(Table III) are consistent with those expected from the structural assignment for these compounds. Methyl and methyne moieties of the isopropoxy groups show a multiplet and complex multiplet, respectively, indicating inequivalency of the isopropoxy groups and coupling with phosphorus. The P–CH_2 group exhibits two complex multiplets in these compounds, revealing that the two protons are not equivalent and each of them couples geminally as well as to an NH proton and the phosphorus atom. When the NH proton was irradiated, the two complex multiplets collapsed to two triplets. The methyl group of the amine moiety gives a doublet due to coupling to the NH proton. Irradiation of the NH proton resulted in the collapse of this doublet to a single peak.

The ^{13}C NMR (Table IV) further confirms the inequivalency of the isopropoxy groups by exhibiting a multiplet for the methyl carbons. The methyne carbons exhibit two doublets (except for **2**, which shows a doublet), indicating two different environments for the isopropoxy group. The large value for the P–C coupling is consistent for these types of compounds.[5b] Appearance of a doublet for the NCH_3 carbon in compounds **1** and **3** may be due to either long-range coupling with phosphorus or the diastereoscopic nature. Chemical shifts of other carbon moieties are consistent with the structures for these compounds.

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Nature of the Catalytically Inactive Cobalt Hydride Formed upon Hydrogenation of Aromatic Substrates. Structure and Characterization of the Binuclear Cobalt Hydride $[\{Pr^i_2P(CH_2)_3PPr^i_2\}Co]_2(H)(\mu\text{-}H)_3$

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The homogeneous, catalytic hydrogenation of aromatic rings still remains a curiosity despite the work reported in the literature.[4] This is largely due to the fact that forcing conditions and poor turnovers have limited the applicability of these systems even though reported stereoselectivities are much higher than in conventional heterogeneous systems. Cobalt-derived catalysts are a good case in point. Complete cis stereoselectivity is observed for the hydrogenation of benzene at 0–20 °C and 1 atm H_2 pressure using $(\eta^3\text{-}C_3H_5)Co[P(OMe)_3]_3$ or $(\eta^3\text{-}C_8H_{13})Co[(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2]$, but turnover numbers are extremely low, ranging from 10 to 100 mol of substrate/mol of catalyst before the formation of catalytically inert mono-[5] or polynuclear hydrides,[6] respectively. Our interest in the related polynuclear hydrides of rhodium[7] such as $[(dippp)Rh]_2(\mu\text{-}H)_2$ (dippp ≡ 1,3-bis(diisopropylphosphino)propane) was incentive to examine the nature of the catalytically inactive cobalt hydride formed during the hydrogenation of arenes using the cobalt catalyst precursor $(\eta^3\text{-}C_3H_5)Co(dippp)$ (**1**). It is interesting to note that the analogous rhodium–allyl complex, $(\eta^3\text{-}C_3H_5)Rh(dippp)$, reacts with H_2 to form the binuclear dihydride $[(dippp)Rh]_2(\mu\text{-}H)_2$ with no evidence of hydrogenation of aromatic substrates.[7] In this report, we describe the characterization of a dark blue cobalt hydride complex that is isolated from the catalytic hydrogenation of aromatic substrates.

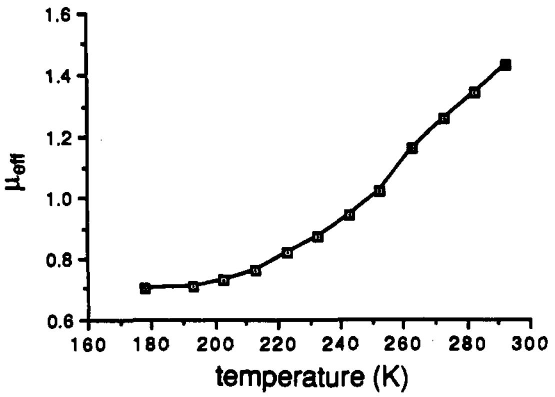
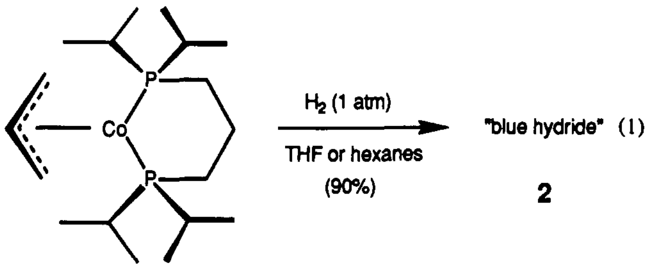


Figure 1. Temperature dependence of μ_{eff} for $[(dippp)Co]_2(H)(\mu\text{-}H)_3$ (**2**) between +20 and −95 °C.

The purple cobalt–allyl derivative **1** serves as a catalyst precursor for the hydrogenation of benzene at 0 °C and ≤1 atm H_2 pressure, generally producing 10–30 equiv of cyclohexane before H_2 uptake is slowed and the catalyst solution turns to a deep, dark blue color. The blue hydride **2** can be isolated from this solution, but it can also be synthesized independently in high yield by stirring a solution of the allyl derivative **1** in a nonaromatic solvent such as THF or hexanes under H_2 at room temperature (eq 1). This blue hydride does not act as a catalyst for the hydrogenation of benzene.



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The blue hydride **2** shows paramagnetic behavior in solution at 20 °C ($\mu_{eff} = 1.4 \pm 0.1$ μ_B (Evan's method)[8]); however, when it is cooled to −95 °C, its ^1H NMR spectrum appears to be that of a diamagnetic compound, particularly since the resonances for the dippp ligand appear in their typical positions. Unfortunately, only very broad, featureless peaks could be discerned in the hydride region. Interestingly, as the temperature is lowered, the magnetic susceptibility also decreases until a value for μ_{eff} of 0.7 μ_B at −95

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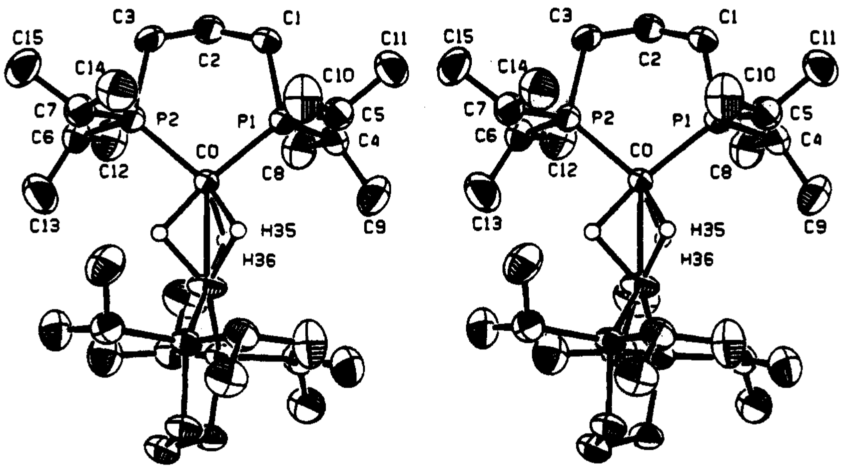
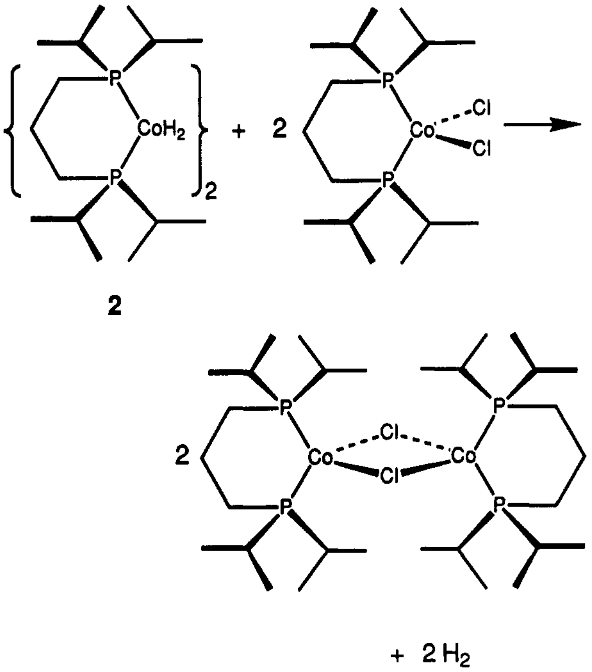


Figure 2. Stereoview of the solid-state structure of $[(\mathrm{dippp})\mathrm{Co}]_2(\mathrm{H})(\mu\text{-H})_3$ (**2**) at 21 °C.

°C (Figure 1). Molecular weight measurements of **2** in solution by the isopiestic (Signer) method[9] were not reproducible. In the solid state, the mass spectrum showed the presence of a parent ion at m/z 674 consistent with a binuclear structure.

Although both bridging and terminal hydride ligands could be inferred from the IR data (ν(Co–H) 1981 cm^{-1}, ν(Co–H–Co) 1001 cm^{-1}, δ(Co–H) 756 cm^{-1}), the actual number of hydride ligands present per molecule was deduced by chemical means. When toluene solutions of the blue hydride **2** and air-stable $(\mathrm{dippp})\mathrm{CoCl}_2$ were mixed, a vigorous reaction occurred, with liberation of hydrogen gas, resulting in a green solution from which the chloro-bridged dimer $[(\mathrm{dippp})\mathrm{Co}]_2(\mu\text{-Cl})_2$ was isolated quantitatively (eq 2).[10] Toepler pump analysis of the evolved gas gave 1.9 ± 0.2 mol of H_2/mol of **2**, assuming the binuclear formulation for the blue hydride. This suggested that four hydrides were coordinated to two cobalt centers.



(2)

In the solid state, susceptibility measurements indicate that the blue hydride is diamagnetic from 6 to 280 K. We have carried out a single-crystal X-ray diffraction study on the blue hydride at both 21 and at −155 °C to provide more information on the structure of this compound. The structure of the complex in the solid state at 21 °C is shown in Figure 2. The room-temperature structure had elucidated the overall molecular architecture although it was only possible to unequivocally locate three bridging hydrides, two of which were related by the C_2 axis of the molecule. The location of the fourth hydride could not be determined, even at low temperature, but it is presumed to be a terminal hydride disordered over four possible, equivalent sites on the two metal centers in the molecule.

There is a very short Co–Co bond distance of 2.2811 (7) Å in the molecule, and this can be explained by the presence of three bridging hydride ligands.[11] The shortest Co–Co bond distance reported in the literature is 2.185 Å in $[(\eta^5\text{-C}_5\mathrm{H}_5)\mathrm{Co}]_2(\mu\text{-bis(trimethylsilyl)acetylene})$.[12] The latter consists of the bridging acetylene ligand oriented perpendicular to the two cobalt centers, resulting in a short metal–metal bond that has been rationalized in terms of a cobalt–cobalt double bond. There is one other example of a polyhydrido-bridged cobalt complex $\{[\{(\mathrm{Ph_2AsCH_2})_3\mathrm{CCH_3}\}\mathrm{Co}]_2(\mu\text{-H})_3\}(\mathrm{BPh_4})$,[13] which contains three bridging hydride ligands and a Co–Co bond length of 2.377 (8) Å. Other examples of Co–Co bond lengths in binuclear cobalt compounds are 2.372 (2) Å in $[(\mathrm{PPh_3})_2\mathrm{N}][\{(\eta^5\text{-C}_5\mathrm{H}_5)\mathrm{Co}\}_2(\mu\text{-CO})_2]^{\bullet-}$,[14] 2.370 (1) Å in $[(\eta^5\text{-C}_5\mathrm{H}_5)\mathrm{Co}]_2(\mu\text{-NO})$,[15] 2.3272 (2) Å in $[(\eta^5\text{-C}_5\mathrm{Me}_5)\mathrm{Co}]_2(\mu\text{-CO})_2(\mu\text{-CHCH}_3)$,[16] and 2.327 (2) Å in $[(\eta^5\text{-C}_5\mathrm{Me}_5)\mathrm{Co}]_2(\mu\text{-CO})_2$.[17]

The dihedral angle between the two $\mathrm{CoP_2}$ planes of the blue hydride **2** is 77°. This nearly perpendicular arrangement of the end fragments of the binuclear molecule is a result of the bulky isopropyl substituents on phosphorus, the rather large P–Co–P angle of 99.4°, and the short Co–Co bond causing these isopropyl groups to interlock into one another. A similar geometry is found in $[\{(\mathrm{C_6H_{11}})_2\mathrm{P}(\mathrm{CH_2})_3\mathrm{P}(\mathrm{C_6H_{11}})_2\}\mathrm{Ni}]_2(\mu\text{-H})_2$,[18] where the dihedral angle is 63°. As a result, the inner core of the blue hydride **2** is well protected, and this probably accounts for its low degree of reactivity. For example, attempts to regenerate an active arene hydrogenation catalyst by dehydrogenation using 3,3-dimethylbutene have been unsuccessful.

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(10) Reduction of $(\mathrm{dippp})\mathrm{CoCl}_2$ with sodium amalgam in toluene generated $[(\mathrm{dippp})\mathrm{Co}]_2(\mu\text{-Cl})_2$ as dark green crystals. Anal. Calcd (found) for $\mathrm{C_{30}H_{68}Co_2Cl_2P_4}$; (fw 741.58): C, 48.59 (48.74); H, 9.24 (9.20); Cl, 9.56 (9.33). Details of this synthesis and the structure of the cobalt(I) dimer will reported separately.

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The solution structure of this blue hydride is complicated by the weak paramagnetism observed. If the structure in solution is binuclear, as it is in the solid state, it is possible that the origin of the magnetic moment may be due to a thermally accessible triplet state.[19] However, another possibility is that fragmentation to generate reactive paramagnetic monomers in equilibrium with diamagnetic dimers may be occurring in solution; this is consistent both with the inability to obtain reproducible solution molecular weights and with the temperature dependence of μ_{eff}. Further work on the nature of the species in solution and the chemical reactivity of the blue hydride **2** is underway.

Experimental Section

All manipulations were conducted under nitrogen or argon by standard glovebox, Schlenk, or vacuum-line techniques.[20] Experiments in the glovebox were performed under a prescrubbed, circulating atmosphere of nitrogen in a Vaccuum Atmospheres HE-553-2 Dri-Lab equipped with a MO-40-2H Dri-Train and a −30 °C freezer. Infrared spectra were recorded on a Pye-Unicam SP-1100 and a Nicolet 5DX Fourier transform spectrophotometer with the samples as KBr pellets or in solution between 0.1-mm NaCl plates. The abbreviations for the infrared bands are as follows: sh, shoulder; m, medium, w weak. NMR spectra were obtained on a Varian XL-300 or a Bruker WH-400 NMR spectrometer. Chemical shifts (δ) are reported in units of parts per million (ppm) relative to tetramethylsilane (TMS) (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), downfield shifts being positive. ^{1}H NMR spectra are recorded relative to residual protiated solvent: benzene-d_6, 7.15; toluene-d_8, 2.09. $^{31}P\{^1H\}$ spectra are recorded relative to external reference $P(OMe)_3$ at 141.00 ppm. The chemical shifts of the paramagnetic complexes are uncorrected for the paramagnetic shift of the solvent. All coupling constants are reported in Hertz, and abbreviations are as follows: s, singlet; t, triplet; m, multiplet, br, broad.

Magnetic susceptibilities were determined in solution at ambient temperature by the Evans' method[8] using benzene as solvent. The measurements (±10%) were carried out by using a Precision coaxial cell (Wilmad Glass Co.) on a Varian EM-360 CW NMR spectrometer. Variable-temperature data were recorded on the Varian XL-300 spectrometer equipped with a variable-temperature probe, using toluene as solvent and internal reference; these susceptibilities were corrected for parallel sample geometry.[21] The diamagnetic susceptibilities of benzene and toluene were taken from the literature.[22]

UV–visible spectra were recorded at 25 °C on a Perkin-Elmer 552A UV–vis spectrophotometer. The samples were prepared in the glovebox and transferred to a 10-mm cuvette fused to a 4-mm Kontes Hi Vacuum Teflon valve.

The magnetic susceptibility of $[(dippp)CoH_2]_2$ (**2**) in the solid state was recorded by Mr. Phil Matsunaga at the University of California, Berkeley, on a SHE SQUID magnetometer at 5 and 40 kg from 6 to 280 K. The samples were placed in KEL-F airtight containers loaded in the globebox. Each run required ~100 mg of compound ground into a fine powder.

Microanalyses were determined by Mr. Peter Borda in the UBC Microanalytical Laboratory.

Unless otherwise noted, all solvents and reagents were obtained from local commercial suppliers. Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and hexanes were predried by refluxing for at least 48 h over CaH_2, prior to distillation from sodium–benzophenone ketyl under argon. Benzene, toluene, and diethyl ether were dried and distilled from sodium–benzophenone ketyl under argon. Pyridine was dried and distilled from CaH_2 under argon. The deuterated solvents C_6D_6 and C_7D_8 for the NMR experiments were purchased from MSD Isotopes, dried over 4-Å molecular sieves, and deaerated by three freeze–pump–thaw cycles prior to use.

Hydrogen gas, supplied by Matheson, was purified by passage through a column of activated 5-Å molecular sieves and MnO supported on vermiculite.[20] Deuterium gas was obtained from MSD Isotopes and used as received.

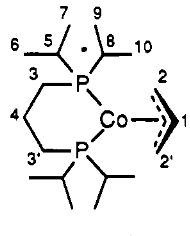
The ligand 1,3-bis(diisopropylphosphino)propane (dippp) was prepared according to a published procedure.[23]

(dippp)CoCl$_2$. Cobalt(II) chloride (5.28 g, 0.041 mol) was suspended in dry toluene (200 mL) in a 500-mL round-bottom flask with a side arm under an inert atmosphere. The ligand, dippp (10.1 g, 0.036 mol), was slowly added by syringe, and the mixture was stirred for 24 h to give a deep blue solution. The residual $CoCl_2$ was removed by filtration, and the filtrate was concentrated in vacuo. The solution was cooled at −20 °C for 24 h, and blue needlelike crystals precipitated. These were separated from the supernatant by cannula, washed with minimum cold hexanes, and dried under vacuum. Yield: 13.1 g (89%). The complex, $(dippp)CoCl_2$, is air-stable in the solid state but decomposes slowly in solution.

Anal. Calcd (found) for $CoCl_2P_2C_{15}H_{34}$ (fw 406.22): C, 44.35 (44.23); H, 8.44 (8.50); Cl, 17.46 (17.26). Mp: 114 °C. MS: *m/z* 405 (1.4%, M^+), 370 (1.3%, $\{Co(dippp)\text{-}Cl\}^+$), 233 (100%, $\{dippp - Pr^i\}^+$), 191 (16.7%, $\{Pr^i{}_2P(CH_2)_3PH\}^+$), 148 (31.4%, $\{Pr^iP(CH_2)_3PH\}^+$). μ_{eff} (C_6H_6): 3.7 ± 0.1 μ_B. UV [C_6H_6; λ, nm (ϵ, L mol^{-1} cm^{-1})]: 323 (4400), 609 (1100), 659 (1000), 737 (1600).

(η^3-C_3H_5)Co(dippp) (1). $(dippp)CoCl_2$ (6.67 g, 16.4 mmol) was dissolved in dry THF (150 mL) in a 300-mL glass reactor. The solution was cooled at −20 °C, and a solution of allylmagnesium chloride (24.4 mL, 1.7 M, 41.0 mmol) was slowly added. The initial blue color of the solution changed to green, before eventually turning purple. The mixture was warmed to room temperature and stirred for 20 h. All solvents were removed in vacuo, the residue was taken up in dry hexanes (300 mL), and the mixture was filtered through a plug of Celite. The purple filtrate was then concentrated in vacuo and cooled at −30 °C. Purple crystals of (η^3-C_3H_5)Co(dippp) (**1**) were obtained overnight. These were separated from the supernatant by pipet, washed with minimum cold hexanes, and dried in vacuo. Yield: 3.63 g (59%). The cobalt–allyl complex also may be purified by sublimation under vacuum (oil bath at 65 °C).

Anal. Calcd (found) for $CoP_2C_{18}H_{39}$ (fw 376.39): C, 57.44 (56.85); H, 10.44 (10.31). Mp: 92–94 °C. MS: *m/z* 376 (9.3%, M^+), 333 (1.1%, $\{(\eta^3\text{-allyl})Co(dippp) - C_3H_7\}^+$), 233 (100%, $\{dippp - Pr^i\}^+$), 191 (19.1%, $\{Pr^i{}_2P(CH_2)_3PH\}^+$), 148 (24.6%, $\{Pr^iP(CH_2)_3PH\}^+$). IR (KBr, cm^{-1}): ν(C–H(allyl)) 3031 (w). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz, ppm): 47.1 (br s, $\Delta\nu_{1/2}$ = 942 Hz). ^{1}H NMR (C_6D_6, 300 MHz, ppm): H(anti), 1.43 (d, *J*(H(anti)–H(central)) = 9.5 Hz, 2 H); H(syn), 3.38 (br s, 2 H); H(central), 4.70 (m, 1 H); CH_3CHCH_3, 0.60–1.30 (br, complex, 28 H); $CH_2CH_2CH_2$, 1.78 (br, unresolved, 4 H); $CH_2CH_2CH_2$, 1.92 (br, unresolved, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.429 MHz, ppm): Cl, 98.8 (s); C2 and C2′, 50.2 (s); C3 and C3′, 28.6 (dt); C4, 21.1 (t); C5 and C8, 23.5 (t); C6, C7, C9 and C10, 20.3, 20.0, 19.3, and 18.6.



$[(dippp)CoH_2]_2$ (2). A solution of (η^3-C_3H_5)Co(dippp) (**1**) (0.516 g, 1.37 mmol) in dry hexanes (15 mL) in an 80-mL glass reactor was degassed and then stirred under an atmosphere of H_2 for 24 h. The initial purple color of the solution turned dark blue instantly after hydrogen was admitted. The solution was filtered through a Celite plug, concentrated, and cooled at −30 °C. Dark blue crystals of $[(dippp)CoH_2]_2$ (**2**) were collected after 24 h. Yield: 0.388 g (84%).

Anal. Calcd (found) for $Co_2P_4C_{30}H_{72}$ (fw 674.66): C, 53.41 (53.73); H, 10.76 (10.79). mS: *m/z* 674 (0.3%, M^+), 673 (1.5%, $\{M - H\}^+$), 672 (4.6%, $\{M - 2H\}^+$), 671 (0.2%, $\{M - 3H\}^+$), 670 (0.5%, $\{M - 4H\}^+$), 629 (0.2%, $\{M - 2H - Pr^i\}^+$), 554 (0.7%, $\{M - 2H - Pr^i{}_2PH\}^+$), 233 (10.0%, $\{dippp - Pr^i\}^+$), 118 (100%, $\{Pr^i{}_2PH\}^+$). IR (KBr, cm^{-1}): ν(Co–H) 1981 (w), ν(Co–H–CVo) 1001 (m, sh), δ(Co–H) 756 (w, sh). μ_{eff} (C_6H_6): 1.4 ± 0.1 μ_B. UV [hexanes; λ, nm (ϵ, L mol^{-1} cm^{-1})]: 253 (6200), 358 (2600), 495 (510), 617 (460). $^{31}P\{^1H\}$ NMR (C_7D_8, 121.421 MHz, ppm): −200 (very br s, $\Delta\nu_{1/2}$ = 2500 Hz), 355 (very br s, $\Delta\nu_{1/2}$ = 6200 Hz). $^{31}P\{^1H\}$ NMR (−90 °C, C_7D_8, ppm): 88.3 (very br s, $\Delta\nu_{1/2}$ = 3760 Hz). ^{1}H NMR (20 °C, C_7D_8, 400 MHz, ppm): $CH(CH_3)_2$, 0.29 (br s) and 1.44 (br s); unknown, −1.38 (br s), −0.25 (br s), and 1.79 (br s); $CH(CH_3)_2$, 4.19 (br s). ^{1}H NMR (−95 °C, C_7D_8, ppm): $CH(CH_3)_2$, 2.4 (br s); $CH(CH_3)_2$, 1.2–1.7 (br d); $PCH_2CH_2CH_2P$, 1.8 (br s); $PCH_2CH_2CH_2P$, 1.1 (br s). The hydrogen evolution experiment was performed by Dr. Warren Piers at Caltech by addition of a toluene solution of $(dippp)CoCl_2$ (2.2 equiv) to a toluene solution of $[(dippp)CoH_2]_2$ (**2**).

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Table I. Crystallographic Data for $[(dippp)CoH_2]_2$ (**2**)

chem formula	$C_{30}H_{72}Co_2P_4$	Z	4
fw	674.66	T	21 °C
space group	$C2/c$	ρ_c	1.22 g/cm^3
a	11.438 (3) Å	λ	0.71069 Å
b	16.458 (4) Å	μ	10.88 cm^{-1}
c	19.561 (3) Å	transm factors	0.897–1.00
β	92.37 (2)°	R	0.032
V	3679 (1) Å^3	R_w	0.043

Table II. Positional Parameters and B(eq) Values for **2**

atom	x	y	z	B(eq), Å^2
Co	0.45773 (3)	0.15175 (3)	0.19607 (2)	3.66 (2)
P(1)	0.51542 (6)	0.21029 (4)	0.10605 (3)	2.90 (3)
P(2)	0.30967 (6)	0.08750 (4)	0.15273 (3)	3.05 (3)
C(1)	0.4352 (3)	0.1912 (2)	0.0232 (1)	3.6 (1)
C(2)	0.3809 (3)	0.1074 (2)	0.0153 (1)	3.8 (1)
C(3)	0.2759 (2)	0.0943 (2)	0.0595 (1)	3.7 (1)
C(4)	0.6684 (2)	0.1870 (2)	0.0828 (1)	3.7 (1)
C(5)	0.5165 (3)	0.3237 (2)	0.1076 (1)	3.9 (1)
C(6)	0.3087 (3)	−0.0247 (2)	0.1648 (2)	4.0 (1)
C(7)	0.1658 (2)	0.1178 (2)	0.1874 (1)	4.0 (1)
C(8)	0.6885 (3)	0.0958 (2)	0.0803 (2)	5.1 (2)
C(9)	0.7586 (3)	0.2269 (2)	0.1316 (2)	5.6 (2)
C(10)	0.3979 (3)	0.3559 (2)	0.1273 (2)	6.0 (2)
C(11)	0.5559 (3)	0.3641 (2)	0.0421 (2)	5.1 (2)
C(12)	0.4163 (3)	−0.0629 (2)	0.1337 (2)	5.6 (2)
C(13)	0.3004 (4)	−0.0486 (2)	0.2392 (2)	6.2 (2)
C(14)	0.1448 (3)	0.2077 (2)	0.1779 (2)	5.8 (2)
C(15)	0.0600 (3)	0.0686 (3)	0.1600 (2)	5.7 (2)
H(1)	0.3723	0.2315	0.0181	4.3
H(2)	0.4901	0.1985	−0.0135	4.3
H(3)	0.3555	0.0998	−0.0328	4.6
H(4)	0.4406	0.0668	0.0280	4.6
H(5)	0.2375	0.0436	0.0448	4.4
H(6)	0.2218	0.1399	0.0515	4.4
H(7)	0.6795	0.2088	0.0369	4.4
H(8)	0.5728	0.3399	0.1442	4.7
H(9)	0.2393	−0.0461	0.1399	4.8
H(10)	0.1721	0.1082	0.2369	4.8
H(11)	0.6808	0.0727	0.1261	6.1
H(12)	0.6304	0.0709	0.0486	6.1
H(13)	0.7673	0.0849	0.0647	6.1
H(14)	0.7516	0.2044	0.1777	6.7
H(15)	0.8374	0.2164	0.1159	6.7
H(16)	0.7447	0.2857	0.1328	6.7
H(17)	0.4029	0.4147	0.1347	7.2
H(18)	0.3396	0.3443	0.0905	7.2
H(19)	0.3748	0.3293	0.1695	7.2
H(20)	0.6326	0.3427	0.0306	6.1
H(21)	0.4989	0.3527	0.0046	6.1
H(22)	0.5616	0.4230	0.0491	6.1
H(23)	0.4111	−0.1222	0.1367	6.7
H(24)	0.4195	−0.0466	0.0856	6.7
H(25)	0.4872	−0.0442	0.1588	6.7
H(26)	0.2310	−0.0233	0.2580	7.4
H(27)	0.2941	−0.1078	0.2427	7.4
H(28)	0.3706	−0.0301	0.2651	7.4
H(29)	0.2132	0.2380	0.1959	6.9
H(30)	0.1321	0.2196	0.1291	6.9
H(31)	0.0756	0.2239	0.2025	6.9
H(32)	−0.0094	0.0841	0.1846	6.8
H(33)	0.0464	0.0798	0.1111	6.8
H(34)	0.0745	0.0105	0.1666	6.8
H(35)	$^1/_2$	0.217 (3)	$^1/_4$	8 (1)
H(36)	0.573 (4)	0.121 (3)	0.233 (3)	12 (1)

Table III. Intramolecular Distances for **2**[a]

Co–P(1)	2.1357 (8)	C(2)–C(3)	1.525 (4)
Co–P(2)	2.1416 (8)	C(4)–C(8)	1.520 (5)
Co–Co*	2.2841 (7)	C(4)–C(9)	1.526 (4)
P(1)–C(1)	1.856 (3)	C(5)–C(10)	1.520 (5)
P(1)–C(4)	1.866 (3)	C(5)–C(11)	1.529 (4)
P(1)–C(5)	1.867 (3)	C(6)–C(13)	1.514 (5)
P(2)–C(3)	1.853 (3)	C(6)–C(12)	1.530 (5)
P(2)–C(6)	1.862 (3)	C(7)–C(14)	1.510 (5)
P(2)–C(7)	1.873 (3)	C(7)–C(15)	1.535 (4)
C(1)–C(2)	1.519 (4)		
Co–H(36)*	1.52 (5)	C(10)–H(17)	0.98
Co–H(36)	1.56 (5)	C(10)–H(18)	0.98
Co–H(35)	1.57 (4)	C(10)–H(19)	0.98
C(1)–H(2)	0.98	C(11)–H(20)	0.98
C(1)–H(1)	0.98	C(11)–H(21)	0.98
C(2)–H(4)	0.98	C(11)–H(22)	0.98
C(2)–H(3)	0.98	C(12)–H(23)	0.98
C(3)–H(5)	0.98	C(12)–H(24)	0.98
C(3)–H(6)	0.98	C(12)–H(25)	0.98
C(4)–H(7)	0.98	C(13)–H(27)	0.98
C(5)–H(8)	0.98	C(13)–H(26)	0.98
C(6)–H(9)	0.98	C(13)–H(28)	0.98
C(7)–H(10)	0.98	C(14)–H(29)	0.98
C(8)–H(12)	0.98	C(14)–H(31)	0.98
C(8)–H(11)	0.98	C(14)–H(30)	0.98
C(8)–H(13)	0.98	C(15)–H(34)	0.98
C(9)–H(15)	0.98	C(15)–H(32)	0.98
C(9)–H(16)	0.98	C(15)–H(33)	0.98
C(9)–H(14)	0.98		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Within a few moments the solution had turned dark green and gas evolution was complete. Measurement of the gas evolved was by Toepler pump analysis and found to be 1.9 ± 0.2 mol (average of three determinations) per dimer of **2**.

X-ray Crystallographic Analysis. Dark blue crystals of $[(dippp)CoH_2]_2$ (**2**) were obtained by cooling a hexanes solution of the complex at −20 °C. In the glovebox, the crystals were loaded into 0.3- or 0.5-mm glass capillaries (Charles Supper Co.), which were then sealled under nitrogen.

At 21 °C. Crystallographic data appear in Table I. The final unit-cell parameters were obtained by least-squares techniques on the setting angles for 25 reflections with $2\theta = 27.0–34.0°$. The intensities of three standard reflections, measured every 150 reflections throughout the data collection, decayed uniformly by 2.3%. The data were processed[24] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans for four reflections). A total of 4586 reflections were collected on a Rigaku AFC6S diffractometer; of these, 4367 were unique ($R_{int} = 0.030$), and those 2725 having $I \geq 3\sigma(I)$ were employed in the solution and refinement of the structure.

The structure analysis was initiated in the centrosymmetric space group $C2/c$ on the basis of the Patterson function, the choice of space group being confirmed by the subsequent successful solution and refinement of the structure. The structure was solved by conventional heavy-atom methods, the coordinates in the Co and P atoms being determined from the Patterson function and those of the remaining nonhydrogen atoms from a subsequent difference Fourier synthesis. The non-hydrogen atoms were refined with anisotropic thermal parameters. The bridging hydrogen atoms were refined with isotropic thermal parameters, and all carbon-bound hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B(H) = 1.2B$(bonded atom)). The remaining metal hydride atom could not be located and is probably a terminal hydride disordered over four possible sites (two at each metal). Neutral-atom scattering factors and anomalous dispersion corrections for all atoms were taken from ref 25. Final atomic coordinates and equivalent isotropic thermal parameters [$B_{eq} = {}^4/_e\sum_i\sum_j\beta_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j)$], bond lengths, and bond angles appear in Tables II–IV, respectively. Anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes are included as supplementary material.

At −155 °C. The same crystal as above was carefully removed from the capillary and mounted on the goniostat by using standard inert-atmosphere handling techniques. After the crystal was cooled to −155 °C, its quality was checked and determined to be adequate.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the original $C2/c$ unit cell. Subsequent solution and refinement of the structure confirmed the choice. Data were collected

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(24) TEXSAN/TEXRAY structure analysis package which includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(25) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor D. Reidel: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102, 149.

Table IV. Intramolecular Bond Angles for **2**[a]

P(1)–Co–P(2)	99.36 (3)	C(2)–C(1)–P(1)	115.3 (2)
P(1)–Co–Co*	128.92 (3)	C(1)–C(2)–C(3)	113.5 (2)
P(2)–Co–Co*	131.55 (3)	C(2)–C(3)–P(2)	115.5 (2)
C(1)–P(1)–C(4)	100.8 (1)	C(8)–C(4)–C(9)	110.3 (3)
C(1)–P(1)–C(5)	100.7 (1)	C(8)–C(4)–P(1)	110.8 (2)
C(1)–P(1)–Co	119.0 (1)	C(9)–C(4)–P(1)	112.0 (2)
C(4)–P(1)–C(5)	101.8 (1)	C(10)–C(5)–C(11)	111.0 (3)
C(4)–P(1)–Co	115.7 (1)	C(10)–C(5)–P(1)	110.3 (2)
C(5)–P(1)–Co	116.1 (1)	C(11)–C(5)–P(1)	115.0 (2)
C(3)–P(2)–C(6)	100.6 (1)	C(13)–C(6)–C(12)	111.1 (3)
C(3)–P(2)–C(7)	100.9 (1)	C(13)–C(6)–P(2)	112.4 (2)
C(3)–P(2)–Co	119.30 (9)	C(12)–C(6)–P(2)	110.4 (2)
C(6)–P(2)–C(7)	102.0 (1)	C(14)–C(7)–C(15)	110.8 (3)
C(6)–P(2)–Co	116.6 (1)	C(14)–C(7)–P(2)	110.7 (2)
C(7)–P(2)–Co	114.7 (1)	C(15)–C(7)–P(2)	115.1 (2)
H(36)*–Co–H(36)	72 (3)	H(15)–C(9)–H(16)	109.49
H(36)*–Co–H(35)	72 (2)	H(15)–C(9)–H(14)	109.43
H(36)*–Co–P(1)	170 (2)	H(15)–C(9)–C(4)	109.51
H(36)*–Co–P(2)	89 (2)	H(16)–C(9)–H(14)	109.43
H(36)*–Co–Co*	43 (2)	H(16)–C(9)–C(4)	109.51
H(36)–Co–H(35)	71 (2)	H(14)–C(9)–C(4)	109.46
H(36)–Co–P(1)	104 (2)	H(17)–C(10)–H(18)	109.47
H(36)–Co–P(2)	132 (2)	H(17)–C(10)–H(19)	109.48
H(36)–Co–Co*	42 (2)	H(17)–C(10)–C(5)	109.49
H(35)–Co–P(1)	98 (1)	H(18)–C(10)–H(19)	109.46
H(35)–Co–P(2)	145.2 (2)	H(18)–C(10)–C(5)	109.46
H(35)–Co–Co*	43 (1)	H(19)–C(10)–C(5)	109.48
H(2)–C(1)–H(1)	109.47	H(20)–C(11)–H(21)	109.49
H(2)–C(1)–C(2)	107.98	H(20)–C(11)–H(22)	109.47
H(2)–C(1)–P(1)	108.00	H(20)–C(11)–C(5)	109.47
H(1)–C(1)–C(2)	107.98	H(21)–C(11)–H(22)	109.47
H(1)–C(1)–P(1)	107.99	H(21)–C(11)–C(5)	109.46
H(4)–C(2)–H(3)	109.47	H(22)–C(11)–C(5)	109.46
H(4)–C(2)–C(1)	108.46	H(23)–C(12)–H(24)	109.48
H(4)–C(2)–C(3)	108.46	H(23)–C(12)–H(25)	109.45
H(3)–C(2)–C(1)	108.44	H(23)–C(12)–C(6)	109.50
H(3)–C(2)–C(3)	108.45	H(24)–C(12)–H(25)	109.44
H(5)–C(3)–H(6)	109.46	H(24)–C(12)–C(6)	109.48
H(5)–C(3)–C(2)	107.95	H(25)–C(12)–C(6)	109.47
H(5)–C(3)–P(2)	107.97	H(27)–C(13)–H(26)	109.47
H(6)–C(3)–C(2)	107.95	H(27)–C(13)–H(28)	109.47
H(6)–C(3)–P(2)	107.97	H(27)–C(13)–C(6)	109.49
H(7)–C(4)–C(8)	107.86	H(26)–C(13)–H(28)	109.46
H(7)–C(4)–C(9)	107.84	H(26)–C(13)–C(6)	109.47
H(7)–C(4)–P(1)	107.84	H(28)–C(13)–C(6)	109.48
H(8)–C(5)–C(10)	106.65	H(29)–C(14)–H(31)	109.49
H(8)–C(5)–C(11)	106.66	H(29)–C(14)–H(30)	109.46
H(8)–C(5)–P(1)	106.66	H(29)–C(14)–C(7)	109.48
H(9)–C(6)–C(13)	107.60	H(31)–C(14)–H(30)	109.46
H(9)–C(6)–C(12)	107.59	H(31)–C(14)–C(7)	109.48
H(9)–C(6)–P(2)	107.61	H(30)–C(14)–C(7)	109.46
H(10)–C(7)–C(14)	106.54	H(34)–C(15)–H(32)	109.49
H(10)–C(7)–C(15)	106.54	H(34)–C(15)–H(33)	109.48
H(10)–C(7)–P(2)	106.54	H(34)–C(15)–C(7)	109.49
H(12)–C(8)–H(11)	109.49	H(32)–C(15)–H(33)	109.45
H(12)–C(8)–H(13)	109.47	H(32)–C(15)–C(7)	109.46
H(12)–C(8)–C(4)	109.49	H(33)–C(15)–C(7)	109.45
H(11)–C(8)–H(13)	109.46	Co–H(35)–Co*	93 (3)
H(11)–C(8)–C(4)	109.47	Co–H(36)–Co*	96 (3)
H(13)–C(8)–C(4)	109.46		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

in the usual manner using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. An absorption correction was made, with maximum and minimum values of 0.925 and 0.876, respectively.

Full-matrix refinement of the non-hydrogen atoms followed by a difference Fourier map located some of the hydrogen atoms. Although the bridging hydride was present in this map, it was left out of the initial refinement. After several cycles, all hydrogen atoms "behaved" normally and a difference Fourier map was generated. In it there was one large peak (0.5 e/Å^3) in a proper position to bridge the two Co atoms. All other peaks within bonding distance of the Co atoms were less than 0.25 e/Å^3 in intensity. Although there was a peak on the 2-fold axis, it was 14th on the list, with an intensity of 0.21 e/Å^3, and was apparently too close to the center of the Co–Co bond to be a hydride. When the hydride was introduced at the 2-fold site and refinement concluded, it behaved properly although the thermal parameter is considerably higher than those of any of the remaining hydrogen atoms.

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Supplementary Material Available: (a) For the data set at 21 °C, tables of crystal and diffractometer data, *U* values, torsion or conformational angles, and least-squares planes for **2**, (b) for the data set at −155 °C, a full report on **2** of all details concerning crystal and diffractometer data and tables of fractional coordinates, anisotropic thermal parameters, and bonded distances and angles for **2**, and (c) VERSORT, ORTEP, and space filling model drawings for **2** (42 pages); listings of observed and calculated structure factor amplitudes for **2** at 21 and −155 °C (38 pages). Ordering information is given on any current masthead page.

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Reactivity of μ-Me$_2$NB$_2$H$_5$ toward the As–N Bond

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During our studies on the reactivity of BH$_3$·THF with mono-, bis-, and tris(dimethylamino) methyl-substituted arsines,[1-3] we observed that μ-Me$_2$NB$_2$H$_5$ formed whenever the BH$_3$·THF was in excess relative to the number of available nitrogen base sites. Decomposition of the N–B-bonded adducts of the aminoarsines gives Me$_2$NBH$_2$, which reacts with the excess BH$_3$·THF to yield μ-Me$_2$NB$_2$H$_5$.

This route to the μ-Me$_2$NB$_2$H$_5$ is analogous to the nearly quantitative synthesis of Burg and Randolph,[4] wherein the Me$_2$NBH$_2$ that is formed from the reaction of Me$_2$NH with B$_2$H$_6$ is reacted with additional B$_2$H$_6$. A variation on this reaction was also reported by Spielman and was used by us in our synthesis of μ-Me$_2$NB$_2$H$_5$.[5,6] Several other synthetic routes to μ-Me$_2$NB$_2$H$_5$ have been reported.[7-9]

There is a somewhat limited literature on the reactivity of μ-Me$_2$NB$_2$H$_5$ with group 15 bases.[4,10-15] In almost all cases, the products are simple 1:1 adducts. The work of Hahn and Schaeffer established that the products from the reactions with NH$_3$, MeNH$_2$, Me$_2$NH, and Me$_3$N are substituted diborazanes.[10] The adducts formed with Me$_3$N, pyridine, Me$_3$P, Me$_2$PH, and MePH$_2$ were shown by Burg and Sandhu to exist with reversible disso-

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