Electrochemical studies show that incorporation of quinone groups into crown ethers couples redox reactions with binding of group IA cations. In contrast to expectations from ion pairing, K^+ with 6QC yields the largest potential shift, followed by $Rb^+ > Na^+ > Cs^+ > Li^+$. Structural studies show that the observed ion selectivity derives from the crown loop, not the quinoid moiety, owing to the latter's ability to pivot with respect to the macrocycle plane and thereby to accommodate a range of cations. EPR studies demonstrate the intramolecular nature of interaction between the cations and the ligands. In its semiquinone form only 6QC shows a metal hyperfine coupling constant with Na.

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Supplementary Material Available: Tables of atomic coordinates, bond angles, bond lengths, anisotropic thermal parameters, hydrogen atomic positions, and torsional angles, and an outline of the searches of the Cambridge Crystallographic Database (52 pages); listing of structure factor tables (69 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(CO)^+$, a d^0 Metal Alkyl Carbonyl Complex. Coordination Chemistry of the Four-Membered Azazirconacycle $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})^+$

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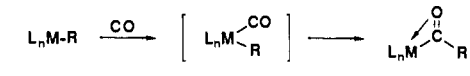
Abstract: The cationic complex $Cp_2Zr(CH_3)(THF)^+$ (**1**, as the BPh_4^- salt) reacts with 2,6-diethylpyridine to afford the chelated secondary zirconocene–alkyl complex $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})^+$ (**2**). Treatment of complex **2** with CO, CH_3CN, ^tBuCN, and $(PhCH_2)(Et)_3N^+Cl^-$ affords $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(CO)^+$ (**3**), $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(CH_3CN)^+$ (**4**), $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(^tBuCN)^+$ (**5**), and $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(Cl)$ (**6**), respectively. The thermally sensitive d^0 carbonyl complex **3** is a rare example of a d^0 M(alkyl)–CO adduct and is unambiguously characterized in solution by low-temperature NMR and IR spectroscopy, ^{13}C-labeling and hydrolysis experiments, and decomposition studies. IR and NMR data establish that **3** contains a terminal CO ligand. An X-ray structure analysis of **6** establishes that the CH(Me)(6-ethylpyrid-2-yl) ligand adopts a chelated structure; the similarity of the spectroscopic data for **3**–**6** implies that **3**–**5** have similar chelated structures. At room temperature, **3** in CD_2Cl_2 rapidly decomposes to afford a complex mixture of products. ^1H NMR monitoring of the decomposition of **3** reveals formation of a transient cationic zirconocene–acyl intermediate **9**, which undergoes 1,2-H shift to afford a mixture of isomeric/oligomeric zirconocene–enolates. Treatment of this mixture with $(PhCH_2)(Et)_3N^+Cl^-$ affords $Cp_2Zr(OCH{=}C\{Me\}\{6\text{-ethylpyrid-2-yl}\})Cl$ (**10**) as a mixture of *E*/*Z* isomers, establishing the presence of zirconocene–enolate species. Hydrolysis of the decomposition products of **3** affords a mixture of thermally sensitive tautomers, enol **11**/aldehyde **11'**, which are characterized by NMR, FTIR, and mass spectroscopy.

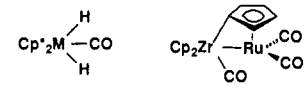
Introduction

It is generally assumed that the insertion reactions of d^0 metal alkyl and hydride complexes with CO, olefins, and related π-acid substrates involve initial coordination of substrate to the metal center (e.g., eq 1). However the intermediate $L_nM(R)$(substrate) adducts are rarely observed and are presumed to be unstable due to the lack of conventional $d \rightarrow \pi^*$ back-bonding and the rapidity of the subsequent insertion reactions.[1] The characterization of these elusive species is of fundamental importance for understanding the scope and selectivity of insertion reactions and for the design of new reactive organometallic complexes.



There are few well-characterized d^0 metal–carbonyl complexes. The thermally sensitive $Cp^*_2M(H)_2(CO)$ adducts (M = Zr, Hf) (Chart I) are formed by carbonylation of $Cp^*_2ZrH_2$ at low temperature, and they undergo CO reduction processes when warmed.[2] These complexes exhibit ν_{CO} bands which are decreased by ca. 100 cm^{-1} from that of free CO (Zr 2044, Hf 2036, vs 2143 cm^{-1} for free CO). The low ν_{CO} values are surprising for d^0 complexes and were ascribed to back-bonding form the b_1 M–H bonding MO (antisymmetric combination of the M–H bonds)[3] to the in-plane CO π^*-orbital.[4] In contrast, ν_{CO} values for M–CO complexes in which only σ-donation is important are higher than the free CO value: e.g., H_3BCO 2165 cm^{-1},[5] $Ag(CO)B(OTeF_5)_4$ 2204

Chart I



M = Zr, Hf

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Table I. Key ^1H and ^{13}C NMR Data for 2,6-Diethylpyridine and Complexes **2–6**

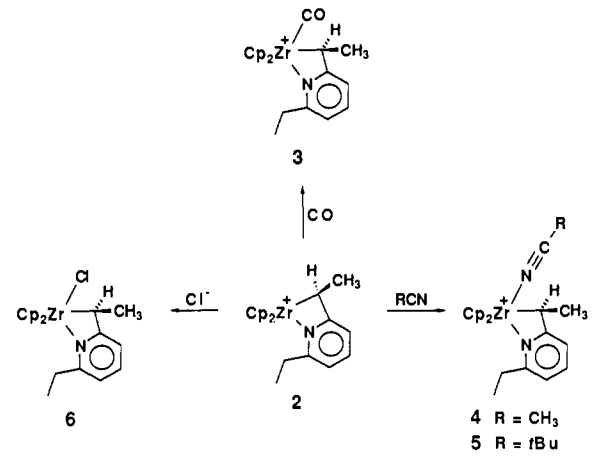
		2,6-diethylpyridine	2	3	4	5	6
$CH(CH_3)$	^1H (δ)		3.97	2.69	2.45	2.45	2.52
	^{13}C (δ)		51.7	30.5	37.2	36.3	43.9
	$^1J_{CH}$ (Hz)		133	140	136	135	134
CH_2CH_3	^1H (δ)	2.75	2.16, 2.08	2.69	2.66	2.68	2.92, 2.76
	^{13}C (δ)	31.7	32.1	29.0	29.7	29.6	29.8
	$^1J_{CH}$ (Hz)	125	128	128	127	127	127
CH_2CH_3	^1H (δ)	1.26	1.03	1.41	1.53	1.40	1.32
	^{13}C (δ)	14.0	14.5	15.1	13.5	13.5	13.8
	$^1J_{CH}$ (Hz)	126	128	127	128	128	127

cm^{-1},[6] and Au(Cl)(CO) 2158 cm^{-1}.[7]

The bimetallic Zr–Ru bonded complex $Cp_2Zr(CO)(\mu\text{-}\sigma,\pi\text{-}C_5H_4)Ru(CO)_2$ (Chart I), which is arguably a Zr(IV) complex in a Zr^+/Ru^- description, is formed by carbonylation of $Cp_2Zr\{(Ru(CO)_2Cp\}_2$ and undergoes rapid exchange with free CO at 0 °C.[8a] This species displays a much lower ν_{CO} value (1840 cm^{-1}), in part due to a weak semibridging interaction with the Ru center. The carbonyl/isovaleraldehyde adducts, $Cp^*_2M(CO)(\eta^2\text{-}O{=}CHCH_2CHMe_2)$ (M = Zr, Hf), have been described, and they also exhibit relatively low ν_{CO} values (1940, 1930 cm^{-1}, respectively) indicative of substantial contribution from the M^{II}(aldehyde) resonance forms.[8b] A Ti(IV)–CO adduct formulated as $\{[Cp_2Ti(CO)]_2(\mu\text{-}(CN)_2C{=}C(CN)_2)\}^{2+}TCNE^{2-}$ has also been described (ν_{CO} = 2055 cm^{-1}).[9] There are several d^0 metal isocyanide complexes, including $Cp^*_2Ti(Me)(CN\text{-}^tBu)^+$ which was observed at low temperature,[10] and several isolable iminoacyl/isocyanide systems, e.g., $Cp_2Ti\{\eta^2\text{-}C(N\text{-}^tBu)Me\}(CN\text{-}^tBu)^+$.[11] To the best of our knowledge, olefin and acetylene complexes of d^0 metals are unknown.[12]

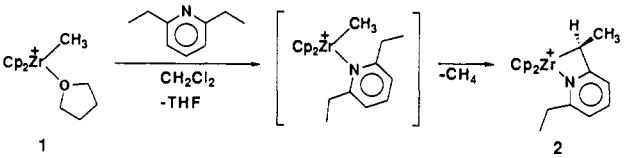
Cationic $Cp_2Zr(R)(L)^+$ complexes (L = labile ligand) catalyze the oligomerization and polymerization of olefins and exhibit a variety of other catalytic and stoichiometric reactions, many of which involve insertion of an olefin, alkyne, or CO into the Zr–R bond as the key step.[13,14] During recent studies of the carbonylation reactions of these complexes, we discovered the title compound, $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(CO)^+$, which is a relatively stable Zr(IV) alkyl carbonyl complex. We describe here the synthesis and characterization of this unusual compound and several analogues which were prepared in order to elucidate its structure.

Scheme I



Results and Discussion

Synthesis of $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})^+$ (2). The cationic complex $Cp_2Zr(Me)(THF)^+$ (**1**)[15] reacts with 2,6-diethylpyridine via ligand substitution and CH activation/CH_4 elimination to afford the secondary zirconocene–alkyl complex $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})^+$ (**2**) (eq 2).[16,17] NMR



data for **2** (Table I and Experimental Section) establish that metalation has occurred at the α-CH_2 site, and the data are consistent with a chelated structure in solution. The ^1H and ^{13}C spectra contain resonances for two inequivalent Cp ligands and the expected patterns for a CH(Me)(6-ethylpyrid-2-yl) ligand. The ^1H NMR resonances for the diastereotopic methylene hydrogens (δ 2.16 (m), 2.08 (m)) and the methyl hydrogens (δ 1.03) of the CH_2CH_3 side chain are shifted significantly upfield from the corresponding resonances of free 2,6-diethylpyridine (δ 2.75 (q), 1.26 (t)), consistent with N-coordination. Similar upfield shifts have been noted previously for related cationic pyridine and substituted-pyridine complexes. The $^1J_{CH}$ value of 133 Hz for $ZrCH(CH_3)$ is larger than expected for a normal, η^1-CH(Me)(6-ethylpyrid-2-yl) ligand and is consistent with incorporation of the CH(Me) fragment in a small ring (e.g., cyclobutane 134 Hz,[18] $Cp_2Zr\{\eta^2\text{-}C,N\text{-}(CH(CH_2(6\text{-methylpyrid-2-yl}))py)\}^+$, J_{CH} = 136 Hz, and $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)^+$, J_{CH} = 145 Hz).[19]

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However, it should be noted that this value is only ca. 5 Hz greater than the $^1J_{CH}$ coupling constant for the py-CH_2CH_3 side chain of **2** (Table I).

Synthesis and Identification of $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(CO)^+$ (3). Complex **2** reacts with carbon monoxide (1–3 atm) below 0 °C to afford the d^0 M–CO adduct $Cp_2Zr\{CH(Me)(6\text{-ethylpyrid-2-yl})\}(CO)^+$ (**3**) (Scheme I). Although the thermal sensitivity of **3** precluded its isolation, low-temperature NMR, IR, ^{13}C-labeling, and hydrolysis experiments unambiguously establish its formation in solution. The ^1H and ^{13}C NMR spectra include resonances for two inequivalent Cp ligands and an intact CH(Me)(6-ethylpyrid-2-yl) ligand. The ^{13}C NMR spectrum of **3** at −40 °C exhibits a resonance at δ 206.1 for the coordinated CO. This resonance is significantly upfield of the ^{13}C carbonyl resonances of cationic $Cp_2Zr\{C(O)CH_3\}(L)^+$ η^2-acyl complexes (δ 315.0, L = THF, CH_3CN) and early transition metal–acyl complexes in general[20,21] and is near that reported for $Cp^*_2HfH_2(CO)$ (δ 224.4). The ^{13}C-labeled complex $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(^{13}CO)^+$ (**3**-^{13}CO) was prepared by treating **2** with ^{13}CO. The ^1H and ^{13}C NMR spectra of **3**-^{13}CO at −40 °C are identical to the spectra of **3**. The lack of $^2J_{H-^{13}C}$ coupling between ^{13}CO and $CH(CH_3)$ in both the ^1H and ^{13}C NMR spectra of **3**-^{13}CO rules out acyl structures.[22] The $ZrCH(Me)$ ^{13}C resonance of **3**-^{13}CO is slightly broadened but not split.[23] The solution (CH_2Cl_2) FT-IR spectrum of **3** exhibits a ν_{CO} absorbance at 2095 cm^{-1}, which shifts to 2048 cm^{-1} for **3**-^{13}CO. This value is ca. 40 cm^{-1} lower than that of free CO (2135 cm^{-1} in CH_2Cl_2)[24] and 55 cm^{-1} higher than the values for the neutral group 4 $Cp^*_2MH_2(CO)$ complexes. The coordinated CO of **3** is labile; at ambient temperature, exchange with free CO is rapid on the NMR time scale. Hydrolysis of **3** at lower than −78 °C affords 2,6-diethylpyridine as the major (97%) organic product.

The NMR data for **3** do not conclusively establish the structure of the CH(Me)(6-ethylpyrid-2-yl) ligand but, when compared to data for related complexes (vide infra), indicate that both C and N are coordinated. Ligands of this type can coordinate in a variety of ways.[25] The Zr–C_α J_{CH} value (140 Hz) is larger than expected for an unstrained CH(Me)(6-ethylpyrid-2-yl) ligand and suggests that the py group is probably coordinated to Zr, either via normal σ-donation from N or through the py π-system in an η^2-benzyl (cf. $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)^+$)[26] or η^3-azaallyl mode.[27,28]

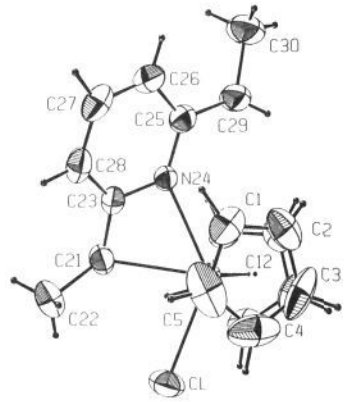


Figure 1. ORTEP view of $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(Cl)$ (**6**).

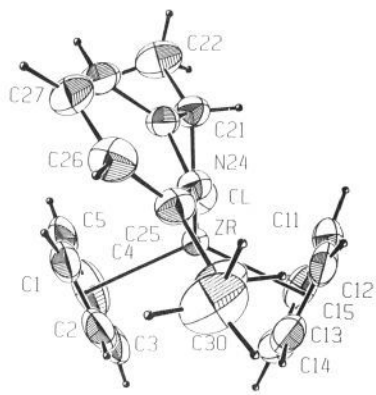
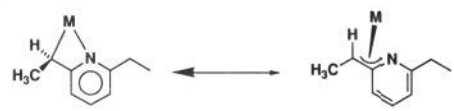


Figure 2. Alternate ORTEP view of $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(Cl)$ (**6**).

Chart II



A B

However, the ^1H NMR resonances for the CH_2CH_3 side chain of **3** (δ 2.68 (q), 1.39 (t))[29] are essentially unchanged from those *of free 2,6-diethylpyridine (Table I), which is inconsistent with* normal N-coordination. Also, the ^{13}C NMR resonance ($\delta \sim 163$) for the ipso carbon in **3** (which would interact with Zr in an η^2-benzyl type structure) is not shifted upfield as observed for other η^2-benzyl derivatives (e.g., $\delta_{C\text{-ipso}} = 126$ in $Cp_2Zr(\eta^2\text{-}CH_2Ph)(CH_3CN)^+$). Thus normal N or η^2-benzyl coordination modes are unlikely. In an effort to probe this question further, several thermally stable analogues of **3** were prepared.

Synthesis of $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(L)^+$ (L = CH_3CN (4), ^{t}BuCN (5)) and $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})Cl$ (6). As summarized in Scheme I, the azametallacycle **2** reacts rapidly with CH_3CN and ^{t}BuCN to yield the isolable nitrile adducts $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})(L)^+$ (L = CH_3CN (**4**), ^{t}BuCN (**5**)) and with Cl^- sources to yield the neutral complex $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})Cl$ (**6**). NMR data (Table I and the Experimental Section) establish that **4**–**6** are structurally similar to **3**. In each case the expected ^1H and ^{13}C resonances for diastereotopic Cp ligands and intact CH(Me)(6-ethylpyrid-2-yl) ligands are observed. In each case, the ^1H NMR resonances for the py-CH_2CH_3 side chain are near that of the corresponding resonances of free 2,6-diethylpyridine, and ^{13}C NMR resonances of the py ipso carbons appear in the normal range ($\delta \sim 163$). However, the $J_{C_\alpha H}$ values (134–136 Hz) are slightly larger than expected for undistorted ZrCH(Me)(6-ethylpyrid-2-yl) ligands.

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Table II. Summary of Crystallographic Data for $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH(CH_3)(6\text{-ethylpyrid-2-yl}))Cl$ (**6**)

empirical formula	$C_{19}H_{22}ClNZr$
fw	391.07
cryst size, mm	0.16 × 0.35 × 0.55
cryst color	yellow
T, K	295
space group	$P2_1/c$
a, Å	8.422 (2)
b, Å	14.431 (3)
c, Å	14.036 (3)
β, deg	93.01 (2)
V, Å^3	1703 (1)
Z	4
d(calcd), g/cm^3	1.53
cell dimens determ, no. reflns, θ range	24 rflns, $21 < 2\theta < 24$
radiation	Mo Kα (λ = 0.7107 Å)
scan ratio, Ω/θ	1
scan range, deg·Ω	0.7 + 0.35 tan (θ)
scan speed, deg/min	1.5–5.0
theta range, deg	$2 < \theta < 30$
data collected, h; k; l	−11,11; −2,20; −13,13
no. rflns collected	6429
no. unique rflns	4277
reflns used, $F > 2\sigma_F$	2755
R_{int}	0.027
max decay corr factor	1.045
abs coeff, cm^{-1}	7.9
empirical abs corr range	1.001–1.074
struct soln method	Patterson/Fourier
refinement[a]	all non-H anisotropic, H isotropic
total params	287
R	0.038
R_w	0.047
weight[a]	P = 0.04, Q = 0.0
SDOUW[b]	1.067
max param shift/esd	0.11
max density, final diff density map, e$^-$/Å^3	0.641

[a] $w = [\sigma_F^2 + (PF)^2 + Q]^{-1}$. [b] Standard deviation of unit weight.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH(CH_3)(6\text{-ethylpyrid-2-yl}))Cl$ (**6**)

	Bond Distances		
Zr–Cl	2.572 (1)	N24–C23	1.365 (5)
Zr–N	2.381 (3)	N24–C25	1.364 (5)
Zr–C21	2.421 (4)	C25–C26	1.378 (6)
C21–C23	1.407 (5)	C26–C27	1.400 (6)
C25–C29	1.498 (6)	C27–C28	1.347 (6)
Zr–C (Cp1)	2.2523 (3)	C28–C23	1.413 (5)
Zr–C (Cp2)	2.2630 (3)	C21–C22	1.515 (6)
	Bond Angles		
Zr–C21–C23	86.8 (2)	Cl–Zr–N24	134.40 (8)
Cl–Zr–C21	77.17 (9)	C21–Zr–N24	57.3 (1)
C(Cp1)–Zr–C(Cp2)	130.11 (1)		

X-ray Structure of 6. Crystals of **6** were obtained from cold toluene/pentane and subjected to X-ray diffraction analysis as summarized in Table II. ORTEP views of the cation structure are shown in Figures 1 and 2, and selected bond distances and angles are given in Table III. Complex **6** adopts a five-coordinate, bent metallocene structure with the C, N, and Cl ligands occupying the three coordination sites in the wedge between the Cp ligands. The Cp_2M metrical parameters are normal.[30] The Cl^- ligand occupies a lateral site cis to the C of the CH(Me)(6-ethylpyrid-2-yl) ligand, and the N is clearly coordinated.

The CH(Me)(6-ethylpyrid-2-yl) ligand is best described as being intermediate between a chelated η^2-C,N alkyl/pyridine structure **A** and an η^3-azaallyl structure **B** (Chart II) and is very similar to the CH(R)(py) ligands in $Cp_2Zr\{\eta^2\text{-}N,C\text{-}CH(SiMe_3)(pyrid\text{-}2\text{-}yl)\}Cl$ (**7**)[31] and $Cp_2Zr\{\eta^2\text{-}C,N\text{-}CH_2(6\text{-methylpyrid-2-yl})\}\{CH_2(6\text{-methylpyrid-2-yl})\}$ (**8**).[32] The Zr–C_α(21)–C_β(23) angle is acute (86.8 (2)°). The Zr–C_α distance in **6** (2.421 (4) Å) is considerably longer than those of simple $Cp_2Zr(R)(X)$ complexes (Cp_2ZrMe_2, $Cp_2Zr(CH_3)(THF)^+$, ca. 2.25 Å),[14,33] but is similar to those of **7** (2.38 (1) Å) and **8** (2.406 (4) Å). The Zr–C_β(23) distance (2.73 Å) is slightly longer than those in $Cp_2Zr(\eta^2\text{-}CH_2Ph)(L)^+$ complexes (ca. 2.6 Å). The four-membered ring is folded along the C_β(23)–N vector, and the py plane is rotated ca. 44.8° out of the Zr–C–Cl–N plane. As a result Zr lies 1.48 Å out of the py plane. The four-membered rings of **7**, **8**, and related complexes are folded in a similar manner. The folding in **7** was ascribed in part to relief of steric interactions between the α-$SiMe_3$ group and a Cp ligand; however, an analogous effect involving the α-Me group in **6** is unlikely as there are no close Cp/Me H–H contacts. This observation and the puckering in **8**, which lacks an α-substituent, suggest that the folding is at least partially electronic in origin. The constraints of the four-membered ring preclude the proper alignment for optimum N–Zr σ-bonding, even when the Zr–C–py bond angle is compressed to <90°, and some η^3-azaallyl character in the bonding (i.e., structure **B**, Chart II) is thus favored. In **6**, the C_α(21)–C_β(23) bond distance is short (1.407 (5) Å vs 1.498 (6) Å for C(25)–C(29)), and there is some alternation of bond distances in the py ring (C(23)–C(28) 1.413 (5), C(28)–C(27) 1.347 (6), C(27)–C(26) 1.400 (6), C(26)–C(25) 1.378 (5) Å), which is consistent with a significant contribution from resonance structure **B**. The Zr–N distance (2.381 (2) Å) in **6** is longer than that in the unstrained five-membered azametallacycle $Cp_2Zr\{CH_2CH_2(6\text{-methylpyrid-2-yl})\}^+$ (2.303 (2) Å), indicating weaker N–Zr bonding, but is similar to the Zr–N distance in **8** (2.407 (4) Å).

Solution Structures of 3–6. As described above, the NMR parameters for **3–6** are all normal except for the somewhat larger Zr*C*H(Me(py)) J_{CH} values. The X-ray analysis of **6** establishes that the ZrCH(Me)(6-ethylpyrid-2-yl) ligand adopts a chelated structure. The acute Zr–C–py angle should produce a large J_{CH} value, but the Zr–C_{ipso} and Zr–N interactions may be too weak to significantly perturb the ^{1}H NMR shifts of the py ethyl side chain or the ^{13}C shift of the ipso carbon from their normal values. On this basis, we conclude that the solution structures of **3–6** are similar to the solid-state structure of **6**. The range of J_{CH} values observed for **3–6** (134–140 Hz) may reflect small differences in the conformation of the ZrCH(Me)(6-ethylpyrid-2-yl) ligand which result from the different steric and electronic demands of CO, RCN, and Cl^- ligands. The potential energy surfaces for distortion of CH(Me)(pyrid-2-yl) ligands are likely to be rather flat.[34] Structures for **3–5** with CO or RCN cis to N are unlikely on steric grounds.

Fate of Complex 3. The bright yellow CH_2Cl_2 solutions of complexes **3** and **3**-^{13}CO are not stable at 23 °C and turn red within minutes. The decomposition was monitored by ^{1}H NMR spectroscopy. Initial ^{1}H NMR spectra reveal formation of a transient cationic zirconocene–acyl intermediate $Cp_2Zr(C(O)CH\{Me\}\{6\text{-ethylpyrid-2-yl}\})^+$ **9** (within ca. 20 min at ambient temperature).[35] Later ^{1}H NMR spectra (longer than 20 min, less than 2 days) are very complex and establish that intermediate **9** decomposes to a mixture of species. A broad resonance at δ 8.99 attributable to $ZrOC\mathit{H}{=}CCH_3$ suggested the presence of

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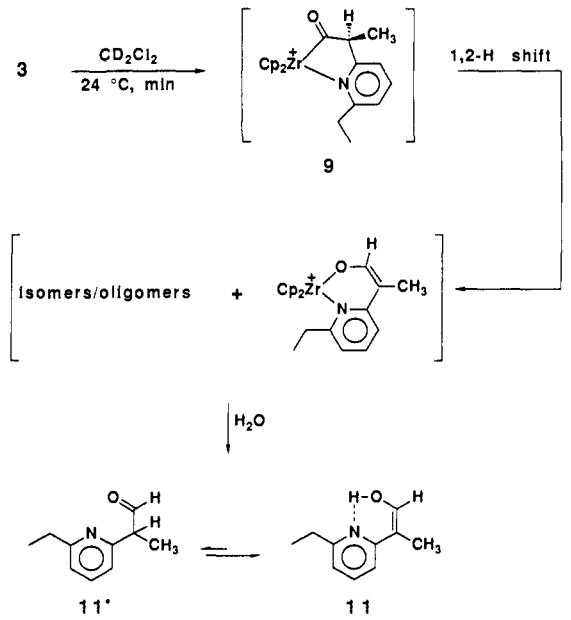
(35) Key data for intermediate **9**: ^{1}H NMR (CD_2Cl_2) δ 7.82 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, para py-H), 7.04 (obscured by BPh_4^-, 1 H, meta py-H), 7.02 (obscured by BPh_4^-, 1 H, meta py-H), 6.24 (s, 5 H, Cp), 5.47 (s, 5 H, Cp), 2.59 (q, $^3J_{HH}$ = 7.5 Hz, 2 H, $C\mathit{H}_2CH_3$), 2.54 (q, $^3J_{HH}$ = 6.5 Hz, 1 H, $ZrC\mathit{H}(CH_3)$), 1.75 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, $ZrCH(C\mathit{H}_3)$), 1.34 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, $CH_2C\mathit{H}_3$); ^{13}C NMR (CD_2Cl_2) δ 319.8 (Zr*C*O).

Scheme II



Zr–enolate species. Treatment of the complex decomposition mixture of **3** with $(PhCH_2)(Et)_3N^+Cl^-$ affords $Cp_2Zr(OCH{=}C\{Me\}\{6\text{-ethylpyrid-2-yl}\})Cl$ (**10**),[36] establishing that **9** decomposes to a mixture of isomeric/oligomeric zirconocene–enolate species. Hydrolysis of the decomposition mixture of **3** affords a mixture of thermally sensitive tautomers, enol **11**/aldehyde **11'**, which were unambiguously characterized by NMR, FTIR, and mass spectroscopy.

These observations are most consistent with a decomposition mechanism (Scheme II) which involves initial CO insertion into the Zr–C bond followed by a 1,2-H shift to afford a mixture of isomeric/oligomeric zirconocene–enolates, the hydrolysis of which affords the enol/aldehyde tautomers. Similar acyl/enolate rearrangements have been reported for acyl and iminoacyl complexes of early transition metals.[37]

Summary

Carbonylation of the four-membered cationic azazirconacycle **2** yields the d^0 carbonyl complex $Cp_2Zr\{CH(Me)(6\text{-ethylpyrid-2-yl})\}(CO)^+$ (**3**).[38] IR and NMR data establish that **3** contains a terminal CO ligand, and comparison of the data of **3** to data for related adducts **4**–**6** and other MCH(R)py complexes **7** and **8** establishes that the ZrCH(Me)(6-ethylpyrid-2-yl) ligand adopts a chelated structure. By analogy to the structure of neutral chloride derivative **6**, the CO ligand of **3** is likely to be cis to the Zr–C, although this was not conclusively established. Other than the Zr–Ru bonded species $Cp_2Zr(CO)(\mu\text{-}\sigma,\pi\text{-}C_5H_4)Ru(CO)_2$, **3** is the only known d^0 carbonyl complex containing a σ-hydrocarbyl ligand. The lowering of ν_{CO} for **3** from the free CO value is ascribed to back-bonding from the *Zr–C*H(Me)(py) bonding orbital to the CO π^*-orbital, analogous to the back-bonding interactions proposed to explain the low ν_{CO} values for $Cp^*_2MH_2(CO)$ (M = Zr, Hf). EHMO calculations indeed indicate significant $Zr\text{–}CH_3/\pi^*$ overlap in the lateral isomer of $Cp_2ZrR_2(CO)$.[3] The higher ν_{CO} value for **3** vs $Cp^*_2MH_2(CO)$ is consistent with a difference in charge; i.e., σ-donation should be stronger and back-bonding to the CO π^*-orbital weaker for cationic **3** than for neutral $Cp^*_2MH_2(CO)$. Furthermore, back-bonding from only one bonding orbital is possible for **3**. The most surprising feature of the carbonylation chemistry described here is that **3** is stable enough to be observed and characterized. The slow CO insertion of **3** may be linked to the chelated structure of the CH(Me)(6-ethylpyrid-2-yl) ligand and/or the steric crowding at the migrating secondary carbon.[39] This work suggests several strategies for the synthesis of stable/observable d^0 metal olefin/alkyne complexes, which we are actively pursuing.

Experimental Section

General. All manipulations were performed under nitrogen atmosphere or vacuum, using a Vacuum Atmospheres Drybox, Schlenk techniques, or a high-vacuum line. CH_2Cl_2 was distilled from CaH_2. Hexane was distilled from Na/benzophenone. CH_3CN and ^{t}BuCN were predried with 4-Å molecular sieves, distilled from CaH_2, and stored over 4-Å molecular sieves. CD_2Cl_2 was distilled from P_2O_5. All solvents were stored in evacuated bulbs and vacuum transferred into reaction flasks or NMR tubes. 2,6-Diethylpyridine was vacuum distilled and stored over molecular sieves. CO and ^{13}CO (99.9% ^{13}C) were purchased from Air Products and MSD Isotopes, respectively. NMR spectra were recorded on Bruker AC-300 or AMX-360 MHz spectrometers in sealed tubes. ^1H and ^{13}C chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^1H NMR couplings were identified via homonuclear decoupling experiments in cases where they were not readily apparent. ^{13}C NMR assignments are based on DEPT and gated $\{^1H\}$ experiments and comparisons to data of related compounds. All spectra of cationic complexes exhibited normal BPh_4^- resonances: ^1H NMR (CD_2Cl_2) δ 7.35 (m, 8 H), 7.05 (t, J = 7.4 Hz, 8 H), 6.90 (t, J = 7.4 Hz, 4 H); ^{13}C NMR (CD_2Cl_2) δ 165.4 (q, J = 49.3 Hz), 136.6, 126.0, 122.2. FTIR spectra were recorded on a Mattson Cygnus 25 spectrometer. Mass spectral analyses were performed on a VG Trio-1 benchtop GC–MS; the relative intensities are reported in parentheses. Elemental analyses were performed by E & R Laboratories Inc. $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (**1**) was prepared as described in ref 14h.

$[Cp_2Zr(\eta^2\text{-}C,N\text{-}CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})][BPh_4]$ (2). To a slurry of **1** (200 mg, 0.319 mmol) in CH_2Cl_2 (7 mL) was added 2,6-diethylpyridine (86 mg, 0.638 mmol). The mixture was stirred at 23 °C for 10 min, resulting in a clear purple solution. The solution was stirred for 24 h at 23 °C and then filtered through a glass wool plug. Hexane (~10 mL) was added to the filtrate to induce slow precipitation of the product. The purple solid was separated by filtration, washed with hexane (3 × 10 mL), and dried in vacuo (yield 191 mg, 89%). **2**: ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 7.88 (t, J = 7.9 Hz, 1 H, para py-H), 7.30 (d, J = 8.0 Hz, 1 H, meta py-H), 7.05 (obscured by BPh_4^-, 1 H, meta py-H), 6.63 (s, 5 H, Cp), 6.01 (s, 5 H, Cp), 3.97 (q, $^3J_{HH}$ = 6.5 Hz, 1 H, $ZrCH(CH_3)$), 2.16 (sextet (overlapping doublet of quartets), $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.08 (sextet (overlapping doublet of quartets), $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 1.75 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, $ZrCH(CH_3)$), 1.03 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, 23 °C) δ 163.0 (ortho py-C), 157.8 (ortho py-C), 143.0 (para py-C), 119.8 (meta py-C), 119.7 (meta py-C), 117.5 (Cp), 116.6 (Cp), 51.7 ($ZrCH(CH_3)$, $^1J_{CH}$ = 133 Hz), 32.1 (CH_2CH_3), 17.7, 14.5. Anal. Calcd for $C_{43}H_{42}BNZr$: C, 76.53; H, 6.27; N, 2.08. Found: C, 76.26; H, 6.34; N, 2.02.

(36) Complex **10** was obtained as a ca. 12:1 mixture of cis/trans (olefin geometry) isomers. Key spectroscopic data: major isomer, ^1H NMR ($C_6D_2Cl_2$) δ 8.26 (q, $^3J_{HH}$ = 1.3 Hz, 1 H, $ZrOCH{=}CCH_3$), 7.17 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, meta py-H), 6.90 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, meta py-H), 6.65 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, meta py-H), 5.89 (s, 10 C, Cp-H), 2.81 (q, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2CH_3), 2.15 (d, $^3J_{HH}$ = 1.3 Hz, 3 H, $=C(CH_3)$), 1.32 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3); minor isomer, ^1H NMR (CD_2Cl_2) δ 8.38 (q, $^3J_{HH}$ = 1.3 Hz, 1 H, $ZrOCH{=}CCH_3$), 2.21 (d, $^3J_{HH}$ = 1.3 Hz, 3 H, $=C(CH_3)$).

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(38) **2** also reacts with excess ^{t}BuNC at 25 °C to form a metastable d^0 isocyanide adduct (analogous to **3**), which undergoes insertion ($t_{1/2}$ < 15 min) to yield an iminoacyl/isocyanide complex. $Cp_2Zr(CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})(^t\text{BuNC})^+$: ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 7.68 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, para py-H), 7.05 (obscured by BPh_4^-, 1 H, meta py-H), 6.81 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, meta py-H), 6.18 (s, 5 H, Cp), 5.34 (s, 5 H, Cp), 2.78 (m, 2 H, CH_2CH_3), 2.10 (q, $^3J_{HH}$ = 6.2 Hz, 1 H, $ZrCH(CH_3)$), 1.69 (s, 9 H, coordinated $(CH_3)_3CNC$), 1.68 (obscured by $(CH_3)_3CNC$, 3 H, $ZrCH(CH_3)$), 1.42 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_2CH_3). $Cp_2Zr(C\{N\text{-}^t\text{Bu}\}CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})(^t\text{BuNC})^+$: ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 7.70 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, para py-H), 7.19 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, meta py-H), 7.15 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, meta py-H), 5.89 (s, 5 H, Cp), 5.43 (s, 5 H, Cp), 4.86 (q, $^3J_{HH}$ = 7.0 Hz, 1 H, $CH(CH_3)$), 2.87 (q, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2CH_3), 1.78 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, $CH(CH_3)$), 1.67 (s, 9 H, coordinated $(CH_3)_3CNC$), 1.34 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 1.34 (s, 9 H, $Zr(C{=}NC(CH_3)_3)$).

(39) Unlike the primary zirconocene alkyl/pyridine complex $Cp_2Zr(\eta^2\text{-}C,N\text{-}CH_2\{6\text{-methylpyridyl-2-yl}\})^+$ (ref 16b), **3** does not insert olefins, terminal alkynes, or nitriles. Guram, A. S.; Jordan, R. F. Unpublished results.

[$Cp_2Zr(CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})(CO)][BPh_4]$ (3). An NMR tube containing a purple solution of **2** (36 mg, 0.053 mmol) in CD_2Cl_2 (0.3 mL) was charged with CO (~1 atm) via vacuum transfer at −197 °C. The tube was warmed to 0 °C to afford a bright yellow solution of thermally unstable **3** (yield: 100% by NMR). Complex **3** could not be isolated as a solid and was characterized in solution. Hydrolysis of **3** at −78 °C gave 2,6-diethylpyridine (97% yield by NMR), which was characterized by comparison of its ^1H NMR spectrum with that of a commercially available sample. **3**: ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 7.79 (t, J = 7.9 Hz, 1 H, para py-H), 7.05 (obscured by BPh_4^-, 1 H, meta py-H), 6.91 (obscured by BPh_4^-, 1 H, meta py-H), 6.14 (s, 5 H, Cp), 5.34 (s, 5 H, Cp), 2.69 (q, $^3J_{HH}$ = 7.5 Hz, 2 H, CH_2CH_3), 2.19 (q, $^3J_{HH}$ = 6.5 Hz, 1 H, $ZrCH(CH_3)$), 1.75 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, $ZrCH(CH_3)$), 1.41 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_2CH_3); ^1H NMR (360 MHz, CD_2Cl_2, −23 °C) δ 7.79 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, para py-H), 7.05 (obscured by BPh_4^-, 1 H, meta py-H), 6.91 (obscured by BPh_4^-, 1 H, meta py-H), 6.12 (s, 5 H, Cp), 5.29 (s, 5 H, Cp), 2.68 (multiplet (overlapping doublet of quartets for each H), 2 H, CH_2CH_3), 2.14 (q, $^3J_{HH}$ = 6.4 Hz, 1 H, $ZrCH(CH_3)$), 1.73 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, $ZrCH(CH_3)$), 1.39 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_2CH_3). ^{13}C NMR (90 MHz, CD_2Cl_2, −40 °C) δ 206.1 (CO), 164.3 (ortho py-C), 162.8 (ortho py-C), 142.4 (para py-C), 116.1 (meta py-C), 114.0 (meta py-C), 109.8 (Cp), 107.7 (Cp), 30.5, (29.1, 29.0, 28.9) (three rotamers of CH_2CH_3), 15.1, (12.5, 12.4, 12.3) (three rotamers of CH_2CH_3); FTIR (CH_2Cl_2, 0.1 mm NaCl cell) ν_{CO} 2095 cm^{-1}.

[$Cp_2Zr(CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})(^{13}CO)][BPh_4]$ (3-^{13}CO). This thermally sensitive complex was prepared from the reaction of **2** with ^{13}CO using the procedure described for the preparation of **3** (yield: 100% by NMR). **3**-^{13}CO: ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 7.79 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, para py-H), 7.05 (obscured by BPh_4^-, 1 H, meta py-H), 6.91 (obscured by BPh_4^-, 1 H, meta py-H), 6.14 (s, 5 H, Cp), 5.34 (s, 5 H, Cp), 2.69 (q, $^3J_{HH}$ = 7.5 Hz, 2 H, CH_2CH_3), 2.19 (q, $^3J_{HH}$ = 6.5 Hz, 1 H, $ZrCH(CH_3)$), 1.75 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, $ZrCH(CH_3)$), 1.41 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_2CH_3); ^1H NMR (360 MHz, CD_2Cl_2, −40 °C) δ 7.78 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, para py-H), 7.05 (obscured by BPh_4^-, 1 H, meta py-H), 6.93 (obscured by BPh_4^-, 1 H, meta py-H), 6.08 (s, 5 H, Cp), 5.24 (s, 5 H, Cp), 2.68 (multiplet (overlapping doublet of quartets of each H), 2 H, CH_2CH_3), 2.12 (q, $^3J_{HH}$ = 6.4 Hz, 1 H, $ZrCH(CH_3)$), 1.72 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, $ZrCH(CH_3)$), 1.39 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_2CH_3); ^{13}C NMR (90 MHz, CD_2Cl_2 −40 °C) δ 206.1 (CO), 164.4 (ortho py-C), 162.8 (ortho py-C), 142.5 (para py-C), 116.2 (meta py-C), 114.1 (meta py-C), 109.9 (Cp), 107.9 (Cp), 30.6 (slightly broadened), (29.1, 29.0, 28.9) (three rotamers of CH_2CH_3), 15.2, (12.6, 12.5, 12.4) (three rotamers of CH_2CH_3); FTIR (CH_2Cl_2, 0.1 mm NaCl cell) ν_{CO} 2048 cm^{-1}.

[$Cp_2Zr(CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})(CH_3CN)][BPh_4]$ (4). Method A. To a purple solution of complex **2** (50 mg, 0.074 mmol) in CH_2Cl_2 was added CH_3CN (~14 mg, 0.342 mmol). The reaction mixture was shaken for 5 s to give a bright yellow solution. Solvent and excess CH_3CN were removed under vacuum, and the yellow solid was dried under vacuum for 3 h to afford complex **4** in a quantitative yield. This sample was used for elemental analysis, ^1H NMR, and FTIR studies.

Method B. Excess CH_3CN (0.2 mL) was directly added to solid **2** (20 mg, 0.30 mmol). The resulting bright yellow solution was allowed to stand at 23 °C for 1 min. Excess CH_3CN was removed under vacuum to afford complex **4** in a quantitative yield. Isolated **4** contained 0.4–0.5 excess equiv of CH_3CN which could not be removed even on extended periods of vacuum drying. This sample was used for ^{13}C NMR studies. **4**: ^1H NMR (300 MHz, CD_2Cl_2, 23 °C) δ 7.70 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, para py-H), 6.92 (obscured by BPh_4^-, 2 H, meta py-H's), 6.28 (s, 5 H, Cp), 5.50 (s, 5 H, Cp), 2.66 (m, 2 H, CH_2CH_3), 2.45 (q, $^3J_{HH}$ = 6.1 Hz, 1 H, $ZrCH(CH_3)$), 1.87 (s, 3 H, coordinated CH_3CN), 1.53 (d, $^3J_{HH}$ = 6.2 Hz, 3 H, $ZrCH(CH_3)$), 1.38 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_2CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, 23 °C) δ 164.3 (ortho py-C), 163.5 (ortho py-C), 141.0 (para py-C), 115.6 (meta py-C), 114.3 (meta py-C), 113.0 (Cp), 111.8 (Cp), 37.2 ($CH(CH_3)$, $^1J_{CH}$ = 136 Hz), 29.7 (CH_2CH_3), 15.7 (CH_2CH_3), 13.5 ($C(H)CH_3$), 2.81 (CH_3CN), CN resonance not observed; FTIR (KBr pellet) ν_{CN} 2307, 2278 cm^{-1}. Anal. Calcd for $C_{45}H_{45}BN_2Zr$: C, 75.50; H, 6.34; N, 3.91. Found: C, 75.37; H, 6.37; N, 4.17.

[$Cp_2Zr(CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})(^tBu\text{-}CN)][BPh_4]$ (5). Complex **5** was isolated as a yellow oil in a quantitative yield from the reaction of **2** with ^tBuCN. The methods described for the preparation of **4** were used here with analogous results. **5**: ^1H NMR (300 MHz, CD_2Cl_2, 23 °C) δ 7.71 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, para py-H), 6.92 (obscured by BPh_4^-, 2 H, meta py-H's), 6.28 (s, 5 H, Cp), 5.50 (s, 5 H, Cp), 2.67 (m, 2 H, CH_2CH_3), 2.44 (q, $^3J_{HH}$ = 6.1 Hz, 1 H, $ZrCH(CH_3)$), 1.59 (d, $^3J_{HH}$ = 6.2 Hz, 3 H, $ZrCH(CH_3)$), 1.50 (s, 9 H, coordinated $(CH_3)_3CCN$), 1.39 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, 23 °C) δ 164.2 (ortho py-C), 163.4 (ortho py-C), 141.1 (para py-C), 115.7 (meta py-C), 114.3 (meta py-C), 113.1 (Cp), 111.8 (Cp), 36.3 ($CH(CH_3)$, $^1J_{CH}$ = 136 Hz), 29.6 (CH_2CH_3), 28.0 ($C(CH_3)_3$), 15.6 (CH_2CH_3), 13.5 ($C(H)CH_3$), 2.81 (CH_3CN), ($CH_3)_3CCN$ resonances were not found even after 18 000 scans; FTIR (KBr pellet) ν_{CN} 2264, 2232 cm^{-1}. Anal. Calcd for $C_{48}H_{51}BN_2Zr$: C, 76.06; H, 6.78; N, 3.70. Found: C, 75.99; H, 6.95; N, 3.52.

$Cp_2Zr(CH\{CH_3\}\{6\text{-ethylpyrid-2-yl}\})Cl$ (6). To a purple solution of **2** (135 mg, 0.200 mmol) in CH_2Cl_2 was added solid $[(PhCH_2)Et_3N]Cl$ (70 mg, 0.308 mmol). The reaction mixture was stirred for 5 min to afford a bright yellow solution. CH_2Cl_2 was removed under vacuum, and the residue was extracted with toluene (3 × 3 mL). The extract was filtered through glass wool, layered with pentane (4 mL), and allowed to stand in the freezer overnight to afford **6** as a yellow crystalline solid (yield: 59 mg, 76%). This sample was used for X-ray diffraction analysis and NMR studies. A second crop (11 mg) was collected from the mother liquor by adding pentane (5 mL) and cooling. **6**: ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 7.51 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, para py-H), 6.74 (d, $^3J_{HH}$ = 8.2 Hz, meta py-H's), 6.68 (d, $^3J_{HH}$ = 7.4 Hz, meta py-H's), 6.11 (s, 5 H, Cp), 5.69 (s, 5 H, Cp), 2.92 (sextet (overlapping doublet of quartets), $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.76 (sextet (overlapping doublet of quartets), $^3J_{HH}$ = 7.6 Hz, 1 H, CH_2CH_3), 2.52 (q, $^3J_{HH}$ = 6.1 Hz, 1 H, $ZrCH(CH_3)$), 1.62 (d, $^3J_{HH}$ = 6.1 Hz, 3 H, $ZrCH(CH_3)$), 1.32 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2 23 °C) δ 167.3 (ortho py-C), 164.6 (ortho py-C), 139.0 (para py-C), 116.5 (meta py-C), 113.4 (Cp), 113.3 (meta py-C), 111.5 (Cp), 43.9 ($CH(CH_3)$, $^1J_{CH}$ = 134 Hz), 29.8 (CH_2CH_3), 15.6 (CH_2CH_3), 13.8 ($C(H)CH_3$).

X-ray Analysis. Crystals of **6** were grown by cooling a concentrated toluene/pentane solution and sealed in capillaries under N_2. Details of the X-ray analysis are summarized in Table II.

Enol 11/Aldehyde 11′. An NMR tube containing a purple solution of **2** (20 mg, 0.030 mmol) in CD_2Cl_2 (0.3 mL) was charged with CO (~3 atm) via vacuum transfer at −197 °C. The tube was warmed to 0 °C to afford a bright yellow solution of thermally unstable **3** (yield: 100% by NMR). This solution was allowed to stand at 23 °C for 2 days. To the resulting red solution was added 1 drop of H_2O, and the two-phase mixture was shaken for 5 min at 23 °C to afford a yellow organic phase. Purification of the organic phase by low-temperature (−78 °C) column chromatography on alumina using pentane and then EtOAc as eluents gave a mixture of unstable tautomers **11** and **11′** (yellow oil; yield 3.1 mg, 63%; ratio ~7:1). Enol (**11**): ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 14.8 (br, 1 H, OH), 7.66 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, para py-H), 7.02 (br d, J_{HH} ca. 1 Hz, 1 H, $=CH(OH)$), 6.96 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, meta py-H), 6.90 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, meta py-H), 2.80 (q, $^3J_{HH}$ = 7.6 Hz, 2 H, CH_2CH_3), 1.86 (d, $^4J_{HH}$ = 1.2 Hz, 3 H, $CH(CH_3)$), 1.30 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3); ^{13}C NMR (90 MHz, CD_2Cl_2, 23 °C) δ 153.4 (=CH(OH)), 138.0 (para py-C), 118.4 (meta py-C), 116.2 (meta py-C), 30.7 (CH_2CH_3), 14.9 (CH_3), 13.3 (CH_3) (the low concentration of sample used for prevention of decomposition precluded identification of the three quaternary carbons); FTIR (NaCl film) ν_{OH} 3356 cm^{-1}. Aldehyde (**11′**): ^1H NMR (360 MHz, CD_2Cl_2, 23 °C) δ 9.81 (d, $^3J_{HH}$ = 1.2 Hz, 1 H, CH=O), 7.60 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, para py-H), 7.07 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, meta py-H), 7.02 (d (partially obscured by enol $CH(OH)=$), 1 H, meta py-H), 3.74 (quartet of doublets, $^3J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1 H, $CH(CH_3)CHO$), 2.79 (obscured by enol CH_2, 2 H, CH_2CH_3), 1.43 (d, $^3J_{HH}$ = 7.1 Hz, 3 H, $CH(CH_3)$), 1.27 (t, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3); FTIR (NaCl film) $\nu_{HC=O}$ 1734 cm^{-1}; MS (EI, 70 eV) m/e 163 (6) {molecular ion}, 162 (7) {M − 1}, 135 (55), 134 (100) {base peak, M − CH_2CH_3}, 119 (26), 84 (15), 77 (14), 49 (18).

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Supplementary Material Available: Tables of complete bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and positional parameters for **6** (6 pages); table of observed and calculated structure factors for **6** (10 pages). Ordering information is given on any current masthead page.