Novel and Efficient Palladium Complexes with β-Ketoiminate Ligands for the Polymerization of Norbornene

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A series of the noble palladium complexes containing β-ketoiminate ligands with internal bases, [Pd(η³-allyl)(β-ketoiminate)], [Pd(Me)(PPh₃)(β-ketoiminate)] and [Pd(Me)(β-ketoiminate)], have been successfully prepared. Crystallographically determined structures showed that these complexes are distorted square planar and pendant bases of the β-ketoiminate ligands fail to coordinate to the metal in the first two classes of complexes while bases do coordinate in the 3ʳᵈ class complexes. These complexes are active towards norbornene polymerization on activation with H(OEt₂)₂BAr′₄ (Ar′ = 3,5-bistrifluoromethylphenyl) and modified methylalumioxane (MMAO). MMAO is more efficient for the activation for polymerization. Generally, the polymerization activity increases with the following order; [Pd(allyl)(β-ketoiminate)] < [Pd(Me)(PPh₃)(β-ketoiminate)] < [Pd(Me)(β-ketoiminate)].

Key Words: Palladium complexes, β-Ketoiminate ligands, Norbornene polymerization, Activators, Structures

Introduction

Up to date, polyolefins have been mainly produced with early transition metal-based catalysts. Recently, late transition metals, in particular nickel and palladium, have attracted much attention as olefin polymerization catalysts due to their less electrophilicity and greater heteroatom tolerance[1,2] even though some group 10 transition metal complexes, especially [P₂M]²⁺[A]₂ (P: diphosphine; M = Pd, Pt; A⁻ = OTf⁻, BF₄⁻, PF₆⁻, SbF₆⁻, ClO₄⁻), act as excellent Lewis acid catalysts.[3] Early pioneering works by Keim *et al.*[4] initiated the research in this field and discrete Ni and Pd monoalkyl complexes containing α-diimines prepared by Brookhart highlighted key features in the olefin polymerization catalyzed by late transition metal complexes.[5] Grubbs' neutral Ni complexes with salicylaldiminato ligands were followed to produce highly linear polyethylene at a rate comparable with highly active metallocene catalysts.[6] Many catalytic systems have been followed and they generally contain bidentate P^O, N^O, P^P and N^N ligands with bulky aryl substituents.[1,2,7] However, late transition metal complexes with tri or higher dentate ligands are generally known to be inactive or less active for olefin polymerizations than ones with bidentate ligands.[8]

On the other hand, norbornene and its derivatives have drawn much interest due to their polymers showing unique physical properties such as high glass transition temperature, optical transparency, low dielectric properties and birefringence, which can be applicable in the new optical information storage media, microelectronics, packing and gas separation.[9,10] Norbornene is known to be polymerized by ring-opening metathesis polymerization (ROMP), cationic polymerization and vinyl addition polymerization. Since the first adoption of a TiCl₄/Al'Bu₃ catalyst, various catalysts from Ni, Co, Cr, Ti, Zr and Pd complexes have been used for norbornene vinyl polymerization and recently well reviewed.[11] Some of these complexes are active towards olefin polymeri-

zation without cocatalysts[6(a),12] but most of them require cocatalysts such as phosphine scavengers, methylaluminoxane (MAO), boranes with or without alkylaluminum, and borates.[13]

Recently, some early and late transition metal complexes with β-ketoiminate or β-diketiminate, a bidentate monoanionic ligand have been prepared and tested for the olefin polymerization.[7(a),14] Among these complexes, bis(β-ketoiminato) Ni(II) complexes[13(e)] are active for the polymerization of even polar monomers such as MMA. Since we have been involved in the research for the synthesis of group 4 and 5 complexes containing N-alkoxy-β-ketoiminate, a terdentate dianionic ligand as promising metalloorganic chemical vapor deposition (MOCVD) precursors,[15] we have kept an eye on Ni and Pd complexes which are formulated as (N^O)MR(L) (M = Ni, Pd; L = neutral ligands) and showed high activities towards olefin polymerization. The outcome would be interesting if L is connected to the N^O system because L should be replaced with incoming olefin monomer during the process of polymerization. Since β-ketoiminate complexes have drawn interest due to their higher thermal stability than the β-diketonate analogues and their versatility, by changing the imine substituents, for tailoring their reactivity and volatility,[16] some palladium complexes containing β-ketoiminate derivatives, one of N^O type ligands with pendant bases have been prepared to test their potential application as olefin polymerization catalysts.

Herein we report the novel and well-characterized palladium complexes containing tridentate monoanionic functional β-ketoiminate ligands, which are highly active towards norbornene and ethylene.

Experimental Section

All the works involving moisture-sensitive compounds were carried out using standard Schlenk or dry-box techniques. All reagents, purchased from Aldrich Chemical Co.,

were used as supplied commercially without further purification. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded by using 5 mm tube on a Varian Unity Inova 400 (400.256 and 100.657 MHz, respectively) or a Varian Gemini 2000 (199.976 and 50.289 MHz, respectively) spectrometer and were referenced to tetramethylsilane (TMS).[31] P{^{1}H} NMR spectra were recorded on a Varian (162.027 MHz) FT-NMR spectrometer and were referenced to external PPh₃ (-5.3 ppm relative to 85% H₃PO₄). All manipulations were conducted under an inert atmosphere. Elemental analyses were performed with EA-1110 (CE Instruments) in the Inha University.

Ligand **1-3**,[16(b)] **4-10** and **14-15**,[16(c)] and **11-13**.[17] [Pd(η³-CH₂CMeCH₂)(μ-Cl)]₂,[18] [Pd(PPh₃)MeCl]₂[19] [Pd(COD)MeCl],[20] H(OEt₂)₂BAr′₄ and NaBAr′₄ (Ar′ = 3,5-(CF₃)₂C₆H₃)[21] have been prepared according to literature procedures. Complexes **1b** and **4b** were already reported elsewhere.[22] MMAO (Tosoh Finechem Co., 5.7% Al content in toluene) was used as supplied.

Synthesis of complexes.

Pd(η³-CH₂CMeCH₂)(CH₃C(O)CHC(NCH₂CH₂CH₂-OCH₃)CH₃) (1a): A mixture of distilled diethyl ether (30 mL), Tl(OC₂H₅) (0.63g, 2.54 mmol), and Ligand CH₃C(O)CHC(NHCH₂CH₂CH₂OCH₃)CH₃ (0.44g, 2.54 mmol) was stirred at room temperature for 1 hr and then the solvent was removed in vacuum. After the above mixture added to diethyl ether and was stirred at -20 °C and then added to suspension of [{Pd(η³-CH₂CMeCH₂)(μ-Cl)}₂] (0.50 g 1.27 mmol) in diethyl ether (40 mL). After it was stirred at -20 °C for 2 h, the mixture was filtered through celite on a frit into a Schlenk flask at -20 °C and then the solvent was removed in vacuum and washed with distilled hexane and dried in vacuum to give a pale yellow solid. (yield: 0.53 g, 63%)

^{1}H-NMR (199.976 MHz, CDCl₃): δ 4.77(s, 1H, C(O)C*H*=C(N)), 3.77(t, 2H, J_{HH} = 7.0Hz, NCH₂CH₂C*H₂*OCH₃), 3.59(d, 1H, J_{HH} = 2.6Hz, allyl), 3.37(t, 2H, J_{HH} = 5.8Hz, NC*H₂*CH₂CH₂-OCH₃), 3.32(s, 3H, NCH₂CH₂CH₂OC*H₃*), 3.00(d, 1H, J_{HH} = 2.6Hz, allyl), 2.87(s, 1H, allyl), 2.66(s, 1H, allyl), 2.15(s, 3H, C*H₃* of allyl), 1.97(s, 3H, C(N)C*H₃*), 1.93(s, 3H, C*H₃*C(O)), 1.87(m, 2H, NCH₂C*H₂*CH₂OCH₃); ^{13}C-NMR (50.289 MHz, CDCl₃): δ 176.60(s, CH₃*C*(O)CH), 164.55(s, CH=*C*(N)CH₃), 130.54(s, CH₂*C*(CH₃)CH₂), 97.76(s, C(O) *C*H=C(N)), 70.33 (s, NCH₂CH₂CH₂O*C*H₃), 59.02(s, *C*H₂ of allyl), 58.78(s, NCH₂CH₂*C*H₂OCH₃), 57.32(s, N*C*H₂CH₂CH₂OCH₃), 53.77 (s, *C*H₂ of allyl), 32.16(s, NCH₂*C*H₂CH₂OCH₃), 26.82(s, *C*H₃C(O)CH), 23.61(s, *C*H₃ of allyl), 21.07(s, CH=C(N)*C*H₃); Anal. Calcd. For C₁₃H₂₃NO₂Pd: C, 47.07; H, 6.99; N, 4.22. Found: C, 47.24; H, 7.30; N, 4.01.

Complexes **4a-12a**, **4b-13b** and **12c-15c** were prepared according to the procedures described for complex **1a**, **1b** and **6c**, respectively.

Pd(η³-CH₂CMeCH₂)(CH₃C(O)CHC(NCH₂C₆H₄OCH₃)-CH₃) (4a): yield: 0.63g, 65%. ^{1}H-NMR (199.976 MHz, CDCl₃): δ 7.23~7.18(m, 2H, NCH₂C₆*H₄*OCH₃), 6.91(t, 1H, J_{HH} = 3.8Hz, NCH₂C₆*H₄*OCH₃), 6.85(d, 1H, J_{HH} = 4.0Hz, NCH₂C₆*H₄*OCH₃), 4.95(d, 1H, J_{HH} = 6.6Hz, NC*H₂*C₆H₄-OCH₃), 4.41(s, 1H, C(O)C*H*=C(N)), 3.85(s, 3H, NCH₂C₆H₄-OC*H₃*), 3.50(d, 1H, J_{HH} = 1.4Hz, allyl), 2.75(s, 1H, allyl), 2.48(d, 1H, J_{HH} = 1.2Hz, allyl), 2.34(s, 1H, allyl), 2.03(s, 3H,

*C*H₃ of allyl), 1.85(s, 3H, C(N)C*H₃*), 1.87(s, 3H, C*H₃*C(O)); ^{13}C-NMR (50.289 MHz, CDCl₃): δ 177.34(s, CH₃*C*(O)CH), 166.21(s, CH=*C*(N)CH₃), 156.21, 128.70, 127.36, 127.00, 120.58, 109.56(s, NCH₂C₆H₄OCH₃), 98.22(s, C(O)*C*H=C(N)), 58.08(s, N*C*H₂C₆H₄OCH₃), 58.00(s, *C*H₂ of allyl), 55.36(s, *C*H₂ of allyl), 54.83(s, N*C*H₂C₆H₄OCH₃), 27.08(s, *C*H₃C(O) CH), 23.22(s, 3H, *C*H₃ of allyl), 21.35(s, CH=C(N)*C*H₃); Anal. Calcd. For C₁₇H₂₃NO₂Pd: C, 53.76; H, 6.10; N, 3.69. Found: C, 53.93; H, 6.27; N, 3.33.

Pd(η³-CH₂CMeCH₂)(CH₃C(O)CHC((NCH₂CH₂C₅-H₄N)CH₃) (C₅H₄N = 2-pyridyl) (6a): yield 0.66g, 71%. ^{1}H-NMR (199.976 MHz, CDCl₃): δ 8.54(d, 1H, J_{HH} = 4.6Hz, C*H* of Pyridine), 7.57(dt, 1H, J_{HH} = 1.4, 7.6Hz, C*H* of Pyridine), 7.16~7.08(m, 2H, C*H* of Pyridine), 4.76(s, 1H, C(O)C*H*= C(N)), 4.06(dt, 2H, J_{HH} = 2.8, 8.8Hz, NC*H₂*CH₂Pyridine), 3.62 (br s, H of allyl), 3.14(br s, H of allyl), 3.05(t, 2H, J_{HH} = 9.0Hz, NCH₂C*H₂*Pyridine), 2.88(br s, H of allyl), 2.71(br s, H of allyl), 2.17(s, 3H, C*H₃* of allyl), 1.98(s, 3H, C(N)C*H₃*), 1.85(s, 3H, C*H₃*C(O)); ^{13}C-NMR (50.289 MHz, CDCl₃): δ 176.73(s, CH₃*C*(O)CH), 164.63(s, CH=*C*(N)CH₃), 159.50, 149.65, 136.41, 123.57, 121.53(s, Pyridine), 130.72(s, CH₂*C*(CH₃)CH₂), 98.23(s, C(O)*C*H=C(N)), 60.26(s, N*C*H₂CH₂Pyridine), 59.10 (s, *C*H₂ of allyl), 54.23(s, *C*H₂ of allyl), 40.72(s, NCH₂*C*H₂-Pyridine), 26.99(s, *C*H₃C(O)CH), 23.81(s, *C*H₃ of allyl), 21.28(s, CH=C(N)*C*H₃); Anal. Calcd. For C₁₆H₂₂N₂OPd: C, 52.68; H, 6.08; N, 7.68. Found: C, 52.82; H, 6.15; N, 7.72.

Pd(η³-CH₂CMeCH₂)(PhC(O)CHC(NCH₂CH₂CH₂OCH₃)-Ph) (7a): yield: 0.71g, 61%. ^{1}H-NMR (199.976 MHz, CDCl₃): δ 7.78~7.71, 7.42~7.24(m, 10H, C₆*H₅*C(O)CH(N)C₆*H₅*), 5.37(s, 1H, C(O)C*H*=C(N)), 3.74(d, 1H, J_{HH} = 2.8Hz, allyl), 3.57(dt, 2H, J_{HH} = 1.8, 8.0Hz, NCH₂CH₂C*H₂*OCH₃), 3.20~ 3.14(m, 6H, NCH₂CH₂CH₂OC*H₃*, NC*H₂*CH₂CH₂OCH₃, H of allyl), 3.05(s, 1H, allyl), 2.74(s, 1H, allyl), 2.22(s, 3H, C*H₃* of allyl), 1.85(m, 2H, NCH₂C*H₂*CH₂OCH₃); ^{13}CNMR (50.289 MHz, CDCl₃): δ 172.54(s, Ph*C*(O)CH), 168.16 (s, CH=*C*(N)Ph), 141.62, 141.21, 129.06, 128.32, 128.03, 127.78, 127.08, 126.94(s, C₆H₅C(O)CH(N)C₆H₅), 130.72(s, CH₂*C*-(CH₃)CH₂), 96.73(s, C(O)*C*H=C(N)), 70.49(s, NCH₂ CH₂-CH₂OCH₃), 60.20(s, NCH₂CH₂*C*H₂OCH₃), 58.65(s, *C*H₂ of allyl), 58.48(s, *C*H₂ of allyl), 53.56(s, N*C*H₂CH₂CH₂OCH₃), 33.59(s, NCH₂*C*H₂CH₂OCH₃), 23.81 (s, *C*H₃ of allyl); Anal. Calcd. For C₂₃H₂₇NO₂Pd: C, 60.60; H, 5.97; N, 3.07. Found: C, 60.55; H, 6.20; N, 2.84.

Pd(η³-CH₂CMeCH₂)(PhC(O)CHC(NCH₂CH₂OCH₃)Ph)-(8a): yield: 0.56g, 50%. ^{1}H-NMR (199.976 MHz, CDCl₃): δ 7.79~7.74, 7.44~7.27(m, 10H, C₆*H₅*C(O)CH(N)C₆*H₅*), 5.41(s, 1H, C(O)C*H*=C(N)), 3.79~3.71(m, 3H, NC*H₂*CH₂OCH₃, allyl), 3.52(t, 2H, NCH₂C*H₂*OCH₃), 3.21(s, 3H, NCH₂CH₂OC*H₃*), 3.13(d, 1H, J_{HH}= 2.8Hz, allyl), 3.08(s, 1H, allyl), 2.75(s, 1H, allyl), 2.24(s, 3H, C*H₃* of allyl); ^{13}C-NMR (50.289 MHz, CDCl₃): δ 173.02(s, Ph*C*(O)CH), 169.13(s, CH=*C*(N)Ph), 141.54, 141.04, 129.18, 128.70, 128.34, 128.06, 127.88, 127.26, 127.12(s, C₆H₅C(O)CH(N)C₆H₅), 130.83(s, CH₂*C*(CH₃)CH₂), 96.87(s, C(O)*C*H=C(N)), 74.17(s, NCH₂ CH₂OCH₃), 60.32(s, NCH₂*C*H₂OCH₃), 59.94(s, *C*H₂ of allyl), 59.14(s, *C*H₂ of allyl), 53.43(s, N*C*H₂CH₂OCH₃), 23.85(s, *C*H₃ of allyl); Anal. Calcd. For C₂₂H₂₅NO₂Pd: C, 59.80; H, 5.70; N, 3.17. Found: C, 59.93; H, 5.69; N, 2.98.

Pd(η³-CH₂CMeCH₂)(PhC(O)CHC(NCH₂C₆H₄OCH₃)Ph) (10a): yield: 1.02g, 80%. ¹H-NMR (199.976 MHz, CDCl₃): δ 7.85~7.80, 7.35~7.17(m, 11H, C₆H₅C(O)CH(N)C₆H₅, NCH₂-C₆H₄OCH₃), 7.47(d, 1H, J$_{HH}$ = 7.6Hz, NCH₂C₆H₄ OCH₃), 7.00(t, 1H, J$_{HH}$= 7.4Hz, NCH₂C₆H₄OCH₃), 6.80(d, 1H, J$_{HH}$= 7.6Hz, NCH₂C₆H₄OCH₃), 5.53(s, 1H, C(O)CH=C(N)), 4.83 (q, 2H, J$_{HH}$= 16.4Hz, NCH₂C₆H₄OCH₃), 3.74(s, 3H, NCH₂-C₆H₄OCH₃), 3.62(d, 1H, J$_{HH}$ = 2.8Hz, allyl), 2.88(s, 1H, allyl), 2.52(d, 1H, J$_{HH}$ = 2.6Hz, allyl), 2.32(s, 1H, allyl), 1.80(s, 3H, CH₃ of allyl); ¹³C-NMR (50.289 MHz, CDCl₃): 173.08(s, PhC(O)CH), 169.10(s, CH=C(N)Ph), 155.79, 141.65, 140.72, 130.73, 129.17, 128.30, 128.09, 127.92, 127.17, 126.45, 120.56, 109.46(s, C₆H₅C(O)CH(N)C₆H₅, NCH₂C₆H₄ OCH₃), 130.91(s, CH₂C(CH₃)CH₂), 96.69(s, C(O)CH=C(N)), 59.20(s, NCH₂C₆H₄OCH₃), 59.01(s, CH₂ of allyl), 55.36(s, CH₂ of allyl), 54.64(s, NCH₂C₆H₄OCH₃), 23.17(s, CH₃ of allyl); Anal. Calcd. For C₂₇H₂₇NO₃Pd: C, 64.35; H, 5.40; N, 2.78. Found: C, 64.55; H, 5.55; N, 2.52.

Pd(η³-CH₂CMeCH₂)(PhC(O)CHC((NCH₂CH₂C₅H₄N)Ph) (C₅H₄N = 2-pyridyl) (12a): yield: 0.37g, 30%. ¹H-NMR (400 MHz, CDCl₃): δ 8.44, 7.80~7.75, 7.51~7.02, 6.89(m, 13H, C₆H₅C(O)CH(N)C₆H₅, CH of Pyridine), 5.38(s, 1H, C(O)CH= C(N)), 3.89(t, 2H, J$_{HH}$= 7.0Hz, NCH₂-CH₂Pyridine), 3.79 (br s, 1H, allyl), 3.39(br s, 1H, allyl), 3.06(br t, 3H, NCH₂CH₂-Pyridine, allyl), 2.83(br s, 1H, allyl), 2.27(s, 3H, CH₃ of allyl); Anal. Calcd. For C₂₆H₂₆N₂OPd: C, 63.87; H, 5.36; N, 5.73. Found: C, 63.96; H, 5.62; N, 5.42.

Pd(CH₃C(O)CHC((NCH₂CH₂C₅H₄N)CH₃)(PPh₃)Me (C₅H₄N = 2-pyridyl) (6b): Ligand CH₃C(O)CHC((NCH₂CH₂-C₅H₄N)CH₃ (0.20 g, 1.0 mmol) was dissolved in 20 mL of THF and this solution was added to a mixture of distilled THF (30 mL) and Tl(OC₂H₅) (0.30 g, 1.20 mmol) dropwise. The resulting solution was stirred at room temperature for 1hr and then the solvent was removed in vacuum. 30 mL of THF was added and [Pd(PPh₃)MeCl]₂ (0.51 g, 0.60 mmol) in 70 mL of THF was added to this solution dropwise. After stirring at room temperature for 8 hr, the mixture was filtered through celite on a frit into a Schlenk flask and then the solvent was removed in vacuum. The product was washed with distilled hexane and extracted with methylene chloride. The solvent was removed in vacuum to give a green solid. (yield: 0.25 g, 43%) ¹H-NMR (199.976 MHz, CDCl₃): δ 8.54(d, 1H, J = 6.2Hz), 7.68-7.05(m, 18H) (PPh₃ and Pv), 4.72(s, 1H, C(O)-CH=C(N)), 3.88(m, 2H, NCH₂CH₂Py), 3.10(dt, 2H, J = 7.8,7.4Hz, NCH₂CH₂Py), 1.98(s, 3H, C(N)CH₃), 1.85(s, 3H, CH₃C(O)), 0.21(d, J = 3.2Hz, 3H, CH₃); ¹³C-NMR (50.289 MHz, CDCl₃): δ 179.00(CH₃C(O)CH), 156.68(CH=C(N)CH₃), 152.98, 135.05, 134.98, 134.87, 134.76, 130.05, 128.42, 128.11, 127.95, 127.85, 127.07, 126.61, 121.45, 109.53(PPh₃ and Py), 97.56(C(O)CH=C(N)), 40.74(NCH₂CH₂), 31.88 (NCH₂CH₂), 23.84(CH₃C(O)CH), 16.82(CH=C(N)CH₃), -0.819 (CH₃); ³¹P-NMR(162.027 MHz, CDCl₃): δ 44.77; Anal. Calcd. For C₃₁H₃₃N₂OPPd: C, 63.43; H, 5.71; N, 4.77; Found C, 63.56; H, 5.95; N, 4.86.

Pd(PhC(O)CHC((NCH₂CH₂C₅H₄N)Ph)(PPh₃)Me (C₅H₄N = 2-pyridyl) (12b): yield: 0.58 g, 81%. ¹H-NMR (199.976 MHz, CDCl₃): δ 8.42(d, 1H, J = 6.2Hz), 7.77-6.99(m, 28H) (PPh₃, Ph and Pv), 5.37(s, 1H, C(O)CH=C(N)), 3.80 (m, 2H,

NCH₂-CH₂-Py), 3.16(t, 2H, J = 15.6Hz, NCH₂CH₂Py), 0.35(d, J = 3.0Hz, 3H, CH₃); ¹³C-NMR (50.289 MHz, CDCl₃): δ 172.54 (PhC(O)CH), 160.15(CH=C(N)Ph), 142.36, 142.69, 142.64, 140.88, 136.09, 135.04, 134.93, 131.87, 131.40, 130.29, 130.27, 128.76, 128.48, 128.38, 128.27, 127.68, 127.41, 127.21, 127.16, 123.64, 121.17 (PPh₃, Ph and Pv), 96.52 (C(O)CH=C(N)), 52.04 (NCH₂CH₂), 42.88 (NCH₂CH₂), 0.92 (CH₃); ³¹P-NMR (162.027 MHz, CDCl₃): δ 43.73; Anal. Calcd. For C₄₁H₃₇N₂OPPd: C, 69.25; H, 5.24; N, 3.94; Found C, 69.33; H, 5.16; N, 3.74.

Pd(CF₃C(O)CHC(NCH₂CH₂CH₂OCH₃)CF₃)(PPh₃)Me (13b): yield: 0.56 g, 85%. ¹H-NMR (199.976 MHz, CDCl₃): δ 7.70-7.36(m, 15H, PPh₃), 5.581(s, 1H, C(O)CH=C(N)), 3.811(br, 2H, NCH₂CH₂), 3.438(t, 2H, J = 8.6Hz, CH₂CH₂-OMe), 3.320(s, 3H, OCH₃), 2.127(m, 2H, NCH₂CH₂CH₂), 0.278 (d, 3H, J = 2.8Hz, CH₃); ¹³C-NMR (50.289 MHz, CDCl₃): δ 165.99 (CF₃C(O)CH), 154.90 (CH=C(N)CF₃), 135.05~128.05 (PPh₃), 120.75, 117.90 (CF₃), 87.35 (C(O)CH=C(N)), 70.27 (NCH₂CH₂), 58.56 (CH₂CH₂OMe), 49.18 (OCH₃), 34.29 (NCH₂-CH₂CH₂), 0.14 (CH₃); ³¹P-NMR (162.027 MHz, CDCl₃): δ 42.99; Anal. Calcd. For C₂₈H₂₈F₆NO₂PPd: C, 50.81; H, 4.26; N, 2.12; Found: C, 51.23; H, 4.46; N, 1.65.

Pd(CH₃C(O)CHC((NCH₂CH₂C₅H₄N)CH₃)Me (C₅H₄N = 2-pyridyl) (6c): Ligand MeC(O)CHC((2-NHCH₂CH₂)Pyridine) Me(0.25 g, 1.22 mmol) was dissolved in 20 ml of THF and this solution was added to a mixture of distilled THF (30 mL) and Tl(OC₂H₅) (0.30 g, 1.20 mmol) dropwise. The resulting solution was stirred at room temperature for 1hr and then the solvent was removed in vacuum. 30 mL of THF was added and Pd(NH₂CH₂C₆H₅)₂MeCl (0.45 g, 1.20 mmol) in 70 mL of THF was added to this solution dropwise. After stirring at room temperature for 8 hr, the mixture was filtered through celite on a frit into a Schlenk flask and then the solvent was removed in vacuum. The product was washed with distilled hexane and extracted with methylene chloride. The solvent was removed in vacuum. (yield: 0.21 g, 52%)

¹H-NMR (199.976 MHz, CDCl₃): δ 8.53(d, 1H, J = 2.6Hz), 7.71(dt, 1H, J = 0.8, 8.6Hz), 7.32-7.27(m, 1H), 7.16-7.12(dt, 1H, J = 0.6,7.4 Hz)(Pv), 4.78(s, 1H, C(O)CH=C(N)), 3.29 (br, 4H, NCH₂CH₂Py), 1.94(s, 3H, C(N)CH₃), 1.82(s, 3H, CH₃C(O)), 0.62(s, 3H, CH₃); ¹³C-NMR (50.289 MHz, CDCl₃): δ 175.78(CH₃C(O)CH), 163.83(CH=C(N)CH₃), 161.65, 153.22, 137.92, 124.17, 122.95(Pv), 98.04(C(O) CH=C(N)), 46.58 (NCH₂CH₂), 41.75(NCH₂CH₂), 26.67(CH₃C(O)CH), 22.43 (CH=C(N)CH₃), 3.74(CH₃); Anal. Calcd. For C₁₃H₁₈N₂OPd: C, 48.09; H, 5.59; N, 8.63. Found: C, 48.24; H, 5.37; N, 8.65.

Pd(PhC(O)CHC((NCH₂CH₂C₅H₄N)Ph)Me (C₅H₄N = 2-pyridyl) (12c): yield: 0.19 g, 49%. ¹H-NMR (199.976 MHz, CDCl₃): δ 8.66(d, 1H, J=5.4Hz), 7.83(m 2H), 7.73(t 1H, J = 7.6Hz), 7.37-7.20(m, 10H), (Ph), 5.52(s, 1H, C(O)CH= C(N)), 3.21(br, 4H, NCH₂CH₂Py), 0.87(s, 3H, CH₃); ¹³C-NMR (50.289 MHz, CDCl₃): δ 171.78(PhC(O)CH), 162.18(CH= C(N)Ph), 153.47, 141.84, 140.99, 138.05, 129.03, 128.54, 128.34, 128.03, 127.19, 127.09, 124.31, 123.06(Ph), 96.40 (C(O)CH=C(N)), 49.16(NCH₂CH₂), 42.28(NCH₂CH₂), 5.28 (CH₃); Anal. Calcd. For C₂₃H₂₂N₂OPd: C, 61.55; H, 4.94; N, 6.24. Found: C, 61.89; H, 5.48; N, 6.31.

Pd(CH₃C(O)CHC((NCH₂C₅H₄N)CH₃)Me (C₅H₄N = 2-pyri-

dyl) (14c): yield: 0.29g , 61%. ^{1}H-NMR (199.976 MHz, CDCl$_3$): δ 8.48(d, 1H, J = 5.8Hz), 7.76(dt, 1H, J = 0.8,8.6Hz), 7.389~7.190(m, 2H), (*Pv*), 4.95(s, 1H, C(O)C*H*=C(N)), 4.89 (s, 2H, NC*H*$_2$), 2.04(s, 3H, C(N)C*H*$_3$), 1.95(s, 3H, C*H*$_3$C(O)), 0.64(s, 3H, C*H*$_3$); ^{13}C-NMR (50.289 MHz, CDCl$_3$): δ 176.72 (CH$_3$C(O)CH), 165.41(CH=C(N)CH$_3$), 162.05, 149.42, 136.83, 123.15, 121.48 (*Pv*), 98.52(C(O)CH=C(N)), 58.98(NCH$_2$), 27.00(CH$_3$C(O)CH), 20.80(CH=C(N)CH$_3$), 1.54(CH$_3$); Anal. Calcd. For C$_{12}$H$_{16}$N$_2$OPd: C, 46.39; H, 5.19; N, 9.02; Found C, 46.50; H, 5.53; N, 8.61.

Pd(PhC(O)CHC((NCH$_2$C$_5$H$_4$N)Ph)Me (C$_5$H$_4$N = 2-pyridyl) (15c): yield: 0.22g, 55%. ^{1}H-NMR (199.976 MHz, CDCl$_3$): δ 8.31(dt, 1H, J = 6.4Hz), 7.86(dd 1H, J = 0.8,4.8Hz), 7.81(dd 1H, J = 0.8, 4.8Hz), 7.38-7.10 (m, 10H), 7.16(t, 1H, J = 7.8Hz) (*Ph* and *Pv*), 5.58(s, 1H, C(O)C*H*=C(N)), 4.81(s, 2H, NC*H*$_2$), 0.88(s, 3H, C*H*$_3$); ^{13}C-NMR(50.289 MHz, CDCl$_3$): δ 175.06 (PhC(O)CH), 164.29(CH=C(N)Ph), 162.71, 161.16, 150.05, 148.97, 141.17, 138.95, 137.70, 136.72, 130.03, 128.94, 128.43, 127.99, 127.20, 125.41, 124.09, 120.78 (*Ph* and *Pv*), 96.40 (C(O)CH=C(N)), 44.28(NCH$_2$), 5.28(CH$_3$); Anal. Calcd. For C$_{22}$H$_{20}$N$_2$OPd: C, 60.77; H, 4.64; N, 6.44; Found C, 60.43; H, 4.60; N, 6.34.

Pd(PhCH$_2$NH$_2$)$_2$MeCl (16): Pd(COD)MeCl (1.00 g, 3.77 mmol) was dissolved in 20 mL of CH$_3$CN and this solution was added to a mixture of distilled THF (30 mL) and C$_6$H$_5$-CH$_2$NH$_2$ 0.81 g (7.58 mmol) dropwise. After stirring at room temperature for 30 min, the mixture was filtered and then the product was removed in vacuum. The product was washed with distilled CH$_3$CN. The solvent was removed in vacuum to give a white solid. (yield: 1.35 g, 95%)

^{1}H-NMR (199.976 MHz, CDCl$_3$): δ 7.34-7.27(m, 10H), 3.99 (dt, 4H, J = 2.2, 15Hz), 2.75(br, 4H), 0.40(s, 3H); ^{13}C-NMR (50.289 MHz, CDCl$_3$): δ 139.21, 129.21, 128.39, 128.31(*Ph*), 49.80(PhCH$_2$), -3.91(CH$_3$); Anal. Calcd. For C$_{15}$H$_{21}$ClN$_2$Pd: C, 48.53; H, 5.70; N, 7.55. Found: C, 48.67; H, 6.16; N, 7.52. Mp. 130 °C dec. white solid

Homopolymerization of norbornene with catalysts activated with [H(Et$_2$O)$_2$]$^+$BAr$_4^{f-}$. In an inert (N$_2$) atmosphere. [H(Et$_2$O)$_2$]$^-$BAr$_4^{f-}$(catalyst : cocatalyst = 1 : 1) were placed into a small vial. To this was added approximately 5mL of solvent, and the mixture gently shaken to dissolve the solids. This solution was then added to 0.005 g of catalyst, 1000 equivalents of norbornene dissolved in approximately 10 mL of solvent in a 20 mL vial containing a stir bar. The solution was stirred rapidly for about 5 min after which time polymerization was quenched by adding acidified methanol. The solid was washed with methanol and dried under vacuum. The resultant polymer was found to be insoluble in all common laboratory solvents.

Homopolymerization of norbornene with catalysts activated with MMAO. In an inert (N$_2$) atmosphere. MMAO (catalyst : cocatalyst = 1 : 1000) were placed into a small vial. To this was added approximately 5 mL of solvent, and the mixture gently shaken to dissolve the solids. This stock solution was then added to 0.005 g of catalyst. 1000 equivalent of norbornene dissolved in approximately 10 mL of solvent in a 20 mL vial containing a stirring bar. The solution was stirred rapidly for about 2 min, after which time polymerization was

complete. The reaction was quenched by addition of acidified methanol. The solid was washed with methanol and dried under vacuum.

Structural determination. The crystals suitable for the X-ray crystallography were grown from the methylene chloride solutions in the freezer maintained at -20 °C.

The diffraction data for compounds **1a, 4b,** and **12c** were collected on a Bruker CCD diffractometer with MoK$_\alpha$ (λ = 0.71073) radition employing 2 kW sealed tube X-ray source operating at 1.6 kW. The crystals were mounted on glass fibers under epoxy. The reflections were successfully indexed by an automated indexing routine built in the SMART program (SMART Area-Detector Software Package. Bruker AXS, Inc., Madison WI, 1995). The CCD data were integrated and scaled using a Bruker SAINT (SAX Area-Detector Integration Program, version 4.050, Bruker AXS, Inc., Madison WI, 1995), and the structures were solved and refined using XPREP (part of the SHELXTL, Crystal Structure Determination Package, version 5.04, Bruker AXS, Inc., Madison WI, 1995) and SHELX-97 (Sheldrick, G. M. Institut fur Anorganische chemie der Universitat, Gotingen, F. R. G., 1997). Hydrogen atoms were located in the calculated positions.
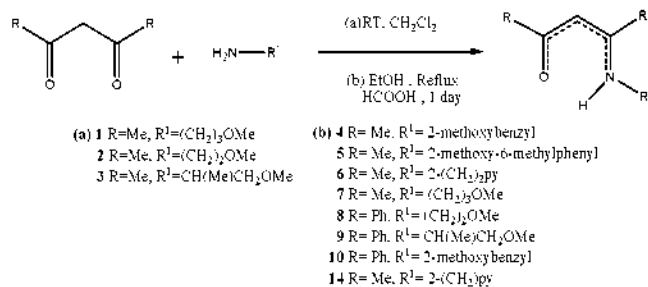
The crystallographic data for compounds **1a** and **12c** (CCDC 608594, 608596) are listed in Table 1.[23] (The crystal structure and crystallographic data for compound **4b** (CCDC 608595) was published elsewhere.[22])

Results and Discussion

Ligand synthesis. Most of the functional β-ketoimines used in this study have been prepared by condendation reactions between corresponding β-diketones and amines described in the literature (scheme 1) with moderate to good yields. However, some of them were synthesized *via* TMS intermediates as shown in scheme 2 and lower yields were generally observed due to multistep reactions.

In all the β-ketoimines, enamine forms are predominant and the proton on the N atom couples with α protons if any.

Complex synthesis. Three classes of palladium(II) complexes have been prepared to investigate the ligand effect on the structure of the complex and the polymerization activity. These complexes are originally designed to have the formula of [Pd(N^O^L)R], which resembles the well-known salicyl-aldiminato complexes but L is incorporated into the (N^O) ligand (N^O ligand with an internal base). The target complexes

(a) 1 R=Me, R^1=(CH$_2$)$_3$OMe
2 R=Me, R^1=(CH$_2$)$_2$OMe
3 R=Me, R^1=CH(Me)CH$_2$OMe

(b) 4 R= Me, R^1= 2-methoxybenzyl
5 R= Me, R^1= 2-methoxy-6-methylphenyl
6 R= Me, R^1= 2-(CH$_2$)$_2$py
7 R= Me, R^1= (CH$_2$)$_3$OMe
8 R= Ph, R^1= (CH$_2$)$_2$OMe
9 R= Ph, R^1= CH(Me)CH$_2$OMe
10 R= Ph, R^1= 2-methoxybenzyl
14 R= Me, R^1= 2-(CH$_2$)py
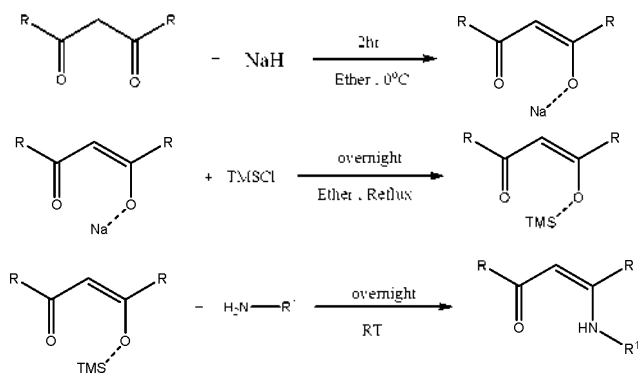
Scheme 1

11 R=Ph, R^1= 2-methoxy-6-methylphenyl
12 R=Ph. R^1= 2-(CH$_2$)$_2$py
13 R=CF$_3$. R^1=(CH$_2$)$_3$OMe
15 R=Ph, R^1= 2-(CH$_2$)py
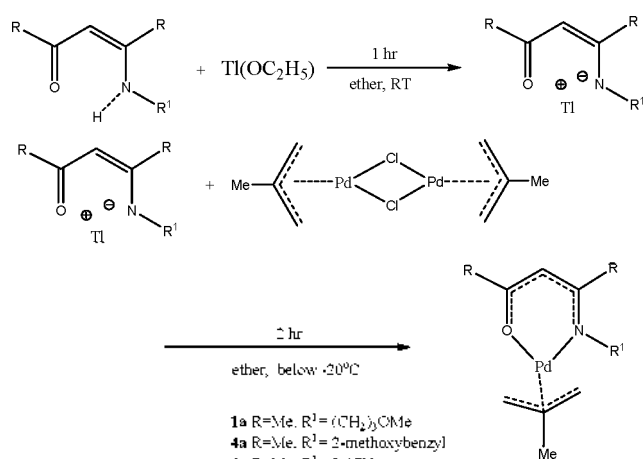
Scheme 2

1a R=Me. R^1= (CH$_2$)$_3$OMe
4a R=Me. R^1= 2-methoxybenzyl
6a R=Me. R^1= 2-(CH$_2$)$_2$py
7a R=Ph. R^1= (CH$_2$)$_3$OMe
8a R=Ph. R^1= (CH$_2$)$_3$OMe
10a R=Ph, R^1= 2-methoxybenzyl
12a R=Ph. R^1= 2-(CH$_2$)$_2$py

Scheme 3
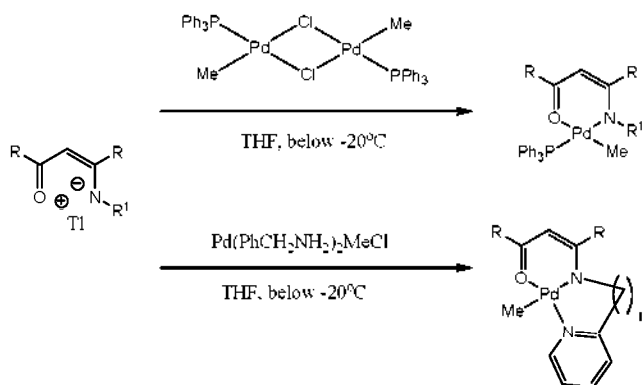
1b R=Me. R^1=(CH$_2$)$_3$OMe   6c R=Me. R^1=2-(CH$_2$)$_2$py. n=2
4b R=Me. R^1=2-methoxybenzyl   12c R=Ph. R^1=2-(CH$_2$)$_2$py. n=2
6b R=Me. R^1=2-(CH$_2$)$_2$py   14c R=Me, R^1=2-(CH$_2$)py. n=1
12b R=Ph, R^1=2-(CH$_2$)py   15c R=Ph. R^1=2-(CH$_2$)py. n=1
13b R=CF$_3$. R^1=(CH$_2$)$_3$OMe

Scheme 4

have been obtained only in the class (III).

The class (I) of the complexes contain a η^3-methallyl ligand with functional β-ketoiminate one. In addition to β-keto-iminate ligands, both methyl and triphenylphosphine ligands and a methyl ligand are present in the class (II) and (III) of the complexes, respectively. The preparative methods are described in scheme 3 and 4.

In the deprotonation step. NaH, Na(OMe). KH. *n*-BuLi, and Tl(OEt) have been found to produce deprotonated β-ketoiminate anions successfully. However, starting palladium halides reacts with only thallium salts of β-ketoimine to produce corresponding target complexes with β-ketoiminate ligands.

In the preparation of methallyl complexes. 2-methyl allyl produced more stable complexes than nonsubstituted allyl. Even with 2-methyl allyl ligand. complexes 13a is not stable enough to obtain satisfactory elemental analysis result. Considering the fact that corresponding phenyl β-ketoiminates and 2-substituted allyl analogues show much more stability, steric bulkiness seems to be more important for the stability than electronic effect in this class of complexes. As will be discussed below. the pendant bases in the functional β-ketoiminates fail to coordinate to the metal in the class (I) complexes.

The class (II) was originally designed to obtain alkyl complexes with tridentate β-ketoiminates but phosphines cannot be removed in the final products. The similar chemical shifts in ^{31}P NMR spectra suggest that these complexes share almost identical coordination geometry. The palladium complex with the same formula as class (II) has been prepared in the reaction of Pd(COD)MeCl with potassium salt of a β-ketoiminate in the presence of PPh$_3$.[14f] It is rather surprising that ligands 14 and 15. where N bonded methylene chains are shortened by a methylene unit from the similar ligands 6 and 12, fail to produce complexes in the class (II). Since ligands 14 and 15 produced class (III) complexes successfully. steric hinderance exerted by bulky triphenylphosphine may be the reason.

In the preparation of class (III) of complexes. reactions between β-ketoiminates and Pd(COD)MeCl, one of the most utilized starting complexes with no phosphines in palladium chemistry, fail to produce alkyl complexes with tridentate β-ketoiminates. In our efforts to find out the proper starting material, Pd(PhCH$_2$NH$_2$)$_2$MeCl. obtained quantitatively from the reaction between Pd(COD)MeCl and PhCH$_2$NH$_2$. was found to produce target complex efficiently. Tridentate functional β-ketoiminates finally replace 2 amines and Cl ligands to produce complexes which can be formulated as (L^O^N)PdR.

Structures of palladium complexes. The structures of three complexes. 1a. 4b. and 12c. one of which represents each class. respectively, were crystallographically determined and the crystallographic data were summarized in Table 1.

As shown in Figure 1, it is found that the methallyl coordinates to metal in a η^3 mode and the pendant base. an ethereal O atom. of the β-ketoiminate is left uncoordinated in complex 1a. The coordination geometry of complex 1a is best described as distorted square planar with N and O in the β-

Palladium Complexes with β-Ketoiminate Ligands

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ketoiminate ligand and 2 terminal carbon atoms of the π-methallyl ligand as the corners of the square. Interestingly, a molecule adopts a structure whose geometrical parameters exhibit more contributing of (a) form, while the other more contributing of (b) form.

The pattern of bond distances from metal to methallyl ligand is different in two forms; in (a) terminal carbons (2.091(16) and 2.046(16) Å) are located closer to metal than central carbon (2.192(14) Å) but reverse (2.167(19) and 2.141(19) Å vs 2.08(2) Å) is true in (b). Slight different Pd-terminal carbon distances may be due to different trans influences of N and O atom. In the (b) form, the difference in trans influence is less than that in the form (a). For [(η³-2-methallyl)-Pd(trifluoroacetate)]₂, where the terminal carbons of the methallyl ligands are trans to the oxygens of two trifluoroacetate bridging ligands,[24] and [Pd(η³-allyl)(tri-*o*-tolylphosphine)(triflate)], where one of the terminal carbons is trans to the oxygen of triflate ligand,[25] the Pd-C distances (2.096(5) and 2.073(5); 2.085(3) Å) are comparable to that found in (a) form. When the trans influence is quite different, the bond distances of Pd-allyl terminal carbon show substantial difference.[25,26] The allyl carbon-carbon distances C31-C32 (1.46(3) and 1.41(3) Å) and C31-C33 (1.41(3) and 1.36(3) Å) are only slightly different. When the allyl coor-

dinates in a η¹, η² mode as found in [Ni(P^O)(allyl)]⁺.[27] substantial differences in allyl carbon-carbon distances (1.373(22), 1.314(24) Å) and metal-carbon distances (M-C$_t$, 1.995(11) and 2.024(11); M-C$_c$, 1.998(11) Å) are observed. In complex **1a**, two carbon-carbon bond distances in an methallyl ligand are slightly different; 1.46(3), 1.41(3) and 1.41(3), 1.36(3) Å, respectively. In a free β-ketoimine ligand, enamine form (b) is predominant but it is interesting that two forms, enamine (C5'-C6', 1.31(2); C6'-C7', 1.42(2); C7'-O1', 1.270(17); C5'-N1', 1.33(2); C4'-N1', 1.44(2) Å) and enol-imine (C5-C6, 1.560(18); C6-C7, 1.37(2); C7-O1, 1.37(2); C5-N1, 1.25(2); C4-N1, 1.488(17) Å), are present simultaneously in a complex. There is no indication of any inter-

(a)   (b)
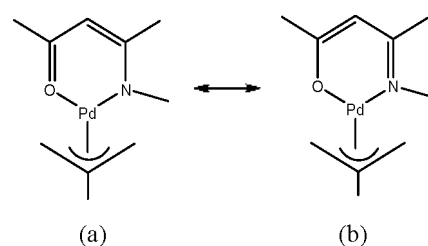
Scheme 5

Table 1. Crystallographic Data for Compounds **1a** and **12c**.

|	**1a**	**12c**	**4b**
Empirical formula	C$_{42}$H$_{62}$N$_2$O$_4$Pd$_2$	C$_{23}$H$_{22}$N$_2$OPd	C$_{32.50}$H$_{35}$ClNO$_2$PPd
Formula weight	871.74	448.83	644.44
Temperature	293(2) K	173(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Space group	triclinic, P1	Orthorhombic, P2(1)2(1)2(1)	Orthorhombic, Pbcn
a	10.187(8) Å	10.0740(8) Å	31.334(3) Å
b	10.656(8) Å	10.9425(8) Å	12.0633(13) Å
c	10.792(9) Å	18.1835(13) Å	16.0742(17) Å
α	91.505(14)°	90°	90°
β	100.561(14)°	90°	90°
γ	114.820(13)°	90°	90°
Volume	1038.2(14) Å³	2004.5(3) Å³	6075.9(11) Å³
Z	2	4	8
Density (calc.)	2.789 Mg/m³	1.487 Mg/m³	1.409 Mg/m³
Absorption coeff.	1.813 mm⁻¹	0.940 mm⁻¹	0.781 mm⁻¹
F(000)	904	912	2648
Crystal size	0.38 × 0.30 × 0.18 mm³	0.18 × 0.20 × 0.35 mm³	0.20 × 0.25 × 0.50 mm³
Reflections collected	5496	12831	36782
Independent reflections	4622[R(int) = 0.0329]	4735 [R(int) = 0.0536]	7355 [R(int) = 0.0881]
Data / restraints / parameters	4622 / 3 / 487	4735 / 0 / 245	7355 / 0 / 349
Goodness-of-fit on F2	0.996	0.973	1.124
Final R indices [I>2σ(I)]	R$_1$ = 0.0426, wR$_2$ = 0.1057	R$_1$ = 0.0338, wR$_2$ = 0.0569	R$_1$ = 0.0797, wR$_2$ = 0.1746
R indices (all data)	R$_1$ = 0.0515, wR$_2$ = 0.1102	R$_1$ = 0.0457, wR$_2$ = 0.0596	R$_1$ = 0.1368, wR$_2$ = 0.2013
Absolute structure parameters	0.14(7)	-0.02(3)	none
Largest diff. peak and hole	0.816 and -0.929 e.Å⁻³	0.944 and -0.549 e.Å⁻³	1.063 and -2.160 e.Å⁻³

(a)

(b)

(c)
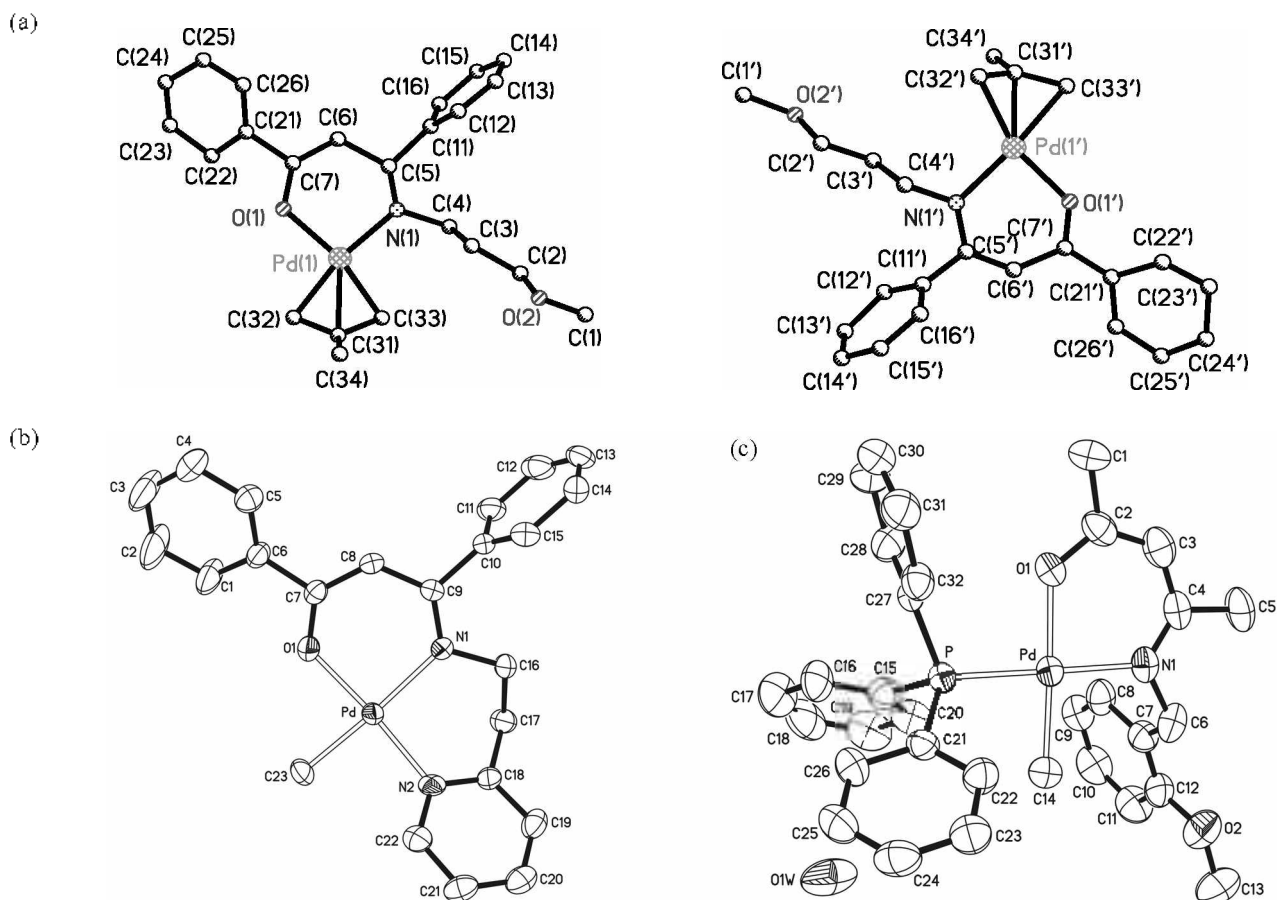
Figure 1. (a) The structure of **1a**. Selected bond distances and angles: Pd(1)-N(1) 2.044(16), Pd(1)-C(33) 2.046(18), Pd(1)-O(1) 2.051(14), Pd(1)-C(32) 2.091(16), Pd(1)-C(31) 2.192(16), Pd(1')-O(1') 2.064(11), Pd(1')-C(31') 2.08(2), Pd(1')-N(1') 2.095(13), Pd(1')-C(33') 2.141(19), Pd(1')-C(32') 2.167(19), O(1')-C(7') 1.270(17), O(1)-C(7) 1.32(2), N(1)-C(5) 1.25(2), N(1)-C(4) 1.488(17), N(1')-C(5') 1.33(2), N(1')-C(4') 1.44(2), C(32)-C(31) 1.46(3), C(33')-C(31') 1.36(3) Å; N(1)-Pd(1)-C(33) 98.9(6), N(1)-Pd(1)-O(1) 95.0(5), C(33)-Pd(1)-O(1) 163.0(6), N(1)-Pd(1)-C(32) 166.9(7), C(33)-Pd(1)-C(32) 69.1(8), O(1)-Pd(1)-C(32) 96.1(7), N(1)-Pd(1)-C(31) 132.0(6), C(33)-Pd(1)-C(31) 38.8(7), O(1)-Pd(1)-C(31) 131.5(6), C(32)-Pd(1)-C(31) 39.8(7), O(1')-Pd(1')-C(31') 130.2(7), O(1')-Pd(1')-N(1') 90.1(5), C(31')-Pd(1')-N(1') 137.3(6), O(1')-Pd(1')-C(33') 95.5(6), C(31')-Pd(1')-C(33') 37.5(7), N(1')-Pd(1')-C(33') 174.4(7), O(1')-Pd(1')-C(32') 160.2(6), C(31')-Pd(1')-C(32') 38.8(8), N(1')-Pd(1')-C(32')106.5(7), C(33')-Pd(1')-C(32') 68.0(8) ° (b) The structure of **12c**. Selected bond distances and angles: Pd-O(1) 2.016(2), Pd-C(23) 2.037(3), Pd-N(2) 2.040(3), Pd-N(1) 2.100(3), O(1)-C(7) 1.298(4), N(1)-C(9) 1.303(4), N(1)-C(16) 1.472(4), N(2)-C(18) 1.341(4), N(2)-C(22) 1.354(4), C(7)-C(8) 1.373(4), C(8)-C(9) 1.437(4) Å; O(1)-Pd-C(23) 84.70(13), O(1)-Pd-N(2) 174.13(10), C(23)-Pd-N(2) 91.43(13), O(1)-Pd-N(1) 91.30(10), C(23)-Pd-N(1) 175.55(14), N(2)-Pd-N(1) 92.71(10) °. (c) The structure of **4b**. Selected bond distances and angles: Pd-C(14) 2.051(6), Pd-O(1) 2.060(4), Pd-N(1) 2.116(5), Pd-P 2.2418(15), O(1)-C(2) 1.287(8), N(1)-C(4) 1.315(8), N(1)-C(6) 1.458(8), C(2)-C(3) 1.387(10), C(3)-C(4) 1.402(9) Å; C(14)-Pd-O(1) 175.5(3), C(14)-Pd-N(1) 92.6(2), O(1)-Pd-N(1) 90.92(19), C(14)-Pd-P 87.5(2), O(1)-Pd-P 89.07(13), N(1)-Pd-P 177.17(14) °.

action between metal and the ethereal O atom.

In the crystal structure of complex **4b** as reported elsewhere,[23] the pendant base, an ethereal O atom, of the β-ketoiminate is left uncoordinated as in complex **1a**. The structure of complex **4b** shows a slightly distorted square planar arrangement comprising the plane with N and O in the β-ketoiminate ligand, a phosphine, and a methyl ligand. As expected from the small coupling constant (3.0-3.6Hz) between phosphine and methyl protons and chelating nature of β-ketoiminate, the methyl group on palladium is positioned cis to the phosphine. The Pd-P bond length of 2.2418(15) Å is comparable to those in phosphine complexes (2.20-2.32 Å).[25,29,30] The Pd-methyl bond distance (2.051(6) Å) is rather long but in agreement with values (2.01-2.05 Å) for related complexes.[28-34] The β-ketoiminate ligand can be described as an enolimine, similar to salicylaldiminate, on the basis of bond

lengths (C2-O, 1.287(8); C2-C3, 1.387(10); C3-C4, 1.402(9); C4-N1, 1.315(8) Å).

In the crystal structure of complex **12c**, the internal base, an N atom in the pyridine ring, of the β-ketoiminate finally coordinates to the metal. The structure is slightly distorted square planar and the functional β-ketoiminate ligand spans almost in the same plane around the metal. The Pd-methyl bond distance (2.037(3) Å) is in agreement with values (2.01-2.05 Å) for related complexes[28-34] but shorter than that in **4b** possibly due to lack of the phosphine. The β-keto-iminate ligand can be also described as an enolimine, similar to salicylaldiminate, on the basis of bond lengths (C7-O1, 1.298 (4); C7-C8, 1.373(4); C8-C9, 1.437(4); C9-N1, 1.303(8); N1-C16, 1.472(4) Å). The Pd-N bond distance of β-ketoiminate ligand (2.100(3) Å) is longer than that of pyridine (2.040(3) Å) possibly due to partial contribution of enamine character.

Palladium Complexes with β-Ketoiminate Ligands

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Table 2. Norbornene Polymerization Results without cocatalysts.

Catalyst	Solvent	Yield (%)	Activity (kg/Pd·mol·hr)
1b		20.0	14.3
6b		13.0	9.0
12b	CH₂Cl₂	15.0	11.5
12c		16.5	9.1
14c		23.0	8.9
15c		17.5	8.5

Amount of catalyst: 0.01 g, [Monomer]:[catalyst] = 1000, solvent volume = 3 mL, reaction time = 6 h, reaction temperature = 25 °C.

Table 3. Norbornene Polymerization Results with a Cocatalyst, [H(Et₂O)₂]⁺BAr₄⁻.

Catalyst	Solvent	Yield (%)	Activity (kg/Pd·mol·hr)
[Pd(methallyl)Cl]₂	CH₂Cl₂	95	263
	PhCl	77	204
	PhMe	13.5	21.3
6a	CH₂Cl₂	35	191
	PhCl	60	328
	PhMe	25	138
1b	CH₂Cl₂	43.5	324
	PhCl	52.3	390
	PhMe	21.1	157
6b	CH₂Cl₂	45.2	295
12b	CH₂Cl₂	57.5	456
	PhCl	94.6	749
	PhMe	14.1	112
13b	CH₂Cl₂	85.1	771
	PhCl	90.2	810
	PhMe	56.6	509
6c	CH₂Cl₂	84.5	477
6cᵃ	CH₂Cl₂	62.7	355
6cᵇ	CH₂Cl₂	16.5	93
12c	CH₂Cl₂	67.2	531
	PhCl	48.8	379
	PhMe	40.7	318
14c	CH₂Cl₂	79.4	1026
15c	CH₂Cl₂	86.6	657
16	CH₂Cl₂	90.7	329
	PhCl	97.3	348
	PhMe	62.9	224

Reaction temperature: 25 °C, solvent volume = 15 mL, [monomer] / [catalyst] = 1000, reaction time = 5 min. 14c = 3 min. ᵃ[cocatalyst] / [catalyst] = 4, ᵇ[cocatalyst] / [catalyst] = 10

However, the Pd-N bond distance of pyridine is rather shorter than those found in phosphino-pyridine complex (2.21-2.23 Å).[30] This may be ascribed to the presence of bulky substituents on the pyridine ring.

Similar enolimine structures of coordinated β-ketoiminate ligands (Cᴄ-O. 1.285(2), 1.2893(19); Cɴ-N. 1.320(2), 1.323(2); Cᴄ-Cᴄ. 1.362(3). 1.368(2); Cɴ-Cᴄ. 1.411(2), 1.401(2)) (Cᴄ, Cɴ and Cᴄ are carbon next to O, one next to N, and centeral one of the β-ketoiminate ligand, respectively) were reported in the Ni(β-ketoiminate ligand)₂ complexes.[14(e)]

Polymerization of norbornene. During our efforts to investigate the reactivities of the class (I) complexes containing β-ketoiminate ligand, the inactivity of these complexes towards

Table 4. Norbornene Polymerization Results with a Cocatalyst, MMAO.

Catalyst	Solvent	Yield (%)	Activity (kg/Pd·mol·hr)
1b	PhMe	62.0	7600
6b	CH₂Cl₂	95.0	24600
12b	CH₂Cl₂	97.5	26100
	PhCl	95.0	22000
	PhMe	41.5	5030
13b	CH₂Cl₂	91.5	29300
	PhCl	89.0	24200
	PhMe	73.5	11200
6c	CH₂Cl₂	94.0	37100
12c	CH₂Cl₂	91.0	51400
	PhCl	94.0	53000
	PhMe	65.5	34800
14c	CH₂Cl₂	97.5	93400
15c	CH₂Cl₂	95.0	77100
16	CH₂Cl₂	100	28300
	PhCl	92.5	20500
	PhMe	48.0	6200

Reaction temperature: 25 °C, solvent volume = 15 mL, Al/Pd = 1000. b and c type catalysts: 1000 equivalents norbornenes, reaction time = 2 min. 14c reaction time: 1 min.

olefin, acetylene, and phosphines is rather suprising. In NMR experiments, no changes are monitored after addition of external L type ligands even after a day. This suggests that β-ketoiminate and methallyl ligands in these complexes coordinate rather strongly and no transformation of bonding modes (η³→ η¹) of the methallyl ligand occurs under these conditions. Finally, removal of the methallyl ligand by introduction of proton source. HBAr₄ was tried to activate for olefin polymerization and a success was observed. The polymerization results of the selected complexes are summarized in Table 3.

Without cocatalysts, class (I) complexes are found to be inactive but class (II) and (III) complexes show activities even though much slower reaction rates and lower activities than those with cocatalysts are observed in the olefin polymerization (Table 2). The polymers are insoluble in common organic solvents, indicating high molecular weight or highly crosslinked ones. As shown in Table 3, the higher activities in the class (I) complexes on activation with cocatalysts are generally observed in polar solvents (PhCl > CH₂Cl₂ > PhMe), indicating the polar character of the active species, while reference complex. [Pd(methallyl)Cl]₂, showed the highest activity in CH₂Cl₂.

In the class (II) complexes, activation can be done by HBAr₄ or MAO. It is found that MAO is more efficient than HBAr₄ by at least 1 or 2 order in activity as shown in Table 3 and 4. In this class, activity increases in the following order; **1b** < **6b** < **12b** < **13b** (HBAr₄ activation). Electron-withdrawing nature of Ph and CF₃ may render the metal center to be more electrophilic to facilitate the coordination of olefin and higher activity.

All the activities obtained in this study are less than but in the same order as one with a nonfunctionalized β-ketoiminate reported earlier.[14(f)] However, much more catalyst and MAO were used in that case ([NB]/[Pd] = 200. [Al]/[Pd] = 5000).

On activation with HBAr'₄, the solvent effect is almost same as that in the 1st class complexes; PhCl > CH₂Cl₂ > PhMe, suggesting the similar polar nature of active species. On activation of MMAO, the same solvent effect, higher activity in polar solvents, was observed even though the activities in methylene chloride are slightly higher than those in chlorobenzene. However, it is not as significant as that found with HBAr'₄. Complex 16, Pd(PhCH₂NH₂)₂MeCl, showed the similar solvent effect on activity.

In the class (III), activity increases in the following order: 6c < 12c < 15c < 14c (HBAr'₄ or MMAO activation). In this class, it is evident that activity in toluene is in the same order as those in polar solvents even though it is still lower. The reason for this phenomenon is not clear yet. Addition of more than 4 equivalents of HBAr'₄ resulted in much less activity, suggesting decomposition of active species to inactive one. The length of backbone also affects the activity possibly due to different rate of opening a vacant site for olefin. As expected from the ring strain, 15c with a short backbone showed higher activity than 12c. It is interesting to observe reverse effect of the substituent on the activity in a higher ring-strain system; 15c with electron-withdrawing Ph substituents showed less activity than 14c with Me.

As expected from the easy formation of a vacant site for the olefin coordination, the polymerization activity on activation of HBAr'₄ generally increases with the following order: [Pd(methallyl)(β-ketoiminate)] < [Pd(Me)(PPh₃)(β-ketoiminate)] < [Pd(Me)(β-ketoiminate)] under the same conditions. On MMAO activation, 14c showed the best activity in this study.

Polymerization mechanism. As mentioned above, the class (I) of the complexes without cocatalysts was inactive and should be activated by the addition of HBAr'₄ for the olefin polymerization. There are two possible pathways described in Scheme 6 in the reaction with HBAr'₄. In order to determine the actual outcome, an NMR experiment has been done.

Initially it is thought that proton removes the methallyl ligand preferentially but contrary to our expectation, a free β-ketoimine with typical peak at 10.8 ppm was observed in an NMR experiment, suggesting the preferential protolysis of β-ketoimine occurs.

However, [Pd(methallyl)Cl]₂ which should produce the same intermediate on activation with NaBAr'₄ showed less activity towards norbornene polymerization and different activities with complexes containing other β-ketoiminate ligands were observed even though the differences are not
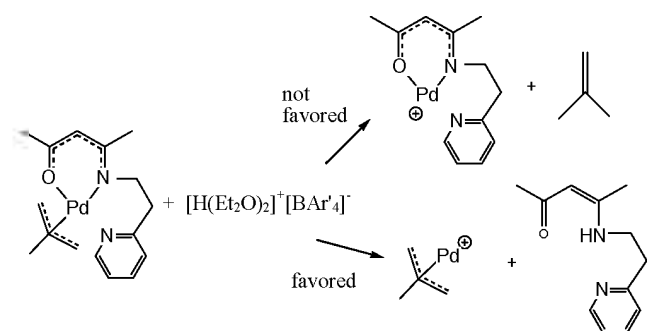
Scheme 6
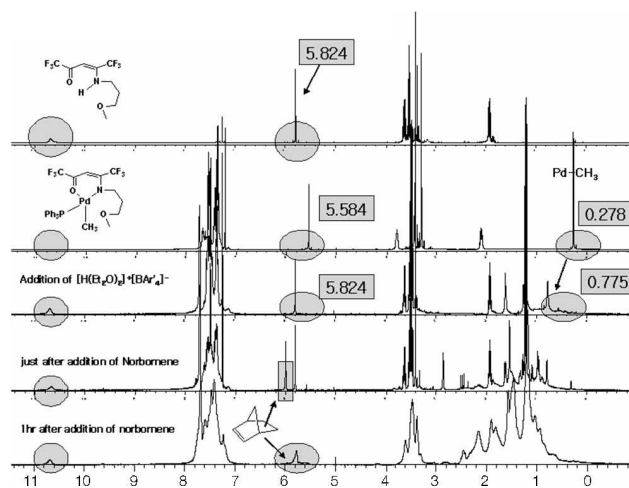
Figure 2. ¹H NMR spectra of the reactions between **13b** and [H(Et₂O)₂]⁺BAr'₄⁻
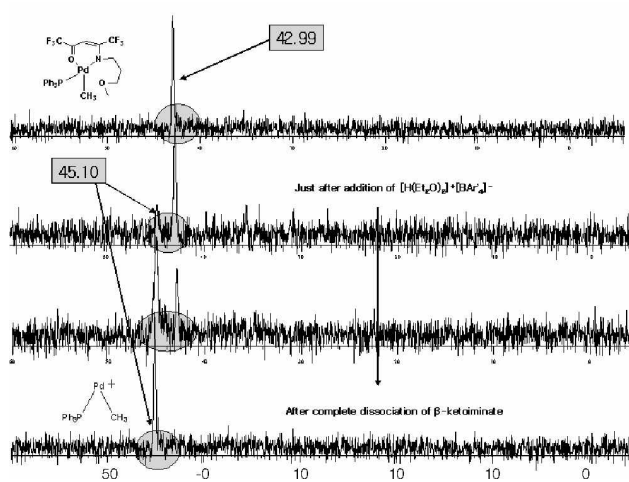
Figure 3. ³¹P NMR spectra of the reactions between **13b** and [H(Et₂O)₂]⁺BAr'₄⁻

great. The different and generally higher polymerization activities than [Pd(methallyl)Cl]₂ in this class of complexes also found. Preactivation of catalysts by introducing HBAr'₄ before addition of norbornene resulted in no polymerization and only activation of the precatalysts in the presence of olefins leads to polymerization, suggesting the quite unstable character of active species.

Unfortunately, the polymers are not soluble in common organic solvents and the characteristics of the polymer cannot be further investigated.

In the class (II) of the complexes, detailed mechanism was investigated with **13b**. In this case, free β-ketoimine ligand was formed while methyl and phosphine ligands were survived on activation with HBAr'₄. The survival of methyl and phosphine ligands was confirmed by ¹H and ³¹P NMR spectra (Figure 2 and 3). The chemical shift of methyl ligand was downshifted from 0.278 to 0.775, which is often observed during the process of obtaining + charge in the complex.[5(e),27,35]

The chemical shift of PPh₃ was almost same (42.99 ppm vs. 45.10 ppm) but quite different from those of free PPh₃ (0 ppm). Possible formation of phosphonium salt can be excluded
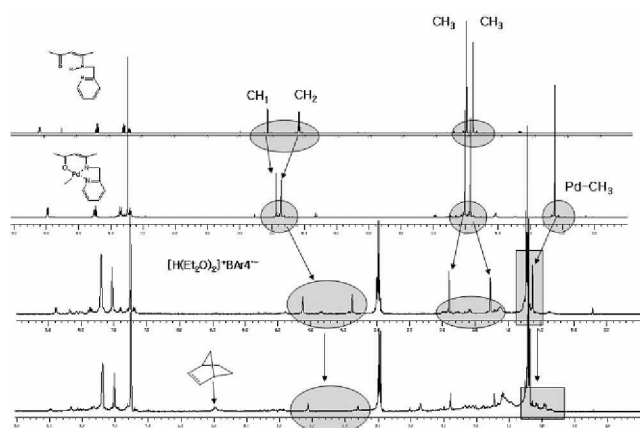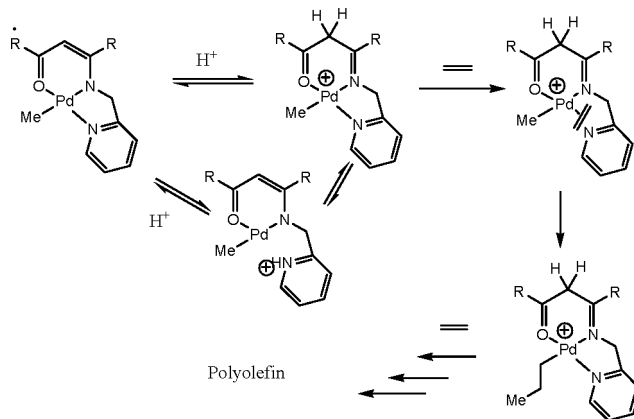
Figure 4. ^{1}H NMR spectra of the reactions between **14c** and $[H(Et_2O)_2]^+BAr_4^-$

Scheme 7

excluded by the chemical shift obtained from the reaction between PPh$_3$ and HBAr'$_4$ (14.932 and 11.903 ppm). HBF$_4$ (12.506 and 9.293 ppm) and HCl (3.243 ppm). Unfortunately, the splitting of the methyl peak in the product by the coordinated phosphine was not observed but a little broader peak (W$_{1/2}$ = 12Hz) was resulted. Therefore, it is assumed that $[Pd(Me)(PPh_3)]^-$ was formed as an active species. The activity difference between **13b** and **1b** seems to rely on the tendency of protolysis of β-ketoiminate. Since ligand **13** is more acidic than **1**, it is expected that the deprotonated **13** is less basic and M-L bond strength is weaker.

In the class (III) of the complexes, preferential removal of methyl ligand is assumed but it is survived after addition of approximate 1 equivalent of HBAr'$_4$ (Figure 4). However, the methyl peak appeared downfield (from 0.64 to 1.12) significantly in the ^{1}H NMR spectrum. Formation of a free β-ketoiminate ligand was not observed. The peaks representing CH of β-ketoiminate and CH$_2$ next to the pyridine shift from 4.95 and 4.89 to 3.87 and 4.60, respectively, while integration ratio changes from 1:2 to 2:2. Two methyl peaks of β-ketoiminate also shift from 2.04 and 1.95 to 2.40 and 1.76. In the free β-diketone ligands, methine peaks in the keto form appear in the range of 3.5-4.0 ppm. However, this complex was found to convert to pyridinium complexes during the accumulation of the ^{13}C NMR data overnight. Therefore, confirmation of CH$_2$ (resonance at around 70 ppm) cannot be done but one peak at 65.864 ppm was observed. From these observations, it may be concluded that protonation would lead to formation of the intermediate where β-ketoimine coordinates to the metal in the keto form (Scheme 7).

14c with electron-donating substituent Me showed higher activity than **15c** with Ph possibly due to stabilization of protonated intermediate. This protonated β-ketoiminate would deviate from the planity due to change of hybridization, which leads to dissociation of internal base. Also complexes with longer backbone showed lower activity due to lower tendency of dissociation of internal base which is originated from higher tolerance toward distortion with lower ring strain of 6-member ring.

Even though reported examples of this type of coordination in the β-ketoiminate complexes are rare, there are some exam-

ples in the β-diketonate complexes.[36] *In situ* formation of $[PdMeCl(MeC(O)CMe_2C(Me)NCH_2Py)]$ by mixing MeC-$(O)CMe_2C(Me)NCH_2Py)$ with Pd(cod)MeCl confirms the possibility of coordination of keto form of β-ketoimine. This complex was activated with MMAO to produce polynorbornene but activity (48000 kg/Pd mol·hr in CH$_2$Cl$_2$ and 8300 kg/Pd mol·hr in toluene) is much lower than that (93400 kg/Pd mol·hr in CH$_2$Cl$_2$) with **14c**. Activation with NaBAr'$_4$ also produces polynorbornene but activity is not high (630 and 210 kg/Pd mol·hr. respectively). This complex did not show any activity towards olefin polymerization without cocatalysts. Attempts to isolate $[PdMeCl(MeC(O) CMe_2C(Me)NCH_2Py)]$ failed due to instability.

However, protonation by HBF$_4$ resulted in the protonation onto pyridine of β-ketoiminate ligand. (new peak at 9.20 ppm in the ^{1}H NMR spectrum) Therefore, counter anion appears to be important for the activation of catalyst precursors even though the reason is not clear yet. The catalytic activity of **14c** in CH$_2$Cl$_2$ on activation with HBF$_4$ (667 kg/Pd mol·hr) is found to be lower than that with HBAr'$_4$ (1030 kg/Pd mol·hr). In toluene, the activities decrease further to 250 and 420 kg/Pd mol·hr, respectively.

Conclusion

Three classes of the new palladium complexes with modified β-ketoiminate ligands containing pendant bases, [Pd(methallyl)-(β-ketoiminate)], [Pd(Me)(PPh$_3$)(β-ketoiminate)] and [Pd(Me)-(β-ketoiminate)], have been successfully prepared. The structures of three complexes representing the each class were crystallographically determined which showed that coordination geometries are distorted square planar and internal bases on the β-ketoiminate ligands fail to coordinate to the metal in the first two classes while bases do coordinate in the class (III) complexes. On activation with H(OEt$_2$)$_2$BAr'$_4$ and MMAO, these complexes showed high activities towards norbornene and ethylene polymerization. MMAO is more efficient for the activation for polymerization. Generally, the polymerization activity increases with the following order: [Pd(methallyl)(β-ketoiminate)] < [Pd(Me)(PPh$_3$)(β-ketoiminate)] < [Pd(Me)(β-ketoiminate)]. NMR experiments revealed that β-ketiminates in all classes react with [H(OEt$_2$)$_2$][BAr'$_4$] preferentially to produce active cationic species. In the class (I) and (II)

complexes, the dissociation of β-ketoiminates was observed but these ligands were found to be coordinated in the class (III) complexes. Higher polymerization activity was observed in the polar solvent.

References

1. Ittel, S. D.; Johnson, J. K.; Brookhart, M. *Chem Rev.* **2000**, *100*, 1169.
2. Mecking, S. *Angew. Chem. Int. Ed.* **2001**, *40*, 534.
3. Brunkan, N. M.; Gagne, M. R. *Organometallics* **2002**, *21*, 1576 and references therein.
4. Keim, W. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 191 and references therein.
5. (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (c) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (d) Svejda, S. A.; Johnson, L. K. Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 10634. (e) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (f) Schultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539. (g) Schultz, L. H.; Brookhart, M. *Organometallics* **2001**, *20*, 3975.
6. (a) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (b) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Basleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.
7. (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem. Int. Ed.* **1999**, *38*, 428. (b) Imanishi, Y.; Naga, N. *Prog. Polym. Sci.* **2001**, *26*, 1147.
8. (a) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487. (b) Kooistra, T. M.; Hekking, K. F. W.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. M.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2003**, 648. (c) Borkar, S.; Saxena, P. K. *Polym. Bull.* **2000**, *44*, 167. (d) Bistovsek, G. J. P.; Baugh, S. P. D.; Hoarau, O.; Gibson, V. C.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Inorg. Chim. Acta* **2003**, *345*, 279.
9. Hennis, A. D.; Polley, J. D.; Long, G. S.; Sen, A.; Yandulov, D.; Lipian, J.; Benedikt, G. M.; Rhodes, L. F. *Organometallics* **2001**, *20*, 2812 and references therein.
10. Yang, H.; Li, Z.; Sun, W. H. *J. Mol. Catal. A: Chemical* **2003**, *206*, 23 and references therein.
11. (a) Janiak, C.; Lassahn, P. G. *Macromol. Rapid Commun.* **2001**, *22*, 479. (b) Janiak, C.; Lassahn, P. G. *J. Mol. Catal. A: Chemical* **2001**, *166*, 193.
12. (a) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059. (b) Held, A.; Bauers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301.
13. Lassahn, P. G.; Janiak, C.; Oh, J. S. *Macromol. Rapid Commun.* **2002**, *23*, 16 and references therein.
14. (a) Safir, L.; Novak, B. M. *Macromolecules* **1995**, *28*, 5396. (b) Arndt, M.; Gosmann, M. *Polym. Bull.* **1998**, *41*, 433. (c) Zhu, Y. Z.; Liu, J. Y.; Li, Y. S.; Tong, Y. J. *J. Orgnomet. Chem.* **2004**, *689*,
   1295. (d) Zhao, C. T.; Ribeiro, M. R.; Portela, M. F. *J. Mol. Catal. A: Chemical* **2002**, *185*, 81. (e) He, X.; Yao, Y.; Luo, X.; Zhang, J.; Liu, Y.; Zhang, L.; Wu, Q. *Organometallics* **2003**, *22*, 4952. (f) Wang, L. Y.; Li, Y. F.; Zhu, F. M.; Wu, Q. *European Polym. J.* **2006**, *42*, 322. (g) Bao, F.; Lu, X.; Kang, B.; Wu, Q. *European Polym. J.* **2006**, *42*, 928. (h) Gui, G.; Bao, F.; Gao, H.; Zhu, F.; Wu, Q. *Appl. Organomet. Chem.* **2005**, *19*, 627.
15. (a) Min, Y.; Cho, Y. J.; Kim, D.; Lee, J. H.; Kim, B. M.; Lim, S. K.; Lee, I. M.; Lee, W. I. *Chem. Vapor Depos.* **2001**, *7*, 146. (b) Min, Y.; Cho, Y. J.; Kim, D.; Lee, J. H.; Kim, B. M.; Lim, S. K.; Lee, I. M.; Lee, W. I. *J. Phys. IV Fr.* **2001**, *11*, 675. (c) Hong, S. H.; Lim, S. K.; Lee, I. M.; Min, Y.; Kim, D.; Lee, W. I. *Thin Solid Films* **2002**, *409*, 82. (d) Lim, S. K.; Lee, J. C.; Sohn, D. S.; Lee, W. I.; Lee, I. M. *Chem. Mater.* **2002**, *14*, 1548. (e) Lim, S. K.; Choi, B. H.; Min, Y.; Kim, D.; Yoon, I.; Lee, S. S.; Lee, I. M. *J. Organomet. Chem.* **2004**, *689*, 224.
16. (a) Bastianini, A.; Battiston, G. A.; Benetollo, F.; Gerbasi, R.; Porchia, M. *Polyhedron* **1997**, *16*, 1105. (b) Doherty, S.; Errington, R. J.; Housley, N.; Ridland, J.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **1999**, *18*, 1018 and references therein. (c) Lee, D. H.; Park, S.-E.; Cho, K.; Kim, Y.; Athar, T.; Lee, I. M. *Tetrahedron Lett.* **2007**, 8281.
17. Neumayer, D. A.; Belot, J. A.; Feezel, R. L.; Reedy, C.; Stern, C. L.; Marks, T. J. *Inorg. Chem.* **1998**, *37*, 5625.
18. Zhang, Y. P.; Yuan, Z.; Puddephatt, R. J. *Chem. Mater.* **1998**, *10*, 2293.
19. Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303.
20. Rulke, R. E.; Ernsting, J. M.; Speck, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.
21. Brookhart, M.; Grant, B.; Volpe, Jr., A. F. *Organometallics* **1992**, *11*, 3920.
22. Lee, D. H.; Cho, M. H.; Kwon, I. H.; Jun, I. C.; Lee, I. M.; Jin, M. J. *Catal. Commun.* **2008**, *9*(6), 1517.
23. CCDC-608594(1a), CCDC-608595(4b), and 608596(12c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via www.ccdc.cam.ac.uk/data_request/cif*. The crystal structure of **4b** was reported elsewhere. (see supporting information; Lee, D. W.; Jung, J. Y.; Lee, I. M.; Jin, M. J. *Eur. J. Org. Chem.* **2008**, 356.
24. Goddard, R.; Krüger, C.; Mynott, R.; Neumann, M.; Wilke, G. *J. Organomet. Chem.* **1993**, *454*, C20.
25. Lipian, J.; Mimna, R. A.; Fondran, J. C.; Yandulov, D.; Shick, R. A.; Goodall, B. L.; Rhodes, L. F.; Huffman, J. C. *Macromolecules* **2002**, *35*(24), 8969.
26. Faller, J. W.; Blankenship, C.; Whitmore, B.; Sena, S. *Inorg. Chem.* **1985**, *24*, 4483.
27. Malinoski, J. M.; Brookhart, M. *Organometallics* **2003**, *22*, 5324.
28. Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935.
29. Daugulis, O.; Brookhart, M. *Organometallics* **2002**, *21*, 5926.
30. Chen, H. P.; Liu, Y. H.; Peng, S. M.; Liu, S. T. *Organometallics* **2003**, *22*, 4893.
31. Li, K.; Darkwa, J.; Guzei, I.; Mapolie, S. F. *J. Organomet. Chem.* **2002**, *660*, 108.
32. Müller, G.; Klinga, M.; Osswald, P.; Leskela, M.; Rieger, B. Z. *Naturforsch., B: Chem. Sci.* **2002**, *57*, 803.
33. Chen, Y. C.; Chen, C. L.; Chen, J. T.; Liu, S. T. *Organometallics* **2001**, *20*, 1285.
34. Reddy, K. R.; Surekha, K.; Lee, G. H.; Peng, S. M.; Chen, J. T.; Liu, S. T. *Orgnaometallics* **2000**, *19*, 2637.
35. Liu, W.; Brookhart, M. *Organometallics* **2004**, *23*, 6099.
36. (a) van Leeuwen, P. W. N. M. *Rec. Trav. Chim.* **1968**, *87*, 396. (b) Nakamura, Y.; Kawaguchi, S. *Chem. Commun.* **1968**, 716. (c) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: London, England, 1978; p 13.