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Acylation of Pyridine Rings Mediated by Group 4 Metal Aryl Oxide Compounds: High Yield Formation of α,α'-Disubstituted-2,6-pyridinedimethoxide Ligands

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Abstract: The room-temperature carbonylation (typically 1000 psi) of solutions of the dialkyl compounds $Zr(OAr')_2(R)_2$ (OAr') = 2,6-di-*tert*-butylphenoxide; R = CH_3, CH_2Ph) in the presence of 1 equiv of a suitable pyridine leads to the formation of a series of α,α'-disubstituted-2,6-pyridinedimethoxide compounds $(Ar'O)_2Zr[OCH(R)\text{-pyr-}CH(R)O]$ [R = CH_3 (**1**), CH_2Ph (**2**); pyr = NC_5H_3, **a**; NC_5H_2-4-Ph, **b**; NC_5H_2-4-Me, **c**]. Spectroscopic studies, ^1H and ^{13}C NMR, of the compounds show in all cases an approximately 50/50 mixture of the threo and meso diastereomers to be present in the initial reaction product mixture. Partial recrystallization of the zirconium benzyl product (**2b**) obtained by using 4-phenylpyridine yielded crystals of the pure threo diastereoisomer. A single-crystal X-ray diffraction of this product confirmed the stereochemistry and showed the five-coordinate zirconium metal center to be chelated by the tridentate pyridinedimethoxide ligand was well as the two 2,6-di-*tert*-butylphenoxide groups. Recrystallization of all the other derivatives yielded crystals containing both the threo and meso forms. In the presence of excess pyridine carbonylation of the compounds $M(OAr')_2(CH_3)_2$ (M = Zr, Hf) yields the six-coordinate adducts $M(OAr')_2[OCH(R)NC_5H_3CH(R)O](C_5H_5N)$ [M = Zr (**3**), Hf (**4**)]. The stoichiometry of the adducts was confirmed by a single-crystal X-ray diffraction analysis of the zirconium compound $Zr(OAr')_2[OCH(CH_3)C_5H_3CH(CH_3)O](C_5H_5N)$ (**3**). In this case, the crystals were found to contain a 50/50 mixture of the threo and meso diastereomers, leading to a disorder involving the α-methyl groups. Hydrolysis of these compounds allows isolation of the corresponding α,α'-disubstituted pyridinedimethanol ligands in good yield. A mechanistic study of the carbonylation reaction employing a competition reaction between pyridine and pyridine-d_5 showed the absence of a significant kinetic isotope effect. This and other studies are interpreted in terms of the reaction involving nucleophilic attack of intermediate metal–acyl groups at the 2- and 6-positions of the pyridine rings. Crystal data for $ZrO_4NC_{55}H_{65}$ (**2b**) at −135 °C: $a = 12.933\ (5)$, $b = 14.088\ (5)$, $c = 14.336\ (5)$ Å; $\alpha = 67.44\ (3)$, $\beta = 80.02\ (3)$, $\gamma = 81.61\ (3)°$; $Z = 2$; $d_{calcd} = 1.256$ g cm^{-3} in space group $P\bar{1}$; for $ZrO_4N_2C_{42}H_{58}$ (*3*) at 22 °C: $a = 10.599\ (5)$, $b = 18.153\ (5)$, $c = 11.155\ (4)$ Å; $\beta = 105.73\ (4)°$; $Z = 2$; $d_{calcd} = 1.199$ g cm^{-3} in space group $P2_1$.

Introduction

The carbonylation of high-valent early d-block, lanthanide and actinide metal-alkyl compounds has been shown to lead to a variety of interesting products.[1-3] Hydrolysis of these products has in some instances been shown to lead to useful organic materials.[1-5] The key step in this carbonylation chemistry is the initial formation of a metal–acyl intermediate, and it is the ensuing reactivity of this functionality that determines the final products of the reaction.[1] For electron-deficient transition metals the acyl group has been shown to adopt an η^2 bonding mode in which the oxygen atom is strongly bound to the metal center. A considerable amount of discussion has taken place concerning how this η^2 binding of acyl and related ligands affects their reactivity.[1,6] In particular, the diverse range of reactivity of these groups was initially accommodated into a bonding picture involving significant amounts of carbene character for the acyl carbon atom. Recent theoretical work has suggested that a more appropriate description of this reactivity involves carbenium ion character for the carbon atom. While studying the chemistry of group 4 metal–alkyl compounds of the type $(ArO)_2MR_2$ (M = Ti, Zr, Hf; ArO = a bulky aryl oxide ligand),[7] we have investigated their reactivity toward carbon monoxide and organic isocyanides. In the case of RNC molecules, reaction with 2 equiv of reagent led to the sequential formation of mono- and bis(η^2-iminoacyl) derivatives $(ArO)_2M(\eta^2\text{-}R'NCR)(R)$ and $(ArO)_2M(\eta^2\text{-}RNCR)_2$.[8] Thermolysis of the bis(η^2-iminoacyl) compounds was found to lead to enediamido compounds formed by an intramolecular coupling of the iminoacyl units.[9,10] In the case of the mono(η^2-iminoacyl) compound, carbonylation led directly to an enamidolate product presumably via a mixed acyl, iminoacyl intermediate.[9,10] In contrast to this behavior, the carbonylation of the substrate dialkyl compounds in hydrocarbon solvents was found not to lead to a single tractable product. Instead, for the zirconium and hafnium derivatives white, sparingly soluble products were obtained. In the case of titanium, evidence for reduction of the metal center was also found. In a modification of the carbonylation reactions, it was found that the addition of pyridine (≥1 equiv) to solutions of the zirconium and hafnium alkyls prior to carbonylation yielded colorless solutions containing only one product in high yields. Analysis of these products indicated that they contained α,α'-disubstituted-pyridinedimethoxide ligands apparently formed by sequential insertion of two acyl groups into the ortho CH bonds of the substrate pyridine.[11] In this paper, we report on our synthetic and mechanistic examination of this reactivity and an evaluation of the potential synthetic utility of the reaction for the formation of pyridinedimethanols, ligands that have recently attracted attention.[12]

Results and Discussion

Synthesis and Spectroscopic Properties of Compounds. The dialkyl compounds $Z(OAr')_2(R)_2$ (R = CH_3, CH_2Ph) have been

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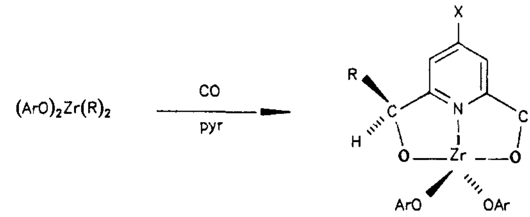
Scheme I



(1):R=CH$_3$; (2):R=CH$_2$Ph

(a):X=H; (b):X=Ph; (c):X=CH$_3$

previously shown to undergo cyclometalation of the 2,6-di-*tert*-butylphenoxide (Ar'O) ligand upon mild thermolysis.[13] They have also been shown to initially form 1:1 adducts with bipyridine in hydrocarbon solvents.[14] In the case of the dibenzyl compound, the coordination of the bipyridine ligand is followed by an alkyl transfer to the heterocyclic ring.[14] The addition of simple pyridine ligands (NC_5H_5; NC_5H_4-4-Ph and NC_5H_4-4-Me) to hydrocarbon solutions of $Zr(OAr')_2Me_2$ and $Zr(OAr')_2(CH_2Ph)_2$ causes no reaction at ambient temperatures as monitored by ^1H NMR spectroscopy. When a mixture of the dialkyl compounds and these pyridine ligands (1 equiv) is carbonylated at 25 °C (1000 psi CO) for periods of 4–12 h, a colorless hydrocarbon solution is typically formed. Removal of solvent from the reaction mixture allows the isolation of a series of pyridinedimethoxide complexes (**1**, R = CH_3) and (**2**, R = CH_2Ph), as shown (Scheme I). Purification of compounds **1** and **2** can be readily achieved by recrystallization from hexane or toluene/hexane mixtures. The spectroscopic properties of **1** and **2** are highly informative. The presence of two chiral centers within the α,α'-disubstituted pyridinedimethoxide ligands results in the possibility of two diastereoisomers (meso and threo) being present. In the threo (*R,R* and *S,S*) isomers, the molecular geometry should result in equivalent aryl oxide ligands; while for the meso (*R,S* and *S,R*) form, the two aryl oxide ligands should be nonequivalent. In both the ^1H and ^{13}C NMR spectra of all of the crude reaction product mixtures, three types of aryl oxide *tert*-butyl groups in the approximate ratio for 2:1:1 are observed. This observation combined with other spectra data (vide infra) indicates that the carbonylation reactions produce a 50/50 mixture of threo and meso compounds. In the ^1H NMR spectrum of the methyl derivatives **1**, the α-CHMeO resonances appear as one quartet and one doublet for each of the diastereoisomers. The two methyl group doublets, due to the threo an meso isomers, are well resolved and of approximately equal intensity. The α-C*H*MeO quartet patterns for each isomer are found to overlap considerably and occur in the δ 5–6 ppm region of the spectrum. In the ^{13}C NMR spectrum of these copounds, the two *C*H(Me)O carbon atoms appear in the δ 80–85 ppm region. Recrystallization of the methyl compounds **1** from hexane solution was found to lead to an exact 50/50 mixture of the threo and meso isomers. On the basis of an X-ray diffraction study (vide infra), it appears that the diastereoisomers cocrystallize together.

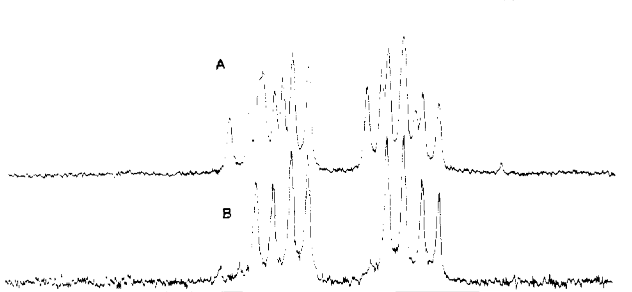
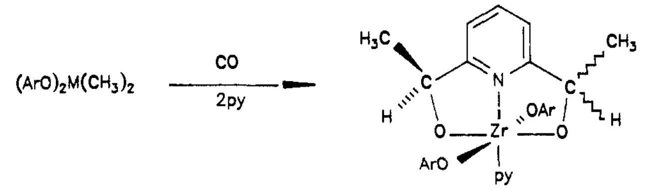


Figure 1. ^1H NMR spectrum (200 MHz, C_6D_6) of the benzyl proton resonances of (A) *meso*- and *threo*-**2b** and (B) recrystallized, *threo*-**2b**. In spectrum A the presence of both diastereoisomers results in two overlapping ABX patterns for the α-CH(CH_2Ph)O benzylic protons. In B only one fo the ABX patterns (eight lines) is present.

Scheme II



(3):M=Zr; (4):M=Hf

In the case of the benzyl derivatives **2**, the ^1H and ^{13}C NMR spectra of the crude reaction products also show an approximately 50/50 mixture of diastereoisomers. Due to the fact that the benzyl methylene protons are diastereotopic, they appear as an ABX pattern for each of the isomers so that a cluster of 16 lines is observed for this group (Figure 1). Recrystallization of the unsubstituted pyridine compound **2a** was found to lead to crystals again containing equal amounts of the diastereomers. However, in the case of the 4-phenyl derivative **2b**, the crystals obtained from a toluene/hexane mixture was found to contain mainly the threo isomer; i.e., only one oAr' resonance. This was confirmed by a single-crystal X-ray diffraction analysis (vide infra). The meso isomer was found to be enriched within the remaining supernatant liquid. The ^1H NMR spectrum of the crystalline material, *threo*-**2b**, is shown in Figure 1 for comparison with the crude reaction product mixture of isomers.

When the carbonylation of the dimethyl compounds $M(OAr')_2(CH_3)_2$ (M = Zr, Hf) is carried out in the presence of an excess of pyridine (≥2 equiv), the pyridine adducts $(OAr')_2M[OCH(Me)NC_5H_3CH(Me)O](NC_5H_5)$ [M = Zr, (**3**), Hf (**4**)] were obtained (Scheme II). Addition of pyridine to **1a** was found to lead to **3**. This process was found to be reversible. Hence, heating solid **3** under vacuum led to the formation of **1a** and free pyridine. The benzyl complex **2a** does not appear to readily coordinate excess pyridine, possibly due to the more bulky benzyl substituent. The spectroscopic properties for **3** and **4** are very similar to those of **1a** except for the extra pyridine signals. Again, the ^1H and ^{13}C NMR spectra of **3** and **4** indicate the presence of equimolar amounts of the meso and threo forms of the α,α'-dimethylpyridinedimethoxide ligands. Recrystallization of **3** from hexane yielded crystals containing equal amounts of the isomer, as indicated both by their spectroscopic properties and by a single-crystal X-ray diffraction analysis.

Attempts to liberate the α,α'-disubstituted pyridinedimethoxide ligands from the metal coordination sphere proved successful. Hence, hydrolysis of compounds **1** or **2** followed by elution on silica led to the separation and isolation of the parent dimethanols in reasonable yields (50–75%), based upon zirconium. The ^1H and ^{13}C NMR spectra of these organic molecules again indicated an approximately 50/50 mixture of threo and meso forms. Attempts to separate the diastereoisomers by thin-layer chromatography proved unsatisfactory.[12] However, hydrolysis of crystals of *threo*-**2b** did lead to the threo form of the dimethanol in >95% purity. The hydrolysis of unpurified reaction mixtures obtained directly from the carbonylation of $Zr(OAr')_2(CH_2Ph)_2$ was also found to contain varying amounts of dibenzylmethanol, $(PhCH_2)_2CHOH$, as identified by ^1H and ^{13}C NMR spectroscopy. We believe this product comes about via the double alkylation of CO leading to an η^2-ketone complex of the type $L_nZr[\eta^2\text{-}CO(PhCH_2)_2]$. The formation of η^2-bound ketone ligands by carbonylation of dialkyl substrates is well established.[15,16] Hydrolysis

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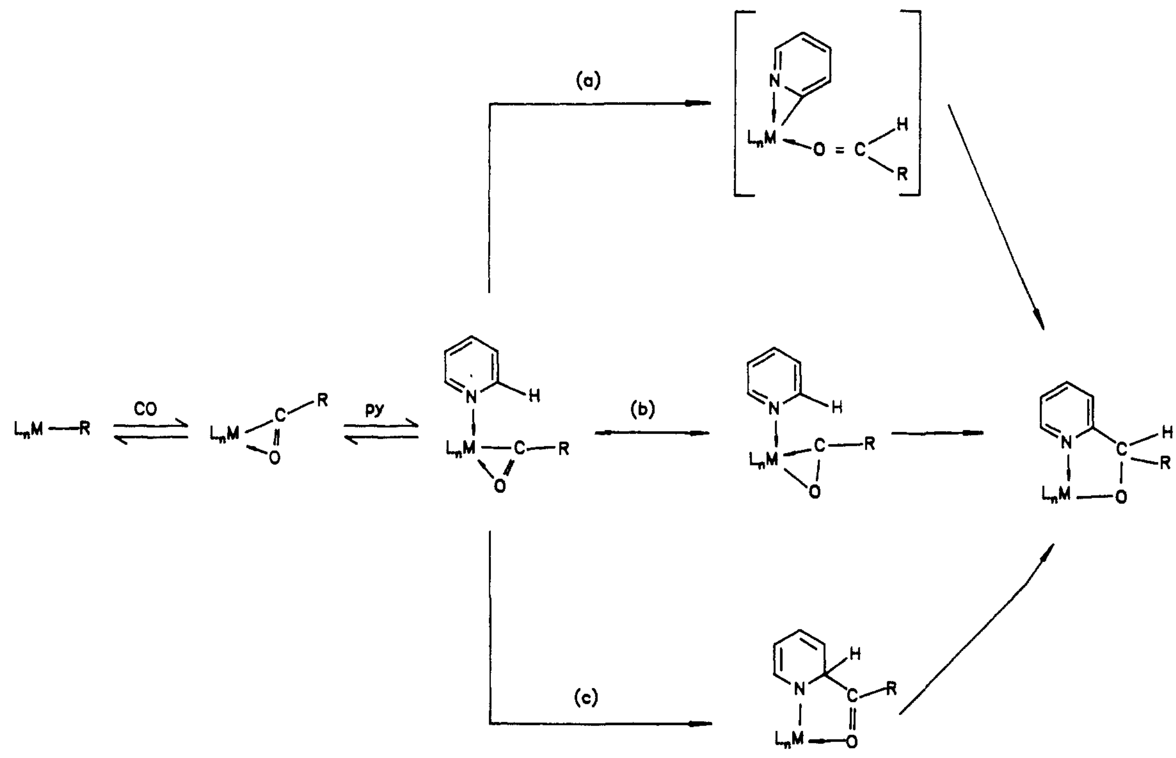
Scheme III



of this function would then lead to the observed alcohol. The carbonylation of $Zr(OAr')_2(CH_2Ph)_2$ in the absence of pyridine was found to lead to a sparingly soluble white compound. Hydrolysis of this material allowed the isolation of $(PhCH_2)_2CHOH$ in 20–30% yield, based upon zirconium.

Mechanistic Considerations. Theoretical calculations by Hoffman and co-workers on the electronic structure of η^2-acyl compounds point to the electrophilic nature of the carbon atom as being pivotal to their reactivity.[6] Work by Tilley et al. has shown that the addition of pyridine or tertiary phosphine ligands to solutions of the silaacyl complex $Cp^*Ta(\eta^2\text{-}COSiMe_3)Cl_3$ leads to the formation of adducts in which the donor ligand is bound to the acyl carbon atom.[17] However, Tilley has also shown that η^2-silaacyl groups can attack pyridine to generate silylpyridinemethoxide groups.[18] It is not believed that the coordination of the pyridine to the acyl carbon atom precedes the formation of the pyridinemethoxide group.[18]

In discussing the formation of the pyridinedimethoxide groups via carbonylation of the $(Ar'O)_2MR_2$ substrates, a number of reasonable pathways must be considered (Scheme III). In all pathways, it is believed that the initial step involves the formation of an η^2-acyl group via migratory insertion of CO into a metal–alkyl bond. In pathway b, the potential carbenoic character of the acyl carbon atom (oxycarbenoid resonance) is recognized that that direct insertion into the ortho CH bond of a coordinated pyridine ligand takes place. There is evidence in the literature for the insertion of a samarium η^2-acyl group into the aromatic CH bond of diphenylacetylene.[19] An alternative pathway, a, proceeds via an η^2-C,N-bound pyridyl intermediate formed by cyclometalation of the pyridine ligand itself. The cyclometalation of pyridine at the ortho position is well-known for both early- and later-transition-metal systems.[20,21] Insertion of the aldehyde group back into the metal–carbon bond then leads to the desired product (Scheme III). The last pathway c involves direct (nucleophilic) attack by the acyl group at the ortho carbon followed by a facile 1,2 hydrogen shift to produce the final product. Trying to discriminate among these three mechanisms is not easy given the fact that the reactions are all multistep, involving a number of possible equilibria.

At attempt was made to try and detect the presence of a significant kinetic isotopic effect (k_H/k_D) for the activation of the pyridine CH bond. Hence, the dimethyl compound $Zr(OAr')_2Me_2$ was carbonylated in the presence of equimolar amounts (10 equiv per Zr of each) of C_5H_5N and C_5D_5N. Analysis of the final product mixture showed the resulting pyridinedimethoxide **3** to contain a 50/50 mixture of deuterio and non-deuterio products. Hence, within experimental error, there appears to be no preference for acylation of pyridine over pyridine-d_5. This result can be interpreted as indicating that pathways a and b, in which the ortho CH bond is being directly broken, are not operative. This assumes that the rate-determining step is not simply the coordination of pyridine to the metal center, which would also result in a lack of discrimination. However, Tilley and co-workers have also mechanistically investigated the formation of pyridinemethoxyide lignds from silaacyl metal complexes.[18] Their work conclusively ruled out the possible intermediacy of an η^2-C,N-pyridyl species, as just such a complex was independently synthesized and shown to generate a different mixture of isomers than that produced in the acyl/pyridine reaction.[18] Further strong evidence against the η^2-C,N-pyridyl pathway comes from the fact that it would preclude overall acylation of both sides of the pyridine substrate to produce pyridinedimethoxide ligands. Once a pyridinemethoxide group is generated and chelated to the metal, a second cyclometalation of the remaining ortho CH bond seems highly unlikely. These arguments hence leave behind pathways b and c as the possible mechanisms. It is well-known that pyridine

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for $(Ar'O)_2Zr[OCH(CH_2Ph)NC_5H_2PhCH(CH_2Ph)]$ (**2b**)[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Zr	0.22534 (5)	0.19945 (4)	0.17292 (4)	1.52 (1)	C(141)	0.2908 (5)	−0.3011 (4)	0.3776 (4)	1.8 (1)
O(20)	0.2162 (3)	0.2765 (3)	0.0253 (3)	1.82 (9)	C(142)	0.2274 (5)	−0.3641 (4)	0.3623 (5)	2.3 (1)
O(30)	0.2150 (3)	0.2810 (3)	0.2606 (3)	1.88 (9)	C(143)	0.2343 (6)	−0.4692 (5)	0.4181 (5)	3.1 (2)
O(121)	0.3772 (3)	0.1532 (3)	0.1659 (3)	1.94 (9)	C(144)	0.3043 (6)	−0.5129 (5)	0.4895 (5)	3.2 (2)
O(161)	0.0866 (3)	0.1406 (3)	0.2192 (3)	2.1 (1)	C(145)	0.3681 (5)	−0.4507 (5)	0.5043 (5)	2.7 (2)
N(11)	0.2488 (4)	0.0242 (3)	0.2388 (3)	1.6 (1)	C(146)	0.3628 (5)	−0.3473 (5)	0.4489 (4)	2.3 (1)
C(12)	0.3472 (5)	−0.0229 (4)	0.2446 (4)	1.8 (1)	C(161)	0.0612 (5)	0.0376 (4)	0.2631 (5)	2.2 (1)
C(13)	0.3635 (5)	−0.1285 (4)	0.2879 (4)	1.7 (1)	C(162)	−0.0043 (5)	0.0173 (5)	0.3663 (5)	2.5 (2)
C(14)	0.2769 (5)	−0.1877 (4)	0.3260 (4)	1.5 (1)	C(163)	−0.1002 (5)	0.0921 (5)	0.3629 (4)	2.2 (2)
C(15)	0.1761 (5)	−0.1371 (4)	0.3180 (4)	1.9 (1)	C(164)	−0.1017 (5)	0.1682 (5)	0.4012 (5)	2.3 (2)
C(16)	0.1640 (4)	−0.0309 (4)	0.2739 (4)	1.7 (1)	C(165)	−0.1891 (5)	0.2374 (5)	0.4001 (5)	2.6 (2)
C(21)	0.2615 (5)	0.2903 (4)	−0.0724 (4)	1.7 (1)	C(166)	−0.2747 (6)	0.2324 (6)	0.3604 (5)	3.2 (2)
C(22)	0.2329 (5)	0.2282 (5)	−0.1211 (4)	2.1 (1)	C(167)	−0.2763 (6)	0.1584 (6)	0.3177 (5)	4.0 (2)
C(23)	0.2919 (5)	0.2359 (5)	−0.2146 (4)	2.3 (1)	C(168)	−0.1879 (5)	0.0890 (5)	0.3203 (5)	3.4 (2)
C(24)	0.3701 (5)	0.3003 (5)	−0.2595 (4)	2.6 (2)	C(221)	0.1436 (5)	0.1567 (5)	−0.0765 (4)	2.4 (1)
C(25)	0.3882 (5)	0.3669 (5)	−0.2141 (4)	2.1 (1)	C(222)	0.1789 (6)	0.0603 (5)	0.0102 (5)	3.0 (2)
C(26)	0.3337 (4)	0.3640 (4)	−0.1218 (4)	1.8 (1)	C(223)	0.0423 (5)	0.2116 (5)	−0.0401 (5)	3.1 (2)
C(31)	0.1677 (5)	0.2977 (4)	0.3468 (4)	1.8 (1)	C(224)	0.1141 (6)	0.1209 (6)	−0.1571 (5)	3.9 (2)
C(32)	0.2150 (5)	0.2490 (4)	0.4380 (4)	2.0 (1)	C(261)	0.3480 (5)	0.4488 (4)	−0.0805 (4)	2.0 (1)
C(33)	0.1590 (5)	0.2581 (5)	0.5268 (4)	2.4 (1)	C(262)	0.4270 (5)	0.5228 (5)	−0.1532 (5)	3.0 (2)
C(34)	0.0627 (5)	0.3146 (5)	0.5262 (5)	2.6 (2)	C(263)	0.2422 (5)	0.5118 (5)	−0.0752 (5)	2.7 (2)
C(35)	0.0228 (5)	0.3694 (5)	0.4357 (4)	2.2 (1)	C(264)	0.3882 (5)	0.4029 (5)	0.0234 (4)	2.5 (1)
C(36)	0.0750 (5)	0.3647 (4)	0.3427 (4)	1.6 (1)	C(321)	0.3233 (5)	0.1886 (5)	0.4407 (4)	2.6 (2)
C(121)	0.4299 (5)	0.0538 (5)	0.1982 (4)	2.1 (1)	C(322)	0.3656 (5)	0.1613 (6)	0.5444 (5)	3.5 (2)
C(122)	0.4979 (5)	0.0343 (5)	0.1081 (4)	2.3 (1)	C(323)	0.4048 (5)	0.2529 (6)	0.3588 (5)	3.6 (2)
C(123)	0.5759 (5)	0.1132 (4)	0.0542 (4)	2.2 (1)	C(324)	0.3173 (6)	0.0851 (5)	0.4300 (5)	3.6 (2)
C(124)	0.5654 (5)	0.1839 (5)	−0.0419 (5)	2.4 (2)	C(361)	0.0366 (5)	0.4383 (4)	0.2411 (4)	1.9 (1)
C(125)	0.6380 (6)	0.2558 (5)	−0.0915 (5)	3.4 (2)	C(362)	0.1208 (5)	0.5131 (5)	0.1831 (5)	2.4 (2)
C(126)	0.7214 (6)	0.2583 (5)	−0.0431 (5)	3.6 (2)	C(363)	−0.0653 (5)	0.5040 (5)	0.2583 (5)	2.7 (2)
C(127)	0.7318 (6)	0.1894 (6)	0.0521 (6)	3.8 (2)	C(364)	0.0141 (5)	0.3833 (5)	0.1735 (4)	2.3 (1)
C(128)	0.6607 (5)	0.1178 (5)	0.1016 (5)	2.8 (2)					

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2.3)]$.

ligands are susceptible to nucleophilic attack at their 2-, 4-, and 6-positions.[22] This is one method for the production of 2-alkylpyridine compounds.[22] We, hence, believe that the formation of the pyridinemethoxide ligands occurs via a nucleophilic acylation of pyridine within the metal coordination sphere (c, Scheme III). It is interesting to note in this context that the initial alkyl substrate $(Ar'O)_2Zr(CH_2Ph)_2$ will alkylate bipyridine and related heterocyclic compounds.[14] It is also of note that the introduction of the pyridine ligand into the metal coordination sphere may, itself, modify the reactivity of the acyl ligand. The introduction of electron density at the metal center may reduce drastically the electrophilicity (carbene-like) nature of the acyl carbon and may even lead to more facile formation of an η^1-acyl moiety, which may be responsible for the reactivity.[23]

Crystallographic Studies. In order to gain insight into the structure and stereochemistry of the pyridinedimethoxide derivatives, it was decided to carry out single-crystal X-ray diffraction analyses of the two types of compounds obtained in this study. Because of the stereochemical possibilities, crystals of pure *threo*-**2b** and mixed *threo*- and *meso*-**3** were chosen for study. Bulk crystalline samples of the latter compound were spectroscopically shown to contain both the threo and meso isomeric forms, although it was not know if both isomers were cocrystallizing within the same unit cell.

***threo*-$(Ar'O)_2Zr[OCH(CH_2Ph)NC_5H_2PhCH(CH_2Ph)O]$ (2b).** An ORTEP view of the molecular structure of *threo*-**2b** is shown in Figure 2. Table I contains the fractional coordinates and anisotropic thermal parameters, while Table II contains some selected bond distances and angles. The geometry about the zirconium atom in **2b** is best considered as highly distorted trigonal bipyramidal. The central nitrogen atom of the pyridinedimethoxide ligand and the two aryl oxide oxygen atoms define an almost perfect trigonal plane: angles of 117.6 (1), 121.0 (1), and 121.4 (1)°. However, the remaining two oxygen atoms of the tridentate pyridine chelate cannot attain a perfectly trans, axial geometry,

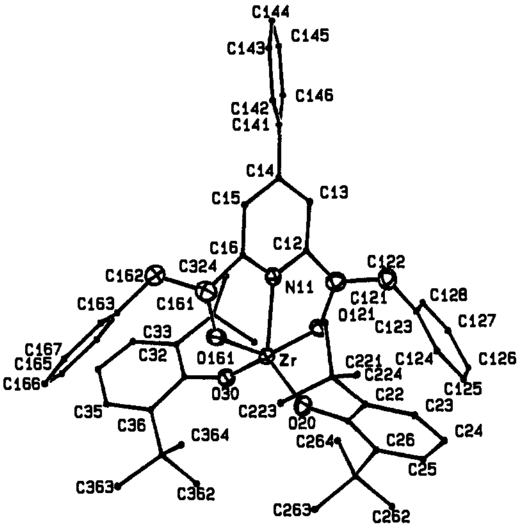

Figure 2. ORTEP view of $(Ar'O)_2Zr[OCH(CH_2Ph)NC_5H_2PhCH(CH_2Ph)O]$ (**2b**).

Table II. Selected Bond Distances and Angles for **2b**

	Distances, Å		
Zr–O(20)	1.989 (3)	Zr–O(30)	1.982 (3)
Zr–O(121)	1.975 (3)	Zr–O(161)	1.987 (3)
Zr–N(11)	2.274 (4)		
	Angles, deg		
O(20)–Zr–O(30)	117.6 (1)	O(20)–Zr–O(121)	99.3 (1)
O(20)–Zr–O(161)	101.2 (1)	O(20)–Zr–N(11)	121.4 (1)
O(30)–Zr–O(121)	100.7 (1)	O(30)–Zr–O(161)	99.9 (1)
O(30)–Zr–N(11)	121.0 (1)	O(121)–Zr–O(161)	139.7 (1)
O(121)–Zr–N(11)	69.8 (1)	O(161)–Zr–N(11)	69.9 (1)
Zr–O(20)–C(21)	146.2 (3)	Zr–O(30)–C(31)	147.7 (3)
Zr–O(121)–C(121)	131.1 (3)	Zr–O(161)–C(161)	130.8 (3)

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(22) *Rodd's Chemistry of the Carbon Compounds*, 2nd ed.; Coffey, S., Ed.; Elsevier: New York, 1976.

(23) (a) Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1987**, *6*, 891. (b) Chebi, D.; Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.*, submitted for publication.

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $(Ar'O)_2Zr[OCH(CH_3)NC_5H_3CH(CH_3)O](py)$ (3)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
Zr	0.15643 (4)	0.09890	0.09980 (6)	3.634 (9)	C(42)	−0.2159 (8)	−0.0350 (5)	0.012 (1)	6.9 (2)
O(20)	0.2322 (4)	0.0846 (2)	−0.0459 (4)	4.4 (1)	C(43)	−0.3082 (7)	0.0095 (6)	−0.062 (1)	7.4 (2)
O(30)	0.3196 (4)	0.1331 (2)	0.2253 (4)	3.78 (9)	C(44)	−0.2751 (8)	0.0777 (6)	−0.094 (1)	7.5 (3)
O(40)	0.1423 (4)	−0.0038 (3)	0.1565 (6)	4.8 (1)	C(45)	−0.1442 (5)	0.0998 (7)	−0.0507 (7)	5.6 (2)
O(41)	0.0341 (4)	0.1807 (3)	0.0134 (5)	4.4 (1)	C(46)	0.0320 (8)	−0.0493 (4)	0.1370 (9)	6.1 (2)
N(10)	0.0648 (5)	0.1264 (3)	0.2765 (6)	4.2 (1)	C(47)	0.012 (1)	−0.0748 (6)	0.262 (1)	8.7 (3)
N40)	−0.0543 (5)	0.0568 (3)	0.0234 (6)	4.7 (1)	C(48)	−0.0860 (7)	0.1721 (6)	−0.074 (1)	7.2 (2)
C(11)	0.1311 (5)	0.1045 (5)	0.3920 (6)	4.6 (1)	C(49)	−0.170 (2)	0.2375 (8)	−0.098 (2)	6.6 (5)
C(12)	0.0848 (7)	0.1162 (6)	0.4941 (8)	6.3 (2)	C(50)	−0.103 (2)	0.189 (3)	−0.196 (2)	14 (1)
C(13)	−0.312 (7)	0.1540 (6)	0.481 (1)	7.0 (2)	C(221)	0.3630 (8)	0.2126 (4)	−0.1283 (8)	5.2 (2)
C(14)	−0.0978 (7)	0.1762 (5)	0.3652 (9)	6.4 (2)	C(222)	0.2268 (9)	0.2454 (5)	−0.149 (1)	6.9 (2)
C(15)	−0.0483 (6)	0.1626 (4)	0.2688 (9)	5.4 (2)	C(223)	0.440 (1)	0.2655 (5)	−0.198 (1)	7.3 (2)
C(21)	0.2862 (6)	0.0753 (4)	−0.1436 (8)	4.5 (2)	C(224)	0.4426 (8)	0.211 (5)	0.0070 (9)	6.1 (2)
C(22)	0.3545 (6)	0.1349 (4)	−0.1828 (8)	4.7 (2)	C(261)	0.1992 (9)	−0.0584 (5)	0.177 (1)	7.1 (2)
C(23)	0.4113 (6)	0.1206 (5)	−0.2812 (7)	5.3 (2)	C(262)	0.270 (1)	−0.0860 (5)	−0.043 (1)	9.9 (3)
C(24)	0.4065 (7)	0.0540 (5)	−0.3372 (9)	5.8 (2)	C(263)	0.059 (1)	−0.0373 (6)	−0.189 (1)	9.7 (3)
C(25)	0.3401 (7)	−0.0020 (5)	−0.3028 (8)	5.6 (2)	C(264)	0.197 (1)	−0.1257 (7)	−0.259 (1)	11.7 (3)
C(26)	0.2747 (7)	0.0059 (4)	−0.2061 (8)	5.3 (2)	C(321)	0.5392 (6)	0.0302 (5)	0.3166 (8)	5.3 (2)
C(31)	0.4210 (5)	0.1570 (4)	0.3206 (7)	3.9 (1)	C(322)	0.5298 (9)	0.0354 (6)	0.176 (1)	7.2 (2)
C(32)	0.5265 (5)	0.1082 (4)	0.3678 (6)	4.5 (1)	C(32)	0.4370 (8)	−0.0228 (4)	−0.3382 (9)	5.8 (2)
C(33)	0.6226 (7)	0.1310 (6)	0.4712 (9)	6.5 (2)	C(324)	0.6681 (8)	−0.0077 (6)	0.378 (1)	7.6 (3)
C(34)	0.6237 (8)	0.1999 (7)	0.525 (1)	7.3 (3)	C(361)	0.3220 (7)	0.2925 (4)	0.3240 (8)	4.8 (2)
C(35)	0.5242 (7)	0.2463 (5)	0.4725 (9)	5.9 (2)	C(362)	0.2179 (8)	0.2807 (4)	0.2006 (9)	5.4 (2)
C(36)	0.4206 (6)	0.2288 (4)	0.3670 (8)	4.6 (2)	C(363)	0.2517 (9)	0.3079 (5)	0.423 (1)	6.4 (2)
C(41)	−0.0846 (6)	−0.0098 (4)	0.0557 (9)	5.3 (2)	C(364)	0.400 (1)	0.3623 (5)	0.305 (1)	7.9 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $({}^4/_3)[a^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table IV. Selected Bond Distances and Angles for $(Ar'O)_2Zr[OCH(CH_3)NC_5H_3CH(CH_3)O](py)$ (3)

	Distances, Å		
Zr–O(20)	2.015 (6)	Zr–O(30)	2.006 (5)
Zr–O(40)	1.988 (5)	Zr–O(41)	2.034 (5)
Zr–N(10)	2.473 (7)	Zr–N(40)	2.295 (6)
	Angles, deg		
O(20)–Zr–O(30)	98.4 (2)	O(20)–Zr–O(40)	102.5 (2)
O(20)–Zr–O(41)	93.1 (2)	O(20)–Zr–N(10)	175.8 (2)
O(20)–Zr–N(40)	102.6 (3)	O(30)–Zr–O(40)	101.2 (2)
O(30)–Zr–O(41)	115.0 (2)	O(30)–Zr–N(40)	158.5 (3)
O(40)–Zr–O(41)	137.9 (2)	O(40)–Zr–N(10)	81.7 (2)
O(40)–Zr–N(40)	69.9 (2)	O(41)–Zr–N(10)	83.9 (2)
O(41)–Zr–N(40)	68.7 (2)	N(10)–Zr–N(40)	79.1 (3)
Zr–O(20)–C(21)	178.8 (5)	Zr–O(30)–C(31)	172.8 (5)
Zr–O(40)–C(46)	129.5 (6)	Zr–O(41)–C(48)	126.7 (6)

resulting in an O–Zr–O angle of only 139.7 (1)°. The four Zr–O distances are all comparable and are well within the range typically found for zirconium(IV) aryl oxide and alkoxide compounds.[8,24] The Zr–N(pyridyl) distance of 2.274 (4) Å is, however, considerably shorter than the distance typically found to terminal pyridine derivatives of this metal. One can compare the distance of 2.403 (1) Å found in the complex $Cp_2Zr(\eta^2\text{-}H^*{}_2C{=}CO)(py)$[25] and 2.407 (4) Å for the chelated pyridiylmethyl ligand in $Cp_2Zr(CH_2\text{-}py\text{-}6Me)_2$.[23] The shortening of the bond to the pyridine nitrogen may reflect the nitrogen atom being pulled in toward the metal by the methoxide oxygen atoms of the chelated ligand. The threo form of the pyridinedimethoxide ligand is clearly confirmed.

$(Ar'O)_2Zr[OCH(CH_3)NC_5H_3CH(CH_3)O](NC_5H_5)$ (3). An ORTEP view of the molecular structure of 3 is shown in Figure 3. Fractional coordinates and isotropic thermal parameters are contained in Table III, while some selected bond distances and angles are collected in Table IV. The geometry about the zirconium atom in 3 is best described as a distorted octahedron. The aryl oxide ligands are arranged approximately trans to the two pyridine nitrogen atoms. Again, as in the structure of **2b**, the two oxygen atoms of the pyridinedimethoxide ligand are held back from being mutually trans, with an O–Zr–O angle of 137.9 (2)°. The Zr–O distances are, again, comparable and well within the expected range of values. The Zr–N distances between the chelated and terminal pyridine ligands are dramatically different. The shortening of the pyridinedimethoxide Zr–N distance, 2.295 (6) Å, over the distance of 2.473 (7) Å for the terminal pyridine ligand may, again, be due to the presence of the chelating oxygen atoms. The introduction of the extra pyridine ligand in compound 3 dramatically increases the steric congestion within the coordination sphere over the five-coordinate compounds **1** and **2**. This is highlighted by the increase in the Zr–O–Ar′ angles on going from **2b** to **3**. In the five-coordinated **2b**, angles of 146.2 (3) and 147.7 (3)° are observed, while in six-coordinate 3, the corresponding angles are 178.8 (5) and 172.8 (5)°. Previous work by our group has shown that this angle is extremely flexible for early d-block aryl oxide compounds and can readily respond to steric demands.[24,26]

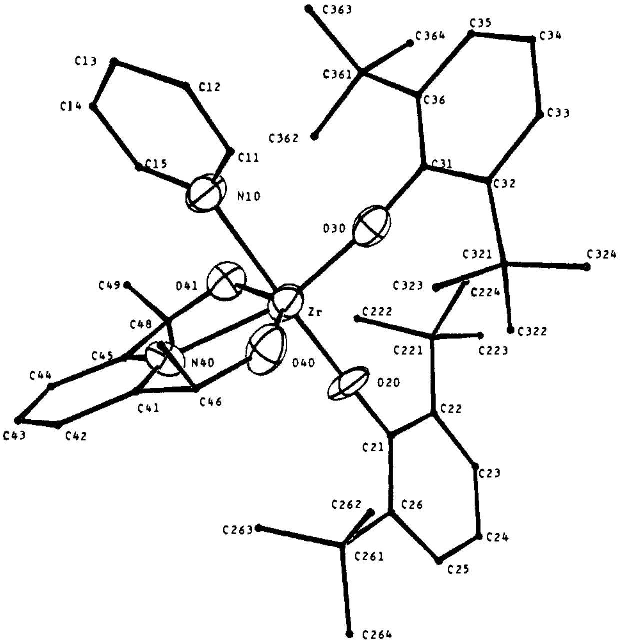

Figure 3. ORTEP view of $(Ar'O)_2Zr[OCH(CH_3)NC_5H_3CH(CH_3)O](py)$ (3).

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(24) Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.*, submitted for publication.

(25) Moore, K. J.; Straus, D. A.; Armantrout, J.; Santasiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

Table V. Crystal Data and Data Collection Parameters

	2b	**3**
formula	$\mathrm{ZrO_4NC_{55}H_{65}}$	$\mathrm{ZrO_4N_2C_{42}H_{58}}$
fw	895.36	746.16
space group	$P\bar{1}$	$P2_1$
a, Å	12.933 (5)	10.599 (5)
b, Å	14.088 (5)	18.153 (4)
c, Å	14.336 (5)	11.155 (4)
α, deg	67.44 (3)	90
β, deg	80.02 (3)	105.73 (4)
γ, deg	81.61 (3)	90
V, Å^3	2366 (2)	2066 (3)
density$_{\mathrm{calcd}}$, g/cm^3	1.256	1.199
crystal size, mm	0.32 × 0.25 × 0.08	0.63 × 0.47 × 0.36
temp, °C	−135	22.0
radiation wavelength	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	ω–2θ	ω–2θ
h,k,l limits:	−13 to 13, −13 to 15, 0 to 15	−13 to 13, 0 to 23, 0 to 11
2θ range, deg	4.00–45.00	4.00–45.00
scan width, deg	0.58 + 0.35 tan θ	0.90 + 0.35 tan θ
take-off angle, deg	1.90	4.90
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP
F_{0000}	948.0	792.0
ρ factor used in weighting	0.040	0.070
no. of unique data collected	6152	4034
no. of data with $I > 3.0\sigma(I)$	4772	2841
no. of variables	550	450
largest shift/esd in final cycle	0.01	0.12
R	0.058	0.043
R_W	0.074	0.058
goodness of fit	1.740	0.908

[a] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

During refinement of the structure of **3**, it was found that one of the α-methyl substituents was disordered evenly on either side of the pyridine plane. Hence, the crystals chosen for study contained a 50/50 mixture of the *meso*-(*S*,*R*) and *threo*-(*S*,*S*) diastereoisomers. Presumably other crystals within the sample contain the other *R*,*S* and *R*,*R* pair. The reason for disorder only occurring for one of the α-methyl groups may reflect a need to accommodate the bulky *tert*-butyl group of one of the aryl oxide ligands (Figure 3).

Experimental Section

All operations were carried out under a dry nitrogen atmosphere either in a Vacuum Atmospheres Dri-lab or by standard Schlenck techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone under a nitrogen atmosphere. The compounds $\mathrm{(Ar'O)_2M(CH_3)_2}$ (M = Zr, Hf) and $\mathrm{(Ar'O)_2Zr(CH_2Ph)_2}$ were prepared by previously reported procedures. Pyridine, 4-phenylpyridine, and 4-methylpyridine were obtained commercially (Aldrich) and dried over KOH pellets and molecular sieves prior to use. All pressure reactions were carried out in a Parr Series 4561 minireactor with a 300-cm^3 total internal capacity. ^{1}H and ^{13}C NMR spectra were recorded either on a Varian Associates Gemini-200 or General Electric QE-300 spectrometer.

Carbonylation Reactions. An essentially identical procedure was adopted for all of the carbonylation reactions. A mixture of the metal–alkyl substrate (1 mmol) and pyridine (≥1 equiv) in benzene solution (10 cm^3) is placed into a small (40-cm^3 total volume) glass vial, which is positioned within the minireactor bomb. After being flushed with CO, the bomb is pressurized to 800 psi and allowed to stand for 12 h. The reaction mixture was not stirred. After being depressurized, the solvent was removed from the reaction mixture under vacuum and the crude products were analyzed by ^{1}H NMR spectroscopy. Purification was achieved either by simple washing with hexane or by recrystallization from suitable solvent mixtures as indicated below.

$\mathbf{(Ar'O)_2Zr[OCH(CH_3)NC_5H_3CH(CH_3)O]}$ (1a). Anal. Calcd for $\mathrm{ZrC_{37}H_{53}NO_4}$: C, 66.62; H, 8.012; N, 2.10. Found: C, 66.93; H, 9.06; N, 1.66. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.43 (s), 1.45 (s, overlapping *Bu^t* groups of meso and threo form), 1.08 (d), 1.11 (d, CH*Me*O), 5.45 (m, C*H*MeO).

$\mathbf{(Ar'O)_2Zr[OCH(CH_3)NC_5H_2PhCH(CH_3)O]}$ (1b). Anal. Calcd for $\mathrm{ZrC_{43}H_{57}NO_4}$: C, 69.50; H, 7.73; N, 1.88. Found: C, 69.56; H, 7.50; N, 1.74. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.65, 1.64 (s, *Bu^t*), 1.41 (d), 1.43 (d, CH*Me*O), 5.80 (m, C*H*MeO). ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 31.9, 32.6 ($\mathrm{C}\mathit{Me}_3$ of meso), 32.2 ($\mathrm{C}\mathit{Me}_3$ of threo), 25.1, 25.2 (CH*Me*O), 82.2, 82.7 (*C*HMeO), 35.9 ($\mathit{C}\mathrm{Me}_3$).

$\mathbf{(Ar'O)_2Zr[OCH(CH_3)NC_5H_2MeCH(CH_3)O]}$ (1c). Anal. Calcd for $\mathrm{ZrC_{38}H_{55}NO_4}$: C, 67.01; H, 8.14; N, 2.06. Found: C, 67.13; H, 8.67; N, 1.99. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.48 (s), 1.49 (s, *Bu^t*), 1.15 (d), 1.18 (d, CH*Me*O), 5.52 (m, C*H*MeO). ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 31.4, 32.1 ($\mathrm{C}\mathit{Me}_3$ of meso); 31.7 ($\mathrm{C}\mathit{Me}_3$ of threo), 35.4 ($\mathit{C}\mathrm{Me}_3$ of both isomers), 24.5, 24.7 (CH*Me*O) 81.4, 81.9 (*C*HMeO), 21.3 (py-4*Me*).

$\mathbf{(Ar'O)_2Zr[OCH(CH_2Ph)NC_5H_3CH(CH_2Ph)O]}$ (2a). ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.54 (s), 1.58 (s, *Bu^t* of meso and threo), 2.8–3.1 (m, $\mathrm{CHC}\mathit{H}_2\mathrm{Ph}$ of both isomers), 5.85 (m, $\mathrm{C}\mathit{H}\mathrm{CH_2Ph}$). ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 31.4, 32.3 ($\mathrm{C}\mathit{Me}_3$ of meso), 31.9 ($\mathrm{C}\mathit{Me}_3$ of threo), 35.4 ($\mathit{C}\mathrm{Me}_3$ of both meso and threo), 44.6, 44.9 ($\mathit{C}\mathrm{H_2Ph}$), 87.0, 86.8 ($\mathit{C}\mathrm{HCH_2Ph}$).

$\mathbf{(Ar'O)_2Zr[OCH(CH_2Ph)NC_5H_2PhCH(CH_2Ph)O]}$ (2b). Anal. Calcd for $\mathrm{ZrC_{55}H_{65}NO_4}$: C, 73.78; H, 7.32; N, 1.56. Found: C, 73.41; H, 7.39; N, 1.99. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.55 (s), 1.57 (s, *Bu^t* of meso), 1.59 (s, Bu^t of threo), 2.8–3.2 (m, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$ of both isomers; see Figur 1), 5.9 m, ($\mathrm{C}\mathit{HC}\mathit{H}_2\mathrm{Ph}$). ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 31.6, 32.4 ($\mathrm{C}\mathit{Me}_3$ of meso), 32.1 ($\mathrm{C}\mathit{Me}_3$ of threo), 35.6 ($\mathit{C}\mathrm{Me}_3$ of both isomers), 45.1 ($\mathit{C}\mathrm{H_2Ph}$ of meso), 45.3 ($\mathit{C}\mathrm{H_2Ph}$ of threo), 87.0 ($\mathit{C}\mathrm{HCH_2Ph}$ of meso), 87.2 ($\mathit{C}\mathrm{HCH_2Ph}$ of threo).

$\mathbf{(Ar'O)_2Zr[OCH(CH_3)NC_5H_3CH(CH_3)O](NC_5H_5)}$ (3). Anal. Calcd for $\mathrm{ZrC_{42}H_{58}N_2O_4}$: C, 67.61; H, 7.84; N, 3.75. Found: C, 67.62; H, 8.21; N, 3.75. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 1.27 (d), 1.31 (d, α-CH*Me*O), 5.75 (q, α-C*H*MeO of both isomers), 1.35 (s), 1.36 (s, *Bu^t*). ^{13}C NMR ($\mathrm{C_6D_6}$, 30 °C): δ 31.4, 32.1 ($\mathrm{C}\mathit{Me}_3$ of meso), 31.7 ($\mathrm{C}\mathit{Me}_3$ of threo), 24.4, 24.5 (α-CH*MeO*), 81.1, 82.1 (α-*C*HMeO), 35.3 ($\mathit{C}\mathrm{Me}_3$2 of both isomers).

$\mathbf{(Ar'O)_2Hf[OCH(CH_3)NC_5H_3CH(CH_3)O](NC_5H_5)}$ (4). Anal. Calcd for $\mathrm{HfC_{42}H_{58}N_2O_4}$: C, 60.53; H, 7.01; N, 3.36. Found: C, 60.10; H, 7.18; N, 2.95. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): the ^{1}H NMR of **4** is almost identical with that of **3** except for the position of the α-$\mathrm{CHC}\mathit{H}_3\mathrm{O}$ multiplet at δ 5.84 ppm. ^{13}C NMR: δ 24.9, 25.0 ($\mathrm{CHC_6D_6}$, 30 °C): δ 24.9, 25.0 (α-CH*Me*O), 81.5, 8i.1 (α-*C*HMeO), 31.7 ($\mathrm{C}\mathit{Me}_3$ of threo), 31.4, 32.1 (C*Me*O of meso).

***threo*- and *meso*-$\boldsymbol{\alpha,\alpha'}$-Dibenzylpyridinedimethanols.** A sample of **2a** was hydrolyzed with water and introduced onto a preparative TLC plate. Elution with benzene allowed the separation of 2,6-di-*tert*-butylphenol from the product pyridinedimethanol. High-resolution mass spectrum: Calcd for $\mathrm{C_{21}NO_2H_{21}}$, 320.1651; found, 320.1648. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 3.51 (b, O*H*), 4.95 (br t, $\mathrm{C}\mathit{H}\mathrm{CH_2Ph}$ of both isomers), 2.7–3.0 (two overlapping, unresolvable ABX patterns due to both isomers), 6.9–7.7 (m, aromatics).

***threo*-$\boldsymbol{\alpha,\alpha'}$-Dibenzylpyridinedimethanol.** A sample of *threo*-**2b** was hydrolyzed and the pyridinedimethanol separated by TLC. High-resolution mass spectrum: Calcd for $\mathrm{C_{27}NO_2H_{25}}$, 396.1964; Found 396.1960. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 3.59 (br, O*H*), 5.00 (t, $\mathrm{C}\mathit{H}\mathrm{CH_2Ph}$), 3.02, 3.10 (ABX, $\mathrm{CHC}\mathit{H}_2\mathrm{Ph}$), 7.0–7.5 (m, aromatics).

Crystallographic Studies. The X-ray diffraction analyses of both **2b** and **3** were carried out in the Purdue Chemistry Department Crystallography Center. Crystal data and data collection parameters are given in Table V. In both cases suitable crystals were located and mounted in a 0.5-mm capillary surrounded by epoxy resin. During data collection three representative reflections were monitored every 5000 s of beam time. The intensity of the standards remained constant. Hence no decay correction was applied. Lorentz and Polarization corrections were applied to the data, as well as an empirical absorption correction. The structures were solved by using the Patterson heavy atom method, which revealed the position of the Zr atom. The remaining atoms were located by using DIRDIF and in succeeding difference Fourier synthesis. Hydrogen atoms were located and added to the structure factor calculations but were not refined.

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Supplementary Material Available: Tables of crystallographic data (**2b**) and positional parameters, thermal parameters, full bond distances, and bond angles (**2b** and **3**) (23 pages); listings of observed and calculated structure factors (**2b** and **3**) (46 pages). Ordering information is given on any current masthead page.

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(26) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron*, in press.