九州大学大学院総合理工学報告
第28巻　第3号　335-342頁　平成18年12月

Engeering Sciences Reports, Kyushu University
Vol. 28, No. 3, pp. 335–342, DEC. 2006

Spectroscopic and Crystallographic Studies on the Insertion Reaction of Aryl Isocyanides into the Bond between Palladium and Carbon, which Contribute to Understanding the *trans*-[$Br_2Ni(CNAr)_2$]-Catalyzed Ethylene Polymerization

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(Received October 31, 2006)

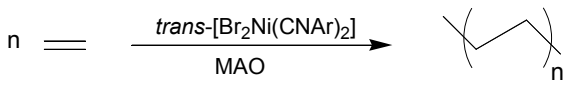
The insertion of two sterically different isocyanides into a Pd-Me bond was investigated by spectroscopy and crystallography; this contribute to better understanding of ethylene polymerization catalyzed by *trans*-[$Br_2Ni(CNAr)_2$]. Thus, the reaction of MePdCl(COD) (COD = cyclooctadiene) with a small isocyanide (CNC_6H_3-2,6-Me_2) or a bulky isocyanide (CNC_6H_3-2,6-Ph_2) demonstrated that isocyanide immediately inserted into the Pd-Me bond. Altough the C_6H_3-2,6-Ph_2 group is more bulky than the C_6H_3-2,6-Me_2 moiety, the anisotropic structure of ortho phenyl groups could provide enough space for the insertion by their appropriate rotations. Similarly, the molecular structure of *trans*-[ClPd{C(Me)=NC_6H_3-2,6-Ph_2}(CNC_6H_3-2,6-Ph_2)$_2$] (**5b**) provided another example of appropriate rotations of phenyl rings, which ingeniously avoid the inter-ligand repulsions.

Key words: *organometallic chemistry, palladium complex, aryl isocyanide, insertion reaction*

1. Inroduction

Organometallic complexes have been actively investigated as the catalyst for ethylene polymerization since the discovery of the metallocene catalyst.[1)] Brookhart and co-workers found Ni complexes bearing α-diimine ligands showing high catalytic activity for ethylene polymerization in 1995,[2)] opening the field of the "post-metallocene catalyst".[3)] We have recently found that the *trans*-[$Br_2Ni(CNAr)_2$] (Ar = aryl group) showed considerably high activity for ethylene polymerization in the presence of methylaluminoxane (MAO) (Scheme 1).[4)] The catalytically active species must be molecule; this is supported by the catalytic activity depends on the structure of the isocyanide ligands. For instance, the Ni complex having CNC_6H_3-2,6-Ph_2 showed the activity 40 times higher than that of CNC_6H_3-2,6-Me_2.

Although the performance of



Scheme 1

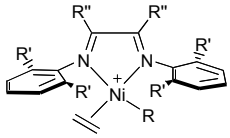
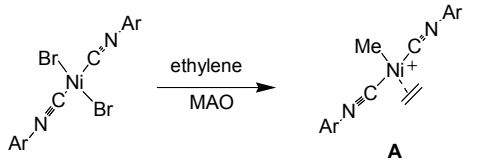


Fig. 1 The proposed active intermediate for Brookhart's catalyst



Scheme 2

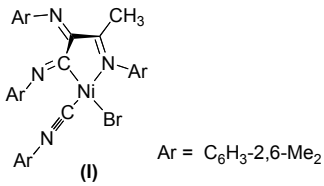


Fig. 2 The azanickellacyclopentene complex (I)

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trans-[$Br_2Ni(CNAr)_2$] is unique as a post-metallocene catalyst, the mechanism is totally unknown. From the analogy to well-investigated intermediates of the Brookhart's catalyst, which are cationic alkyl nickel species bearing coordinated ethylene as shown in Fig. 1, cationic species **A** may be generated from *trans*-[$Br_2Ni(CNAr)_2$] by way of mono-methylation and subsequent halogen abstraction by MAO (Scheme 2). However, this mechanism is problematic due to the trans-configuration of **A** between Me group and ethylene, which prevents insertion of ethylene between the Ni-Me bond. Possible insertion of the isocyanide ligand in **A** between the Ni-Me bond posed another problem for the mechanistic consideration, which could produce new nickel intermediates having a Ni-C(=NAr)Me moiety. It is really attractive to consider alternative mechanisms, in which intermediates having a Ni-C(=NAr)Me moiety or its analogues play an important role in the *trans*-[$Br_2Ni(CNAr)_2$]-catalyzed ethylene polymerization. In fact, a support of this possibility was available by the discovery that a nickel complex **I**, which can be formed by insertion of three molecules of CNAr to Ni-Me species generated from *trans*-[$Br_2Ni(CNAr)_2$] with MAO, actually behaves as an ethylene polymerization catalyst (Fig. 2).[5)]

We felt high probability of the mechanisms involving insertion of CNAr into Ni-Me species. However, a problem of this mechanism is the activity of ethylene polymerization depends on the structures of isocyanides, typically, *trans*-[$Br_2Ni(CNC_6H_3$-2,6-$Ph_2)_2$] >> *trans*-[$Br_2Ni(CNC_6H_3$-2,6-$Me_2)_2$]. As described in section 2.4 in detail, the molecular modeling study strongly suggests that there is a substantial difference in steric hindrance between CNC_6H_3-2,6-Ph_2 and CNC_6H_3-2,6-Me_2; the former is more bulky than the latter. A question is whether CNC_6H_3-2,6-Ph_2 may be too bulky for the smooth insertion into the Ni-Me bond; this provides difficulties in generating the catalytically active species. In order to solve this problem, we were interested in the model reaction using palladium as central metal to

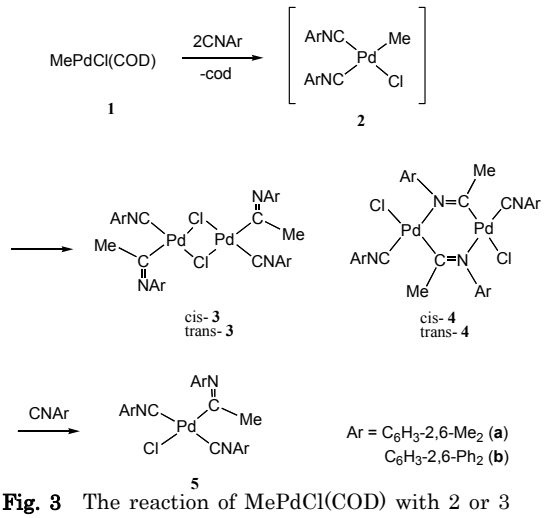


Fig. 3 The reaction of MePdCl(COD) with 2 or 3 equivalents of ArNC.

investigate how facile the insertion of CNC_6H_3-2,6-Ph_2 and CNC_6H_3-2,6-Me_2 into Pd-Me bond of *in situ* generated $MePdCl(CNAr)_2$. Palladium is in the same triad as nickel, affording more stable methyl complexes. High stability of the palladium-methyl complexes are useful for the mechanistic studies of the *trans*-[$Br_2Ni(CNAr)_2$] catalyzed ethylene polymerization, in which insertion of CNAr to $MeNiX(CNAr)_2$ is possibly involved as the mechanism.

2. Results and Dicussion

2.1 The spectroscopic study of the insertion reaction of CNC_6H_3-2,6-Me_2 into a Pd-Me bond

Vincente and co-workers have recently reported the insertion reaction of CNC_6H_3-2,6-Me_2 to Pd-Me bond, which is the small isocyanide described above, into a Pd-(C_6H_4-2-NH_2) bond.[6)] There was no report on the insertion reaction of CNC_6H_3-2,6-Me_2 into a Pd-Me bond, which is more important for the consideration of the mechanism of the MAO-assisted *trans*-[$Br_2Ni(CNAr)_2$]-catalyzed ethylene polymerization. As a related study, Anderson and co-workers reported spectroscopic studies on the insertion reaction of CN^{t}Bu into a Pd-Me bond.[7)] This report has shown the reaction of MePdCl(COD) and three equivalents of CN^{t}Bu to give the Pd complex having a structure similar to **5** shown in Fig. 3. In the related study to this Anderson's research, Uson and co-workers discussed the possibility

of intermediates similar to **3** and **4**.[8)]

We carried out the reaction of MePdCl(COD) with two or three equivalents of CNC_6H_3-2,6-Me_2 in CD_2Cl_2, and monitored the formed products by ^{1}H NMR spectroscopy. As shown in Fig. 3, the reaction of MePdCl(COD) and two equivalents of CNC_6H_3-2,6-Me_2 was expected to form **2a** by the ligand exchanging of COD and CNC_6H_3-2,6-Me_2. If **2a** is unstable and insertion of CNAr rapidly takes place, **3a** and **4a** could be formed. Addition of another equivalent of CNC_6H_3-2,6-Me_2 was likely to give **5a** as a single stable product. The actual ^{1}H NMR spectra (the range of Me on aryl group) for these reactions are shown in Fig 4. The reaction of MePdCl(COD) with two equivalents of CNC_6H_3-2,6-Me_2 afforded significant amount of precipitation, whereas addition of additional CNC_6H_3-2,6-Me_2 resulted in dissolution of the precipitates. A ^{1}H resonance due to the Pd-Me group is generally observed around or higher than 1 ppm; however, no singlet was observed around 1 ppm on ^{1}H NMR spectra. The spectrum obtained by addition of three equivalents of CNC_6H_3-2,6-Me_2 was unequivocally showed that the sole species assignable to **5a** exist in the solution. Thus, the signal of Me group originated from Pd-Me was seen at 2.68 ppm, significantly downfield from 1 ppm, suggesting the insertion reaction of isocyanide to form the Me(Pd)C=N(C_6H_3-2,6-Me_2) moiety. The signals due to the coordinated CNC_6H_3-2,6-Me_2 were observed at 2.10 and 2.40 ppm, respectively. The integral ratio of these three singlets was 3:6:12, which is in accord with the structure of **5a**. It is well known that the signals of aromatic protons are generally seen in 7-8 ppm. The signals of triplet (2H) and doublet (4H) at 7.29 and 7.16 ppm were thus assignable to para and meta protons of the coordinated CNC_6H_3-2,6-Me_2, respectively. In contrast, the multiplet (3H) at 6.88-6.95 ppm appeared unusually upfield as the aromatic protons. The upfield shift of aromatic protons is often observed, when the electron donating group such as nitrogen functional groups having a lone pair electron. Compared with the N≡C group of isocyanide (Ar-N≡C→Pd) acting as an electron acceptor, the N=C group of the imidoyl (Ar-N=C(Me)-Pd) could behave as an electron donor, giving the upfield shift described above. Two IR absorptions were visible at 2174 and 1666 cm^{-1} due to the stretching vibration of the coordinated isocyanide (*C*≡*N*-Ar) and imidoyl group (*C*=*N*-Ar), respectively (Table 1). Thus all of the ^{1}H and IR data are consistent with the structure of **5a**.

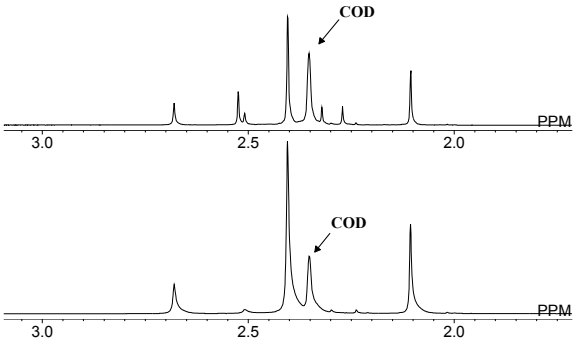


Fig. 4 ^{1}H NMR spectra of the reaction of MePdCl(COD) with 2 (above) or 3 (below) equivalents of CNC_6H_3-2,6-Me_2 in CD_2Cl_2

Table 1 Representative IR absorptions of obtained mixtures under each condition

condition	2eq. of CNAr		3eq. of CNAr
	solution	precipitate	
C≡N(cm^{-1})	2175	2189	2174
C=N(cm^{-1})	1630-1660	1663	1666
	1590	1560	

The ^{1}H NMR spectrum of the reaction of two equivalents of CNC_6H_3-2,6-Me_2 with MePdCl(COD) was complicated, suggesting the existence of more than two palladium species besides **5a**. The IR spectrum also gave several absorptions including the peaks due to **5a**. As described above, no ^{1}H resonance around 1 ppm indicates rapid insertion of CNC_6H_3-2,6-Me_2 into the Pd-Me bond. At present, we postulate the species formed by addition of two equivalents of CNC_6H_3-2,6-Me_2 would be a mixture of **3a** and **4a**, which are presumably a mixture of cis and trans isomers. This hypothesis is supported by the IR analyses of the precipitates and the solid recovered from the solution. The precipitate had absorption at 1560 cm^{-1} due to the bridging imidoyl group of **4a**, whereas the absorptions of the sample obtained from the solution were mainly observed at the range of 1630-1660 cm^{-1} which can be assignable to **3a** and **5a**. It is important

that dual species existing in the reaction mixture of two equivalents of CNC_6H_3-2,6-Me_2 with MePdCl(COD) were converted to a single product **5a** by addition of another equivalent of CNC_6H_3-2,6-Me_2. these results suggest that the spectral change is not inconsistent with the scheme shown in Fig. 3.

These spectroscopic results demonstrated that the small isocyanide, CNC_6H_3-2,6-Me_2, quickly inserted into the Pd-Me bond of intermediary $MePdCl(CNC_6H_3$-2,6-$Me_2)_2$ to form the imidoyl structure. This provided a good basis to investigate the homologous reaction of more bulky CNC_6H_3-2,6-Ph_2 with MePdCl(COD).

2.2 The spectroscopic study of the insertion reaction of CNC_6H_3-2,6-Ph_2 into a Pd-Me bond

Similar pathways to Fig. 3 (Ar = C_6H_3-2,6-Me_2) can be drawn for the reactions of MePdCl(COD) and two or three equivalents of CNC_6H_3-2,6-Ph_2 [Fig. 3 (Ar = C_6H_3-2,6-Ph_2)]. The change of actual ^{1}H NMR spectra (the range of Me) for the reactions of CNC_6H_3-2,6-Ph_2 with MePdCl(COD) are shown in Fig. 5. In contrast to the above described reaction with the small isocyanide, the reaction with two equivalents of CNC_6H_3-2,6-Ph_2 kept homogeneous. The ^{1}H NMR showed two singlets due to the Me groups at 0.98 and 1.62 ppm. A small singlet appeared at 1.15 ppm will be discussed later. On addition of another equivalent of CNC_6H_3-2,6-Ph_2, the singlet at 1.62 ppm disappeared, and all of the ^{1}H resonances, both methyl and aryl regions, became consistent with the structure of **5b**. Thus, the signals observed at 7.61-7.40 ppm are due to all of the protons on aryl groups of the CNC_6H_3-2,6-Ph_2 ligand coordinated to the Pd center. The two triplets at 6.60 and 6.71 ppm were due to the protons on the para and meta position of C_6H_3-2,6-Ph_2 of the imidoyl group, respectively. The multiplets observed at 6.80-6.86 ppm and a doublet at 7.10 ppm were due to the protons of C_6H_3-2,6-Ph_2 and ortho protons of C_6H_3-2,6-Ph_2 of the imidoyl group, respectively. The IR spectrum showed two

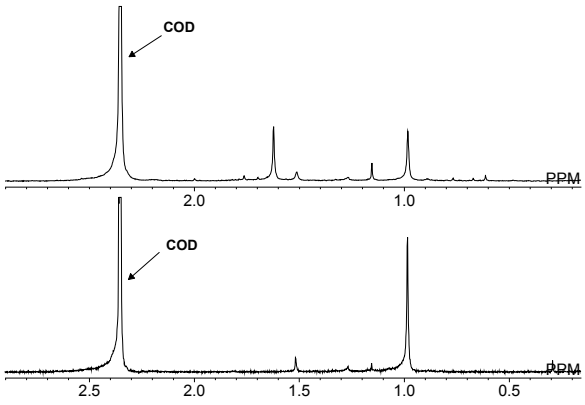


Fig. 5 ^{1}H NMR spectrum of the reaction of MePdCl(COD) with 2 (above) or 3 (below) equivalents of CNC_6H_3-2,6-Ph_2 in CD_2Cl_2

Table 2. Representative IR absorptions of obtained mixtures under each condition

condition	2eq. of CNAr	3eq. of CNAr
C≡N(cm^{-1})	2172	2175
C=N(cm^{-1})	1653	1653
	1583	1585

absorptions at 2175 and 1653 cm^{-1} due to the stretching vibration of the coordinated isocyanide (C≡N-Ar) and imidoyl group (C=N-Ar), respectively, which is also consistent with the structure of **5b**.

A solution formed by the reaction of two equivalents of this bulky isocyanide with MePdCl(COD) apparently contained **5b** and another species showing a ^{1}H resonance at 1.62 ppm. The IR absorptions mainly appeared at 2172 and 1653 cm^{-1}, which are assignable to the isocyanide ligand and non-bridging imidoyl groups. This suggests that the species showing the singlet at 1.62 ppm on the NMR could be **3b**. Evidence for the presence of **4b** may be a small absorption at 1583 cm^{-1}, which may correspond to the singlet at 1.15 ppm on the ^{1}H NMR spectrum.

All of these results suggest that the insertion of isocyanide into the Pd-Me bond is also rapid even with the bulky isocyanide such as $CNC_6H_3$2,6-Ph_2. For the explanation of the spectroscopic data described above consistently, existence of **2b** in solution must be excluded, which might be detectable in solution when the bulky isocyanide slowly undergoes the insertion between the Pd-Me bond. One may claim that the ^{1}H resonances due to the methyl groups

appeared at 0.98-1.62 ppm as described above, which could be assignable to Pd-Me moieties. Since the methyl group of the imidoyl moiety in **5a** appeared significantly downfield from this region, we have to explain the unusual chemical shift of the imidoyl methyl group in **5b**. This should be due to the long range shielding effect induced by local magnetic field of the benzene ring, which can clearly be visible in the molecular structure of **5b** described in the next section.

2.3 The molecular structure of the complex **5b** formed by insertion of the bulky isocyanide, CNC_6H_3-2,6-Ph_2

The described above spectroscopic studies indicated that even the bulky isocyanide, CNC_6H_3-2,6-Ph_2, quickly insert into the Pd-Me bond. The insertion reaction proceeded so smoothly even at room temperature. However, considerations using the molecular model described later indicate that bulkiness of CNC_6H_3-2,6-Ph_2 may provide sterically very crowded circumstances on the molecular structure of **5b**. In fact, inter-ligand steric repulsions around the Pd centre looked enormous when we built the simple molecular model for **5b**. In other words, the bulkiness of isocyanide may affect the thermodynamic stability of **5b**, though it does not give little effect on the kinetic formation of **5b**. The crystallography to determine the molecular structure of **5b** was thus carried out.

The single crystals were grown from a CH_2Cl_2/hexane solution containing a mixture obtained by the reaction of MePdCl(COD) with 4 equivalents of CNC_6H_3-2,6-Ph_2. There was no problem on the crystallographic data, and the molecular structure of **5b** was revealed to be just the same as we expected. The ORTEP drawing is illustrated in Fig. 6.

Arrangement of the four groups connecting to the Pd atom is square planer, and two CNC_6H_3-2,6-Ph_2 ligands coordinated to the Pd centre are in trans configuration. The imidoyl group, C(Me)=NC_6H_3-2,6-Ph_2, exists at the opposite site of the chlorine atom. The two CNC_6H_3-2,6-Ph_2 ligands are bonded to the Pd atom with bond lengths of 1.990(5) and 1.972(5) Å for Pd-C, whereas those of 1.154(6) and 1.143(6) Å for C≡N. The C(Me)=NC_6H_3-2,6-Ph_2 group has a typical structure of the imidoyl group, of which N(1)-C(1) bond distance [1.277(6) Å] suggested the existence of a N=C double bond, whereas the angles of C(1)-N(1)-C(3) [125.0(4) deg.] and C(2)-C(1)-Pd(1) [116.6(3) deg.] contribute to sp^2 hybridization of C(1) and N(1). The arrangement of the phenyl groups, which are located at the ortho-positions of three C_6H_3-2,6-Ph_2 moieties, was demonstrated to avoid the steric repulsions of the Ph rings ingeniously. This is achieved by rotation of the Ph planes in the CNC_6H_3-2,6-Ph_2 groups. Thus, the possible rotation to avoid the steric

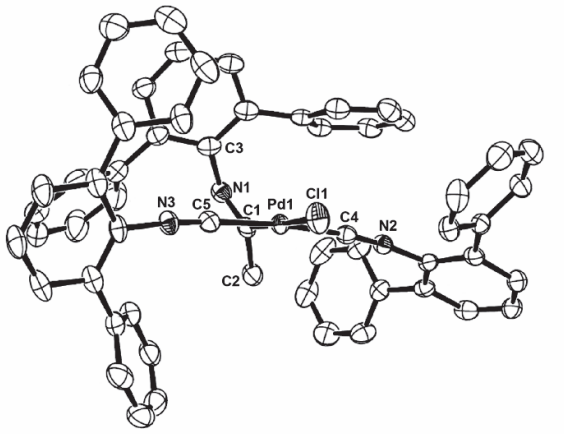


Fig. 6 The molecular structure of **5b**. Ellipsoids represent 50% probability; hydrogen atoms are omitted for clarity.

Table 3 Representative bond lengths and angles for **5b**

Pd(1)-Cl(1)	2.439(1)	Cl(1)-Pd(1)-C(1)	175.7(1)
Pd(1)-C(1)	2.022(5)	Cl(1)-Pd(1)-C(4)	96.7(1)
Pd(1)-C(4)	1.990(5)	C(4)-Pd(1)-C(5)	173.0(2)
Pd(1)-C(5)	1.972(5)	C(1)-N(1)-C(3)	125.0(4)
N(1)-C(1)	1.277(6)	C(2)-C(1)-Pd(1)	116.6(3)
N(2)-C(4)	1.154(6)		
N(3)-C(5)	1.143(6)		

Table 4 Crystallographic data for **5b**

Crystal system	monoclinic
Space group	$P2_1/c$
a, (Å)	9.561(2)
b, (Å)	17.843(4)
c, (Å)	27.205(5)
β, (deg.)	94.7442(9)
V, (Å^3)	4632.8(16)
Z	4
μ(MoKα) (cm^{-1})	15.28
No. of reflections measured	total: 27045, unique: 7638 (R_{int} = 0.069)
Good ness of fit on F^2	1.006
Final R indices [λ>2σ(λ)]	R_1 = 0.0530
R indices (all data)	wR_2 = 0.1490
Largest diff. peak and hole	2.54 and -0.77 eÅ^{-3}

repulsions explain both the thermodynamic stability of **5b**; this explanation can be extended to interpretation of the facile insertion of CNC_6H_3-2,6-Ph_2 into the Pd-Me bond discussed above.

The crystallographic study of **5b** also gave a clear answer to the question why the ^1H resonance due to the imidoyl methyl group in **5b** appeared at unusually higher field. In the molecular structure of **5b**, the methyl group is located at the face of two phenyl moieties of the CNC_6H_3-2,6-Ph_2 ligands. It is well known that the ring current of the aromatic ring gives local magnetic field leading to substantial change of the chemical shifts of protons nearby in the NMR spectroscopy(see Experimental section). The proton spatially located on the face of the phenyl ring generally gives significant upfield shifts by 1-2 ppm. The location of the methyl group is fitted just in this case, and its chemical shift (0.98 ppm) is explained by the long range shielding of the phenyl rings nearby.

2.4 Considerations on the steric effect of isocyanides

As described above, we started this research from our hypothesis that CNC_6H_3-2,6-Ph_2 may be sterically too bulky to promote insertion into the Pd-Me bond, which is facilely accomplished by smaller CNC_6H_3-2,6-Me_2. This hypothesis seemed to be reasonable, when we saw the structures of two isocyanides, CNC_6H_3-2,6-Ph_2 and CNC_6H_3-2,6-Me_2, determined by semi-empirical MO (PM3) calculations, of which CPK model illustrations are shown in Fig. 7. It is well known that a methyl group is isotropic, and free rotation along with the C(Me)-C(aryl) bond in CNC_6H_3-2,6-Me_2 provides a spherical sterically exclusive region, of which diameter is ca. 5 Å. According to the estimation of the spherical sterically exclusive region, free rotation of the phenyl group affords a sphere of which diameter is ca. 8 Å. In this sense, CNC_6H_3-2,6-Ph_2 must be more bulky than CNC_6H_3-2,6-Me_2. However, a feature of phenyl group is its anisotropic structure, and planarity of the phenyl group would provide

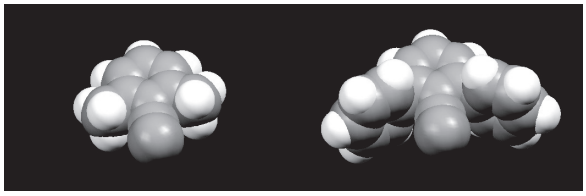
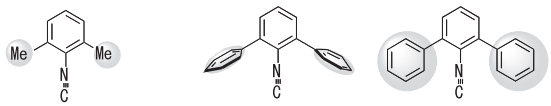


Fig. 7 The space filling model of CNC_6H_3-2,6-Me_2 (left) and CNC_6H_3-2,6-Ph_2 (right), simulated by PM3 method



a b(edge) b(face)

Fig. 8 The isocyanides; CNC_6H_3-2,6-Me_2 [a], CNC_6H_3-2,6-Ph_2 [b(edge)] and [b(face)]

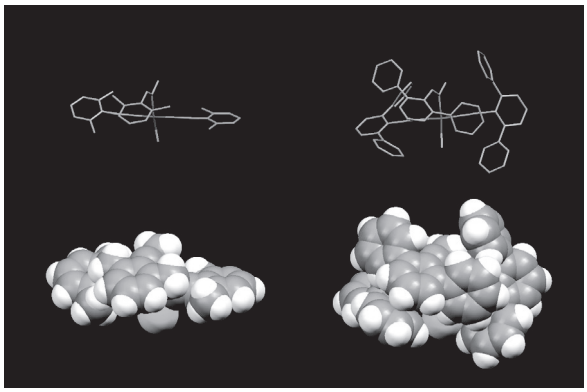


Fig. 9 The skeleton model (upper) and space filling model (bottom) of complex **5a** (left), There were simulated by MOPAC based on the structure of *trans*-[Pd{C(=NC_6H_3-2,6-Me_2)$C_6H_4NH_2$-2}I(CNC_6H_3-2,6-Me_2)]. Those of the complex **5b** (right) were determined by crystallographic data

much smaller steric influence. This is typically seen in Fig. 8, in which the rotation gives two extreme configuration, “edge” and “face”. If the rotation is restricted so as to minimize the steric repulsion among the ligands, the C_6H_3-2,6-Ph_2 groups would not afford severe steric hindrance to the complex **5b**. The molecular structure of **5a** was shown in Fig. 9, was estimated from the crystallographically determined structure of *trans*-[Pd{C(=NC_6H_3-2,6-Me_2)$C_6H_4NH_2$-2}I(CN C_6H_3-2,6-Me_2)], of which the $C_6H_4NH_2$-2 moiety was replaced by the Me group. The steric circumstance around the palladium in **5a** is not crowded, and there is enough space for the free rotation of the methyl groups in C_6H_3-2,6-Me_2 moieties. In sharp contrast, the ortho-phenyl groups in **5b** are apparently large, and caused substantial steric repulsions

among the ligands bonded to the palladium atom. In other words, it is apparent that coordination of all of the ligands in **5b** is accomplished by the fact that the motion of the phenyl groups should be severely restricted to minimize the inter-ligand steric interactions. This is accomplished by anisotropic structure of the phenyl groups which enable to alternate their steric influence by appropriate rotation. The importance of the anisotropic structure of the phenyl groups in the C_6H_3-2,6-Ph_2 groups can be expanded to the explanation for the facile insertion of CNC_6H_3-2,6-Ph_2. Although the phenyl group in CNC_6H_3-2,6-Ph_2 is more bulky than the methyl group in CNC_6H_3-2,6-Me_2, the phenyl groups can produce enough space for the insertion into the Pd-Me bond by their appropriate rotations. In other words, success of the CNC_6H_3-2,6-Ph_2 ligand in the *trans*-[Br_2Ni(CNAr)$_2$]-catalyzed polymerization of ethylene could be attributed to the steric flexibility of CNC_6H_3-2,6-Ph_2 derived from the anisotropic structure of the phenyl groups, which facilely produces the catalytically active species by the insertion reaction into the intermediary Ni-Me bond as well as giving the appropriate steric influence on the active species for the ethylene polymerization. Importance of appropriate steric influence of the ligand on the ethylene polymerization has been well established in the chemistry of the Brookhart's catalysts.

Concluion

We reported in this paper a model study for elucidating the mechanisms of *trans*-[Br_2Ni(CNAr)$_2$]-catalyzed polymerization of ethylene. We believe that insertion of the isocyanide ligand into a Ni-Me bond formed by pretreatment of MAO with *trans*-[Br_2Ni(CNAr)$_2$] plays an important role in catalysis. The spectroscopic as well as the crystallographic studies using palladium homologues as models for this insertion reaction solve a question whether the bulky CNC_6H_3-2,6-Ph_2 really inserts between the Ni-Me bond. Although complete elucidation of the polymerization mechanisms requires further investigation, the results described in this paper supports a possible mechanism shown in Fig. 10. Thus, *trans*-[MeBrNi(CNAr)$_2$] species formed by the pretreatment of nickel catalyst with MAO is followed by the insertion of CNAr into the Ni-Me bond. The resulting imidoyl intermediate **6** reacts with ethylene to afford the intermediate **7**. Replacement of the Br ligand by a methyl group is accomplished by methylation with MAO to form **8**, and insertion of coordinated ethylene into the Ni-Me bond of **8** initiates the ethylene polymerization.

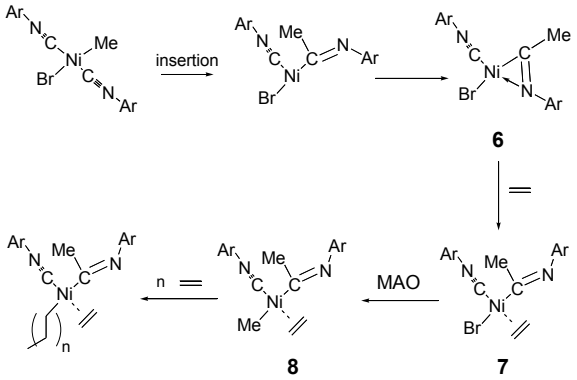


Fig. 10 The possible mechanism for ethylene polymerization of *trans*-[Br_2Ni(CNAr)$_2$]

We are planning further elucidation of the polymerization mechanisms and the catalyst design to improve the catalytic activity and polymerization behavior. The present study suggests that model studies using palladium will help for these future plans.

Acknowledgement

The authors are grateful to Mr. Masao Tanabiki and memberes of TOSOH Co. Ltd. for helpful discussions. Help for crystallographic studies by Dr. Yusuke Sunada and Taisuke Matsumoto is acknowledged.

Experimental section

General.: All experiments were carried out under an argon atmosphere. All solvents were distilled over CaH_2 prior to use (CD_2Cl_2 and CH_2Cl_2). All NMR experiments were carried out using CD_2Cl_2 solution placed in a 5Φ NMR tube and degassed several times. The tube was sealed in flame, while the solution was kept in a liquefied nitrogen bath in vacuum. The ^{1}H NMR spectra were taken with a JEOL Lambda 400 spectrometer. Chemical shifts were recorded in ppm from the internal standard (^{1}H: solvent). IR spectra were recorded in cm^{-1} on a JASCO FT/IR-550 spectrometer.

NMR identification of the species formed by the reaction of MePdCl(COD) with isocyanides:

(I) *MePdCl(COD) with two or three equivalents of CNC_6H_3-2,6-Me_2*: In a NMR tube were placed CNC_6H_3-2,6-Me_2 (2.7 mg, 20 μmol, or 4.1 mg, 30 μmol) and MePdCl(COD) (2.8 mg, 10 μmol), and then CD_2Cl_2 (ca. 0.3 mL) was transferred to by vacuum.

Spectral data for [ClPd[C(Me)=NC_6H_3-2,6-Me_2](CNC_6H_3-2,6-Me_2)$_2$] (5a); ^{1}H NMR (395MHz, CD_2Cl_2, r.t.); δ7.61 (d, 1H, Ph, J = 7.2Hz). 7.59 (d, 1H, Ph, J = 7.2Hz), 7.50-7.40 (m, Ph, 21H), 7.10 (d, 4H, J = 7.7Hz), 6.86-6.80 (m, 3H), 6.71 (t, 4H, Ph, J = 7.7Hz), 6.60 (t, 2H, Ph, J = 7.7Hz), 0.98 (s, Me, 3H). IR: $\nu_{C\equiv N}$ 2175, 1652 cm^{-1}

(II) *MePdCl(COD) with two or three equivalents of CNC_6H_3-2,6-Ph_2*: The reaction of CNC_6H_3-2,6-Ph_2 (7.7 mg, 30 μmol, or 12 mg, 45 μ mol) and MePdCl(COD) (4.0 mg, 15 μmol) was carried out in similar fashion.

Isolation and crystallographic study of ClPd[C(Me)=NC_6H_3-2,6-Ph_2](CNC_6H_3-2,6-Ph_2)$_2$ (5b): In CH_2Cl_2 (10 mL), CNC_6H_3-2,6-Ph_2 (123 mg, 0.48 mmol) and MePdCl(COD) (34.4mg, 0.13 mmol) were dissolved at -78°C, and the mixuture was stirred for 2h at room temperature. The resulting solution was removed in vacuo, and the residue was washed with hexane. The desired complex **5b** was formed as white powder. Recrystallization of this crude product from CH_2Cl_2-hexane gave **5b** as needle in 99% yield (119 mg). ^{1}H NMR (395MHz CD_2Cl_2, r.t.); δ7.61 (d, 1H, Ph, J = 7.2Hz). 7.59 (d, 1H, Ph, J= 7.2Hz), 7.50-7.40 (m, Ph, 21H), 7.10 (d, 4H, Ph, 7.7Hz), 6.86-6.80 (m, Ph, 3H), 6.71 (t, 4H, Ph, J = 7.7Hz), 6.60 (t, 2H, Ph, J = 7.7Hz), 0.98 (s, Me, 3H). IR: $\nu_{C\equiv N}$ 2175, 1652 cm^{-1}.

Crystallographic studies: X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The data were collected at 293(1) K using ω scans in the θ range of -110.0° ≤ θ ≤ 70°. Data were collected and processed using CrystalClear (Rigaku) on a Pentium computer. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[9] and expanded using Fourier techniques.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least squares refinement on F^2 was based on 10380 observed reflections and 610 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber.[11] All calculations were performed using the CrystalStructure[12),13)] crystallographic software package. Details of final refinement are summarized in Table 4, and the numbering scheme employed is shown in Fig. 6.

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