

[(Triphos)Ni(η^2 -BH₄)]: An Unusual Nickel(I) Borohydride Complex

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Reduction of [(triphos)NiCl₂] (**1**) with an excess of NaBH₄ in THF produces the paramagnetic Ni(I) complex [(triphos)Ni(η^2 -BH₄)] (**2**). X-ray crystallography shows **1** to be a square-planar Ni(II) species in which the phosphine ligand is bidentate, whereas **2** has pseudotetrahedral geometry at the Ni(I) center, with a tridentate phosphine and the borohydride ligand occupying a single coordination site. Density functional theory calculations show the unpaired electron in **2** to reside in an orbital located mainly on the Ni atom.

Well-defined Ni(I) complexes are relatively rare, although phosphine ligands are known to support this unusual oxidation state,¹ which has been invoked in several biologically relevant processes involving nickel-containing enzymes such as hydrogenase, carbon monoxide dehydrogenase, and methyl-*S*-coenzyme M reductase.² Ni-mediated borohydride reductions have been carried out on a wide range of functional groups in organic synthesis.³ Monomeric Ni(I) complexes are paramagnetic (d⁹ electron configuration) and demonstrate redox properties unique to a group 10 radical.⁴ The capacity of the potentially tridentate, bulky ligand 1,1,1-tris(diphenylphosphinomethyl)ethane [(MeC(CH₂PPh₂)₃, triphos] to form stable complexes with 3d metals in low oxidation states has been clearly demonstrated.⁴ In particular, it stabilizes the 1+ oxidation state of both cobalt and nickel. For example, the complexes [(triphos)NiX] (X = Cl, Br) have been

prepared by reduction of the dihalide with sodium borohydride,⁵ and [(triphos)MI] (M = Co, Ni) can be formed directly from the metal diiodide without the necessity of an added reducing agent. It is unsurprising, therefore, that a similar Ni(I) species can be formed with the borohydride moiety. Here we report the synthesis and structural and spectroscopic studies of the first characterized nickel(I) borohydride complex.⁶

The complex [(triphos)NiCl₂] (**1**; Figure 1) is formed in high yield by the addition of triphos to NiCl₂ in dry THF.^{7,8} **1** is a moderately air-stable orange powder. The ³¹P{¹H} NMR spectrum at 25 °C shows a single resonance at –21.0 ppm indicating a fluxional ligand; at –60 °C, this resolves into two peaks at –21.6 and –22.6 ppm in a 1:2 ratio. The structure of complex **1** was determined by X-ray crystallography,^{9,10} as detailed in Table 1 and Figure 1. This reveals a mononuclear, square-planar Ni(II) center with *cis*-chloro ligands and a bidentate triphos moiety in which the third

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- (8) To 50 mL of a THF solution of NiCl₂ (0.30 g, 2.31 mmol) was added an equimolar amount of triphos (1.45 g, 2.31 mmol). An immediate color change from green to orange was observed. The solution was stirred for 30 min and filtered. Orange crystals of **1** were isolated after concentrating the resulting solution and cooling overnight at 4 °C. Yield: 1.40 g; 80%. Anal. Expt (theory): C, 65.30 (65.29); H, 5.19 (5.21). ¹H NMR (THF-*d*₈, 300 MHz, ppm): 7.9–7.1 (br, 30H, C₆H₅), 1.88 (s, 6H, CH₃), 1.69 (s, 3H, CH₃). ³¹P{¹H} NMR (THF-*d*₈, 400 MHz, ppm): –21.0 (25 °C), –21.6 (1P), –22.6 (2P) (–60 °C).
- (9) Orange crystals of **1** were grown by slow evaporation of a THF solution at 4 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fiber, and frozen in the cold-nitrogen stream of the goniometer. A hemisphere of data were collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3°. The detector distance was 5 cm. The data were reduced (SAINT, ref 10a) and corrected for absorption (SADABS, ref 10b). The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL, ref 10c). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model. The drawing was generated using the program ORTEP-3 (ref 10d).
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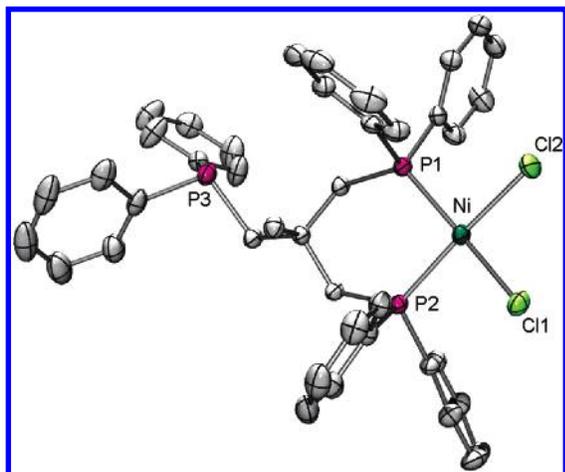


Figure 1. ORTEP plot of **1** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–P1, 2.1643(7); Ni–P2, 2.1693(7); Ni–Cl1, 2.1900(9); Ni–Cl2, 2.2120(7); Cl1–Ni–P1, 172.58(3); Cl2–Ni–P2, 176.77(3).

Table 1. Crystal, Collection, and Refinement Parameters for **1** and **2**^a

	1	2
empirical formula	C ₄₁ H ₃₉ Cl ₂ NiP ₃	C ₄₁ H ₄₃ BNiP ₃
fw	754.24	698.18
cryst size, mm	0.40 × 0.15 × 0.10	0.15 × 0.125 × 0.025
a, Å	25.685(3)	20.475(2)
b, Å	13.8498(12)	10.3065(11)
c, Å	22.0402(18)	16.9806(18)
α, deg	90	90
β, deg	97.656(3)	90
γ, deg	90	90
V, Å ³	7770.6(12)	3583.3(7)
θ range for data collection (deg)	1.60–27.50	1.99–27.50
d(calcd), Mg/m ³	1.289	1.294
cell meas temp, K	173(1)	173(1)
space group	C2/c	Pna2(1)
Z	8	4
h, k, l min to max ranges	–30 ≤ h ≤ 32 –17 ≤ k ≤ 17 –28 ≤ l ≤ 28	–24 ≤ h ≤ 25 –13 ≤ k ≤ 13 –22 ≤ l ≤ 21
reflns collected	26210	23632
independent reflns	8507 [R(int) = 0.0412]	7259 [R(int) = 0.1102]
final R indices	R1 = 0.0405, wR2 = 0.0892	R1 = 0.0489, wR2 = 0.0623
R indices (all data)	R1 = 0.0826, wR2 = 0.0982	R1 = 0.1259, wR2 = 0.0725
data/restraints/parameters	8507/0/425	7259/1/548
GOF	1.021	0.941
final diff map, e/Å ³	0.857 and –0.275	0.351 and –0.358

^a wR2 = $(\sum[w(F_o^2 - F_c^2)^2]/\sum[F_o^4])^{1/2}$. R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. Weight = $1/[\sigma^2(F_o^2) + (XP)^2 + (YP)]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, $X = 0.0436$ (**1**) or 0.0137 (**2**), and $Y = 5.82$ (**1**) or 0.00 (**2**).

phosphorus atom is unbound and resides distally from the Ni atom. This bonding mode for triphos has been observed commonly in other square-planar 16-electron complexes such as [(triphos)PtCl₂]¹¹ and [(triphos)Pt(CH₃)₂],¹² as well as in some 18-electron species such as [(triphos)Re(CO)₃].¹³

Reduction of **1** with a stoichiometric amount of NaBH₄ in CH₂Cl₂/EtOH is known to produce [(triphos)NiCl],⁵

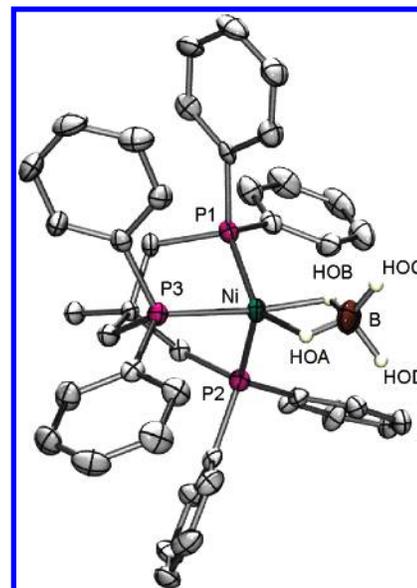


Figure 2. ORTEP plot of **2** (50% probability ellipsoids). Hydrogen atoms of the triphos ligand are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–P1, 2.2501(12); Ni–P2, 2.2475(13); Ni–P3, 2.2463(13); Ni–HOA, 1.83(5); Ni–HOB, 1.59(5); B–HOA, 1.03(5); B–HOB, 1.09(5); B–HOC, 1.00(5); B–HOD, 1.15(5); P1–Ni–P2, 93.87(5); P1–Ni–P3, 89.50(5); P2–Ni–P3, 94.90(5).

however, the addition of a large excess of NaBH₄ in ethanol to complex **1** in THF results in the formation of yellow crystals of [(triphos)Ni(η²-BH₄)] (**2**).¹⁴ Single-crystal X-ray diffraction¹⁵ reveals **2** to be monomeric (Table 1 and Figure 2). This complex exhibits reasonable stability in a THF solution and in powder form, but upon exposure to oxidants (e.g., O₂) or halogenated solvents (CH₂Cl₂), it decomposes gradually.

2 is only the second stable nickel borohydride complex to be characterized, [Tp*Ni(η³-BH₄)] {Tp* = hydrotris(3,5-dimethylpyrazoyl)borate}¹⁶ having been reported recently. The X-ray structure of **2** clearly reveals the borohydride ligand to coordinate in a symmetrical η² manner. The Ni center is pseudotetrahedral if the borohydride ligand is assumed to occupy a single coordination site and the Ni, B, HOA, and HOB atoms are coplanar.

The Ni–B distance of 2.24 Å in **2** is larger than the sum of the covalent radii of nickel and boron (1.84 Å),¹⁷ and the

(14) To a 50-mL THF solution of **1** (0.50 g, 0.754 mmol) was added 10 mL of a ethanol solution of NaBH₄ (0.20 g, 5.303 mmol), resulting in a yellow solution. This was then refluxed for 20 min before filtration. Concentration of the resulting solution and cooling overnight at 4 °C afforded yellow crystals of **2**. Yield: 0.37 g, 53%. ¹H NMR (THF-*d*₈, 400 MHz, ppm, from +25 to –70 °C): δ 8.0–7.1 (br, 30H, C₆H₅), 1.60 (s, 6H, CH₂), 1.01 (s, 3H, CH₃), –0.58 (¹J_{HB} = 81 Hz) (q, 4H, BH₄). ³¹P{¹H} NMR (THF-*d*₈, 300 MHz, ppm): δ 27.17. ¹¹B NMR (THF-*d*₈, 300 MHz, ppm): δ –42.98 (¹J_{BH} = 82 Hz). IR (KBr, cm^{–1}): ν(B–H_i) = 2354s, ν(B–H_b) = 2007w. Owing to the reactivity of the complex, elemental analysis proved difficult to obtain; ¹H, ¹¹B, and ³¹P NMR spectra (THF-*d*₈) are presented in the Supporting Information.

(15) Yellow crystals of **2** were grown by slow diffusion using a THF/ethanol mixture at 4 °C. For details of the X-ray structure determination, see ref 9. In contrast to **1**, all hydrogen atoms of **2** were found in Fourier difference maps and refined using common isotropic thermal parameters.

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four hydrogen atoms of the BH₄ group are tetrahedrally arranged around the boron. The Ni–H distances span a wide range, 1.59(5)–1.83(5) Å, comparable to those in other nickel hydride and borohydride complexes.^{16,18} Complex **2** is structurally very similar to its Co(I) analogue [(triphos)-Co(η^2 -BH₄)].¹⁹ However, the hapticity of the borohydride ligand appears very sensitive to the oxidation state and nature of the metal and its associated ligand set in late-transition-metal borohydride complexes. Thus, BH₄[−] adopts a tridentate binding mode in the Ni(II) species [Tp*Ni(η^3 -BH₄)]¹⁶ but a monodentate mode in the Cu(I) analogue of **2**, viz., [(triphos)-Cu(η^1 -BH₄)].²⁰

The magnetic susceptibility of **2** in the solid state was measured by the Gouy method and in solution in THF-*d*₈ by the Evans technique.²¹ μ_{eff} values of 2.47 and 2.57 μ_{B} , respectively, indicate the presence of a single unpaired electron with an orbital contribution to the spin-only moment. Attempts to obtain a reproducible electron paramagnetic resonance spectrum have thus far been frustrated by sample decomposition.

Density functional theory (DFT) calculations have been carried out to explore the nature of the unpaired electron in the model complex [MeC(CH₂PH₂)₃]Ni(η^2 -BH₄) (**2'**; Figure 3).^{22–26} The optimized geometry of this system, in which the phenyl groups of the triphos ligand have been replaced by hydrogen atoms, is in good agreement with that found

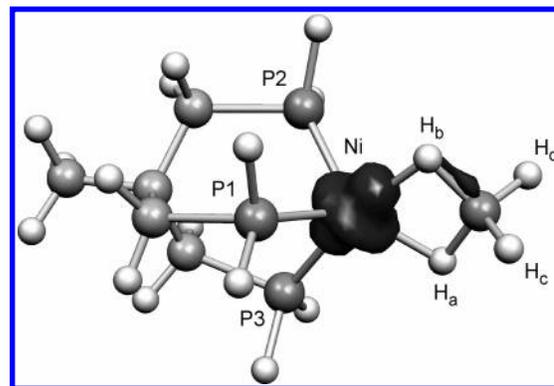


Figure 3. Representation of the model complex **2'** and its spin polarization. Selected bond distances (Å) and angles (deg): Ni–P1, 2.230; Ni–P2, 2.224; Ni–P3, 2.299; Ni–H_a, 1.699; Ni–H_b, 1.741; B–H_a, 1.279; B–H_b, 1.275; B–H_c, 1.205; B–H_d, 1.205; P1–Ni–P2, 95.89; P1–Ni–P3, 90.16; P2–Ni–P3, 89.60.

experimentally for complex **2**. The computed total spin densities for **2'** (Ni, 0.855; B, 0.138; P1, 0.001; P2, 0.004; P3, 0.053; H_a, 0.000; H_b, −0.007; H_c, −0.008; H_d, −0.008) clearly reveal the unpaired electron to be located predominantly on the metal, with only a minor presence on boron (Figure 3). Negligible spin populations are found on the phosphorus and bridging hydrogen atoms.

Although complex **2** is paramagnetic, it displays relatively sharp resonances in its NMR spectra in THF-*d*₈ between 25 and −70 °C, which are easily assigned to the triphos and borohydride ligands (see the Supporting Information). For example, the ¹¹B NMR spectrum shows a quintet at −42.98 ppm ($w_{1/2}$ = 5 Hz), albeit measurably broader than that obtained for free BH₄[−] under the same conditions (−41.08 ppm; $w_{1/2}$ = 1.4 Hz). This sharpness is in accord with the spin densities calculated for **2'** (qv). With a quartet centered at −0.58 ppm in the ¹H NMR spectrum (J_{BH} = 82 Hz), the borohydride ligand remains fluxional between 25 and −70 °C. The ³¹P{¹H} NMR spectrum under the same conditions shows a single resonance at 27.17 ppm.

In summary, the capability of the bulky triphos ligand to switch from a bidentate to a tridentate binding mode, in tandem with the reducing nature and size of the borohydride ligand, promotes the change from square-planar **1** to the unusual tetrahedral complex **2**. Complex **2** is only the second characterized stable borohydride of nickel and the first such example in which this metal is in the 1+ oxidation state.

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Supporting Information Available: X-ray data in the form of a CIF for complexes **1** and **2**; ¹H, ³¹P, and ¹¹B NMR spectra for complex **2** in THF-*d*₈ and Cartesian coordinates for the optimized geometry of **2'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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