

Reduction of Carbon Monoxide by Tandem Electron Transfer and Migratory Insertion of a Masked Zirconium(IV) Hydride. Formation of a Zirconium Formyl–Ylide Complex

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In the presence of carbon monoxide, the Zr(III) tetrahydroborate complex $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{BH}_4[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ disproportionates to give two diamagnetic species: the bis-(tetrahydroborate) complex $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\text{BH}_4)_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ and the dicarbonyl derivative $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$. The bis(tetrahydroborate) undergoes a further slow reaction with CO to generate a zirconium–formyl complex in which the formyl unit is stabilized by phosphine coordination; in other words, electron transfer in tandem with hydride migratory insertion have been used to reduce CO. The structure of the formyl–ylide species $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\text{BH}_4)(\text{HCOPPr}^i_2\text{CH}_2\text{SiMe}_2)\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2\text{BH}_3)$ was determined by both solution (NMR spectroscopy) and solid-state (X-ray crystallography) methods. Not only does one end of the tridentate amido–diphosphine ligand bind to the formyl carbon but the other phosphine donor is coordinated to a BH_3 molecule. Presumably, it is this latter interaction that initially frees up a reactive Zr–H bond that subsequently undergoes migratory insertion with CO to generate the formyl unit.

Introduction

During the last few decades, fundamental aspects of the Fischer–Tropsch reaction have come under intense scrutiny.¹ This was fueled by increased oil prices and the potential use of synthesis gas (CO/H_2) as an alternative feedstock for the preparation of liquid hydrocarbons.^{2–7} On the homogeneous front, the reaction of CO with a metal hydride to generate a metal formyl was presumed^{5,6,8,9} to be an important first step in this process. From efforts to prepare metal formyl complexes, much fundamental knowledge about the relative migratory aptitudes of hydride and alkyl ligands as well as detailed knowledge of metal–ligand bond strengths has accrued.^{8–10} While there are a number of examples of early metal hydride derivatives that react with CO to form a metal formyl as a presumed intermediate,^{11–16}

the reaction of a metal tetrahydroborate unit (M–BH_4) with CO has been found to undergo different reactions.¹⁷ In this report we detail the reaction of a zirconium(III) tetrahydroborate complex with CO that ultimately results in the formation of an unusual ylide–formyl derivative, presumably first by electron transfer followed then by hydride migratory insertion.

Results and Discussion

We have previously reported the preparation of mononuclear Zr(III) complexes having the general formula $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{X}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, where X = halide, hydride, hydrocarbyl, or tetrahydroborate,¹⁸ by reduction of the starting Zr(IV) dichloro derivative $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **1**, with Na/Hg to generate excellent yields of the Zr(III) chloro complex $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **2**. In the process of investigating the reactivity patterns of this very rare oxidation state of zirconium, we discovered that, in the presence of carbon monoxide, a very clean disproportionation reaction could be observed for the chloro derivative $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **2**, and for the tetrahydroborate derivative $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{BH}_4[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **3**. Thus, the reaction of CO with these

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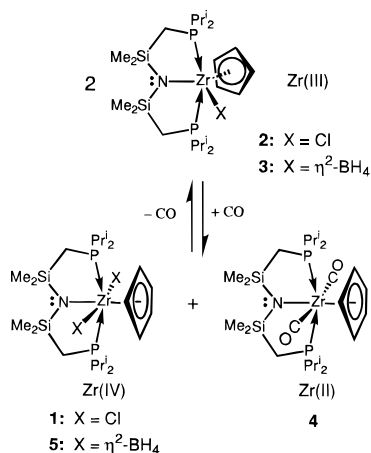
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Scheme 1



species produces the corresponding Zr(IV) complex with either two chloride or two tetrahydroborate ligands and, in addition, the Zr(II) dicarbonyl complex $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **4**. This is outlined in Scheme 1. Within minutes of addition of CO to a solution of the Zr(III) chloro derivative **2**, there is observed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy an equal mixture of two diamagnetic products: the starting dichloro $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **1**, and the dicarbonyl $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **4**. Similarly, the tetrahydroborate **3** gives an equal mixture of the bis(tetrahydroborate) **5** and the dicarbonyl **4**. This reaction is an equilibrium as evidenced by the fact that slow removal of CO from solutions of the Zr(IV)/Zr(II) mixtures results in the re-formation of the Zr(III) starting complexes as evidenced by ESR spectroscopy; addition of CO re-establishes the diamagnetic compounds. In fact, this equilibrium makes isolation of the products of the disproportionation reaction somewhat difficult since contamination by the Zr(III) starting derivatives is problematic. However, while we have been unable to isolate the pure bis(tetrahydroborate) complex, the dicarbonyl **4** can be isolated pure, albeit in low yield, from the reaction of the chloro derivative **2** with CO. The structure of the bis(tetrahydroborate) **5** was established by solution NMR spectroscopy as being similar to the starting dichloro complex **1**, that is having essentially trans disposed, bidentate BH₄ units, since the backbone resonances of the PNP ligand are equivalent even down to -85°C . While such disproportionation reactions are well-known for Ti(III),¹⁹ the instances found in Zr(III) chemistry are rare.²⁰ Presumably this reaction proceeds via dinuclear intermediates after coordination by CO, but this is speculation since we have no corroborating evidence. We also observe this kind of disproportionation when the Zr(III) complexes are allowed to react with excess acetonitrile; however, the products were only characterized by NMR spectroscopy since the corresponding Zr(II) derivative with acetonitrile as a ligand was found to be thermally unstable above -20°C .

The mixture of the dichloro complex **1** and the dicarbonyl **4** is stable indefinitely under a CO atmosphere; however, if the mixture of the bis(tetrahydrobo-

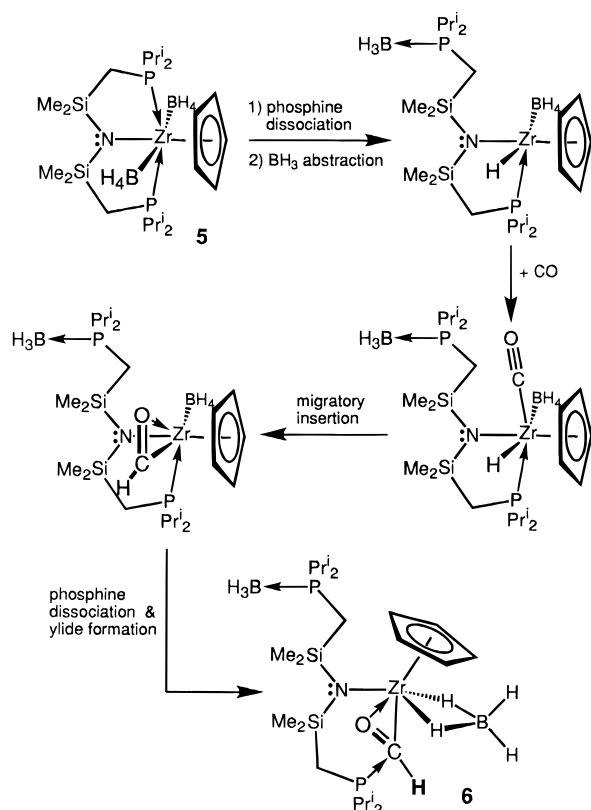
rate) **5** and the dicarbonyl **4** is allowed to stir under excess CO for an extended time and monitored by ^1H NMR spectroscopy, resonances for a new material were observed to grow in at the expense of those resonances due to the bis(tetrahydroborate) derivative **5**. Isolation of this new material away from the dicarbonyl complex **4** was possible by fractional crystallization. Elemental analyses were consistent with the empirical formulation of a CO adduct of the bis(tetrahydroborate), " $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\text{BH}_4)_2\text{CO}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ ", **6**; however, the NMR spectroscopic parameters were indicative of considerable asymmetry. In the ^1H NMR spectrum of **6**, particularly noteworthy was the presence of a doublet at 3.02 ppm due to coupling of a phosphorus-31 nucleus ($J_{\text{H-P}} = 27.4$ Hz); the cyclopentadienyl protons appeared as a sharp singlet at 6.41 ppm. Other resonances in the ^1H NMR spectrum due to the PNP ligand were rather complicated; four singlets due to the silylmethyl groups (SiMe_2) and a set of complicated overlapping multiplets due to the isopropyl methyls and methine protons were observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displayed two peaks, one broad singlet at 31.2 ppm and a sharp singlet at 39.7 ppm. Selective ^{31}P decoupled ^1H NMR experiments showed that the resonance at 3.02 ppm in the ^1H NMR spectrum is coupled to the ^{31}P resonance at 39.7 ppm with $J_{\text{H-P}} = 27$ Hz. When the reaction was performed with carbon-13-labeled CO, the doublet at 3.02 ppm in the ^1H NMR spectrum became a doublet of doublets at 3.10 ppm ($^1J_{\text{C-H}} = 162$ Hz) and the sharp singlet resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 39.7 ppm was observed as a doublet ($J_{\text{P-C}} = 55.1$ Hz). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the enriched material showed a doublet at 60.7 ppm ($J_{\text{P-C}} = 55$ Hz); this chemical shift is considerably outside the range normally associated with a formyl type ligand⁸ and is rather indicative of some further reduced form of CO. In accord with this, the solution infrared spectrum did not show any absorptions characteristic of a terminal or a bridging carbonyl ligand or even a carbonyl functional group. In the B-H stretching region of the IR spectrum, there were observed absorptions characteristic of a bidentate BH₄ ligand bound to Zr (terminal B-H bond stretches at 2423 and 2378 cm^{-1} and a band at 2146 cm^{-1} corresponding to the bridging boron-hydrogen stretch) as well as additional terminal B-H stretches at 2355 and 2345 cm^{-1} ; for the sake of completeness, the IR spectrum of the bis(tetrahydroborate) complex **5** shows strong absorptions due to the terminal boron-hydrogen stretches at 2429 and 2381 cm^{-1} and a band at 2134 cm^{-1} corresponding to the bridging boron-hydrogen stretch, and these absorptions are virtually identical to that of the Zr(III) tetrahydroborate complex $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{BH}_4[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$, **3**, which has been structurally characterized as having a bidentate BH₄ unit. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of complex **6** has a singlet at -101.3 ppm and a doublet at -127.2 ppm; the latter is probably due to the coupling with one phosphorus-31 nucleus ($J_{\text{B-P}} = 47.4$ Hz).

On the basis of the spectroscopic data, the structure of **6** could be assigned as due to a species containing a formyl-yliide unit (Scheme 2); this was confirmed by an X-ray crystal structure as shown in Figure 1. Listed in Tables 1 and 2 are selected bond lengths and bond angles, respectively, for compound **6**: the atomic pa-

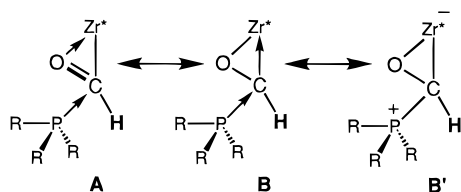
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Scheme 2



rameters are given in Table 3. There is considerable structural change in the coordination mode of the ancillary PNP ligand as one end of the ligand has a dangling phosphine bound to a terminal BH_3 unit in a typical Lewis-acid-Lewis-base type interaction, while the other phosphine arm is now bound to the carbon of the formyl ligand. The other parts of the molecule are essentially unchanged from the starting tetrahydroborate derivative **3**: the Cp unit is bound in an η^5 -fashion, and the remaining BH_4 unit is bidentate. The formyl-ylide core of the molecule shows a O-C1 bond length of 1.429(5) Å and a P1-C1 distance of 1.765(4) Å; the latter distance is only slightly shorter than the other P-C bond distances around this particular phosphorus atom. The O-C1 bond distance, however, is somewhat in between a typical C-O double or single bond and, thus, perhaps indicates some resonance contribution from the oxycarbene⁹ forms **B** and **B'** shown in zirconate form **B'**, the ylide formalism is explicit.



One possible mechanistic pathway for the formation of **6** has some implications on the reactivity of tetrahydroborate complexes in general.²¹ We suggest (Scheme 2) that the first step is phosphine dissociation from **5** followed by removal of BH_3 by the free phosphine ligand to form a zirconium hydride; subsequent coordination of CO and a migratory insertion step generate an η^2 -formyl ligand. Rearrangement to the final product is

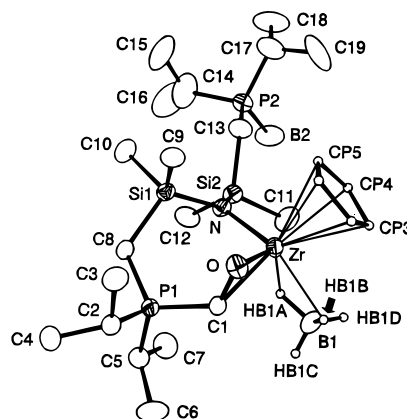


Figure 1. Molecular structure and numbering scheme for **6**.

Table 1. Selected Bond Lengths (Å) for **6**

Zr-O	1.987(3)	Zr-Cent	2.2855(9)
Zr-N	2.135(3)	Zr-HB1A	2.09(4)
Zr-Cp1	2.534(6)	Zr-HB1B	2.31(4)
Zr-Cp2	2.527(5)	Si1-N	1.731(4)
Zr-Cp3	2.555(6)	Si2-N	1.733(4)
Zr-Cp4	2.573(6)	P1-C1	1.765(4)
Zr-Cp5	2.560(6)	P1-C2	1.832(4)
Zr-C1	2.254(4)	P1-C5	1.818(5)
Zr-B1	2.594(6)	P1-C8	1.795(4)
O-C1	1.429(5)	P2-B2	1.927(7)

Table 2. Selected Bond Angles (deg) for **6**

O-Zr-N	104.63(13)	Zr-O-C1	80.78(21)
O-Zr-C1	38.73(14)	Zr-N-Si1	115.11(17)
N-Zr-C1	95.70(14)	Zr-N-Si2	122.76(18)
C1-P1-C2	110.90(21)	Si1-N-Si2	122.11(20)
C1-P1-C5	107.41(21)	Zr-C1-P1	129.48(22)
C1-P1-C8	114.15(20)	Zr-C1-O	60.49(19)
P1-C1-O	116.1(3)	Zr-C1-H1	115.2(3)
P1-C1-H1	110.0(3)	O-C1-H1	116.6(4)
O-Zr-Cent	105.68(9)	C1-Zr-Cent	141.84(12)

via phosphine dissociation and coordination to the formyl carbon.²²⁻²⁴ To the best of our knowledge, there is the first time that a metal formyl has been stabilized by phosphine ligation; earlier work has shown that phosphine addition results in the C-O bond cleavage of a dinuclear tantalum formyl unit.¹¹ In our complex, the two phosphine arms of the ancillary ligand serve both to activate the zirconium center by removal of a BH_3 to unmask a hydride and to stabilize the resulting reactive formyl ligand by formation of a phosphorus ylide unit.²⁵

Attempts to provide additional evidence for this mechanistic proposal have been thwarted by our inability to independently prepare the bis(tetrahydroborate) **5** or to isolate it away from the dicarbonyl complex **4**. In fact, an obvious method to prepare **5** via the reaction of excess LiBH_4 with the dichloride **1** failed to give any of the desired material; attempted oxidation of the Zr(III) tetrahydroborate complex **3** with PbCl_2 to generate the mixed chloro-tetrahydroborate $\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{BH}_4)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ also was unsuccessful.

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Table 3. Atomic Parameters x , y , and z and B_{iso} Values (\AA^2)

	x	y	z	B_{iso}^a
Zr	0.59612(4)	0.85878(5)	0.138626(16)	3.334(20)
P1	0.68673(9)	1.11441(11)	0.06067(4)	2.98(5)
P2	0.86911(10)	0.92905(15)	0.35646(5)	3.90(6)
Si1	0.69846(10)	1.16080(13)	0.17736(4)	3.33(6)
Si2	0.80563(11)	0.91100(14)	0.23448(5)	3.66(6)
O	0.52305(22)	0.9919(3)	0.08702(11)	3.94(15)
N	0.7087(3)	0.9827(3)	0.18801(12)	3.19(18)
CP1	0.4318(5)	0.8835(6)	0.1695(3)	8.6(5)
CP2	0.4185(4)	0.7701(8)	0.14117(22)	7.9(4)
CP3	0.4837(7)	0.6694(6)	0.1645(3)	12.0(6)
CP4	0.5338(5)	0.7264(9)	0.2075(3)	12.2(6)
CP5	0.5037(6)	0.8542(9)	0.21052(23)	11.3(5)
C1	0.6127(3)	0.9665(4)	0.06808(15)	3.21(21)
C2	0.6108(4)	1.2365(4)	0.01540(15)	3.49(22)
C3	0.5224(4)	1.2977(5)	0.03501(18)	4.43(24)
C4	0.6778(4)	1.3520(5)	−0.00019(19)	5.1(3)
C5	0.7936(4)	1.0547(5)	0.03513(18)	4.07(24)
C6	0.7575(5)	0.9896(7)	−0.01698(20)	6.7(3)
C7	0.8637(4)	0.9551(6)	0.07098(22)	6.0(3)
C8	0.7387(3)	1.2072(4)	0.11764(16)	3.32(21)
C9	0.5652(4)	1.2287(5)	0.17330(18)	4.7(3)
C10	0.7844(4)	1.2739(5)	0.22539(18)	5.6(3)
C11	0.8093(4)	0.7158(5)	0.23357(20)	5.9(3)
C12	0.9364(4)	0.9669(6)	0.22802(19)	5.4(3)
C13	0.7767(4)	0.9597(5)	0.29700(16)	4.39(25)
C14	0.9470(5)	1.0882(7)	0.3665(3)	9.6(5)
C15	0.8917(6)	1.2176(7)	0.3771(3)	10.0(5)
C16	1.0457(7)	1.0849(11)	0.3820(5)	19.5(9)
C17	0.7898(4)	0.9284(7)	0.40251(19)	6.3(3)
C18	0.8558(6)	0.9172(8)	0.45659(21)	9.3(5)
C19	0.7094(5)	0.8175(8)	0.3927(3)	10.0(5)
B1	0.6696(5)	0.6441(6)	0.10097(24)	5.5(4)
B2	0.9545(6)	0.7647(8)	0.3621(3)	7.0(4)

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid.

ful. Thus the proposal that the formyl unit results from external CO and not perhaps via the dicarbonyl **4** is difficult to substantiate. However, it should be pointed out that the electron transfer process that leads to disproportionation (Scheme 1) occurs much more rapidly than the reduction of CO (Scheme 2), and this is good evidence that it is the Zr(IV) bis(tetrahydroborate) complex **5** that reduces CO and not the Zr(III) tetrahydroborate derivative **3**. In addition, the tendency for phosphine dissociation is probably more pronounced in the Zr(IV) complex **5** than in the Zr(III) species **3** simply because the former has a higher formal coordination number than the latter.

One of the standard methods of generating early metal hydrides is via initial formation of the tetrahydroborate ligand followed by addition of an external Lewis base such as an amine or a phosphine.^{26–29} In our case the presence of the internal chelated Lewis base is a new permutation of this reaction and suggests that other intramolecular Lewis bases or, by extension, intramolecular Lewis acids may be capable of generating reactive intermediates.

Experimental Section

General Methods. The ¹H, ³¹P, and ¹³C NMR spectra were recorded on a Varian XL-300, a Bruker AC-200, a Bruker WH-400, or a Bruker AM-500 spectrometer. Proton spectra were referenced using the partially deuterated solvent peak as the

internal reference, C₆D₅H at 7.15 ppm and C₆D₅CD₂H at 2.09 ppm relative to Me₄Si. The ³¹P{¹H} NMR spectra were referenced to external P(OMe)₃ set at +141.00 ppm relative to 85% H₃PO₄. The ¹³C{¹H} NMR spectra were referenced to the C₆D₆ signal at 128.0 ppm or to the CD₃C₆D₅ signal at 20.4 ppm. ¹H{³¹P} NMR spectra were recorded on the Bruker AMX 500 spectrometer.

UV–vis spectra were recorded on a Perkin-Elmer 5523 UV/vis spectrophotometer stabilized at 20 °C. Mass spectral studies were carried out on a Kratos MS 50 using an EI source. IR spectra were recorded on a Bomem MB-100 spectrometer. Solution samples were recorded in a 0.1 mm KBr cell, and solid samples were recorded as KBr pellets. Carbon, hydrogen, nitrogen, and chloride analyses were performed by the microanalyst of this department.

The ESR spectra were recorded on Varian E-3 spectrometer calibrated with a sample of VO(acac)₂, $g = 1.965$. ESR simulations were done on a Macintosh Ix using ESR II from Calleo Scientific Software. The values of line broadening and coupling constants were obtained from the simulated spectra.

The starting complexes Zr(η^5 -C₅H₅)Cl₂[N(SiMe₂CH₂PPrⁱ)₂]₂, **1**, and Zr(η^5 -C₅H₅)Cl[N(SiMe₂CH₂PPrⁱ)₂]₂, **2**, were prepared as previously described;³⁰ all other reagents were obtained from standard sources.

Zr(η^5 -C₅H₅)BH₄[N(SiMe₂CH₂PPrⁱ)₂]₂, **3.** To a solution of Zr(η^5 -C₅H₅)Cl[N(SiMe₂CH₂PPrⁱ)₂]₂ (800 mg, 1.37 mmol) in toluene (40 mL) was added solid LiBH₄ (150 mg, 6.84 mmol), and the mixture was stirred at room temperature. After being stirred for 12 h, the slurry was filtered through a layer of Celite and the filtrate was concentrated to give a black oil. The oil was dissolved in Et₂O (5 mL) and cooled at −40 °C to give black rectangular crystals (650 mg, 84%). ESR (toluene): $g = 1.958$; $a(^{31}\text{P}) = 20.7$ G, 2P; $a(^{14}\text{N}) = 2.0$ G, 1N; $a(^1\text{H}) = 2.8$ G, 4H; line width used for simulation, 2.8 G. UV–vis (toluene, 1 cm quartz cell): $\lambda_{\text{max}} = 332$ nm; $\epsilon_{\text{max}} = 2800$ L mol^{−1} cm^{−1}. IR (cm^{−1}, KBr): 2953, 2871, 2401 (s, B–H_i), 2379 (s, B–H_t), 2126 (s, B–H_b), 1457 (m, Zr–H), 1373, 1244, 1124. Anal. Calcd for C₂₃H₅₃NBSi₂P₂Zr: C, 49.00; H, 9.47; N, 2.48. Found: C, 48.82; H, 9.46; N, 2.48.

Zr(η^5 -C₅H₅)(HCOPPrⁱ₂CH₂SiMe₂)N(SiMe₂CH₂PPrⁱ)₂-BH₃, **6.** A solution of the tetrahydroborate complex Zr(η^5 -C₅H₅)BH₄[N(SiMe₂CH₂PPrⁱ)₂]₂ (500 mg, 0.89 mmol) in toluene (40 mL) was stirred under 1 atm of carbon monoxide for 3 days. The solvent and excess CO were rapidly removed under high vacuum, and the residue was extracted with cold (−10 °C) hexanes; the hexanes-insoluble residue was then dissolved in minimum toluene; after the sample was left to stand at −40 °C, off white crystals of the product were obtained (108 mg, 40%). The carbon-13-labeled material was made using ¹³CO obtained from MSD Isotopes (98% ¹³C). ¹H NMR (δ , 500 MHz, C₇D₈): 0.23, 0.35, 0.61, 0.69 (s, each 3H, Si(CH₃)₂); 0.60 (overlapping d of d, 6H, [P(CH(CH₃)₂)₂]₂, ³J_{H–H} = 7.6 Hz, ³J_{P–H} = 15.3 Hz); 0.94 (overlapping d of d, 6H, [P(CH(CH₃)₂)₂]₂, ³J_{H–H} = 7.1 Hz, ³J_{P–H} = 15.3 Hz); 1.03 (two overlapping d, 2H, SiCH₂P); 0.98–1.11 (m, 14H, [P(CH(CH₃)₂)₂]₂, and SiCH₂P); 1.54 (sept, 1H, P[CH(CH₃)₂]₂, ³J_{H–H} = 7.1 Hz); 1.77 (sept, 1H, P[CH(CH₃)₂]₂, ³J_{H–H} = 7.1 Hz); 1.80 (sept, 2H, P[CH(CH₃)₂]₂, ³J_{H–H} = 7.6 Hz); ¹²C-isotopomer, 3.02, ¹³C-isotopomer, 3.10 (d of d, 1H, CHO, ²J_{P–H} = 27.4 Hz, ¹J_{C–H} = 161.9 Hz); 6.41 (s, 5H, C₅H₅). ³¹P{¹H} NMR (δ , 121.4 MHz, C₇D₈): 31.20 (br, 1P); 39.72 (d, 1P, ²J_{P–C} = 55.1 Hz). Gated decoupled ¹³C NMR (δ , 75.4 MHz, C₇D₈): 60.73 (d of d, CHO, ²J_{P–C} = 55.7 Hz, ¹J_{C–H} = 162.2); 113.5 (d, C₅H₅, ¹J_{C–H} = 170.8 Hz). ¹¹B{¹H} NMR (δ , 96.2 MHz, C₇D₈): −101.33 (br s, BH₄); −127.23 (br d, (BH₃)₂P[CH(CH₃)₂]₂, ¹J_{P–B} = 47.4 Hz). ¹H{¹¹B} NMR (δ , 500 MHz, C₇D₈): 1.22 (s, 3H, probably (BH₃)₂P[CH(CH₃)₂]₂); some changes in the minor resonances located around 0.2–0.4 ppm (probably, BH₄). IR (cm^{−1}, KBr): 2423 (s, B–H_i), 2378 (s, B–H_t), 2355

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(s, B–H_i); 2345 (s, B–H_i); 2146 (s, B–H_b), 1460 (m, Zr–H). Anal. Calcd for C₂₄H₅₇B₂NOP₂Si₂Zr: C, 47.52; H, 9.47; N, 2.31. Found: C, 47.93; H, 9.45; N, 2.64.

Zr(η^5 -C₅H₅)(CO)₂[N(SiMe₂CH₂PPri₂)₂], 4. Addition of excess CO (1 atm) to a degassed solution of Zr(η^5 -C₅H₅)Cl[N(SiMe₂CH₂PPri₂)₂], **2** (300 mg, 0.051 mmol), in toluene (10 mL) resulted in the formation of an orange solution; rapid removal of the excess CO and the toluene under high vacuum and subsequent extraction of the residues with hexanes (10 mL) produced a solution of the dicarbonyl **4**. After filtration through a layer of Celite followed by cooling to –40 °C there was obtained brown-red crystals (31 mg, 20% based on Zr–(II)). ¹H NMR (δ , 300 MHz, C₆D₆): 0.31 (s, 12H, Si(CH₃)₂); 0.68 (m, 4H, SiCH₂P); 0.85–1.0 (m, 24H, P[CH(CH₃)₂]₂); 1.70 (br sept, 4H, P[CH(CH₃)₂]₂), ³J_{H–H} = 7.4 Hz); 4.75 (t, ~5H, C₅H₅, ³J_{P–H} = 1.5 Hz). Gated decoupled ¹³C NMR (δ , 75.4 MHz, C₇D₈): 92.12 (s, Cp, ¹J_{C–H} = 171.5 Hz); 249.0 (s, CO). ³¹P{¹H} NMR (δ , 121.421 MHz, C₆D₆): 37.91 (s). IR (cm^{–1}, toluene): 1965 (w, CO); 1871 (s, CO); 1845 (shoulder, CO). Anal. Calcd for C₂₅H₄₉NO₂P₂Si₂Zr: C, 49.63; H, 8.16; N, 2.32. Found: C, 49.72; H, 8.35; N, 2.27.

Zr(η^5 -C₅H₅)(BH₄)₂[N(SiMe₂CH₂PPri₂)₂], 5. This compound was not isolated pure but was characterized spectroscopically in solution. ¹H NMR (δ , 300 MHz, C₆D₆): 0.44 (s, 12H, Si(CH₃)₂); 0.89 (br m, 4H, SiCH₂P); 1.0–1.1 (m, 24H, P[CH(CH₃)₂]₂); 2.00 (br sept, 4H, P[CH(CH₃)₂]₂), ³J_{H–H} = 7.4 Hz); 6.28 (t, ~5H, C₅H₅, ³J_{P–H} = 1.5 Hz). ¹³C NMR (δ , 75.4 MHz, C₆D₆): 109.53 (s, Cp). ³¹P{¹H} NMR (δ , 121.421 MHz, C₆D₆): 5.80 (s). ¹¹B{¹H} NMR (δ , 96.2 MHz, C₇D₈): –92.00 (s, BH₄). IR (cm^{–1}, solution): 2427 (s, B–H_i), 2381 (s, B–H_i), 2130 (s, B–H_b).

Zr(η^5 -C₅H₅)(CH₃CN)_x[N(SiMe₂CH₂PPri₂)₂]. The reaction of Zr(η^5 -C₅H₅)Cl[N(SiMe₂CH₂PPri₂)₂], **2**, with CH₃CN was carried out at low temperature. A solution of **2** (30 mg in 0.5 mL of C₇D₈) was transferred into a NMR tube and degassed three times by freeze–pump–thaw cycles; using a constant volume gas apparatus, 2 equiv of CH₃CN vapor was condensed at –196 °C, and the tube was sealed. The sample was transferred into a –60 °C bath, and after standing for 1 h, the sample solution became deep red. The NMR spectroscopic analysis shows the presence of two complexes, Zr(η^5 -C₅H₅)Cl₂[N(SiMe₂CH₂PPri₂)₂], **1**, and Zr(η^5 -C₅H₅)(CH₃CN)_x[N(SiMe₂CH₂PPri₂)₂]. Warming the sample to room temperature shows a rapid decrease in the intensity of the resonances associated with the acetonitrile complex. ¹H NMR (δ , 300 MHz, C₇D₈) (at 10 °C): 0.02 (s, 6H, Si(CH₃)₂); 0.15 (s, 6H, Si(CH₃)₂); 1.12–1.26 (m, 24H, P[CH(CH₃)₂]₂); 2.00 (br sept, 2H, P[CH(CH₃)₂]₂), ³J_{H–H} = 6.5 Hz); 2.36 (br sept, 2H, P[CH(CH₃)₂]₂), ³J_{H–H} = 6.5 Hz); 2.78 (s, 3H, CH₃CN); 5.66 (s, 5H, C₅H₅). ³¹P{¹H} NMR (δ , 121.421 MHz, C₇D₈) (at –18 °C): 32.92 (s).

X-ray Crystallography. Crystals of **6** were grown from neat toluene at –30 °C. X-ray measurements were made on a crystal measuring 0.40 × 0.50 × 0.60 mm mounted in a sealed Lindemann capillary tube under N₂. The crystal data are given in Table 4. Data were collected at 25 °C on a Nonius CAD-4 diffractometer using the ω scan mode and Mo K α radiation (λ = 0.709 30 Å) using a procedure described elsewhere.³⁰ After anisotropic refinement of all non-hydrogen, methyl, formyl, and borane hydrogen atoms were located

Table 4. Crystal Data^a

compd	6
formula	C ₂₄ H ₅₇ B ₂ NOP ₂ Si ₂ Zr
fw	606.68
color, habit	colorless, block
cryst system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	13.303(3)
<i>b</i> , Å	9.5813(7)
<i>c</i> , Å	27.518(7)
β , deg	103.42(5)
<i>V</i> , Å ³	3411.8(12)
<i>Z</i>	4
ρ_{calc} , g/cm ³	1.18
<i>F</i> (000)	1296
μ , cm ^{–1}	41.0
cryst size, mm	0.40 × 0.50 × 0.60
transm factors	0.843–0.992
scan type	ω
data collcd	$\pm h, +k, +l$
$2\theta_{\text{max}}$, deg	45
cryst decay, %	negligible
tot. reflns	4680
tot. unique reflns	4447
<i>R</i> _{merge}	0.018
reflcs with <i>I</i> ≥ 3 σ (<i>I</i>)	3626
no. of variables	314
<i>R</i>	0.038
<i>R</i> _w	0.042
gof	4.53
max Δ/σ (final cycle)	0.005
resid density, e/Å ³	–0.43 to 0.42

^a Temperature 298 K, Nonius CAD-4 diffractometer, Mo K α radiation (λ = 0.709 30 Å), $\sigma^2(F^2)$ = [*S*²(*C* + 4*B*)]/*Lp*² (*S* = scan rate, *C* = scan count, *B* = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and $\text{gof} = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for *R*, *R*_w, and *gof* are based on those reflections with *I* ≥ 3 σ (*I*).

and fixed via inspection of a difference Fourier map, temperature factors being based on the atom to which they are bonded. Borate hydrogen atoms were located and refined. Methylene and sp² hydrogen atoms were fixed in calculated positions (*d*_{C–H} = 1.08 Å). All crystallographic calculations were conducted with the PC version of the NRCVAX program package locally implemented on an IBM-compatible 80486 computer.

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Supporting Information Available: Text giving experimental details and complete listings of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond angles and bond lengths for **6** (4 pages). Ordering information is given on any current masthead page.

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