Zwitterionic Nickel(II) Complexes: Synthesis, Characterization, Decomposition, and Stoichiometric and Catalytic Reactivities

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Abstract

Zwitterionic nickel(II) compounds with a borate-containing anionic bidentate phosphine ligand (PBP⁻) have been synthesized and some of them crystallographically characterized. The methyl complex, (PBP⁻)Ni⁺CH₃(NCCH₃), reacts with H₂ to form an 12-membered macrocycle containing three Ni nuclei and reacts with carbon monoxide (CO) to afford the acetyl complex (PBP⁻)Ni⁺COCH₃(CO). The square planar acetyl complex is stable in solution under one atmosphere of CO but undergoes irreversible decomposition under high CO pressure at room temperature. X-Ray crystallographic characterization of a decomposition product revealed fragmentation of the anionic borate under high pressure. (PBP⁻)Ni⁺COCH₃(CO) is an active catalyst for ethylene-CO copolymerization, but its productivity is low likely due to its instability under high CO pressure.

Key words: Anionic phosphine, zwitterionic nickel compound, CO-ethylene copolymerization

1. Introduction

Zwitterionic transition metal complexes bearing an anionic phosphine ligand display electronic properties between the isoelectronic cationic and neutral analogs [1]. Peters extensively studied a variety of the zwitterionic complexes and explored the concept for catalyst development and to gain insights of reaction mechanisms. Particularly related to the present work, Peters and coworker have shown that zwitterionic palladium complexes with an anionic bidentate phosphine ligand are as active as the cationic analog with a neutral ligand as catalysts for ethylene-CO copolymerization [2].

Palladium catalysts [3] have generally shown much better productivities and activities than do Ni catalysts [4] for CO-ethylene copolymerization and are the catalysts adopted by commercial processes [5]. However, palladium is much more expensive than nickel. A nickel catalyst that is somewhat less active and productive than the palladium catalysts might still have a cost advantage. We reasoned that the enhanced electron-donating ability of anionic phosphine ligand [1,2] might alleviate a possible catalyst resting state in Ni-catalyzed CO-ethylene copolymerization [6] and recently reported a zwitterionic Ni catalyst that possessed an extraordinary initial activity for catalyzing the copolymerization [7]. Our exploration along this line began with the nickel analogs of the palladium complexes reported by Peters. We account here the synthesis and characterization of these zwitterionic nickel complexes and their stoichiometric and catalytic reactivities.

2. Results and Discussion

Synthesis and Stoichiometric Reactions. Reaction of ligand **1** with an excess amount of in situ formed (TMEDA)NiMe₂ [8] provided an effective entrance to the nickel chemistry (Scheme 1). Compound **2** was isolated in a moderate yield based on the stoichiometry of the ligand.

Scheme 1. Synthesis and reactivity of zwitterionic Ni complexes.

Unlike the Pd analog [2], reaction of **2** with a proton source in THF did not lead to any isolable product. Rather a strongly coordinating Lewis base was necessary to stabilize the methyl zwitterionic nickel complex. The formation of **3** was nearly quantitative in acetonitrile but separation of the $\text{ASN}^+\text{BPh}_4^-$ salt from **3** proved challenging due to their similarity in solubility in various solvents. As the result, in situ generated **3** was used directly for subsequent synthesis.

Upon exposure to one atmosphere of H_2 , the orange acetonitrile solution of **3** turned red within minutes and gave copious red-orange precipitate. The precipitate did not dissolve in any common organic solvents. When H_2 was allowed to slowly diffuse into the solution without disturbance, X-ray quality crystals were obtained, and the structure of the macrocyclic product (**4**) was determined (Figure 1). The metallomacrocyclic **4** is an ensemble of three Ni(II) centers

Figure 1. The structure of compound **4** with 35% probability ellipsoids. Hydrogen atom positions have been omitted for clarity. Selected bond lengths and angles: N(1)-Ni(2) 1.883(4) Å, N(2)-Ni(3) 1.883(4) Å, N(3)-Ni(1) 1.879(4) Å, C(39)-Ni(1) 1.995(4) Å, C(79)-Ni(2) 1.995(4) Å, C(119)-Ni(3) 2.012(4) Å, Ni(1)-P(2) 2.1765(14) Å, Ni(1)-P(1) 2.2257(14) Å, Ni(2)-P(4) 2.1511(13) Å, Ni(2)-P(3) 2.2097(12) Å, Ni(3)-P(6) 2.1488(12) Å, Ni(3)-P(5) 2.1982(12) Å, N(3)-Ni(1)-C(39) 92.01(18)°, N(1)-Ni(2)-C(79) 88.48(18)°, N(2)-Ni(3)-C(119) 90.47(18)°.

and three monoanionic $-\text{CH}_2\text{C}\equiv\text{N}-$ bridges, producing an irregular hexagon structure. The metal sites exhibit slightly distorted square planar geometries, comprised of the bidentate phosphine ligand, the nitrogen atom of the activated acetonitrile, and a Ni-C bond produced from C-H bond activation. The Ni-N-C-C bridges are nearly linear, but the C-C-Ni bond angles are bent

(116.4(3), 104.7(3) and 103.8(3)°), which are indicative of sp^3 hybridized carbon atoms from the activated methyl groups. The Ni-C bond lengths are typical for σ Ni-alkyl complexes.

When **3** was exposed to H_2 in an NMR tube in CD_3CN , CH_4 and H-D molecules were observed in the 1H NMR spectrum. Therefore, the formation of **4** is the result of first hydrogenolysis of the Ni-Me bond and then σ -bond metathesis between the Ni-H bond and the H-C bond in CH_3CN [9]. The postulated Ni-H intermediate was not observed, indicating that hydrogenolysis must be the rate-limiting step.

Upon exposure to one atmosphere of CO, the orange acetonitrile solution of **3** immediately turned yellow. The $ASN^+BPh_4^-$ salt carried over from the formation of **3** was precipitated by addition of a copious amount of diethyl ether. The crude product, **5**, which contained a small but unneglectable amount of acetonitrile-coordinated species, was precipitated by addition of hexane into the mother liquor. Re-dissolving the crude product in diethyl ether and exposure to CO one more time was necessary in order to completely substitute and remove CH_3CN . Compound **5** was stable in solution under one atmosphere of CO for several days. This is in contrast to its palladium analog, which is not stable under similar conditions [2]. However, **5** decomposed quickly in the absence of CO at room temperature in solution under N_2 . For this reason, solution-phase characterizations of **5** were all carried out under CO. The C=O stretching vibration of the acetyl group (ν_{ac} at 1688 cm^{-1}) and the $C\equiv O$ stretching vibration of the coordinated CO ligand (ν_{CO} at 2053 cm^{-1}) are red-shifted in the infrared spectrum of **5** compared to those of its cationic analog [6], $(DPPP)Ni^+$ -acetyl (ν_{ac} at 1698 cm^{-1} and ν_{CO} at 2082 cm^{-1} , $DPPP = 1,3$ -bis(diphenylphosphino)propane). This is consistent with the notion that the anionic phosphine ligand is more electron-donating than its neutral analog. In addition to spectroscopic methods and elemental analysis, the structure of **5** was confirmed by X-ray crystallography (Figure 2).

Figure 2. The structure of compound **5** with 35% probability ellipsoids. Hydrogen atom positions have been omitted for clarity. Selected bond lengths and angles: C1-Ni1 1.762(2) Å, C2-Ni1 1.946(2) Å, C2-C3 1.501(3) Å, C1-O1 1.135(3) Å, Ni(1)-P(1) 2.2118(6) Å, Ni(1)-P(2) 2.2748(6) Å, C1-Ni1-C2 85.06(9)°, O2-C2-C3 123.8(2)°.

Structural elucidation of **5** reveals a square planar Ni(II) complex with a single carbonyl and an acyl group bound to the metal. The metal carbon length is as expected for a single bond (1.946(2) Å) and the geometry of the acetyl group is consistent with a sp^2 hybridized geometry about the acyl carbon atom.

Copolymerization Catalyzed by 5 and Stability of 5. Compound **5** did catalyze the copolymerization of CO and ethylene to produce the alternating copolymer (Table 1). Increase in

Table 1. Productivities of **5** and its Pd analog as catalysts for CO-ethylene copolymerization.

Entry	catalyst	CO (psi)	Ethylene (psi)	Reaction Time (min)	Yield (g)	Productivity (kg·mol ⁻¹)
1 ^a	5	50	600	120	0.27	21
2 ^a	5	300	300	120	0.034	2.6
3 ^b	Pd analog	100	100	60	0.36	39

^a Polymerization conditions: 0.013 mmol of **5** in 10 mL toluene at 45 °C.

^b Data adopted from ref. 2. Polymerization conditions: 0.0093 mmol of Pd catalyst in 10 mL THF at room temperature.

CO pressure and decrease in ethylene pressure decrease the productivity of **5** (entry 2). Complex **5** completely deactivates within 2 h even under 50 psi of CO. Longer reaction time did not increase the polyketone yield. The optimal productivity of **5** (entry 1) is somewhat lower than those of the zwitterionic and cationic Pd catalysts reported by Peters but on the same order of magnitude. These productivities are several orders of magnitudes lower than those observed in commercial processes using cationic Pd catalysts³ likely because the solvent in the latter cases is methanol and excess of acids and quinones are added to regenerate the deactivated catalysts. In our case, the presence of an acid, protic solvent, or quinone completely deactivates **5**.

In order to understand the possible mechanism for catalyst deactivation, we subjected **5** to high pressure CO and monitored the decomposition process by in situ FT-IR (Figure 3). The

Figure 3. Decomposition of **5** under high-pressure CO monitored by in situ FT-IR. The bottom spectrum was recorded immediately after exposure of a diethyl ether solution of **5** to 200 psi of CO. The middle spectrum was recorded after 2 h exposure to 200 psi of CO. Top spectrum was recorded after 2 h exposure to 200 psi of CO and then 2 h exposure to 500 psi of CO. Excess of free CO is subtracted from the spectra.

initial spectrum of a diethyl ether solution of **5** under 200 psi of CO is identical to that under one atmosphere of CO. The band at 1688 cm^{-1} is attributable to the C=O stretching vibration of the acetyl group (ν_{ac}), and the band at 2053 cm^{-1} is attributable to the C $\equiv$ O stretching vibration of the coordinated CO ligand (ν_{CO}). The 5-coordinate **5**-CO was not observed. Decomposition was obvious after 2 h under 200 psi of CO. After an additional 2 h under 500 psi of CO, the ν_{ac} and ν_{CO} bands of **5** became barely observable. A decomposed solution was kept under high pressure for several days, and some yellow crystals precipitated from the solution. The structure of this decomposition product, **6** (Scheme 1), was characterized by X-ray crystallography (Figure 4). Compound **6** is a five-coordinate nickel complex with a side-bound P-CH₂ ligand. There are very few structurally characterized examples of this type of side-bound P-CH₂ ligand in organometallic complexes, with the known structures having been reported for low-coordinate Ni compounds [10]. However, **6** exhibits similar structural characteristics as the previously reported examples, with nearly identical Ni-P bond lengths and a slightly lengthened Ni-C distance. The observation of **6** as a decomposition product suggests fragmentation of the borate center of the ligand in the decomposition process. One would suspect that the relatively strong nucleophilicity of the aliphatic borate moiety, Ph₂PCH₂B⁻, is detrimental for its stability. Therefore, a stable anionic borate center with improved resistance to electrophilic attack is necessary for improvement of the catalytic productivity.

Figure 4. The structure of compound **6** with 35% probability ellipsoids. Hydrogen atom positions have been omitted for clarity. Selected bond lengths and angles: Ni(1)-P(3) 2.1567(9) Å, C(51)-Ni(1) 2.044(3) Å, C(52)-Ni(1) 1.827(3) Å, C(51)-P(3) 1.754(3) Å, Ni(1)-P(1) 2.2018(8) Å, Ni(1)-P(2) 2.2294(9) Å, C(52)-Ni(1)-C(51) 97.96(13)°, C(52)-Ni(1)-P(3) 116.79(10)°, C(51)-Ni(1)-P(3) 49.28(9)°.

3. Conclusion

Several zwitterionic nickel(II) compounds with Peters' borate-containing anionic bidentate phosphine ligand (PBP⁻) have been isolated and characterized. The methyl complex (**3**) reacts with H₂ to form a 12-member metallomacrocycle (**4**) and reacts with CO to afford the acetyl complex (**5**). Complex **5** catalyzes the alternating copolymerization of CO and ethylene, but the catalytic productivity is low. The low productivity is attributed to the instability of **5** under high pressure CO. The decomposition of **5** under high pressure CO is likely due to the high reactivity of the aliphatic borate moiety, Ph₂PCH₂B⁻.

4. Experimental

All manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glove box or using standard Schlenk techniques. Solvents were dried using an MBraun MS-SPS-800 solvent purification system. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. Chemical shifts (δ) were reported in ppm. For ¹H and ¹³C spectra, solvent peaks were used as chemical shift references. For ³¹P spectra, an external 85% H₃PO₄ was used as the reference. Elemental analysis was carried out by Microanalysis, INC., Delaware. Ligand **1** was synthesized following a procedure in the literature [11] (TMEDA)NiMe₂ was in situ generated following a procedure in the literature [7].

4.1. Synthesis of **2**.

Ligand **1** (2.00 g, 2.9 mmol) was suspended in 40 mL of anhydrous acetonitrile in a 100 mL Schlenk flask. The flask was cooled to 0 °C, and to it was added (TMEDA)NiMe₂ (15 mL of 0.468 M solution in THF, 7.0 mmol). The mixture was stirred at 0 °C for 1 h and then at room temperature for 16 h. The solvent was removed under vacuum, and the resultant brown oily substance was stirred over anhydrous diethyl ether (30 mL) and solidified after 8 h. The liquid was decanted, and the crude product was crystallized from a mixture of THF and diethyl ether (1:1 volume ratio) at -45 °C. A bright yellow crystalline product was obtained after crystallization (1.10 g, 49% yield). ¹H NMR (acetone-d₆, 300 MHz): δ -0.45 (d, J = 6 Hz, 6H, Ni(CH₃)₂), 1.66 (br t, 4H, CH₂PPh₂), 2.28 (m, 8H, N(CH₂CH₂)₂), 3.75 (m, 8H, N(CH₂CH₂)₂), 6.57-6.68 (m, 6H), 6.95 (b, 4H), 7.04-7.13 (m, 12H), 7.46 ("t", J = 8 Hz, 8H); ¹³C{¹H} NMR (acetone-d₆, 75 MHz): δ 1.8 (dd, J = 84 and 24 Hz, Ni(CH₃)₂), 23.0 (br, CH₂PPh₂), 22.6 (N(CH₂CH₂)₂), 63.6 (N(CH₂CH₂)₂), 122.2, 126.5, 127.9, 128.2, 133.2, 135.8 (d, J = 5 Hz, ortho PPh₂), 141.8 ("t", J = 14 Hz, ipso PPh₂), 166.8 (br, ipso BPh₂). ³¹P{¹H} NMR (acetone-d₆, 121 MHz): δ 32.8 (s). Anal. Calcd. For C₄₈H₅₆BN₂NiP₂: C 74.06; H 7.25; N 1.8. Found: C 73.44; H 7.02; N 1.5.

4.2. Formation of **3**.

Compound **2** (500 mg, 0.64 mmol) was partially dissolved in anhydrous acetonitrile (13 mL) in a 100 mL Schlenk flask. In a 25 mL Schlenk flask, [HN(*i*Pr)₂Et][BPh₄] was dissolved in anhydrous acetonitrile (2 mL), and the solution was added to the flask with the nickel compound. Immediate methane formation was visible, and the reaction was allowed to stir at room temperature for 30 min. Anhydrous diethyl ether (15 mL) was added to precipitate the [ASN][BPh₄] side product. The product, along with [ASN][BPh₄] remaining in solution, was filtered to a new 100 mL flask. Solvent was removed under vacuum to afford the yellow-orange powder product containing ~10 mol% of [ASN][BPh₄] impurity (300 mg, ~60% yield). ¹H NMR (acetonitrile-d₆, 300 MHz): δ -0.35 ("t", J = 8 Hz, 3H, NiCH₃), 1.68 (br t, J = 32 Hz, 4H,

CH_2PPh_2), 6.68-6.78 (m), 6.95 (b), 7.24-7.33 (m), 7.39-7.46 (m), 7.60 (br); $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , 121 MHz): δ 52.8 (d, $J = 54$ Hz) and 36.2 (d, $J = 54$ Hz).

4.3. Synthesis of **4**.

The crude compound **3** (50 mg) was dissolved in anhydrous acetonitrile (10 mL) in a 20 mL Schlenk tube. The Schlenk tube was briefly evacuated, and H_2 (1 atm) was introduced. The solution was allowed to sit without stirring. A large amount of red-orange crystals formed overnight. The crystals were isolated by filtration (48 mg, 98% yield). The crystals could not be dissolved in any solvents that did not cause decomposition. Its solid state structure was determined by X-ray crystallography.

4.4. Synthesis of **5**.

The crude compound **3** (200 mg) was dissolved in anhydrous acetonitrile (10 mL) in a 50 mL Schlenk flask. The solution was exposed to CO (1 atm) at room temperature and stirred for 30 min. The volume of the solution was then reduced to about 2 mL under vacuum. After the solution was exposed to CO (1 atm) again, diethyl ether (10 mL) was added to precipitate $[\text{ASN}][\text{BPh}_4]$ carried over from formation of **3**. The $[\text{ASN}][\text{BPh}_4]$ precipitate was removed by filtration under CO (1 atm), and hexane was added to the solution to precipitate a yellow crude product. The yellow crude product was re-dissolved in diethyl ether (10 mL) under CO (1 atm). A layer of hexane (20 mL) was laid on top of the solution and allowed to diffuse at 0 °C. A yellow crystalline precipitate was obtained after a few days. The crystalline solid was isolated by filtration (114 mg, 62% yield). ^1H NMR (C_6D_6 , under 1 atm CO, 300 MHz): δ 1.82 (s, 3H, $\text{NiC}(\text{O})\text{CH}_3$), 2.01 (br, 2H, CH_2PPh_2), 2.08 (br, 2H, CH_2PPh_2), 6.75-6.89 (m, 10H), 7.21-7.30 (m, 12H), 7.35 (t, $J = 7$ Hz, 4H), 7.76 (d, $J = 7$ Hz, 4H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , under 1 atm CO, 121 MHz): δ 17.6 (b). Anal. Calcd. For $\text{C}_{41}\text{H}_{37}\text{BNiO}_2\text{P}_2$: C 71.04; H 5.38; N 0.0. Found: C 70.88; H 5.02; N 0.0.

4.5. Polymerization catalyzed by **5**.

Catalyst **5** (0.0125 mmol, 12 mg) was dissolved in a 125-mL Parr reactor with 10 mL toluene in a glove box. Then, the reactor was pressurized with ethylene and CO. The reactor was kept in a pre-heated oil bath at 45 °C for 2 h. The pressure was released. Polyketone was then isolated by filtration. After dried overnight in a vacuum oven, a white powder was obtained and weighed. The yields are given in Table 1. ^1H NMR of the polyketone product can be found in Supplemental Information.

4.6. X-ray crystallographic study of **4**, **5**, and **6**.

Single crystals of **4** were obtained directly from the synthesis (see above). Single crystals of **5** were obtained by slow evaporation of a diethyl ether solution of **5** in an H-tube under CO (1 atm) at room temperature. Single crystals of **6** were obtained after a diethyl ether solution of **5** was pressurized with CO (1000 psi) and kept at room temperature for several days.

X-ray Data Collection and Structure Determination: X-ray intensity data for compounds **4**, **5**, and **6** were collected on a Bruker CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Mo $K\alpha$ $\lambda = 0.71073$ Å or **4** and **6**, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å for compound **5**). Crystals were mounted on a cryoloop using Paratone oil and placed under a stream of nitrogen at 100 K. The detector was placed at a distance of 4.000 cm from the crystal. Crystal data and structure refinement parameters are summarized in Table 2.

Table 2: Crystal data and structure refinement parameters for **4**, **5** and **6**.

Compound	4	5	6
Empirical formula	C ₁₂₀ H ₁₀₆ B ₃ N ₃ Ni ₃ P ₆	C ₄₁ H ₃₇ BNiO ₂ P ₂	C ₅₂ H ₄₆ BNiOP ₃
Formula weight	1984.46	693.17	849.32
Wavelength	0.71073 Å	1.54178	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2(1)/c	P-1
Unit cell dimensions	a = 12.464(2) Å b = 20.080(3) Å c = 24.708(4) Å α = 85.186(2)° β = 77.524(2)° γ = 77.089(2)°	a = 12.464(2) Å b = 20.080(3) Å c = 24.708(4) Å β = 94.845(3) °	a = 11.7078(16) Å b = 13.8338(19) Å c = 14.849(2) Å α = 91.862(2)° β = 96.781(2)° γ = 107.771(2)°
Volume	5881.3(16) Å ³	3476.4(4)	2268.2(5) Å ³
Z	2	4	2
Density (calculated)	1.121 Mg/m ³	1.324	1.244 Mg/m ³
Absorption coefficient	0.602 mm ⁻¹	1.324 mm ⁻¹	0.570 mm ⁻¹
F(000)	2072	1448	888
Crystal size	0.20 x 0.03 x 0.02 mm	0.19 x 0.14 x 0.08 mm	0.20 x 0.20 x 0.07 mm
Theta range for data collection	2.19 to 27.18°	6.34 to 66.56°	2.15 to 24.70°
Index ranges	-16 ≤ h ≤ 16, -26 ≤ k ≤ 26, -31 ≤ l ≤ 31	-10 ≤ h ≤ 11, -17 ≤ k ≤ 17, -23 ≤ l ≤ 24	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	49371	18773	15829
Independent reflections	26144 [R(int) = 0.0698]	5085 [R(int) = 0.0232]	7795 [R(int) = 0.1166]
Completeness to theta	96.2%	95.7%	98.5 %
Max. and min. transmission	0.7456 and 0.6127	0.7529 and 0.6594	0.7452 and 0.6314
Data / restraints / parameters	26114 / 0 / 1216	5085 / 0 / 425	7795 / 0 / 523
Final R indices [I > 2σ(I)]	R1 = 0.0642, wR2 = 0.1627	R1 = 0.0314, wR2 = 0.888	R1 = 0.0458, wR2 = 0.1247
R indices (all data)	R1 = 0.1181, wR2 = 0.2028	R1 = 0.0346, wR2 = 0.0914	R1 = 0.0592, wR2 = 0.1357
Largest diff. peak and hole	0.771 and -0.430 Å ⁻³	0.353 and -0.282 Å ⁻³	0.700 and -0.642 Å ⁻³

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