Synthetic and Mechanistic Investigation of the Rearrangement of η^2-Iminoacyl Ligands of Group 4 Metals to Vinylamido Groups via a Facile 1,2-Hydrogen Shift

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Reaction of the metallocene dichloride compounds Cp_2MCl_2 (M = Zr, Hf) with (2-(6-methylpyridyl)-methyl)lithium ($LiCH_2$-py-6Me) leads to the bis(alkyl) compounds $Cp_2M(CH_2\text{-py-6Me})_2$ (M = Zr (**1a**), Hf (**1b**)). A single-crystal X-ray diffraction analysis of **1a** shows the compound to contain one chelated and one terminal pyridylmethyl ligand in the solid state. Solution studies with ^1H and ^{13}C NMR spectroscopy indicate equivalent pyridylmethyl ligands for **1**, presumably due to rapid dissociation and recoordination of the pyridine nitrogen atoms. Treatment of compounds **1** with 2,6-dimethylphenyl isocyanide (xyNC) leads initially to the formation of the corresponding η^2-iminoacyl derivatives $Cp_2M(\eta^2\text{-xyNCCH}_2\text{-py-6Me})(CH_2\text{-py-6Me})$ (M = Zr (**2a**), Hf (**2b**)). The η^2 binding of the iminoacyl group is strongly implied by the downfield shift of the iminoacyl carbon atom in the ^{13}C NMR spectrum: δ 246.7 ppm for **2a** and δ 254.4 ppm for **2b**. The iminoacyl compounds **1** exhibit thermal instability in solution. Over a period of hours at 25–30 °C they rearrange via a 1,2-hydrogen shift to the corresponding vinylamido compounds $Cp_2M[\text{xyNCH=CH-py-6Me}](CH_2\text{-py-6Me})$ (M = Zr (**3a**), Hf (**3b**)) in almost quantitative yield. Further reaction of **3** with xyNC finally leads to the bis(vinylamido) compounds $Cp_2M[\text{xyNCH=CH-py-6Me}]_2$ (**5**) via the corresponding intermediate η^2-iminoacyl **4**. On the basis of ^1H NMR data and a single-crystal X-ray diffraction analysis of **5b**, a trans arrangement can be assigned for the hydrogen atoms attached to the vinyl group. Treatment of Cp_2HfCl_2 with 1 equiv of $LiCH_2$-py-6Me or $Cp_2Hf(CH_2\text{-py-6Me})_2$ **1b** leads to the formation of $Cp_2Hf(CH_2\text{-py-6Me})Cl$ (**6**). Again treatment of **6** with xyNC generates the intermediate η^2-iminoacyl compound $Cp_2Hf(\eta^2\text{-xyNCCH}_2\text{-py-6Me})Cl$ (**7**), which isomerizes to the corresponding vinylamido compound **8**. A kinetic study of the conversion of **2a,b** to **3a,b** and **7** to **8** shows the reactions to be first order in η^2-iminoacyl at 28 °C and the 1,2-hydrogen shifts to proceed at essentially the same rate, demonstrating little dependence on metal and ancillary ligation. The use of the deuterated reagent $LiCD_2\text{-py-6CD}_3$ allows the formation of $Cp_2Hf(\eta^2\text{-xyNCCD}_2\text{-py-6CD}_3)Cl$ **7**. The isomerization of **7** to **8** proceeds at a much slower rate than for the protio compound, yielding k_H/k_D = 11 (2) at 28 °C. The introduction of a phenyl substituent onto the α-carbon of the alkyl ligand totally inhibits the 1,2-hydrogen shift. Hence, the compound $Cp_2Hf[\text{CH(Ph)-py}]Cl$ (**9**) reacts with xyNC to yield the stable, structurally characterized η^2-iminoacyl $Cp_2Hf[\text{xyNCCH(Ph)-py}]Cl$ (**10**). These results combined with the thermal stability of the corresponding benzyl-derived η^2-iminoacyl compounds are discussed in terms of possible mechanisms for the overall 1,2-hydrogen shift. Crystal data at 22 °C for $Cp_2Zr(CH_2\text{-py-6Me})_2$ (**1a**): a = 7.679 (3) Å, b = 11.239 (3) Å, c = 12.672 (2) Å, α = 95.67 (2)°, β = 100.57 (2)° γ = 68.37 (3)°, Z = 2, d_{calcd} = 1.432 g cm^{-3} in space group $P\bar{1}$ Crystal data for $Cp_2Hf(\text{xyNCH=CH-py-6Me})_2$ (**5b**) at −155 °C: a = 14.490 (7) Å, b = 8.925 (4) Å, c = 15.943 (9) Å, β = 91.03 (3)°, Z = 2, d_{calcd} = 1.263 g cm^{-3} in space group $I2$. Crystal data for $Cp_2Hf[\eta^2\text{-xyNCCH(Ph)-py}]Cl$ (**10**) at 22 °C: a = 11.012 (1) Å, b = 14.821 (1) Å, c = 19.067 (2) Å, β = 103.263 (8)°, Z = 4, d_{calcd} = 1.613 g cm^{-3} in space group $P2_1/n$. In the solid-state structure of **10** the phenyl and pyridyl groups were disordered.

Introduction

The migratory insertion of carbon monoxide into high-valent, early-d-block, lanthanide and actinide metal–alkyl and –hydride bonds is a reaction that has been and continues to be the focus of considerable research interest.[1-3] The carbonylation of these metal alkyl and hydride compounds is found to produce a diverse range of new organic fragments that are typically retained within the metal coordination sphere in the absence of hydrolysis.[1] Despite the plethora of products available from these reactions, a crucial (sometimes elusive) intermediate is the initially formed metal–acyl or metal–formyl compound. For these electron-deficient metals a η^2 binding of the acyl or formyl group typically takes place with a strong metal–oxygen bond.[1,4] This bonding situation has received significant theoretical study, especially in regard to its impact on the reactivity of the functionality.[5] Such reactivity includes a large number of interesting carbon–carbon bond-forming reactions.[1,6] However, in certain cases the η^2-acyl group itself is found to undergo a rearrangement reaction to produce an enolate complex.[7,8] The nature of the enolate

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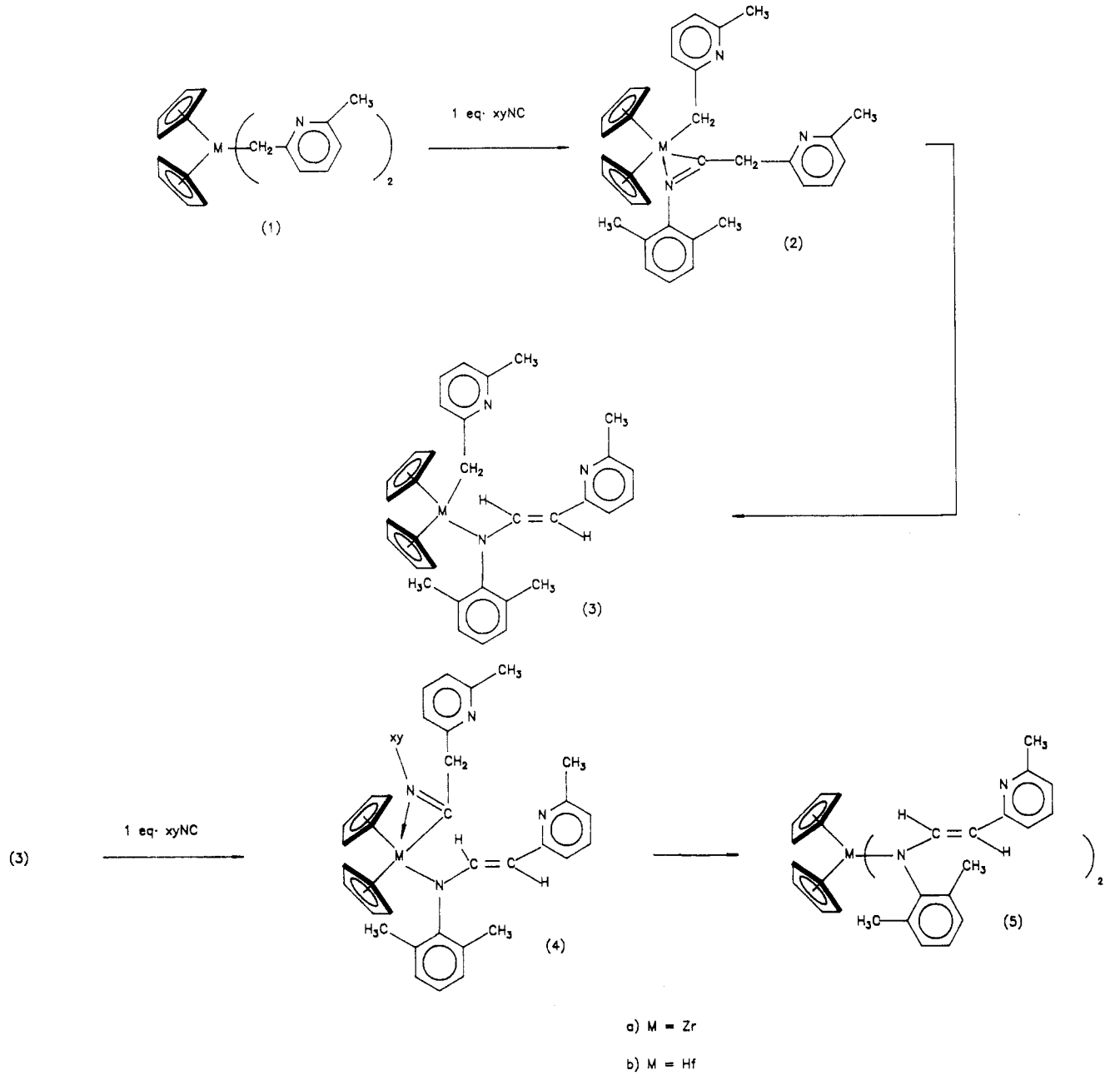
Scheme I



ligands is such that no subsequent organometallic chemistry of note can occur. During our studies of the early-d-block metal chemistry of pyridylmethyl ligands,[9] we have identified a very facile, analogous isomerization of a series of η^2-iminoacyl ligands to produce vinylamido groups. In this paper we report not only on the synthetic aspects of this rearrangement but also upon some mechanistic studies of the reactivity.

Results and Discussion

Synthesis and Spectroscopic Properties of Compounds. The reaction of the metallocene compounds Cp_2MCl_2 (M = Zr, Hf) with 2 equiv of the lithium reagent $LiCH_2$-py-6Me (CH_2-py-6Me = 2-(6-methylpyridyl)methyl) in hydrocarbon solvents leads to the formation of the corresponding pyridylmethyl compounds **1a** and **1b** (Scheme I). The compounds 1 constitute new examples of a rapidly growing class of compounds containing 2-pyridylmethyl and related ligands.[10-12] Ligation of this type has previously been shown to adopt a variety of

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bonding modes with metals of the s, p, and d blocks.[10-12] In a series of important studies Raston and co-workers have synthesized and characterized an extensive series of metal derivatives of α-silylated pyridylmethyl ligands. Typical coordination modes identified are (i) terminal, i.e. only C-bound, (ii) C,N-chelating, and (iii) binucleating, in which the ligand spans two metal centers. Of direct relevance to this work is the reported structure of $Cp_2ZrCl[CH(SiMe_3)\text{-}py]$.[10a] Here the complex was found to achieve an 18-electron configuration for the metal center in the solid state by C,N-chelation of the pyridylmethyl ligand. In the case of compounds **1**, chelation of both ligands seems highly unlikely, given the 20-electron nature of the resulting metal complex. The ^1H and ^{13}C NMR spectra of the bis(alkyl) compounds **1a** and **1b** show only one set of pyridylmethyl group resonances even at −75 °C in toluene-d_8 solution. This result, however, does not prove that both ligands are equivalent in solution and are only carbon-bound. Instead, it is possible that exchange of nonequivalent pyridylmethyl ligands is taking place in solution by rapid dissociation/coordination of pyridyl nitrogen atoms. The bis(pyridylmethyl) compounds $(Ar'O)_2M(CH_2\text{-}py\text{-}6Me)_2$ (M = Hf, Th) were shown in the solid state to be isomorphous and isostructural, containing both alkyl ligands C,N-chelated to the six-coordinate metal center.[9] However, in solution the expected diastereotopic CH_2-py-6Me protons were found to resonate as a sharp singlet even at low temperatures. Strong evidence for the chelation of the pyridylmethyl ligands remaining in solution was obtained from the $^1J(^{13}C\text{–}^1H)$ coupling constants for the CH_2-py-6Me methylene group. The value of the coupling constants of methylene groups has been shown to be extremely sensitive to the size of the ring in which the group is contained, e.g. ranging from 123 Hz for cyclohexane to 161 Hz for cyclopropane.[13] In the case of the aryloxide compounds $M(OAr')_2(CH_2\text{-}py\text{-}6Me)_2$ coupling constants of 146 Hz (M = Hf) and 139 Hz (M = Th) were measured in solution, inconsistent with an unstrained, i.e. nonchelated, methylene group. Instead the values compare well with the coupling constant of 134 Hz reported for cyclobutane, where the C–CH_2–C angle of 90° is very close to the M–CH_2–py angles of 91.9 (3)° (M = Hf) and 91.6 (8)° (M = Th) observed in the solid state.[9,13] A correlation between the M–CH_2–Ph angles observed in the solid state and the $^1J(^{13}C\text{–}^1H)$ methylene group coupling constants measured in solution has been demonstrated for metal benzyl complexes.[14]

In the case of the pyridylmethyl compounds **1** obtained in this study, the corresponding coupling constants measured from the ^{13}C NMR spectra are 134 Hz for **1a** and 121 Hz for **1b**. In the case of the zirconium compound **1a** structural studies show one terminal and one C,N-chelated pyridylmethyl ligand to be present in the solid state (vide infra). The higher coupling constant obtained for this compound strongly indicates that in solution one of the pyridyl nitrogen atoms remains bound to the metal center, although rapid exchange of C,N-chelated and terminal alkyl groups must also be occurring. In the case of the hafnium complex the coupling constant of 121 Hz is identical with that observed for purely C-bound pyridylmethyl ligands. Hence, on the basis of this criteria it would appear that C,N-chelation of the ligands does not occur to any appreciable extent for the hafnium complex **1b** in solution. Whether this can be attributed to the very slightly smaller covalent radius of Hf(IV) compared to that Zr(IV) is unclear.

In common with other metallocene dialkyls of the type Cp_2MR_2 (M = Ti, Zr, Hf), compounds **1** will react with 1 equiv of the aryl isocyanide reagent xyNC (xy = 2,6-dimethylphenyl) rapidly in hydrocarbon solution to produce the corresponding η^2-iminoacyl compounds **2a** and **2b** (Scheme I). In the ^1H NMR spectra of **2** the presence of two CH_2-py methylene groups is clearly observed, the one attached to the iminoacyl group resonating downfield of the noninserted M–CH_2-py-6Me ligand. In the ^{13}C NMR spectrum the presence of the η^2-iminoacyl group is confirmed by the characteristic downfield resonance for the iminoacyl carbon atom at δ 246.7 (**2a**) and δ 254.4 (**2b**).[15]

Unlike previously reported η^2-iminoacyl compounds of the type $Cp_2M(\eta^2\text{-}R'NCR)(R)$,[1,16,17] both **2a** and **2b** exhibit thermal instability in solution. Over a period of hours at room temperature changes in the ^1H NMR spectra of **2** show its clean conversion into the new compound **3**. After the formation of **3** is complete (several hours, 28 °C), no further changes in the spectra take place. The ^1H and ^{13}C NMR spectra of **3** indicate a structure containing a trans vinylamido group formed by rearrangement of the initial η^2-iminoacyl ligand via an overall 1,2-hydrogen shift (Scheme I). In the ^1H NMR spectra of **3a** and **3b** a highly characteristic AX pattern is observed due to the new vinylic protons with a $^3J(^1H\text{–}^1H)$ coupling constant of 12–13 Hz consistent with a mutually trans arrangement. The downfield-shifted C*H* proton at δ 8.76 ppm (**3a**) and δ 8.63 ppm (**3b**) can be assigned to the vinylic proton adjacent to the amido nitrogen atom, while the other vinylic proton adjacent to the pyridyl group resonates more upfield at δ 4.78 ppm (**3a**) and δ 4.77 ppm (**3b**). In the ^{13}C NMR spectra of **3a** and **3b** the new vinylic carbon atoms are readily identified, while there is a complete absence of any η^2-iminoacyl carbon resonance. Besides the resonances due to the new vinylamido ligand, the remaining M–CH_2-py-6Me ligand is also present. In the ^{13}C NMR spectrum the $^1J(^{13}C\text{–}^1H)$ coupling constant for the methylene group of **3a** and **3b** is found to be 123 and 121 Hz, respectively, consistent with this group being only carbon-bound to the metal center.

Further reaction between the vinylamido compounds **3** and 1 equiv more of xyNC takes place much more slowly in solution over a period of hours at 25 °C to produce the corresponding bis(vinylamido) compounds **5a** and **5b** (Scheme I). This reaction presumably proceeds via the intermediate η^2-iminoacyl compound **4**, although it was not spectroscopically (^1H NMR) detected. The ^1H and ^{13}C NMR spectroscopic properties of **5a** and **5b** show the presence of two equivalent vinylamido ligands with trans-vicinal hydrogen atoms. In the ^{13}C NMR spectrum the $^1J(^{13}C\text{–}^1H)$ coupling constant for the trans *CH*=*CH* groups lies within the expected 150–170-Hz region. The trans arrangement of the substituents about the vinyl linkage was confirmed by a single-crystal X-ray diffraction study of **5b** (vide infra).

When the dichloride Cp_2HfCl_2 was treated with only 1 equiv of $LiCH_2$-py-6Me the mono(alkyl) compound $Cp_2Hf(CH_2\text{-}py\text{-}6Me)Cl$ (**6**) was obtained. Compound **6**

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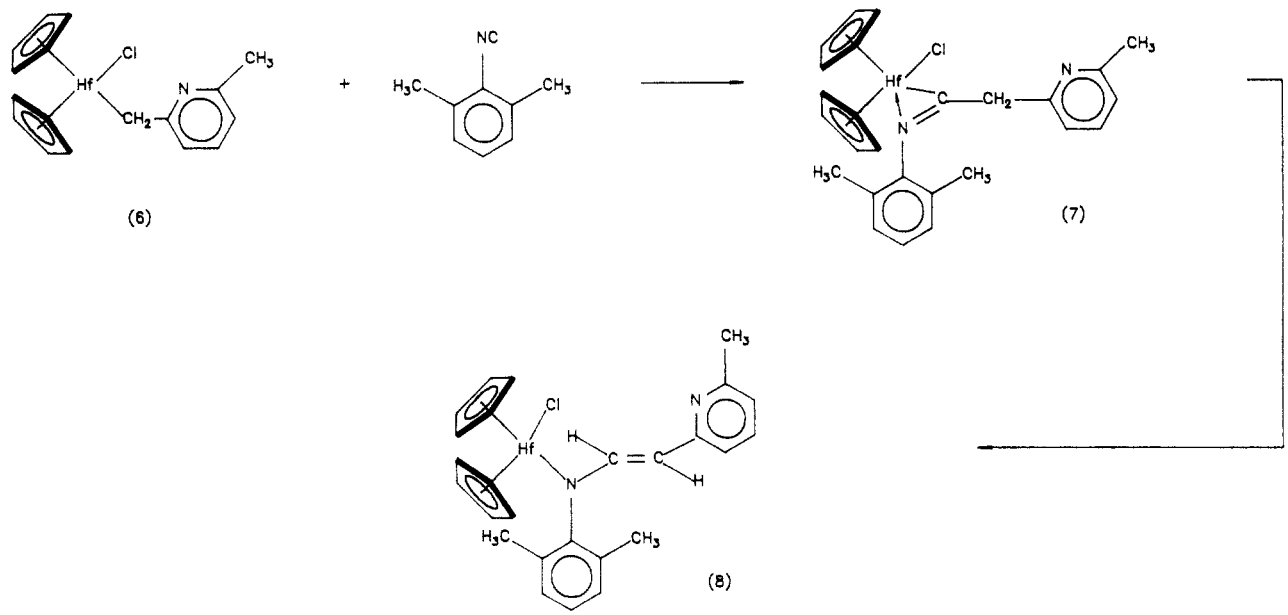
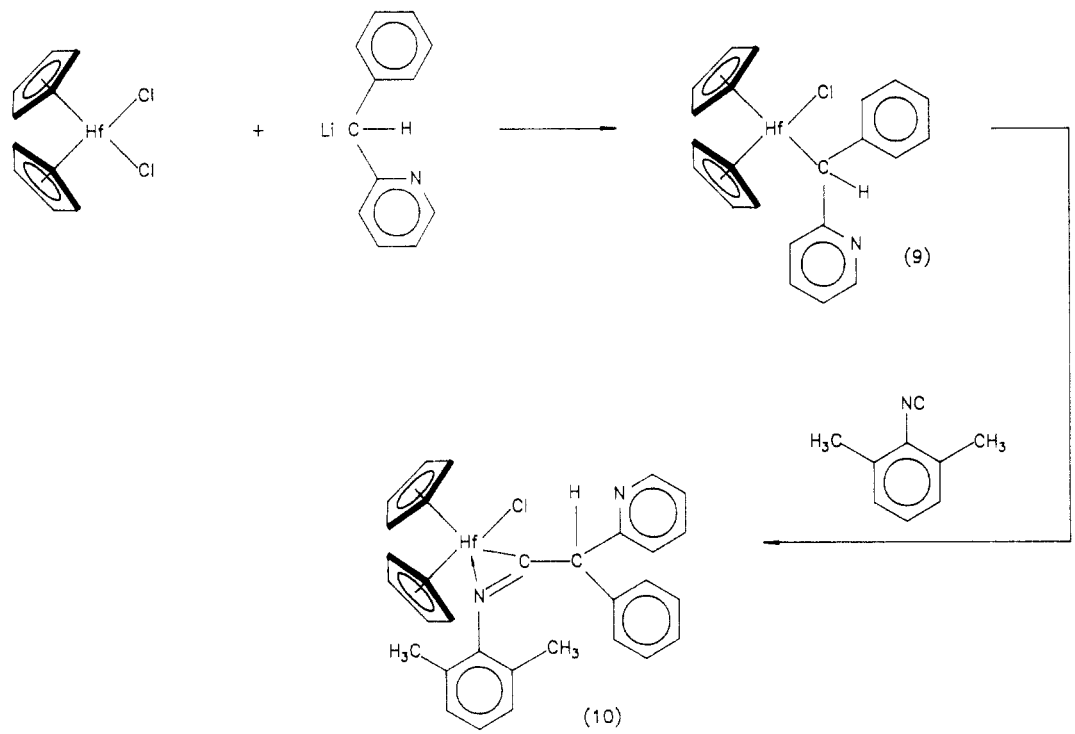
Scheme II



Scheme III



could also be isolated in high yield by heating equimolar amounts of Cp_2HfCl_2 and $Cp_2Hf(CH_2\text{-py-6Me})_2$ **1b** in toluene at 100 °C for a few minutes. Ligand redistribution reactions of this type have been well documented.[18] In the ^{13}C NMR spectrum of **6** the $^1J(^{13}C-^1H)$ coupling constant was found to be only 121 Hz. Hence, it appears that even with a chloride ancillary ligand the pyridylmethyl group does not C,N-chelate in solution to the Cp_2Hf unit. Reaction of **6** with 1 equiv of xyNC takes place rapidly in solution to produce the corresponding η^2-iminoacyl compound **7**: δ 253.5 ppm for the NC carbon atom. However, as with the previous η^2-iminoacyl compounds formation of the new vinylamido compound **8** takes place as solutions of **7** are left at room temperature (Scheme II).

In an attempt to inhibit the isomerization reaction, the alkyl compound $Cp_2Hf[CH(Ph)\text{-py}]Cl$ **9** was synthesized from Cp_2HfCl_2 and 1 equiv of LiCH(Ph)-py (Scheme III). Compound **9** was itself found to exhibit thermal instability over periods of days in solution, generating 2-benzylpyridine and unidentified hafnium products. In the room-temperature ^1H NMR spectrum of freshly prepared **9**, only one Cp resonance was resolvable despite the presence of the chiral Hf–CH(Ph)-py center. However, when toluene-d_8 solutions of **9** were cooled, the Cp resonance was found to broaden and separate into two equal-intensity singlets. Similar changes in the ^1H NMR spectrum of the related compound $Cp_2Zr[CH(SiMe_3)\text{-py}]Cl$ was noted by Raston and co-workers. A possible explanation of this observation is the presence of rapid ligand exchange taking place in solution between hafnium metal centers. The reaction of freshly prepared **9** with 1 equiv

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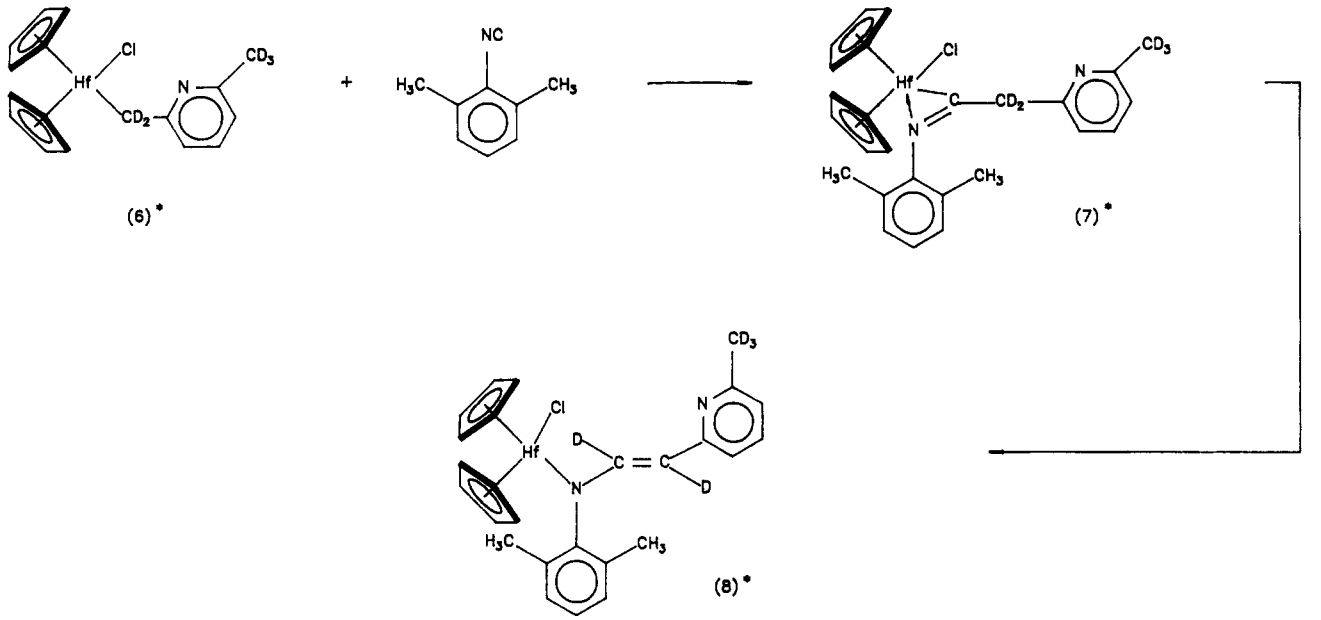
Scheme IV



of xyNC takes place smoothly in hydrocarbon solvent to generate the η^2-iminoacyl complex **10** (Scheme III). In the case of **10** two nonequivalent Cp resonances are clearly resolved, δ 5.71 and 5.89 ppm, in the room-temperature ^{1}H NMR spectrum, while the characteristic η^2-iminoacyl carbon resonance is also observed at δ 252.5 ppm in the ^{13}C NMR spectrum. It is also interesting to note that two equal-intensity, nonequivalent CH_3 resonances for the *2,6-dimethyl*phenyl–N group are also observed, implying hindered rotation about the aryl–N bond. In contrast the case for the η^2-iminoacyl intermediates **2** and **7**, the presence of the extra phenyl substituent in **10** totally inhibits the 1,2-hydrogen shift so that single crystals of stable **10** could be isolated for a structure determination to be performed.

Mechanistic Studies. The facile, room-temperature isomerization of the η^2-iminoacyl compounds **2a**, **2b**, and **7** to produce the corresponding vinylamido compounds contrasts with the thermal stability of the corresponding benzyl compounds $Cp_2M(\eta^2\text{-xyNCCH}_2\text{Ph})(CH_2Ph)$ (M = Zr, Hf). These compounds show no change in toluene-d_8 solution after months at 100 °C. After 15 days at 120 °C some minor decomposition of the zirconium complex was observed to produce a variety of unidentified products.

A kinetic study of the conversion of the η^2-iminoacyl compounds **2a**, **2b**, and **7** to the vinylamido derivatives **3a**, **3b**, and **8** was undertaken. At 28 °C in toluene-d_8 all three rearrangement reactions were found to obey first-order kinetics for the disappearance of the η^2-iminoacyl compounds as monitored by ^{1}H NMR spectroscopy. All three compounds rearrange at comparable rates. Hence, it appears that the reaction is not very sensitive to the change in metal center on going from Zr to Hf (Figure 1) or to the change of the adjacent ligand from Cl to CH_2-py-6Me.

In order to try and measure the magnitude of any kinetic isotope effect that might be present for the isomerization reaction, the compound $Cp_2Hf(CD_2\text{-py-}6CD_3)Cl$ (**6**-d_5) was synthesized. Treatment of **6**-d_5 with xyNC led to the formation of the η^2-iminoacyl compound **7**-d_5 (Scheme IV). The rearrangement of **7**-d_5 to **8**-d_5 via an overall 1,2-deuterium shift was found to be considerably slower at 28 °C than for the corresponding protio compound. Hence, there is a sizable kinetic isotope effect of k_H/k_D = 11 (2) for the reaction at this temperature. A kinetic isotope effect of k_H/k_D = 5.9 (5) was reported by Marks and Moloy for the first-order isomerization of $Cp^*_2Th(\eta^2\text{-COCD}_2\text{Bu}^t)Cl$ at 115 °C.

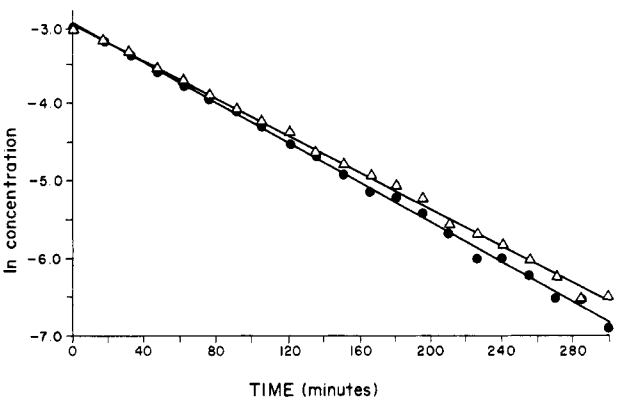
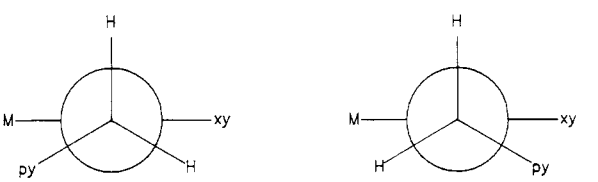


Figure 1. First-order plot for the disappearance of $Cp_2M(\eta^2\text{-xyNCCH}_2\text{-py-6Me})(CH_2\text{-py-6Me})$ (M = Zr (●), Hf (△)) at 28 °C in toluene-d_8 solution.

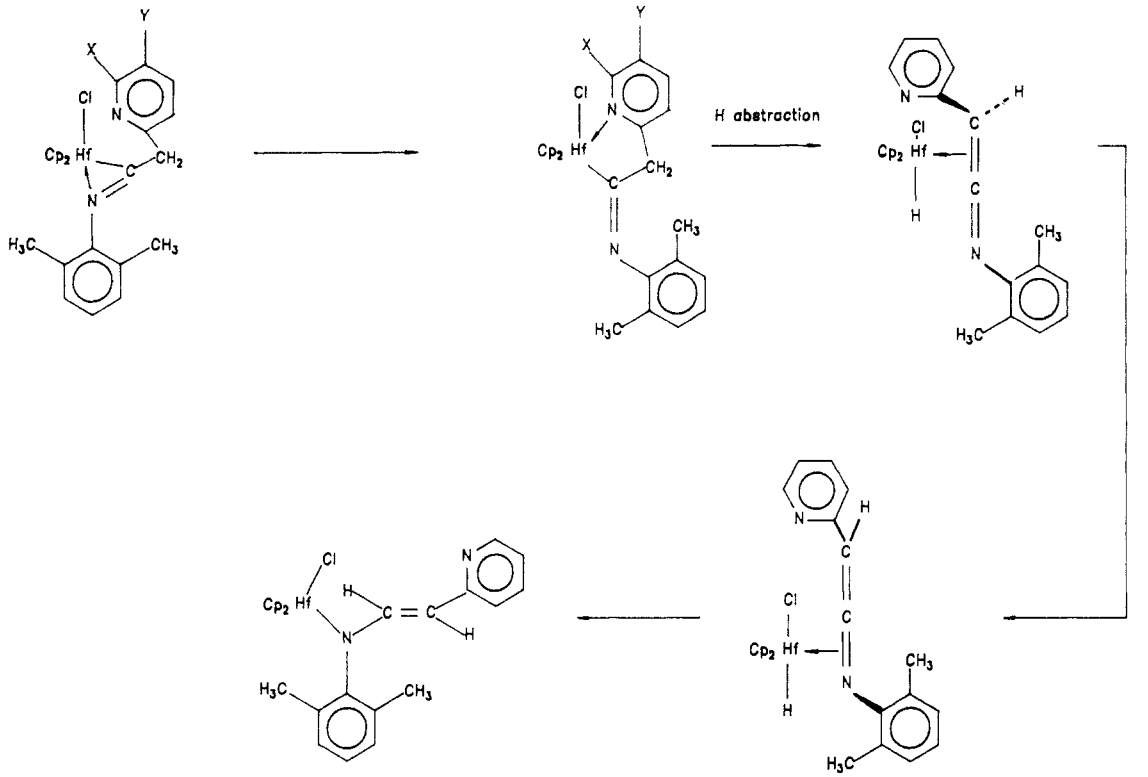
Chart I



The intramolecular rearrangement of high-valent, electron-deficient metal η^2-acyl ligands to produce enolate groups has been argued to be support for a bonding picture involving oxycarbenoid character.[5,7,8] The 1,2-hydrogen and 1,2-silyl migration reactions to the acyl carbon atom are certainly carbene-like reactivity.[19] In the case of η^2-iminoacyl groups an amidocarbene resonance picture can be similarly invoked.[15] The 1,2-hydrogen shift to the carbene-like carbon center then leads to the vinylamido group. The exclusive trans configuration that is observed for the products can then be rationalized as a consequence of steric pressure between the nitrogen 2,6-dimethylphenyl substituent and the pyridyl substituent (Chart I). The

(19) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971.

Scheme V



introduction of a phenyl group onto the pyridylmethyl carbon as in compound **10** presumably restricts the hydrogen atom from obtaining a suitable configuration for migration. Indeed, the solid-state structure of **10** (vide infra) shows the pyridyl and phenyl substituents to be oriented so that the CH bond is in a position totally precluding a 1,2-hydrogen shift.

A major question that arises from this work is how one rationalizes the accelerated rearrangement observed for the η^2-iminoacyl groups containing the pyridylmethyl substituent compared to that for their benzyl counterpart. The replacement of a phenyl ring by the pyridyl ring results in a reaction occurring in hours at 25 °C compared to months at 120 °C. One possibility is that the pyridyl group greatly increases the tendency of the methylene hydrogen atoms to migrate to the iminoacyl carbon. It is well-known that CH bonds adjacent to a 2- or 4-pyridyl group are much more acidic than benzylic protons due to the electron-withdrawing properties of the pyridyl nitrogen.[20] This accounts for the ready deprotonation of 2,6-dimethylpyridine by $LiBu^n$ to produce $LiCH_2$-py-6Me. However, a different explanation for the dramatic differences in reactivity may be that the pyridyl group does not accelerate an existing pathway but instead introduces an alternative pathway of lower energy. In particular, it is interesting to note the possibiliy that coordination of the pyridyl nitrogen to the metal center would result in formation of a five-membered metallacycle in which the iminoacyl group is now only carbon-bound. Abstraction of a β-hydrogen from this ring by the metal produces a metal hydride ketenimine complex.[1c,21] Insertion of the metal–hydride function across the C–N bond would lead to the vinylamido group (Scheme V). Of course, β-hydrogen abstraction could take place directly from the methylene group of the η^2-iminoacyl ligand. However, the η^2-binding of these ligands has the effect of bending the alkyl group attached to the iminoacyl carbon atom away from the metal;[1] cf. the Hf–C–CH(py)(Ph) angle of 163° in the η^2-iminoacyl compound **10** (vide infra). Hence, a β-hydrogen abstraction process would be highly unlikely for an η^2-iminoacyl group in which the nitrogen atom remains tightly bound to the metal center.

In order to investigate this reactivity further, attempts were made to obtain the pyridylmethyl compounds $Cp_2Hf(CH_2$-py)Cl (**11**) and $Cp_2Hf(CH_2$-py-5Me)Cl (**12**) containing a simple unsubstituted pyridyl group (CH_2-py) and a 5-methylpyridyl group (CH_2-py-5Me), respectively. These changes from the 6-methylpyridyl compounds so far studied should not result in a dramatic change in the nature of the methylene group protons. However, the removal of the 6-methyl substituent should increase the coordinating ability of the pyridyl nitrogen.[22] Unfortunately, although reaction of Cp_2HfCl_2 with $LiCH_2$-py and $LiCH_2$-py-5Me resulted in the formation of **11** and **12**, respectively, the compounds were found to undergo decomposition over periods of hours at room temperature so that pure samples of **11** and **12** were not isolable. However, treatment of solutions containing **11** and **12** with xyNC was found not to lead to solutions of the corresponding η^2-iminoacyl compound but instead to the rapid formation of the isomerized vinylamido derivatives. The vinylamido compounds were readily characterizable in solution by ^1H and ^{13}C NMR spectroscopy but were not obtained pure from the contaminants in solution. On the basis of these rather unsatisfactory experiments it appears that isomerization of the η^2-iminoacyl occurs very rapidly when the pyridylmethyl nitrogen atom is not blocked by the presence of a methyl group in the 6-position. This would imply that coordination of the pyridine nitrogen does indeed play

(20) *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Cofey, S., Ed.; Elsevier: New York, 1976; Vol. IV, Part F (Heterocyclic Compounds).
(21) (a) Bassett, J. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1779. (b) Yarrow, D. J.; Ibers, J. A.; Tatsumo, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *95*, 8590. (c) Otsuka, S.; Nakamura, A.; Yoshidra, T. *J. Organomet. Chem.* **1967**, *7*, 339.

(22) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans* **1978**, 1490.

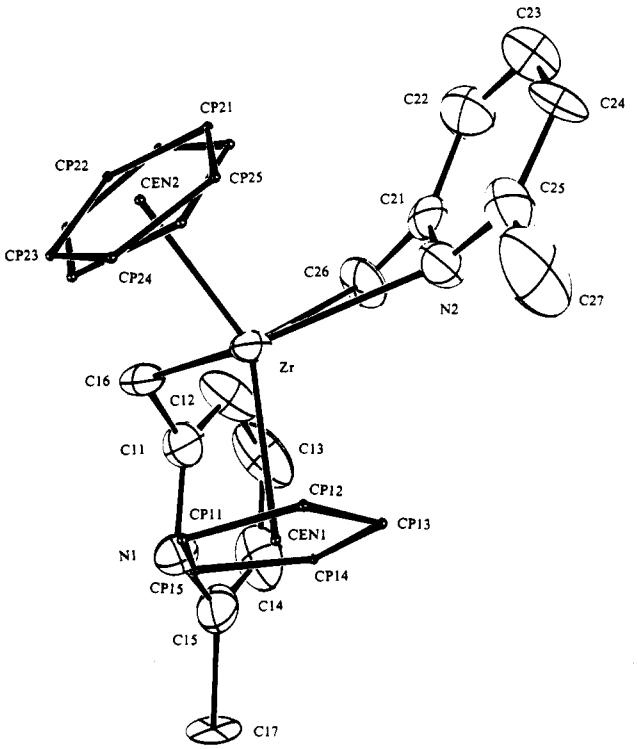


Figure 2. ORTEP view of $Cp_2Zr(CH_2\text{-py-}6Me)_2$ (**1a**).

an important role in allowing the isomerization to take place. The significant amounts of impurities within these solutions, however, may mean that the rate of the isomerization process is being perturbed by other reactions taking place.

We have also evaluated the effect of added pyridine upon the stability of the benzyl-derived η^2-iminoacyl complex $Cp_2Hf(\eta^2\text{-xyNCCH}_2\text{Ph})Cl$. Monitoring toluene-$d_8$ solutions of this compound both on its own as well as in the presence of 2–5 equiv of pyridine showed very little difference in stability. The compound was found to be unstable, however, when heated in solution in neat pyridine-d_5. The ^1H NMR spectrum after several days at 120 °C showed downfield doublets in the region consistent with the presence of vinylamido groups. The reactions were by no means clean. In the context of these studies it is of great interest to note the recently reported work of Tilley et al.[23] The η^2-acyl complex $Cp^*TaCl_3(\eta^2\text{-COCH}_2CMe_3)$ was shown to be stable in solution for days at room temperature. However, the addition of pyridine at −65 °C was found to lead to an intermediate pyridine adduct that isomerizes at −10 °C to the cis enolate $Cp^*TaCl_3(py)(OCH{=}CHCMe_3)$. The more facile isomerization observed by Tilley and co-workers in this case may be supportive of the idea that an $\eta^2 \rightarrow \eta^1$ rearrangement induced by an incoming ligand might precede a facile isomerization process in which β-hydrogen abstraction is a key step.

Structural Studies. In order to gain more insight into the structures of the compounds involved in this work, single-crystal X-ray diffraction analyses of the simple alkyl $Cp_2Zr(CH_2\text{-py-}6Me)_2$ (**1a**), the η^2-iminoacyl $Cp_2Hf[\eta^2\text{-xyNCCH(Ph)-py}]Cl$ (**10**), and the vinylamido compound $Cp_2Hf[xyNCH{=}CH\text{-py-}6Me]_2$ (**5b**) were performed.

$Cp_2Zr(CH_2\text{-py-}6Me)_2$ (1a). An ORTEP view of the molecular structure of **1a** is shown in Figure 2. Fractional coordinates are collected in Table I, while some selected bond distances and angles are given in Table II. The

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $Cp_2Zr(CH_2\text{-py-}6Me)_2$ (1a)

atom	*x*	*y*	*z*	*B*, Å^{2a}
Zr	0.06807 (5)	0.38584 (4)	0.25070 (3)	2.237 (6)
N(1)	0.2629 (6)	0.7521 (4)	0.4009 (3)	3.30 (8)
N(2)	0.0113 (5)	0.3197 (4)	0.0573 (3)	2.96 (7)
C(11)	0.3692 (6)	0.6848 (4)	0.3699 (4)	3.09 (9)
C(12)	0.5250 (7)	0.7446 (5)	0.3273 (5)	4.1 (1)
C(13)	0.5650 (9)	0.8700 (6)	0.3153 (5)	5.1 (1)
C(14)	0.452 (1)	0.9349 (5)	0.3421 (5)	4.7 (1)
C(15)	0.3008 (8)	0.8731 (5)	0.3846 (4)	3.7 (1)
C(16)	0.3182 (6)	0.5504 (4)	0.3823 (4)	2.99 (8)
C(17)	0.1692 (9)	0.9372 (5)	0.4127 (5)	4.9 (1)
C(21)	0.1986 (6)	0.3782 (4)	0.0620 (3)	3.04 (8)
C(22)	0.2921 (7)	0.3214 (5)	−0.0022 (4)	4.0 (1)
C(23)	0.1906 (8)	0.2144 (6)	−0.0757 (5)	4.5 (1)
C(24)	−0.0049 (9)	0.1615 (5)	−0.0865 (5)	4.5 (1)
C(25)	−0.0881 (7)	0.2153 (5)	−0.0181 (4)	3.8 (1)
C(26)	0.2809 (6)	0.4884 (5)	0.1434 (4)	3.33 (9)
C(27)	−0.2955 (9)	0.1585 (7)	−0.0244 (6)	5.4 (2)
C(P11)	−0.2088 (6)	0.3919 (5)	0.3321 (4)	3.8 (1)
C(P12)	−0.2798 (6)	0.3461 (5)	0.2195 (4)	3.8 (1)
C(P13)	−0.2109 (6)	0.4474 (5)	0.1641 (5)	4.1 (1)
C(P14)	−0.0920 (7)	0.5523 (5)	0.2407 (5)	3.9 (1)
C(P15)	−0.0922 (6)	0.5178 (5)	0.3449 (4)	3.64 (9)
C(P21)	0.207 (1)	0.2033 (8)	0.2385 (7)	2.8 (1)*
C(P22)	0.289 (1)	0.2763 (8)	0.3472 (7)	2.7 (1)*
C(P23)	0.145 (1)	0.2634 (8)	0.4021 (7)	2.6 (1)*
C(P24)	−0.025 (1)	0.1822 (7)	0.3325 (7)	2.4 (1)*
C(P25)	0.014 (1)	0.1492 (8)	0.2307 (7)	2.7 (1)*
C(P21A)	0.271 (1)	0.2491 (9)	0.2924 (8)	3.5 (2)*
C(P22A)	0.218 (1)	0.280 (1)	0.3896 (9)	3.9 (2)*
C(P23A)	0.031 (2)	0.224 (1)	0.376 (1)	4.3 (2)*
C(P24A)	−0.041 (1)	0.156 (1)	0.2658 (9)	4.0 (2)*
C(P25A)	0.108 (1)	0.172 (1)	0.217 (1)	4.1 (2)*

[a] Values marked with an asterisk are for anisotropically refined atoms, given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Zr(CH_2\text{-py-}6Me)_2$ (1a)

Zr–N(2)	2.407 (4)	Zr–C(16)	2.422 (4)
Zr–C(26)	2.406 (5)		
N(2)–Zr–C(16)	133.7 (1)	N(2)–Zr–C(26)	57.5 (1)
C(16)–Zr–C(26)	76.2 (2)	Zr–N(2)–C(21)	89.7 (2)
Zr–N(2)–C(25)	138.5 (3)	Zr–C(10)–C(11)	121.5 (3)
Zr–C(26)–C(21)	88.5 (3)		

molecule can be seen to contain a routine metallocene unit with a Cp–Zr–Cp angle of 128.1 (3)°. One of the cyclopentadiene ligands is disordered in **1a**, with two possible orientations differing by a rotation of 36°. It can be seen that one of the pyridylmethyl ligands adopts a nonchelating bonding mode with a $Zr–CH_2–py$ angle of 121.5 (3)°, resulting in the pyridyl nitrogen being well removed from the metal center. The other pyridylmethyl ligand is C,N-bound to the metal, resulting in a formal 18-electron configuration for the zirconium metal center. The formation of the four-membered ring results in an acute $Zr–CH_2–py$ angle of 88.5 (3)° for this group. The $Zr–CH_2$ distances between the two alkyl ligands are comparable, 2.407 (6) and 2.422 (4) Å, with the chelated pyridylmethyl group having a slightly longer distance than for the terminal group. However, both of these Zr–C distances are longer than typical ones for zirconium(IV) alkyl compounds. Compare values of 2.279 (4), 2.288 (10), and 2.388 (12) Å for the bis(alkyls) $Cp_2Zr(R)_2$ (R = CH_2SiMe_3, CH_2CMe_3, and $CHPh_2$, respectively).[24] The distances are not quite as long, however, as the 2.431 (5) Å $Zr–CH_3$

(23) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149 and references therein.

(24) Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081.

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $Cp_2Hf[\eta^2$-xyNCCH(Ph)-py]Cl (10)

atom	x	y	z	B, Å^{2a}
Hf	0.25790 (2)	0.02816 (2)	0.24270 (1)	3.365 (5)
Cl	0.2753 (2)	−0.1272 (1)	0.2981 (1)	6.00 (5)
N(20)	0.3311 (4)	−0.0422 (3)	0.1594 (2)	3.2 (1)
C(10)	0.3255 (5)	0.0408 (4)	0.1422 (3)	2.8 (1)
C(11)	0.3719 (6)	0.0780 (4)	0.0782 (3)	3.5 (1)
C(21)	0.3705 (6)	−0.1192 (4)	0.1242 (3)	3.9 (1)
C(22)	0.4828 (6)	−0.1608 (5)	0.1566 (4)	5.1 (2)
C(23)	0.5174 (8)	−0.2373 (6)	0.1232 (5)	7.3 (2)
C(24)	0.4447 (9)	−0.2706 (5)	0.0606 (5)	7.9 (2)
C(25)	0.3345 (9)	−0.2291 (5)	0.0301 (4)	7.1 (2)
C(26)	0.2923 (7)	−0.1523 (5)	0.0602 (4)	4.8 (2)
C(27)	0.5642 (7)	−0.1254 (6)	0.2250 (5)	6.7 (2)
C(28)	0.1694 (8)	−0.1074 (6)	0.0252 (4)	6.3 (2)
C(P11)	0.0653 (6)	0.0650 (6)	0.1490 (4)	5.4 (2)
C(P12)	0.0444 (6)	−0.0196 (6)	0.1748 (4)	5.6 (2)
C(P13)	0.0353 (7)	−0.0120 (6)	0.2457 (4)	6.0 (2)
C(P14)	0.0538 (7)	0.0778 (6)	0.2658 (4)	5.9 (2)
C(P15)	0.0721 (6)	0.1259 (5)	0.2057 (5)	5.9 (2)
C(P21)	0.4723 (6)	0.0945 (5)	0.2917 (4)	4.8 (2)
C(P22)	0.4464 (8)	0.0418 (5)	0.3458 (4)	6.1 (2)
C(P23)	0.3442 (8)	0.0799 (6)	0.3681 (4)	6.1 (2)
C(P24)	0.3136 (7)	0.1585 (6)	0.3284 (4)	5.7 (2)
C(P25)	0.3883 (7)	0.1661 (5)	0.2804 (4)	4.8 (2)
C(1111)	0.2804 (5)	0.1433 (4)	0.0330 (3)	3.6 (1)
C(1112)	0.2558 (6)	0.1347 (5)	−0.0402 (3)	4.3 (2)
C(1113)	0.1761 (8)	0.1921 (6)	−0.0826 (4)	6.6 (2)
C(1114)	0.1166 (8)	0.2589 (6)	−0.0542 (5)	6.5 (2)
C(1115)	0.1392 (8)	0.2680 (5)	0.0191 (5)	6.1 (2)
C(1116)	0.2226 (6)	0.2104 (5)	0.0628 (4)	4.4 (2)
C(1121)	0.5011 (6)	0.1178 (5)	0.1091 (3)	3.8 (1)
C(1122)	0.5988 (6)	0.0619 (5)	0.1169 (4)	4.4 (2)
C(1123)	0.7157 (6)	0.0931 (6)	0.1476 (5)	6.3 (2)
C(1124)	0.7353 (7)	0.1786 (7)	0.1711 (5)	6.4 (2)
C(1125)	0.6379 (7)	0.2363 (6)	0.1628 (5)	6.3 (2)
C(1126)	0.5201 (6)	0.2066 (5)	0.1310 (4)	4.8 (2)
C(5001)	0.467 (1)	0.4661 (8)	0.0498 (6)	9.1 (3)*
C(5002)	0.653 (2)	0.527 (1)	0.025 (1)	14.8 (5)*
C(5003)	0.589 (2)	0.488 (1)	0.071 (1)	14.3 (5)*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

distance found in the η^2-iminoacyl complex $Cp_2Zr(\eta^2$-MeNCCHPh$_2$)(CH$_3$) reported by Lappert et al.[17] The distance to the bound pyridyl nitrogen, Zr–N = 2.407 (4) Å, is very close to the 2.403 (1) Å distance reported for the simple pyridine ligand in $Cp_2Zr(\eta^2$-H$_2$C=CO)(py).[25] Hence, the formation of the four-membered ring in **1a** does not lead to any significant lengthening of the Zr–N(pyridyl) bond. In the hafnium complex (Ar'O)$_2$Hf(CH$_2$-py-6Me)$_2$ (Ar'O = 2,6-di-*tert*-butylphenoxide) both the Hf–C and Hf–N distances of 2.307 (5) and 2.374 (4) Å are shorter than those found in **1a**.[9]

An interesting feature of the chelated pyridylmethyl group in **1a** concerns the fact that the metal center is not contained within the plane of the pyridine ring; i.e., the pyridine rings' formal lone pairs of electrons do not point directly at the metal center. A number of previous studies of the bonding of pyridine, quinoline, and related heterocyclic ligands to metal centers have shown that distortions of the metal–nitrogen bonds similar to this can readily take place, especially in order to relieve steric congestion.[22,26,27] Previous work by Raston et al. on related pyridylmethyl ligation has shown similar distortions, and a bonding

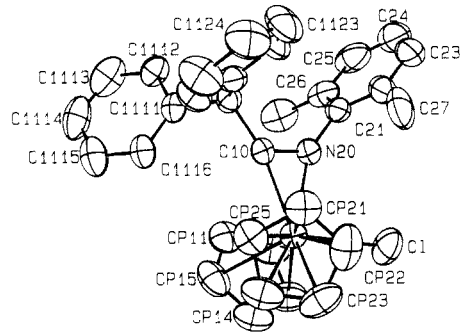


Figure 3. ORTEP view of $Cp_2Hf[\eta^2$-xyNCCH(Ph)-py]Cl (**10**).

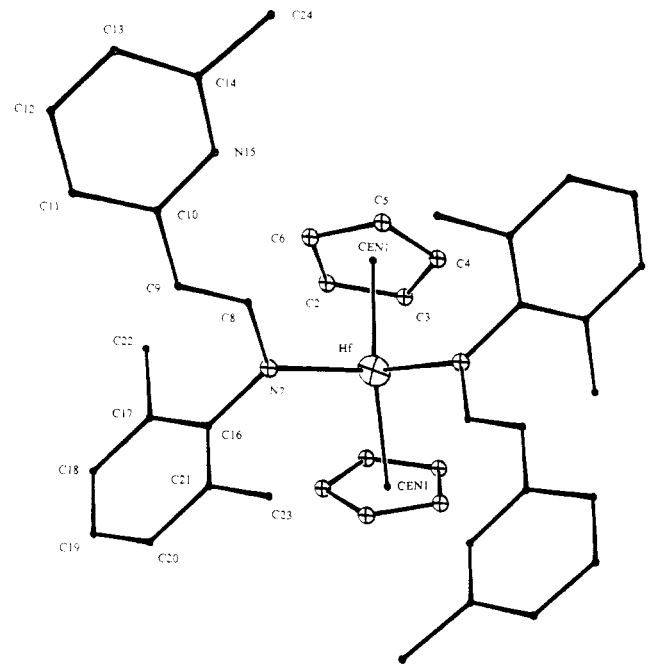


Figure 4. ORTEP view of $Cp_2Hf[$xyNCH=CH-py-6Me$)_2$ (**5b**).

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Hf[\eta^2$-xyNCCH(Ph)-py]Cl (10)

Hf–Cl	2.523 (2)	Hf–N(20)	2.202 (4)
Hf–C(10)	2.218 (5)	C(10)–N(20)	1.27 (7)
Cl–Hf–N(20)	82.2 (1)	Cl–Hf–C(10)	115.5 (1)
C(10)–Hf–N(20)	33.4 (2)		

picture describing the ligand as an azaallyl moiety has been used to account for it.[10]

$Cp_2Hf[\eta^2$-xyNCCH(Ph)-py]Cl (10). An ORTEP view of the molecular structure of **10** is shown in Figure 3. The fractional coordinates are given in Table III, while Table IV contains some selected bond distances and angle. Compound **10** represents another example of an 18-electron group 4 metallocene derivative of the type $Cp_2M(\eta^2$-RCX)(Y) (X = O, NR').[1] Previous mechanistic, structural, and theoretical studies of η^2-acyl and η^2-iminoacyl compounds of this type have demonstrated two overall structural types to exist.[1,5] The carbon atoms and heteroatoms of the acyl or iminoacyl group are oriented within the equatorial girdle of the metallocene unit. Hence, two different rotamers are possible. In the case of **10** the nitrogen atom of the iminoacyl group is adjacent to the chlorine atom. The same type of conformation is also shown in the compounds $Cp_2Zr(\eta^2$-MeNCCHPh$_2$)-(CH$_3$) and $Cp_2Zr(\eta^2$-Bu^{t}NCCH$_2$Ph)(OAr).[17] The C–N distance of 1.271 (7) Å found in **10** is comparable to related distances in other η^2-iminoacyl compounds.[1,15] Similarly, the Hf–C and Hf–N distances are as one would expect. In

(25) Moore, K. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.
(26) Deeming, A. J.; Rothwell, I. P. Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Chem. Commun.* **1979**, 670.
(27) Newkome, G. R.; Fronczek, F. R.; Gupta, V. K.; Puckett, W. E.; Pantoleo, D. C.; Kiefer, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 1982.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for $Cp_2Hf[xyNCH{=}CH\text{-}py\text{-}6Me]_2$ (5b)[a]

atom	x	y	z	B_{iso}, Å^2
Hf(1)	-10000*	-217*	-10000*	23
C(2)	-10722 (11)	-2088 (21)	-10980 (10)	22
C(3)	-9776 (13)	-2439 (19)	-10924 (10)	28
C(4)	-9312 (13)	-1335 (20)	-11318 (11)	25
C(5)	-9931 (11)	-240 (61)	-11585 (9)	27
C(6)	-10824 (11)	-707 (19)	-11385 (10)	23
N(7)	-8869 (8)	1379 (14)	-10117 (8)	16
C(8)	-8718 (11)	2435 (17)	-9501 (9)	15
C(9)	-8042 (11)	3438 (21)	-9440 (10)	21
C(10)	-7936 (12)	4517 (25)	-8789 (9)	18
C(11)	-7154 (11)	5494 (19)	-8754 (10)	22
C(12)	-7073 (13)	6476 (20)	-8099 (12)	30
C(13)	-7738 (11)	6543 (20)	-7509 (10)	22
C(14)	-8486 (11)	5560 (19)	-7585 (10)	19
N(15)	-8564 (9)	4635 (55)	-8193 (9)	24
C(16)	-8167 (10)	1441 (18)	-10775 (9)	18
C(17)	-7398 (11)	546 (18)	-10718 (10)	22
C(18)	-6734 (11)	664 (20)	-11339 (10)	26
C(19)	-6850 (13)	1635 (23)	-12009 (11)	35
C(20)	-7609 (13)	2563 (21)	-12045 (11)	31
C(21)	-8289 (11)	2482 (18)	-11411 (9)	20
C(22)	-7264 (12)	-248 (71)	-9971 (11)	57
C(23)	-9071 (13)	3571 (22)	-11476 (12)	32
C(24)	-9251 (14)	5639 (24)	-6962 (11)	39
C(25)	5393 (21)	6011 (38)	529 (20)	31 (7)
C(26)	5266 (17)	4061 (31)	302 (16)	19 (5)
C(27)	5000*	2977 (34)	0*	21 (5)
C(28)	5611 (24)	4472 (54)	821 (22)	64 (11)
C(29)	5851 (32)	6259 (61)	1133 (29)	87 (12)

[a] Fractional coordinates are $\times 10^4$ for non-hydrogen atoms; hydrogen atoms. B_{iso} values are $\times 10$. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609. Parameters marked by an asterisk were not varied.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Hf[xyNCH{=}CH\text{-}py\text{-}6Me]_2$ (5b)

Hf-N(7)	2.18 (1)	N(7)-C(8)	1.38 (2)
C(8)-C(9)	1.33 (2)		
N(7)-Hf-N(7)′	98.5 (7)	Hf-N(7)-C(8)	119.7 (10)
Hf-N(7)-C(16)	127.9 (10)	C(8)-N(7)-C(16)	112.3 (12)

the refinement of the structure of **10** it became impossible to differentiate the phenyl and pyridyl rings. Presumably complete disordering of the nitrogen atom occurs among the two rings, as the pyridylmethyl group formed by deprotonation of 2-benzylpyridine is racemic.

$Cp_2Hf[xyNCCH{=}CH\text{-}py\text{-}6Me]_2$ (5b). An ORTEP view of the molecular structure of **5b** is shown in Figure 4. The fractional coordinates are collected in Table V, while Table VI contains some selected bond distances and angles. Considerable difficulty was encountered in obtaining crystals of **5b** suitable for X-ray diffraction analysis, and the results of the study are not as good as one would wish. However, there is no doubt from the data as to the molecular structure of **5b**. A crystallographically imposed 2-fold axis within the molecule makes the two Cp and vinylamido ligands equivalent. It can be seen (Figure 4) that the trans geometry for the olefinic group inferred from spectroscopic data is confirmed by the structural results. The Hf-N(7) distance of 2.182 (12) Å is slightly longer than distances typically found to amido ligands bound to Zr(IV) and Hf(IV); cf. the M-N distances of 2.072 (2) Å in $Cp_2Zr(NMe_2)(OAr)$[17] and 2.04 (1) Å in $Hf[N(SiMe_3)_2]_3Cl$.[28] This elongation is probably the consequence of a decrease in nitrogen p to metal d π-bonding due not only to the electronic nature of **5b** (only one π-bond allowed to achieve an 18-electron configuration) but also possibly due to conjugation of the nitrogen lone pair with the vinyl substituent.

(28) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Abdul-Malik, K. M.; Praistloy, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere either in a Vacuum Atmospheres Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium–benzophenone and stored under a nitrogen atmosphere. The lithium reagents $LiCH_2$-py-6Me and LiCH(Ph)-py were obtained as yellow solids by treating 2,6-dimethylpyridine or 2-benzylpyridine with $LiBu^n$ (1 equiv) in hexane. The ^1H and ^{13}C NMR spectra were recorded on either a Varian Associates Gemini 200 or a General Electric QE-300 instrument.

$Cp_2Zr(CH_2\text{-}py\text{-}6Me)_2$ (1a). To a suspension of Cp_2ZrCl_2 (2.0 g, 6.8 mmol) in diethyl ether (50 cm^3) was gradually added a solution of $LiCH_2$-py-6Me (1.7 g, 15 mmol) also in Et_2O (50 cm^3). The resulting red-orange mixture was stirred for 12 h before the solvent was removed in vacuo. The residue was extracted with hexane (100 cm^3), and the deep orange filtrate was concentrated to yield the product as orange crystals, yield 1.8 g (61%). Anal. Calcd for $ZrC_{24}H_{26}N_2$: C, 66.47; H, 6.04; N, 6.46. Found: C, 66.35; H, 6.14; N, 6.58. ^1H NMR ($C_6D_5CD_3$, 30 °C): δ 5.53 (s, C_5H_5), 2.15 (s, Zr-CH_2), 2.28 (s, 6*Me*), 6.0–7.4 (aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 110.2 (C_5H_5), 43.6 (Zr-CH_2, $^1J(^{13}C\text{-}^1H)$ = 134 Hz), 24.0 (6*Me*).

$Cp_2Hf(CH_2\text{-}py\text{-}6Me)_2$ (1b). A procedure identical with that used for **1a** above, only with Cp_2HfCl_2 (2.0 g) and $LiCH_2$-py-6Me (1.5 g) yielded **1b** as an orange-brown crystalline solid from hexane; yield 2.0 g (72%). Anal. Calcd for $HfC_{24}H_{26}N_2$: C, 55.33; H, 5.03; N, 5.38. Found: C, 55.15; H, 5.03; N, 5.38. ^1H NMR ($C_6D_5CD_3$, 30 °C): δ 5.71 (s, C_5H_5), 1.90 (s, Hf-CH_2), 2.46 (s, 6*Me*), 6.0–7.4 (aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 111.4 (C_5H_5), 63.6 (Hf-CH_2, $^1J(^{13}C\text{-}^1H)$ = 121 Hz), 24.8 (6*Me*).

$Cp_2Zr(\eta^2\text{-}xyNCCH_2\text{-}py\text{-}6Me)(CH_2\text{-}py\text{-}6Me)$ (2a). The addition of 2,6-dimethylphenyl isocyanide (1 equiv) to solutions of **1a** in C_6D_6 led to the rapid formation of unstable **2a** in solution. ^1H NMR (C_6D_6, 30 °C): δ 5.53 (s, C_5H_5), 2.63 (s, Zr-CH_2), 3.42 (s, NCCH_2-py-6Me), 2.28 (s), 2.44 (s, 6*Me*), 1.70 (s, xy *Me*). ^{13}C NMR (C_6D_6, 30 °C): δ 246.7 (N*C*).

$Cp_2Hf(\eta^2\text{-}xyNCCH_2\text{-}py\text{-}6Me)(CH_2\text{-}py\text{-}6Me)$ (2b). ^1H NMR (C_6D_6, 30 °C): δ 5.51 (s, C_5H_5), 2.27 (s, Hf-CH_2), 3.49 (s, NCCH_2-py-6Me), 1.91 (s, xy *Me*). ^{13}C NMR (C_6D_6, 30 °C): δ 254.4 (N*C*).

$Cp_2Zr(xyNCH{=}CH\text{-}py\text{-}6Me)(CH_2\text{-}py\text{-}6Me)$ (3a). To a solution of **1a** (0.5 g, 1.15 mmol) in benzene (20 cm^3) was added xyNC (0.17 g, 1.3 mmol). The resulting mixture was stirred overnight. Removal of solvent followed by recrystallization of the resulting crude product from hot hexane yielded orange needles of **3a**, yield 0.52 g (80%). Anal. Calcd for $ZrC_{33}H_{35}N_3$: C, 70.17; H, 6.25; N, 7.44. Found: C, 69.49; H, 6.20; N, 7.20. ^1H NMR (C_6D_6, 30 °C): δ 2.40 (s), 2.53 (s, 6*Me*), 2.77 (s, Zr-CH_2), 5.76 (s, C_5H_5), 2.11 (s, xy *Me*), 8.76 (d), 4.78 (d, NC*H*=C*H*, $^3J(^1H\text{-}^1H)$ = 12 Hz). ^{13}C NMR (C_6D_6, 30 °C): δ 113.0 (C_5H_5), 55.5 (Zr-CH_2, $^1J(^{13}C\text{-}^1H)$ = 123 Hz), 99.1 (C=*C*H-py-6Me, $^1J(^{13}C\text{-}^1H)$ = 154 Hz), 146.7 (xyN*C*H=CH, $^1J(^{13}C\text{-}^1H)$ = 164 Hz).

$Cp_2Hf(xyNCH{=}CH\text{-}py\text{-}6Me)(CH_2\text{-}py\text{-}6Me)$ (3b). A procedure identical with that used for **3a** only with **1b** (0.5 g, 0.95 mmol) and xyNC (0.13 g, 0.99 mmol) yielded **3b** as a yellow solid, yield 0.51 g (82%). Anal. Calcd for $HfC_{33}H_{35}N_3$: C, 60.87; H, 5.26; N, 6.45. Found: C, 59.62; H, 5.56; N, 5.90. ^1H NMR (C_6D_6, 30 °C): δ 2.40 (s), 2.52 (s, 6*Me*), 2.54 (s, Hf-CH_2), 5.73 (s, C_5H_5), 2.14 (s, xy *Me*), 8.63 (d), 4.77 (d, NC*H*=C*H*, $^3J(^1H\text{-}^1H)$ = 13 Hz). ^{13}C NMR (C_6D_6, 30 °C): δ 112.1 (C_5H_5), 57.2 (Hf-CH_2, $^1J(^{13}C\text{-}^1H)$ = 121 Hz), 100.3 (CH=*C*H-py-6Me, $^1J(^{13}C\text{-}^1H)$ = 177 Hz), 147.8 (xyN*C*H=CH, $^1J(^{13}C\text{-}^1H)$ = 165 Hz).

$Cp_2Zr(xyNCH{=}CH\text{-}py\text{-}6Me)_2$ (5a). To a solution of **1a** (0.5 g, 1.15 mmol) in benzene (20 cm^3) was added xyNC (0.34 g, 2.59 mmol). The mixture was stirred overnight before the solvent was removed to yield the crude product. Recrystallization from hot toluene yielded the product as orange-red crystals, yield 0.39 g (49%). Anal. Calcd for $ZrC_{42}H_{44}N_4$: C, 72.47; H, 6.37; N, 8.05. Found: C, 72.16; H, 6.20; N, 7.71. ^1H NMR (C_6D_6, 30 °C): δ 2.10

Table VII. Crystal Data and Data Collection Parameters

	1a	10	5b
formula	$ZrN_2C_{24}H_{26}$	$HfClN_2C_{38}H_{37}$	$HfC_{42}H_{44}N_2$
fw	433.71	735.67	783.33
space group	$P\bar{1}$	$P2_1/n$ (No. 14)	$I2$
a, Å	7.679 (3)	11.012 (1)	14.490 (7)
b, Å	11.239 (3)	14.821 (1)	8.925 (4)
c, Å	12.672 (2)	19.067 (2)	15.943 (9)
α, deg	95.67 (2)	90	90
β, deg	100.57 (2)	103.263 (8)	91.03 (3)
γ, deg	108.37 (3)	90	90
V, Å^3	1006 (1)	3028.8 (9)	2061 (1)
Z	2	4	2
d_{calcd}, g cm^{-3}	1.432	1.613	1.262
cryst dimens, mm	0.73 × 0.29 × 0.22	0.56 × 0.52 × 0.50	0.23 × 0.23 × 0.34
temp, °C	22.0	22.0	−155
radiation (wavelength, deg)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
linear abs coeff, cm^{-1}	5.46	35.32	25.36
abs cor applied	empirical	empirical	empirical
scan method	ω–2θ	ω–2θ	ω–2θ
h,k,l limits	−9 to 9, −14 to 14, 0–16	−11 to 11, 0–15, 0–20	0–15, 0–10, +16 to −15
2θ rang, deg	4.00–55.00	4.00–45.00	6.00–45.00
scan width, deg	0.90 + 0.35 tan θ	0.41 + 0.35 tan θ	2.0 + dispersion
takeoff angle, deg	4.90	1.90	2.00
no. of unique data	4587	4115	1464
no. of data with $I > 3.0\sigma(I)$	3411	3148	1378
largest shift/esd in final cycle	0.19	0.22	0.05
R	0.050	0.029	0.054
R_w	0.065	0.039	0.049
goodness of fit	1.033	1.226	0.802

(s, 6*Me*), 2.45 (s, xy *Me*), 5.89 (s, C_5H_5), 9.24 (d), 4.76 (d, NC*H*=C*H*-py-6Me, $^3J(^1H–^1H)$ = 13 Hz). ^{13}C NMR (C_6D_6, 30 °C): δ 114.3 (C_5H_5), 98.3 (CH=*C*H-py-6Me, $^1J(^{13}C–^1H)$ = 154 Hz), 135.9 (xyN*C*H=CH, $^1J(^{13}C–^1H)$ = 157 Hz).

Cp_2Hf(xyNCH=CH-py-6Me)$_2$ (5b). This compound was obtained by use of a procedure identical with that for **5a** only with **1b** (0.5 g, 0.95 mmol) and xyNC (0.26 g, 1.98 mmol); yield 0.38 g (50%). Anal. Calcd for $HfC_{42}H_{44}N_2$: C, 64.40; H, 5.66; N, 7.15. Found: C, 64.07; H, 5.62; N, 6.18. ^1H NMR (C_6D_6, 30 °C): δ 2.15 (s, 6*Me*), 2.50 (s, xy *Me*), 5.90 (s, C_5H_5), 9.19 (d), 4.79 (d, NC*H*=C*H*, $^3J(^1H–^1H)$ = 12 Hz). ^{13}C NMR (C_6D_6, 30 °C): δ 113.2 (C_5H_5), 99.6 (CH=*C*H-py-6Me, $^1J(^{13}C–^1H)$ = 154 Hz), 149.2 (xyN*C*H=CH, $^1J(^{13}C–^1H)$ = 166 Hz).

$Cp_2HfCl(CH_2$-py-6Me) (6). To a suspension of Cp_2HfCl_2 (5.0 g, 13.2 mmol) in toluene (30 cm^3) was added $LiCH_2$-py-6Me (1.57 g, 13.8 mmol). The mixture was stirred at room temperature for 2 h before being warmed in an oil bath at 100 °C for 90 min. Removal of the toluene solvent followed by extraction with Et_2O yielded the product as a dark brown solid. Compound **6** was also obtained by heating a mixture of **1b** and Cp_2HfCl_2 in C_6D_6 at 100 °C, as evidenced by changes in the ^1H NMR spectrum. Anal. Calcd for $HfC_{17}H_{18}NCl$: C, 45.35; H, 4.03; N, 3.11; Cl, 7.87. Found: C, 45.05; H, 3.36; N, 2.57; Cl, 8.13. ^1H NMR (C_6D_6, 30 °C): δ 5.75 (s, C_5H_5), 2.34 (s, Hf–CH_2), 2.50 (s, 6*Me*), 6.5–7.2 (aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 112.7 (C_5H_5), 61.6 (Hf–*C*H$_2$, $^1J(^{13}C–^1H)$ = 121 Hz), 25.1 (6*Me*, $^1J(^{13}C–^1H)$ = 126 Hz).

$Cp_2Hf(\eta^2$-xyNCCH$_2$-py-6Me)Cl (7). Addition of xyNC (1 equiv) to **6** in C_6D_6 showed the formation of unstable **7** in solution. ^1H NMR (C_6D_6, 30 °C): δ 6.00 (s, C_5H_5), 3.91 (s, NCCH_2), 2.62 (s, 6*Me*), 2.32 (s, xy Me). ^{13}C NMR (C_6D_6, 30 °C): δ 253.5 (*N*C).

Cp_2Hf(xyNCH=CH-py-6Me)Cl (8). To a solution of **6** (0.5 g, 1.1 mmol) in benzene (15 cm^3) was added xyNC (0.32 g, 1.2 mmol), and the mixture was stirred. After a period of hours the product **8** precipitated from the reaction mixture and was washed with hexane and dried. Anal. Calcd for $HfC_{26}H_{27}N_2Cl$: C, 53.30; H, 4.90; N, 4.73; Cl, 6.07. Found: C, 53.7; H, 4.7; N, 4.8; Cl, 6.1. ^1H NMR (C_6D_6, 30 °C): δ 5.92 (s, C_5H_5), 2.48 (s, 6*Me*), 2.26 (xy *Me*), 9.21 (d), 4.90 (d, NC*H*=C*H*, $^3J(^1H–^1H)$ = 13 Hz). ^{13}C NMR (C_6D_6, 30 °C): δ 113.6 (C_5H_5), 101.6 (CH=*C*H-py-6Me, $^1J(^{13}C–^1H)$ = 155 Hz), 147.3 (xyN*C*H=CH, $^1J(^{13}C–^1H)$ = 164 Hz).

Cp_2Hf[CH(Ph)-py]Cl (9). To a suspension of Cp_2HfCl_2 (2.0 g, 5.26 mmol) in benzene (20 cm^3) was gradually added LiCH(Ph)-py (0.97 g, 5.5 mmol) with stirring. After 16 h the resulting mixture was filtered and the solvent evaporated in vacuo. The crude product was purified by washing with hexane before being dried. In both the solid state and hydrocarbon solution compound **9** was found to undergo slow decomposition to 2-benzylpyridine and unidentified hafnium compounds. Anal. Calcd for $HfC_{22}H_{20}NCl$: C, 51.58; H, 3.94; N, 2.73; Cl, 6.92. Found: C, 51.78; H, 3.91; N, 2.84; Cl, 7.01. ^1H NMR (C_6D_6, 30 °C): δ 5.65 (s, C_5H_5), 3.38 (s, Hf–C*H*Ph-py). ^{13}C NMR (C_6D_6, 30 °C): δ 111.4 (C_5H_5), 48.9 (Hf–*C*HPh-py, $^1J(^{13}C–^1H)$ = 130 Hz). At −60 °C the single Cp resonance at δ 5.65 ppm is split into two equal-intensity peaks at δ 5.40 and 5.85 ppm in the ^1H NMR spectrum.

$Cp_2Hf(\eta^2$-xyNCCH(Ph)-py)Cl (10). To a solution of **9** (0.75 g, 1.46 mmol) in benzene (15 cm^3) was added xyNC (0.19 g, 1.46 mmol). After it was stirred for 16 h, the mixture was filtered and the solvent removed in vacuo to yield the crude product. Recrystallization by cooling of a saturated toluene solution yielded long white crystals of pure product suitable for X-ray diffraction studies. Anal. Calcd for $HfC_{30}H_{29}NCl$: C, 57.86; H, 4.54; N, 4.35; Cl, 5.5]. Found: C, 57.61; H, 4.84; N, 4.23; Cl, 5.55. ^1H NMR (C_6D_6, 30 °C): 5.71 (s), 5.89 (s, C_{H5}), 3.92 (s, C*H*Ph-py), 1.92 (s), 1.95 (s, xyMe_2). ^{13}C NMR (C_6D_6, 30 °C): δ 252.5 (*N*C), 108.7, 109.0 (C_5H_5), 61.7 (*C*HPh-py), 18.4, 18.5 (xy Me_2).

Deuteration Experiments. Preparation of 2,6-$(CD_3)_2C_5H_3N$. A mixture of 5 cm^3 (42.9 mmol) of 2,6-dimethylpyridine with 25 cm^3 (433 mmol) of CH_3CO_2D (98% purity) was heated at 110 °C for 2 h. After neutralization of the solution with sodium carbonate the deuterated product was extracted with 20 mL of dichloromethane. The solvent was removed by evaporation, and the procedure was repeated with use of another 25 cm^3 of CH_3CO_2D; 2.2 cm^3 of deuterated product was recovered. Analytical data: 92.5 (5)% deuterated on the basis of the mass and ^1H NMR spectra.

Preparation of $Cp_2Hf(CD_2$-py-6$CD_3)_2$. A solution of 1.61 g (4.23 mmol) of Cp_2HfCl_2 in 10 cm^3 of benzene was mixed with 1.0 g (8.47 mmol) of $LiCD_2$-py-6CD_3 (prepared from 2,6-$(CD_3)_2C_5H_3N$ and LiBu^n). The mixture was stirred for 2 h and the product filtered and dried under vacuum. The product was extracted with 10 cm^3 of ether, yielding 2.06 g (92%) of the product. Analytical data: the mass spectrum indicated 94.5% deuteration. ^1H NMR (C_6D_6, 30 °C): δ 5.70 (s, C_5H_5), 6.5–7.2 (m, aromatics).

Preparation of $Cp_2Hf(Cl)(CD_2$-py-6$CD_3)$ (6-d_5). This compound was prepared in situ in an NMR tube with use of 0.04 g (0.075 mmol) of $Cp_2Hf(CD_2$-py-6$CD_3)_2$ dissolved in 2 cm^3 of C_6D_6 followed by addition of 0.03 g (0.076 mmol) of Cp_2HfCl_2 and thermolysis of the solution at 110 °C for 30 min. ^1H NMR (C_6D_6, 30 °C): δ 5.70 (s, C_5H_5) 6.45–7.15 (m, aromatics).

$Cp_2Hf(\eta^2$-xyNCCD$_2$-py-6CD_3)Cl (7-d_5). Addition of xyNC (1 equiv) to 6-d_5 in C_6D_6 showed the formation of unstable 7-d_5

in solution. ^{1}H NMR (C_6D_6, 30 °C): δ 5.65 (C_5H_5), 1.85 (s, xy *Me*), 6.45–7.15 (m, aromatics).

Cp_2Hf(xyNCD=CD-py-6CD_3)Cl (8-d_5). To a solution of 6-d_5 (0.040 g, 9.1×10^{-2} mmol) in deuterated benzene (1.5 cm^3) was added 0.015 g (11.4×10^{-2} mol) of xyNC. After a period of days the product 8-d_5 was formed in quantitative yield. ^{1}H NMR (C_6D_6, 30 °C): δ 2.28 (s, xy *Me*), 5.93 (s, C_5H_5), 6.05–7.15 (m, aromatics).

Crystallographic Studies. The X-ray diffraction analysis of **1a** and **10** was carried out in the Purdue Chemistry Department Crystallography Center, while that of **5b** was carried out the Indiana University Molecular Structure Center. Crystal data and data collection parameters are collected in Table VII.

$Cp_2Zr(CH_2$-py-6Me$)_2$ (1a) and Cp_2Hf[xyNCCH(Ph)-pyl]Cl (10). In both cases suitable crystals were located and mounted in a 0.5-mm capillary surrounded by epoxy resin. Data collection and refinement were carried out with use of the standard procedures of the Purdue crystallographic facility. In both cases the monitoring of five standard reflections over time showed no significant decay. The positions of the hydrogen atoms were calculated with the assumption of an idealized geometry and a bond distance of 0.95 Å. For methyl groups, one hydrogen atom was located in the difference Fourier map, its position was idealized, and the remaining positions were calculated. The hydrogen atoms were not refined. No correction for estimation was applied. In the case of **1a** one of the Cp rings was found to be resolved, while for **10** the pyridyl and phenyl groups could not be differentiated.

Cp_2Hf[xyNCH=CH-py-6Me$]_2$ (5b). A suitable crystal was located, transferred to the goniostat with use of standard inert-atmosphere handling techniques employed by the IUMSC, and cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to a monoclinic body-centered cell. As indexed, the possible space group choices were $I2$, Im, and $I2/m$. Subsequent solution and refinement of the structure confirmed the noncentrosymmetric $I2$ as the proper choice.

Data were collected in the usual manner by use of a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ values in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. There was considerable difficulty in locating several of the carbon atoms, but once located, they were "well behaved". An apparent solvent molecule was visible in difference Fouriers and was included as a partial-occupancy disordered fragment. Several of the hydrogen atom positions were visible in a difference Fourier phased on the nonhydrogen atoms. Positions were calculated for all hydrogens by the assumption of an idealized geometry with d(C–H) = 0.95 Å, and they were included as fixed-atom contributors in the final cycles. A ψ scan of several reflections near $\chi = 90°$ indicated that no absorption correction was necessary. A final difference Fourier was essentially featureless, with the largest peak being 1.6 e/Å^3 located adjacent to the metal position. On the basis of refinement of both enantiomers, the reported coordinates correspond to the correct choice for the given crystal.

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Supplementary Material Available: Tables of general temperature factors and bond distances and angles for **1a**, **5b**, and **10** (28 pages); tables of structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.