Synthesis and Investigation of a New Family of Alkylzirconium Complexes. Crystal and Molecular Structure of [Hydrotris(3,5-dimethylpyrazolyl)borato]-*tert*-butoxy[η^2-1-(*tert*-butylimino)ethyl]methylzirconium(IV)

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Received June 20, 1983

The reaction of [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)Cl_2 (pz = pyrazolyl ring) with excess MeMgBr, $PhCH_2MgCl$, or LiC≡CR leads to the preparation of a new family of stable alkylzirconium complexes, [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)R_2. The Me and CH_2Ph derivatives react rapidly with *t*-BuNC to yield [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)(η^2-C(R)$NCMe_3$)R complexes. The solid-state structure of [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)(η^2-C(Me)$NCMe_3$)Me has been determined crystallographically. The crystals form in the monoclinic space group $P2_1/c$ with $a = 11.137$ (3) Å, $b = 16.112$ (2) Å, $c = 17.051$ (4) Å, $\beta = 93.78$ (2)°, $V = 3053$ Å^3, and $Z = 4$. In addition to clearly defining the η^2-coordination of the iminoacyl ligand, the structure shows that the O-*t*-Bu group enters into substantial multiple bonding with the electron-deficient Zr atom. The Zr–O–C bond angle is 174.4 (6)°, and the Zr–O bond length is 1.924 (6) Å. The monoalkyl complexes [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-$Bu)_2R'$ (R′ = Me, C≡CR) are also readily prepared from [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-$Bu)_2Cl$ but do not react with *t*-BuNC. These complexes are also formed in reactions of the dialkyl complexes with 1 equiv of *t*-BuOH.

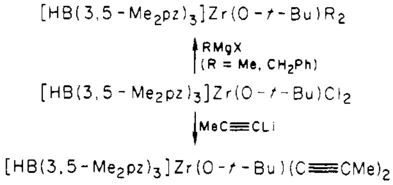
Introduction

The chemistry of zirconium alkyls has been of considerable recent interest. The starting material for a majority of this chemistry has been commercially available Cp_2ZrCl_2.[1] More recently, compounds in the Cp*Zr[2] and $Cp*_2Zr$[3] (Cp* = η^5-C_5Me_5) systems have been reported. Few reports of complexes containing auxilary ligands other than Cp or Cp* have appeared.[4]

To this end, we have previously reported the preparation of a family of zirconium halide complexes containing a tris(1-pyrazolyl)borate ligand.[5] It is anticipated that these complexes will be useful starting materials for the exploration of new organometallic chemistry. To date, the Zr complex showing the greatest potential for further derivatization is [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)Cl_2[6] (pz = pyrazolyl ring). Presented in this paper is the conversion of this compound into [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)R_2 (R = Me, CH_2Ph, C≡CMe) derivatives and the reactions of these new complexes with *t*-BuNC. The solid-state structure of one of these insertion products, [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)(η^2-C(Me)$NCMe_3$)Me, has been characterized by a single-crystal X-ray structural investigation. The synthesis of [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-$Bu)_2X$ (X = Cl, Me, C≡CMe) complexes is also reported.

Results

Synthesis of Alkyl Compounds. The preparation of the starting material for the dialkyl complexes prepared in this study, [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)Cl_2 (pz = pyrazolyl ring), has been previously described.[6] The reaction of this dihalide complex with a slight excess of RMgX (R = Me, CH_2Ph; X = Cl, Br) or a twofold excess of propynyllithium in THF, yields the desired dialkyl complexes as shown in eq 1. These complexes are extremely soluble,



$$\begin{array}{c}[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)R_2\\ \Big\uparrow{\scriptstyle RMgX\ (R\,=\,Me,\ CH_2Ph)}\\ [HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2\\ \Big\downarrow{\scriptstyle MeC\equiv CLi}\\ [HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)(C\equiv CMe)_2\end{array} \qquad (1)$$

even in pentane, and proved difficult to crystallize. They have been characterized by ^1H and ^{13}C NMR, mass spectrometry, and the reaction chemistry described below. In the NMR, the expected 2:1 pattern for each pyrazolyl ring type resonance is observed (one pyrazolyl group is trans to the *tert*-butoxide group while the remaining two pyrazolyl groups are trans to the alkyl substituents in these pseudooctahedral molecules). The various resonances for the alkyl groups are equivalent except the methylene hydrogen atoms of the benzyl groups that are diastereotopic and appear as an AB quartet. Mass spectra do not show molecular ions, but one observes characteristic clusters of peaks (R = Me, C≡CMe, $M^+ - 15$ (CH_3); R = CH_2Ph, $M^+ - 91$ (CH_2Ph)) for these compounds with appropriate isotopic distributions as expected for Zr and B.

All of these compounds are air and moisture sensitive but show surprising thermal stability in solution at 70 °C. After 30 h, only [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)$(CH_2Ph)_2$ shows marked decomposition. Slight decomposition is noted for [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)Me_2 after 30 h whereas no decomposition is observed for [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)(C≡CMe)$_2$.

Earlier[6] it was noted that it was difficult to isolate [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-$Bu)_2Cl$ free of either the mono or tributoxy analogues. It has now been shown (eq 2) that

$$[HB(3,5\text{-}Me_2pz)_3]ZrCl_3 + 2KO\text{-}t\text{-}Bu \xrightarrow[\text{reflux}]{\text{benzene}} [HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_2Cl + 2\ KCl \qquad (2)$$

using a slight excess of KO-*t*-Bu in refluxing benzene leads to the desired complex just slightly contaminated with the tributoxy derivative. Crystallization of this mixture from hexane yields white crystalline material free of the more soluble tributoxy complex. Another route to this complex

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is the exchange reaction shown in eq 3. In a similar

$$[\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})\mathrm{Cl_2} + [\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_3 \rightarrow 2[\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_2\mathrm{Cl} \quad (3)$$

exchange reaction, it has been shown that [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)Cl$_2$ can be prepared from [HB(3,5-Me$_2$pz)$_3$]ZrCl$_3$ and [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)$_2$Cl.

When [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)$_2$Cl is treated with excess RLi (R = Me, C≡CMe) in THF, the corresponding monoalkyl complexes are formed in good yield (eq 4). The

$$[\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_2\mathrm{Cl} \xrightarrow[\mathrm{THF}]{\mathrm{RLi}} [\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_2\mathrm{R} + \mathrm{LiCl} \quad (4)$$

$$\mathrm{R} = \mathrm{Me},\ \mathrm{C{\equiv}CMe}$$

monoalkyl complexes can be isolated as crystalline solids from pentane and show characteristic ^{1}H and ^{13}C NMR spectra. They are sensitive to air and moisture but exhibit good thermal stability, showing only slight decomposition at 70 °C after 30 h.

The preparation of [HB(3,5-Me$_2$pz)$_3$]ZrR$_3$ or [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)ClR complexes has been unsuccessful. Mixing [HB(3,5-Me$_2$pz)$_3$]ZrCl$_3$ with 3 equiv or an excess of a variety of alkylating reagents consumes the starting material but has not yet led to the isolation of the desired trialkyl complexes. The reaction of [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)Cl$_2$ with 1 equiv of RMgX or RLi reagents leads only to the reisolation of starting material. The direct preparation of amido complexes has also been unsuccessful. The reaction of [HB(3,5-Me$_2$pz)$_3$]ZrCl$_3$ or [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)Cl$_2$ with LiNEt$_2$ or LiNHPh leads to the consumption of the starting material, but no amido complexes have been characterized.

Reactions of [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)R$_2$. Chemistry directed at the zirconium–carbon bond has been carried out with variable success. It has been demonstrated that 1 equiv of *t*-BuOH reacts completely with [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)R$_2$ (R = Me, C≡CMe) yielding the [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)$_2$R complexes as shown in eq 5. A simple extension of this reaction was employed

$$[\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})\mathrm{R_2} + t\text{-}\mathrm{BuOH} \xrightarrow{\mathrm{benzene}} [\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_2\mathrm{R} + \mathrm{RH} \quad (5)$$

$$\mathrm{R} = \mathrm{Me},\ \mathrm{C{\equiv}CMe}$$

in an effort to prepare a series of amido complexes. To date, the reaction of the dimethyl complex with 1 equiv of amine (*t*-BuNH$_2$, Et$_2$NH, PhNH$_2$) has failed to yield any detectable amido complex at room temperature. Even after 22 h at 68 °C, the dimethyl complex fails to react with *t*-BuNH$_2$ to afford an amido complex. The ^{1}H NMR reveals only the starting dimethyl complex.

Efforts to substitute halogen for methyl in [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)Me$_2$ have been unsuccessful. Reactions with HCl/diethyl ether or Br$_2$/CH$_2$Cl$_2$ lead only to decomposition of the starting material. The reaction of equimolar amounts of [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)Me$_2$ and [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)Cl$_2$ yielded only starting materials and no trace of monoalkyl product.

These new alkylzirconium complexes do not appear to react smoothly with CO. Clear, colorless solutions of the dimethyl complex turn yellow when placed under a CO atmosphere, but no immediate changes are observed in the NMR spectra. Eventually (38 h) some decomposition of the starting material is evident by NMR with trace amounts of acetone observed in the volatile products.

In contrast, the dimethyl and dibenzyl compounds readily react with *t*-BuNC at room temperature to form the η^2-iminoacyl monoinsertion products shown in eq 6.

$$[\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})\mathrm{R_2} \xrightarrow[\mathrm{benzene}]{t\text{-}\mathrm{BuNC}} [\mathrm{HB}(3,5\text{-}\mathrm{Me_2pz})_3]\mathrm{Zr}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})(\eta^2\text{-}\mathrm{C(R)NCMe_3})\mathrm{R} \quad (6)$$

$$\mathrm{R} = \mathrm{Me},\ \mathrm{CH_2Ph}$$

These complexes crystallize from hydrocarbon solvents providing suitable crystals for an X-ray crystallographic study of the dimethyl adduct (vide infra). The ^{13}C NMR spectra for both compounds show that all of the pyrazolyl groups are nonequivalent, as expected for these seven-coordinate complexes. The iminoacyl carbon atom resonance for these complexes is found at high field in the 243–244 ppm range, characteristic for iminoacyl carbons.[7] The ^{13}C NMR spectrum for [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)(η^2-C(CH$_2$Ph)NCMe$_3$)(CH$_2$Ph) shows two benzyl resonances. The gated decoupled ^{13}C spectrum yields the $J_{\mathrm{C-H}}$ values for the CH$_2$ of each benzyl group allowing for their assignment. The downfield resonance (49.6 ppm ($J_{\mathrm{C-H}}$ = 114.0 Hz)) is assigned to the methylene carbon of the CH$_2$Ph group coordinated to the zirconium. This low value[8] for $J_{\mathrm{C-H}}$ is similar to that measured for [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)(CH$_2$Ph)$_2$ ($J_{\mathrm{C-H}}$ = 113.0 Hz). The upfield resonance (43.7 ppm ($J_{\mathrm{C-H}}$ = 124.4 Hz)) is assigned to the methylene carbon of the CH$_2$Ph group that is bonded to the carbon atom of the inserted isocyanide group. The ^{1}H NMR spectrum also shows two different CH$_2$Ph groups for this molecule. At 90 MHz the resonances for the methylene protons of the CH$_2$Ph groups appear as an AB quartet (δ 3.89 (J = 17.4 Hz)) and a broad singlet (δ 2.83). At 400 MHz this broad singlet is resolved into an AB quartet. As noted most clearly in this 400-MHz spectrum, each resonance (except the complex Ph region) is flanked by a similar appearing resonance at about 10% the integrated intensity. In the spectrum of [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu-*d*$_9$)(η^2-C(CD$_2$Ph)NCMe$_3$)(CD$_2$Ph), both the major and minor peaks of the appropriate resonances were absent. Similar peaks are noted in the ^{13}C NMR spectrum. It is believed that these resonances arise from a second isomer of this complex in which the η^2-iminoacyl ligand is rotated differently than in the primary isomer. Upon heating to 70 °C, this compound gave no indication of interconversion of these two isomers. Small resonances in the ^{1}H NMR spectrum of [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)(η^2-C(Me)NCMe$_3$)Me indicate the presence of a low concentration of a second rotamer in this case also. Similar rotational isomers were noted by Lappert et al. for Cp$_2$Zr(η^2-iminoacyl)R complexes.[7]

Excess *t*-BuNC at room temperature also yields the monoinsertion products. Heating with excess isocyanide does lead to changes in the NMR spectra, but no multiple insertion products have been characterized. The [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)$_2$R complexes do not react with *t*-BuNC.

Crystal Structure. The molecular structure for [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)(η^2-C(Me)NCMe$_3$)Me is shown in Figure 1. The *t*-BuNC group has inserted into one of the Zr–Me bonds of the starting material to form the η^2-iminoacyl ligand. Although other η^2-iminoacyl complexes

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[7] Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35.

[8] Analogous benzyl coupling constants in (η^5-C$_5$H$_5$)Ta(CH$_2$CMe$_3$)(CH$_2$Ph)Cl$_2$ are 126 (trans isomer) and 128 Hz (cis isomer)[9a] and range from 117 to 139 Hz for Ta(CH$_2$Ph)$_n$Cl$_{5-n}$ (n = 2–5) complexes,[9b] and the coupling constant is 112 Hz for [H$_2$B(3,5-Me$_2$pz)$_2$]Ta(CH$_2$Ph)$_3$Cl.[10]

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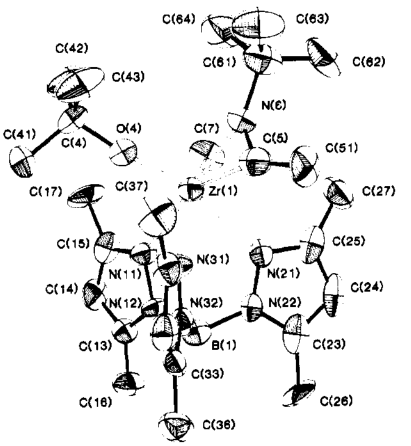

Figure 1. ORTEP diagram showing the structure of [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)(η^2-C(Me)NCMe$_3$)Me.

of zirconium have been prepared,[7,11] this appears to be the first for which the solid-state structure has been reported. The bond distances and angles of the η^2-iminoacyl ligand are typical of similar ligands bound to other metals.[12] The Zr–C(5) bond length of 2.20 (1) Å is comparable to the Zr–C distance of 2.197 (6) and 2.186 (4) Å for the η^2-acyl complexes $Cp_2Zr(\eta^2$-C(Me)O)Me[13] and $Cp_2Zr(\eta^2$-C(Me)-O)(OC)$_3$MoCp.[14] The C(5)–N(6) distance of 1.27 (2) Å is comparable to the 1.280 (6)-Å distance found in Cp_2Ti-(η^2-C(Ph)N-2,6-$Me_2C_6H_3$).[12] Essentially equal Zr–C(5) and Zr–N(6) bond distances are found here as was also observed for the above Ti complex, clearly indicating an η^2-coordination of the iminoacyl ligand.

The overall coordination geometry about the Zr is rather irregular. We have previously reported the structures of two somewhat similar seven-coordinate Ta molecules, [HBpz$_3$]TaMe$_3$Cl[15] and [H(μ-H)B(3,5-Me$_2$pz)$_2$]TaMe$_3$Cl,[16] both of which adopt fairly regular capped octahedral structures. This seven-coordinate Zr molecule has a quite different structure that is best described as a distorted octahedron with the η^2-iminoacyl ligand occupying a single site (the N(6)–Zr–C(5) angle is 33.6 (4)°). The N–Zr–N angles formed from the pyrazolyl ring donor atoms are all essentially equal and are substantially less than 90° (76.4° average). This allows the face formed by the other three ligands to open considerably. Particularly notable is the O(4)–Zr–C(7) angle of 101.4 (3)°. In fact, the Me ligand (C(7)) seems to be pushed away from the other ligands of this face by a close contact of 3.065 Å with N(6). The C(5)–C(37) contact is also fairly close at 3.287 Å. The O(4)–C(7) and O(4)–N(6) distances are normal at 3.291 and 2.974 Å, respectively. The closest Me–Me contact (excluding CMe$_3$ contacts) is intramolecular between C(7) and C(17) at 3.439 Å, with all others greater than 3.58 Å.

The Zr–O bond length of 1.924 (6) Å is very short and implies significant multiple bond character arising from pπ–dπ donation from oxygen to the highly coordinatively unsaturated Zr atom. For comparison, the Zr–O bond length is 1.94 Å in [Cp$_2$ZrCl]$_2$O[17a] and averages 1.959 Å in [Cp$_2$ZrO]$_3\cdot C_7H_8$,[17b] molecules in which multiple Zr–O bonding has also been suggested. A bond length of 1.910 Å has been reported for Cp$_2$Zr(O-*t*-Bu)Ru(CO)$_2$Cp.[18] The Zr–O–C(4) bond angle is 174.4 (6)°, the largest M–O–C bond angle yet observed. A large M–O–C angle has been reported for [CpCl$_2$Ti]$_2$O$_2$C$_2$Me$_4$ of 166.2°[19] and 169.6° for Cp$_2$Zr(O-*t*-Bu)Ru(CO)$_2$Cp.[18] More typical metal-*t*-butoxide angles are in the range of 134–153° for a family of Mo and W complexes,[20] and an angle of 132.4° is found for [HB(3,5-Me$_2$pz)$_3$]Mo(NO)Cl(OCHMe$_2$).[21] It does not appear that intramolecular contacts force this large angle. The CMe$_3$ group is bent in the direction of C(7), and no Me–Me contacts with either C(7) or the other CMe$_3$ group are less than 4 Å.

Discussion

Stable alkylzirconium complexes lacking β-hydrogen atoms are readily prepared with the auxiliary ligand combination of a [HB(3,5-Me$_2$pz)$_3$] and one or two alkoxide groups. The preparation of polypyrazolylborate alkylzirconium complexes lacking the strongly electron-donating alkoxide ligands has been unsuccessful. Others have noted the ability of π-donating alkoxide and amide ligands to stabilize high valent or coordinatively unsaturated alkylmetal complexes.[22]

The strong donating ability of the alkoxide ligand is clearly demonstrated in the structure of [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)(η^2-C(Me)NCMe$_3$)Me (a molecule with two additional electrons donated by the ligands than the simple alkyls) by a short M–O distance and a large M–O–C angle. With the assumption that the Zr–Me distance is a reference point for a pure single bond, a Zr–O single bond distance of 2.21 Å is predicted,[23] 0.29 Å longer than observed. This short bond distance coupled with the nearly linear Zr–O–C group indicates substantial Zr–O multiple bonding with possibly both lone pairs on oxygen being involved in pπ–dπ donation to the metal.

The inability to prepare analogous amido complexes is surprising. Numerous attempts to displace Cl ligands with amides for all of the [poly(pyrazolyl)borato]zirconium complexes have failed. Even more surprising is the failure of primary and secondary amines to react with the new alkylzirconium complexes. In contrast, *tert*-butyl alcohol reacts rapidly (eq 5). The successful alkoxide–chloride exchange reactions (eq 3) suggest a possible route to these derivaitves may be the reaction of [HB(3,5-Me$_2$pz)$_3$]ZrCl$_3$ with known M–(NR$_2$)$_n$ complexes. Although these alkoxide–chloride exchange reactions are rapid, alkyl–chloride exchange was not observed. This presumably reflects the better bridging ability of alkoxide vs. alkyl groups.

The [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)R$_2$ (R = Me, CH$_2$Ph) complexes react rapidly with *t*-BuNC to form η^2-iminoacyl

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derivatives, but CO does not. $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_2R$ complexes will not react, even with *t*-BuNC. The ability of isocyanides to react more effectively than CO most likely reflects the greater basicity[24] of the former ligands allowing the carbon lone pair to interact with the "hard" Zr d° metal center. A similar explanation has recently been invoked to explain the lack of reactivity of $[(\eta^5\text{-}C_5Me_5)Zr(BH_4)H(\mu\text{-}H)]_2$ toward CO.[2b] The lack of reactivity of the $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_2R$ complexes with isocyanides could be a simple steric problem but more likely is due to the effective multiple bonding of two alkoxide ligands with the empty Zr orbitals. It has recently been established for $Cp_2ZrMe(X)$ complexes that the equilibrium constant for the formation of η^2-acyl complexes in the presence of CO decreases in the order Me > Cl > OEt.[25]

Experimental Section

General Procedure. All operations were carried out under an atmosphere of prepurified nitrogen with the use of standard Schlenk techniques or an efficient drybox. All solvents were dried, degassed, and distilled prior to their use. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer. Proton NMR spectra were recorded on Varian EM-390 and Brüker WH-400 spectrometers, and chemical shifts are reported in δ vs. Me_4Si. Carbon-13 NMR spectra were recorded on a IBM NR-80 spectrometer with C_6D_6 or $CDCl_3$ as the solvent and internal standard. Chemical shifts are reported in ppm vs. Me_4Si, with the C_6D_6 resonance assigned at 128.0 ppm and the $CDCl_3$ resonance at 77.0 ppm. All carbon-13 spectra were run with ^1H decoupling (unless otherwise noted), and all resonances are singlets. Mass spectra were run as solids by using a Finnigan 4021 GC–mass spectrometer using an ionization voltage of 70 eV. $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ and $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ were prepared as previously described.[5,6] Elemental analyses were performed by Robertson Laboratory. Melting points were determined in sealed capillaries and are uncorrected. The MeMgBr (Aldrich) and $PhCH_2MgCl$ were standardized prior to use by a titration with isopropyl alcohol (1.0 M in xylene) using 2,2′-biquinoline (Me) and 1,10-phenanthroline ($PhCH_2$) as indicators.[26]

[Hydrotris(3,5-dimethylpyrazolyl)borato]di-*tert*-butoxychlorozirconium(IV) $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_2Cl\}$. $[HB(3,5\text{-}Me_2pz)_3]ZrCl_3$ (2.79 g, 5.62 mmol) was combined with potassium *tert*-butoxide (1.30 g, 11.6 mmol) in a 250-mL round-bottom flask. Benzene (150 mL) was added via syringe, and the reaction was heated at reflux for 1 h. After the solution was allowed to cool to room temperature, the cloudy, colorless solution was filtered through a medium-fritted disk, and all the volatiles were removed under vacuum, leaving a white solid residue (2.89 g, 90%). The analytical sample was obtained by recrystallizing twice from pentane: mp 254–256 °C; ^1H NMR spectrum ($CDCl_3$) δ 5.73, 5.64 (1, 2; s, s; 4-H(pz)), 2.61, 2.53, 2.35, 2.28 (6, 3, 3, 6; s, s, s, s; 3-CH_3, 5-CH_3(pz)), 1.34 (18, s, $OC(CH_3)_3$); ^{13}C NMR spectrum ($CDCl_3$, the rings in this compound are nonequivalent and are labeled A and B, the ratio of A:B is 2:1) δ 151.7 (A), 150.5 (B), 145.4 (B), 144.0 (A) (3-C, 5-C(pz)), 106.2 (A), 105.9 (B) (4-C(pz)), 78.8 (OC), 31.9 ($OC(CH_3)_3$), 16.1 (A), 16.0 (B), 12.9 (B), 12.8 (A) (3-CH_3, 5-CH_3(pz)); the mass spectrum shows multiple clusters at *m*/*e* 553 ($M^+ - 15$, (CH_3)) and 495 ($M^+ - 73$, (O-*t*-Bu)); no molecular ion (M^+)was observed. Anal. Calcd for $C_{23}H_{40}N_6BO_2Zr$: C, 48.46; H, 7.07. Found: C, 48.26; H, 7.25.

[Hydrotris(3,5-dimethylpyrazolyl)borato]-*tert*-butoxydimethylzirconium(IV) $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Me_2\}$. $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ (3.00 g, 5.64 mmol) was dissolved in THF (50 mL) and cooled to −78 °C. MeMgBr (2.85 M in diethyl ether, 4.45 mL, 12.7 mmol) was added slowly via syringe. The reaction temperature was gradually allowed to reach room temperature over 3 h where it stirred overnight (16 h). All volatiles were removed under vacuum. Benzene (50 mL) was added to dissolve the crude residue. Dioxane (2.2 mL) was then added dropwise, and the solution was allowed to stir for 1 h. The cloudy, white solution was filtered through a medium-fritted disk, yielding a clear, colorless filtrate. All volatiles were removed under vacuum leaving the product as a white solid (2.58 g, 93%): mp 217–221 °C dec; ^1H NMR spectrum (benzene-d_6) δ 5.63, 5.38 (1, 2; s, s; 4-H(pz)), 2.59, 2.42, 2.18, 2.04 (3, 6, 3, 6; s, s, s, s; 3-CH_3, 5-CH_3(pz)), 1.63 (9, s, $OC(CH_3)_3$), 0.63 (6, s, Zr(CH_3)'s); ^{13}C NMR spectrum (benzene-d_6, the pz rings are nonequivalent in this compound and are labeled A and B, the ratio of A:B is 2:1) δ 152.3 (B), 150.8 (A), 144.8 (A), 143.7 (B) (3-C, 5-C(pz)), 107.3 (B), 106.2 (A) (4-C(pz)), 79.6 (OC), 36.7 ($ZrCH_3$'s), 32.4 ($OC(CH_3)_3$), 15.3 (B), 14.8 (A), 13.0 (B), 12.5 (A) (3-CH_3, 5-CH_3(pz)); the mass spectrum shows a cluster (base peak) at *m*/*e* 475 ($M^+ - 15(CH_3)$); no molecular ion (M^+) was observed.

[Hydrotris(3,5-dimethylpyrazolyl)borato]di-*tert*-butoxymethylzirconium(IV) $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_2Me\}$. $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Me_2$ (0.50 g, 1.0 mmol) was dissolved in benzene (15 mL). *tert*-Butyl alcohol (96 μL, 1.0 mmol) was added slowly via microsyringe at room temperature. The evolution of a gas was noted. The reaction was stirred at room temperature for 15 min. All volatiles were removed in a vacuum leaving the product as a white solid (0.48 g, 86%). The analytical sample was obtained by crystallization from pentane. Pure $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_2Me$ was obtained as clear, colorless crystals: mp 177–179 °C; ^1H NMR spectrum (benzene-d_6) δ 5.56, 5.54 (2, 1; s, s; 4-H(pz)), 2.73, 2.53, 2.10, 2.06 (6, 3, 6, 3; s, s, s, s; 3-CH_3, 5-CH_3(pz)), 1.46 (18, s, $OC(CH_3)_3$), 0.59 (3, s, $ZrCH_3$); ^{13}C NMR spectrum (benzene-d_6, the rings are nonequivalent in this compound and are labeled A and B, the ratio of A:B is 2:1) δ 151.3 (A), 150.2 (B), 145.1 (B), 143.8 (A) (3-C, 5-C(pz)), 106.4 (A), 105.7 (B) (4-C(pz)), 77.3 (OC), 32.8 ($OC(CH_3)_3$), 24.6 ($ZrCH_3$), 16.2 (A), 15.9 (B), 12.9 (A), 12.6 (B) (3-CH_3, 5-CH_3(pz)); the high-resolution mass spectrum shows a cluster for $M^+ - 15$ (CH_3). Calcd for $^{12}C_{24}{}^1H_{43}{}^{14}N_6{}^{10}B^{16}O_2{}^{90}Zr$, $^{12}C_{24}{}^1H_{43}{}^{14}N_6{}^{11}B^{16}O_2{}^{90}Zr$, $^{12}C_{24}{}^1H_{43}{}^{14}N_6{}^{11}B^{16}O_2{}^{92}Zr$, $^{12}C_{24}{}^1H_{43}{}^{14}N_6{}^{11}B^{16}O_2{}^{94}Zr$: 532.2389, 533.2353, 535.2356, 537.2369. Found: 532.2320, 533.2325, 535.2299, 537.2292. No molecular ion (M^+) was observed. This complex can also be prepared from $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_2Cl$ and excess methyllithium. Anal. Calcd for $C_{24}H_{43}N_6BO_2Zr$: C, 52.44; H, 7.88. Found: C, 51.91; H, 8.38.

[Hydrotris(3,5-dimethylpyrazolyl)borato]-*tert*-butoxy-[η^2-1-(*tert*-butylimino)ethyl]methylzirconium(IV) $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)(\eta^2\text{-}C(Me)NCMe_3)Me\}$. $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Me_2$ (0.30 g, 0.61 mmol) was dissolved in benzene (3 mL) in a 25-mL round-bottom flask. *tert*-Butyl isocyanide (60 μL, 0.61 mmol) was added via a microsyringe. The reaction was stirred at room temperature for 15 min. The volatiles were removed under vacuum leaving a white residue. The residue was redissolved in pentane (50 mL) at room temperature, this solution was filtered, and the solvent was evaporated to a volume of about 15 mL. Cooling to 0 °C yielded clear, colorless crystals (0.21 g, 60%) that were collected and dried in an N_2 stream: mp 179–181 °C; ^1H NMR spectrum (benzene-d_6) δ 5.70, 5.47 (2, 1; s, s; 4-H(pz)), 2.78, 2.17, 2.16, 2.09 (3, 6, 3, 6; s, s, s, s; 3-CH_3, 5-CH_3(pz)), 1.94 (3, s, $NC(CH_3)$), 1.59 (9, s, $OC(CH_3)_3$), 1.24 (9, s, $NC(CH_3)_3$), 0.38 (3, s, $ZrCH_3$); ^{13}C NMR spectrum (benzene-d_6, the rings in this compound are nonequivalent) δ 243.6 ($ZrC(CH_3)N$), 150.9, 149.4, 149.0, 143.7, 143.4, 143.0 (3-C, 5-C(pz)), 106.3, 106.0, 105.7 (4-C(pz)), 76.0 (OC), 61.4 (NC), 32.8 ($OC(CH_3)_3$), 30.2 ($NC(CH_3)_3$), 23.9, 22.3 ($ZrCH_3$, $ZrC(CH_3)N$), 16.6, 15.9, 14.6, 13.0, 12.8 (1, 1, 1, 2, 1 intensity ratio, 3-CH_3, 5-CH_3(pz)); IR spectrum (cm^{-1} in CH_2Cl_2) ν(C=N) 1542; the mass spectrum shows a multiple cluster at *m*/*e* 558 ($M^+ - 15$, (CH_3)); the molecular ion (M^+) was not observed. Anal. Calcd for $C_{26}H_{46}N_7BOZr$: C, 54.34; H, 8.07. Found: C, 53.90; H, 8.52.

[Hydrotris(3,5-dimethylpyrazolyl)borato]-*tert*-butoxydi-1-propynylzirconium(IV) $\{[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)(C{\equiv}CMe)_2]$. $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)Cl_2$ (2.00 g, 3.76 mmol) and propynyllithium (0.69 g, 15 mmol) were combined in a 250-mL round-bottom flask. THF (75 mL) was added via syringe to this mixture at −78 °C. The reaction temperature was allowed to gradually reach room temperature (3 h) where it stirred overnight (16 h). All volatiles were removed under vacuum leaving

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a yellow-orange residue. This residue was extracted with pentane (225 mL) at room temperature and filtered through a medium-fritted disk yielding a clear, yellow-orange filtrate. All volatiles were removed under vacuum at room temperature leaving a yellow-orange solid (1.71 g, 84%), mp 145–153 °C dec. The compound (1.0 g) was dissolved in hexane (100 mL) and filtered, and the volume of the filtrate was concentrated to ca. 30 mL. After the mixture was left standing at 0 °C overnight, yellow-orange crystalline material was obtained (0.58 g, 58%): ^{1}H NMR spectrum (benzene-d_6) δ 5.57, 5.39 (1, 2; s, s; 4-H(pz)), 3.17, 2.76, 2.09, 2.01 (3, 6, 3, 6; s, s, s, s; 3-CH$_3$, 5-CH$_3$(pz)), 1.73 (9, s, OC(CH$_3$)$_3$), 1.61 (6, s, C≡CCH$_3$); ^{13}C NMR spectrum (benzene-d_6, the rings in this compound are nonequivalent and are labeled A and B, the ratio A:B is 2:1) δ 153.5 (B), 151.6 (A), 144.8 (A), 143.5 (B) (3-C, 5-C(pz)), 106.8 (B), 106.2 (A) (4-C(pz)), 97.1, 68.4 (C≡C), 80.6 (OC), 32.5 (OC(*C*H$_3$)$_3$), 16.4 (B), 15.5 (A), 12.6 (B), 12.4 (A) (3-CH$_3$, 5-CH$_3$(pz)), 4.6 (C≡C*C*H$_3$); IR spectrum (cm^{-1} in CH$_2$Cl$_2$) ν(C≡C) 2093; the mass spectrum shows multiple clusters at *m/e* 523 (M$^+$ – 15, (CH$_3$)) and 460 (M$^+$ – 78, (2C≡CCH$_3$)); no molecular ion (M$^+$) was observed.

[Hydrotris(3,5-dimethylpyrazolyl)borato]di-*tert*-butoxy-1-propynylzirconium(IV) {[HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)$_2$-(C≡CMe)}. [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)$_2$Cl (2.00 g, 3.51 mmol) and propynyllithium (0.32 g, 7.02 mmol) were combined in a 250-mL round-bottom flask. THF (75 mL) was added via syringe to this mixture at –78 °C. The temperature of the reaction was allowed to gradually (3 h) reach room temperature where it stirred overnight (16 h). All volatiles were removed under vacuum leaving a pale yellow residue. Benzene (50 mL) was used to extract this residue and after filtration gave a clear, colorless filtrate. All volatiles were removed under vacuum leaving an off-white residue (1.83 g, 91%). The analytical sample was obtained by crystallization twice from pentane. White crystals, mp 185–187 °C, were obtained that underwent sample degradation upon further crystallization attempts: ^{1}H NMR spectrum (benzene-d_6) δ 5.54 (3, s, 4-H(pz)), 2.99, 2.57, 2.08 (6, 3, 9; s, s, s; 3-CH$_3$, 5-CH$_3$(pz)), 1.75 (3, s, C≡CCH$_3$), 1.49 (18, s, OC(CH$_3$)$_3$); ^{13}C NMR spectrum (benzene-d_6, the rings are nonequivalent in this compound and are labeled A and B, the ratio of A:B is 2:1) δ 151.9 (A), 150.4 (B), 145.8 (B), 143.8 (A) (3-C, 5-C(pz)), 106.3 (A), 106.0 (B) (4-C(pz)), 98.1, 68.0 (C≡C), 77.9 (OC), 32.7 (OC(*C*H$_3$)$_3$), 16.7 (A), 16.0 (B), 12.8 (A), 12.6 (B) (3-CH$_3$, 5–CH$_3$(pz)), 5.0 (C≡C*C*H$_3$); the mass spectrum shows multiple clusters at *m/e* 572 (M$^+$), 557 (M$^+$ – 15, (CH$_3$)), 532 (M$^+$ – 40, (HC≡CCH$_3$)) and 499 (M$^+$ – 73, (O-*t*-Bu)); IR spectrum (cm^{-1} in CH$_2$Cl$_2$) ν(C≡C) 2105. Anal. Calcd for C$_{26}$H$_{43}$N$_6$BO$_2$Zr: C, 54.43; H, 7.55. Found: C, 52.89; H, 7.47.

[Hydrotris(3,5-dimethylpyrazolyl)borato]-*tert*-butoxy-dibenzylzirconium(IV) {[HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)-(CH$_2$Ph)$_2$}. [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)Cl$_2$ (1.71 g, 3.21 mmol) was dissolved in THF (50 mL) and cooled to –78 °C. PhCH$_2$MgCl (0.61 M in diethyl ether; 12.0 mL, 7.32 mmol) was added dropwise. The reaction temperature was allowed to gradually warm up to room temperature where it stirred overnight (16 h). All volatiles were removed under vacuum leaving a bright yellow residue. Benzene (50 mL) was added to dissolve this residue, and dioxane (1.3 mL) was added dropwise forming an insoluble magnesium chloride–dioxane complex that was removed by filtration of the cloudy, yellow solution through a medium-fritted disk. All volatiles were removed under vacuum leaving the crude product. Further purification is effected by extracting the crude compound (0.75 g) with pentane (200 mL) at room temperature. After a filtration and removal of the pentane under vacuum, the product can be obtained as a bright yellow solid (0.45 g, 60%). Examination of the insoluble material determined that all of the desired compound had been extracted: ^{1}H NMR spectrum (benzene-d_6) δ 6.94 (10, m, Ph), 5.55, 5.37 (1, 2; s, s; 4-H(pz)), 2.76 (4, AB quartet, J = 12.0 Hz, *C*H$_2$Ph), 2.43, 2.24, 2.15, 2.03 (3, 6, 3, 6; s, s, s, s; 3-CH$_3$, 5-CH$_3$(pz)), 1.35 (9, s, OC(CH$_3$)$_3$); ^{13}C NMR spectrum (CDCl$_3$, the rings in this compound are nonequivalent and are labeled A and B, the ratio of A:B is 2:1) δ 152.2 (B), 151.2 (A), 145.2 (A), 144.2 (B) (3-C, 4-C(pz)), 151.2 (C1(Ph)), 127.4, 126.7 (C2, 3, 5, 6(Ph)), 120.2 (C4(Ph)), 107.7 (B), 106.0 (A) (4-C(pz)), 81.8 (OC), 67.5 (CH$_2$Ph), 31.8 (OC(*C*H$_3$)$_3$), 16.2 (B), 15.3 (A), 13.3 (B), 12.9 (A) (3-CH$_3$, 5-CH$_3$(pz)); the mass spectrum shows a multiple cluster at *m/e* 551 (M$^+$ – 91, (CH$_2$Ph)); no molecular ion (M$^+$) was observed.

Table I. Coordinates of Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses[a]

atom	*x*	*y*	*z*	B_{eq}
Zr(1)	0.1869 (1)	0.2129 (1)	0.0665 (1)	3.10
O(4)	0.2693 (5)	0.2852 (4)	−0.0018 (3)	4.06
C(4)	0.3208 (10)	0.3447 (7)	−0.0539 (7)	5.57
C(41)	0.4568 (11)	0.3173 (8)	−0.0593 (8)	8.29
C(42)	0.3124 (13)	0.4310 (7)	−0.0176 (8)	7.91
C(43)	0.2509 (13)	0.3398 (8)	−0.1337 (7)	7.72
C(5)	0.0246 (10)	0.1702 (8)	−0.0028 (6)	4.53
C(51)	−0.0649 (9)	0.1081 (7)	−0.0439 (6)	5.44
N(6)	0.0105 (7)	0.2470 (6)	0.0110 (5)	3.78
C(61)	−0.0907 (11)	0.3055 (7)	−0.0138 (7)	5.92
C(62)	−0.2045 (10)	0.2856 (9)	0.0320 (8)	7.92
C(63)	−0.1222 (13)	0.3017 (9)	−0.1035 (8)	8.79
C(64)	−0.0412 (12)	0.3946 (7)	0.0086 (9)	8.71
C(7)	0.1415 (9)	0.3033 (6)	0.1658 (6)	4.99
N(11)	0.3706 (7)	0.1914 (5)	0.1490 (4)	3.50
N(12)	0.4078 (7)	0.1144 (4)	0.1762 (4)	2.87
C(13)	0.5105 (9)	0.1212 (7)	0.2223 (5)	3.52
C(14)	0.5435 (9)	0.2032 (8)	0.2253 (6)	4.71
C(15)	0.4562 (10)	0.2462 (7)	0.1797 (6)	4.37
C(16)	0.5684 (10)	0.0521 (7)	0.2638 (6)	5.19
C(17)	0.4469 (12)	0.3402 (6)	0.1649 (8)	6.60
N(21)	0.1310 (8)	0.1054 (5)	0.1579 (4)	3.65
N(22)	0.2076 (7)	0.0434 (5)	0.1823 (4)	3.15
C(23)	0.1528 (11)	−0.0089 (7)	0.2306 (6)	4.56
C(24)	0.0390 (11)	0.0199 (8)	0.2383 (6)	5.25
C(25)	0.0282 (11)	0.0916 (8)	0.1915 (6)	4.44
C(26)	0.2133 (12)	−0.0861 (7)	0.2656 (7)	6.61
C(27)	−0.0791 (10)	0.1445 (8)	0.1812 (6)	5.99
N(31)	0.2693 (7)	0.0890 (5)	0.0152 (4)	3.17
N(32)	0.3247 (6)	0.0290 (5)	0.0623 (5)	3.35
C(33)	0.3587 (8)	−0.0364 (6)	0.0186 (7)	3.83
C(34)	0.3242 (10)	−0.0180 (7)	−0.0579 (7)	4.22
C(35)	0.2678 (9)	0.0609 (7)	−0.0579 (6)	4.07
C(36)	0.4204 (9)	−0.1115 (6)	0.0510 (7)	5.07
C(37)	0.2217 (10)	0.1094 (7)	−0.1274 (6)	5.43
B(1)	0.3347 (11)	0.0369 (7)	0.1536 (7)	3.75

[a] Equivalent isotropic temperature factors $B = {}^8/_3\,\pi^2\Sigma_i\Sigma_j u_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$ in Å^2.

Table II. Bond Distances (Å) with Estimated Standard Deviations in Parentheses

Zr(1)-O(4)	1.924 (6)	Zr(1)-C(5)	2.20 (1)
Zr(1)-N(6)	2.194 (8)	Zr(1)-C(7)	2.32 (1)
Zr(1)-N(11)	2.430 (7)	Zr(1)-N(21)	2.439 (8)
Zr(1)-N(31)	2.389 (8)	O(4)-C(4)	1.45 (1)
C(4)-C(41)	1.59 (2)	C(4)-C(42)	1.53 (2)
C(4)-C(43)	1.52 (2)	C(5)-C(51)	1.55 (2)
C(5)-N(6)	1.27 (2)	N(6)-C(61)	1.51 (1)
C(61)-C(62)	1.57 (2)	C(61)-C(63)	1.55 (2)
C(61)-C(64)	1.58 (2)	N(11)-N(12)	1.38 (1)
N(11)-C(15)	1.38 (1)	N(12)-C(13)	1.35 (1)
N(12)-B(1)	1.53 (1)	C(13)-C(14)	1.37 (2)
C(13)-C(16)	1.45 (2)	C(14)-C(15)	1.39 (2)
C(15)-C(17)	1.54 (2)	N(21)-N(22)	1.36 (1)
N(21)-C(25)	1.33 (1)	N(22)-C(23)	1.35 (1)
N(22)-B(1)	1.53 (1)	C(23)-C(24)	1.37 (2)
C(23)-C(26)	1.52 (2)	C(24)-C(25)	1.40 (2)
C(25)-C(27)	1.47 (2)	N(31)-N(32)	1.38 (1)
N(31)-C(35)	1.32 (1)	N(32)-C(33)	1.36 (1)
N(32)-B(1)	1.56 (2)	C(33)-C(34)	1.37 (2)
C(33)-C(36)	1.48 (1)	C(34)-C(35)	1.42 (2)
C(35)-C(37)	1.48 (2)		

[Hydrotris(3,5-dimethylpyrazolyl)borato]-*tert*-butoxy-[η^2-1-(*tert*-butylimino)benzylmethyl]benzylzirconium(IV) {[HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)(η^2-C(CH$_2$Ph)NCMe$_3$)CH$_2$Ph}. [HB(3,5-Me$_2$pz)$_3$]Zr(O-*t*-Bu)(CH$_2$Ph)$_2$ (1.30 g, 2.02 mmol) was dissolved in benzene (10 mL). *tert*-Butyl isocyanide (212 μL, 2.02 mmol) was added via microsyringe. The reaction was stirred at room temperature for 15 min. The volatiles were removed under vacuum leaving a light yellow residue (1.28 g, 87%). The analytical sample was obtained by dissolving the crude product (0.50 g) in hexane (75 mL) at room temperature followed by filtration and reduction of the filtrate to a volume of about 20 mL. Light yellow

Table III. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

O(4)-Zr(1)-C(5)	105.8 (3)	N(21)-N(22)-C(23)	110.1 (8)	Zr(1)-C(5)-N(6)	72.8 (6)
O(4)-Zr(1)-C(7)	101.4 (3)	C(23)-N(22)-B(1)	128.1 (8)	Zr(1)-N(6)-C(5)	73.6 (6)
O(4)-Zr(1)-N(21)	165.9 (3)	N(22)-C(23)-C(26)	123 (1)	C(5)-N(6)-C(61)	131.0 (9)
C(5)-Zr(1)-N(6)	33.6 (4)	C(23)-C(24)-C(25)	106 (1)	N(6)-C(61)-C(63)	111.6 (9)
C(5)-Zr(1)-N(11)	153.6 (3)	N(21)-C(25)-C(27)	125 (1)	C(62)-C(61)-C(63)	110.3 (9)
C(5)-Zr(1)-N(31)	82.2 (3)	Zr(1)-N(31)-N(32)	122.8 (5)	C(63)-C(61)-C(64)	109 (1)
N(6)-Zr(1)-N(11)	168.9 (3)	N(32)-N(31)-C(35)	106.6 (7)	Zr(1)-N(11)-C(15)	131.6 (6)
N(6)-Zr(1)-N(31)	114.0 (3)	N(31)-N(32)-B(1)	121.6 (7)	N(11)-N(12)-C(13)	110.3 (7)
C(7)-Zr(1)-N(21)	84.4 (3)	N(32)-C(33)-C(34)	106.5 (9)	C(13)-N(12)-B(1)	129.1 (8)
N(11)-Zr(1)-N(21)	76.7 (3)	C(34)-C(33)-C(36)	128.8 (9)	N(12)-C(13)-C(16)	123.7 (9)
N(21)-Zr(1)-N(31)	76.2 (3)	N(31)-C(35)-C(34)	109.2 (9)	C(13)-C(14)-C(15)	106.5 (9)
O(4)-C(4)-C(41)	105.7 (8)	C(34)-C(35)-C(37)	127.1 (9)	N(11)-C(15)-C(17)	122.1 (9)
O(4)-C(4)-C(43)	108.2 (9)	N(12)-B(1)-N(32)	108.7 (8)	Zr(1)-N(21)-N(22)	122.3 (6)
C(41)-C(4)-C(43)	111.5 (9)	O(4)-Zr(1)-N(6)	92.2 (3)	N(22)-N(21)-C(25)	106.6 (8)
Zr(1)-C(5)-C(51)	157.8 (8)	O(4)-Zr(1)-N(11)	91.1 (2)	N(21)-N(22)-B(1)	121.8 (8)
C(51)-C(5)-N(6)	129 (1)	O(4)-Zr(1)-N(31)	94.2 (2)	N(22)-C(23)-C(24)	107.9 (9)
Zr(1)-N(6)-C(61)	155.4 (7)	C(5)-Zr(1)-C(7)	112.1 (4)	C(24)-C(23)-C(26)	129 (1)
N(6)-C(61)-C(62)	110.3 (9)	C(5)-Zr(1)-N(21)	83.4 (3)	N(21)-C(25)-C(24)	110 (1)
N(6)-C(61)-C(64)	105.0 (9)	N(6)-Zr(1)-C(7)	85.6 (3)	C(24)-C(25)-C(27)	126 (1)
C(62)-C(61)-C(64)	110.4 (9)	N(6)-Zr(1)-N(21)	101.2 (3)	Zr(1)-N(31)-C(35)	130.5 (6)
Zr(1)-N(11)-N(12)	123.1 (5)	C(7)-Zr(1)-N(11)	83.3 (3)	N(31)-N(32)-C(33)	110.9 (7)
N(12)-N(11)-C(15)	105.3 (7)	C(7)-Zr(1)-N(31)	154.5 (3)	C(33)-N(32)-B(1)	127.4 (8)
N(11)-N(12)-B(1)	120.6 (7)	N(11)-Zr(1)-N(31)	76.3 (3)	N(32)-C(33)-C(36)	124.7 (9)
N(12)-C(13)-C(14)	108.4 (9)	Zr(1)-O(4)-C(4)	174.4 (6)	C(33)-C(34)-C(35)	106.9 (9)
C(14)-C(13)-C(16)	127.8 (9)	O(4)-C(4)-C(42)	108.4 (9)	N(31)-C(35)-C(37)	123.6 (9)
N(11)-C(15)-C(14)	109.5 (9)	C(41)-C(4)-C(42)	111.2 (9)	N(12)-B(1)-N(22)	110.6 (8)
C(14)-C(15)-C(17)	128 (1)	C(42)-C(4)-C(43)	112 (1)	N(22)-B(1)-N(32)	108.6 (8)
Zr(1)-N(21)-C(25)	131.0 (7)				

crystals (0.29 g, 58%) were isolated from the solution: mp 167–169 °C dec; ^{1}H NMR spectrum (benzene-d_6) δ 6.77, 6.34 (10, m, m; Ph), 5.43, 5.28, 5.24 (1, 1, 1; s, s, s; 4-H(pz)), 3.89 (2, AB quartet, J = 17.4 Hz, (ZrCH$_2$Ph)), 2.83 (2, br s, NC(CH$_2$Ph)), 2.52, 2.25, 2.14, 1.88, 1.58 (3, 3, 6, 3, 3; s, s, s, s, s, 3-CH$_3$, 5-CH$_3$(pz)), 1.66 (9, s, NC(CH$_3$)$_3$), 1.31 (9, s, OC(*CH*$_3$)$_3$); ^{13}C NMR spectrum (CDCl$_3$, the rings in this compound are nonequivalent) δ 244.0 (*C*-(CH$_2$Ph)N), 154.0, 137.1 (C-1(Ph)), 150.4, 149.5, 149.1, 143.4, 143.2, 143.0 (3-C, 5-C(pz)), 128.5, 127.2, 126.8, 126.3 (C2, 3, 5, 6(Ph)), 125.1, 118.4 (C4(Ph)), 106.1, 105.5 (1:2 intensity ratio, (4-C(pz)), 77.1 (OC), 62.2 (NC), 49.6 (Zr*C*H$_2$Ph), 43.7 (C(*C*H$_2$Ph)N), 32.3, 30.7 (C(*C*H$_3$)$_3$), 16.9, 16.0, 15.1, 13.0, 12.8 (1, 1, 1, 2, 1 intensity ratio, 3-CH$_3$, 5-CH$_3$(pz)); IR spectrum (cm^{-1} in CH$_2$Cl$_2$) ν(C=N) 1539; the mass spectrum shows a multiple cluster at m/e 634 (M$^+$ – 91, (CH$_2$Ph)); no molecular ion (M$^+$) was observed. Anal. Calcd for C$_{38}$H$_{54}$N$_7$BOZr: C, 62.79; H, 7.49. Found: C, 62.84; H, 7.42. The deuterated analogues were prepared by the identical procedure as the nondeuterated complexes. LiAlD$_4$ reduction of methyl benzoate yielded PhCD$_2$OH which was converted to PhCD$_2$Cl by treatment with SOCl$_2$. The *tert*-butyl-d_9 group was introduced from potassium *tert*-butoxide prepared from KH and the commercially available (Aldrich) perdeuterioalcohol.

X-ray Structure Determination. The crystals grown from pentane were predominantly in the form of plates bounded by {201} and {011} with (201) and ($\bar{2}0\bar{1}$) being the most developed faces. Few crystals were in the form of a bipyramid bounded by {110} and {011}. The agreement between the unit cell dimensions of the two crystals of the different habits was about 0.01 Å. The bipyramidal crystals were more convenient for the X-ray analysis (see more uniform absorption corrections) and therefore were used first. When the first crystal decomposed in the X-ray beam, we could not find any more bipyramid specimens of sufficiently high quality and thus used a plate type crystal to finish the data collection. The crystals are monoclinic of space group $P2_1/c$ with unit cell dimensions: for a bipyramid, a = 11.144 (3) Å, b = 16.117 (2) Å, c = 17.048 (3) Å, β = 93.84 (2)°, V = 3055 Å^3; for a plate, a = 11.131 (3) Å, b = 16.108 (2) Å, c = 17.055 (4) Å, β = 93.72 (2)°, V = 3051 Å^3, Z = 4, D(calcd) = 1.25 g cm^{-3}, λ(Mo Kα) = 0.710 73 Å, linear absorption coefficient μ = 3.81 cm^{-1}, F(000) = 1216, T = 291 K.

The data were collected with an Enraf-Nonius CAD-4 diffractometer: graphite monochromator; ω–2θ scan mode; 0.9° + 0.35° tan θ scan range; variable scan speed; orientation checked every 100 reflections; intensity of three standard reflections were monitored every 2.5 h of exposure time. The unit cell parameters were obtained from a least-squares fit to the setting angles ϕ, χ, ω, and θ for 25 general reflections. The crystals, sealed in a glass capillary, showed monotonic, isotropic decay in the X-ray beam, and therefore the data were measured in several concentric shells by using two crystals: bipyramid 0.2 × 0.2 × 0.2 mm, 2θ range 4–36°, 2019 reflections measured, 1364 observed with $I > 3\sigma(I)$, decay correction maximum 1.146, average 1.067, absorption corrections made maximum and minimum transmission 0.948 and 0.934; plate 0.2 × 0.2 × 0.1 mm, 2θ range 30–48°, 3678 reflections measured, 1188 observed with $I > 3\sigma(I)$, decay correction maximum 1.065, average 1.031, absorption corrections made maximum and minimum transmission 0.966 and 0.938. In the last 2θ shell 43–48° less than 20% of the reflections were observed. The data from the two crystals were scaled togehter by using 459 common reflections and showed a good agreement with a discrepancy factor of R = 0.025. All together 2093 observed and symmetry independent reflections were available.

The Zr position was determined from a Patterson map, and the rest of the structure was found in difference Fourier maps. The structure was refined by full-matrix least-squares minimizing $\sum w|\mathrm{F}_o - F_c|^2$, $w = (\sigma^2(F) + 0.0007F^2)^{-1}$ with anisotropic temperature factors for all non-hydrogen atoms. In the difference Fourier maps all non-methyl H atoms were found as well as those on the methyl bound to Zr and half of the methyls on the tris(pyrazolyl)borate ligand (C–H distances were in the range 0.83–1.22 Å). Although the highest remaining maxima were close to the other methyl groups, they did not form consistent patterns and the other H atoms could not be located with sufficient confidence. The located H atoms were used in structure factor calculations but not refined. The final R = 0.055, wR = 0.068, and S = 2.85 where $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and $S = (\sum w(|F_o| - |F_c|)^2/\sum w)^{1/2}$. On the final difference Fourier map maximum and minimum were 0.40 and –0.41 e A^{-3}, respectively.[27] The non-hydrogen atomic coordinates are listed in Table I, and important bond distances and angles are in Tables II and III. An ORTEP[28] drawing of the molecule is shown in Figure 1.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a partial support of this project. We

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(27) Data reduction carried out by using Enraf-Nonius Structure Determination Package, Frenz, B. A. (1982), refinement with SHELX-76 program for crystal structure determination, Sheldrick, G. M. (1976), Cambridge University, England.

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also thank the Eastman Kodak Co. for a fellowship (to M.E.T.). The use of the facilities at the University of South Carolina Regional NMR Center, funded by the National Science Foundation (Grant CHE82-07445), is acknowledged.

Registry No. {[HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-$Bu)_2$Cl}, 87307-02-6; {[HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-Bu)Me_2}, 87307-03-7; {[HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-$Bu)_2$Me}, 87307-04-8; {[HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-Bu)(η^2-C(Me)NCMe_3)Me}, 87307-05-9; {[HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-Bu)(C≡CMe$)_2$}, 87307-06-0; {[HB(3,5-$Me_2PZ)_3$]ZR(O-*t*-$Bu)_2$-(C≡CMe)}, 87318-58-9; {[HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-$Bu)_2$(CY_2Ph$)_2$}, 87307-07-1; {[HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-Bu)(η^2-C(CH_2Ph)-NCMe_3)CH_2Ph}, 87307-08-2; [HB(3,5-$Me_2PZ)_3$]ZrCl_3, 80041-67-4; [HB(3,5-$Me_2PZ)_3$]Zr(O-*t*-Bu)Cl_2, 84695-13-6; KO-*t*-Bu, 865-47-4; MeBr, 74-83-9; *t*-BuOH, 75-65-0; *t*-BuNC, 7188-38-7; MeC≡CLi, 4529-04-8; PhCH_2Cl, 100-44-7; PhCD_2OH, 21175-64-4; PhCD_2Cl, 33712-34-4; methyl benzoate, 93-58-3.

Supplementary Material Available: Tables of fractional coordinates of H atoms and anisotropic thermal motion parameters and listings of structural factor amplitudes for [HB(3,5-$Me_2pz)_3$]Zr(O-*t*-Bu)(η^2-C(Me)NCMe_3)Me (12 pages). Ordering information is given on any current masthead page.

Phosphinomethyl Complexes of Zirconium: Preparation, Complexation Capabilities, and Structural and Chemical Characteristics

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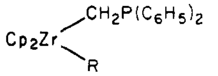
Received July 19, 1983

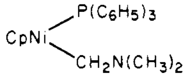
Syntheses of $Cp_2Zr(Cl)CH_2PPh_2$ (1) and $Cp_2Zr(CH_2PPh_2)_2$ (4) are described as is the X-ray crystal structure determination of the latter: monoclinic, space group $P2_1/a$, $a = 17.377$ (1) Å, $b = 12.844$ (1) Å, $c = 13.250$ (1) Å, $\beta = 96.084$ (6); $V = 2940.6$ (3) Å^3, $Z = 4$. As was found earlier for 1, the geometry about Zr is normal, and no Zr–P interaction is evident. Reduction of 1 with Na/Hg produces a fairly stable paramagnetic Zr(III) species formulated as $Cp_2ZrCH_2PPh_2$. The latter is monomeric and, similar to a simple Zr(III) alkyl model compound, decomposes in solution mostly via intermolecular H transfer from a Cp ring to Zr-bound carbon. Mechanisms for the chemistry of these Zr(III) species are suggested on the basis of an isotopic labeling study. Reaction of 1 with $Cr(CO)_5THF$ produces crystalline $Cp_2Zr(Cl)CH_2PPh_2Cr(CO)_5$: monoclinic, space group $P2_1/n$, $a = 11.346$ (9) Å, $b = 13.696$ (7) Å, $c = 17.609$ (13) Å, $\beta = 99.88$ (6)°, $V = 2696$ (3) Å^3, $Z = 4$. Reaction of 4 with (norbornadiene)$Cr(CO)_4$ produces $Cp_2Zr(\mu\text{-}CH_2PPh_2)_2Cr(CO)_4$, containing a severely hindered six-membered ring in a twist-boat conformation: monoclinic, space group $P2_1/n$, $a = 12.932$ (5) Å, $b = 16.966$ (3) Å, $c = 19.160$ (5) Å, $\beta = 97.88$ (3) Å, $V = 4164$ Å^3, $Z = 4$. Both Cr complexes display relatively normal Zr and Cr geometric environments with no unexpected interactions evident.

Introduction

As one part of an ongoing study of compounds containing both "early" and "late" transition metals, we recently reported the synthesis and some chemistry of zirconocene derivatives containing the (diphenylphosphino)methyl ligand.[2] These compounds are the first examples of such complexes containing either a group 4 or 5 metal and are unique in displaying exclusively η^1 bonding between ligand and metal (compounds 1–4). By way of comparison, Schmidbaur and others have reported the preparation of a number of phosphinomethyl complexes of group 8 metals, all of which display exclusively η^2 bonding in a three-membered M–C–P ring.[3] Related structures containing sulfur or nitrogen in place of phosphorus have also been reported;[4] only in the case of a single nitrogen system has evidence been obtained for an η^1-bonded species as well (compound 5).[4c] A theoretical



1, R = Cl
2, R = *n*-C_8H_{17}
3, R = $(CH_2)_4CH{=}CH_2$
4, R = $CH_2P(C_6H_5)_2$



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