# Trimethylphosphine-bis(benzyl)nickel: Synthesis and Characterization

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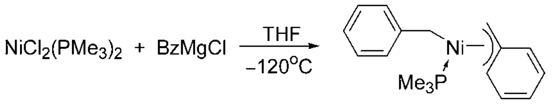
Dedicated to Richard R. Schrock on the occasion of his 60th birthday.

**Abstract:** The reaction of $NiCl_2(PMe_3)_2$ with 2 equivs. of benzylmagnesium chloride in THF at −120 °C affords $Ni(\eta^1\text{-}CH_2C_6H_5)(\eta^3\text{-}CH_2C_6H_5)PMe_3$. The formation of this thermally unstable compound is accompanied by bisbenzyl and Ni(0) side products. Single crystal X-ray analysis confirms the presence of the $\eta^1$-benzyl and $\eta^3$-benzyl ligands. Reaction of $Ni(\eta^1\text{-}CH_2C_6H_5)(\eta^3\text{-}CH_2C_6H_5)PMe_3$ with 2-(diphenylphosphino)benzoic acid and activation with $B(C_6F_5)_3$ gave the expected product [2-(diphenylphosphino)benzoate tris(pentafluorophenyl)borate-$\kappa^2$P,O]($\eta^3$-benzyl)nickel.

**Keywords:** ethylene polymerization; nickel-benzyl complexes, nickel catalysis, phosphines

Nickel-allyl complexes are key intermediates in a number of catalytic and stoichiometric reactions.[1,2] Substantial long-standing efforts[3] have been dedicated towards bis(benzyl)nickel-type structures and an increasing number of nickel $\eta^3$-benzyl complexes have been reported since the mid 1980 s.[4] However, the number of bis(-benzyl) nickel (II) species remains limited, in part because of a lack of suitable starting materials. The reaction of nickel(II) dihalides with benzyl-Grignard species does not provide the target compounds and leads to black metallic reduction products [Ni(0)] and bisbenzyl.[3,5] Stabilization of bis(alkyl)Ni(II) complexes is typically improved by phosphines, such as triethylphosphine[6] and trimethylphosphine, which have been successfully employed for different *ortho*-substituted benzyl nickel complexes.[7] Nevertheless, the only isolated and characterized bis(benzyl)nickel(II) compound [2,2′-dipyridine-bis(benzyl)nickel][8] is supported by the bidentate 2,2′-bipyridine ligand.



**Scheme 1.** Synthesis of trimethylphosphine-bis(benzyl)nickel.

Our interest in benzyl nickel complexes based on ligands such as diphenylphosphine benzoic acid, α-iminocarboxamides, and pyridinecarboxamides for use in tandem polymerization reactions[2] led us to consider alternative synthetic methods. In this contribution, we provide details for the synthesis, characterization and reactivity of $Ni(\eta^1\text{-}CH_2C_6H_5)(\eta^3\text{-}CH_2C_6H_5)PMe_3$ (Scheme 1). To the best of our knowledge, this compound is unique in having two benzyl fragments on a nickel center supported by a single two electron donor ligand.

A solution of nickel dichloride bis(trimethylphosphine) $[NiCl_2(PMe_3)_2]$[9] in THF at −120 °C was treated with a 2 M solution of benzylmagnesium chloride (BzMgCl) in THF under argon. After dropwise addition, the reaction flask was closed and kept at −90 °C overnight. Evaporation of volatiles at −40 °C, extraction with pentane, filtration, and removal of the solvent provided a viscous purple oil. Black metallic solids remained on the frit, which suggests the formation of metallic nickel. $^1$H NMR spectroscopy shows bisbenzyl[10] and $Ni(PMe_3)_4$,[11] which account for ~ 20% of the integrated proton resonances. New peaks are observed at (in ppm) 2.42, 1.13 and 0.70, which are consistent with $\eta^3$-$CH_2C_6H_5$, $\eta^1$-$CH_2C_6H_5$ and $PMe_3$ signals, respectively, in the appropriate integration ratios. Repeated reactions gave rise to the same signals without perturbation of their relative integrations.

Purification of the product was accomplished by multiple recrystallizations. Complete separation from $Ni(PMe_3)_4$ is difficult and accounts for the low yield of the isolated pure product (11%). Decomposition of a $C_6D_6$ solution takes place quickly at room temperature. Single crystals suitable for X-ray diffraction studies were obtained from a pentane solution at −35 °C.[12] The results of the study are summarized in Figure 1 and confirm the molecular structure of the product to be $Ni(\eta^1\text{-}CH_2C_6H_5)(\eta^3\text{-}CH_2C_6H_5)PMe_3$. Selected bond

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lengths and angles are shown in Table 1. The C(8)–Ni(1) [1.977(4) Å] bond distance ($\eta^1$-benzyl group) is shorter than the C(1)–Ni(1) [2.001(4) Å], C(2)–Ni(1) [2.019(4) Å], and especially C(3)–Ni(1) [2.245(4) Å] bonds, which correspond to the $\eta^3$-coordinated benzyl.

**Table 1.** Selected bond lengths and angles for trimethylphosphine-bis(benzyl)nickel.

| Selected bond lengths (Å) and angles (°) | |
|---|---|
| Ni(1)–C(1) | 2.001(4) Å |
| Ni(1)–C(2) | 2.019(4) Å |
| Ni(1)–C(3) | 2.245(4) Å |
| Ni(1)–C(8) | 1.977(4) Å |
| Ni(1)–P(1) | 2.1244(10) |
| C(1)–C(2) | 1.439(5) |
| C(8)–C(9) | 1.465(5) |
| C(8)–Ni(1)–C(1) | 162.80(16) |
| C(8)–Ni(1)–C(2) | 120.94(16) |
| C(8)–Ni(1)–P(1) | 104.93(12) |
| C(1)–Ni(1)–P(1) | 91.05(11) |
| C(2)–Ni(1)–P(1) | 131.35(11) |
| C(8)–Ni(1)–C(3) | 96.74(16) |
| P(1)–Ni(1)–C(3) | 154.20(11) |

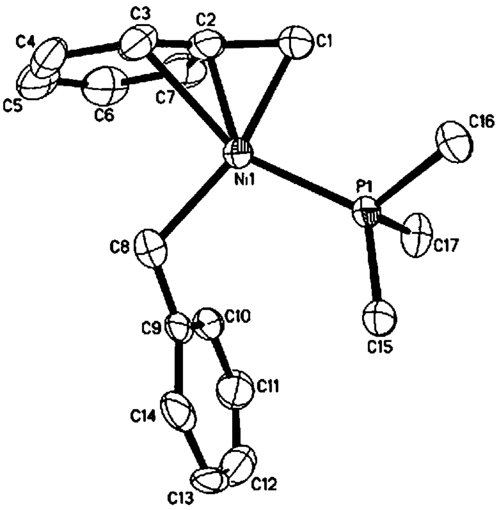
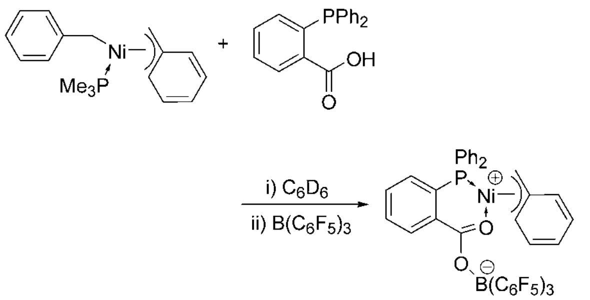


**Figure 1.** ORTEP drawing of Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)-$PMe_3$ (hydrogen atoms omitted, 50% ellipsoids).

The nickel atom is bound by C(8), P(1), C(1) and C(2) in a square planar fashion. Nickel itself is almost perfectly in the plane (0.15 Å deviation), while the C(3) ring atom of the $\eta^3$-benzyl group is out of the plane by

**Table 2.** Crystallographic collection and refinement parameters for Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)$PMe_3$.

| Empirical formula | $C_{17}H_{23}NiP$ |
|---|---|
| Molecular weight (g mol$^{-1}$) | 317.03 |
| Description | red crystals |
| Size (mm$^3$) | 0.22 × 0.18 × 0.16 |
| Temperature (K) | 168(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 10.6492(6) |
| $b$ (Å) | 12.3399(7) |
| $c$ (Å) | 14.2222(8) |
| α (°) | 64.5700(10) |
| β (°) | 88.7230(10) |
| γ (°) | 75.1490(10) |
| Volume (Å$^3$) | 1623.21(16) |
| $Z$ | 4 |
| Calculated density (Mg/m$^3$) | 1.297 |
| Absorption coefficient (mm$^{-1}$) | 1.279 |
| F(0 0 0) | 672 |
| θ range for data collection (°) | 1.59 to 26.37 |
| Index range | $-13 \leq h \leq 13$ |
| | $-15 \leq k \leq 15$ |
| | $-17 \leq l \leq 17$ |
| Reflections collected | 15522 |
| Independent reflections | 6540 [R(int) = 0.0464] |
| Data/restraints/parameters | 6540/0/488 |
| Goodness-of-fit on F$^2$ | 1.006 |
| Final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0415, wR2 = 0.0929 |
| $R$ indices (all data) | R1 = 0.0843, wR2 = 0.1087 |
| Transmission (ratio of max. to min.) | 0.8215 and 0.7662 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.592 and –0.508 e.Å$^{-3}$ |



**Scheme 2.** Synthesis of [2-(diphenylphosphino)benzoate tris(pentafluorophenyl)borate-$\kappa^2$P,O]($\eta^3$-benzyl)nickel using Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)$PMe_3$.

0.96 Å. The $\eta^3$-benzyl ring, as well as the $\eta^1$-benzyl ring, are almost perpendicular to the plane spanned by C(8)–P(1)–C(1)–C(2) (79° and 78°, respectively). The crystallographic collection and refinement parameters are summarized in Table 2.

Solution NMR characterization is consistent with the solid state results. Specifically, the $^1$H NMR spectrum shows two non-equivalent aromatic rings, in addition to the $\eta^1$-$\mathit{CH_2}C_6H_5$, $\eta^3$-$\mathit{CH_2}C_6H_5$ and $PMe_3$ signals described above. The methylene protons on each benzyl fragment are equivalent, however they are diastereotopic in the solid structure. It is known that $\eta^3$-benzyl groups can exist as isomers that arise from pseudorotamers of the $\eta^3$-benzyl ligand.[13] This suprafacial rearrangement, which exchanges the C(3) and C(7) carbons averages out the methylene protons on the NMR time scale. The two benzyl groups do not exchange in the NMR time scale at temperatures which prevent decomposition. The $^{31}$P{$^1$H} NMR spectrum shows a single broad peak. After standing at room temperature for more than 60 minutes, the $^1$H NMR spectrum changes to a compound that has not been identified.

The reactivity of Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)$PMe_3$ was examined by the addition of 2-(diphenylphosphino)benzoic acid and two equivalents of $B(C_6F_5)_3$ in deuterated benzene in a sequential two step reaction. The previously characterized product [2-(diphenylphosphino)benzoate tris(pentafluorophenyl)borate-$\kappa^2$P,O]($\eta^3$-benzyl)nickel[2c] was obtained and characterized by $^1$H, $^{31}$P, and $^{19}$F NMR spectroscopy. Estimated NMR scale yields are approximately 60%.

In summary, we have shown the synthesis and characterization of Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)$PMe_3$. This compound is a rare example of a bisbenzyl-nickel complex and the first to be supported by a single additional two electron donor ligand. The $\eta^1$- and $\eta^3$-binding modes were confirmed by solution and solid state characterization techniques. Because of the expected lability of the $\eta^3$-binding mode, this complex is coordinatively unsaturated and is therefore unstable towards thermal decomposition. Reactivity was demonstrated by the reaction shown in Scheme 2. However, the low yield of the preparation of Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)$PMe_3$ and the low stability are likely to preclude wide use as a starting material for benzyl nickel compounds.

## Experimental Section

### General Methods

Manipulations were performed under argon or nitrogen by using Schlenk techniques[14] and/or a glove-box. All chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[15] Deuterated benzene was purchased from Cambridge Isotope Laboratories, Inc. and dried over Na/K. $NiCl_2(PMe_3)_2$ was prepared according to the literature.[9a,16] $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra were recorded on a Varian UNITY INOVA 400 MHz spectrometer operating at 399.95 MHz, 100.58 MHz, and 161.91 MHz, respectively, and were referenced to the residual solvent peak. The $^{31}$P{$^1$H} NMR spectrum was referenced to $H_3PO_4$.

### Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)$PMe_3$

Bis(trimethylphosphine)nickel dichloride (1.00 g, $3.55 \times 10^{-3}$ mol) was suspended in THF (100 mL) and cooled to $-120$ °C. Dropwise addition of benzylmagnesium chloride (3.55 mL, 2 M in THF, $7.10 \times 10^{-3}$ mol) under argon turned the reaction mixture purple. The reaction mixture was left at $-90$ °C overnight and was allowed to warm to $-40$ °C. All volatiles were removed under vacuum. The resulting dark purple solid was quickly extracted with pentane at room temperature, filtered and all volatiles were removed to give a dark red viscous oil, which was contaminated with bisbenzyl and $Ni(PMe_3)_4$. The crude material was purified by multiple crystallizations from pentane at $-35$ °C to give dark red crystals suitable for X-ray crystallography. The product is stable as a solid at $-35$ °C for 1–2 weeks and decomposes in solution, even at $-35$ °C. Yield: 124 mg (11%); $^1$H NMR ($C_6D_6$, 298 K): $\delta = 7.16$ (t, 2H, $^3J_{H,H} = 7.5$ Hz, *meta*-H-Ph), 7.06 (t, 2H, $^3J_{H,H} = 7.5$ Hz, *meta*-H-Ph), 7.01 (t, 1H, $^3J_{H,H} = 7.5$ Hz, *para*-H-Ph), 6.85 (t, 1H, $^3J_{H,H} = 7.5$ Hz, *para*-H-Ph), 6.68 (d, 2H, $^3J_{H,H} = 7.5$ Hz, *ortho*-H-Ph), 6.63 (d, 2H, $^3J_{H,H} = 7.5$ Hz, *ortho*-H-Ph), 2.42 (s, 2H, $CH_2$), 1.13 (s, 2H, $CH_2$), 0.70 (br s, 9H, $PMe_3$); $^{13}$C{$^1$H} NMR ($C_6D_6$, 298 K): $\delta = 130.4$ (Ph), 130.2 (Ph), 122.4 (Ph), 121.9 (Ph), 120.0 (br, Ph), 30.6 ($CH_2$), 23.5 (br, $CH_2$), 15.6 (br, $PMe_3$); $^{31}$P{$^1$H} NMR ($C_6D_6$, 298 K): $\delta = -16.7$ ($\nu_{1/2} = 460$ Hz). X-ray data: Cambridge Crystallographic Data Centre CCDC 244083.

### [2-(Diphenylphosphino)benzoate Tris(pentafluorophenyl)borate-$\kappa^2$P,O]-($\eta^3$-benzyl)nickel(II)

2-(Diphenylphosphino)benzoic acid (10 mg, $6.53 \times 10^{-5}$ mol) and Ni($\eta^1$-$CH_2C_6H_5$)($\eta^3$-$CH_2C_6H_5$)$PMe_3$ (11 mg, $6.53 \times 10^{-5}$ mol) were added in $C_6D_6$ and stirred for 5 min. $B(C_6F_5)_3$ (34 mg, $1.31 \times 10^{-4}$ mol) was added and the reaction mixture was filtered after 5 min. The resulting red solution was characterized by NMR spectroscopy and the product was isolated as red crystals by pentane diffusion into the benzene solution at room temperature. Yield: 19 mg, (60%); NMR spectra match those previously reported.[2c]

### Supplementary Material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 244083. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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