11−N2)	76.7	(C16−C21)−(Ni1−N1−C4−C14−N2)	76.7
(C25−C30)−(Pd1−N1−C1−C11−N2)	77.4	(C28−C33)−(Ni1−N1−C4−C14−N2)	80.0

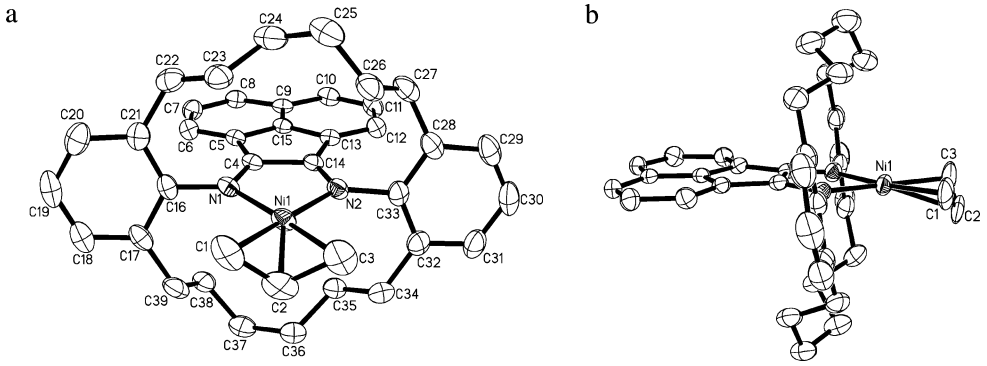


Figure 2. X-ray crystal structure of the Ni(II)-allyl complex **14** showing important atoms labeled: (a) front view and (b) side view (C2 is only shown for one position and the BAF counterion was removed for clarity; the atoms were drawn with 50% thermal ellipsoids).

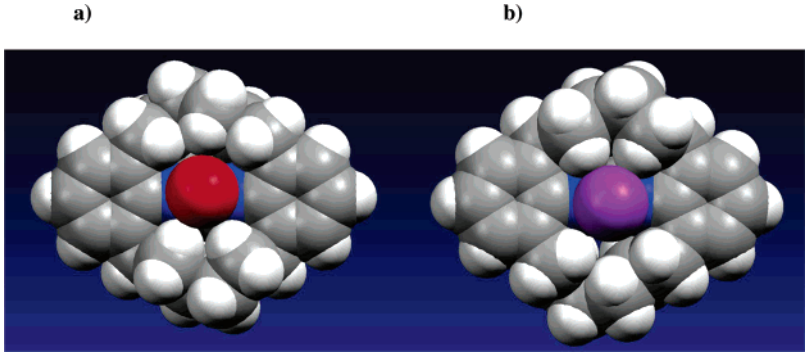
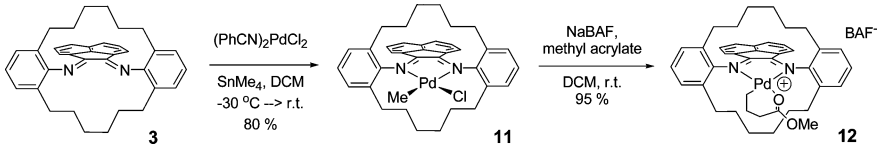
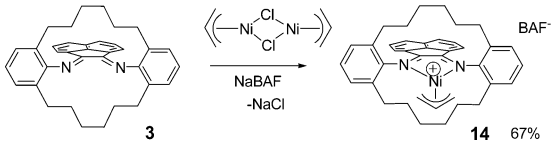


Figure 3. Space-filling representation for the X-ray crystal structures of complexes **10** and **14**: (a) $PdCl_2$ complex **10**; (b) Ni(II)-allyl complex **14**. (The two chloride atoms in **10** and the allyl fragment in **14** are removed for better visualization of the sterics in the binding pocket. Color code: red = Pd; purple = Ni; gray = C; white = H; blue = N.)

Scheme 5



Scheme 6



polymerization activity. Figure 3 also shows that some hydrogen atoms in the alkyl bridge are very close to the metal centers in complexes **10** and **14**. The shortest distances between the Pd center and alkyl hydrogens in complex **10** are 2.66 and 2.75 Å, while in Ni(II) complex **14** the shortest distances are 2.56 and 2.57 Å. The close proximity between alkyl hydrogens and the metal centers may lead to C−H activation and further catalyst deactivation via the pathway proposed by Brookhart and co-workers.[9] This may be an alternative mechanism to account for their low catalytic activity. The structural analysis suggests that, while ligand bulkiness is important for achieving active catalyst and high molecular weight polymer, a too crowded catalytic center may prohibit catalytic activity. In future ligand design, a balance of steric bulkiness in axial directions and accessibility of the metal center from the front side has to be reached in order to achieve highly active polymerization catalysts.

Conclusions

An efficient synthetic route was developed for the preparation of novel alkyl-bridged cyclophane-type ligands. With α-diimine as a template, ring-closing metathesis afforded efficient cyclization to form two alkyl bridges at one time. Using this methodology, the new macrocyclic α-diimine ligand **3**, containing two C6 alkyl bridges, was successfully synthesized. A series of Pd(II) and Ni(II) complexes of **3** were successfully

(23) The X-ray shows decane cocrystallizing as an impurity to give an empirical formula of $C_{36}H_{36}Cl_2N_2Pd\cdot{}^1/_2C_{10}H_{22}$. CCDC 254673 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 CB2 1EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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(26) Careful layering of a DCM solution of **14** with decane and slow evaporation of the solvents afforded high-quality single crystals. The entire complex including the BAF counterion has an empirical formula of $C_{71}H_{53}BF_{24}N_2Ni$. CCDC 254674 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 CB2 1EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

prepared and characterized. The X-ray crystal structures of complexes **10** and **14** show that the complexes exhibit coordination geometry similar to their acyclic analogues and the alkyl bridges do not introduce significant ring strain into the complexes. The preactivated Pd(II) complex **12** and the allyl nickel complex **14** exhibited low activities for ethylene polymerization. Careful structural analysis indicates that the alkyl bridges impose significant sterics to the catalytic centers, which may cause a reduction of polymerization activity. The proximity of some alkyl hydrogens to the metal centers may also result in catalyst deactivation via intramolecular C−H activation followed by decomposition. This study points out that a number of molecular parameters including the binding pocket size, the geometry of the ligand, and a balance of steric bulkiness in axial directions and accessibility of the metal center from the front side have to be considered in future polymerization catalyst designs.

Experimental Section

General Procedures. All manipulations of air- and/or water-sensitive compounds were performed using the standard Schlenk techniques. Organometallic compounds were handled in a nitrogen-filled Vacuum Atmospheres drybox. High-resolution mass spectra were recorded on Micromass LCT or Micromass Autospec. Elemental analyses were performed by Atlantic Microlab (Nocross, GA). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-500 or -400 spectrometers. Chemical shifts are reported relative to the residual solvent.

Materials. Toluene, dichloromethane, and diethyl ether are obtained from the purified solvent system.[27] High-pressure polymerizations were performed in a mechanically stirred 600 mL Parr autoclave. Ultrahigh pure grade ethylene gas was purchase from Airgas and used without further purification. A 7% Al (wt %) solution of modified methylaluminoxane (MMAO) in toluene (d = 0.88 g/mL) containing 12% isobutyl groups was purchased from Akzo Nobel. Acenaphthenequinone, 1-hexene, 2-bromometaxylene, allylmagnesium chloride, *p*-toluedine, and chloromethyltrimethylsilane were purchased from Aldrich Chemical Co. Trimethylsilylmethyl azide was purchased from TCI America. (DME)$NiBr_2$ was obtaind from Strem, and the second-generation Grubbs catalyst was a generous donation from Materia, Inc.

Synthesis of 6. A solution of 1-bromo-2,6-bis(bromomethyl)-benzene **5** (13.2 g, 38.5 mmol) in THF/Et_2O (1:1 mixture; 100 mL) was cooled to −78 °C and stirred for 20 min. A solution of allylmagnesium chloride in THF (2 M, 2.5 equiv) was added dropwise at −78 °C. The resulting solution was stirred overnight and was allowed to warm to room temperature naturally. The reaction was quenched with aqueous ammonium chloride, then extracted with ether, washed with brine, and dried over magnesium sulfate. The crude mixture was chromatographed using silica and hexane as eluent to give a colorless liquid in 90% yield.

6: ^{1}H NMR$_{(CDCl_3)}$ δ 7.15 (m, 1H); 7.05 (m, 2H); 5.93−5.84 (m, 2H); 5.09−4.98 (m, 4H); 2.88−2.83 (m, 4H); 2.41−2.34 (m, 4H); ^{13}C NMR$_{(CDCl_3)}$ 141.6, 137.8, 127.9, 126.7, 114.9, 36.4, 33.8 ppm. Anal. Calcd for $C_{14}H_{17}Br$: C 63.41, H 6.46. Found: C 63.05, H 6.49.

Synthesis of 7. A solution of **6** (2.65 g, 10 mmol) in ether was added dropwise to a flask filled with magnesium metals (0.3 g, 1.2 equiv) and ether (40 mL). The formation of the Grignard reagent is signaled by the refluxing action of ether. If this does not occur, adding drops of dibromoethane activates the magnesium, and the reaction is refluxed until all the magnesium metals are gone. The reaction mixture was then cooled to room temperature, and trimethylsilylmethyl azide (1.55 g, 1.2 equiv) in ether was added dropwise. The reaction was continued overnight at room temperature. Addition of water and stirring for 30 min followed by the usual extraction workup gave a crude mixture, which upon column chromatography (silica, 10%ethyl acetate in hexane) gave the amine products **7** in 72% yield.

7: ^{1}H NMR$_{(CDCl_3)}$ δ 6.96 (d, J = 7.5 Hz, 2H); 6.72 (t, J = 7.5 Hz, 1H); 5.97−5.89 (m, 2H); 5.14−5.02 (m, 4H); 3.64 (s, br, 2H); 2.64−2.60 (m, 4H); 2.43−2.38 (m, 4H); ^{13}C NMR$_{(CDCl_3)}$ 141.8, 138.3, 127.3, 125.8, 118.2, 115.1, 34.3, 32.9, 31.2 ppm. Anal. Calcd for $C_{14}H_{19}N$: C 83.53, H 9.51, N 6.96. Found: C 83.58, H 9.41, N 6.59.

Synthesis of 8. To a mixture of acenaphthenequinone and aniline **7** (2.6 equiv) in methanol was added drops of formic acid. The mixture was refluxed for 2 days, after which a yellow solid precipitates out of the solution. Washing with cold methanol and drying gave the diimine product as a yellow solid in 82% yield.

8: ^{1}H NMR$_{(CDCl_3)}$ δ 7.90 (d, J = 10.3 Hz, 2H); 7.38 (t, J = 9.6 Hz, 2H); 7.21−7.16 (m, 6H); 6.67 (d, J = 8.9 Hz, 4H); 5.76−5.69 (m, 4H); 4.82 (m, 8H); 2.66−2.49 (m, 8H); 2.34−2.21 (m, 8H); ESMS exptl (M + H) = 549.32, obsvd (M + H) = 549.25; HRMS calcd for $C_{40}H_{40}N_2$ $[M + H]^+$ 549.3270, found 549.3278. Anal. Calcd for $C_{40}H_{40}N_2$: C 87.55, H 7.35, N 5.10. Found: C 87.57, H 7.35, N 5.13.

Synthesis of 9. A solution of **8** and Grubbs' second-generation catalyst in toluene was heated to 90 °C under nitrogen atmosphere. The solution turns black after 1 h, indicating the decompositon of the catalyst. Re-addition of the catalyst in DCM was done every 2 h for four times. The mixture was stirred at 90 °C overnight. Evaporation of the solvent and column chromatography (silica, 4:6 DCM/hexane) gave the cyclophane **9** in 70% yield.

9: ^{1}H NMR$_{(TCE\ 90\ °C)}$ δ 8.00 (d, J = 8.2 Hz, 2H); 7.59 (s, br, 2H); 7.25 (br, 1H); 7.01 (d, J = 7.4 Hz, 4H); 7.00 (t, J = 7.3, 2H); 5.99 (s, 1H); 5.53 (s, 4H); 2.46 (br, 12H); 1.93 (br, 4H); HRMS calcd for $C_{36}H_{32}N_2$ $[M + H]^+$ 493.2644, found 493.2647.

Synthesis of 3. Hydrogenation of the cyclophane **9** using Pd on carbon in DCM/MeOH (1:1) was done under hydrogen atmosphere for 3 h. The mixture was filtered thru Celite (DCM/MeOH eluent) and after evaporation was subjected to column chromatography (silica, DCM/hexane, 4:6) to give **3** in 92% yield.

3: ^{1}H NMR$_{(CD_2Cl_2)}$ δ 8.04 (d, J = 8.4 Hz, 2H); 7.59 (s, br, 2H); 7.11 (d, J = 7.4 Hz, 4H); 7.02 (t, J = 7.6, 2H); 2.32 (br, 8H); 1.84 (br, 4H); 1.46 (br, 4H); 1.27 (br, 8H); ^{13}C NMR$_{(CDCl_3)}$ 148.1, 131.1, 128.6, 128.3, 127.2, 34.3, 31.6, 22.7 ppm; HRMS calcd for $C_{36}H_{36}N_2$ $[M + H]^+$ 497.2957, found 497.2935.

Synthesis of $PdCl_2$ Cyclophane Complex 10. A mixture of $(PhCN)_2PdCl_2$ (18 mg, 0.07 mmol) and the macrocyclic ligand **3** (34.5 mg, 0.07 mmol) in CH_2Cl_2 (4 mL) was stirred at room temperature overnight. After evaporation of all volatile components, the residue was washed with pentane and dried. High-quality single crystals of the complex were prepared by layering decane on a concentrated CH_2Cl_2 solution of the complex. The structure of the complex **10** was confirmed by X-ray single-crystal structure analysis. **10**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, 2H, J = 8.2 Hz), 7.55 (t, 2H, J = 7.4 Hz), 7.32 (t, 2H, 6.8 Hz), 7.24−7.26 (m, 4H), 6.66 (d, 2H, J = 7.3 Hz), 3.41 (br, 4H), 2.79 (br, 4H), 2.51−2.55 (m, 4H), 1.98−2.03 (m, 4H), 1.54 (br, 4H), 1.26−1.33 (br, 4H); ^{13}C NMR (125 MHz, $CDCl_3$ in ppm) δ 147.1, 144.0, 134.2, 133.1, 131.0, 130.1, 129.2, 129.1, 125.7, 125.6, 34.4, 28.5, 25.8 ppm.

Synthesis of Pd(Me)Cl Cyclophane Complex 11. A solution of $(PhCN)_2PdCl_2$ (416 mg, 1.08 mmol) in CH_2Cl_2 (18 mL) was cooled to −35 °C. Then tetramethyltin (0.52 mL, 3.80 mmol) was added, and the mixture was stirred at −35 °C for two more hours. The ligand **3** (593 mg, 0.832 mmol) dissolved

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in 10.0 mL of CH_2Cl_2 was added to the in situ generated Pd(Me)Cl from the above solution. The resulting red solution was warmed to RT and allowed to stir overnight. The solution was filtered through Celite and subjected to flash chromatography (DCM) under N_2 flow, providing **11** as a dark red solid (722 mg, 81%).

11: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, 1H, J = 8.3 Hz), 8.13 (d, 1H, J = 8.3 Hz), 7.51−7.61 (m, 2H), 7.21−7.32 (m, 6H), 6.88 (d, 1H, J = 7.2 Hz), 6.65 (d, 1H, J = 7.3 Hz), 3.28−3.35 (m, 2H), 3.09−3.16 (m, 2H), 2.61−2.89 (m, 4H), 2.51−2.60 (m, 4H), 1.80−1.93 (m, 4H), 1.48−1.55 (m, 2H), 1.33−1.44 (m, 2H), 1.19−1.27 (m, 4H), 0.94 (s, 3H, Pd-*Me*); ^{13}C NMR (125 MHz, $CDCl_3$ in ppm) δ 169.29, 164.78, 144.55, 144.26, 143.86, 132.81, 132.19, 131.42, 130.96, 129.74, 129.43, 129.38, 129.02, 127.59, 127.02, 126.79, 124.07, 123.98, 33.87, 28.15, 25.86, 25.36, 24.42, 5.05 ppm; HRMS calcd for $C_{37}H_{39}N_2ClPd$ in CH_3CN $[M - Cl + CH_3CN]^+$ 658.2428, found 658.2424.

Synthesis of Allyl Ni Cyclophane Complex 14. A solution of ligand **3** (94 mg, 0.19 mmol), nickel allyl chloride dimer (31 mg, 0.6 equiv), and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAF) (170 mg, 0.19 mmol) in diethyl ether (7 mL) was stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite, and the solvent was evaporated in vacuo. The residue was washed with 10 mL of pentane and dried, affording 180 mg (67% yield) of reddish brown solid. High-quality single crystals were obtained by recrystallization in toluene. The structure of complex **14** was confirmed by X-ray single-crystal structure analysis.

14: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, 2H, J = 8.2 Hz), 7.72 (s, BAF^- H), 7.61 (t, 2H), 7.56 (s, BAF^- H), 7.32 (m, 6 H), 6.92 (d, 2H, J = 7.2 Hz), 5.32 (m, 1H), 3.65 (s, b, 2H), 2.96−2.45 (m, 12H), 1.88−1.26 (m, 14H); HRMS calcd for $C_{71}H_{53}BF_{24}N_2Ni$ $[M - BAF]^+$ 595.2623, found 595.2603.

Ethylene Polymerization by Preactivated Pd^{II} Complexes 12. In a nitrogen-purged glovebox, 10 μmol of catalyst was dissolved in 10 mL of toluene. Into a 600 mL Parr reactor purged under nitrogen, 55 mL of toluene solvent was loaded followed by purging with 50 psi ethylene three times (5 min each) at RT. After the catalyst solution was introduced at RT, the reactor was immediately charged with ethylene to the desired pressure (1 atm to 400 psi). The polymerization was allowed to run for overnight. The desired temperature was reached within 5 min after the catalyst was loaded into the reactor. The reaction was stopped by the release of ethylene, and removal of solvent afforded PEs.

Ethylene Polymerization by Ni-Allyl Complex 14.[13,28] A 600 mL Parr autoclave was heated under vacuum at 135 °C for several hours and was flushed with ethylene twice. It was then cooled to RT and backfilled with ethylene twice before reducing the pressure inside. A solution of **14** (7.3 mg, 5 μmol) in toluene (100 mL), which was prepared inside the glovebox, was transferred into the Parr reactor under nitrogen stream. The autoclave was sealed and the ethylene pressure raised to 200 psi. The solution was vigorously stirred under ethylene pressure, and the temperature of the system was equilibrated to be 5 degrees less than the desired polymerization temperature for 15 min. The autoclave was then vented, and the pressure inside was reduced. The activator, $B(C_6H_5)_3$ (20 equiv, 51 mg, 100 μmol), dissolved in toluene (100 mL), was transferred into the autoclave, which was subsequently sealed and pressurized to 200−400 psi ethylene pressure under vigorous stirring. Polymerization was run at temperatures from 70 to 90 °C overnight. The reaction was stopped by the release of ethylene, and removal of solvent afforded PEs.

Supporting Information Available: Detailed information on X-ray crystal structural analyses for complexes **10** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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