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Synthesis, structure and norbornene polymerization activity of a bulky β-diketiminato palladium(II) complex

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ABSTRACT

A new bulky β-diketiminato palladium(II) complex was synthesized by direct reaction of $(^{i}Pr_2Ph)_2$nacnacH ($(^{i}Pr_2Ph)_2$nacnac = $CH\{C(Me)N(C_6H_3\text{-}2,6\text{-}^{i}Pr_2)\}_2$) with $Pd(OAc)_2$ which yielded $[(^{i}Pr_2Ph)_2$nacnac]Pd(OAc) as a mononuclear species with chelating nacnac and acetato ligands. Preliminary investigations into the polymerization of norbornene in the presence of BF_3OEt_2 were performed.

The first examples of monoanionic β-diketiminato ligands for applications in coordination chemistry date back to 1968 [1]. However, the ligand class remained in relative obscurity until 1995 when Brookhart published a seminal paper detailing applications of bulky α-diimine ligands in Ni(II) and Pd(II) chemistry for olefin polymerization [2]. This work initiated widespread interest in the utilization of α- and β-diimine and subsequently β-diketiminato ligands for applications across the periodic table [3]. β-diketiminato ligands with bulky *ortho*-substituents on the *N*-phenyl groups only date back to 1997 and have become increasingly popular due to both their ease of synthesis and ability to sterically protect the metal center [4a]. The popularity of β-diketiminato ligands is such that they even have their own nickname, nacnac, being the nitrogen analogues of acetylacetonato (acac) ligands. Despite the explosion in β-diketiminato coordination chemistry, relatively few (nacnac)Pd(II) complexes have been reported [4].

Concurrent with a general interest in applications of diimine ligands [5], we are interested in the polymerization of cyclic olefins by late transition-metal catalysts. Cyclic olefin polymers are referred to as "advanced materials" due to a unique combination of physical properties such as good mechanical strength, optical transparency and low birefringence [6]. Norbornene is a representative cyclic olefin monomer which can be polymerized by ring opening metathesis, cationic or radical, and vinyl addition polymerization mechanisms. Each polymerization mechanism leads to a polymer type that is different in structure and properties from the other. Palladium based catalysts usually polymerize norbornene via a vinyl addition mechanism [6,7].

In this communication we report the synthesis of a bulky mononuclear β-diketiminato Pd(II) complex, $[(^{i}Pr_2Ph)_2$nacnac]Pd(OAc) ($(^{i}Pr_2Ph)_2$nacnac = $CH\{C(Me)N(C_6H_3\text{-}2,6\text{-}^{i}Pr_2)\}_2$) and preliminary catalytic activity for the polymerization of norbornene in the presence of boron trifluoride etherate, BF_3OEt_2.

The bulky $(^{i}Pr_2Ph)_2$nacnacH ligand was prepared by the condensation of 2,6-diisopropylaniline with acetylacetone according to the literature procedure [4a]. The reaction of $(^{i}Pr_2Ph)_2$nacnacH with one equiv $Pd(OAc)_2$ in toluene affords a red solution from which red crystals of $[(^{i}Pr_2Ph)_2$nacnac]Pd(OAc) (**1**) are isolated in 75% yield (Scheme 1) [8]. Complex **1** was characterized by NMR, MS and elemental analysis. To better understand the coordination environment and nuclearity of **1**, single-crystal X-ray diffraction experiments were also performed.

The NMR spectra of **1** are consistent with a planar structure and C_{2v} symmetry in solution. The isopropyl groups and the aromatic hydrogen atoms above and below the PdNCCCN plane are equivalent with the isopropyl methyl groups being in chemically distinct environments. The characteristic ^1H NMR resonance for the central CH group of the nacnac ligand in **1** is located at 4.84 ppm. The EI mass spectra show an intense molecular ion peak at m/e 582, consistent with formation of a mononuclear species.

1 co-crystallized with two molecules of dichloromethane. The crystal structure of **1** shows a mononuclear species with the Pd(II) center adopting a typical square planar coordination geometry with chelating nacnac and acetato ligands (Fig. 1) [9]. The nacnac and the OAc ligands in **1** are almost exactly co-planar where the

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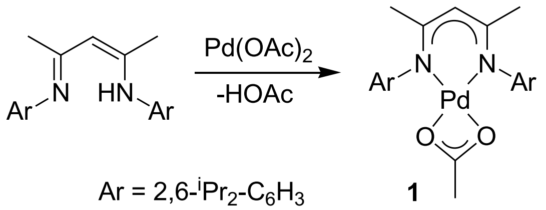
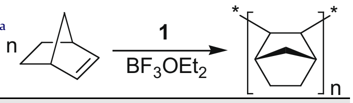


Scheme 1. Synthesis of [(^{i}Pr$_2$Ph)$_2$nacnac]Pd(OAc) (**1**).

Table 1
Norbornene (NB) polymerization results[a]



Solvent	Time (min)	NB/Pd	Yield (%)	Activity kg$_{NB}$/(mol$_{Pd}$ h)
Toluene	30	2100	2.1	8.3
Toluene	150	2800	36	38
TCB	40	3000	45	190

[a] Polymerization conditions: 35 μmol precatalyst, 20 mL solvent, 30 eq BF_3OEt_2, > 2000 eq monomer, 22 °C. TCB = 1,2,4-trichlorobenzene.

dihedral angle between the planes defined by N1–Pd1–N2 and O1–Pd1–O2 is only 1.4°. The backbone of the nacnac ligand is also essentially planar as evidenced by the torsional angle defined by Pd1–N1–C13–C14 of only 0.2° and a dihedral angle between the N1–Pd1–N2 and C13–C14–C15 planes of 1.3°. This is in contrast to a previously reported structure employing less bulky unsubstituted phenyl groups which adopts a dinuclear acetato-bridged structure, [(Ph$_2$nacnac)Pd(μ-OAc)]$_2$ with significantly twisted nacnac ligands [4e]. An analogous structure employing an acac ligand in place of the OAc group was, however, reported to be a mononuclear species [4d].

Neutral palladium precatalysts typically require an activator such as methylaluminoxane or $B(C_6F_5)_3$ to initiate norbornene polymerization. Boron trifluoride etherate, BF_3OEt_2, has recently emerged as a simple but effective activator that is relatively inexpensive and easy to use [10]. Excess amounts of BF_3OEt_2 are required to increase the ionic character of the active species and thus increase chain propagation rates.

While precatalyst **1**, in the presence of 30 eq BF_3OEt_2, displayed moderate overall yields in the polymerization of norbornene, there was a pronounced induction period of up to an hour before rapid precipitation of polynorbornene and gelation of the solution (Table 1) [11]. The prolonged induction period is likely due to the steric bulk of the nacnac ligand retarding the rate at which OAc abstraction occurs by BF_3OEt_2. Yields did not exceed 50%, which is likely due to catalyst co-precipitation with the polymer. The induction period was noticeably reduced when 1,2,4-trichlorobenzene was used as solvent in place of toluene. The resulting polynorbornenes were insoluble in common solvents such as toluene, methylene chloride, dmso, benzene, chloroform and 1,2,4-trichlorobenzene. IR analysis of the polynorbornene showed no absorbance in the 1600–1670 cm^{-1} range indicating that the polymerization occurred via a vinyl addition pathway.

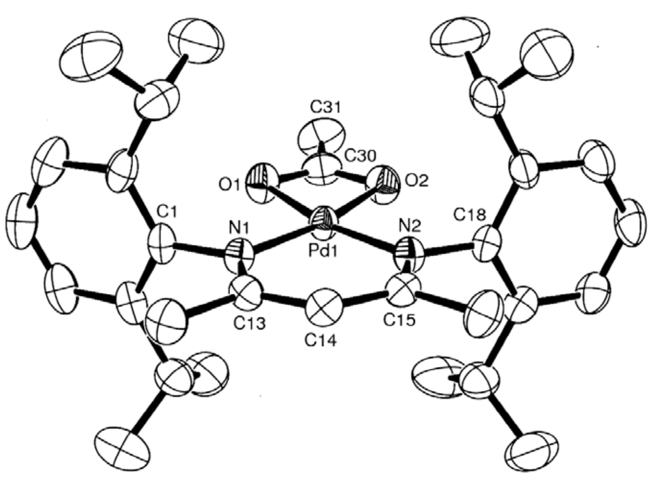


Fig. 1. ORTEP plot of **1** at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) = 1.961(4), Pd(1)–N(2) = 1.958(4), Pd(1)–O(1) = 2.108(4), Pd(1)–O(2) = 2.110(4), N(2–Pd(1)–N(1) = 92.21(17), O(1)–Pd(1)–O(2) = 62.14(15).

In conclusion, we have synthesized a new bulky acetato-β-diketiminatopalladium(II) complex employing (^{i}Pr$_2$Ph)$_2$nacnac as the ligand resulting in a mononuclear species with chelating monoanionic nacnac and acetato ligands. Preliminary investigations into the polymerization of norbornene using BF_3OEt_2 as the activator resulted in a catalyst system that exhibited relatively modest activity compared to previously reported Pd(II) systems. Investigations into alternative activation routes and polymerization of functionalized norbornene monomers are currently underway.

Acknowledgments

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Appendix A. Supplementary material

CCDC 692076 contains the supplementary crystallographic data for **1**· $(CH_2Cl_2)_2$. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.08.006.

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[8] Synthesis of **1**. Under dinitrogen, a Schlenk flask was charged with *N*,*N*-(2,6-diisopropylphenyl)-2,4-pentanediimine (0.1 g, 0.24 mmol), $Pd(OAc)_2$ (54 mg, 0.24 mmol) and toluene (10 mL) and stirred for 24 h at ambient temperature. The resulting red solution was filtered and the solvent was removed under vacuum to yield a red powder. The compound was crystallized from a saturated methylene chloride solution at −20 °C (0.104 g, 75%). ^{1}H NMR (C_6D_6, ppm): δ 7.12 (t, *J* = 7.5 Hz, 2H, CH_{Ar}), 7.06 (d, *J* = 7.5 Hz, 4H, CH_{Ar}), 4.84 (s, 1H, C*H*), 3.72 (sept, 4H, C*H*(CH$_3$)$_2$), 1.72 (d, 12H, CH(C*H*$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.21 (d, 12H, CH(C*H*$_3$)$_2$), 1.06 (s, 3H, C*H*$_3$CO$_2$) ppm. ^{13}C NMR (C_6D_6): δ 190.0 (CH$_3$*C*O$_2$), 156.0 (C=N), 144.5 (CH$_{Ar}$), 142.7 (C$_{Ar}$), 127.8 (C$_{Ar}$), 124.1 (CH$_{Ar}$), 96.0 (CH), 29.1 (CH$_3$), 24.9 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$), 22.6 (CH(CH$_3$)$_2$), 22.5 (CH$_3$CO$_2$). Anal. Calcd for $C_{31}H_{44}N_2O_2Pd$: C, 63.85; H, 7.61; N, 4.80. Found: C, 63.97; H, 7.79; N, 5.05. EI-MS (*m/z*): calcd for $C_{31}H_{44}N_2O_2Pd$ [M]$^+$: 582.2, found: 582.0.

[9] Crystal data for **1** · $(CH_2Cl_2)_2$: $C_{33}H_{48}Cl_4N_2O_2Pd$, FW = 752.93, monoclinic, crystal dimensions 0.25 × 0.20 × 0.20 mm, space group $P21/n$, a = 14.4850(4) Å, b = 14.9227(5) Å, c = 18.0734(6) Å, α = 90°, β = 105.0190(12)°, γ = 90°, V = 3773.2(2) $Å^3$, Z = 4, D_{calc}: 1.325 Mg/m^3, MoKα radiation (λ = 0.71073 Å; μ = 0.804 mm^{-1}). 35015 collected reflections, 7419 unique (R_{int} = 0.1142), Final R indices [$I > 2\sigma(I)$] were R_1 = 0.0612, wR_2 = 0.1389. Data was collected at −100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program. Cell refinement and data reductions used the programs DENZO and SCALEPACK. SIR97 was used to solve the structure and SHELXL97 was used to refine the structure. The value of R_{int} (0.11) was very large, apparently due to the irregular shape of the crystal. A full triclinic data set was obtained to obtain the best possible structure. The large range of $U_{eq(max)}/U_{eq(min)}$ for both C and H atoms is because C atoms are in very different environments. Some are held rigidly by cyclic moieties, while others have great rotational and vibrational freedom, such as the isopropyl groups on the ortho positions of phenyl groups.

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[11] In a typical polymerization reaction, the catalyst and dry solvent were added to a Schlenk flask under N_2 atmosphere. The monomer was added and the flask sealed with a septum. While stirring, BF_3OEt_2 was injected via syringe and the solution was left to stir at room temperature for the desired time or until gelation occurred due to polymer precipitation. The reaction was quenched by addition of HCl/ethanol (10% v/v), filtered and washed with ethanol. The final product was dried under vacuum until constant weight.