ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 23 (2004) 1587–1594

POLYHEDRON

www.elsevier.com/locate/poly

Pyridineenolato and pyridineenamido complexes of zirconium, titanium and aluminum

Ui Gab Joung [a], Tae Ho Kim [a], Dae June Joe [a], Bun Yeoul Lee [a,*], Dong Mok Shin [b], Young Keun Chung [b]

[a] *Department of Molecular Science and Technology, Ajou University, San 5, Wonchondong, Suwon 442-749, Republic of Korea*
[b] *School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, Republic of Korea*

Received 11 February 2004; accepted 8 March 2004
Available online 15 April 2004

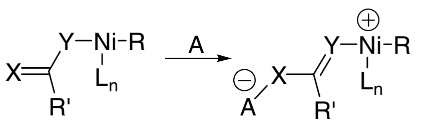
Abstract

Deprotonation of 2-acetylpyridine with KH in THF afford a potassium enolate compound (**2**) which reacts with $Zr(NEt_2)_2Cl_2(THF)_2$ and $Ti(NMe_2)_2Cl_2$ to yield $[CH_2{=}C(C_5H_4N)O\text{-}\kappa^2N,O]_2M(NR_2)_2$ (M = Zr, R = Et, **3**; M = Ti, R = Me, **4**) in 84% and 76% yield, respectively. Deprotonation of imines derived from 2-acetylpyridine, $(2,6\text{-}Me_2C_6H_3)N{=}C(C_5H_4N)(CH_3)$ (**5**) and $(2,6\text{-}i\text{Pr}_2C_6H_3)N{=}C(C_5H_4N)(CH_3)$ (**6**), affords potassium enamides, $K[(2,6\text{-}Me_2C_6H_3)N\text{–}C(C_5H_4N)({=}CH_2)]$ (**7**) and $K[(2,6\text{-}i\text{Pr}_2C_6H_3)N\text{-}(C_5H_4N)({=}CH_2)]$ (**8**). Reactions of the potassium salt **7** with $Zr(NEt_2)_2Cl_2(THF)_2$ and $Ti(NMe_2)_2Cl_2$ afford pyridineenamido complexes, $[(2,6\text{-}Me_2C_6H_3)NC(C_5H_4N)({=}CH_2)\text{-}\kappa^2N,N]_2M(NR_2)_2$ (M = Zr, R = Et, **9**; M = Ti, R = Me, **10**). Reaction of **8** with $Zr(NEt_2)_2Cl_2(THF)_2$ affords $[(2,6\text{-}i\text{Pr}_2C_6H_3)NC(C_5H_4N)({=}CH_2)]_2Zr(NEt_2)_2$ (**11**) but the reaction of **8** with $Ti(NMe_2)_2Cl_2$ yields $[(2,6\text{-}i\text{Pr}C_6H_3)NC(C_5H_4N)({=}CH_2)]TiCl(NMe_2)_2$ (**12**). Addition of excess $AlMe_3$ to **3** or **4** results in transmetallation of Zr or Ti to Al to afford an aluminum enolate complex, $[CH_2{=}C(C_5H_4N)(OAlMe_3)\text{-}\kappa^2N,O]AlMe_2$ (**13**). Addition of $AlMe_3$ to **12** results in the formation of a transmetallated complex, $[(2,6\text{-}i\text{Pr}_2C_6H_3)NC(C_5H_4N)({=}CH_2)]AlMe_2$ (**14**). The solid structures of **4, 11, 13** and **14** were determined by X-ray crystallography.

Keywords: Enolato; Enamido; Zirconium; Titanium; Aluminum

1. Introduction

A great deal of effort has been devoted in developing single site polymerization catalysts in both academic and industrial fields [1]. Metal complexes beyond metallocenes using various ligand systems including chelating diamido [2] and phenoxy-imine [3–5] have been developed and expansion from group 4 metal complexes to complexes based on the late transition metals [6] has been achieved. Bazan and Lee have described some metal complexes based on carboxylato [7], carboxamido [8] and enamido ligands [9]. The complexes are characteristic since the ligands have an electron-rich atom to which a Lewis acidic cocatalyst can bind to afford zwitterionic active complexes (Eq. (1)). A novel activation reaction was successfully applied to nickel complexes and recently it was expanded to the early transition metal complexes with an enamido ligand [10]. Herein, we report preparation of pyridineenolato and pyridineenamido complexes of titanium, zirconium and aluminum. The complexes have an electron-rich methylene carbon to which a Lewis acidic cocatalyst can bind.



(1)

A = Lewis acid; X = O, CH2; Y = O, R''N

---

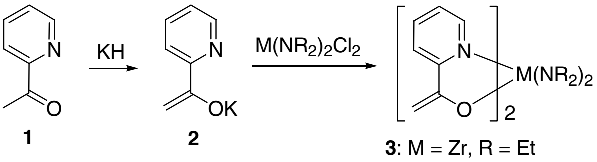
[*] Corresponding author. Tel.: +82-31-219-1844; fax: +82-31-219-1592.
E-mail address: bunyeoul@ajou.ac.kr (B.Y. Lee).

0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.03.009

2. Results and discussion

2.1. Synthesis and characterization

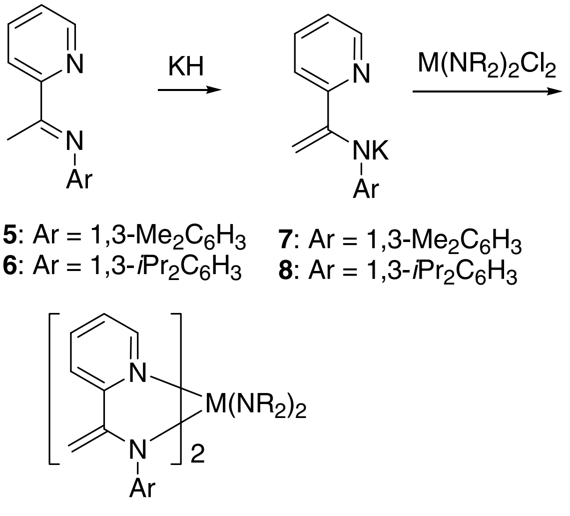
Deprotonation of 2-acetylpyridine is successfully conducted by KH in THF (Eq. (2)). Addition of $Zr(NEt_2)_2Cl_2(THF)_2$ and $Ti(NMe_2)_2Cl_2$ to the potassium enolate salt **2** results in clean formation of the desired enolato complexes, $[CH_2{=}C(C_5H_4N)O\text{-}\kappa^2 N,O]_2M(NR_2)_2$ (M = Zr, R = Et, **3**; M = Ti, R = Me, **4**) in 84% and 76% yield, respectively (Eq. (2)). The characteristic methylene proton signals are observed at 4.99 and 4.82 ppm for **3** and at 4.99 and 4.78 ppm for **4** as singlets in the ^1H NMR spectra (C_6D_6). The $=CH_2$ carbon signals are observed at 87.63 and 85.48 ppm for **3** and **4,** respectively, in the ^{13}C NMR spectra (C_6D_6). Single crystals of **4** suitable for X-ray crystallography were obtained by recrystallization in toluene and the solid structure was confirmed.



3: M = Zr, R = Et
4: M = Ti, R = Me

(2)

Syntheses of the imine compounds **5** [11] and **6** [12] have been reported. The deprotonation is carried out cleanly by KH in THF (Eq. (3)). The potassium salts are readily soluble in a cosolvent of benzene and THF (v/v, ~5:1) and are characterized by the ^1H and ^{13}C NMR spectra. Reaction of the potassium salts with $Zr(NEt_2)_2Cl_2(THF)_2$ and $Ti(NMe_2)_2Cl_2$ yields the desired pyridineenamido complexes **9**–**11** (Eq. (3)). The complexes were isolated by recrystallization in toluene.

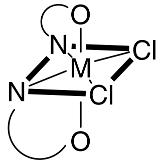


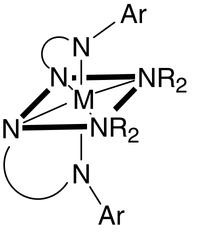
5: Ar = 1,3-$Me_2C_6H_3$ **7**: Ar = 1,3-$Me_2C_6H_3$
6: Ar = 1,3-*i*$Pr_2C_6H_3$ **8**: Ar = 1,3-*i*$Pr_2C_6H_3$

(3)

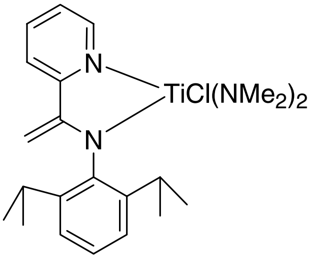
9: Ar = 1,3-$Me_2C_6H_3$, M = Zr, R = Et
10: Ar = 1,3-$Me_2C_6H_3$, M = Ti, R = Me
11: Ar = 1,3-*i*$Pr_2C_6H_3$, M = Zr, R = Et

The enamido ligand is ambiphilic. Either nitrogen or methylene carbon can coordinate to the metal center [9]. Observation of two singlet signals at 4.8–3.7 ppm in the ^1H NMR spectra (C_6D_6) and observation of a signal at 79–89 ppm in the ^{13}C NMR spectra support that the nitrogen coordinates as depicted in Eq. (3). If two pyridineenamido ligands and two dialkylamido ligands coordinate to the metal center to form an octahedral complex, eight stereochemical structures are possible as the case in the phenoxy-imine complexes [4]. In case of the phenoxy-imine complexes, the most stable isomer was calculated to have the structure shown below and actually only the most stable complex was obtained. X-ray crystallographic studies of a single crystal of **11** obtained by recrystallization in toluene reveal that the complex has similar stereochemical structure as observed for the phenoxy-imine complexes, with a *cis*-relationship between the two dialkylamide ligands and a *trans*-relationship between the two amido nitrogen atoms. Since similar signal patterns are observed for **9** and **10** in the ^1H and ^{13}C NMR spectra, we presume they have a similar stereochemical structure as observed for **11**.





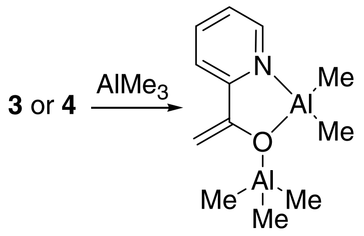
In the case of the reaction of potassium salt **8** with $Ti(NMe_2)_2Cl_2$, the desired complex is not obtained. The major product isolated by recrystallization in toluene can be assigned to the structure **12** by the analysis of the ^1H NMR spectrum. The relative intensity of the dimethylamido methyl signal is twice that observed for **10** and only one broad septet isopropyl CH signal and two doublet isopropyl CH_3 signals are observed. In the ^1H NMR spectrum of **11,** two septet isopropyl CH signals and four doublet isopropyl CH_3 signals are observed.



12

Transformation of the bis(dialkylamido) complex to the dichloro or dialkyl complex is desired because the latter is effectively activated with a common cocatalyst such as MAO or $B(C_6F_5)_3$. When chlorinating reagent,

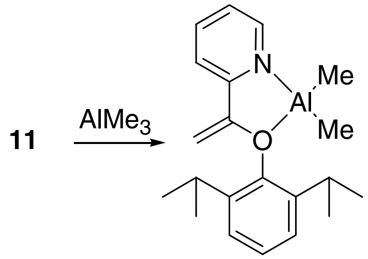
Me_3SiCl or Me_2SiCl_2, is reacted with **3–4** and **9–11,** a complex mixture of products is observed in the ^1H NMR spectra. When alkylating reagent, $AlMe_3$ (10 equivalents) is reacted with the enolate complex **3**, aiming to obtain the dimethyl zirconium complex, the ^1H NMR spectrum indicates that a complex is formed cleanly. The complete set of signals for the pyridineenolate ligand is observed in the ^1H NMR spectra but two methyl signals are observed at −0.04 and −0.27 ppm with integration values of 9 and 6. The ^1H and ^{13}C NMR spectra of the reaction product between **4** and $AlMe_3$ are exactly the same as those observed for the reaction product of **3**. Single crystals suitable for X-ray crystallography were obtained by recrystallization in pentane at −30 °C and the molecular structure was determined. The product is an $AlMe_3$-coordinated enolatodimethylaluminum complex (Eq. (4)).



13

(4)

Several sets of signals are observed in the ^1H NMR spectrum when sterically hindered complex **11** is reacted with $AlMe_3$. The main product is deposited from pentane solution at −30 °C as single crystals, which are suitable for X-ray crystallography. The X-ray crystallographic studies of the product reveal that the main product is a transmetallated aluminum complex as shown in Eq. (5).



14

(5)

2.2. X-ray crystallographic studies

The solid structure of **4** and selected bond distances and angles are shown in Fig. 1. It shows a distorted octahedral structure with a *trans*-relationship between the two oxygen atoms and a *cis*-relationship between the two dimethylamido ligands. All atoms in the pyridineenolate ligand and the titanium atom are situated in a plane and hence the dihedral angle of C(8)–C(13)–O(2)–Ti(1), C(11)–C(12)–N(2)–Ti(1) and C(9)–C(8)–C(13)–O(2) are measured to be 1.9°, −179.4° and −179.7°, respectively. The C(6)–C(7) distance (1.335(4) Å) and the C(13)–C(14) distance (1.324(4) Å) are indicative of a double bond between these two atoms. The O(1)–C(6) distance (1.327(4) Å) and the O(2)–C(13) distance (1.336(4) Å) are indicative of a shortened single bond by resonance. The dimethylamido nitrogen atoms are almost trigonal planar (sum of bonding angles, 359.8° and 357.1°) indicating π-electron donation to the titanium metal.

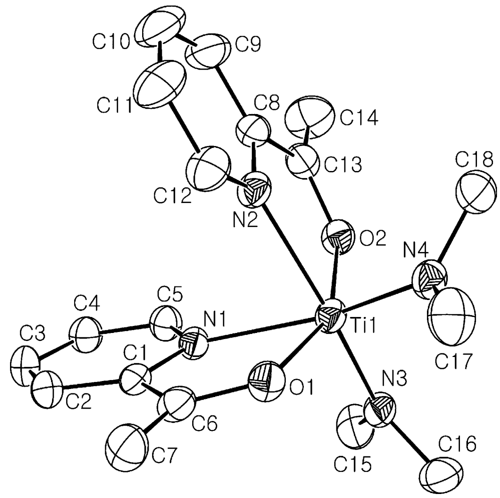


Fig. 1. Thermal ellipsoid plot (30% probability level) of the structure of **4**. Selected bond distances (Å) and angles (°): Ti(1)–O(1), 1.949(2); Ti(1)–O(2), 1.923(2); Ti(1)–N(1), 2.282(2); Ti(1)–N(2), 2.269(2); Ti(1)–N(3), 1.929(2); Ti(1)–N(4), 1.914(3); O(1)–C(6), 1.327(4); O(2)–C(13), 1.336(4); C(6)–C(7), 1.335(4); C(13)–C(14), 1.324(4); O(2)–Ti(1)–O(1), 154.51(9); N(4)–Ti(1)–N(1), 159.75(10); N(3)–Ti(1)–N(2), 164.92(10); C(6)–O(1)–Ti(1), 126.10(18); C(13)–O(2)–Ti(1), 126.12(19).

The solid structure of **11** and selected bond distances and angles are shown in Fig. 2. It also shows a distorted octahedral structure. The two amido nitrogen atoms are in a *trans*-relationship and the two dimethylamido ligands are situated in a *cis*-relationship. The Zr–N distances are in the order of $Zr–NEt_2$ (2.078(3) and 2.058(3) Å) <Zr–N(amido) (2.278(3) and 2.279(2) Å) <Zr–N(pyridine) (2.420(3) and 2.429(3) Å). A ring, (Zr(1)–N(3)–C(20)–C(25)–N(4)), formed by chelation is coplanar (dihedral angles of N(3)–C(20)–C(25)–N(4) and C(20)–C(25)–N(4)–Zr(1) are 1.6° and −0.3°, respectively) while the other ring (Zr(1)–N(1)–C(1)–C(6)–N(2)) is slightly out of coplanarity (dihedral angles of N(1)–C(1)–C(6)–N(2) and C(1)–C(6)–N(2)–Zr(1) are 11.3° and −19.1°, respectively). The aryl rings are almost perpendicular to the plane formed by chelation (dihedral angles of C(6)–N(2)–C(8)–C(9) and C(25)–N(4)–C(27)–C(28) are −76.4° and 78.5°, respectively). The C(6)–C(7) distance (1.366(5) Å) and the C(25)–C(26) distance (1.347(4) Å) are indicative of a double bond although they are slightly longer than the corresponding distances observed for the enolate complex **4**. All the diethylamido nitrogens and amido nitrogens show trigonal planar

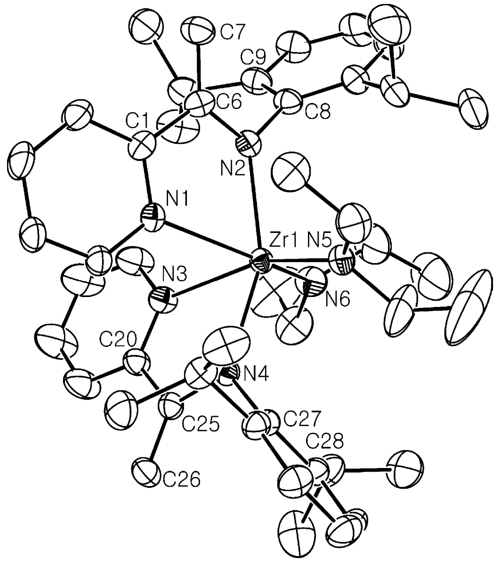


Fig. 2. Thermal ellipsoid plot (30% probability level) of the structure of **11**. Selected bond distances (Å) and angles (°): Zr(1)–N(1), 2.420(3); Zr(1)–N(2), 2.278(3); Zr(1)–N(3), 2.429(3); Zr(1)–N(4), 2.279(2); Zr(1)–N(5), 2.078(3); Zr(1)–N(6), 2.058(3); N(2)–C(6), 1.390(4); N(4)–C(25), 1.391(4); C(6)–C(7), 1.366(5); C(25)–C(26), 1.347(4); N(2)–Zr(1)–N(4), 155.95(9); N(6)–Zr(1)–N(1), 147.50(12); N(5)–Zr(1)–N(3), 158.64(10); C(25)–N(4)–Zr(1), 123.20(19); C(6)–N(2)–Zr(1), 120.5(2).

structure and hence the sum of bonding angles around N(2), N(4), N(5) and N(6) are calculated to be 359.9°, 359.6°, 359.7° and 359.9°, respectively.

The solid structure of **13** and selected bond distances and angles are shown in Fig. 3. Two aluminum atoms show a distorted tetrahedral structure. All the atoms on the pyridineenamide ligand and the two aluminum atoms are almost situated in a plane (dihedral angles of C(4)–C(5)–N(1)–Al(1) and C(5)–N(1)–Al(1)–Al(2) are −178.2° and 177.7°, respectively). The oxygen atom shows almost a trigonal planar structure (sum of bonding angle, 358.0°). The Al(1)–O(1) distance (1.847(6) Å) is shorter than the Al(2)–O(1) distance (1.934(6) Å) and the Al(1)–C distances (1.941(9) and 1.929(9) Å) are shorter as well than the Al(2)–C distances (1.951(10), 1.962(11) and 1.972(11) Å).

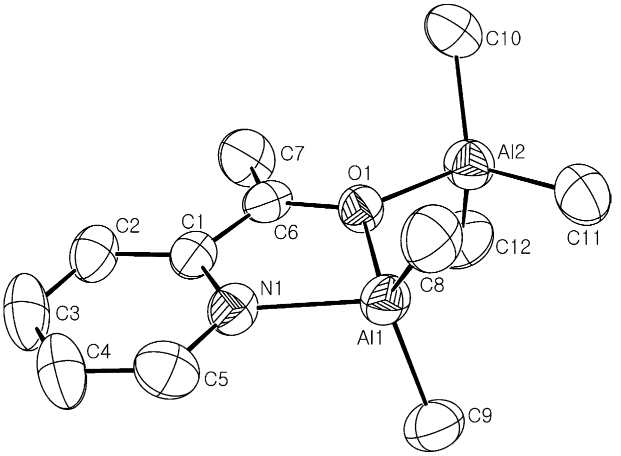


Fig. 3. Thermal ellipsoid plot (30% probability level) of the structure of **13**. Selected bond distances (Å) and angles (°): Al(1)–O(1), 1.847(6); Al(1)–N(1), 1.980(8); Al(1)–C(8), 1.941(9); Al(1)–C(9), 1.929(9); Al(2)–O(1), 1.934(6); Al(2)–C(10), 1.951(10); Al(2)–C(11), 1.962(11); Al(2)–C(12), 1.972(11); O(1)–C(6), 1.390(10); C(6)–C(7), 1.306(11); C(6)–O(1)–Al(1), 117.0(6); C(6)–O(1)–Al(2), 124.1(6); Al(1)–O(1)–Al(2), 116.9(3).

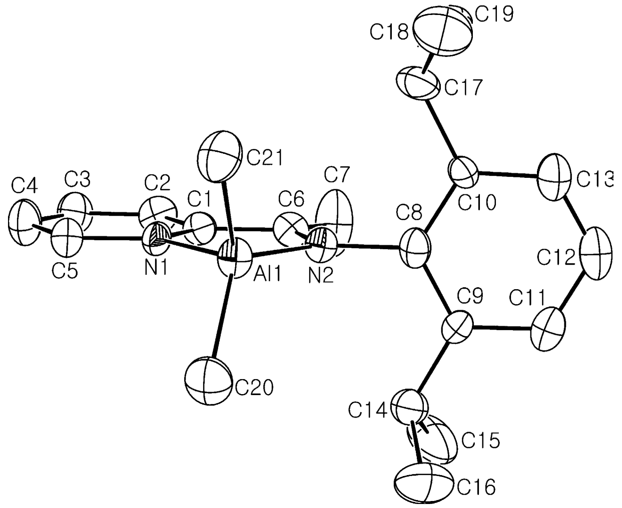


Fig. 4. Thermal ellipsoid plot (30% probability level) of the structure of **14**.

The solid structure of **14** is shown in Fig. 4. The final *R* indices for the refinement are too high ($R_1 = 0.1573$, $wR_2 = 0.3676$) to do quantitative analysis for the bond distances and angles, but it can be seen that Al(1), C(6), N(2) and all the atoms in the pyridine ring are coplanar and the 2,6-diisopropyl benzene ring is perpendicular to the plane.

3. Experimental

3.1. General considerations

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, THF and C_6D_6 were distilled from benzophenone ketyl. $Zr(NEt_2)_2Cl_2(THF)_2$ [13] and $Ti(NMe_2)_2Cl_2$ [14] were prepared according to the literature method. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out on a Perkin–Elmer 2400 CHN microanalyzer.

*3.2. Synthesis of $CH_2{=}C(C_5H_4N)OK$ (**2**)*

2-Acetylpyridine (1.00 g, 8.25 mmol) and KH (0.331 g, 8.25 mmol) were weighed in a flask and cold THF (10 ml, −30 °C) was added. The solution was stirred for 4 h at room temperature. The precipitated solid was filtered and washed with THF to give a white solid (1.13 g, 86%). The solid was not soluble in pyridine, benzene or THF.

3.3. Synthesis of $[CH_2{=}C(C_5H_4N)O\text{-}\kappa^2N,O]_2Zr(NEt_2)_2$ *(**3**)*

$ZrCl_2(NEt_2)_2(THF)_2$ (1.41 g, 3.14 mmol) was dissolved in THF (20 ml) and solid **2** (1.00 g, 6.28 mmol) was added in one portion at room temperature. The solution was stirred overnight. Solvent was removed by vacuum. The product was extracted with toluene (15 ml × 2) and the toluene was removed by vacuum to give a yellow solid (1.25 g, 84%) which was analytically pure. ^1H NMR (C_6D_6): δ 8.51 (dt, $J = 5.6$, 1.2 Hz, 1H, py-H^6), 7.01 (d, $J = 8.0$ Hz, 1H, py-H^3), 6.60 (ddd, $J = 8.0$, 7.2, 1.2 Hz, 1H, py-H^4), 6.29 (ddd, $J = 7.2$, 5.6, 1.2 Hz, 1H, py-H^5), 4.99 (s, 1H, $=CH_2$), 4.82 (s, 1H, $=CH_2$), 3.73 (q, $J = 6.8$ Hz, 4H, CH_2CH_3), 1.21 (t, $J = 6.8$ Hz, 6H, CH_2CH_3) ppm. $^{13}C\{^1H\}$NMR (C_6D_6) δ 162.31, 157.90, 146.68, 137.33, 122.37, 119.86, 87.63 ($=CH_2$), 44.54 (CH_2CH_3), 16.11 (CH_2CH_3) ppm. *Anal.* Calc. ($C_{22}H_{32}N_4O_2Zr$): C, 55.54; H, 6.78; N, 11.78. Found: C, 55.72; H, 6.53; N, 11.38%.

3.4. Synthesis of $[CH_2{=}C(C_5H_4N)O\text{-}\kappa^2N,O]_2Ti(NMe_2)_2$ *(**4**)*

The complex was synthesized using the same procedure and conditions as for **3,** but with $TiCl_2(NMe_2)_2$ (0.500 g, 2.42 mmol) and the potassium salt **2** (0.770 g, 4.84 mmol). The analytically pure red solid was isolated by extraction with toluene (0.690 g, 76%). Single crystals suitable for X-ray crystallography were obtained by recrystallization in toluene at −30 °C. ^1H NMR (C_6D_6): δ 8.57 (dt, $J = 5.6$, 1.2 Hz, 1H, py-H^6), 7.01 (dd, $J = 6.8$, 1.2 Hz, 1H, py-H^3), 6.64 (ddd, $J = 8.8$, 6.8, 1.2 Hz, 1H, py-H^4), 6.34 (ddd, $J = 7.2$, 5.6, 1.2 Hz, 1H, py-H^5), 4.99 (s, 1H, $=CH_2$), 4.78 (s, 1H, $=CH_2$), 3.57 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$NMR (C_6D_6) δ 163.88, 157.12, 146.39, 136.99, 122.34, 119.47, 85.48 ($=CH_2$), 48.20 (CH_3) ppm. *Anal.* Calc. ($C_{18}H_{24}N_4O_2Ti$): C, 57.46; H, 6.43; N, 14.89. Found: C, 57.03; H, 6.73; N, 14.59%.

3.5. Synthesis of $K[(2,6\text{-}Me_2C_6H_3)N\text{–}C(C_5H_4N)(=CH_2)]$ *(**7**)*

A solution of **5** (1.20 g, 5.35 mmol) in THF (20 ml) was added to a slurry of KH (0.429 g, 1.07 mmol) in THF (5.0 ml) and the resulting mixture was stirred for one day at room temperature. The dark brown solution was filtered and solvent was removed under vacuum. The residue was triturated in pentane to give a greenish yellow solid. The yield was 1.15 g (82%). ^1H NMR (C_6D_6:THF-d_8, 5:1): δ 7.95 (d, $J = 8.0$ Hz, 1H, py-H^6), 7.44 (d, $J = 5.2$ Hz, 1H, py-H^3), 7.24 (d, $J = 7.2$ Hz, 2H, ph-$H^{3\text{ and }5}$), 7.13 (td, $J = 8.0$, 1.6 Hz, 1H, py-H^5), 6.95 (t, $J = 7.2$ Hz, 1H, ph-H^4), 6.62 (dd, $J = 7.2$, 5.2 Hz, 1H, py-H^4), 4.11 (s, 1H, $=CH_2$), 3.29 (s, 1H, $=CH_2$), 2.30 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$NMR (C_6D_6:THF-d_8, 5:1) δ 169.57, 158.59, 154.57, 148.16, 135.32, 131.75, 128.65, 121.93, 120.77, 118.79, 69.40 ($=CH_2$), 19.21 (CH_3) ppm.

3.6. Synthesis of $K[(2,6\text{-}iPr_2C_6H_3)N(C_5H_4N)(=CH_2)]$ *(**8**)*

This salt was synthesized using the same procedure and conditions for **7,** but with **6** (1.61 g, 5.74 mmol) and KH (0.461 g, 11.5 mmol). The mixture was stirred for two days. The yield was 1.61 g (88%). ^1H NMR (C_6D_6:THF-d_8, 5:1): δ 7.99 (d, $J = 8.0$ Hz, 1H, py-H^6), 7.70 (d, $J = 5.2$ Hz, 1H, py-H^3), 7.33 (d, $J = 7.2$ Hz, 2H, ph-$H^{3\text{ and }5}$), 7.20 (t, $J = 7.2$ Hz, 1H, ph-H^4), 7.12 (td, $J = 8.0$, 1.6 Hz, 1H, py-H^5), 6.64 (td, $J = 8.0$, 1.2 Hz, 1H, py-H^4), 4.15 (s, 1H, $=CH_2$), 3.52 (septet, $J = 7.2$ Hz, 2H, $CH(CH_3)_2$), 3.26 (s, 1H, $=CH_2$), 1.51 (d, $J = 7.2$ Hz, 6H, $CH(CH_3)_2$), 1.16 (d, $J = 7.2$ Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$NMR (C_6D_6:THF-d_8, 5:1) δ 164.24, 157.92, 155.83, 147.85, 142.87, 135.49, 123.54, 122.45, 120.84, 119.90, 71.60 ($=CH_2$), 27.81 ($CH(CH_3)_2$), 26.75 ($CH(CH_3)_2$), 26.02 ($CH(CH_3)_2$) ppm.

3.7. Synthesis of $[(2,6\text{-}Me_2C_6H_3)NC(C_5H_4N)(=CH_2)\text{-}\kappa^2N,N]_2Zr(NEt_2)_2$ *(**9**)*

$ZrCl_2(NEt_2)_2(THF)_2$ (0.523 g, 1.16 mmol) and potassium salt **7** (0.609 g, 2.32 mmol) were weighed in a flask and THF (30 ml) was added. The resulting solution was stirred for two days. Solvent was removed under vacuum to give a black residue which was dissolved in toluene (40 ml). The solution was filtered and solvent was reduced to ~10 ml, at which point yellow solids precipitated. The deposited solid was collected by filtration (0.486 g, 61%). ^1H NMR (C_6D_6): δ 8.80 (br d, $J = 4.8$ Hz, 1H, py-H^6), 7.41 (d, $J = 8.4$ Hz, 1H, py-H^3), 7.20 (d, $J = 7.2$ Hz, 1H, ph-$H^{3\text{ or }5}$), 7.14 (d, $J = 7.2$ Hz, 1H, ph-$H^{3\text{ or }5}$), 7.03 (t, $J = 7.2$ Hz, 1H, ph-H^4), 6.71 (br t, $J = 7.2$ Hz, 1H, py-H^5), 6.23 (br t, $J = 6.0$ Hz, 1H, py-H^4), 4.60 (s, 1H, $=CH_2$), 3.89 (s, 1H, $=CH_2$), 3.22 (dq, $J = 14$, 7.2 Hz, 2H, NCH_2CH_3), 2.75 (dq, $J = 14$, 7.2 Hz, 2H, NCH_2CH_3), 2.64 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 0.71 (t, $J = 7.2$ Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$NMR (C_6D_6) δ 158.77, 153.27, 151.58, 147.79, 137.10, 136.59, 134.97, 129.32, 128.80, 124.06, 121.19, 120.98, 83.30 ($=CH_2$), 42.07 (CH_2CH_3), 22.36 (CH_3), 20.46 (CH_3), 13.36 (CH_2CH_3) ppm. *Anal.* Calc. ($C_{38}H_{50}N_6Zr$): C, 66.92; H, 7.39; N, 12.32. Found: C, 67.23; H, 7.45; N, 12.11%.

3.8. Synthesis of $[(2,6\text{-}Me_2C_6H_3)NC(C_5H_4N)(=CH_2)\text{-}\kappa^2N,N]_2Ti(NMe_2)_2$ *(**10**)*

The complex was synthesized using the same procedure and conditions for **9,** but with $TiCl_2(NMe_2)_2$ (0.174 g, 0.840 mmol) and the potassium salt **7** (0.440 g, 1.68 mmol). The solution was stirred for two days at 50 °C. The complex was purified by recrystallization in toluene at −30 °C. The yield was 0.140 g (29%). ^{1}H NMR (C_6D_6): δ 8.70 (d, $J = 4.8$ Hz, 1H, py-H^6), 7.48 (d, $J = 8.4$ Hz, 1H, py-H^3), 7.23 (d, $J = 7.6$ Hz, 1H, ph-H$^{3 \text{ or } 5}$), 7.15 (d, $J = 7.6$ Hz, 1H, ph-H$^{3 \text{ or } 5}$), 7.04 (t, $J = 7.2$ Hz, 1H, ph-H^4), 6.74 (td, $J = 7.6$, 2.0 Hz, 1H, py-H^5), 6.21 (td, $J = 6.4$, 0.8 Hz, 1H, py-H^4), 4.50 (s, 1H, $=CH_2$), 3.89 (s, 1H, $=CH_2$), 2.63 (s, 6H, CH_3), 2.45 (s, 3H, CH_3). $^{13}C\{^1H\}$NMR (C_6D_6) δ 158.09, 153.88, 153.69, 147.67, 136.45, 135.68, 134.51, 129.56, 129.02, 123.73, 121.13, 120.83, 78.95 ($=CH_2$), 48.13 (NCH_3), 23.21 (CH_3), 20.13 (CH_3) ppm. *Anal.* Calc. ($C_{34}H_{42}N_6Ti$): C, 70.09; H, 7.27; N, 14.42. Found: C, 69.71; H, 7.52; N, 14.11%.

*3.9. Synthesis of [(2,6-iPr$_2$C$_6$H$_3$)NC(C$_5$H$_4$N)(=CH$_2$)]$_2$Zr(NEt$_2$)$_2$ (**11**)*

The complex was synthesized using the same procedure and conditions for **9,** but with $ZrCl_2(NEt_2)_2(THF)_2$ (0.707 g, 1.57 mmol) and the potassium salt **8** (1.00 g, 3.14 mmol). The solution was stirred for one day at room temperature. The crystals, which were analytically pure and suitable for X-ray crystallography, were obtained by recrystallization in toluene at −30 °C. The yield was 0.742 g (60%). ^{1}H NMR (C_6D_6): δ 8.70 (d, $J = 5.6$ Hz, 1H, py-H^6), 7.50–7.24 (m, 4H), 6.76 (td, $J = 7.2$, 1.2 Hz, 1H, py-H^5), 6.44 (t, $J = 6.4$ Hz, 1H, py-H^4), 4.79 (s, 1H, $=CH_2$), 4.11 (septet, $J = 6.8$ Hz, 2H, $CH(CH_3)_2$), 3.78 (s, 1H, $=CH_2$), 3.43 (septet, $J = 6.8$ Hz, 2H, $CH(CH_3)_2$), 3.33 (dq, $J = 14$, 6.8 Hz, 2H, NCH_2), 2.77 (dq, $J = 14$, 6.8 Hz, 2H, NCH_2), 1.50 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.48 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.44 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.34 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 0.70 (t, $J = 7.2$ Hz, 6H, NCH_2CH_3) ppm. $^{13}C\{^1H\}$NMR (C_6D_6) δ 159.15, 156.34, 151.30, 147.61, 146.28, 144.65, 137.20, 124.96, 124.70, 124.19, 121.01, 120.85, 89.13 ($=CH_2$), 43.42 (NCH_2), 29.03, 28.00, 27.79, 27.43, 25.76, 24.65, 14.15 (NCH_2CH_3) ppm. *Anal.* Calc. ($C_{46}H_{66}N_6Zr$): C, 69.56; H, 8.38; N, 10.58. Found: C, 69.43; H, 8.42; N, 10.21%.

*3.10. Synthesis of [(2,6-iPr$_2$C$_6$H$_3$)NC(C$_5$H$_4$N)(=CH$_2$)]TiCl(NMe$_2$)$_2$ (**12**)*

The complex was synthesized using the same procedure and conditions for **9,** but with $TiCl_2(NMe_2)_2$ (0.325 g, 1.57 mmol) and the potassium salt **8** (1.00 g, 3.14 mmol). The solution was stirred for one day at room temperature. The single crystals, which were analytically pure, were obtained by recrystallization in toluene at −30 °C. The yield was 0.445 g (63%). ^{1}H NMR (C_6D_6): δ 8.52 (d, $J = 5.2$ Hz, 1H, py-H^6), 7.28–7.10 (m, 4H), 6.87 (td, $J = 7.2$, 0.8 Hz, 1H, py-H^5), 6.49 (t, $J = 6.0$ Hz, 1H, py-H^4), 4.56 (s, 1H, $=CH_2$), 3.75 (s, 1H, $=CH_2$), 3.29 (br septet, $J = 6.8$ Hz, 2H, $CH(CH_3)_2$), 3.01 (s, 12H, NCH_3), 1.26 (d, $J = 7.2$ Hz, 6H, $CH(CH_3)_2$), 1.25 (d, $J = 7.2$ Hz, 6H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$NMR (C_6D_6) δ 156.52, 155.44, 149.01, 147.40, 142.84, 137.12, 125.56, 123.64, 122.55, 119.61, 87.96 ($=CH_2$), 47.2 (br NCH_3), 28.86 ($CH(CH_3)_2$), 27.20 ($CH(CH_3)_2$), 24.18 ($CH(CH_3)_2$) ppm. *Anal.* Calc. ($C_{23}H_{35}N_4ClTi$): C, 61.27; H, 7.84; N, 12.43. Found: C, 60.88; H, 7.89; N, 12.33%.

*3.11. Synthesis of [CH$_2$=C(C$_5$H$_4$N)(OAlMe$_3$)-κ^{2}N,O]AlMe$_2$ (**13**)*

Complex **3** (0.100 g, 0.210 mmol) was dissolved in benzene (3.0 ml) and $AlMe_3$ (0.15 g, 2.10 mmol) was added. The solution was stirred at room temperature overnight. All volatiles were completely removed under high vacuum at room temperature. Pentane was added and the solution was filtered over celite. White crystals were deposited when the solution was stored at −30 °C. The yield was 45 mg (43%). ^{1}H NMR (C_6D_6): δ 7.17 (d, $J = 6.8$ Hz, 1H, py-H^6), 6.72 (td, $J = 6.8$, 0.8 Hz, 1H, py-H^4), 6.62 (d, $J = 8.8$ Hz, 1H, py-H^3), 6.31 (t, $J = 6.4$ Hz, 1H, py-H^5), 5.56 (d, $J = 3.6$ Hz, 1H, $=CH_2$), 4.86 (d, $J = 3.6$ Hz, 1H, $=CH_2$), −0.04 (s, 9H, $AlCH_3$), −0.27 (s, 6H, $AlCH_3$) ppm. $^{13}C\{^1H\}$NMR (C_6D_6) δ 151.54, 150.37, 142.53, 140.59, 124.40, 120.30, 97.94 ($=CH_2$), −6.20 (br, AlC), −7.87 (br, AlC) ppm. *Anal.* Calc. ($C_{12}H_{21}NOAl_2$): C, 57.82; H, 8.51; N, 5.62. Found: C, 57.55; H, 8.15; N, 5.33%.

*3.12. Synthesis of [(2,6-iPr$_2$C$_6$H$_3$)NC(C$_5$H$_4$N)(=CH$_2$)]AlMe$_2$ (**14**)*

The complex was synthesized using the same procedure and conditions for **13,** but with **11** (0.100 g, 0.126 mmol) and $AlMe_3$ (0.024 ml, 0.252 mmol) in benzene (1.0 ml). The solvent was removed by vacuum and the residue was extracted with pentane. Light yellow single crystals were deposited when the pentane solution was stored at −30 °C overnight (20 mg, 24%).

^{1}H NMR (C_6D_6): δ 7.46 (d, $J = 5.6$ Hz, 1H, py-H^6), 7.19 (t, $J = 8.4$ Hz, 1H, py-H^3), 6.70 (ddd, $J = 8.0$, 7.2, 1.2 Hz, 1H, py-H^5), 6.26 (ddd, $J = 7.2$, 5.2, 1.2 Hz, 1H, py-H^4), 4.55 (d, $J = 1.2$ Hz, 1H, $=CH_2$), 3.86 (d, $J = 1.2$ Hz, 1H, $=CH_2$), 3.58 (septet, $J = 7.2$ Hz, 2H, $CH(CH_3)_2$), 1.39 (d, $J = 7.2$ Hz, 6H, $CH(CH_3)_2$), 1.36 (d, $J = 7.2$ Hz, 6H, $CH(CH_3)_2$), −0.28 (s, 8H, $AlCH_3$) ppm. $^{13}C\{^1H\}$NMR (C_6D_6) δ 156.28, 150.26, 147.22, 142.68, 139.13, 126.24, 124.48, 122.90, 120.87, 84.26 ($=CH_2$), 28.35, 26.41, 25.21, −8.49 (AlC) ppm. *Anal.* Calc. ($C_{21}H_{29}N_2Al$): C, 74.96; H, 8.71; N, 8.33. Found: C, 74.62; H, 8.52; N, 8.45%.

Table 1
Crystallographic parameters of **4**, **11**, **13** and **14**[a]

	4	**11**	**13**	**14**
Formula	$C_{18}H_{24}N_4O_2Ti$	$C_{46}H_{66}N_6Zr$	$C_{12}H_{21}Al_2NO$	$C_{21}H_{29}AlN_2$
F_w	376.31	794.27	249.26	336.44
Color	dark brown	yellow	pale yellow	pale yellow
Size (mm)	0.3 × 0.3 × 0.15	0.20 × 0.20 × 0.15	0.20 × 0.15 × 0.15	0.30 × 0.30 × 0.20
a (Å)	8.3150(10)	12.6440(10)	8.865(3)	14.5650(10)
b (Å)	13.9490(10)	17.6100(10)	9.262(3)	8.617(2)
c (Å)	17.1270(10)	20.0200(10)	10.200(2)	17.395(2)
α (°)	90	90	78.869(17)	90
β (°)	97.476(3)	90	88.652(18)	106.349(6)
γ (°)	90	90	73.658(10)	90
V (Å^3)	1969.6(3)	4457.7(5)	788.1(4)	2094.9(6)
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P21/c$	$P2_12_12_1$	$P\bar{1}$	$P21/N$
D_{calc} (g cm^{-3})	1.269	1.184	1.050	1.067
Z	4	4	2	4
μ (mm^{-1})	0.452	0.283	0.168	0.101
Number of data collected	8080	10,110	2699	8672
Number of unique data	4418	10,110	1643	3115
Number of variables	230	491	151	224
R (%)	0.0587	0.0442	0.0811	0.1573
R_w(%)	0.1029	0.0942	0.2321	0.3676
Goodness-of-fit	1.010	1.029	1.329	1.230

[a] Data collected at 293(2) K with Mo Kα radiation (λ (Kα) = 0.7107), $R(F) = \sum \|F_o| - |F_c\| / \sum |F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ with $F_o > 2.0\sigma(I)$.

3.13. Crystallographic studies

Crystals of **4, 11, 13** and **14** coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf-Nonius CCD single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXS-97) [15] and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 1.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center (**4**: CCDC no. 230878; **8**: CCDC no. 230879; **13**: CCDC no. 230880; **14**: CCDC no. 230881). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by grant No. (R05-2002-000155-0) from the Basic Research Program of the Korea Science and Engineering Foundation.

References

[1] (a) Review: H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. 34 (1995) 1143;
(b) A. Togni, R.L. Halterman (Eds.), Metallocenes, Wiley-VCH, New York, 1998;
(c) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 429;
(d) H.G. Alt, A. Köpple, Chem. Rev. 100 (2000) 1205;
(e) G.W. Coates, Chem. Rev. 100 (2000) 1223;
(f) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253;
(g) E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391;
(h) G.W. Coates, J. Chem. Soc. Dalton Trans. (2002) 467;
(i) G.W. Coates, P.D. Hustad, S. Reinartz, Angew. Chem. Int. Ed. 41 (2002) 2236.

[2] (a) J.D. Scollard, D.H. McConville, J. Am. Chem. Soc. 118 (1996) 10008;
(b) J.D. Scollard, D.H. McConville, N.C. Payne, J.J. Vittal, Macromolecules 29 (1996) 5241;
(c) P.N. O'Shaughnessy, K.M. Gillespie, C. Morton, I. Westmoreland, P. Scott, Organometallics 19 (2002) 4496;
(d) C.H. Lee, Y.-H. La, J.W. Park, Organometallics 19 (2000) 344;
(e) L.-C. Liang, R.R. Schrock, W.M. Davis, Organometallics 19 (2000) 2526;
(f) Y.-M. Jeon, J. Heo, W.M. Lee, T. Chang, K. Kim, Organometallics 18 (1999) 4107.

[3] (a) S. Matsui, T. Fujita, Catal. Today 66 (2001) 63;
(b) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 7888;
(c) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S.-i. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 3327;
(d) J. Tian, G.W. Coates, Angew. Chem. Int. Ed. 39 (2000) 3626.

[4] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 123 (2001) 6847.

[5] (a) T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Banselben, Science 287 (2000) 460;
(b) C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149;
(c) E.F. Connor, T.R. Younkin, J.I. Henderson, A.W. Waltman, R.H. Grubbs, Chem. Commun. (2003) 2272.

[6] (a) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283;
(b) S. Mecking, A. Held, F.M. Bauer, Angew. Chem. Int. Ed. 41 (2002) 544;
(c) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169;
(d) S. Mecking, Coord. Chem. Rev. 203 (2000) 325.

[7] (a) Z.J.A. Komon, X. Bu, G.C. Bazan, J. Am. Chem. Soc. 122 (2000) 1830;
(b) Z.J.A. Komon, X. Bu, G.C. Bazan, J. Am. Chem. Soc. 122 (2000) 12379;
(c) B.Y. Lee, Y.H. Kim, H.J. Shin, C.H. Lee, Organometallics 21 (2002) 3481;
(d) Z.J.A. Komon, G.M. Diamond, M.K. Leclerc, V. Murphy, M. Okazaki, G.C. Bazan, J. Am. Chem. Soc. 124 (2002) 15280;
(e) C.B. Shim, Y.H. Kim, B.Y. Lee, Y. Dong, H. Yun, Organometallics 22 (2003) 4272.

[8] (a) B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon, X. Bu, J. Am. Chem. Soc. 123 (2001) 5352;
(b) B.Y. Lee, X. Bu, G.C. Bazan, Organometallics 20 (2001) 5425;
(c) C.B. Shim, Y.H. Kim, B.Y. Lee, D.M. Shin, Y.K. Chung, J. Organomet. Chem. 675 (2003) 72.

[9] Y.H. Kim, T.H. Kim, B.Y. Lee, D. Woodmansee, X. Bu, G.C. Bazan, Organometallics 21 (2002) 3082.

[10] (a) Y.H. Kim, T.H. Kim, N.Y. Kim, E.S. Cho, B.Y. Lee, D.M. Shin, Y.K. Chung, Organometallics 22 (2003) 1503;
(b) Y. Zhang, D.A. Kissounko, J.C. Fettinger, L.R. Sita, Organometallics 22 (2003) 21.

[11] A. Koppl, H.G. Alt, J. Mol. Catl. A: Chem. 154 (2000) 45.

[12] T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskela, J. Organomet. Chem. 606 (2000) 112.

[13] S. Brenner, R. Kempe, P. Arndt, Z. Anorg. Allg. Chem. 621 (1995) 2021.

[14] E. Benzing, W. Kornicker, Chem. Ber. 94 (1961) 2263.

[15] G.M. Sheldrick, SHELXL-97 Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.