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Synthesis and Structural Analysis of Half-Titanocenes Containing η^2-Pyrazolato Ligands, and Their Use in Catalysis for Ethylene Polymerization

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Cp*TiCl$_2$(L) [L = C$_3$H$_3$N$_2$ (**1**), 3,5-Me$_2$C$_3$HN$_2$ (**2**) and 3,5-^{i}Pr$_2$C$_3$HN$_2$ (**3**)], and Cp*Ti(C$_3$H$_3$N$_2$)$_3$ (**4**) were prepared in moderate yields by treating Cp*TiCl$_3$ with the pyrazoles in the presence of Et$_3$N or with their corresponding lithium salts in Et$_2$O. The structures of **1** and **2** determined by X-ray crystallography indicate that these complexes fold a distorted tetrahedral geometry around Ti, and the pyrazolato ligands coordinate to Ti with η^2-*N,N′*-coordination mode. In contrast, one of the pyrazolato ligand in **4** coordinates to Ti with η^1-*N*-bonding, whereas the other two ligands were bound to Ti with η^2-*N,N′*-fashion. The Cp analogues, CpTiCl$_2$(L) [L = C$_3$H$_3$N$_2$ (**5**), 3,5-Me$_2$C$_3$HN$_2$ (**6**), 3,5-^{i}Pr$_2$C$_3$HN$_2$ (**7**), and 3,5-Ph$_2$C$_3$HN$_2$ (**8**)], were also prepared by the reaction of CpTiCl$_3$ with the corresponding lithium salts in Et$_2$O or *n*-hexane. The crystallographic analyses of **5** and **6** revealed that the pyrazolato ligands coordinate to Ti with η^2-*N,N′*-coordination mode. These complexes (**1**−**3**, **5**−**8**) exhibited moderate catalytic activities for ethylene polymerization in the presence of methylaluminoxane (MAO), and the activities were highly affected by the substituent on the pyrazolato ligand employed. Complex **1** exhibited the highest activity affording polymer with uniform molecular weight distribution, suggesting that the polymerization proceeded with uniform catalytically active species. An increase in the steric bulk in the pyrazolato ligand led to a slight decrease in the activity by the Cp* analogues, whereas the activity by the Cp analogues increased upon increasing the steric bulk in the pyrazolato ligand employed.

Introduction

The design and synthesis of efficient transition metal complex catalysts that precisely control olefin coordination polymerization have attracted considerable attention.[1−7] *Nonbridged* half-metallocenes of group 4 transition metals of the type, Cp′M(L)X$_2$ (Cp′ = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand such as OAr, NR$_2$, N = CR$_2$, N = PR$_3$, etc.; X = halogen, alkyl), as exemplified in Chart 1, have emerged as one of the promising candidates for the new efficient catalysts.[6−8] This is because they exhibit unique characteristics for the synthesis of new

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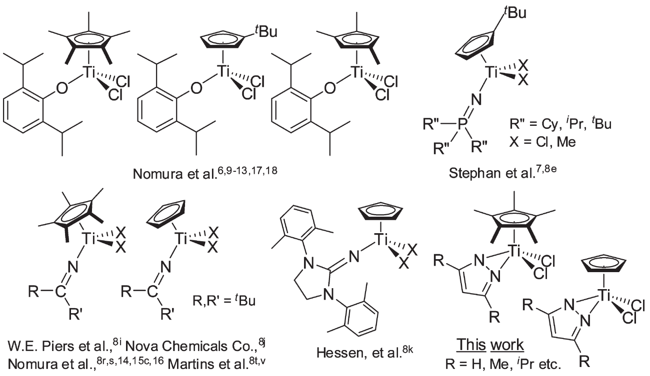
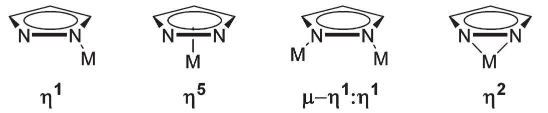
Chart 1



polymers[6,9−20] that are not accessible by conventional Ziegler−Natta catalysts, ordinary metallocene type,[1] and "constrained geometry" (linked Cp-amide) type catalysts.[1,2] Moreover, their syntheses are generally simple involving one or two steps, and the modification in the steric and/or electronic environment of the ligand framework is more facile especially than that in the linked half-metallocene type complexes.[6] We have demonstrated that half-titanocenes containing an anionic ancillary donor ligand of the type, $Cp'TiCl_2(L')$ (L' = O-2,6-$^iPr_2C_6H_3$, $N{=}C^tBu_2$), not only exhibit notable catalytic activities for olefin polymerization[8] but also display unique characteristics especially for copolymerization of ethylene with vinylcyclohexane,[11] 2-methyl-1-pentene,[12] styrene,[13,14] and cyclic olefins such as norbornene,[15] cyclopentene,[16] and cyclohexene.[17] More recently, we reported that these catalysts are also effective for introducing functional groups into polyolefins in an efficient manner.[18,19] It turned out that an efficient catalyst for the desired (co) polymerization can be modified by simple replacement of both the cyclopentadienyl fragment (Cp′) and the anionic ancillary donor ligands (L) employed.[6]

Chart 2



Pyrazolato ligands and their derivatives are capable of exhibiting a variety of coordination modes such as η^1, $\mu{-}\eta^1{:}\eta^1$, η^2 and η^5 (Chart 2), and many studies are known about their coordination behaviors.[20] The η^2-*N*,*N*′-pyrazolato coordination is predominant in the chemistry of early transition metal complexes,[21−23] as demonstrated by Erker and Winter,[21] and this feature brings forth the intriguing possibility of employing pyrazolato ligands as ancillary donor ligand for better stabilization. It is also known that those complexes bear significant structural and chemical resemblance to analogous cyclopentadienyl and β-diketonate derivatives.[21] Although synthesis of zirconocene complexes containing pyrazolato ligands were known, detailed studies for synthesis and structural analysis of a series of half-titanocenes containing pyrazolato ligands have not so far been reported. Moreover, investigation of their application as the catalyst precursors for olefin polymerization has not been explored, although unique stabilization as the anionic ancillary donor ligand by η^2 (or η^5) coordination can be highly expected, as described above.[21] Therefore, in the present contribution, we wish to introduce the synthesis and structural analysis of half-titanocenes containing a series of (substituted) pyrazolato ligands of the type, $Cp'TiCl_2(L)$ [Cp′ = Cp* and Cp, L = $C_3H_3N_2$, 3,5-$Me_2C_3HN_2$, 3,5-$^iPr_2C_3HN_2$, 3,5-$Ph_2C_3HN_2$, Chart 1], and their use as catalyst precursors for ethylene polymerization.[24]

Results and Discussion

1. Synthesis and Structural Analysis of $Cp^*TiCl_2(L)$ [L = $C_3H_3N_2$, 3,5-$Me_2C_3HN_2$ and 3,5-$^iPr_2C_3HN_2$] and $Cp^*Ti(C_3H_3N_2)_3$. The general strategy for the synthesis of $Cp^*TiCl_2(L)$ [L = $C_3H_3N_2$ (**1**), 3,5-$Me_2C_3HN_2$ (**2**) and 3,5-$^iPr_2C_3HN_2$ (**3**)] is depicted in Scheme 1. $Cp^*TiCl_2[C_3H_3N_2]$ (**1**) could be prepared in 52% yield by treatment of Cp^*TiCl_3 with 1.1 equiv of $Li(C_3H_3N_2)$ (prepared in

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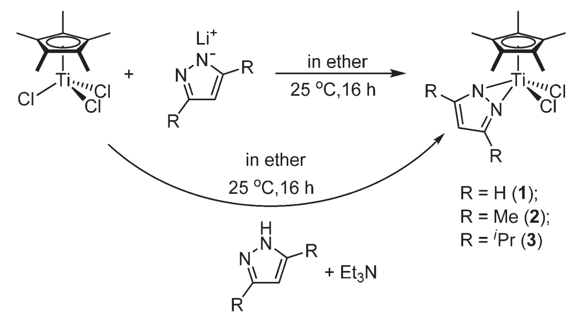
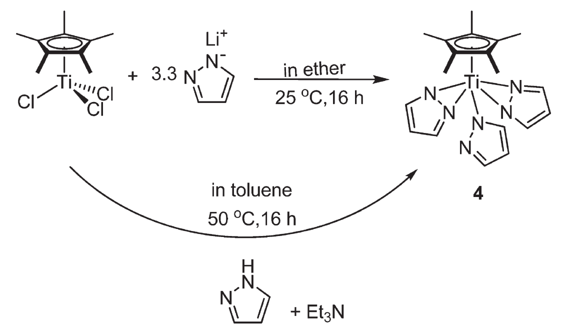
Scheme 1



Scheme 2



advance by treating pyrazole with ^{n}BuLi with in hexane, and isolated as the white solid)[25] and was isolated as deep red microcrystals from the chilled CH_2Cl_2/n-hexane solution (−20 °C). The corresponding 3,5-dimethylpyrazolato and 3,5-diisopropylpryazolato complexes (**2** and **3**) could be isolated by following the same procedure (yield 60% and 82%, respectively). The observed reactivity of lithium pyrazolides toward Cp^*TiCl_3 lies in stark contrast to those of lithium pyrrolides,[24] which afforded bis- and tris-pyrrolide complexes along with the desired monopyrrolide complex thus making the isolation of the pure complex cumbersome. Moreover, the observed trend is quite different from what has been reported in the synthesis of Cp^*TiCl_2[N(Me)(cyclohexyl)][8] where optimization of the reaction conditions (temperature, equiv of lithium salts, etc.) was necessary probably because of the gradual decomposition of the lithium salt in the reaction solution. Complexes **1**−**3** could also be synthesized by the reaction of Cp^*TiCl_3 with pyrazole derivatives (LH) in the presence of Et_3N (Scheme 1), and this observation also lies in stark contrast to pyrrole derivatives, which were not reactive toward Cp^*TiCl_3 under the same conditions.[24] Attempts for preparations of half-titanocenes containing 3,5-diphenylpyrazolato, 3-methylpyrazolato, and 4-bromopyrazolato ligands were not successful by either method.

The attempted synthesis of bis-pyrazolato complex $Cp^*TiCl(C_3H_3N_2)_2$ by the reaction of Cp^*TiCl_3 with 2.2 equiv of $Li(C_3H_3N_2)$ was not successful, and the monopyrazolato complex (**1**) was isolated instead. The use of toluene as a solvent at higher temperatures led to the formation of a mixture of products thus rendering the isolation of pure complex difficult. In contrast, all the three chlorine atoms in Cp^*TiCl_3 could be smoothly replaced with pyrazolato ligand, when Cp^*TiCl_3 was treated with 3.3 equiv of $Li(C_3H_3N_2)$ in Et_2O at room temperature, affording $Cp^*Ti(C_3H_3N_2)_3$ (**4**) in 56% yield (Scheme 2). Synthesis of **4** could also be accomplished by the reaction of Cp^*TiCl_3 with pyrazole (3.3 equiv) in the presence of excess Et_3N in toluene at 50 °C. However, the reaction of Cp^*TiCl_3 with lithium salts of 3-methylpyrazole, 3,5-dimethylpyrazole, and 3,5-diisopropylpyrazole (> 3.0 equiv) in either Et_2O (at room temperature) or toluene (50−80 °C) resulted in the formation of a mixture of products, and attempted isolations of the desired tris-pyrazolato complexes from the mixtures were not successful even after repeated recrystallization procedures.

All the complexes (**1**−**4**) were identified based on ^{1}H and ^{13}C NMR spectra and elemental analyses, and the structures of **1**, **2**, and **4** were determined by X-ray crystallography, as described below. Resonances ascribed to protons in pyrazole were observed at 6.92 and 7.80 ppm in the ^{1}H NMR spectrum of **1**, which were downfield shifted with respect to those in free pyrazole (6.29 and 7.61 ppm) caused by the decrement of electron density on the five-membered heterocyclic ring because of coordination. In a similar fashion, pyrazolato ring protons in **2** and **3** were observed at 6.43 and 6.50 ppm, respectively, which are downfield shifted with respect to those in the corresponding free ligands (5.81 and 5.85 ppm, respectively). As mentioned above, pyrazolato ligands coordinate to metals in a variety of fashions as depicted in Chart 2. Although it is difficult to distinguish various coordination modes of pyrazolato ligand to Ti solely by their NMR spectra, the η^5-bonding mode seems unlikely because the ring protons were slightly downfield shifted (**1**: $\Delta\delta$0.14 and 0.19, **2**: $\Delta\delta$ 0.62, **3**: $\Delta\delta$ 0.65) whereas the protons in a η^5-pyrazolato Ru complex [$Cp^*Ru(\eta^5$-3,5-dimethylpyrazolato) showed a large upfield shift ($\Delta\delta$ 1.42).[26]

The structures of **1** and **2** were determined by X-ray crystallographic analysis (Figure 1), and the selected bond lengths and the angles are summarized in Table 1.[27] The pyrazolato and 3,5-dimethylpyrazolato ligands are coordinated in η^2-*N*,*N*′ fashion with almost identical Ti−N bond lengths [2.031(2)-2.0474(13) Å], which are comparable with most of the reported Ti complexes bearing η^2-*N*,*N*′-coordinated pyrazolato ligands,[21−21] but are slightly longer than those in half-titanocenes containing pyrrolide ligands [1.969(4) and 1.965(2) Å for $Cp^*TiCl_2(2,4\text{-}Me_2C_4H_2N)$ and $Cp^*TiCl_2(3\text{-}Et\text{-}2,4\text{-}Me_2C_4HN)$, respectively].[24] Moreover, the Ti−N bond distances are significantly longer than those in $(1,3\text{-}Me_2C_5H_3)TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ [1.898(2) Å],[8] Cp^*TiCl_2[N(Me)(cyclohexyl)] [1.870(3) Å],[8] and in $Cp^*TiCl_2(N{=}CPh_2)$ [1.827 (2) Å],[28] and the distance is close to the estimated value (2.02 Å) for a titanium−nitrogen single bond according to Pauling's covalent radii.[29] These results thus suggest that titanium forms

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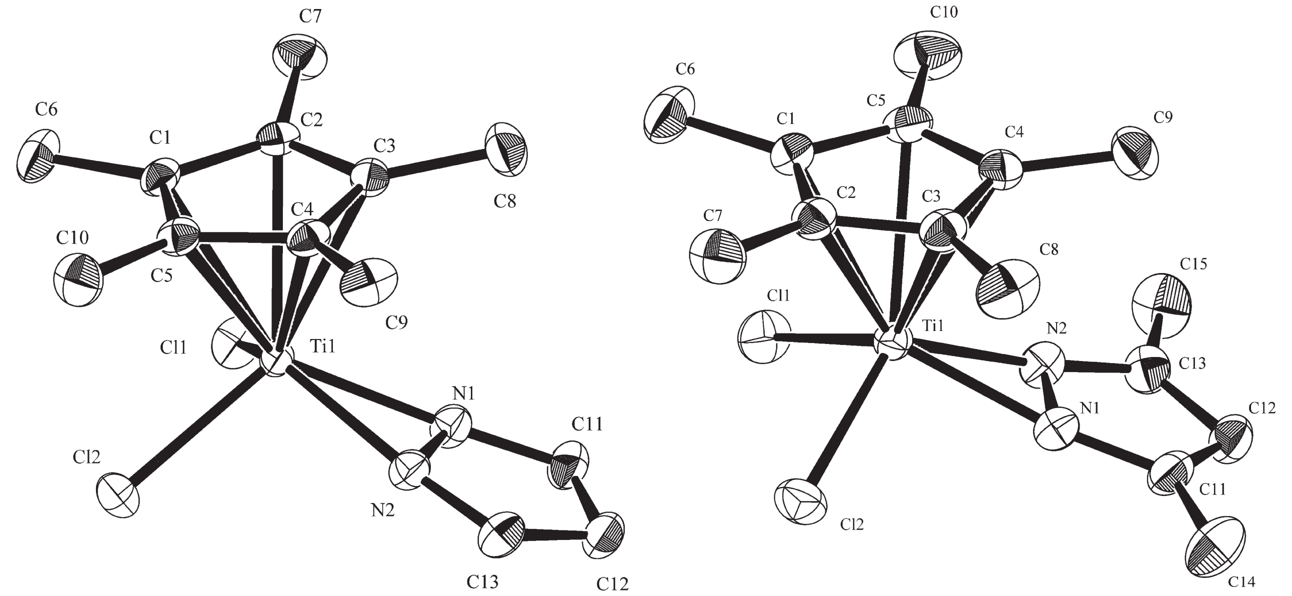

Figure 1. Oak Ridge Thermal Ellipsoid Program (ORTEP) drawings for $Cp^{*}TiCl_2(C_3H_3N_2)$ (**1**, left) and $Cp^{*}TiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**2**, right). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.[27]

Table 1. Selected Bond Distances (Å) and Angles (deg) for $Cp^{*}TiCl_2(C_3H_3N_2)$ (**1**) and $Cp^{*}TiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**2**)[27]

	1	**2**
	Bond Distances (Å)	
Ti(1)−Cl(1)	2.3088(4)	2.3047(13)
Ti(1)−Cl(2)	2.3028(5)	2.3027(13)
Ti(1)−N(1)	2.0429(14)	2.031(2)
Ti(1)−N(2)	2.0474(13)	2.0185(16)
Ti(1)−C(1)	2.3579(16)	2.376(2)
Ti(1)−C(2)	2.3697(16)	2.378(2)
Ti(1)−C(3)	2.3620(17)	2.347(3)
N(1)−C(11)	1.341(2)	1.339(2)
C(11)−C(12)	1.381(2)	1.392(5)
C(12)−C(13)	1.388(2)	1.399(6)
N(2)−C(13)	1.337(2)	1.337(2)
N(1)−N(2)	1.3679(18)	1.381(6)
Ti(1)−Cp	2.037	2.029
	Bond Angles (deg)	
Cl(1)−Ti(1)−Cl(2)	95.684(18)	97.24(3)
Cl(1)−Ti(1)−N(1)	91.46(4)	91.27(9)
Cl(2)−Ti(1)−N(1)	119.25(4)	123.90(8)
Cl(1)−Ti(1)−N(2)	125.34(4)	122.05(9)
Cl(2)−Ti(1)−N(2)	93.70(4)	92.48(10)
N(1)−Ti(1)−N(2)	39.07(5)	39.87(16)
Cp-Ti(1)−Cl(1)	112.86(2)	112.46(6)
Cp-Ti(1)−Cl(2)	113.16(2)	114.05(6)
Cp-Ti(1)−N(1)	118.86(4)	113.93(6)
Cp-Ti(1)−N(2)	112.20(4)	114.15(6)

σ-bonds to both nitrogen atoms in the pyrazolato ligand as a result of delocalization of negative charge over five-membered ring. On the basis of these results, these complexes would be considered as 14e complexes (by 3e donation with the pyrazolato ligand) rather than 16e complexes (by 5e donation). The bonding behavior in the pyrazolato ligand is somewhat similar to that in the amidinate ligands, exemplified by $Cp^{*}Ti[\eta^2\text{-}PhCH(Me)NCH(Me)NCH(Me)Ph]Cl_2$ in which amidinate ligand exhibits η^2-coordination mode with both nitrogen atoms attached with Ti through σ-bonds as indicated by almost equal Ti−N bond lengths [2.114(2) and 2.157(2) Å].[30] The pyrazolato ligand is planar and close to a regular pentagon in both cases, for example, all the bond distances within the heterocyclic ring are almost identical in complex **1** [N(1)−C(11) 1.341(2), C(11)−C(12) 1.381(2), C(12)−C(13) 1.388(2), N(2)−C(13) 1.337(2), N(1)−N(2) 1.3679(18)] and bond angles are close to 108° (see Supporting Information). The coordination spheres around the Ti possess an approximate tetrahedral geometry in both complexes if the center of the nitrogen−nitrogen bond in pyrazolato ligand is considered as a monodentate ligand. As a result of η^2-*N*,*N*′-coordination of pyrazolato ligands, the Cl(1)−Ti−Cl(2) bond angles in **1**, **2** were constrained [**1**; 95.684(18)° and **2**; 97.24(3)°], and these showed unique contrast to those in the half-titanocenes containing pyrrolide ligands in η^1 coordination mode (> 100°).[24]

The Ti−Cl bond lengths [2.3027(13)−2.3088(4) Å] are somewhat longer than those in the Cp*-pyrrolide complexes [$Cp^{*}TiCl_2(2,4\text{-}Me_2C_4H_2N)$: 2.2639(19), 2.2458(19) Å; $Cp^{*}TiCl_2(3\text{-}Et\text{-}2,4\text{-}Me_2C_4HN)$: 2.2548(19), 2.2578(11) Å].[24] The observed slight differences in the Ti−Cl bond lengths (in between the pyrrolide and the pyrazolato analogues) are probably the outcome of better electron donation of the η^2-*N*,*N*′-coordinated pyrazolato ligands than the η^1-coordinated pyrrolide ligands. Moreover, the Ti−Cl bond lengths are comparable with those in $Cp^{*}TiCl_2(2,6\text{-}{}^{i}Pr_2C_6H_3)$ [2.305(2) Å][6] and $Cp^{*}TiCl_2[N(Me)(cyclohexyl)]$ [2.302(1), 2.304(1) Å],[8] but are slightly longer than those in $(1,3\text{-}Me_2C_5H_3)TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ [2.2662(9), 2.2770(9) Å],[8] and $Cp^{*}TiCl_2(N = CPh_2)$ [2.2844 (8) and 2.2735(10) Å].[28] The N−N distances [**1**, 1.3679(18); **2**, 1.381(6) Å] and the N(1)−Ti(1)−N(2) bite angles [**1**, 39.07(5)°; **2**, 39.87(16)°] in the pyrazolato ligands are similar to those in the η^2-*N*,*N*′-pyrazolato complexes of several early transition metals.[21−23]

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[30] Koterwas, L. A.; Fettinger, J. C.; Sita, L. A. *Organometallics* **1999**, *18*, 4183.

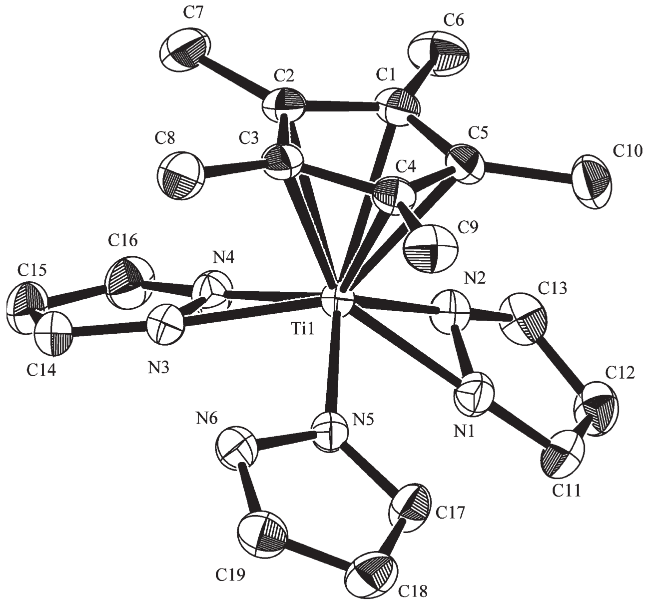


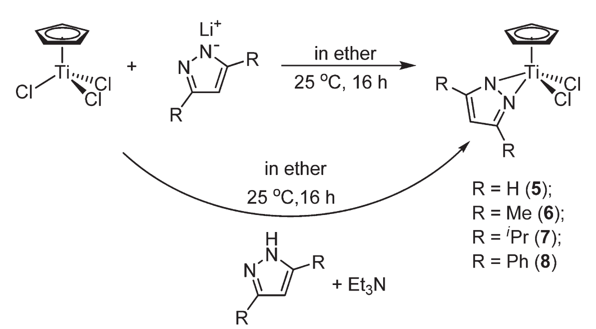
Figure 2. ORTEP drawings for $Cp^*Ti(C_3H_3N_2)_3$ (**4**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[27]

The structure of $Cp^*Ti(C_3H_3N_2)_3$ (**4**) is shown in Figure 2, and the selected bond distances and the angles are summarized in Table 2.[27] Two of the three pyrazolato ligands coordinate to Ti with η^2-*N*,*N′*-bonding modes and the one binds to Ti through η^1-*N*-coordination. The geometry around Ti can be envisioned as a distorted tetrahedral if the center of the nitrogen−nitrogen bond in η^2-*N*,*N′*-coordinated pyrazolato ligand is considered as a monodentate ligand. The Ti−N bond distances in η^2-*N*, *N′*-coordinated pyrazolato ligand [2.0503(16)-2.0735(13) Å] are slightly longer than those in complexes **1** and **2** [2.031(2)-2.0474(13) Å]. In contrast, Ti−N bond length in η^1-*N*-coordinated pyrazolato ligand was significantly longer [2.1136(13)Å] than those with the η^2-*N*,*N′*-coordinated pyrazolato ligands. On the basis of these crystallographic results, the complex **4** should be considered as a 16 electron complex.

Although two different bonding modes (η^2-*N*,*N′* and η^1-*N*) of three pyrazolato ligands in **4** were observed in the crystallographic analysis, only two types of ring protons corresponding to these pyrazolato ligands were observed as triplet (6.52 ppm) and doublet (7.81 ppm) in $CDCl_3$. The variable temperature ^{1}H NMR spectra were measured in toluene-d_8 to investigate any possible dynamic process taking place in **4**, but the spectra did not show any changes in the temperature range of between −80 and 100 °C.

2. Synthesis and Structural Analysis of $CpTiCl_2(L)$ [L = $C_3H_3N_2$, 3,5-$Me_2C_3HN_2$, 3,5-$^i Pr_2C_3HN_2$, and 3,5-$Ph_2C_3HN_2$]. Initial attempts for the synthesis of $CpTiCl_2(C_3H_3N_2)$ (**5**) by the reaction of $CpTiCl_3$ with 1.1 equiv of $Li(C_3H_3N_2)$ in Et_2O were not successful, and the resulting product was a mixture consisting of bis-pyrazolato complex (major) along with the desired mono-pyrazolato complex. In contrast, the reaction of $CpTiCl_3$ with pyrazole in the presence of Et_3N resulted in the clean formation of the desired complex (**5**) in 60% yield, which was obtained as yellow microcrystals from the chilled CH_2Cl_2/*n*-hexane solution (−20 °C). It was found that the by-production of undesired bis-pyrazolato complex can be avoided if reaction of $CpTiCl_3$ with the lithium salt, $Li(C_3H_3N_2)$, is carried out in cold *n*-hexane. In case of the other pyrazolato derivatives **6**−**8**, reactions of the corresponding lithium salts with $CpTiCl_3$ in Et_2O took place cleanly without formation of any undesired bis- or tris-pyrazolato complexes (Scheme 3). The desired complexes (**6**−**8**) were thus isolated in moderate yields (**6**, 53%; **7**, 63%; and **8**, 57%). Complexes **6**−**8** were also accessible through the reaction of the corresponding pyrazole derivatives with Et_3N in Et_2O. Several attempts to prepare the Cp complexes containing 3-methylpyrazolato and 4-bromopyrazolato complexes were not successful, as observed in the Cp* complexes. The reaction of $CpTiCl_3$ with 2.2 and 3.3 equiv of $Li(C_3H_3N_2)$ resulted in the formation of oily products, and the isolation of the pure bis- and tris-pyrazolato complexes could not be accomplished. Furthermore, attempted syntheses of the tris-pyrazolato complexes with 3-methylpyrazolato, 3,5-dimethylpyrazolato, and 3,5-diisopropylpyrazolato ligands were not successful either.

Scheme 3



Complexes **5**−**8** were identified based on ^{1}H and ^{13}C NMR spectra and elemental analyses, and the structures of **5** and **6** were determined by X-ray crystallography, as described below. As observed in the Cp* analogues (**1**, **2**), resonances ascribed to the ring protons in pyrazole were downfield shifted (7.00 and 7.81 ppm) with respect to those in free pyrazole (6.29 and 7.61 ppm). The protons corresponding to pyrazolato ligands in Cp complexes seemed more downfield shifted than those in their Cp* counterparts [**1**, 6.93 and 7.80; **4**, 7.00 and 7.81 ppm; **2**, 6.43; **5**, 6.55 ppm; **3**, 6.50; **6**, 6.60 ppm]. Despite the fact that the magnitude of downfield shift in Cp complexes is greater than those in Cp* analogues, η^5-bonding mode is ruled out on the grounds that $\Delta\delta$ lies in the range 0.23−0.75 ppm well below the value of 1.42 ppm observed in a η^5-pyrazolato Ru complex.[26]

Figure 3 shows the structure for **5**, **6** determined by X-ray crystallographic analysis, and the selected bond lengths and the angles are summarized in Table 3.[27] The analysis results indicate that the pyrazolato ligands coordinate to Ti with η^2-*N*,*N′* mode. The Ti−N bond lengths [2.007(3)−2.030(2) Å] in **5**, **6** are slightly shorter than those in the Cp* counterpart [2.031(2)−2.0474(13) Å], and the facts indicate a better electron donation from Cp* consistent with the NMR data. As observed in the Cp* complexes (**1**, **2**), the Ti−N bond lengths in **5** and **6** are longer than those in the Cp-pyrrolide complexes, $CpTiCl_2(C_4H_4N)$ [1.956(19) Å]

Table 2. Selected Bond Distances (Å) and Angles (deg) for Cp*Ti($C_3H_3N_2$)$_3$ (**4**)[27]

Bond Distances (Å)					
Ti(1)−N(1)	2.0735(13)	Ti(1)−Cp*	2.049	C(15)−C(16)	1.379(2)
Ti(1)−N(2)	2.0587(12)	N(1)−C(11)	1.344(2)	N(4)−C(16)	1.336(2)
Ti(1)−N(3)	2.0635(13)	C(11)−C(12)	1.377(2)	N(3)−N(4)	1.353(19)
Ti(1)−N(4)	2.0503(16)	C(12)−C(13)	1.387(2)	N(5)−C(17)	1.349(2)
Ti(1)−N(5)	2.1136(13)	N(2)−C(13)	1.3369(19)	C(17)−C(18)	1.377(2)
Ti(1)−C(1)	2.3714(14)	N(1)−N(2)	1.347(2)	C(18)−C(19)	1.390(2)
Ti(1)−C(2)	2.3933(14)	N(3)−C(14)	1.334(2)	N(6)−C(19)	1.335(2)
Ti(1)−C(3)	2.3870(14)	C(14)−C(15)	1.396(3)	N(5)−N(6)	1.374(17)

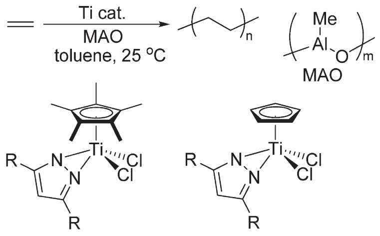
Bond Angles (deg)			
Cp*−Ti(1)−N(1)	120.12(4)	N(1)−Ti−N(2)	38.03(5)
Cp*−Ti(1)−N(2)	108.23(4)	N(1)−Ti−N(3)	130.33(5)
Cp*−Ti(1)−N(3)	109.34(4)	N(1)−Ti−N(4)	110.52(6)
Cp*−Ti(1)−N(4)	113.63(4)	N(1)−Ti−N(5)	81.71(5)
Cp*−Ti(1)−N(5)	110.32(4)	N(2)−Ti−N(3)	122.31(6)
N(2)−Ti−N(4)	86.52(5)	N(3)−Ti−N(5)	85.73(5)
N(2)−Ti−N(5)	119.15(4)	N(4)−Ti−N(5)	117.06(5)
N(3)−Ti−N(4)	38.39(5)		

and CpTiCl$_2$(2,4-Me$_2$C$_4$H$_2$N) [1.968(13) Å]. The pyrazolato ligand in **5** is planar and close to a regular pentagon as indicated by approximately identical bond distances within the heterocyclic ring [N(1)−C(6) 1.341(3), C(6)−C(7) 1.385(4), C(7)−C(8) 1.381(3), N(2)−C(8) 1.337(2), N(1)−N(2) 1.363(2)], and the bond angles are close to 108° (see Supporting Information); similar trends were seen in **6**. The coordination sphere around the Ti atom fold an approximate distorted tetrahedral in both complexes. As a result of η^2-*N*,*N*′-coordination of the pyrazolato ligands, the Cl(1)−Ti−Cl(2) bond angles in **5**, **6** become constrained [**5**, 95.48(2)°, and **6**, 96.63(5)°], and these showed unique contrast to those in the half-titanocenes containing pyrrolide ligands in η^1-*N*-coordination mode (>100°).[24]

The Ti−Cl bond lengths [2.2760(16)-2.3134(9) Å] are longer than those in the Cp-pyrrolide complexes [CpTiCl$_2$(C$_4$H$_4$N): 2.2587(7), 2.252(13) Å; CpTiCl$_2$(2,4-Me$_2$C$_4$H$_2$N): 2.244(4), 2.2561(4) Å].[24] The slight difference in the Ti−Cl bond length is most probably an outcome of better electron donation of η^2-*N*,*N*′-coordinated pyrazolato ligands as compared to η^1-*N*-coordinated pyrrolide ligands, although the Ti−N bond lengths in the pyrazolato complexes are longer than those in the pyrrolide complexes. The N−N distances [**5**, 1.363(2); **6**, 1.396(4) Å] and the N(1)−Ti(1)−N(2) angles [**5**, 39.07(5)°; **6**, 40.56(12)°] in the pyrazolato ligands are comparable with those in the Cp* derivatives (**1**, **2**), and these are in a generally observed range for η^2-*N*,*N*′-pyrazolato complexes of several early transition metals.[21−23]

3. Polymerization of Ethylene Cp′TiCl$_2$(L) [Cp′ = Cp*, Cp; L = C$_4$H$_4$N, 2,5-Me$_2$C$_4$H$_2$N, 2,4-Me$_2$C$_4$H$_2$N, 2,4-Me$_2$-3-EtC$_4$HN] − MAO Catalyst Systems. Ethylene polymerizations using the Cp*TiCl$_2$(C$_3$H$_3$N$_2$) (**1**) were conducted in toluene in the presence of methylaluminoxane (MAO) at 25 °C (Scheme 4), and the results are summarized in Table 4. MAO white solid prepared by removing AlMe$_3$ and toluene from the commercially available samples (PMAO-S, 6.8 wt % in toluene, Tosoh Finechem Co.) was chosen because it was effective in the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when the Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) was used as the catalyst precursor.[9]

Scheme 4



Ti cat.: Cp'TiCl$_2$(L)
Cp' = Cp*; L = C$_3$H$_3$N$_2$ (**1**), 3,5-Me$_2$C$_3$HN$_2$ (**2**), 3,5-^{i}Pr$_2$C$_3$HN$_2$ (**3**);
Cp' = Cp; L = C$_3$H$_3$N$_2$ (**5**), 3,5-Me$_2$C$_3$HN$_2$ (**6**), 3,5-^{i}Pr$_2$C$_3$H$_3$N$_2$ (**7**), 3,5-PhC$_3$HN$_2$ (**8**)

Note that **1** showed remarkable catalytic activities for the ethylene polymerization and the activities by Cp*TiCl$_2$(C$_3$H$_3$N$_2$) (**1**, activity = 6300−9000 kg-PE/mol-Ti·h) were higher than those by Cp*TiX$_2$(C$_4$H$_4$N) (X = Cl, Me, activity = 5400−5970 kg-PE/mol-Ti·h).[24] The resultant polymers under the optimized Al/Ti molar ratios possessed unimodal molecular weight distributions (although their M_n values were somewhat low compared with those obtained by the reported Cp*-aryolox analogues,[6,9,10,12] M_n = 2.46−3.52 × 10^4, M_w/M_n = 2.17−2.47, runs 2,4,5), and these observations are in unique contrast to the facts that resultant polymers prepared by the Cp*-pyrrolide analogue contained a small amount of high molecular weight fraction.[24] Since the by-production of the high molecular weight shoulders by using the Cp*-pyrrolide analogue−MAO catalysts was considered to be due to dissociation of the pyrrolide ligand (pyrrolide transfer from Ti to Al), the formation of unimodal polymers in the present case clearly suggest that the dissociation of the pyrazolato ligand did not take place under these conditions, probably because of an improved stability of the pyrazolato ligand in **1** with η^2-*N*,*N*′ coordination mode rather than that of the pyrrolide ligand (η^1-*N* coordination).

Ethylene polymerization using a series of the Cp* and Cp analogues containing different pyrazolato ligands (**2**, **3**, **5**−**8**) were also conducted under the same conditions, and the results are summarized in Table 4. It turned out that **2**, **3** and **5**−**8** also exhibited moderate catalytic

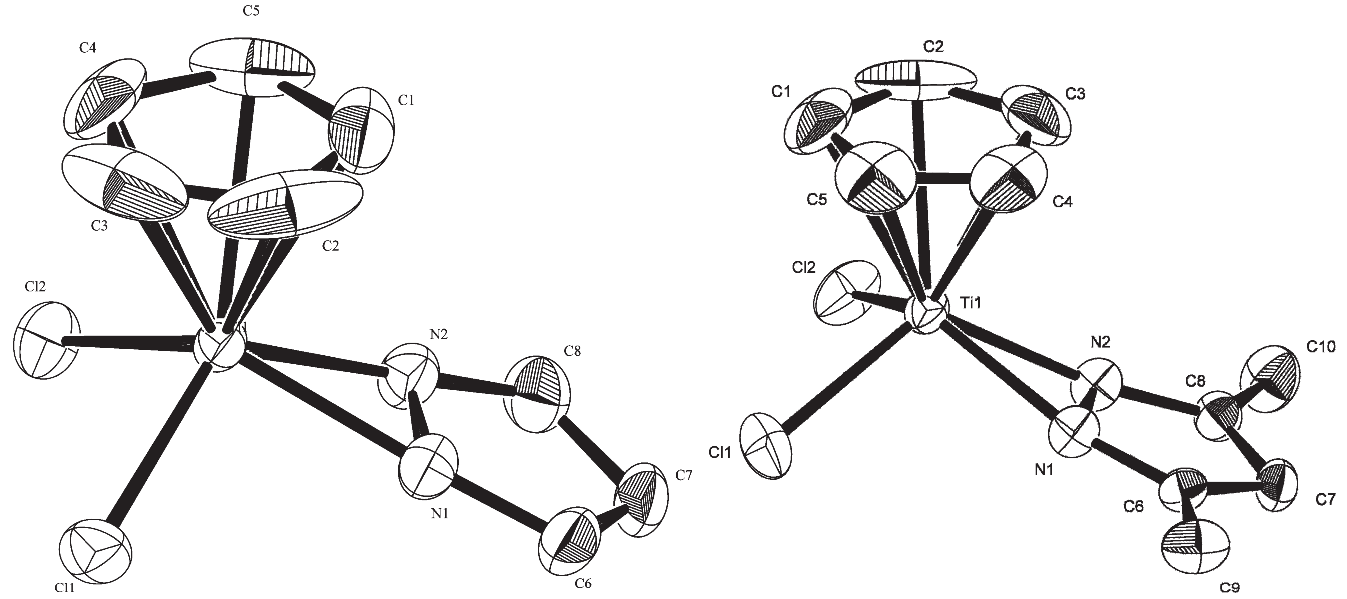


Figure 3. ORTEP drawings for $CpTiCl_2(C_3H_3N_2)$ (**5**, left) and $CpTiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**6**, right). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[27]

Table 3. Selected Bond Distances (Å) and Angles (deg) for $CpTiCl_2(C_3H_3N_2)$ (**5**) and $CpTiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**6**)[27]

	5	**6**
Bond Distances (Å)		
Ti(1)−Cl(1)	2.3018(7)	2.2760(16)
Ti(1)−Cl(2)	2.2904(7	2.3146(10)
Ti(1)−N(1)	2.023(2)	2.022(3)
Ti(1)−N(2)	2.0159(19)	2.007(3)
Ti(1)−C(1)	2.330(2)	2.332(5)
Ti(1)−C(2)	2.322(4)	2.331(7)
Ti(1)−C(3)	2.333(4)	2.321(7)
N(1)−C(6)	1.341(3)	1.336(4)
C(6)−C(7)	1.385(4)	1.407(5)
C(7)−C(8)	1.381(3))	1.373(4)
N(2)−C(8)	1.336(3)	1.335(5)
N(1)−N(2)	1.363(2)	1.396(4)
Ti(1)−Cp	2.023	2.013
Bond Angles (deg)		
Cl(1)−Ti(1)−Cl(2)	95.48(2)	96.63(5)
Cl(1)−Ti(1)−N(1)	92.25(6)	93.93(11)
Cl(2)−Ti(1)−N(1)	121.03(6)	125.65(9)
Cl(1)−Ti(1)−N(2)	123.40(6)	120.86(11)
Cl(2)−Ti(1)−N(2)	91.65(6)	90.35(8)
N(1)−Ti(1)−N(2)	39.07(5)	40.56(12)
Cp−Ti(1)−Cl(1)	113.53(6)	112.81(10)
Cp−Ti(1)−Cl(2)	113.87(6)	112.27(8)
Cp−Ti(1)−N(1)	115.82(7)	111.97(12)
Cp−Ti(1)−N(2)	114.20(8)	118.19(14)

Table 4. Ethylene Polymerization by $Cp'TiCl_2(L)$ [$Cp' = Cp^*$; L = $C_3H_3N_2$ (**1**), $3,5\text{-}Me_2C_3HN_2$ (**2**), $3,5\text{-}{}^iPr_2C_3HN_2$ (**3**): $Cp' = Cp$; L = $C_3H_3N_2$ (**5**), $3,5\text{-}Me_2C_3HN_2$ (**6**), $3,5\text{-}{}^iPr_2C_3HN_2$ (**7**), $3,5\text{-}Ph_2C_3HN_2$ (**8**)] - MAO Catalyst Systems[a]

run	catalyst Cp′; L	amount (μmol)	MAO (mmol)	polymer yield (mg)	activity[b]	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$
1	Cp*; $C_3H_3N_2$ (**1**)	0.2	3.0	241	7230		
2		0.2	3.0	247	7410	2.46	2.47
3		0.1	3.0	105	6300		
4		0.1	3.0	106	6360	2.81	2.40
5		0.1	2.0	150	9000	3.52	2.17
6		0.1	2.0	147	8820		
7		0.1	1.0	25	1500	62.0	2.40
						0.92	2.01
8		0.1	1.0	23	1380		
9	Cp*; $3,5\text{-}Me_2C_3HN_2$ (**2**)	0.1	2.0	122	7320	2.91	2.62
10		0.1	2.0	120	7200		
11	Cp*; $3,5\text{-}{}^iPr_2C_3HN_2$ (**3**)	0.1	2.0	145	8700	2.40	2.44
12		0.1	2.0	141	8460		
13	Cp; $C_3H_3N_2$ (**5**)	0.1	2.0	7	420		
14		0.1	2.0	9	540	130.6	2.31
15	Cp; $3,5\text{-}Me_2C_3HN_2$ (**6**)	0.1	2.0	10	600		
16		0.1	2.0	13	780	124.4	2.29
17	Cp; $3,5\text{-}{}^iPr_2C_3HN_2$ (**7**)	0.1	2.0	14	840	97.4	3.07
						0.36	2.04
18		0.1	2.0	14	840		
19	Cp; $3,5\text{-}Ph_2C_3HN_2$ (**8**)	0.1	2.0	20	1200	89.5	3.03
20		0.1	2.0	19	1140		

[a] Reaction Conditions: toluene total 30 mL, ethylene 6 atm, 10 min, 25 °C, 100 mL scale autoclave, d-MAO (prepared by removing $AlMe_3$ and toluene from commercially available MAO). [b] Activity = kg-PE/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards.

activities for ethylene polymerization in the presence of MAO, and the activities were affected by the substituent on the pyrazolato ligands employed. The activities using a series of the Cp* analogues increased in the order: L = $C_3H_3N_2$ (**1**, 9000 kg-PE/mol-Ti·h) > $3,5\text{-}{}^iPr_2\text{-}C_3HN_2$ (**3**, 8700) > $3,5\text{-}Me_2\text{-}C_3HN_2$ (**2**, 7320). Complex **1** exhibited the highest activity among the Cp* analogues, and introduction of two methyl groups in the pyrazolato ligand (in **2**) led to a slight decrease in activity, whereas the 3,5-diisopropyl analogue exhibited the similar catalytic activity. The facts should thus be an interesting contrast to the facts using the Cp*-pyrrolide analogues, where an introduction of the alkyl substituents into the pyrrolide ligand resulted in the significant decrease in the activity.[24] Moreover, the activity using a series of $CpTiCl_2(L)$ increased in the order: L = $3,5\text{-}Ph_2\text{-}C_3HN_2$

Table 5. Crystal Data and Structure Refinement Parameters for $Cp^*TiCl_2(C_3H_3N_2)$ (**1**), $Cp^*TiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**2**), $Cp^*Ti(C_3H_3N_2)_3$ (**4**), $CpTiCl_2(C_3H_3N_2)$ (**5**), and $CpTiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**6**)[27]

	1	**2**	**4**	**5**	**6**[a]
formula	$C_{13}H_{18}Cl_2N_2Ti$	$C_{15}H_{22}Cl_2N_2Ti$	$C_{19}H_{24}N_6Ti$	$C_8H_8Cl_2N_2Ti$	$C_{40.50}H_{48}Cl_9N_8Ti_4$
fw	321.10	349.16	384.34	250.97	1157.56
cryst color, habit	red, block	red, block	red, block	yellow, block	orange, block
cryst size (mm)	0.40 × 0.40 × 0.35	0.40 × 0.35 × 0.20	0.40 × 0.35 × 0.20	0.25 × 0.20 × 0.18	0.50 × 0.40 × 0.30
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)
a (Å)	6.8153(3)	7.6897(4)	18.0253(8)	7.2026(3)	9.0137(3)
b (Å)	16.1063(6)	15.4162(7)	13.2856(5)	12.0375(5)	10.2644(4)
c (Å)	13.2599(5)	15.6337(8)	16.7750(6)	23.2951(8)	15.0913(7)
V (Å^3)	1454.87(10)	834.34(7))	3807.4(2)	2019.72(13)	1313.36(9)
Z value	4	2	8	8	1
D_{calcd} (g/cm^3)	1.466 g/cm^3	1.390 g/cm^3	1.341 g/cm^3	1.651 g/cm^3	1.463 g/cm^3
F_{000}	664.00	364.00	1616.00	1008.00	588.00
no. of reflns meads.	11789	6930	15269	15074	11031
no. of observations	2424	2831	3115	1583	4373
no. of variables	181	203	259	126	303
R1	0.0244	0.0289	0.0287	0.0293	0.0631
wR2	0.0840	0.1108	0.1010	0.0971	0.1377
goodness of fit	1.002	1.001	1.016	1.004	1.001

[a] The crystal consisted of $[CpTiCl_2(3,5\text{-}Me_2C_3HN_2)]_4\cdot 1/2CH_2Cl_2$. The details are shown in the Supporting Information.

(**8**, 1200 kg-PE/mol-Ti·h) > $3,5\text{-}^iPr_2\text{-}C_3HN_2$ (**7**, 840) > $3,5\text{-}Me_2\text{-}C_3HN_2$ (**6**, 780) > $C_3H_3N_2$ (**5**, 540), suggesting that the activity by the Cp analogues increased upon increasing the steric bulk in the pyrazolato ligand. The latter trend by the Cp analogues seems similar to that in the Cp′-aryloxo analogues[9] as well as Cp′-pyrrolide analogues[24]and that in ordinary metallocenes,[31] in which an introduction of electron donating substituents would stabilize the catalytically active species leading to the higher activity.

Concluding Remarks

In summary, we have established a systematic route for the synthesis of various half-titanocenes containing pyrazolato ligands of the types $Cp'TiCl_2(L)$ [Cp′ = Cp* and L = $C_3H_3N_2$ (**1**), $3,5\text{-}Me_2C_3HN_2$ (**2**) and $3,5\text{-}^iPr_2C_3HN_2$ (**3**); Cp′ = Cp and L = $C_3H_3N_2$ (**5**), $3,5\text{-}Me_2C_3HN_2$ (**6**), $3,5\text{-}^iPr_2C_3HN_2$ (**7**), and $3,5\text{-}Ph_2C_3HN_2$ (**8**)]. The structural analysis results clearly indicate that these complexes are 14e Ti(IV) species, and the pyrazolato ligand coordinates to Ti with η^2-*N,N*′-fashion. The tris(pyrazolato) analogue, $Cp^*Ti(C_3H_3N_2)_3$, was also cleanly prepared by treating Cp^*TiCl_3 with $C_3H_3N_2Li$ in Et_2O, and the crystallographic analysis result indicates that one of the pyrazolato ligand coodinates to Ti with η^1-*N* fashion and the other two coordinate to Ti with η^2-*N,N*′ fashion.

These complexes (**1**−**3**, **5**−**8**) exhibited moderate/notable catalytic activities for ethylene polymerization in the presence of MAO, and the activities were affected by the substituent on the pyrazolato ligand. Complex **1** exhibited the highest activity, and the activity was higher than that by the Cp*-pyrrolide analogue under the same conditions. The resultant polymers possessed rather low molecular weights with uniform molecular weight distributions, suggesting that the polymerization proceeded with uniform catalytically active species. The facts thus showed unique contrast to those prepared by the Cp*-pyrrolide analogue, in which certain degree of pyrrolide transfer (from Ti to Al) was accompanied in the polymerization using the Cp*-pyrrolide analogue in the presence of MAO cocatalyst.[24]

We highly believe that the results presented here should be promising not only from the viewpoint of basic understanding of the chemistry of half-titanocenes containing pyrazolato ligands but also from the standpoint of designing efficient transition metal catalysts for precise olefin polymerization (e.g., improved stabilization of the catalytically active species to avoid the ligand transfer from Ti to Al, etc.). We are exploring a possibility for efficient preparation of new polymers by ethylene copolymerization with strictly encumbered comonomers. We are also exploring syntheses of a series of half-titanocenes containing both pyrazolato and the other anionic ancillary donor ligands for better understanding concerning coordination modes and reactivity in these complexes.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade tetrahydrofuran, diethyl ether, *n*-hexane, dichloromethane, and toluene (Kanto Chemical Co., Inc.) were transferred into bottles containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and were used without further purification. Reagent grade pyrazole, 3,5-dimethylpyrazole, 3,5-diisopropylpyrazole, 3,5-diphenylpyrazole, $CpTiCl_3$ and Cp^*TiCl_3 were purchased from Wako Pure Chemical Ind., Ltd., and were used as received. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received. Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.). Some analysis runs were employed twice to confirm the reproducibility in independent analysis/synthesis runs.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNMLA400 spectrometer (399.65 MHz, ^1H; 100.40 MHz, ^{13}C). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to residual solvent peaks.

Molecular weights and molecular weight distributions for the polyethylene samples were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022

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(31) Influence of cyclopentadienyl fragment in ethylene polymerization by substituted zirconocenes, Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1991**, *479*, 1.

detector (for high temperature, Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Synthesis of Li($C_3H_3N_2$). Li($C_3H_3N_2$) was prepared according to the following procedure.[25] Into a *n*-hexane (50 mL) solution containing pyrazole (2.04 g, 0.03 mol) precooled at −20 °C (in the freezer), *n*-hexane solution containing *n*-BuLi (18.9 mL of 1.58 mol/L solution, 0.03 mol) was added slowly in small portions. Immediate formation of voluminous white precipitates was observed. The reaction mixture was then warmed slowly to room temperature and was stirred for 4 h. The resultant precipitates were thus collected on a glass filter and were adequately washed with *n*-hexane twice and dried in vacuo. Yield 89%. ^{1}H NMR (THF-d_8): δ 6.19 (br, 1H, NCHC*H*), 7.65 (br, 2H, NC*H*). ^{13}C NMR (THF-d_8): δ 101.52, 137.66.

Lithium salts of 3,5-dimethylpyrazole, 3,5-diisopropylpyrazole, and 3,5-diphenylpyrazole were prepared similarly.[25]

Synthesis of Cp*TiCl$_2$($C_3H_3N_2$) (1). All the complexes could be synthesized by following either of the two methods, which have been described in detail for the synthesis of complex **1**.

Method 1. Into an Et$_2$O solution (10 mL) containing Cp*TiCl$_3$ (289 mg, 1.0 mmol) was added Li($C_3H_3N_2$) (81 mg, 1.1 mmol) at −20 °C. The reaction mixture was stirred for 16 h at 25 °C followed by addition of a small amount of CH_2Cl_2 (0.5 mL) to quench the remaining lithium salt. The reaction mixture was filtered through a Celite pad using a glass filter. The filtercake was washed with Et$_2$O, and the combined filtrate and the washings were taken to dryness under reduced pressure to give a solid red residue. The residue was dissolved in a minimum amount of CH_2Cl_2 and layered with hexane. The chilled solution (−20 °C) afforded red microcrystals. Yield 167 mg (52%). δ 2.09 (15H, C_5Me_5), 6.93 (t, 1H, *J* = 1.5 Hz, N NCHC*H*), 7.81 (d, 2H, *J* = 1.5 Hz, NC*H*CH). ^{13}C NMR (CDCl$_3$): δ 13.18, 119.29, 133.95, 134.20. Anal. Calcd for $C_{13}H_{18}Cl_2N_2Ti$: C, 48.63; H, 5.65; N, 8.73%. Found: C, 48.57; H, 5.83; N, 8.50%.

Method 2. A suspension of Cp*TiCl$_3$ (289 mg, 1.0 mmol) and Et$_2$O (10 mL) was cooled in a refrigerator to −20 °C. A mixture of pyrazole (75 mg, 1.1 mmol) and Et$_3$N (110 mg, 1.1 mmol) was added to the above cooled mixture in small portions. The reaction mixture was stirred for 16 h at room temperature, the reaction mixture was then filtered through a Celite pad using a glass filter. The solid residue was washed with Et$_2$O; the filtrate and the washings were combined and evaporated to dryness. Recrystallization of the solid residue with CH_2Cl_2 layered with *n*-hexane afforded red microcrystals of **1**. Yield 157 mg (49%). ^{1}H and ^{13}C NMR data was exactly the same with the sample prepared by method 1.

Cp*TiCl$_2$(3,5-Me$_2$C$_3$HN$_2$) (2). The synthetic procedure of **2** was the same as that for **1** except that lithium salt of 3,5-dimethylpyrazole (114 mg, 1.1 mmol) was used in place of Li($C_3H_3N_2$). Yield 209 mg (method 1: 60%, method 2: 53%). ^{1}H NMR (CDCl$_3$): δ 2.10 (15H, C_5Me_5), 2.33 (6H, Me), 6.43 (s, 1H, NCHC*H*). ^{13}C NMR (CDCl$_3$): δ 12.35, 13.21, 119.05, 133.33, 145.20. Anal. Calcd for $C_{15}H_{22}Cl_2N_2Ti$: C, 51.60; H, 6.35; N, 8.02%. Found: C, 51.27; H, 6.19; N, 8.10%.

Cp*TiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (3). The synthetic procedure of **3** was the same as that for **1** except that lithium 3,5-diisopropylpyrazolato (173 mg, 1.1 mmol) was used in place of Li($C_3H_3N_2$). Yield 332 mg (method 1: 82%, method 2: 79%). ^{1}H NMR (CDCl$_3$): δ 1.31 (d, 12H, *J* = 7.0 Hz, CH*Me*$_2$), 2.11 (s, 15H, C_5Me_5), 3.05 (sep, 2H, *J* = 7.0 Hz, C*H*Me$_2$), 6.50 (s, 1H, NCHC*H*). ^{13}C NMR (CDCl$_3$): δ 13.34, 22.71, 27.49, 113.59, 133.27, 156.05. Anal. Calcd for $C_{19}H_{30}Cl_2N_2Ti$: C, 56.31; H, 7.46; N, 6.91%. Found: C, 56.30; H, 7.24; N, 6.98%.

Cp*Ti($C_3H_3N_2$)$_3$ (4). The synthetic procedure of **8** was the same as that for **1** except that 3.3 equiv of lithium pyrazolato (244 mg, 3.3 mmol) was used, and the desired complex was purified by recrystallization from chilled ether solution. In case of method 2, approximately 10 equiv of pyrazole and Et$_3$N were employed, and reaction was carried out in toluene at 50 °C for 16 h. Yield 216 mg (method 1: 56%, method 2: 48%). ^{1}H NMR (CDCl$_3$): δ 1.75 (s, 15H, C_5Me_5), 6.52 (t, 1H, *J* = 1.5 Hz, NCHC*H*), 7.81 (d, 2H, *J* = 1.5 Hz, NC*H*CH). ^{13}C NMR (CDCl$_3$): δ 11.57, 13.21, 111.31, 129.33, 134.71. Anal. Calcd for $C_{19}H_{24}N_6Ti$: C, 59.38; H, 6.29; N, 21.87%. Found: C, 59.04; H, 6.21; N, 21.51%.

CpTiCl$_2$($C_3H_3N_2$) (5). The synthetic procedure of **4** was the same as that for **1** except that CpTiCl$_3$ (219 mg, 1.1 mmol) was used in place of Cp*TiCl$_3$, and the reaction was carried out in hexane in case of method 1. Yield 150 mg (method 1: 60%, method 2: 62%). ^{1}H NMR (CDCl$_3$): ^{1}H NMR (CDCl$_3$): δ 6.65 (s, 5H, C_5H_5), 7.00 (t, 1H, *J* = 1.5 Hz, NCHC*H*), 7.81 (d, 2H, *J* = 1.5 Hz, NC*H*). ^{13}C NMR (CDCl$_3$): δ 120.21, 121.16, 136.29. Anal. Calcd for $C_8H_8Cl_2N_2Ti$: C, 38.29; H, 3.21; N, 11.16%. Found: 38.63; H, 3.12; N, 11.07%.

CpTiCl$_2$(3,5-Me$_2$C$_3$HN$_2$) (6). The synthetic procedure of **5** was the same as that for **2** except that CpTiCl$_3$ (219 mg, 1.1 mmol) was used in place of Cp*TiCl$_3$, and the product was purified by recrystallization from chilled ether solution. Yield 147 mg (method 1: 53%, method 2: 48%). ^{1}H NMR (CDCl$_3$): δ 2.33 (s, 6H, Me), 6.49 (s, 1H, NCHC*H*), 6.62 (s, 5H, C_5H_5). ^{13}C NMR (CDCl$_3$): δ 12.34, 119.75, 120.37, 147.86. Anal. Calcd for $C_{10}H_{12}Cl_2N_2Ti$: C, 43.05 or 38.74 (+TiC); H, 4.34; N, 10.04%. Found: 40.92; H, 4.08; N, 9.68%.

CpTiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (7). The synthetic procedure of **6** was the same as that for **3** except that CpTiCl$_3$ (219 mg, 1.1 mmol) was used in place of Cp*TiCl$_3$. Yield 208 mg (method 1: 63%, method 2: 58%). ^{1}H NMR (CDCl$_3$): δ 1.31 (d, 12H, *J* = 6.96 Hz, Me), 3.01 (sep, 2H, *J* = 6.96 Hz, C*H*Me$_2$), 6.55 (s, 1H, NCHC*H*) 6.60 (s, 5H, C_5H_5). ^{13}C NMR (CDCl$_3$): δ 22.50, 27.37, 115.27, 120.34, 158.06. Anal. Calcd for $C_{14}H_{22}Cl_2N_2Ti$: C, 50.18; H, 6.02; N, 8.36%. Found: 50.44; H, 6.22; N, 8.49%.

CpTiCl$_2$(3,5-Ph$_2$C$_3$HN$_2$) (8). The synthetic procedure of **6** was the same as that for **1** except that CpTiCl$_3$ (219 mg, 1.1 mmol) was used in place of Cp*TiCl$_3$ and lithum 3,5-diphenylpyrazolato was used instead of Li($C_3H_3N_2$). Yield 234 mg (57%). ^{1}H NMR (CDCl$_3$): δ 6.65 (s, 5H, C_5H_5), 7.03 (s, 1H, NCHC*H*), 7.37−7.52 (m, 6H, Ar) 7.92−7.94 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$): δ 112.24, 121.04, 123.39, 125.93, 129.13, 130.14, 152.12. Anal. Calcd for $C_{20}H_{16}Cl_2N_2Ti$: C, 59.59; H, 4.00; N, 6.95%. Found: 59.87; H, 4.13; N, 6.81%.

Crystallographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The selected crystal collection parameters are listed below (Table 5), and the detailed results were described in the reports in the Supporting Information. All structures were solved by direct method and expanded using Fourier techniques,[32] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complexes **1**, **2**, **4**−**6** were performed using the Crystal Structure[33,34] crystallographic software package.

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Ethylene Polymerization Procedures. Ethylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. Solvent (29.0 mL) and MAO white solid (174 mg, 3.0 mmol), prepared by removing toluene and $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.), were charged into the autoclave in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of **1** via a syringe, the reaction apparatus was pressurized to 5 atm (total 6 atm), and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried in vacuo.

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Supporting Information Available: ^{1}H-, ^{13}C NMR spectra for $Cp^*TiCl_2(C_3H_3N_2)$ (**1**), $Cp^*TiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**2**), $Cp^*Ti(C_3H_3N_2)_3$ (**4**), and $CpTiCl_2(3,5\text{-}Me_2C_3HN_2)$ (**6**). VT ^{1}H NMR spectra for **4**. Crystal structure determinations, reports for **1**, **2**, **4**−**6**, and the crystallographic data are also given as CIF files, ORTEP drawing for $[CpTiCl_2(3,5\text{-}Me_2C_3HN_2)]_4 \cdot 1/2CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.