

Promoting Effect of AlCl_3 on the Fe-catalyzed Dimerization of Bicyclo[2.2.1]hepta-2,5-diene

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The activity of the catalytic system composed of $\text{Fe}(\text{acetylacetonate})_3$ ($\text{Fe}(\text{acac})_3$), triphenylphosphine, and diethylaluminum chloride for the dimerization of bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene, NBD) to produce hexacyclic endo-endo dimer (hexacyclo[7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6}]tetradec-10-ene, H_{nn}) was significantly enhanced by the presence of AlCl_3 , especially at the molar ratios of NBD/ $\text{Fe}(\text{acac})_3$ of 500. XPS analysis of the catalytic systems clearly demonstrates that AlCl_3 facilitates the reduction of $\text{Fe}(\text{acac})_3$ to form active species, $\text{Fe}(\text{II})$ and $\text{Fe}(\text{0})$ species. The layer separation was observed when $[\text{BMIm}]\text{Cl}$ was used along with AlCl_3 , but catalyst recycle was not very successful.

Key Words : Ionic liquids, 2,5-Norbornadiene, Dimerization, Hexacyclic endo-endo isomer

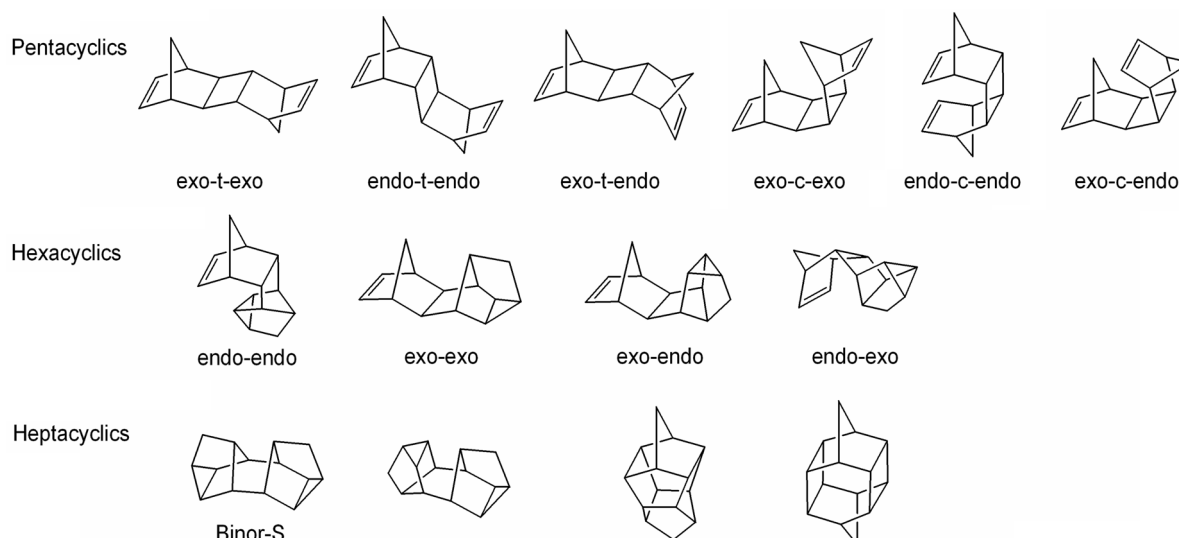
Introduction

The transition metal-catalyzed dimerization of bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene, NBD) has attracted increasing interest as a useful route to obtain ingredients of high density liquid fuels (HDLFs) and polycyclic hydrocarbon compounds. In general, the dimerization of NBD produces a series of isomeric mixtures with various compositions, depending on the type of catalyst employed (Scheme 1). For instance, Rh/C catalyst favors the formation of an isomeric mixture containing hexacyclic exo-endo (H_{xn}) as the major component.^{1,2} It has been also shown that the use of three-component catalytic system consisting of $\text{Co}(\text{acetylacetonate})_3$ ($\text{Co}(\text{acac})_3$), triphenylphosphine (TPP), and diethylaluminum chloride (DEAC) or ethylaluminum dichloride (EADC) produces heptacyclic Binor-S (dodeca-

hydro-1,2,4: 5,6,8-dimetheno-s-indecene) as the major product.^{3,4} In contrast, the dimerization in the presence of an iron-based three-component catalytic system consisting of $\text{Fe}(\text{acetylacetonate})_3$ ($\text{Fe}(\text{acac})_3$), TPP, and DEAC yields hexacyclic endo-endo dimer (hexacyclo[7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6}]tetradec-10-ene, H_{nn}) as the major product.⁵

Of various isomers of NBD dimers, H_{nn} is considered as the most essential component of HDLFs, but the commercialization of the process to produce H_{nn} using a Fe-based catalytic system has been restricted due to the low H_{nn} productivity.

In the continuous line of our study on the development of active and selective catalytic systems for the dimerization of NBD, we have found that the co-presence of AlCl_3 significantly enhances the activity of the catalytic systems based on $\text{Fe}(\text{acac})_3$, producing H_{nn} in high yields.



Scheme 1. Theoretically possible dimers of NBD.

We report here in detail the effect of AlCl_3 on the catalytic activity of Fe-based catalytic systems for the dimerization of NBD as well as the investigation of the active species and the mechanism for the formation of H_{nn} .

Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. NBD, EADC, DEAC, AlCl_3 , TPP, and $\text{Fe}(\text{acac})_3$ were purchased from Aldrich Chemical Co. All the solvents were obtained from Baker Chemical Co. and were distilled over appropriate drying agents prior to use.⁶ 1-Butyl-3-methylimidazolium chloride ($[\text{BMIm}]\text{Cl}$) was prepared using the method described in the literature.⁷⁻⁹

Instruments. The products were analyzed by gas chromatography with an Agilent 6890 GC equipped with a flame ionized detector and a DB wax column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$) and by mass spectrometry with an Agilent 6890-5975 GC-MSD equipped with a HP-5 capillary column ($50 \text{ m} \times 0.2 \text{ mm} \times 0.5 \mu\text{m}$). X-ray photoelectron spectroscopy (XPS) measurements were conducted with a PHI 5800 ESCA System of Physical Electronics equipped with a hemispherical energy analyzer and the monochromatized $\text{Al K}\alpha$ X-ray source of 250 W. The pass energy was 93.9 eV (0.8 eV steps) and 58.7 eV (0.13 eV steps) for the survey and high-resolution spectra, respectively. The collection angle for all the measurements was 45° . Before data acquisition, the catalyst sample was degassed for 3 h at 298 K under a reduced pressure of about 1.0×10^{-9} torr to minimize the surface contamination. Each spectrum obtained was curve-deconvoluted using the XPSPEAK Version 4.1 software.¹⁰ The C 1s peak at 284.6 eV was used to correct the surface charging effect before attempting the chemical state identification.^{11,12}

Dimerization reaction. Dimerization reactions were conducted in a 100 mL 3-necked round bottomed flask fitted with a reflux condenser, a thermocouple well, and a dropping funnel under a nitrogen atmosphere. The flask was charged with a catalyst, additives, toluene as a solvent, and *m*-xylene as an internal standard. The flask was then immersed in an oil bath that was maintained at a specified temperature and NBD was added drop-wise through a dropping funnel. After the reaction was completed, the product mixture was neutralized with an aqueous solution of NaHCO_3 and the upper organic layer was recovered and analyzed by GC, GC-Mass, and ^1H NMR.^{13,14}

Results and Discussion

In most cases, the dimerization of NBD requires the use of large quantities of additives such as alkylaluminum chloride and phosphines.^{1-5,15,16} Alkylaluminum chlorides are known to reduce metal complexes to form an active species and phosphines are believed to function as stabilizers for the resulting active species.^{17,18} To confirm the effects of additives on the NBD dimerization, the dimerization reactions

were conducted in the presence of a Fe-based catalytic system consisting of $\text{Fe}(\text{acac})_3$, TPP, and DEAC or DEAC/ AlCl_3 , and the factors affecting the dimerization were investigated.

As can be seen from Table 1, H_{nn} was produced as the major product when the dimerization was carried out in the presence of a Fe-based catalyst system consisting of $\text{Fe}(\text{acac})_3$, TPP, and DEAC. The dimerization of NBD, however, did not proceed in the absence of DEAC (Table 1, entry 4), suggesting an important role of DEAC in the reduction of Fe(III). The conversion of NBD continuously increased with increasing molar ratio of DEAC/ $\text{Fe}(\text{acac})_3$. The yield and selectivity of H_{nn} increased up to the molar ratio of 20, and then remained almost constant on further increase of the molar ratio. As already mentioned, the role of alkylaluminum chloride is to reduce metal complexes to form active species and thus the reduction of Fe(III) to Fe(II) and Fe(0) species by DEAC can be easily conceivable. The degree of Fe(III) reduction will obviously be dependent on the molar ratio of DEAC/Fe(III). At low to medium molar ratio of DEAC/Fe(III), the formation of Fe(II) species seems to be favored, but, at higher molar ratio of DEAC/Fe(III), Fe(0) species could be dominated. It is hard to conclude at the moment that which species, Fe(II) or Fe(0) is more responsible for the formation of H_{nn} , but experimental results suggest that both species function as active species even though $[\text{Fe}(0)\text{-TPP}]$ species has been proposed as the only active species for the dimerization of NBD.¹⁸

Effect of phosphine was also investigated by performing the dimerization at 85°C for 1 h in the presence of a Fe-based catalytic system. Molar ratios of NBD/ $\text{Fe}(\text{acac})_3$ and DEAC/ $\text{Fe}(\text{acac})_3$ were set at 500 and 20, respectively. As Table 1 indicates, the dimerization proceeded very slowly in the absence of TPP, producing H_{nn} in yield less than 5%. It has been reported that HCl, a catalyst poison, is often produced during the formation of an active species in the alkylaluminum chloride-assisted dimerization of olefinic compounds (Table 1, entry 3). Therefore, in the absence of HCl scavenger like TPP, HCl could attack the active species, resulting in the deactivation of the active species and

Table 1. Activities of various catalytic systems for the dimerization of NBD^{a,b}

Entry	Catalyst	C ^c (%)	S ^d (%)	Y ^e (%)
1	DEAC	0.0	0.0	0.0
2	$\text{Fe}(\text{acac})_3$	0.0	0.0	0.0
3	$\text{Fe}(\text{acac})_3$ -DEAC (1/20)	19.2	46.7	9.0
4	$\text{Fe}(\text{acac})_3$ -TPP (1/8)	0.0	0.0	0.0
5	$\text{Fe}(\text{acac})_3$ -TPP-DEAC (1/8/5)	0.0	0.0	0.0
6	$\text{Fe}(\text{acac})_3$ -TPP-DEAC (1/8/10)	5.2	77.0	4.0
7	$\text{Fe}(\text{acac})_3$ -TPP-DEAC (1/8/20)	85.6	85.2	72.9
8	$\text{Fe}(\text{acac})_3$ -TPP-DEAC (1/8/30)	81.5	77.8	63.5
9	$\text{Fe}(\text{acac})_3$ -TPP-EADC (1/8/20)	0.0	0.0	0.0

^aMolar ratio of NBD/ $\text{Fe}(\text{acac})_3$ = 500, temperature = 85°C , reaction time = 1 h. ^bNumbers in parentheses refer to molar ratios. ^cConversion of NBD. ^dSelectivity of H_{nn} . ^eYield of H_{nn} .

Table 2. Effect of TPP on the NBD dimerization^a

Entry	Molar ratio (TPP/Fe(acac) ₃)	C ^b (%)	S ^c (%)	Y ^d (%)
1	1	28.3	67.8	19.2
2	2	37.1	77.7	28.8
3	3	41.7	75.8	31.7
4	4	49.1	81.9	40.2
5	5	62.7	80.6	50.5
6	8	85.6	85.2	72.9
7	10	92.6	84.4	78.1

^aMolar ratios of NBD/Fe(acac)₃ and DEAC/Fe(acac)₃ were set at 500 and 20, respectively. temperature = 85 °C, reaction time = 1 h.

^bConversion of NBD. ^cSelectivity of H_{nm}. ^dYield of H_{nm}.

consequently producing low yield of dimer. However, in the presence of TPP, the conversion of NBD and the yield of H_{nm} increased continuously with increasing molar ratio of TPP/Fe, implying the important role of TPP in the stabilization of the active species (Table 2).

From these results, it is likely that the degrees of reduction of Fe(acac)₃ by DEAC and stabilization of the active species by TPP are playing pivotal roles in determining the catalytic activity and product selectivity.

Interestingly, the addition of small amounts of AlCl₃ to the three-component catalytic system increased the conversion of NBD and selectivity of H_{nm} (Table 3). The effect of AlCl₃ was more pronounced, especially at the molar ratio of NBD/Fe(acac)₃ of 500 or higher. The yield of H_{nm} increased with increasing molar ratio of AlCl₃/Fe(acac)₃ up to 5, but decreased drastically thereafter, affording large amounts of polymerized side products. It seems that the formation of Fe(II) and Fe(0) species is facilitated by the co-presence of AlCl₃, thereby accelerating the production of H_{nm}. However, at higher molar ratio above 5, excess AlCl₃ is likely to play a role in polymerizing NBD. One might suspect that the

Table 3. Effect of added AlCl₃ at various molar ratios of NBD/Fe(acac)₃^a

Entry	Molar ratio		C ^b (%)	S ^c (%)	Y ^d (%)
	NBD	AlCl ₃			
1	500	0	85.6	85.2	72.9
2	500	1	90.5	85.0	76.9
3	500	2	91.0	85.3	77.7
4	500	5	93.3	85.5	79.8
5	500	10	88.4	64.9	57.3
6	750	0	48.1	86.4	41.6
7	750	1	53.6	87.0	46.6
8	750	2	68.3	86.8	59.3
9	750	5	90.2	87.2	78.7
10	750	10	71.2	76.3	54.3
11	1000	0	21.0	84.2	17.7
12	1000	2	42.5	86.7	36.9
13	1000	5	85.1	87.5	74.4
14	1000	10	16.2	85.2	13.8

^aMolar ratio of Fe(acac)₃/TPP/DEAC = 1/8/20, temperature = 85 °C, reaction time = 1 h. ^bConversion of NBD. ^cSelectivity of H_{nm}. ^dYield of H_{nm}.

ethylaluminum dichloride (EADC) could be formed from the disproportionation of DEAC with AlCl₃ and the resulting EADC facilitated the formation of active species. Contrary to our expectation, the dimerization was completely quenched when EADC was used in place of DEAC and AlCl₃, suggesting that EADC is not able to generate active species by reducing Fe(acac)₃ (Table 1, entry 9).

To have a better insight of the role of AlCl₃ on the formation of active species, the high-resolution XPS analysis of the catalytic systems was conducted. The Fe 2p_{3/2} peaks were deconvoluted using XPSPEAK Version 4.1 software using a Gaussian-Lorentzian peak profile function and a Shirley background.¹⁰ It is reported that the characteristic Fe 2p_{3/2} peaks for Fe(III), Fe(II), and Fe(0) appeared at 711.2, 709.8, and 706.7 eV, respectively.^{11,12,19} As shown in Figure 1, Fe(acac)₃ exhibited distinct peak of Fe 2p_{3/2} at 714.3 and 711.4 eV corresponding to Fe(III). When Fe(acac)₃ was treated with DEAC, TPP, and AlCl₃ at 85 °C (DEAC/TPP/AlCl₃ = 20/8/5), the high-resolution spectrum of Fe 2p_{3/2} showed three component peaks at 714.2, 709.4, and 706.5 eV associated with Fe(III), Fe(II), and Fe(0), respectively. The area ratio of Fe(III)/Fe(II)/Fe(0) was calculated as 1/3.5/1.9, indicating that the Fe(III) was reduced to Fe(II) and Fe(0). The reduction of Fe(acac)₃ by DEAC and TPP (DEAC/TPP = 20/8) also showed three component peaks at 713.2, 709.3, and 706.2 eV corresponding to Fe(III), Fe(II), and Fe(0), respectively, but with the area ratio of Fe(III)/Fe(II)/Fe(0) = 1/1.2/0.3. These results demonstrate that the reduction of Fe(III) to Fe(II) and Fe(0) can be facilitated by the presence of AlCl₃, and both Fe(II) and Fe(0) species are responsible for the formation of H_{nm}.

The effect of temperature on the dimerization of NBD was investigated in the presence of the three-component catalytic system composed of Fe(acac)₃, TPP, and DEAC. As shown in Table 4, the conversion of NBD increased with the rise of temperature when the dimerization reactions were conducted with the molar ratios of NBD/Fe at 250 and 500. However, the yield of H_{nm} increased with the increase of temper-

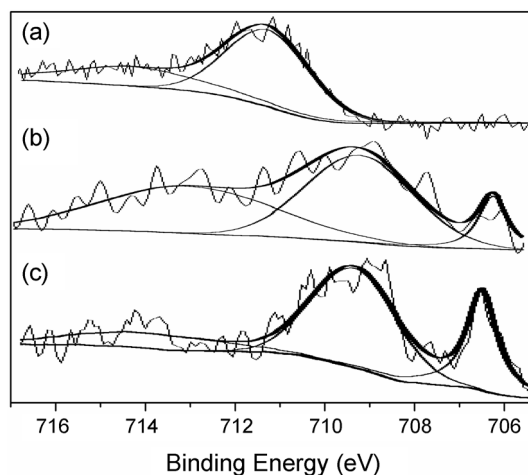
**Figure 1.** Curve-fitted XPS high-resolution Fe 2p_{3/2} spectra of (a) Fe(acac)₃, (b) Fe(acac)₃/TPP/DEAC = 1/8/20, and (c) Fe(acac)₃/TPP/DEAC/AlCl₃ = 1/8/20/5.

Table 4. Effect of temperature on the NBD dimerization^a

Entry	Molar ratio (NBD/ $\text{Fe}(\text{acac})_3$)	Temperature (°C)	C ^b (%)	S ^c (%)	Y ^d (%)
1	250	25	3.8	69.4	2.7
2	250	40	7.3	75.2	5.5
3	250	60	83.3	84.0	70.0
4	250	85	90.4	82.7	74.8
5	250	100	93.7	76.2	71.5
6	500	40	1.9	87.8	1.7
7	500	60	29.2	83.1	24.2
8	500	85	85.6	85.2	72.9
9	500	100	70.6	79.5	56.1

^aMolar ratio of $\text{Fe}(\text{acac})_3/\text{TPP}/\text{DEAC} = 1/8/20$, temperature = 85 °C, reaction time = 1 h. ^bConversion of NBD. ^cSelectivity of H_{nn} . ^dYield of H_{nn} .

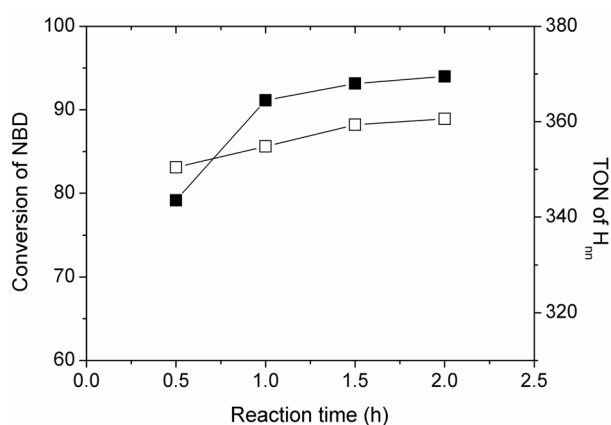


Figure 2. Effect of reaction time on the dimerization reaction of NBD at 85 °C: (□) conversion of NBD; (■) TON of H_{nn} (TON = moles of H_{nn} /moles of $\text{Fe}(\text{acac})_3$, molar ratios of NBD/ $\text{Fe}(\text{acac})_3$ /TPP/DEAC = 500/1/8/20).

ature only up to 85 °C, but decreased on further increase of temperature, most likely due to the formation of polymerized side products.

Effect of reaction time was also examined with or without the presence of added AlCl_3 at 85 °C and the molar ratio of NBD/ $\text{Fe}(\text{acac})_3 = 500$. As can be seen in Figure 2, the conversion increased with the reaction time, but the rate of increase was very slow after 30 min, irrespective of the presence of AlCl_3 .

Recently, ionic liquids (ILs) have been considered as the environmentally benign reaction media which can be applied to the catalysis, separation, or recovery of catalysts.²⁰ For this reason, the possibility of catalyst recycling was tested by adding an ionic liquid, [1-butyl-3-methylimidazolium]Cl ([BMIm]Cl) into the catalytic system consisting of $\text{Fe}(\text{acac})_3$, TPP, DEAC, and AlCl_3 . It is well known that the interaction of [BMIm]Cl with AlCl_3 produces [BMIm] $[\text{AlCl}_4]$, which is immiscible with hydrocarbons.^{7,21–23} It was hoped that most of the active species remains in [BMIm] $[\text{AlCl}_4]$ layer formed *in situ* during the dimerization and therefore can be recovered the organic product layer by a simple layer separation. The dimerization reactions were conducted at 85 °C with the NBD/ $\text{Fe}(\text{acac})_3$ /TPP molar ratio

Table 5. Catalyst recycling study with [BMIm]Cl^a

Cycle No.	Conversion of NBD (%)	Selectivity of H_{nn} (%)	Yield of H_{nn} (%)
1	93.8	87.1	81.7
2	81.5	86.7	70.7
3	4.3	87.8	3.8

^aMolar ratio of NBD/ $\text{Fe}(\text{acac})_3$ /TPP/DEAC = 250/1/8/20, [BMIm]Cl/ AlCl_3 / $\text{Fe}(\text{acac})_3 = 20/20/1$, temperature = 85 °C, reaction time = 1 h.

at 250/1/8. As expected, two distinct layers were observed when [BMIm]Cl was added in the reaction mixtures and the dimerization was not strongly affected by the presence of [BMIm]Cl (see Table 5). The recovered bottom layer was reused for the further dimerization with a fresh charge of NBD, but the NBD conversion and H_{nn} yield were reduced drastically after two cycles, suggesting that the catalyst is deactivated during the dimerization or the active component is lost during the recycles.

Further study is in progress to find out the reason for the catalyst deactivation and to develop a recyclable catalytic system.

To have a better understanding of the mechanism for the formation of H_{nn} , the intermediates involved in the catalytic cycle assisted by $\text{Fe}(0)$ species with a phosphine ligand were theoretically investigated at the B3LYP (6-31+G* for C and H, and LanL2DZ with ECP for P and Fe) level of the theory using Gaussian 03 program.²⁴ For simplicity, PH_3 was used instead of triphenylphosphine for the calculation. As can be seen from the optimized structures and energies of the intermediates (shown in parenthesis in kcal mol⁻¹ relative to the starting $\text{Fe}(\text{NBD})_2\text{PH}_3$ complex), stepwise formation of three σ -bond from three π -bond proceeds smoothly without any too stable or too unstable intermediates, which is a characteristics of an active catalyst (see Figure 3). This is in

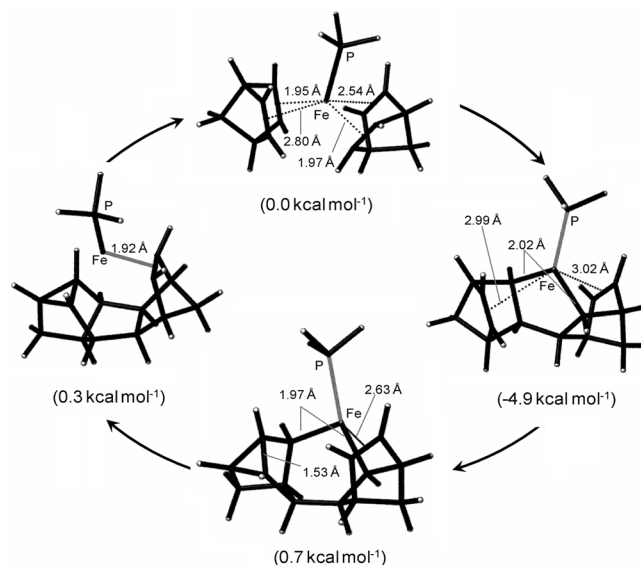


Figure 3. Proposed catalytic cycle for the formation of H_{nn} (potential energies of the intermediates were shown in parenthesis in kcal mol⁻¹ relative to the starting $\text{Fe}(\text{NBD})_2\text{PH}_3$ complex).

good agreement with the previous report that Fe-TPP is an active species for the NBD dimerization conducted in the presence of Fe(acac)₃, TPP, and DEAC.¹⁸

Conclusion

The introduction of AlCl₃ into the catalytic system composed of Fe(acac)₃, TPP, and DEAC was highly effective in promoting the dimerization of NBD, especially at the molar ratios of NBD/Fe(acac)₃ of 500 and higher. XPS analysis of the catalytic systems clearly demonstrates that AlCl₃ facilitates the reduction of Fe(acac)₃ and the formation of Fe(II) and Fe(0) species. Theoretical study clearly shows that Fe(0) species with a phosphine ligand can be an active species for the formation of H_{nn}. The layer separation was observed when [BMIm]Cl was used along with AlCl₃, but catalyst recycle was not fully successful.

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