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COMMUNICATION

The Ligand Redox Behavior and Role in 1,2-Bis[(2,6-diisopropylphenyl)imino]-acenaphthene) Nickel/TMA(MAO) Systems for Ethylene Polymerization

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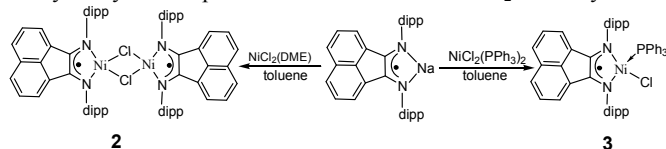
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The BIAN ligands in Brookhart catalysts were proved to be redox-active during the catalyst activation with alkylaluminum or MAO, and the neutral catalytically active species with a radical anionic BIAN rather than the cationic ones with a neutral BIAN ligand were confirmed to be formed in the catalytic system.

In the original report on the Ni and Pd catalysts with α -diimine ligands for olefin polymerization by Brookhart *et al* in 1995,¹ it was reported that the cationic diazadienes(DAD)-based methyl nickel and palladium complexes show only moderately activity for ethylene polymerization, while the 1,2-bis[arylimino]-acenaphthene (BIAN)-based nickel dibromides exhibits extremely high activity when activated with methylaluminoxane (MAO). Based on the NMR study of ethylene, a mechanism involving cationic active species similar to the one supposed for metallocene catalyst systems² was proposed for the Ni and Pd catalyst systems.¹ Although no cationic species has been isolated from the BIAN-based nickel catalyst systems and structurally confirmed so far,³ the supposed mechanism based on DAD-palladium system has been undoubtedly applied to the BIANNiBr₂/MAO systems.⁴ According to the mechanism, the α -diimine ligands in their Ni and Pd complexes are presumed to neutrally coordinate to the central metal.^{1,4} In the other hand, the redox-active character of the α -diimine ligands has received more and more attention in recent years.⁵ It has been known that, in addition to be able to neutrally coordinate to metal ions, the α -diimine ligands can also accept electrons easily and coordinate to metal ions in mono- or di-anionic forms.⁶ The BIAN ligands possessing an extended π -system can even be reduced to *tri*- and *tetra*-anions, and be used as electron sink.⁷ It has also been proved that the π acceptor properties of the BIAN ligands cause electron deficiency at the coordinated metal center rendering these complexes high activities towards organic substrates.⁷ The α -diimines can be reduced by alkali metals, earth alkali metals, and some other low valent metal compounds.^{5d, 8} More recently, it is reported that the α -diimines can also be reduced by alkylaluminum in refluxed n-hexane leading to the π -radical α -diimine aluminium alkyls.⁹ Moreover, coordination of the BIAN to a metal seems to facilitate its reduction.¹⁰ It has been shown that alkylation of Ar-BIANPdCl₂ with

organo-lithium, -magnesium, and -zinc reagents may causes the reduction of the Ar-BIAN ligands,¹⁰ which implies that the neutral ligands in α -diimine Ni and Pd catalyst precursors may also be reduced to the radical anionic form upon activation with MAO or AIR₃. To develop new neutral nickel catalysts for olefin polymerization, we have synthesized a binuclear nickel complex [dipp-BIANNi]₂(μ -Cl)₂ (**2**) and a mononuclear nickel chloride dipp-BIANNiCl(Ph₃P) (**3**) (dipp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) bearing a radical anionic dipp-BIAN ligand, and briefly examined the activation reaction of a known Brookhart catalyst dipp-BIANNiBr₂ (**1**) with AIR₃. The nickel complexes **2** and **3** are structurally similar to the SHOP (Shell Higher Olefin Process) catalysts¹¹ and the Grubbs' neutral olefin polymerization catalysts,¹² and therefore would be expected to be good catalyst precursors for ethylene polymerization. Complexes **2** and **3** were found to show moderate to high activities in ethylene polymerization upon activation with AlMe₃ (TMA), and behave similarly to the known Brookhart catalyst **1** under similar conditions. It was also found that, during activation with TMA, complex **1** can be converted to a Ni-Al binuclear complex dipp-BIANNi(μ -Br)₂AlMe₂ (**4**). In addition, the reaction solutions of 1/TMA, 2/TMA, and 4/TMA show similar ESR signals in toluene in which the anionic BIAN radical was observed. These results throw some lights on the understanding of the real catalytically active species formed in the BIANNiX₂/MAO system.



Scheme 1. The synthesis of the nickel complexes bearing radical BIAN ligands.

The new nickel complexes **2** and **3** can be conveniently synthesized *via* sodium salt metathesis reaction as shown in Scheme 1. Treatment of the dipp-BIANNa^{7b} with NiCl₂(DME) in toluene afford **2** as blue crystals in a yield of 67%. Complex **2** was found to be paramagnetic and highly moisture and air sensitive. X-ray diffraction analysis reveals **2** existing as a chlorine-bridged binuclear. Both metallacycles in **2** are nearly planar with the nickel atoms in them having a distorted tetrahedral geometry (Figure 1. left). The bond length of N–Ni (1.9453 Å (av)) is slightly shorter than those in other nickel complexes with neutral BIAN ligands.¹³ Compared to

free dipp-BIAN ligand,¹⁴ the C–N bond (1.313(3) Å) distances within the metallacycle are elongated while the C–C bond (1.451(3) Å) is shortened, demonstrating the radical anionic nature of the dipp-BIAN ligand in **2**. Similarly, reaction of dipp-BIANNa with NiCl₂(Ph₃P)₂ in toluene affords **3** in moderate yield. Complex **3** can be alternatively prepared by mixing **2** with Ph₃P in toluene. Single crystal X-ray diffraction analysis shows **3** to be a monomeric complex with the nickel atom sitting in a tetrahedral center (Figure 1, right). The C–C bond length (1.458(6) Å) and the C–N bond lengths (1.314(av) Å) in the BIAN backbone of **3** also suggest the presence of a π -radical anionic dipp-BIAN ligand.^{6a,7}

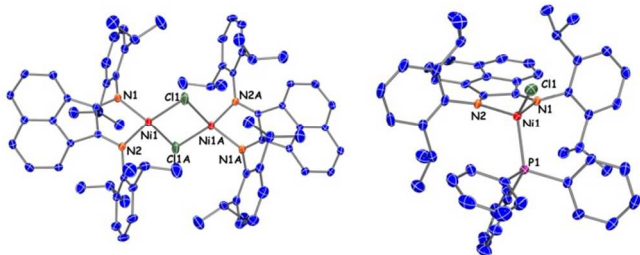


Figure 1. Molecular structures of **2** (left) and **3** (right). Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 30% probability.

Complexes **2** and **3** were tested as catalyst for ethylene polymerization with AIR₃ (R = Me, Et, ^tBu) as alkylating reagent (Table 1). Upon activation with AIR₃ (Al:Ni = 200), **2** and **3** both show moderate to high activities in ethylene polymerization. It is noticed that the catalytic activities of **2** and **3** are strongly dependent on the kind of the AIR₃ used. The system activated with TMA shows higher catalytic activity than those activated with AlEt₃ and Al(^tBu)₃. The system with **3** is slightly less active when compared to that with **2** under the same condition. For comparison, the catalyst system of **1**/TMA was also evaluated for ethylene polymerization.¹⁵ It was found that the **1**/TMA system shows similar catalytic activity to the **2**/TMA system does under the same conditions and the two systems produce polyethylene with similar molecular weight and dispersity. It was also found that addition of AlMe₃ to the solution of **1** in toluene results rapid color change from red-brown to purple-blue that is the same color complexes **2** or **3** show in toluene. These results imply that the catalytically active species formed in these systems may be the same or structurally similar to each other. UV-vis spectroscopic studies on the solutions of **1**, **2**, **1**/TMA, and **2**/TMA in toluene (Figure 2, left) reveal that **1**/TMA and **2** show a similar adsorption around 570 nm, which is assignable to the charge-transfer (CT) transition from a radical anionic BIAN ligand to the central metal in despite of a bathochromic shift happening compared to the absorptions observed in the range of 420–550 nm for other complexes containing a similar radical anionic BIAN ligand.^{6a,16} Complex **1** shows no evident absorption in the corresponding range. When TMA (5 equiv) was added to the solutions of **1** and **2**, another new absorption appears around 805 nm. The ESR spectra of **1**/TMA and **2**/TMA recorded in toluene at room temperature are also very much alike in which a 10-lined signal with $g = 2.0030$ was observed. Computer simulation suggests that the hyperfine structure in the ESR spectra may originate from the coupling of the unpaired electron with the ⁷³Al ($I = 5/2$; $A_{Al} = 6.0$ G), ¹⁴N ($I = 1$; $A_N = 4.7$ G), and ¹H ($I = 1/2$; $A_H = 1.2$ G) nuclei. (Figure 2, right).^{7e} These ESR spectra are similar to that described for the dipp-BIANAlMe₂ in which the aluminum atom is chelated by a radical anionic BIAN ligand,¹⁷ demonstrating that the BIAN ligand in **1** was reduced to radical anionic form in the presence of TMA.

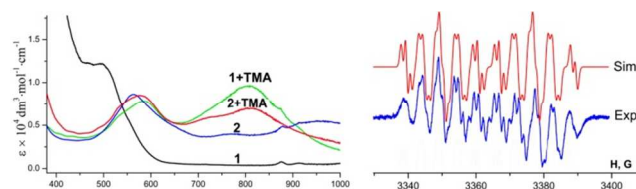
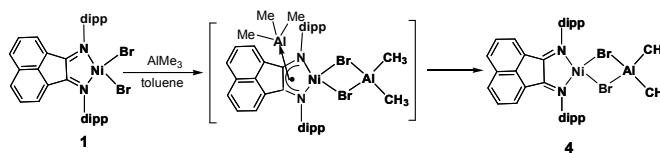


Figure 2. The UV-vis spectra of **1**, **2**, **1**/TMA, and **2**/TMA in toluene (left), and the ESR spectrum of **1**/TMA in toluene (right).



Scheme 2. Reaction of the dipp-BIANNiBr₂ with TMA.

Treatment of **1** with 5 equiv of TMA in toluene affords a blue solution. Careful evaporation of the solvent and crystallization of the residual in toluene/hexane mixture gave complex **4** as deep-blue paramagnetic crystals in a moderate yield. X-ray diffraction analysis reveals **4** to be a Ni–Al binuclear complex with the nickel atom in a tetrahedral coordinating environment (Figure 3). The nickel atom is essentially coplanar with the BIAN backbone with the Ni–N bond distance being 1.974(2) Å. The C–C bond distance of 1.464(3) Å is longer than that in **2** and is more consistent with single bond between sp^2 -hybridized carbon atoms.¹⁸ The C–N bond lengths in the BIAN backbone (1.297(3) Å) are slightly shorter than those in **2** (1.311 Å (av)) and **3** (1.313 Å (av)), and comparable to those (1.274(7)–1.308(7) Å) observed in nickel complexes with a neutral BIAN ligand.¹² Based on these bond parameters, it seems that the dipp-BIAN ligand in the solid state **4** is more likely in close shell neutral form, with the center metal Ni in +1 oxidation state. ESR spectroscopic studies at room and low temperatures also supports the presence of the Ni(I) in the solid state **4**. The anisotropic ESR spectrum of **4** in the solid state (Figure 4, left) is temperature-independent and exhibits an orthorhombic symmetry of the g -tensor. The experimental spectrum is in agreement with the simulated one and is also similar to that observed for a Cp(BIAN)Ni(I) complex.¹⁹ The appearance of g_1 , g_2 , and g_3 components at 2.361, 2.167, and 2.052, respectively, is indicative of a Ni(I) complex. Complex **4** in toluene solution is ESR silent at room temperature. However, when 4 equiv of TMA was added to the solution of **4** in toluene, the 10-lined ESR signal seen in the **1**/TMA and **2**/TMA systems reappeared. In the other hand, when 1 equiv of B(C₆F₅)₃ was added, the solution shows an ESR spectrum with a 7-line signal ($g = 2.0042$), suggesting the existence of the anionic BIAN radical. The hyperfine structure should originate from the coupling of the unpaired electron with the ¹⁴N ($I = 1$) and ¹H ($I = 1/2$) nuclei. Given the existence of the coupling of ²⁷Al with radical in **1**/TMA and **4**/TMA evidenced by their EPR, we tentatively supposed that the formation of the radical anionic BIAN ligand in the presence of TMA (or B(C₆F₅)₃) may be attributed to the interaction of the TMA (or B(C₆F₅)₃) with the anionic radical π -system of the BIAN backbone, which facilitates the electron transition from nickel center to the BIAN ligand.

Upon activation with 200 equiv of TMA, complexes **1**, **2**, and **4** all show high catalytic activities for ethylene polymerization and behave similarly under the same conditions. Typical ethylene polymerization results are summarized in Table 1. Complex **3** shows relatively low catalytic activities due to the presence of the coordinated PPh₃ in the molecule. The catalytic activity of these catalysts is dependent on the AIR₃ used, which may result from the

slower alkylation of the catalyst precursors with larger AlR_3 to form an alkyl-bridged heterodinuclear $\text{BIANNi}(\mu\text{-R})_2\text{AlR}_2$ in refer to literatures²⁰. Furthermore, the bulkier bridging-alkyls in $\text{BIANNi}(\mu\text{-R})_2\text{AlR}_2$ may also hinder the coordination of the monomer to the metal center. When MAO (500 equiv) was used as the activator, it was found that the catalytic activities of **1**, **2**, and **4**, together with the molecular weights of the polymers produced in these reactions are all moderately enhanced in comparison to the data obtained from the TMA activated systems. Furthermore, when 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ was added to the **1**/TMA and **2**/TMA systems, slightly improved catalytic activities were observed and much higher molecular weight polymers were obtained. However, when 1 equiv of trityl borate $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was added to the **1**/TMA and **2**/TMA systems, both systems demonstrate no catalytic activity and no polymer or oligomer was produced. In addition, AlEt_2Cl (200 equiv) activated **4** catalyst system was also found to show relatively high catalytic activity and produce highly branched polyethylene. Similar results were also reported with other diimine nickel catalyst systems.²¹

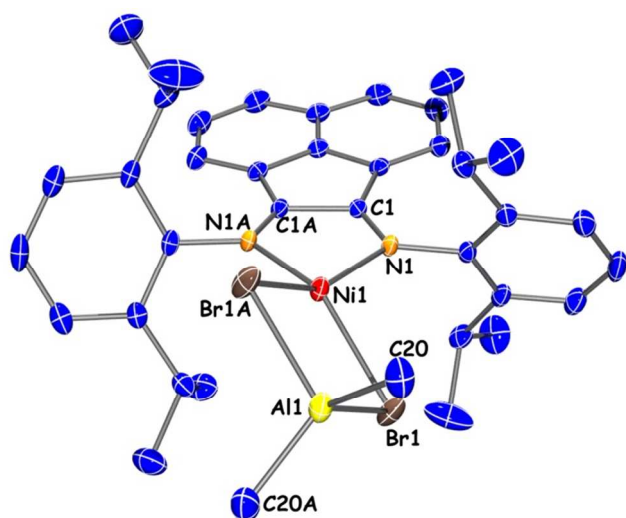


Figure 3. Molecular structure of **4**. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at 30% probability.

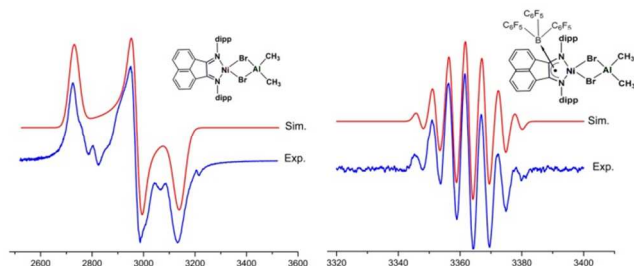


Figure 4. ESR spectrum of **4** in solid (left); and **4**/ $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene.

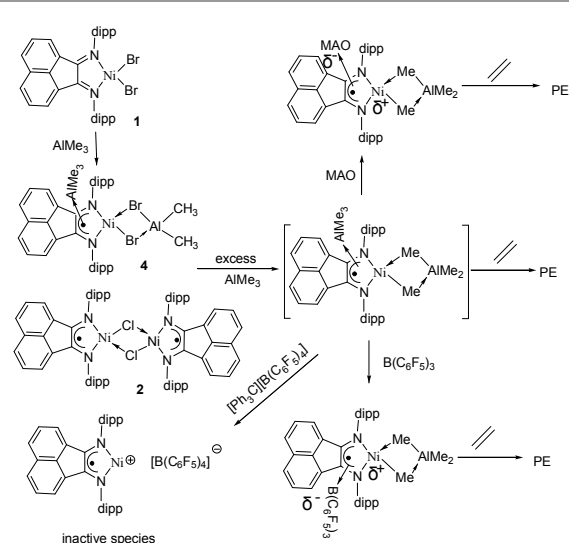
On the basis of the polymerization results as well as the above mentioned UV-vis, ESR, and structural studies, a possible mechanism for the activation and catalytic polymerization procedures of complexes **1**, **2**, and **4** can be proposed as shown in Scheme 3. In the presence of excess TMA, **1**, **2**, and **4** can be alkylated affording the alkyl nickel complex with a radical anionic dippe-BIAN ligand, which should be a catalytically active species for ethylene polymerization. Given the open environment at the nickel center, the alkyl-bridged heterodinuclear complexes possessing a structure analogous to **4** is more favorable.²⁰ Attempts to isolate the

active methyl nickel complex from the reaction of **2** with excess TMA in toluene were not successful so far. The formation of the $(\text{BIAN})\text{Ni}(\mu\text{-Me})_2\text{AlMe}_2$ species during the activation was indirectly confirmed by the addition of trityl borate $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (1 equiv), which is supposed to be capable of abstracting a methyl or alkyl group from the alkylated nickel complex to form a naked, catalytically inactive cationic species. The improvements in catalytic performances of these catalyst systems upon addition of MAO and $\text{B}(\text{C}_6\text{F}_5)_3$ may result from the interaction of the electron enriched radical anionic BIAN ligand with the Lewis acid MAO and $\text{B}(\text{C}_6\text{F}_5)_3$, which makes the central nickel(II) more positively charged and therefore is in favor of the coordination and insertion of ethylene. It is well documented that coordination of carbonyls to $\text{B}(\text{C}_6\text{F}_5)_3$ in SHOP-type catalysts and α -iminocarboximidate-nickel complexes can greatly improve the catalytic activities of these catalysts in ethylene polymerization.²² The formation of the carbonyl adducts was believed to remove the electron density from the nickel and render the metal center more electron deficiency.

Table 1. Ethylene polymerization results with dippe-BIAN Ni complexes^a

run	cat	AlR_3 (ratio)	Activity ^b	M_w^c	D^c	Branches ^d	T_m^e
($\times 10^4$)							
1	2	AlMe_3 (200)	2720	5.07	2.8	32.32	109.7
2	2	AlEt_3 (200)	288	1.80	4.0	n.d.	115.2
3	2	Al^iBu_3 (200)	576	2.03	4.0	n.d.	114.6
4	3	AlMe_3 (200)	1424	3.44	3.5	n.d.	96.5
5	3 ^f	AlMe_3 (200)	904	4.50	3.1	24.62	112.7
6	1	AlMe_3 (200)	2808	5.00	2.8	22.66	110.2
7	4	AlMe_3 (200)	2904	4.89	2.8	29.60	116.0
8	1	MAO(500)	3640	5.75	3.3	34.23	110.3
9	2	MAO(500)	3608	5.40	3.4	39.13	112.5
10	4	MAO(500)	3504	5.32	3.3	38.06	108.3
11	2 ^g	AlMe_3 (200)	–	–	–	–	–
12	2 ^h	AlMe_3 (200)	3128	13.68	3.0	27.61	118.9
13	4	AlEt_2Cl (200)	3464	5.13	2.6	64.52	64.4

^aPolymerization conditions: 5 μmol catalyst based on nickel, 60 mL of toluene, 5 bar of ethylene, 20 $^\circ\text{C}$, 15 min. ^bActivity in unit of $\text{Kg of PE}\cdot\text{mol}(\text{Ni})^{-1}\cdot\text{h}^{-1}$. ^c M_w and D (dispersity) were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 $^\circ\text{C}$ using a light scattering detector. ^dBranches per 1000 carbons determined by ^{13}C NMR spectroscopy at 130 $^\circ\text{C}$. ^eDetermined by DSC. ^fPolymerization time 60 min. ^gOne equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was added. ^hOne equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ was added.



Scheme 3. Proposed mechanism in the dippe-BIAN NiBr₂/MAO catalytic systems.

In summary, two new nickel complexes chelated by a radical anionic dipp-BIAN ligand have been synthesized by the reaction of dipp-BIANNa with nickel dichloride. Treatment of the neutral dipp-BIANNiBr₂ with 5 equiv of TMA in toluene was found to readily produce a Ni-Al binuclear complex with the nickel atom being chelated by the radical anionic dipp-BIAN ligand. ESR studies indicate that the existence of B(C₆F₅)₃ (or TMA) facilitates the formation of the radical anionic dipp-BIAN ligand through the electron transition from nickel center to the BIAN ligand due to the interaction of the Lewis acid B(C₆F₅)₃ (or TMA) with the electron-rich π-system of the BIAN backbone. When activated with excess TMA, these nickel complexes show high catalytic activities for ethylene polymerization and behave in similar manners under the same conditions. The activities of these systems were enhanced by addition of MAO, B(C₆F₅)₃, and AlEt₂Cl. A polymerization reaction mechanism involving neutral catalytically active species rather than cationic one was proposed.

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Notes and references

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