Polymerization Catalysts

Cyclophane-Based Highly Active Late-Transition-Metal Catalysts for Ethylene Polymerization**

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Cyclophane chemistry has evolved into an exciting research area stemming from simple curiosity of the syntheses and structures to the exploitation of physical properties of cyclophanes for various applications including molecular recognition, supramolecular chemistry, and biomimics.[1] A plethora of literature describing cyclophane–metal host–guest chemistry indicates the potential application of cyclophanes as ligands in metal-catalyzed transformations.[1] One major research effort in our group is to explore the use of cyclophanes as ligands for olefin polymerization catalysis. In our ligand design, we strategically position metal binding sites at the core of cyclophanes to chelate transition metals. The cyclophane framework shields all directions of the catalytic metal center except leaving two *cis* coordination sites open in the front: one for monomer coordination and the other for the growing polymer chain. The well-defined cavity and sterically hindered microenvironment of cyclophanes should offer great opportunities for fine-tuning the catalytic properties. The rigid cyclophane framework may also enhance the stability of transition-metal complexes. Despite these promises, however, the use of cyclophanes as ligands for transition-metal polymerization catalysis remains mostly unexplored.[2] Herein, we report the first cyclophane-based late-transition-metal catalyst that shows high activity and thermal stability for ethylene polymerization.

Late-transition-metal olefin polymerization catalysts have received much attention recently because they can produce polyolefins with interesting new branching topologies and have better tolerance to functional groups.[3] One noteworthy example is the Ni^{II}- and Pd^{II}-α-diimine complexes reported by Brookhart and co-workers.[4] The Ni^{II} systems were shown to have comparable activities to those of the early-transition-metal catalysts in polymerizing ethylene into high molecular weight (MW) polyethylenes (PEs) and the Pd^{II} systems were shown to be able tolerate and incorporate polar olefins such as methyl acrylate.[4] The branching topology of the PEs formed by the Pd^{II}-α-diimine catalysts can easily be tuned from linear to hyperbranched to dendritic by simply varying ethylene pressure.[5] Whereas these catalysts exhibit excellent properties as described, one limitation is their relatively high sensitivity to temperature. The catalysts decompose rapidly at 50 °C for Pd^{II}-α-diimine[6] and at 70 °C for Ni^{II}-α-diimine systems.[7] The MW of the PEs formed by Ni^{II} catalysts also decreases precipitously as the temperature of polymerization is raised.[7] These issues hindered the commercialization of these catalysts since gas-phase olefin polymerizations typically operate at temperatures as high as 80–100 °C.[8] Herein, we report novel Pd^{II} and Ni^{II}-α-diimine catalysts containing a cyclophane ligand moiety that demonstrate improved thermal stability and produce high MW PEs at temperature ranges suitable for industrial gas-phase olefin polymerization.

In the acyclic catalyst **A** (Figure 1), the aryl groups are roughly perpendicular to the coordination plane so the isopropyl substitutents on the aryls are positioned at the axial directions to retard associative chain transfer[4] or chain transfer to ethylene monomer.[9] At elevated temperature, however, the aryl groups may freely rotate away from the perpendicular orientation, resulting in increased associative chain transfer or chain transfer to monomer and a resulting decrease in MW of the PE formed by the acyclic catalyst **A**.[7] Moreover, as the aryl groups rotate towards the coordination plane, the isopropyl substituents on the aryl rings reach within close proximity of the metal center giving it an opportunity to react with the C–H bonds (C–H activation) to form metallacycles, which was proposed as one potential deactivation pathway for this family of catalysts.[6] In our cyclophane-based complex **B**, 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 contributes to the retardation of the C–H activation of the ortho subsitutents, hence, should prevent this potential catalyst-deactivation pathway from being available. In addition, it has been observed for other systems that rigid macrocyclic ligands enhance the coordination stability for metal complexes.[2b] Based on these considerations, we

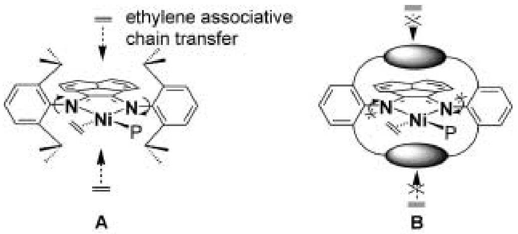

Figure 1. Comparison of the acyclic (**A**) with cyclophane-based (**B**) Ni^{II}–α-diimine complexes.

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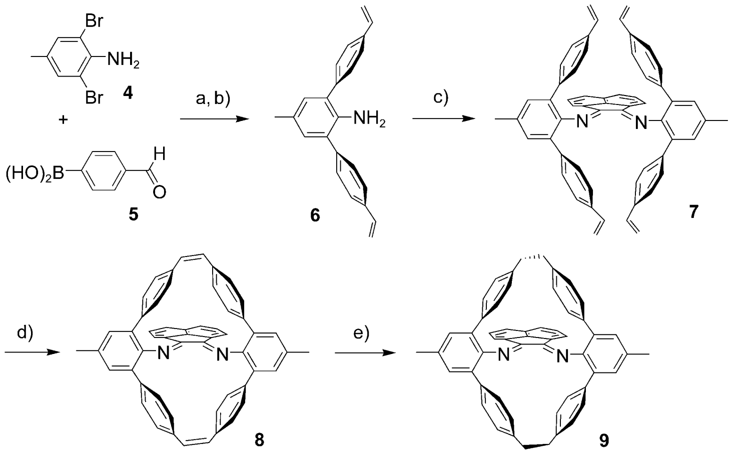
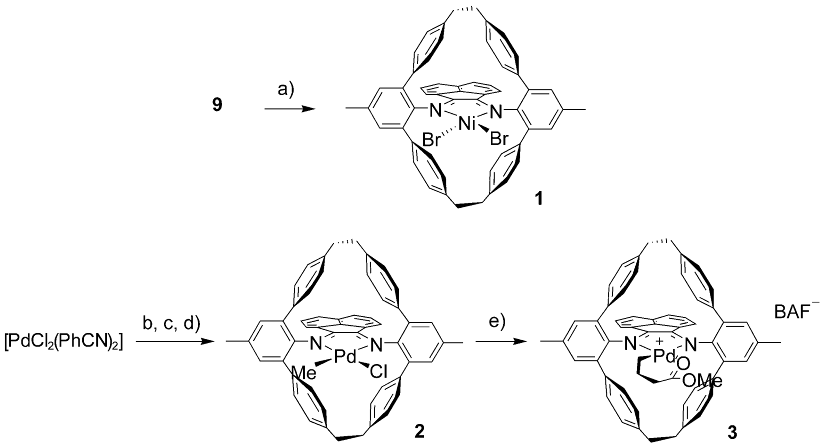
designed the cyclophane-based α-diimine ligand to address the critical thermal sensitivity of the acyclic α-diimine systems. In more general terms, we envision cyclophanes to be a new family of ligand frameworks to be used in the design of metal complexes for polymerization catalysis.

The synthesis of the cyclophane ligand (Scheme 1) began with the Suzuki coupling of commercially available 2,6-dibromo-4-methylaniline (**4**) with 4-formylphenylboronic acid (**5**) followed by the conversion of the dialdehyde into divinyl by using the Wittig reaction to give the product **6** in 64 % total yield. Condensation of **6** with acenaphthenequinone gave the α-diimine **7**. Molecular modeling shows that in α-diimine **7** the styryl phenyl rings are perpendicular to the aniline phenyl rings, rendering the right conformation for ring closing metathesis (RCM)[10] to close the ring. Indeed, the RCM proceeded very efficiently to form the cyclophane **8** in 80 % yield.[11] Compound **8** was hydrogenated to give the cyclophane α-diimine **9**.



Scheme 1. Synthesis of the cyclophane-based ligand. Reaction conditions: a) $[\text{Pd}(\text{PPh}_3)_4]$, 2 M Na_2CO_3, 1,4-dioxane, reflux, (85 %); b) Ph_3PMeBr, THF, KO*t*Bu, (75 %); c) acenaphthenequinone, benzene, PTSA, azeotrope 5 days, (79 %); d) Grubbs generation 2 catalyst, CH_2Cl_2, 50 °C, (80 %); e) Pd/C, H_2, CH_2Cl_2-MeOH, (77 %).

Both Ni^{II} and Pd^{II} complexes with the cyclophane α-diimine ligand **9** were synthesized and characterized.[12] Complexation of **9** with $[\text{NiBr}_2(\text{dme})]$ (dme = dimethoxyethane) in dicholoromethane (Scheme 2) afforded the NiBr_2 complex **1** as the precatalyst for the ethylene polymerization studies. For the synthesis of the Pd complex, the ligand **8** was complexed with Pd(Me)Cl generated in situ[13] (Scheme 2) followed by hydrogenation to provide **2**, which was reacted with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAF) and methyl acrylate (MA) to give the preactivated cationic Pd^{II} complex **3**.



Scheme 2. Synthesis of the cyclophane-based Ni^{II} and Pd^{II} complexes. Reaction conditions: a) $[\text{NiBr}_2(\text{dme})]$, CH_2Cl_2, 18 h, (95 %); b) SnMe_4, CH_2Cl_2, −35 °C, 3 h; c) **8**, −35 °C to RT, 6 h (81 %); d) Pd/C, H_2, CH_2Cl_2-MeOH, (99 %); e) methyl acrylate, NaBAF, CH_2Cl_2, RT, 12 h (97 %).

High quality single crystals suitable for X-ray analysis for the Pd^{II} complex **2** was obtained by carefully layering a slightly concentrated dichloromethane solution of **2** with *n*-decane.[14] X-ray crystal structure of complex **2** (Figure 2) shows that the active Pd^{II} center is in the core of the cyclophane ligand, as we initially envisioned. The bond angles and distances in the Pd^{II} coordination plane are very similar to the values of an acyclic α-diimine-PdMeCl complex reported by Brookhart and co-workers.[6] The resulting angles of the planes that run through the aniline moiety (C13–C18) and the adjacent phenyl groups (C49–C54) and (C20–C25) are 72.0° and 122.8°, respectively. The planes that run through the aniline moiety on the opposite side (C34–C39) and the adjacent phenyl groups (C41–C46) and (C28–C33) are 52.1° and 128.6°, respectively. The large difference in the torsion angles between aryl rings (52.1° for C34–C46/C41–C46 verses 72.0° for C13–C18/C49–C54) is presumably caused by the different sizes of the chloride and methyl groups. The angles between the five-membered palladacyclic coordination plane (Pd1-N2-C2-C1-N1) and the two aniline-derived phenyl planes (C13–C18) and C34–C39) are 91.5° and 91.3°, respectively. A view from the top of the space filling model of **2** indicates that the axial sites for the metal center are completely blocked by the alkane bridge on cyclophane ring, which plays a critical role in obtaining high-molecular-weight polymers at elevated temperatures (see below).

Exposure of the complex **1** to moderated methylalumoxane (MMAO) in toluene generated a highly active catalyst for ethylene polymerization. The activated catalyst had polymerization activities similar to the most active early-transition-metal metallocene catalysts[15] and late-transition-metal catalysts[4a,7,16] with a turnover frequency (TOF) of $1.50\times10^{6}\,\text{h}^{-1}$ (productivity of 42 000 kg of PE mol^{-1} of $\text{Ni}\,\text{h}^{-1}$). To the best of our knowledge, this is the first reported cyclophane-based

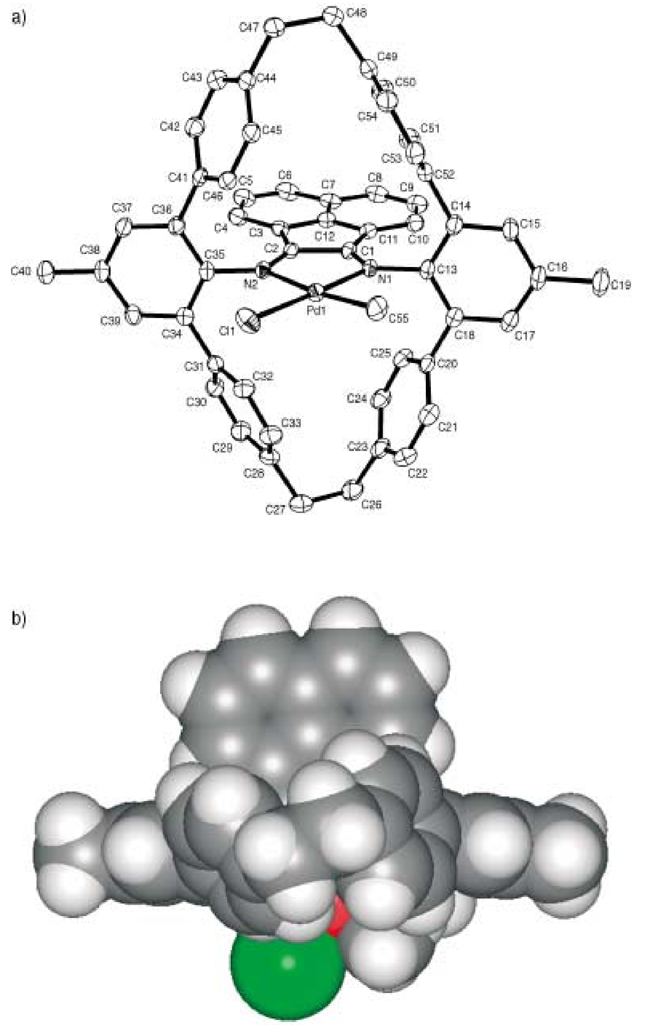


Figure 2. a) X-ray crystal structure of complex **2**. b) Top view space filling model of **2** (red = Pd; green = Cl; black = C; blue = N). ORTEP view of **2** showing important atoms labeled (50% thermal ellipsoids; the fragment of solvated dichloromethane and 1,2-dichloroethane was omitted for clarity). Selected interatomic distances [Å]: Pd1-C55 = 2.018(3), Pd1-N1 = 2.053(2), Pd1-N2 = 2.218(2), Pd1-Cl1 = 2.3149(8), N1-C1 = 1.285(4), N1-C13 = 1.440(4), N2-C2 = 1.279(4), N2-C35 = 1.443(4), C1-C2 = 1.507(4). Selected bond angles [°]: C55-Pd1-N1 = 92.93(12), C55-Pd1-N2 = 171.67(11), N1-Pd1-N2 = 78.99(9), C55-Pd1-Cl1 = 88.15(10), N1-Pd1-Cl1 = 178.60(7), N2-Pd1-Cl1 = 99.90(6), C1-N1-C13 = 121.5(2), C2-N2-C35 = 117.4(2), N1-C1-C2. Selected torsion angles (deg): N1-C1-C2-N2 = −2.8(4), C2-N2-C35-C36 = −82.2(3), C1-N1-C13-C14 = 90.5(3), C1-N1-C13-C18 = −99.1(3).

highly active catalyst for olefin polymerization. The polymerization was run at temperatures of 30–90 °C to probe its thermal stability. At each temperature, the polymerization ran at three different time periods ranging from 5 to 15 min to test the catalyst lifetime. The catalyst remained highly active at temperatures up to 90 °C, as evident by consistent catalyst TOFs. More specifically, as the temperature was increased from 30 to 70 °C, the observed TOF decreased only by 10 %. At even 90 °C, the reduction of TOF for polymerization of 10 min is less than 30 %. This is in contrast to the acyclic Ni^{II}-α-diimine counterparts (e.g., complex **4g** in reference [7]), which generally show a significantly lower productivity at elevated temperatures.[7] The calculated TOFs for polymerization at constant temperature but different periods of time indicate that the active catalyst remained active for a period of time. At temperatures below 70 °C, the catalyst maintained almost constant productivity over 15 minutes. For polymerizations at 70 and 90 °C, the productivity was constant in the first 10 minutes and then started to decrease, thus suggesting that the active species starts to decompose with longer periods of time at higher temperatures (see Table 1).

Besides the high activity and thermal stability, the MWs of the PEs obtained by using complex **1** did not drop as the temperature was raised. Even at 90 °C, the MWs of PEs are still in the range of 300 000 $g\,mol^{-1}$. This again contrasts to the acyclic Ni^{II}-α-diimine systems, for which MWs of PEs usually decrease rapidly with increasing temperature.[7] We attribute the constant MWs at elevated temperatures to the unique cyclophane ligand that keeps the axial sites for the metal center fully blocked even at elevated temperatures (see above). The observed relatively narrow polydispersity indices (PDI) clearly indicate the single-site nature of the catalyst and are suggestive of some living character for the polymerization. The PEs formed contain short chain branches with most being simple methyl branches as revealed by ^{13}C NMR. The branching density increases as the polymerization temperature increases, which are consistent with the acyclic Ni^{II}–α-diimine systems.[7] One interesting observation is that the branching density is considerably higher than the values for the PEs produced by a very similar acyclic Ni^{II}–α-diimine system reported by Rieger and co-workers,[16] which suggests that the cyclophane ligand environment significantly influences the catalytic properties of the complex. The branching was presumably produced by the chain-walking mechanism proposed by Brookhart[4] and Fink.[17] The significantly increased branching density may result from enhanced chain-walking processes caused by the unique cyclophane ligand environment.

Polymerization of ethylene with the preactivated Pd^{II} complex **3** was also carried out.[18] The preactivated Pd^{II} complex **3** showed much higher thermal stability for ethylene polymerization than the acyclic Pd^{II}–α-diimine analogues reported previously.[16] The complex **3** has a half life of more than three hours for ethylene polymerization at 70 °C.[18] In contrast, the acyclic analogues decomposed within minutes even at room temperature.[16] The branching density of the PEs formed by complex **3** at room temperature is around 110 branches/1000 carbons, which is significantly higher than the values for PEs formed by the acyclic Pd^{II}–α-diimine catalysts as estimated from the melting temperatures reported for their PEs.[16] The contrast in both the catalyst thermal stability and the PE microstructures between the cyclophane and acyclic Pd^{II} catalysts once again suggests that the unique cyclophane ligand environment significantly influences the catalytic properties of the complexes. While it has been reported that the introduction of aryl substituents onto a different ligand improved the thermal stability for Ni^{II} complexes in ethylene polymerization in the presence of hydrogen,[19] the big contrast in thermal stability and PE branching density between our cyclophane Ni^{II} and Pd^{II} systems with open

Table 1: Summary of ethylene polymerization data with the Ni complex.[a]

Entry	Moles of catalyst [$\times 10^6$]	T [°C]	t [min]	Yield [g]	TOF[b] [$\times 10^3$ h^{-1}]	$\bar{M}_n$[c] [$\times 10^3$ h^{-1}]	PDI	Branches per 1000 C atoms[d]
1	1	30	5	3.48	1491	320	1.29	66
2	1	30	10	6.70	1436	288	1.30	73
3	1	30	15	9.25	1321	294	1.31	67
4	1	50	5	3.20	1371	248	1.23	80
5	1	50	10	6.85	1468	652	1.28	84
6	1	50	15	9.00	1286	342	1.23	85
7	1	70	5	3.11	1333	323	1.45	91
8	1	70	10	6.10	1307	619	1.43	89
9	1	70	15	7.35	1050	429	1.41	91
10	1	90	5	2.50	1071	252	1.72	97
11	1	90	10	4.70	1007	462	1.64	96
12	1	90	15	4.62	660	292	1.40	96

[a] Experimental conditions: in 200 mL of toluene, cocatalyst MMAO (Al:Ni $\approx$3000), 200 psi ethylene pressure. [b] TOF = turnover frequency, which was calculated as the moles of ethylene per mole of catalyst per hour. [c] $\bar{M}_n$, number-average molecular weight measured by gel-permeation chromatography with polystyrene standards. [d] Branching determined from ^{1}H NMR spectroscopy.

chain analogues containing aryl substituents[16] clearly indicates that the cyclophane ligand environment has a significant impact on the catalytic properties.

In summary, we report here the first cyclophane-based late-transition-metal catalyst that shows high activity and thermal stability for ethylene polymerization. An efficient route was developed for the synthesis of a novel cyclophane-based α-diimine ligand. The Ni^{II} and Pd^{II}-α-diimine complexes with the cyclophane ligand were successfully synthesized and characterized. The Ni^{II} complex exhibits excellent activity for ethylene polymerization with a productivity of 42 000 kg of PE mol $^{-1}$ of Ni h^{-1}. Both the Ni^{II} and Pd^{II} catalysts show significantly higher thermal stability than the acyclic analogs. The cyclophane catalysts also form PEs with significantly higher branching density as compared to the similar acyclic counterparts.[16] All these data suggest the novel cyclophane ligand change the catalytic properties significantly for the Ni^{II} and Pd^{II} complexes. It should be noted that the Ni^{II} complex **1** has sufficiently high productivity and thermal stability at temperature ranges suitable for gas-phase olefin-polymerization processes. The MWs of the PEs formed by complex **1** are also high and rather constant with polymerization temperature. Encouraged by these results, we are currently exploring a family of new cyclophane-based ligands and investigating the polymerization properties of a family of their transition-metal complexes.

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[11] The ring-closing metathesis afforded the bicyclic compound **8** as the major product (80 % yield) and a small amount of monocyclic by-product with ring closing only on one side.

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located about an inversion center. CCDC-222192 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, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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