Organometallics **2002,** *21,* 3481−3484

Synthesis, Molecular Structures, and Norbornene Polymerization of Methallyl Nickel(II) Complexes of 2-(Diphenylamino)benzoate

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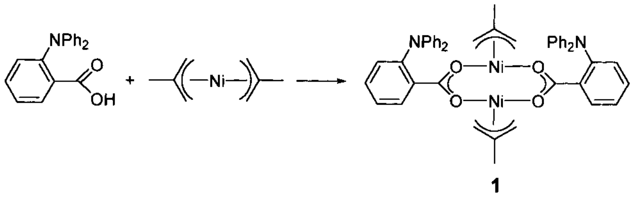
Received February 19, 2002

*Summary: Reaction of 2-(diphenylamino)benzoic acid with bis(methallyl)nickel(II) results in the dinuclear complex bis(η^3-methallyl)bis{μ-[(2-diphenylamino)benzoato-O:O′]}dinickel(II) (**1**), where the nitrogen atom does not coordinate to the nickel. Addition of $B(C_6F_5)_3$ to **1** in benzene affords the nitrogen-coordinating complex [(2-diphenylamino)benzoate tris(pentafluorophenyl)borate-κ^2N,O](η^3-methallyl)nickel(II) (**2**). The structures of **1** and **2** are confirmed by X-ray crystallography. Complex **2** shows good activity for norbornene polymerization, while complex **1** is inactive.*

Late transition metal catalysts for transforming olefins to more valuable oligomers or polymers have attracted considerable attention from both academic and industrial field.[1,2] Usually transition metal complexes are activated by electrophilic abstraction of methyl or hydride by Lewis acids.[3] Recently, it has been reported that nickel complexes containing carboxylato or carboxamidato ligands could be activated by electrophilic addition of Lewis acids to the carbonyl.[4,5] By the addition, the neutral metal complexes become zwitterionic and consequently the electron density of the metal is reduced. The novel activation process was successfully applied to the catalysts for the dimerization, oligomerization, and polymerization of ethylene. The fact that a little variation of the ligand structure may lead to profound change in the catalytic reactivities prompts us to synthesize nickel catalysts chelated by various ligand frameworks containing carbonyl functionalities. Herein, we report the syntheses of a nickel complex derived from 2-(diphenylamino)benzoate and its activation by addition of $B(C_6F_5)_3$ to the carbonyl for norbornene polymerization.

Reaction of 2-(diphenylamino)benzoic acid[6] with bis(methallyl)nickel(II) gives a clean complex with concomitant isobutylene byproduct. Only two methallyl-CH_2 signals are observed (2.36 and 1.71 ppm in C_6D_6) in the ^{1}H NMR spectrum. If the complex is a N,O-chelated square planar structure frequently observed in phosphine analogues,[7] four methallyl-CH_2 proton signals should appear. Furthermore only one methallyl-CH$_2$ carbon signal is observed in the ^{13}C NMR spectrum (50.23 ppm). These observations suggest that the structure is different from the ones observed for phosphine analogues. Broad signals are observed at 7.65 and 6.80 ppm from the protons attached to the 3 and 6 positions in the benzoate ring. The X-ray crystallography reveals that the complex is a dinuclear structure bridged by a carboxylate with a square-planar arrangement of ligands on nickel, as shown in Figure 1. The basic structure is close to that of bis(η^3-methallyl)bis(trifluoroacetato)dinickel.[8] The nitrogen donor does not coordinate to nickel, and each diphenylamino group is located eclipsed. Four C−O bond lengths are almost the same (av 1.250(3) Å), and the four Ni−O bond lengths are also almost in the same range (av 1.911(8) Å). Observation of only one methally-CH$_2$ carbon and only two methally-CH_2 protons in the ^{13}C and ^{1}H NMR spectra can be well explained by the solid structure, which suggests that the solution structure in benzene might be the same as the solid structure. Broad signals of protons on the benzoate ring might result from slow rotation of the benzoate ring containing a bulky diphenylamino group around the C(*ipso*)−CO_2 axis on the NMR time scale.



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Addition of an equimolar amount of $B(C_6F_5)_3$ to the dinuclear complex results in formation of a clean

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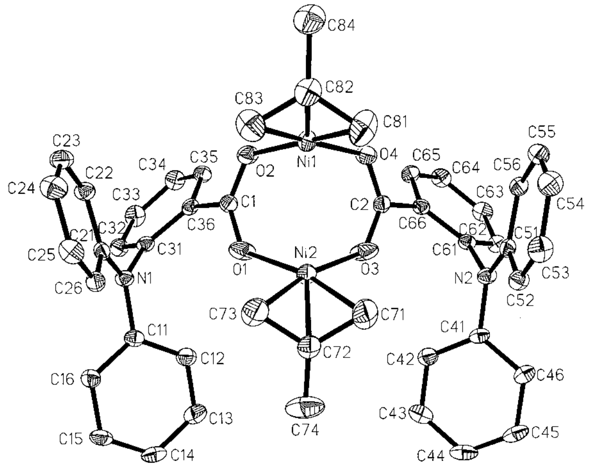


Figure 1. ORTEP view of **1**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ni(1)−O(2), 1.915(2); Ni(1)−O(4), 1.919(2); Ni(2)−O(1), 1.905(2); Ni(2)−O(3), 1.903(2); C(1)−O(1), 1.253(4); C(1)−O(2), 1.246(4); C(2)−O(3), 1.252(4); C(2)−O(4), 1.250(4); Ni(1)−C(81), 1.986(4); Ni(1)−C(83), 1.974(4); Ni(2)−C(71), 1.987(4); Ni(2)−C(73), 1.991(4); N(1)−C(21), 1.411(4); N(1)−C(11), 1.426(4); N(1)−C(31), 1.437(4).

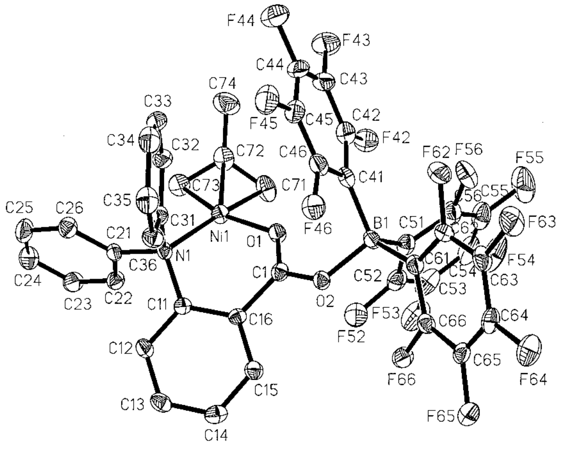


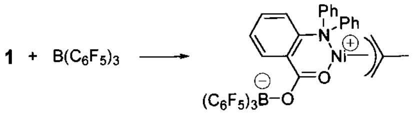
Figure 2. ORTEP view of **2**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ni(1)−O(1), 1.899(3); Ni(1)−N(1), 2.0593; Ni(1)−C(71), 1.986(5); Ni(1)−C(73), 1.989(5); C(1)−O(1), 1.229(4); C(1)−O(2), 1.297(4); B(1)−O(2), 1.546(5); N(1)−C(21), 1.487(4); N(1)−C(11), 1.486(4); N(1)−C(31), 1.474(4).

complex. Very sharp signals are observed from the (diphenylamino)benzoate ligand fragment in the ^{1}H and ^{13}C NMR spectra, but the methallyl-CH_2 protons are very broad at 1.1−1.7 ppm. Only one broad methallyl-CH$_2$ carbon signal at 56.75 ppm and one broad methallyl-CCH$_3$ carbon signal at 149.0 ppm are observed in the ^{13}C NMR spectrum. The ^{11}B NMR and ^{19}F NMR spectra are similar to those observed for [($C_6H_5)_2$-$PC_6H_4C(OB(C_6F_5)_3)O$-κ^2P,O]Ni(η^3-CH_2CMeCH_2).[4] Single crystals were grown by vapor phase addition of pentane to a benzene solution at room temperature. The solid structure is very similar to that of [($C_6H_5)_2PC_6H_4C(OB$-$(C_6F_5)_3)O$-κ^2P,O]Ni(η^3-CH_2CMeCH_2) in terms of molecular connectivity and bond lengths (Figure 2). There are two independent molecules, two benzene molecules and a pentane molecule in the unit cell. The C−ONi distance (1.229(4) or 1.234(4) Å) is characteristic of a C−O double bond, while the C−OB distance (1.297(4) or 1.288(4) Å) is more indicative of a single bond. These measurements support the zwitterionic resonance structure **2**. The N−C distance for **2** (av 1.482(7) Å) is longer than that observed for **1** (av 1.424(11) Å). For **1**, delocalization of nonbonding electrons on nitrogen to the benzene ring makes the N−C bonds shorter. If the solid structure is preserved in solution, four distinct proton signals and two carbon signals should be observed from the methallyl-CH$_2$ fragment in the NMR spectra, but only one broad carbon and proton signal is observed. These observations indicate that the complex is under some fluxional motion in benzene.

Table 1. Norbornene Polymerization Results[a]

complex	temp (°C)	yield (g)	activity (10^{-6} g/mol·h)	M_w[b]	M_w/M_n[b]
1	r.t.	0	0		
B(C_6F_5)$_3$	r.t.	0	0		
2	r.t.	0.15	3.6	633 000	2.1
2	40	0.13	3.1	592 000	2.2
2	50	0.16	3.8	448 000	2.0
2	70	0.16	3.8	358 000	1.9

[a] Polymerization conditions: 10 g norbornene solution in toluene (50 wt %), 0.5 μmol of complex, 5 min. [b] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C based on polystyrene standards.



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When ethylene gas is added to a C_6D_6 solution of **2**, the signals in the ^{1}H NMR spectrum are broadened immediately and a mixture of 1-butene and 2-butene is formed slowly. The rate is so slow that it takes more than 1 day to transform all gaseous ethylene to butene (turnover frequency, 0.5 h^{-1}). In the case of [($C_6H_5)_2$-$PC_6H_4C(OB(C_6F_5)_3)O$-κ^2P,O]Ni(η^3-CH_2CMeCH_2), the ethylene gas was disappeared immediately.[4] However, when norbornene is added to the solution, the solution becomes viscous immediately, implying the complex is active for norbornene polymerization.[9,10] The detailed norbornene polymerization results are summarized in Table 1. Neither complex **1** nor B(C_6F_5)$_3$ alone shows any activity for the norbornene polymerization, but complex **2** is highly active. The activity reaches 3.6 × 10^6 g/mol·h at room temperature, and the value is sustained up to 80 °C. The ^{1}H NMR spectra in $C_2D_2Cl_4$ confirm that the polymers are obtained exclusively by the vinyl-type polymerization. The ^{13}C-CPMAS spectrum of the soluble polynorbornene produced by Ni(acac)$_2$/MAO is different from that of the insoluble polymer produced by Pd(acac)$_2$/MAO. The latter has more signals than the former. The increase of the number of signals was interpreted in terms of cross-

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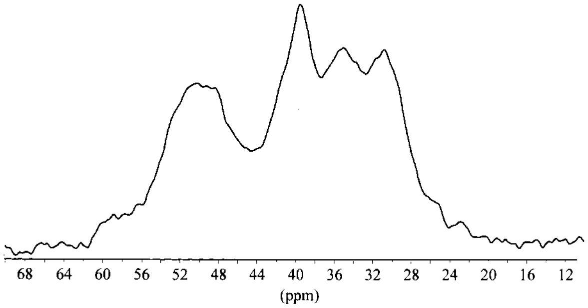

Figure 3. ^{13}C-CPMAS spectrum of polynorbornene.

linking.[11] The ^{13}C-CPMAS spectrum of the polynorbornene produced by **2** at room temperature looks like a combination of both spectra (Figure 3). Even though the determinations of the actual molecular weights are limited,[12] we can measure the molecular weights routinely by using a GPC instrument based on polystyrene standard and compare the data with previously reported ones. The molecular weight of the polymer obtained by **2** at room temperature (M_w = 633 000) is substantially lower than the one obtained by Ni(acac)$_2$/MAO catalyst under similar conditions (M_w = 3 800 000).[11] Narrow molecular distribution (MWD = 1.9−2.2) indicates the presence of a single active species in the polymerization solution. The dependency of the molecular weight on polymerization temperature follows a general trend of the metallocene catalysts: the higher the temperature, the lower the molecular weight.

Experimental Section

General Considerations. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, and benzene were distilled from benzophenone ketyl. Norbornene for polymerization was purchased from Aldrich and dissolved in toluene (Aldrich anhydrous grade) to make a 50 wt % solution. The solution was stirred for 3 days over Na/K alloy at room temperature and vacuum-transferred. NMR spectra were recorded on a Varian Unity 400 or 500 spectrometer. ^{11}B NMR and ^{19}F NMR spectra were calibrated and reported downfield from external BF$_3$·OEt$_2$ and α,α,α-trifluorotoluene, respectively.

2-(Diphenylamino)benzoic Acid. The compound was synthesized according to the literature method.[6] The NMR data are not given in the literature. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (dd, J = 8.0, 1.6 Hz, 1 H, H^{3or6}), 7.53 (ddd, J = 8.0, 7.2, 1.6 Hz, 1 H, H^{4or5}), 7.31 (ddd, J = 7.6, 7.2, 1.2 Hz, 1 H, H^{4or5}), 7.27−7.19 (m, 5 H), 7.05−6.96 (m, 6 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 169.75 (carbonyl), 147.75, 147.61, 134.03, 132.54, 130.07, 129.35, 127.67, 125.52, 123.19 ppm.

Bis(η^3-methallyl)bis{μ-[(2-diphenylamino)benzoato-*O*:*O′*]}dinickel(II) (1). Bis(methallyl)nickel(II) (0.300 g, 1.82 mmol) and 2-(diphenylamino)benzoic acid (0.474 g, 1.63 mmol) were weighed in a vial inside a glovebox. Cold toluene (20 mL, −30 °C) was added, and the solution was stirred overnight. All volatiles were removed by vacuum, and the residue was dissolved in benzene. Deep yellow single crystals, which were analytically pure and suitable for X-ray crystallography, were obtained by vapor phase addition of pentane to a benzene solution at room temperature for 2 days (0.600 g, 92%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.65 (br d, J = 6 Hz, 1 H, H^{3or6}), 7.12 (d, J = 7.6 Hz, 4 H, *o*-ph), 7.06−7.00 (m, 4 H, *m*-ph), 6.97−6.90 (m, 2 H, *p*-ph), 6.80 (br, 1 H, H^{3or6}), 6.77 (tt, J = 7.2, 1.2 Hz, 2 H, H$^{4\text{ and }5}$), 2.36 (br s, 2 H, methallyl-CH$_2$), 2.33 (br s, 3 H, methallyl-CH$_3$), 1.71 (br s, 2 H, methallyl-CH$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 178.19 (carbonyl), 148.84, 145.39, 136.66, 131.69, 131.61, 131.46, 129.44, 125.83, 123.36, 122.82, 121.83, 50.23 (methallyl-CH$_2$), 23.39 (methallyl-CH$_3$) ppm. Anal. Calcd for C$_{46}$H$_{42}$N$_2$Ni$_2$O$_4$: C, 68.7; H, 5.3. Found: C, 68.9; H, 5.6.

Table 2. Crystallographic Parameters[a]

	1	2
formula	$C_{46}H_{42}N_2Ni_2O_4$	$C_{49.5}H_{33}BF_{15}NNiO_2$
fw	804.24	1028.29
a, Å	16.921(2)	15.847(4)
b, Å	8.7318(12)	17.263(5)
c, Å	27.104(4)	18.737(5)
α, deg	90	109.329(5)
β, deg	106.550(2)	103.015(5)
γ, deg	90	102.690(5)
V, Å^3	3838.8(9)	4465(2)
space group	P2(1)/c	P-1
d(calc), g cm^{-1}	1.392	1.530
Z	4	4
μ, mm^{-1}	1.028	0.540
no. of data collected	32 626	39 636
no. of unique data	6754	15 660
no. of variables	521	1288
R (%)	4.87	5.08
R_w (%)	11.9	7.01
goodness of fit	1.004	0.820

[a] All data collected at 150 K with Mo Kα radiation, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 4.0\sigma(F)$, $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]^2]^{1/2}$ with $F_o > 4.0\sigma(F)$.

[(2-Diphenylamino)benzoate tris(pentafluorophenyl)borate-κ^2*N,O*](η^3-methallyl)nickel(II) (2). Bis(η^3-methallyl)bis{μ-[(2-diphenylamino)benzoato-*O*:*O′*]}dinickel(II) (**1**) (0.100 g, 0.124 mmol) and B(C$_6$F$_5$)$_3$ (0.127 g, 0.248 mmol) were weighed in a flask inside a glovebox. Toluene (10 g) was added, and the solution was stirred overnight. Removal of solvent gave quantitatively a greenish yellow powder, which is quite pure by ^{1}H NMR. Single crystals for X-ray crystallography and elemental analysis were grown by vapor phase addition of pentane to a benzene solution at room temperature overnight. One benzene and a half pentane molecule are incorporated per each molecule in the single crystals. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 8.69 (dd, J = 7.6, 1.6 Hz, 1 H, H^{3or6}), 6.85 (t, J = 7.2 Hz, 2 H, *p*-ph), 6.82 (td, J = 7.6, 1.2 Hz, 1 H, H^{4or5}), 6.76 (t, J = 8.4 Hz, 4 H, *m*-ph), 6.68 (ddd, J = 8.0, 7.6, 1.2 Hz, 1 H, H^{4or5}), 6.66 (d, J = 7.6 Hz, 4 H, *o*-ph), 6.18 (dd, J = 8.0 Hz, 1.2 Hz, 1 H, H^{3or6}), 1.82 (s, 3 H, methallyl-CH_3) 1.1−1.7 (br, 4 H, methallyl-CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 172.52 (carbonyl), 148.8 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 149.0 (br, methallyl-*C*CH$_3$), 148.34, 140.0 (dm, $^1J_{CF}$ = 250 Hz, *o*-CF), 137.5 (dm, $^1J_{CF}$ = 250 Hz, *m*-CF), 134.91, 134.11, 129.31, 129.30, 128.76, 127.65, 127.12, 126.84, 124.87, 56.73 (br, methallyl-*C*H$_2$), 21.73 (methallyl-*C*H$_3$) ppm. ^{19}F NMR (376 MHz, C$_6$D$_6$): δ −77.0 (d, $^3J_{FF}$ = 19 Hz, *ortho*-F), −102.30 (t, $^3J_{FF}$ = 20 Hz, *para*-F), −107.76 (br t, $^3J_{FF}$ = 18 Hz, *meta*-F) ppm. ^{11}B NMR (C$_6$D$_6$, 128 MHz): δ −3.1 ppm. Anal. Calcd for C$_{41}$H$_{21}$BF$_{15}$NNiO$_2$·C$_6$H$_6$·1/2(C$_5$H$_{12}$): C, 57.8; H, 3.24. Found: C, 57.6; H, 3.10.

Norbornene Polymerization. The vial containing 10 g of norbornene solution in toluene (50 wt %) was immersed in an oil bath whose temperature had been set to a given value inside a glovebox, and the solution was stirred for 15 min. The catalyst in toluene (0.50 μmol) was added. The solution was stirred vigorously for 5 min. The viscous solution was brought out from the drybox and poured into a flask containing acetone. The white precipitates were collected by filtration and dried

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(12) In the case of the rigid polymers as polythiophenes, the GPC determinations using polystyrene standards overestimate the molecular weights severely. See: Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017.

under vacuum overnight. ^{1}H NMR spectra were obtained at 100 °C in $C_2D_2Cl_4$. The ^{13}C-CPMAS spectrum was measured at 100 °C, pulse angle 90°, relaxation delay 3 s using a Bruker MSL 300.

Crystallographic Studies. Crystals were mounted onto a thin glass fiber with paratone-8277 and immediately placed in a cold nitrogen stream at 150 K on a Bruker SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation). A full sphere of intensity data was collected in 2252 frames with ω scans (width of 0.30° and exposure time of 30 s per frame). The numbers of reflections used for the least-squares refinement of unit cell parameters (at 150 K) were 8192 and 4838 for **1** and **2**, respectively. The empirical absorption corrections based on the equivalent reflections were performed using the program SADABS. The structures were solved by direct methods followed by successive difference Fourier methods. All calculations were performed using SHELXTL (version 5.0.3). Full-matrix refinements were against F^2. Hydrogen atoms were calculated at idealized positions and their atomic positions were refined as riding atoms of their parent carbon atoms. The crystal data and refinement results are summarized in Table 2.

Acknowledgment. The authors are grateful to Prof. G. C. Bazan at U.C. Santa Barbara for helping to publish this result and Dr. X. Bu for the single-crystal diffraction studies. This work was supported by grant No. R05-2002-000-00155-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

Supporting Information Available: Complete details for crystallographic studies of **1** and **2**. The material is available free of charge via the Internet at http://pubs.acs.org.

OM020134G