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Synthesis and Insertion Chemistry of Cationic Zirconium(IV) Pyridyl Complexes. Productive σ-Bond Metathesis

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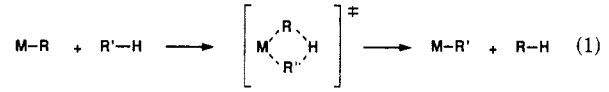
The reaction of $Cp_2Zr(CH_3)(THF)^+$ (1) with pyridine produces CH_4 and a mixture of $Cp_2Zr(\eta^2$-N,C-pyridyl)$(THF)^+$ (2) and $Cp_2Zr(\eta^2$-N,C-pyridyl)(pyridine)$^+$ (3) via ortho-C-H bond activation. Complex 2 is converted to 3 by reaction with excess pyridine. Complex 1 reacts similarly with 2-methylpyridine (α-picoline) to yield the picolyl complex $Cp_2Zr\{\eta^2$-N,C-$NC_5H_3(6\text{-Me})\}(THF)^+$ (6). An intermediate picoline adduct $Cp_2Zr(CH_3)$(picoline)$^+$ (7a) is observed in this reaction. Low-temperature NMR studies of 7a and the $(C_5H_4Me)_2Zr$ analogue 7b reveal a high-field ^1H shift and a reduced J_{C-H} for the ortho C-H of the coordinated picoline suggestive of an agostic interaction. The three-membered Zr-N-C ring structures of 2, 3, and 6 are assigned on the basis of ^1H and ^{13}C NMR spectral data and confirmed by X-ray crystallographic analysis of $Cp_2Zr\{\eta^2$-N,C-$NC_5H_3(6\text{-Me})\}(PMe_3)^+$ (8), which is formed by reaction of 6 with PMe_3. Complex 8 crystallizes in space group Cc with a = 9.571 (4) Å, b = 17.524 (11) Å, c = 21.861 (7) Å, β = 92.55 (3)°, V = 3662.9 (5.1) Å^3, and Z = 4. The picolyl ligand of 8 lies in the plane between the two Cp ligands, and the Zr-C (2.29 (2) Å) and Zr-N (2.21 (1) Å) bond lengths are similar. Complex 6 reacts readily with ethylene, propylene, and 2-butyne to yield insertion products 9-11, which have five-membered chelate ring structures. These reactions proceed via initial THF dissociation from 6 followed by coordination of substrate and insertion into the Zr-C bond. Complex 9 crystallizes in space group $P\bar{1}$ with a = 10.387 (2) Å, b = 12.129 (3) Å, c = 13.844 (4) Å, α = 87.78 (2)°, β = 76.37 (2)°, γ = 76.63 (2)°, V = 1648.8 (9) Å^3, and Z = 2. The chelate ring of 9 is relatively unstrained. Complexes 9 and 10 react with CH_3CN to yield 2-ethenyl-6-methylpyridine and 2-(1-methylethenyl)-6-methylpyridine (14), respectively, and $Cp_2Zr(N{=}CHMe)(CH_3CN)^+$ (13). These reactions proceed by ligand-induced ring opening, β-H elimination, and trapping of the Zr-H product by CH_3CN insertion. Complex 10 reacts similarly with PMe_3 to yield 14 and $Cp_2Zr(H)(PMe_3)_2^+$ (17) via ring opening, β-H elimination, and trapping of the Zr-H product by PMe_3 coordination. These Zr-mediated olefin/picoline coupling reactions illustrate how productive reaction schemes may be constructed by combining σ-bond metathesis, insertion, and β-H elimination reactions.

Electrophilic, d^0 and d^0f^n Cp^*_2MR ($Cp^* = C_5Me_5$, M = group III, lanthanide) complexes exhibit a rich C-H activation/σ-bond metathesis chemistry (eq 1) in which C-H



(1)

R, R' = H, alkyl, aryl, etc.

bonds of a variety of substrates are activated.[1,2] Facile H-H activation chemistry has been observed for cationic Zr(IV) complexes $Cp_2Zr(R)(L)^+$ ($Cp = C_5H_5$, L = two-electron donor), and more recently ligand and counterion C-H bond activations have been observed for these systems.[3,4] These reactions are believed to involve four-center transition states that are accessed by initial coordination of the H-H or C-H bond to the electrophilic metal center (eq 1).[5,6] This chemistry is of great potential utility in catalysis because the Cp^*_2MR' and $Cp_2M(R')(L)^+$ complexes formed by σ-bond metathesis undergo a variety of insertion, elimination, and ligand-exchange reactions to which the σ-bond metathesis chemistry might be coupled. For example, several Cp^*_2MR systems catalyze the dimerization of terminal acetylenes by a mechanism involving σ-bond metathesis and insertion.[1e,f] We recently reported that $Cp_2Zr(R)(L)^+$ complexes catalyze the coupling of olefins with α-picoline by a process involving σ-bond metathesis, insertion, Zr-R bond hydrogenolysis, and ligand exchange.[4a,7] In contrast, the 18-electron complexes $L_nM(R)(H)$, produced by C-H oxidative addition reactions of 16-electron fragments L_nM (generated photochemically or thermally), usually are resistant to insertion, β-H elim-

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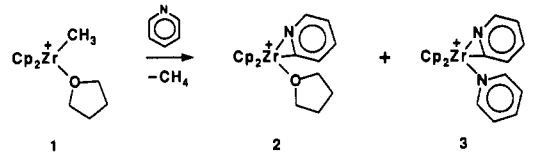
ination, and other reactions.[8]

Our initial efforts to develop the σ-bond metathesis chemistry of $Cp_2Zr(R)(L)^+$ complexes have focused on reactions of C–H bonds of the ligand L. Activation of hydrocarbon C–H bonds by these systems seems less likely due to the presence of the more reactive C–H bonds of L and the BPh_4^- counterion. In extensive studies of $Cp_2Zr(R)(THF)^+$ complexes we have seen no evidence for activation of the THF C–H bonds.[9] This lack of reactivity is a result of a combination of steric and electronic factors that inhibit initial coordination of the THF C–H bonds in these systems. X-ray diffraction studies[9b,f] show that in the solid state the THF ligands of $Cp_2Zr(CH_3)(THF)^+$ (1) and $Cp'_2Zr[(Z)\text{-}C(Me)=C(Me)(^nPr)](THF)^+$ ($Cp' = C_5H_4Me$) are in orientations that place their α-C–H bonds out of the plane that is between the two Cp ligands and in which the Zr LUMO is localized.[10] Moreover, the short Zr–O bond and the perpendicular orientation of the THF ligand in 1,[9b] along with chemical reactivity trends,[3] are consistent with significant O–Zr π-bonding. Such π-bonding would utilize the Zr orbital required for ligand C–H bond activation. This analysis suggests that ligand C–H bond activation should be favored in this system for ligands that (i) coordinate in a manner that orients a ligand C–H bond in the plane containing the Zr–LUMO and (ii) are two-electron donors. With these considerations in mind, we initiated a study of the reactions of 1 with pyridine and related heteroaromatic substrates. This paper describes reactions of 1 with pyridine and 2-methylpyridine (α-picoline) that proceed by σ-bond metathesis/orthometalation leading to η^2-N,C-pyridyl complexes with reactive, three-membered Zr–C–N rings. These reactions can be coupled with insertion and β-H elimination reactions into productive, though stoichiometric, σ-bond metathesis reaction schemes. This chemistry also provides the basis for catalytic, productive σ-bond metathesis reactions.[4a,11] In a succeeding paper, the scope and regioselectivity of this ligand C–H activation chemistry is addressed in a study of the reactions of 1 with a more extensive series of heteroaromatic substrates.[12]

Results

Cationic Cp_2Zr^{IV} Pyridyl Complexes. The cationic methyl complex $Cp_2Zr(CH_3)(THF)^+$ (1)[13] reacts with pyridine at 40–60 °C in THF or CH_2ClCH_2Cl solvent to yield CH_4, a mixture of η^2-pyridyl complexes $Cp_2Zr(\eta^2\text{-}N,C\text{-pyridyl})(THF)^+$ (2) and $Cp_2Zr(\eta^2\text{-}N,C\text{-pyridyl})(py)^+$ (3), and several unidentified Zr products (eq 2). Despite

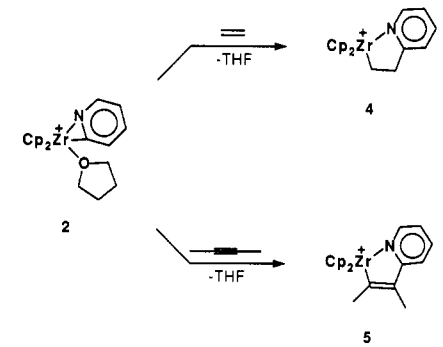


(2)

careful control of reaction stoichiometry and several recrystallizations, THF complex 2 was obtained in only ca. 85% purity; as a result this species was characterized by ^1H NMR spectroscopy only.[14] However, pyridine complex 3 was obtained in pure form by reaction of 1 with neat pyridine or by reaction of the product mixture of eq 2 with pyridine. The pyridine ligand of 3 is not displaced by THF, even in neat THF.

The ^1H and ^{13}C NMR spectra of 3 (Table I) establish the presence of pyridyl and pyridine rings and indicate that only one isomer is present. These data are similar to data for related d^0 pyridyl complexes $Cp^*_2M(\eta^2\text{-}N,C\text{-}NC_5H_4)$ (M = Y, Sc, Lu),[1a,e,f] the latter two of which have been characterized by X-ray crystallography, and $Cp^*HfCl_2(\eta^2\text{-}N,C\text{-}NC_5H_4)$.[15] The ^{13}C spectrum of 3 features a characteristic downfield signal (δ 200.9) for the ipso carbon. It was possible to assign all the resonances in the ^1H spectrum by homonuclear decoupling experiments. At both ambient temperature and −95 °C, only single resonances for the meta and ortho pyridine hydrogens are observed. This is consistent with a structure in which the pyridine ring is perpendicular to the plane between the two Cp ligands or with rapid rotation of the pyridine ring about the Zr–N bond. The structures shown for 2 and 3 are anticipated to be the most stable on the basis of the X-ray structure of 8 (vide infra). In the presence of excess pyridine at ambient temperature, separate ^1H resonances are observed for free and coordinated (1 equiv) pyridine. This establishes that exchange of free and coordinated pyridine is slow on the NMR time scale and that the three-membered Zr–N–C ring is not opened by the coordination of a second pyridine ligand.

In exploratory NMR scale reactions, mixtures of 2 and 3 obtained from eq 2 were reacted with ethylene (1 atm) or excess 2-butyne in CD_2Cl_2 at 23 °C. In both cases THF complex 2 reacted rapidly, yielding compounds whose NMR spectra are consistent with insertion products 4 and 5, respectively (eq 3),[16] while pyridine complex 3 did not react.



(3)

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(13) The counterion is BPh_4^- in all cases.

(14) ^1H NMR of 2 (CD_2Cl_2, 90 MHz, BPh_4^- resonances excluded) δ 7.6–8.3 (m, 4 H), 5.91 (s, 10 H), 3.97 (m, 4 H), 2.03 (m, 4 H).

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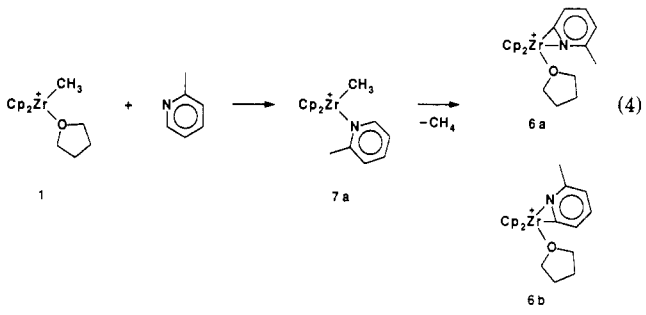
(16) (a) ^1H NMR of 4 (CD_2Cl_2, 90 MHz) δ 6.8–7.6 (m, BPh_4^-), 6.32 (s, 10 H), 3.51 (t, J = 6.9 Hz, 2 H), 1.77 (t, J = 6.9 Hz, 2 H, NC_5H_4 obscured). ^1H NMR for 5 (CD_2Cl_2, 90 MHz) δ 6.8–7.6 (m, BPh_4^-), 6.40 (s, 10 H), 1.94 (q, J = 0.8 Hz, 3 H), 1.70 (q, J = 0.8 Hz, 3 H), NC_5H_4 obscured. (b) Isolation and full characterization of 4 and 5 were precluded by the presence of unreacted 3.

These initial results establish that **1** undergoes σ-bond metathesis reactions with pyridine C–H bonds and that the resulting $Cp_2Zr(\eta^2\text{-N,C-pyridyl})(L)^+$ complexes undergo insertion chemistry provided L is sufficiently labile (i.e., THF, not py). At this point we redirected our attention to reactions of **1** with 2-methylpyridine (α-picoline) with the expectations that this ligand would be more labile than pyridine due to steric effects and that formation of an (unreactive) analogue of **3** would be avoided.

Reaction of 1 with α-Picoline. Complex **1** reacts rapidly ($t_{1/2}$ ca. 6 min) with a slight excess of α-picoline in CH_2Cl_2 solution at 23 °C to produce $Cp_2Zr(\eta^2\text{-N,C-picolyl})(THF)^+$ (**6**, 87%) and CH_4 (1 equiv, Toepler pump), eq 4. ^1H NMR monitoring of this reaction in CD_2Cl_2



(4)

reveals the liberation of free THF and the formation of picoline adduct **7a** prior to aryl C–H activation.

Complex **6** is isolated by crystallization from THF with no contamination by the picolyl picoline analogue of **3**. The ^1H and ^{13}C NMR spectra of **6** exhibit two complete sets of Cp, picolyl, and THF resonances consistent with the presence of two isomers, **6a** and **6b**, in a 1/1 ratio. The presence of characteristic low-field ^{13}C ipso carbon resonances (δ 201.6 and 186.3) and the absence of ^1H ortho H resonances establish that both isomers contain η^2-N,C-picolyl ligands. The two isomers thus must differ in the position of coordinated THF as shown in eq 4. Both interconversion of isomers **6a** and **6b** and exchange of coordinated and free THF are slow on the NMR time scale at 23 °C but rapid at 66 °C. The observed ratio of **6a**/**6b** is the thermodynamic ratio as it does not change after weeks at ambient temperature or after heating to 66 °C and cooling.

Complex **6** is sparingly soluble in THF but more soluble in CH_2Cl_2 and CH_2ClCH_2Cl. As a result of the η^2-pyridyl structure, it is more stable in the latter solvents than are simple alkyl complexes $Cp_2Zr(R)(THF)^+$,[9] decomposing only slowly in CH_2Cl_2 ($t_{1/2}$ ca. 20 days, 40 °C) to a mixture of Cp_2ZrCl_2 and a product formulated as $Cp_2Zr(picolyl)(Cl)$ by ^1H NMR (two isomers).[17] A complex identical by ^1H NMR to the major isomer of the latter species is formed rapidly by reaction of **6** with $[NEt_3CH_2Ph]Cl$ or $[N^nBu_4]Cl$ in CD_2Cl_2 at 23 °C.

Solution Structures of $Cp_2Zr(CH_3)(picoline)^+$ (7a) and $Cp'_2Zr(CH_3)(picoline)^+$ (7b). It is clear that the interaction of the ortho-C–H bond of the picoline ligand with the unsaturated Zr(IV) center at some point along the reaction coordinate is important for C–H activation and CH_4 elimination in eq 4. Intermediate **7a** and the analogous $(C_5H_4Me)_2Zr$ species **7b** were studied in detail by NMR spectroscopy at low temperature (−85 to −50 °C, Table I) to determine if these complexes adopt agostic ground-state structures.[18] The data suggest but do not prove that weak agostic interactions between the picoline ortho-C–H bonds and the Zr center are present in these species.

Analysis of NMR spectroscopic data for d^0 metal pyridine complexes in which agostic interactions involving the ortho-C–H bonds are ruled out by X-ray crystallography or are precluded by the 18-electron count at the metal center reveals that in general (i) the ^1H and ^{13}C resonances for the ortho-C–H remain essentially unchanged or shift downfield slightly upon coordination and (ii) $J_{C\text{-}H}$ increases by 3–10 Hz. For example, the ^1H and ^{13}C py ortho C–H resonances for cationic 18-electron complex **3** (Table I) are shifted downfield by 0.07 and 2.0 ppm, respectively, and $J_{C\text{-}H}$ is increased by 5.0 Hz vs free pyridine.[19] Similarly, for the 18-electron complex $Cp_2Zr(CH_3)(4,4'\text{-}Me_2bipy)^+$, the ortho C–H ^1H and ^{13}C resonances are shifted only slightly and $J_{C\text{-}H}$ is increased by 3 and 5 Hz vs the free ligand.[20,21] In contrast, for **7a** and **7b**, the α-picoline ortho-C–H ^1H resonance is shifted *upfield* by 0.98 and 0.97 ppm, respectively, and the ^{13}C resonance is shifted *upfield* by 7 ppm vs those of free picoline.[22] We recently reported that $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$ complexes have β-agostic structures[23] and that the β-CH_2R resonances are shifted upfield by 1–4 ppm and the β-C resonances shift upfield by 20–25 ppm from the corresponding resonances of the THF complexes, $Cp'_2Zr(CH_2CH_2R)(THF)^+$, which have normal, undistorted structures.[9] By analogy, the upfield ^1H and ^{13}C shifts of the ortho C–H groups of **7a** and **7b** suggest the presence of agostic interactions in these cases. Low-temperature spectra of **7a** and **7b** exhibit only single Cp or $C_5H_4CH_3$ resonances consistent with the in-plane orientation of the picoline ligand which is required for an agostic interaction.

The $J_{C\text{-}H}$ values of agostic systems typically are decreased from corresponding values in normal structures.[18] Due to the limited solubility of **7a** at the low temperatures at which it is stable, it was not possible to measure $J_{C\text{-}H}$

(17) ^1H NMR of $Cp_2Zr(picolyl)(Cl)$ major isomer (360 MHz, CD_2ClCD_2Cl) δ 7.63 (d, J = 7.2 Hz, 1 H, meta), 7.55 (t, J = 7.3, 1 H, para), 6.97 (d, J = 7.3, 1 H, meta), 5.88 (s, 10 H, Cp), 2.59 (s, CH_3); minor isomer (90 MHz, CD_2Cl_2) δ 6.02 (s, Cp), 2.57 (s, CH_3), NC_5H_3Me obscured.

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(19) (a) ^1H NMR of pyridine (CD_2Cl_2, 360 MHz) δ 8.58 (br d, J = 4.1 Hz, 2 H, ortho), 7.66 (tt, J = 7.6, 1.8, 1 H, para), 7.26 (m, 2 H, meta); ^{13}C NMR (CD_2Cl_2, 90 MHz) δ 150.0 (d, J_{CH} = 179 Hz, ortho), 135.7 (dt, J_{CH} = 162, 6, para), 123.7 (dt, J_{CH} = 162, 8, meta). Literature values reported for J_{CH} ortho are in conflict[b,c] and the value reported in ref 19d is in error. (b) Maciel, G. E.; McIver, J. W. Jr.; Ostlund, N. S.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 1. (c) Malinowski, E. R.; Pollora, L. Z.; Larmann, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 2649. (d) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley Interscience: New York, 1972; p 287.

(20) NMR data for ortho-C–H group of free 4,4'-Me_2-bipy $\delta(^1H)$ 8.50, $\delta(^{13}C)$ 149.1 ($J_{C\text{-}H}$ = 177 Hz). NMR data for ortho-C–H group of $Cp_2Zr(CH_3)(4,4'\text{-}Me_2\text{-bipy})^+$ $\delta(^1H)$ 8.45, 8.43, $\delta(^{13}C)$ 152.2, 151.0 ($J_{C\text{-}H}$ = 182, 180 Hz). See ref 9a and 12.

(21) NMR data for pyridine ortho-C–H (δ ^1H, δ ^{13}C, $J_{C\text{-}H}$) in other systems: (a) free pyridine (8.58, 150.0, 179). (b) $Cp^*Hf(C_5H_{10})(py)Cl$ (8.7, 151.5, 183); Blenkers, J.; Hessen, B.; van Bolhuis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459. (c) $Cp^*_2Zr(\eta^2\text{-}OCCH_2)(py)$ (9.26, 8.43; 153.0, 151.0; 182, 189): Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (d) $Ti(OC_6H_3Bu^tCMe_2CH_2)(OAr')(CH_2SiMe_3)(py)$ (8.87): Fanwick, P. E.; Kobriger, L. M.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1986**, *108*, 8095. (e) $[(C_5H_4Me)_2Y(H)(Py)]_2$ (8.75): Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

(22) ^1H NMR of α-picoline (−71 °C, CD_2Cl_2, 360 MHz) δ 8.38 (d, J = 4.7 Hz, 1 H, H6), 7.59 (td, J = 7.7, 1.8, 1 H, H4), 7.16 (d, J = 7.3, 1 H, H3), 7.09 (t, J = 6.8, 1 H, H5), 2.46 (s, 3 H, CH_3); ^{13}C NMR (−45 °C, CD_2Cl_2, 90 MHz) δ 158.2 (s, C2), 148.8 (d, J_{CH} = 177, C6), 136.0 (dd, J_{CH} = 161, 6, C4), 123.0 (d, J_{CH} = 162, C3), 120.5 (dt, J_{CH} = 163, 7, C5), 24.2 (q, J_{CH} = 126, methyl).

(23) (a) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289. (b) Jordan, R. F.; Bradley, P. K. Abstracts of the 198th ACS National Meeting, Miami Beach, FL; Sept 10–15, 1989, INOR 360.

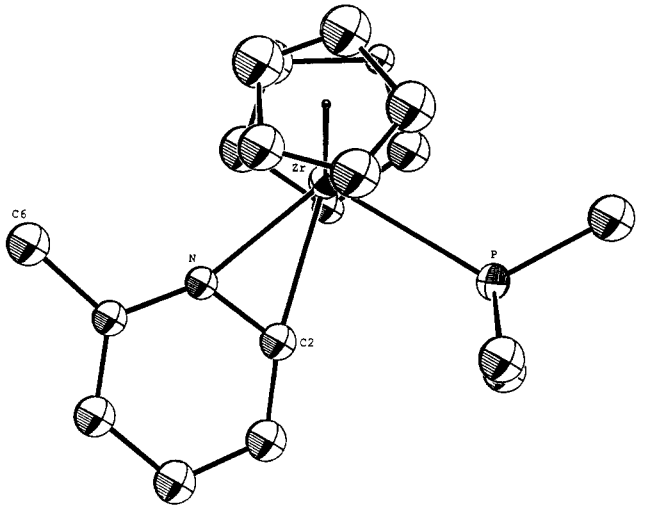
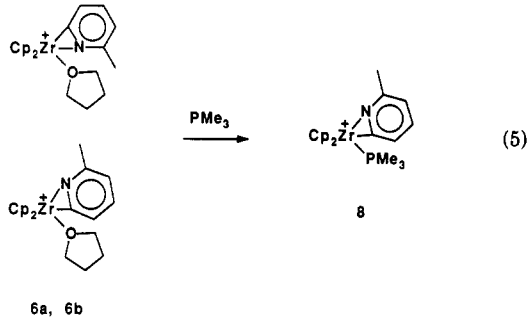


Figure 1. Structure of the cation of 8.

for the ortho hydrogen. However, for the more soluble complex **7b** this J_{C-H} is 9 Hz *smaller* than in the free ligand. The J_{C-H} for the ortho position is thus ca. 14 Hz less than expected for a normal η^1-picoline ligand. While this difference is quite small, it is consistent with the presence of an agostic interaction. For comparison, Teuben and co-workers have reported that one of the ortho-C–H bonds of Cp^*_2Y(3,5-dimethylbenzyl) is agostic.[1e] In this case J_{C-H} is reduced by 16 Hz vs the corresponding value for Cp^*_2Y(3,5-dimethylbenzyl)(THF), which has a normal structure.[24,25]

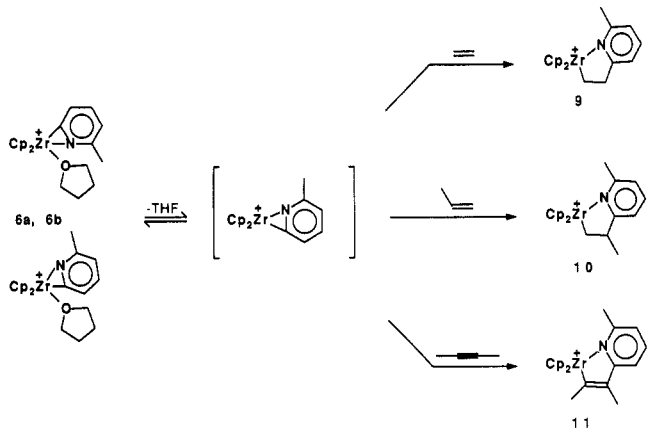
Synthesis and X-ray Structure of $Cp_2Zr(\eta^2$-N,C-picolyl)$(PMe_3)^+$ (8). Complex **6** reacts with a slight excess of PMe_3 in CH_2Cl_2 solution to yield $Cp_2Zr(\eta^2$-N,C-picolyl)$(PMe_3)^+$ (**8**), eq 5. ^1H NMR monitoring of this



(5)

reaction reveals initial rapid formation of a mixture of two isomers of **8**, followed by slower conversion to a single isomer (complete after 24 h, 23 °C).[26] The ^1H and ^{13}C NMR spectra of the thermodynamic isomer exhibit resonances for picolyl and PMe_3 ligands and ^{31}P coupling to the Cp hydrogens, and to C2 and C5 of the picolyl ligand.

Scheme I



The X-ray structure of **8** (thermodynamic isomer) was determined in order to confirm that the cationic pyridyl and picolyl complexes have monomeric, η^2 structures as observed for $Cp^*_2M(\eta^2$-N,C-$NC_5H_4)$ (M = Sc, Lu)[1a,f] and not dimeric μ-pyridyl or η^1 structures as observed for several late metal complexes.[27] The structure contains monomeric cations as shown in Figure 1, and BPh_4^- anions (not shown). Atomic coordinates and selected metrical parameters are listed in Tables II and III. The Cp_2Zr structure is normal and the η^2-picolyl and PMe_3 ligands lie in the plane between the Cp ligands, with C1 of the picolyl ligand occupying the central coordination site.

The Zr–N–C ring is structurally similar to the Sc–N–C ring in $Cp^*_2Sc(\eta^2$-N,C-$NC_5H_4)$[1f] and the Zr–C–C ring in the benzyne complex $Cp_2Zr(\eta^2$-$C_6H_4)(PMe_3)$[28] and is strained. The Zr–N (2.21 (1) Å) and Zr–C1 (2.29 (2) Å) bond lengths are similar, and the N–Zr–C1 angle is highly acute (34.2 (4)°). The Zr–C1 distance is slightly longer than those in the cationic zirconocene complexes **1** (2.256 (10) Å)[9b] and $(C_5H_4Me)_2Zr\{C(Me)=C(Me)(^nPr)\}(THF)^+$ (2.227 (9) Å)[9f] and the neutral complexes $Cp_2Zr(\eta^2$-$C_6H_4)(PMe_3)$ (2.267 (5), 2.228 (5) Å) and $Cp_2Zr(CH_3)_2$ (2.273 (5), 2.280 (5) Å).[29] The Zr–N distance is significantly shorter than Zr–N distances in Zr(IV) py complexes (2.3–2.4 Å) and is 0.05 Å longer (after correction for metal size difference)[30] than the Sc–N distance in $Cp^*_2Sc(\eta^2$-N,C-$NC_5H_4)$. The Zr–P distance (2.693 (4) Å) is similar to those in other cationic zirconocene PMe_3 complexes such as $Cp_2Zr(H)(PMe_3)_2^+$ (2.684 (3), 2.676 (3) Å)[3] and $Cp'_2Zr(CH_2CH_3)(PMe_3)^+$ (2.691 (3) Å),[23] and to that in the neutral complex $Cp_2Zr(\eta^2$-$C_6H_4)(PMe_3)$ (2.687 (3) Å). There is no interaction between the picolyl CH_3 group and the Zr center.

Structures of η^2-Pyridyl and η^2-Picolyl Complexes. Cationic complexes **2**, **3**, and **6** and the neutral complex Cp_2Zr(picolyl)Cl have been assigned monomeric η^2-N,C-pyridyl, Zr–N–C ring structures on the basis of the simi-

(24) The assignment of an agostic structure for Cp^*_2Y(3,5-dimethylbenzyl) is based on the observation of ^{89}Y–C and ^{89}Y–H coupling to one of the ortho-C–H groups in low-temperature spectra. The observed ortho J_{C-H} at 20 °C, which is the average of one normal and one agostic J_{C-H}, is 142.1 Hz; this value is 8.2 Hz less than that for the ortho J_{C-H} for the THF complex Cp^*_2Y(3,5-dimethylbenzyl)(THF) (150.3 Hz), which has a normal structure. Assuming that J_{C-H} for the normal ortho C–H of Cp^*_2Y(3,5-dimethylbenzyl) is 150 Hz, J_{C-H} for the agostic C–H is thus reduced by 16 Hz.

(25) There is no evidence for agostic interactions involving the picoline CH_3 groups of **7a** and **7b**. While the $NC_5H_4CH_3$ ^1H and ^{13}C resonances of the coordinated picoline of **7a** and **7b** are shifted upfield from those of the free ligand, the J_{C-H} values are normal, and similar upfield shifts are observed for the methyl resonances of the disubstituted pyridine ligand of complex **10**, which has a normal structure by X-ray diffraction.

(26) (a) A 2/1 ratio in favor of the thermodynamic isomer is obtained after 45 min at 23 °C. (b) ^1H NMR minor isomer (360 MHz, CD_2Cl_2, BPh_4^- resonances excluded) δ 7.86 (d, J = 7.3 Hz, 1 H, meta), 7.67 (t, J = 7.3, 1 H, para), 7.10 (d, J = 7.3, 1 H, meta), 5.74 (d, J_{PH} = 1.7, 10 H, Cp), 2.40 (s, 3 H, picolyl CH_3), 1.62 (d, J_{PH} = 6.8, 9 H, PMe_3).

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(28) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113.

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(30) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Table I. ^1H and ^{13}C NMR Data

compd (solvt)[a,b]	^1H NMR[c]	assgnt	^{13}C NMR[d]	assgnt
$Cp_2Zr(\eta^2\text{-N,C-}NC_5H_4)(py)^+$ (**3**)[e]	8.65 (dt, J = 4.8, 1.6, 2 H)[f]	py ortho	200.9 (s)[g]	pyridyl C2
	8.39 (dt, J = 5.2, 1.2, 1 H)	pyridyl H6	151.9 (d, J = 184)	py ortho
	8.05 (dt, J = 7.6, 1.2, 1 H)	pyridyl H3	144.8 (d, J = 186)	pyridyl C6
	7.97 (tt, J = 7.6, 1.6, 1 H)	py para	140.8 (d, J = 169)	pyridyl C3 or C4 or py para
	7.84 (td, J = 7.6, 1.0, 1 H)	pyridyl H4	138.6 (d, J = 152)	
	7.54 (m, 2 H)	py meta	131.9 (d, J = 169)	
	7.38 (ddd, J = 1.0, 4.6, 7.3, 1 H)	pyridyl H5	126.8 (d, J = 167)	py meta
			125.7[h]	pyridyl C5
	5.84 (s, 10 H)	Cp	110.4 (d, J = 154)	Cp
$Cp_2Zr(\eta^2\text{-N,C-}NC_5H_3(6\text{-Me}))(THF)^+$ (**6a**, **6b**)	7.75–7.63 (m, 4 H)	pic H3, H4	201.6 (s)[g]	picolyl C2
	7.23 (d, J = 7.2, 1 H)	pic H5	186.3 (s)	
	7.15 (d, J = 6.3, 1 H)		157.2 (s)	picolyl C6
	5.98 (s, 10 H)	Cp	155.5 (s)	
	5.90 (s, 10 H)		139.7 (d, J = 161)	picolyl C4
	3.96 (m), 3.91 (m), (8 H)	THF α-H	139.3 (d, J = 161)	
	2.54 (s, 3 H)	pic CH_3	138.8[i]	picolyl C3
	2.44 (s, 3 H)		127.8 (d, J = 165)	
	1.99 (m), 1.98 (m), (8 H)	THF β-H	132.2 (d, J = 168)	picolyl C5
			128.8 (d, J = 169)	
			111.9 (d, J = 167)	Cp
			110.8 (d, J = 167)	
			78.7 (t, J = 151)	THF α-C
			78.1 (t, J = 149)	
			26.4 (t, J = 134)	THF β-C
			25.9 (t, J = 135)	
			23.0 (q, J = 124)	picolyl CH_3
			21.5 (q, J = 128)	
$Cp_2Zr(CH_3)(picoline)^+$ (**7a**)	7.83 (t, J = 7.5, 1 H)[j]	para H	158.3[k,l]	picoline C2
	7.40 (d, J = 5.6, 1 H)	ortho H	141.9	picoline C6
	7.36 (d, J = 8.0, 1 H)	meta H	140.3	picoline C4
		α to CH_3	128.6	picoline C3
	7.30 (m, J = 7.3, 1 H)[m]	meta H	124.0	picoline C5
		γ to CH_3	114.1	Cp
	6.29 (s, 10 H)	Cp	44.2	Zr–CH_3
	2.20 (s, 3 H)	picoline CH_3	25.1	picoline CH_3
	0.89 (s, 3 H)	Zr–CH_3		
$Cp'_2Zr(CH_3)(picoline)^+$ (**7b**)	7.79 (t, J = 7.7, 1 H)[j]	para H	158.2 (s)[n]	picoline C2
	7.41 (d, J = 6.1, 1 H)	ortho H	141.6 (d, J = 168)	picoline C6
	obscured by BPh_4^-	meta H	141.0 (d, J = 178)	picoline C4
	6.19 (s, 2 H)	Cp′	128.5 (d, J = 168)	picoline C3
	6.15 (s, 2 H)	Cp′	123.6 (d)[o]	picoline C5
	5.98 (s, 4 H)	Cp′	124.5 (s)	Cp′ ipso
	2.16 (s, 3 H)	picoline CH_3	117.3 (d, J = 172)	Cp′
	2.00 (s, 3 H)	Cp′ CH_3	116.5 (d, J = 174)	Cp′
	0.79 (s, 3 H)	Zr–CH_3	110.2 (d, J = 168)	Cp′
			108.4 (d, J = 177)	Cp′
			41.9 (q, J = 120)	Zr–CH_3
			25.2 (q, J = 128)	picoline CH_3
			14.7 (q, J = 128)	Cp′ CH_3
$Cp_2Zr(\eta^2\text{-N,C-}NC_5H_3(6\text{-Me}))(PMe_3)^+$ (**8**)	7.70 (t, J = 7.0, 1 H)	para H	178.6 (d, J_{PC} = 28)[k,p]	picolyl C2
	7.65 (d, J = 7.6, 1 H)	meta H		
	7.26 (d, J = 7.3, 1 H)	meta H	156.1	picolyl C6
	5.80 (d, J_{PH} = 2.0, 10 H)	Cp	139.4	picolyl C4
	2.62 (s, 3 H)	pic CH_3	130.1 (d, J_{PC} = 2)	picolyl C5
	1.62 (d, J_{PH} = 7.6, 9 H)	$P(CH_3)_3$	125.9	picolyl C3
			107.9	Cp
			21.4	picolyl CH_3
			17.2 (d, J_{PC} = 23)	$P(CH_3)_3$
9	7.74 (t, J = 7.8, 1 H)	pic para H	166.1[k]	pic C2
	7.13 (d, J = 7.7, 1 H)	pic meta H	156.0	pic C6
	obscured by BPh_4^-	pic meta H	142.9	pic C4
	6.43 (s, 10 H)	Cp	124.4	pic C5
	3.42 (t, J = 7.1, 2 H)	$ZrCH_2CH_2$–	123.4	pic C3
	1.88 (t, J = 7.1, 2 H)	$ZrCH_2CH_2$–	115.4	Cp
	1.51 (s, 3 H)	pic CH_3	35.9	$ZrCH_2CH_2$–
			22.3	$ZrCH_2CH_2$–
			15.0	pic CH_3
9 (CD_3CN)	7.75 (t, J = 7.7, 1 H)	pic para H		
	7.16 (d, J = 7.8, 2 H)	pic meta H		
	6.38 (s, 10 H)	Cp		
	3.47 (t, J = 7.1, 2 H)	$ZrCH_2CH_2$–		
	2.16 (s, 3 H)	pic CH_3		
	1.62 (t, J = 7.1, 2 H)	$ZrCH_2CH_2$–		

Table I (Continued)

compd (solvt)[a,b]	^{1}H NMR[c]	assgnt	^{13}C NMR[d]	assgnt
10	7.80 (t, J = 7.9, 1 H)	pic para H	170.3[g,k]	pic C2
	7.26 (d, J = 8.1, 1 H)	pic meta H	155.5	pic C6
	7.00 (d, J = 8.0, 1 H)	pic meta H	143.0	pic C4
	6.42 (s), 6.41 (s), (10 H)	Cp	124.6	pic C5
	3.56 (m, 1 H)	$ZrCH_2CH(CH_3)$-	121.8	pic C3
	2.81 (dd, J = 13.5, 11.7, 1 H)	$ZrCH_2CH(CH_3)$- trans to CH_3	115.8, 114.9	Cp
			58.1	$ZrCH_2CH(CH_3)$-
	1.39 (s, 3 H)	pic CH_3	41.2	$ZrCH_2CH(CH_3)$-
	1.36 (d, J = 6.6, 3 H)	$ZrCH_2CH(CH_3)$-	22.6	-CH_3
	0.81 (dd, J = 13.5, 5.4, 1 H)	$ZrCH_2CH(CH_3)$- cis to CH_3	21.9	-CH_3
10 (CD_3CN)	7.81 (t, J = 7.8, 1 H)[f,q]	pic para H		
	7.17 (d, J = 7.8, 1 H)	pic meta H		
	6.36 (s, 10 H)	Cp		
	3.61 (m, 1 H)	$ZrCH_2CH(CH_3)$-		
	2.27 (dd, J = 11.2, 12.8, 1 H)	$ZrCH_2CH(CH_3)$- trans to CH_3		
	2.12 (s, 3 H)	pic CH_3		
	1.27 (d, J = 6.6, 3 H)	$ZrCH_2CH(CH_3)$-		
	0.87 (dd, J = 12.8, 5.2, 1 H)	$ZrCH_2CH(CH_3)$- cis to CH_3		
11	7.80 (t, J = 8.0, 1 H)	pic para H	210.6[k]	$ZrC(CH_3)=C(CH_3)$-
	7.27 (d, J = 8.2, 1 H)	pic meta H	161.2	pic C2
	6.83 (d, J = 7.7, 1 H)	pic meta H	155.3	pic C6
	6.38 (s, 10 H)	Cp	143.1	$ZrC(CH_3)=C(CH_3)$-
	1.91 (s, 3 H)	alkenyl CH_3	131.9	pic C4
	1.80 (s, 3 H)	alkenyl CH_3	121.8	pic C5
	1.39 (s, 3 H)	pic CH_3	118.8	pic C3
			115.5	Cp
			22.4	alkenyl CH_3
			20.9	alkenyl CH_3
			14.5	pic CH_3
11 (CD_3CN)	7.90 (t, J = 7.9, 1 H)	pic para H		
	7.33 (d, J = 8.1, 1 H)	pic meta H		
	7.01 (d, J = 8.0, 1 H)	pic para H		
	6.56 (s, 10 H)	Cp		
	1.89 (s, 3 H)	alkenyl CH_3		
	1.81 (s, 3 H)	alkenyl CH_3		
	1.66 (s, 3 H)	pic CH_3		
2-methyl-6-(1-methylethenyl)-pyridine (**14**)	7.54 (t, J = 7.7, 1 H)	para H	157.82 (s)	ortho C
	7.27 (d, J = 7.9, 1 H)	meta H	157.76 (s)	ortho C
	7.03 (d, J = 7.6, 1 H)	meta H	143.9 (s)	$C(CH_3)=CH_2$
	5.86 (m, 1 H)	$-C(CH_3)=CH_2$ cis to CH_3	136.7 (d, J = 161)	para C
			121.9 (d, J = 162)	meta C
	5.24 (m, 1 H)	$-C(CH_3)=CH_2$ trans to CH_3	116.9 (d, J = 160)	meta C
			115.1 (tq, J = 157, 6)	$C(CH_3)=CH_2$
	2.51 (s, 3 H)	ortho CH_3		
	2.18 (dd, J = 1.6, 0.9)	$-C(CH_3)=CH_2$	24.7 (q, J = 127)	CH_3
			20.6 (q (dd), J = 127, 11, 7)	$C(CH_3)=CH_2$

[a] Solvent is CD_2Cl_2 unless otherwise indicated. [b] BPh_4^- resonances: ^{1}H NMR: 7.35 (br m, 8 H) ortho, 7.04 (t, J = 7.4, 8 H) meta, 6.90 (t, J = 7.2, 4 H) para. ^{13}C NMR: 164.4 (q, J_{BC} = 49) ipso, 136.4 meta, 126.0 ortho, 121.1 para. [c] 360.13 MHz unless indicated. [d] 90.56 MHz unless indicated. [e] ^{1}H assignments confirmed by homonuclear decoupling. ^{13}C assignments based on trends in δ and J_{CH} observed for pyridines and intensities in spectrum of sample containing $Cr(acac)_3$. [f] 200 MHz. [g] 50.31 MHz. [h] Observed in 75.47 MHz {^{1}H} spectrum; J_{CH} not determined. [i] Not observed in coupled spectrum. [j] -85 °C. [k] Proton decoupled. [l] -50 °C. [m] Partially obscured by BPh_4^-; may be a doublet of doublets as seen for free picoline. [n] -45 °C. [o] Obscured by BPh_4^-; not possible to accurately determine J_{CH}. [p] 75.47 MHz. [q] Second pic meta H obscured by BPh_4^-.

larity of their NMR spectral properties to those of the crystallographically characterized compounds $Cp^*_2M(\eta^2$-N,C-pyridyl) (M = Sc, Lu) and **8**. The following observations are consistent with this assignment: (i) two isomers are observed in several cases, (ii) related neutral Ti(III) complexes $Cp_2Ti(\eta^2$-N,C-$NC_5H_3R)$ are monomeric (EPR and molecular weight determination),[31] and (iii) **6** and **8** are far more stable in CH_2Cl_2 than are $Cp_2Zr(R)(THF)^+$ complexes.[9]

Insertion Reactions of 6. Complex **6** reacts rapidly with ethylene, propylene, and 2-butyne in CH_2Cl_2 to yield the single insertion products **9**–**11**, respectively (100% NMR, Scheme I), which were isolated (88–91%) by crystallization from CH_2Cl_2 and characterized by NMR spectroscopy and analysis. The qualitative reactivity order is 2-butyne (minimum at -78 °C) > ethylene > propylene ($t_{1/2}$ ca. 11 min, 20 °C, 1 atm). The propylene reaction is inhibited by THF ($t_{1/2}$ ca. 13 h at 20 °C in presence of 50 equiv of excess THF, 1 atm of propylene). As picolyl complex **6** does not coordinate a second equivalent of THF,[32] this implies that THF dissociation occurs prior to insertion as indicated in Scheme I. Complex **8**, which contains a strongly coordinated PMe_3 ligand, does not react with propylene (9 equiv, CD_2Cl_2, 37 °C).

X-ray Structure of 9. The solid-state structure of **9** consists of discrete monomeric cations and BPh_4^- anions. The cation structure is shown in Figure 2, and atomic coordinates and selected metrical parameters are listed in

(31) (a) Klei, B.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1978**, 659. (b) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *214*, 53.

(32) The ^{1}H NMR spectrum (CD_2Cl_2) of **6** is unchanged in the presence of 50 equiv of excess THF.

Table II. Positional Parameters for 8[a]

atom	x	y	z	B, Å²
Zr	0.500	0.26110 (6)	0.500	3.39 (2)
p	0.6099 (4)	0.2542 (2)	0.3888 (2)	4.08 (8)
N1	0.475 (1)	0.1441 (5)	0.5354 (5)	3.1 (2)*
C1	0.514 (1)	0.1333 (7)	0.4786 (6)	3.9 (3)*
C2	0.520 (2)	0.0619 (8)	0.4550 (7)	4.8 (3)*
C3	0.492 (2)	0.0002 (7)	0.4904 (8)	5.2 (3)*
C4	0.447 (2)	0.0136 (9)	0.5502 (7)	4.9 (3)*
C5	0.446 (1)	0.0854 (7)	0.5728 (6)	3.6 (3)*
C6	0.421 (2)	0.1043 (9)	0.6398 (8)	5.5 (4)*
C11	0.335 (1)	0.3688 (6)	0.4770 (5)	2.5 (2)*
C12	0.282 (2)	0.3261 (9)	0.5304 (7)	5.6 (4)*
C13	0.240 (2)	0.2585 (9)	0.5116 (8)	6.2 (4)*
C14	0.262 (1)	0.2506 (6)	0.4461 (5)	2.9 (2)*
C15	0.316 (2)	0.3200 (9)	0.4274 (7)	5.3 (4)*
C21	0.622 (2)	0.366 (1)	0.5590 (9)	7.7 (5)*
C22	0.603 (2)	0.312 (1)	0.597 (1)	7.9 (5)*
C23	0.692 (2)	0.2542 (9)	0.5841 (8)	6.4 (4)*
C24	0.760 (2)	0.271 (1)	0.5328 (9)	7.4 (4)*
C25	0.723 (2)	0.339 (1)	0.5147 (9)	7.2 (4)*
C31	0.649 (2)	0.342 (1)	0.3469 (8)	6.5 (4)*
C32	0.501 (2)	0.2017 (9)	0.3341 (8)	5.5 (4)*
C33	0.771 (2)	0.201 (1)	0.3887 (8)	6.2 (4)*
C41	0.728 (1)	0.0616 (7)	0.7537 (7)	3.6 (3)*
C42	0.749 (2)	0.1374 (8)	0.7412 (6)	4.1 (3)*
C43	0.664 (2)	0.1974 (8)	0.7646 (7)	4.9 (3)*
C44	0.560 (2)	0.178 (1)	0.8008 (8)	6.3 (4)*
C45	0.536 (2)	0.105 (1)	0.8147 (8)	6.3 (4)*
C46	0.618 (2)	0.0457 (9)	0.7909 (8)	5.5 (4)*
C51	0.387 (1)	0.4765 (7)	0.1608 (6)	3.1 (3)*
C52	0.310 (1)	0.4809 (7)	0.1061 (6)	3.8 (3)*
C53	0.350 (2)	0.4500 (8)	0.0503 (7)	4.1 (3)*
C54	0.474 (2)	0.4101 (8)	0.0500 (7)	4.3 (3)*
C55	0.554 (2)	0.4040 (8)	0.1038 (7)	4.7 (3)*
C56	0.509 (2)	0.4346 (8)	0.1585 (7)	5.0 (3)*
C61	0.451 (1)	0.4748 (7)	0.7761 (6)	3.6 (3)*
C62	0.437 (2)	0.4847 (8)	0.8389 (7)	4.2 (3)*
C63	0.548 (2)	0.4658 (9)	0.8824 (8)	5.9 (4)*
C64	0.667 (2)	0.4405 (9)	0.8638 (8)	6.0 (4)*
C65	0.690 (2)	0.429 (1)	0.8051 (9)	8.1 (5)*
C66	0.579 (2)	0.4467 (9)	0.7609 (7)	5.3 (4)*
C71	0.734 (2)	0.0841 (8)	0.2118 (7)	4.4 (3)*
C72	0.597 (2)	0.0814 (8)	0.1908 (7)	4.9 (3)*
C73	0.516 (2)	0.1488 (9)	0.1709 (7)	5.5 (4)*
C74	0.580 (2)	0.215 (1)	0.1747 (8)	6.4 (4)*
C75	0.712 (2)	0.222 (1)	0.1968 (8)	6.4 (4)*
C76	0.791 (2)	0.1570 (9)	0.2152 (7)	5.7 (4)*
B	0.327 (2)	0.4923 (9)	0.7266 (7)	3.3 (3)*
C1C	0.2870	0.3048	0.4785	0*
C2C	0.6801	0.3084	0.5575	0*

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

Table III. Selected Bond Distances (Å) and Angles (deg) for 8[a]

Zr–P	2.693 (4)	N–C5	1.35 (2)
Zr–N	2.21 (1)	C1–C2	1.36 (2)
Zr–C1	2.29 (2)	C2–C3	1.36 (2)
Zr–CN1	2.208	C3–C4	1.41 (3)
Zr–CN2	2.246	C4–C5	1.35 (2)
N–C1	1.32 (2)	C5–C6	1.53 (2)
CN1–Zr–CN2	132.0	Zr–N–C1	76 (1)
P–Zr–N	109.1 (3)	Zr–C1–N	69 (1)
P–Zr–C1	75.2 (4)	C1–N–C5	122 (1)
N–Zr–C1	34.2 (4)	N–C1–C2	120 (1)

[a] CN*n* denotes centroid of a Cp ring.

Tables IV and V. The structure of the Cp_2Zr framework is normal and the $-CH_2CH_2$(6-methyl-2-pyridyl) ligand is bonded in the plane between the two Cp ligands in an η^2-C,N fashion. The chelate ring does not appear to be unusually strained. The Zr–C8 distance (2.263 (2) Å) is normal. The Zr–N distance (2.303 (2) Å) is shorter than

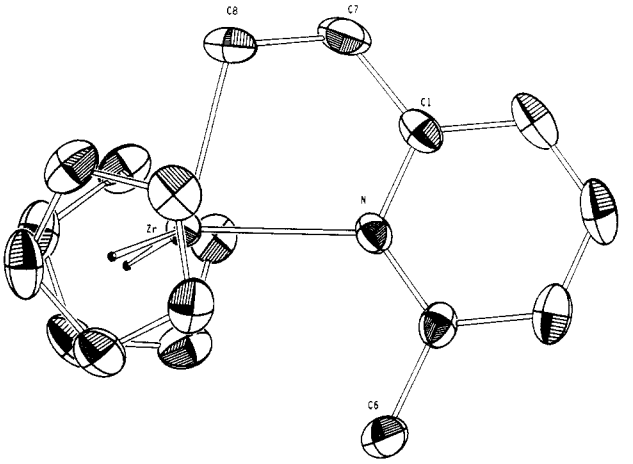


Figure 2. Structure of the cation of **9**.

Table IV. Positional Parameters for 9[a]

atom	x	y	z	B, Å²
Zr	0.13842 (2)	−0.22926 (1)	0.20753 (1)	2.894 (3)
N	0.0767 (2)	−0.2060 (1)	0.3778 (1)	3.48 (3)
C1	0.1721 (2)	−0.2663 (2)	0.4244 (2)	4.26 (5)
C2	0.1478 (3)	−0.2617 (2)	0.5273 (2)	5.84 (6)
C3	0.0309 (3)	−0.1972 (2)	0.5814 (2)	6.44 (7)
C4	−0.0647 (3)	−0.1378 (2)	0.5352 (2)	5.71 (6)
C5	−0.0416 (2)	−0.1423 (2)	0.4322 (2)	4.03 (4)
C6	−0.1466 (3)	−0.0817 (3)	0.3802 (2)	5.82 (7)
C7	0.2939 (2)	−0.3446 (3)	0.3603 (2)	5.88 (7)
C8	0.3329 (2)	−0.3121 (2)	0.2537 (2)	4.97 (6)
C11	0.2507 (3)	−0.0624 (2)	0.1841 (2)	5.54 (6)
C12	0.1139 (3)	−0.0193 (2)	0.1969 (2)	5.41 (6)
C13	0.0706 (3)	−0.0537 (2)	0.1181 (2)	5.85 (7)
C14	0.1867 (4)	−0.1195 (2)	0.0540 (2)	6.36 (7)
C15	0.2965 (3)	−0.1244 (2)	0.0958 (2)	5.83 (6)
C21	0.0501 (2)	−0.4046 (2)	0.2501 (2)	4.48 (5)
C22	0.1607 (3)	−0.4339 (2)	0.1702 (2)	5.16 (6)
C23	0.1295 (3)	−0.3734 (2)	0.0888 (2)	5.93 (6)
C24	−0.0010 (3)	−0.3071 (2)	0.1170 (2)	6.21 (6)
C25	−0.0517 (2)	−0.3255 (2)	0.2185 (2)	5.15 (6)
B	0.5031 (2)	0.2434 (2)	0.2556 (2)	2.91 (4)
C1P	0.4360 (2)	0.2725 (2)	0.1577 (1)	2.88 (4)
C2P	0.4741 (2)	0.3481 (2)	0.0836 (1)	3.25 (4)
C3P	0.4138 (2)	0.3725 (2)	0.0030 (2)	3.89 (5)
C4P	0.3135 (2)	0.3212 (2)	−0.0071 (2)	4.26 (5)
C5P	0.2747 (2)	0.2442 (2)	0.0630 (2)	4.58 (5)
C6P	0.3344 (2)	0.2216 (2)	0.1432 (2)	4.03 (5)
C11P	0.6458 (2)	0.2865 (2)	0.2345 (1)	2.97 (4)
C12P	0.7759 (2)	0.2170 (2)	0.2047 (1)	3.22 (4)
C13P	0.8928 (2)	0.2595 (2)	0.1792 (2)	3.39 (5)
C14P	0.8848 (2)	0.3737 (2)	0.1849 (2)	4.23 (5)
C15P	0.7584 (2)	0.4452 (2)	0.2162 (2)	4.29 (5)
C16P	0.6424 (2)	0.4027 (2)	0.2406 (2)	3.80 (4)
C21P	0.3985 (2)	0.3106 (2)	0.3553 (1)	3.10 (4)
C22P	0.4471 (2)	0.3354 (2)	0.4359 (2)	4.54 (5)
C23P	0.3639 (3)	0.3919 (2)	0.5212 (2)	4.86 (6)
C24P	0.2258 (3)	0.4218 (2)	0.5312 (2)	4.67 (5)
C25P	0.1721 (2)	0.3956 (2)	0.4555 (2)	4.56 (5)
C26P	0.2576 (2)	0.3417 (2)	0.3686 (2)	3.79 (4)
C31P	0.5270 (2)	0.1061 (2)	0.2716 (1)	3.03 (4)
C32P	0.5951 (2)	0.0295 (2)	0.1926 (2)	3.87 (5)
C33P	0.6158 (2)	−0.0863 (2)	0.2029 (2)	4.62 (5)
C34P	0.5691 (2)	−0.1328 (2)	0.2923 (2)	4.70 (5)
C35P	0.5001 (2)	−0.0612 (2)	0.3718 (2)	4.63 (5)
C36P	0.4809 (2)	0.0553 (2)	0.3615 (2)	3.70 (4)

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

those in related neutral Zr(IV) pyridine complexes such as $Cp^*_2Zr(\eta^2\text{-}OCCH_2)(py)$ (2.403 (1) Å)[21c] and $Zr(OAr')_2(OCHMepyCHMeO)(py)$ (2.473 (7) Å)[21d] and is also slightly shorter than M^{IV}–N distances in other complexes

Table V. Selected Bond Distances (Å) and Angles (deg) for 9[a]

Zr–N	2.303 (2)	C2–C3	1.351 (4)
Zr–C(8)	2.263 (2)	C3–C4	1.359 (4)
Zr–CN1	2.202	C4–C5	1.391 (3)
Zr–CN2	2.191	C5–C6	1.485 (4)
Zr–C(6)	3.496 (2)	C7–C8	1.498 (4)
N–C(1)	1.365 (3)	Zr–H6A	2.84
N–C(5)	1.357 (2)	Zr–H8A	2.80
C(1)–C(2)	1.387 (3)	Zr–H8B	2.92
C(1)–C(7)	1.507 (3)		
CN1–Zr–CN2	133.6	N–C1–C7	116.9 (2)
N–Zr–C8	77.26 (8)	C1–C7–C8	116.0 (2)
Zr–N–C1	113.4 (1)	Zr–C8–C7	107.3 (1)
C1–N–C5	119.9 (2)		

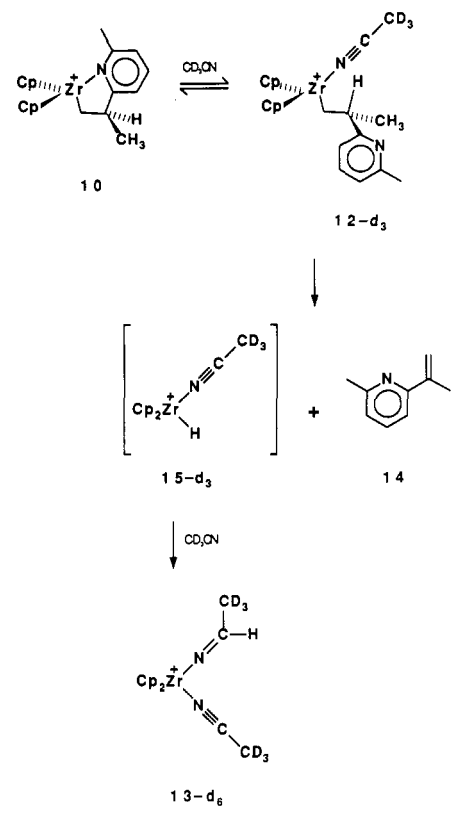
[a] CN*n* denotes centroid of a Cp ring.

in which pyridine is part of a four- or five-membered chelate ring, e.g., $Cp_2Zr\{\eta^2$-C,N-CH_2(6-methyl-2-py)$\}$-(CH_2(6-methyl-2-py) (2.407 (4) Å)[33,34] and Cp*Hf$\{\eta^2$-O,N-OCH(Si(TMS)$_3$)(2-py)$\}$Cl (2.36 (1) Å).[15,35] The most unusual structural feature is the acute N–Zr–C8 angle (77.26 (8)°), which is ca. 20° smaller than the X–Zr–Y angles of 94–97° normally observed for Cp_2ZrXY compounds.[36] This is a result of the constraints imposed by the chelated structure: increasing this angle would require concomitant increases in the angles at C or N. The ring is slightly puckered with C7 lying 0.55 Å out of the Zr–C8–N plane. The ^{1}H NMR results indicate that the ring flexes rapidly in solution. There is no interaction between Zr and the C6 methyl group (Zr–H > 2.8 Å, Zr–C6 = 3.496 (2) Å).

Solution Structures of 9–11. NMR spectroscopic data (Table I) and solution behavior observations establish that **9–11** maintain chelated structures in CH_2Cl_2 solution that are analogous to that established for **9** in the solid state. The ^{1}H and ^{13}C NMR spectra of **10** exhibit signals for two inequivalent Cp ligands as expected for a cyclic structure due to the presence of the β-CH_3 group. For all three compounds **9–11** the $NC_5H_3CH_3$ resonance is shifted significantly upfield from the corresponding resonances of free picoline and disubstituted pyridines. The chemical shift of the methine H of **10** (δ 3.56) is more consistent with the primary Zr alkyl structure indicated than with the isomeric secondary Zr alkyl structure derived from inverse insertion. For comparison, chemical shifts for $Cp'_2Zr(CH_2R)(THF)^+$ are in the range δ 1.2–1.6, while the methine shift for 2-isopropyl-6-methylpyridine is δ 3.01. This structural assignment is confirmed by the results of β-H elimination (vide infra) and hydrogenolysis reactions.[4a] Complexes **9–11** are stable in CH_2Cl_2 solution, and ^{1}H NMR spectra of CD_2Cl_2 solutions are unchanged in the presence of added THF. For comparison, base-free $Cp_2Zr(R)^+$ species rapidly decompose in CH_2Cl_2 by Cl^- abstraction, and in the presence of THF form THF complexes.[9]

β-Elimination Reactions of 9–11. Complexes **9** and **10** do not undergo β-H elimination in CH_2Cl_2 solution at 23 °C. The chelated structures preclude the β-H from attaining the correct orientation for transfer to Zr; furthermore, such a β-H transfer is likely to be highly endothermic and is expected to proceed in the reverse direction.[9f,37] We therefore investigated the reactions of **9** and **10** with several ligands that we anticipated might open the chelate rings and irreversibly trap the Zr–H product resulting from β-H elimination.

Scheme II

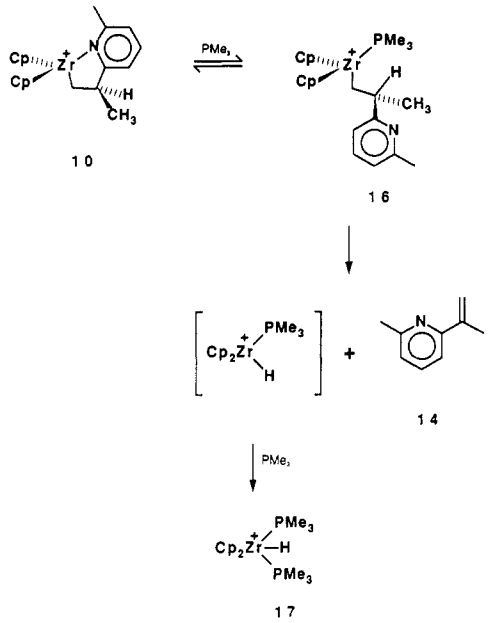


The ^{1}H NMR spectrum of **10** in CD_3CN solution exhibits a single Cp resonance and significant shifts in the other resonances compared to the CD_2Cl_2 spectrum; in particular the $NC_5H_3(CH_3)(CHMeCH_2Zr)$ resonance shifts from δ 1.39 to 2.12, in the direction of free 6-isopropyl-2-methylpyridine (δ 2.51). These observations are consistent with extensive formation of the ring-opened species **12**-d_3 (Scheme II). Under these conditions, rapid reaction ($t_{1/2}$ ca. 2.5 h, 23 °C) to yield the previously characterized azomethine complex **13**-d_6 (95% NMR)[3] and 2-(1-methylethenyl)-6-methylpyridine (**14**, 100% NMR) occurs. This reaction likely occurs via β-H elimination of **12**-d_3 to yield hydride **15**-d_3, which is rapidly trapped by CD_3CN insertion (Scheme II). In a preparative scale reaction in CH_3CN, **14** was isolated in 63% yield by an aqueous workup procedure. Analogous β-H elimination/insertion sequences have been observed for $Cp'_2Zr(CH_2CH_2R)(CH_3CN)^+$ complexes.[38] For comparison, addition of 6 equiv of CH_3CN to a CD_2Cl_2 solution of **10** results in coalescence of the inequivalent ^{1}H NMR Cp resonances but no shifts in the other resonances. This is consistent with minor and rapidly reversible formation of **12**. No net reaction is observed after 15 h at 40 °C. The lack of reaction in this case supports the proposal that ring-opened species **12** is the reactive intermediate in Scheme II.

The reaction of **9** in CH_3CN is similar to that of **10**. A shift in the picolyl methyl resonance from δ 1.51 in CD_2Cl_2

(33) Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1987**, *6*, 891.
(34) Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1987**, *6*, 2498.
(35) See also: (a) Bailey, S. I.; Colgan, D.; Engelhardt, L. M.; Leung, W.; Papasergio, R. I.; Raston, C. L.; White, A. L. *J. Chem. Soc., Dalton Trans.* **1986**, 603.
(36) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: West Sussex, 1986; Chapter 4.
(37) (a) Shock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701. (b) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275.
(38) Jordan, R. F.; Wang, Y.; LaPointe, R. E.; Bradley, P. K.; Borkowsky, S., manuscript in preparation.

Scheme III



to δ 2.16 in CD_3CN suggests significant formation of a ring opened species analogous to **12**; however, reaction to yield **13** and 2-ethenyl-6-methylpyridine is slow ($t_{1/2}$ ca. 63 h, 23 °C). This reaction likely proceeds through a process like that described for **10**, in which the key step is β-hydride elimination.

PMe_3 induces a similar though less efficient β-H elimination reaction of **10**. Addition of 4 equiv of PMe_3 to a CD_2Cl_2 solution of **10** produces significant changes in the ^1H NMR spectrum consistent with extensive formation of ring-opened species **16** (Scheme III). As above, a single Cp resonance is observed, and the $NC_5H_3(CH_3)$-$(CHMeCH_2Zr)$ resonance (δ 2.24) is significantly shifted toward that of free isopropylpicoline. A single PMe_3 resonance (δ 1.06, br s)[39] is observed, indicating that exchange of free and coordinated PMe_3 is rapid. Under these conditions **14** (60%) and $Cp_2Zr(H)(PMe_3)_2^+$ (**17**, 60% NMR) are produced in a slow reaction ($t_{1/2}$ ca. 29 h, 25 °C). This reaction likely proceeds via β-H elimination of **16** followed by rapid trapping of $Cp_2Zr(H)(PMe_3)^+$ by PMe_3. The stable bis-PMe_3 complex **17** has been characterized previously and does not undergo rapid PMe_3 exchange.[3] Analogous β-H elimination reactions have been observed for $Cp'_2Zr(CH_2CH_2R)(PMe_3)^+$ complexes.[23,40]

Alkenyl complex **11** does not undergo β-H elimination, even in the presence of PMe_3 or CH_3CN. This is not surprising since in this case β-H elimination would yield an allene product. The ^1H NMR spectrum of a solution of **11** and PMe_3 in CD_2Cl_2 solution exhibits a picolyl methyl resonance shifted only slightly from δ 1.39 to 1.42 and an unshifted free PMe_3 resonance, indicating that the chelate ring does not open under these conditions. Complex **11** is stable in CD_3CN solution (no production of **13**-d_6 after 64 h at 40 °C).

Discussion

The chemistry of $Cp_2Zr(CH_3)(THF)^+$ (**1**) and related cationic d^0 alkyl complexes is dominated by three key properties: (i) the high Lewis acidity of the Zr(IV) center, (ii) the lability of the THF ligand, and (iii) the presence of a reactive Zr–C bond.[9] Together these properties promote coordination, activation, and insertion of unsaturated substrates (ethylene, acetylenes, ketones, nitriles, etc).[9,41] In this work we have found that these properties also promote ligand C–H activation chemistry.

Complex **1** reacts with pyridine to yield η^2-N,C-pyridyl complexes **2** and **3** and with α-picoline (2-methylpyridine) to yield η^2-N,C-picolyl complex **6**. The presence of three-membered Zr–C–N rings in these complexes is established by NMR spectroscopy and by the X-ray structure of PMe_3 derivative **8**. These reactions involve initial THF displacement by the pyridine substrate, and subsequent ortho-C–H abstraction/C–H activation by the Zr–CH_3 group (σ-bond metathesis). Interaction of the ligand ortho-C–H bond with the Zr(IV) center is almost certainly important at some point along the reaction coordinate. Low-temperature NMR studies of intermediate picoline complex **7a** and the $(C_5H_4Me)_2Zr$ analogue **7b** reveal a high-field ^1H resonance and a lowered J_{C-H} for the ortho-C–H group of the coordinated picoline, suggesting that a weak agostic interaction is present in the ground state of each species. These reactions are similar to pyridine ortho-C–H activation reactions of Cp^*_2LuR, Cp^*_2ScR, Cp^*_2YR, Cp_2TiR, and other systems[1a,e,f,31,42-44] and to C–H abstraction reactions leading to benzyne complexes.[45]

Interestingly, complex **1** reacts more rapidly with 2-methylpyridine than with pyridine itself. Teuben and co-workers observed similar selectivity in the reactions of Cp_2TiR with pyridines.[31] This trend may reflect steric influences on substrate coordination in the intermediate substrate complexes: the 2-Me substituent of 2-methylpyridine should favor a conformation in which the ligand lies in the plane between the Cp ligands, placing the ortho-C–H bond in a favorable orientation for interaction with the Zr(IV) LUMO, while the perpendicular orientation, which is unfavorable for C–H activation, may be preferred for the less crowded unsubstituted pyridine. It is also possible that the in-plane orientation is favored for both the intermediate 2-methylpyridine and pyridine complexes but that the Me substituent in the former case promotes interaction of the ortho-C–H bond with the Zr-centered LUMO.[12,28c]

The Zr–C–N rings of **2** and **6** are highly reactive and undergo single insertions of ethylene, propylene, or 2-butyne to yield ring-expanded products **4**, **5**, and **9**–**11**. The insertion reactions of **6** are strongly inhibited by THF, and **3** and **8**, which contain nonlabile py and PMe_3 ligands,

(39) ^1H NMR of free PMe_3 under similar conditions: δ 1.00 (d, J_{PH} = 1.7 Hz).

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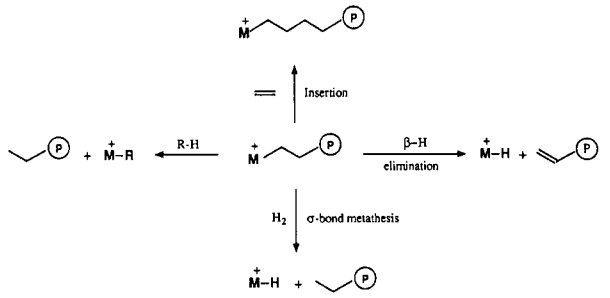
Scheme IV



respectively, are unreactive. These observations imply that initial loss of THF and coordination of substrate is required for insertion. Similar insertions are observed for d^0 metal benzyne complexes and related systems.[28,45,46]

In contrast to the single ethylene insertion observed for **6**, simple $Cp_2Zr(alkyl)(THF)^+$ complexes that contain labile THF ligands polymerize ethylene.[9] This difference is a result of the stability of the chelate ring of **9**. The X-ray structure of **9** and the observation that the chelate ring of this complex is not opened by THF establish that the ring is relatively unstrained. For this reason, ethylene coordination and ring opening (i.e., displacement of the chelated py by ethylene) does not occur, and further ethylene insertion/polymerization by **9** is not observed.

The dialkylpyridine ligands of **9** and **10**, formed by olefin insertion reactions of **6**, can be removed from Zr as vinyl pyridines by β-H elimination reactions. These reactions require the presence of ligands that can (i) displace the py ligand, open the chelate ring, and allow attainment of the correct geometry for β-H elimination, and (ii) trap the Zr–H species resulting from the (endothermic) β-H elimination and thus drive the overall reaction. Solution NMR data establish that both CH_3CN and PMe_3 open the chelate rings of **9** and **10**. In the former case β-H elimination leads to $Cp_2Zr(H)(CH_3CN)^+$ (**15**) which is trapped by CH_3CN insertion to yield $Cp_2Zr(N{=}CHMe)(CH_3CN)^+$ (**13**). In the latter case β-H elimination leads to $Cp_2Zr(H)(PMe_3)^+$, which is trapped by PMe_3 coordination to yield $Cp_2Zr(H)(PMe_3)_2^+$ (**17**).

The overall sequences of ligand substitution and ortho C–H activation (eq 4), insertion (Scheme I), and ligand induced β-H elimination (Schemes II and III) constitute high-yield, Zr-mediated alkenylations of α-picoline by ethylene and propylene. Similar Zr-mediated reaction schemes should be possible with a wide range of heteroaromatic and unsaturated substrates.[12]

Relationship to Olefin Polymerization. Scheme IV summarizes the key reactions of the unsaturated active sites/species in Ziegler–Natta and related olefin polymerization catalyst systems. Polymer chain growth occurs by olefin insertion, and chain transfer occurs by β-H elimination, M–R bond hydrogenolysis, and (possibly) C–H activation.[47] The availability of well-characterized discrete molecular catalysts[48] and the developing mechanistic understanding of these key reactions[49] offer the opportunity of utilizing this chemistry in the development of new types of stoichiometric and catalytic C–H activation and C–C coupling reactions. In this work, pyridines are activated by coordination to **1** and subsequent ortho-C–H bond activation, elaborated by olefin insertion, and removed by β-H elimination. A key aspect of this approach is that the extent of insertion is controlled by the ring size of the intermediate Zr complexes: three-membered Zr–C–N rings of **3** and **6** undergo facile insertion, while the five-membered rings of **9–11** do not. Thus single insertion rather than polymerization[4b,9] is observed. The chemistry described here is stoichiometric because the product derived from the β-H elimination step, either **13** or **17**, is unreactive with olefins and with pyridines. However, related catalytic chemistry is possible when product removal is accomplished by Zr–R bond hydrogenolysis.[4a]

Experimental Section

All manipulations were performed under inert atmosphere or vacuum using a Vacuum Atmospheres drybox or a high-vacuum line. Solvents were purified by distillation from appropriate drying/deoxygenating agents prior to use, stored in evacuated bulbs, and vacuum transferred into reaction flasks or NMR tubes.[50] Ethylene and propylene were obtained from Matheson and used without further purification. 2-Butyne was obtained from Aldrich and distilled from sodium prior to use. Pyridine and α-picoline were purchased from Aldrich and distilled from CaH_2 prior to use. $[Cp_2Zr(CH_3)(THF)][BH_4]$ (**1**) was prepared as previously described.[3] NMR spectra were recorded on JEOL FX-90, Nicolet 200, Bruker MSL-300, or Bruker WP-360 spectrometers in sealed tubes. ^1H and ^{13}C chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. Elemental analyses were performed by Analytische Laboratorien or Oneida Research Services.

$[Cp_2Zr(\eta^2\text{-}N,C\text{-}NC_5H_4)(NC_5H_5)][BPh_4]$ (3). A slurry of **1** (1.15 g, 1.84 mmol) in neat pyridine (20 mL) was stirred overnight at 45 °C, to yield a brown solution. Hexane (10 mL) was added at −78 °C to cause precipitation of a tan solid, which was collected by filtration. The product was washed with hexane and dried in vacuo overnight at 23 °C (yield 1.00 g, 78%). Anal. Calcd for $C_{44}H_{39}BN_2Zr$: C, 75.72; H, 5.64; N, 4.02; Zr, 13.07. Found: C, 75.69; H, 5.68; N, 3.93; Zr, 13.20.

$[Cp_2Zr(\eta^2\text{-}N,C\text{-}NC_5H_3(6\text{-}Me))(THF)][BPh_4]$ (6). Under a N_2 purge α-picoline (0.75 mL, 7.6 mmol) was added to a slurry of **1** (4.27 g, 6.81 mmol) in 45 mL of CH_2Cl_2. The slurry was stirred for 30 min at 23 °C, during which time all of the solid dissolved. The solvent was removed under vacuum, and 40 mL of THF was added, producing a white slurry. The white solid product, which was only slightly soluble in THF, was separated by filtration, washed twice with 15-mL portions of cool THF, and dried in vacuo at 23 °C overnight (yield 4.15 g, 87%). Anal. Calcd for $C_{44}H_{44}BNOZr$: C, 74.96; H, 6.30; N, 1.99; Zr, 12.94. Found: C, 74.76; H, 6.20; N, 1.96; Zr, 12.80.

In a second experiment, designed to measure the yield of CH_4, a slurry of **1** (2.00 g, 3.19 mmol) in CH_2Cl_2 (65 mL) was frozen at −196 °C. α-Picoline (0.3 mL, 3.2 mmol) was added under a N_2 purge, and the flask was evacuated. The flask was warmed to 23 °C and stirred overnight, producing a light yellow solution. Noncondensable volatiles were removed and quantified by using a Toepler pump. Condensable volatiles were collected by a −196 °C trap. The evolved gas (3.05 mmol, 96%) was identified as CH_4 by ^1H NMR (δ 0.15, C_6D_6) and IR. The yield of **6**, isolated as

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Table VI. Summary of Crystallographic Data for 8 and 9

	8	9
emp formula	$C_{43}H_{45}BNPZr$	$C_{42}H_{40}BNZr$
formula wt	708.84	660.82
cryst size, mm	0.10 × 0.20 × 0.46	0.36 × 0.48 × 0.60
cryst color	colorless	amber
T, K	295	295
space group	Cc	$P\bar{1}$
a, Å	9.571 (4)	10.387 (2)
b, Å	17.524 (11)	12.129 (3)
c, Å	21.861 (7)	13.844 (4)
α, deg		87.78 (2)
β, deg	92.55 (3)	76.37 (2)
γ, deg		76.63 (2)
V, Å^3	3662.9 (5.1)	1648.8 (9)
Z	4	2
d(calcd), g/cm^3	1.285	1.331
cell dimens	19 reflctns, 30–35° 2θ	24 reflctns, 37–44° 2θ
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
scan ratio, $2\theta/\omega$	0.67	0.33
scan limit	$2 \le 2\theta \le 40°$	$2 \le 2\theta \le 50°$
scan speed	0.7–5.5°/min	0.6–4.0°/min
scan range	0.8 + 0.35 tan θ	0.7 + 0.35 tan θ
data coll	$\pm h,\pm k,\pm l$	$\pm h,\pm k,\pm l$
no. of reflctns coll	7652	11676
no. of unique intensities	1705	5838
no. of $F > 3\sigma(F)$	1192	4856
decay (max corr on F)	1.02	<1%, no correction
agrmnt btwn equiv reflctns	2.9% on F	1.9% on F
μ, cm^{-1}	3.66	3.54
abs corr. (emp on F^2)	max 1.00, min. 0.91	max. 1.00, min 0.98
struct soln	Patterson	Patterson and DIRDIF
refinement	anisotropic on Zr, P; isotropic on other non-H; fixed H	anisotropic on all non-H; fixed H
data/parameter in LS	1192/197	4856/406
R^a	0.042	0.025
$R_w{}^b$	0.055	0.040
wt (Killean and Lawrence)^d	P = 0.04, Q = 0.0	P = 0.03, Q = 0.0
SDOUW^c	1.086	1.069
max parameter shift/esd	0.07	0.28
max resid e density, e/Å^3	0.48	0.36

^{a} $R = \sum\Delta F_H/\sum F_{o,H}$, where $H = h,k,l$, and F_o is scaled to F_c, ΔF is $||F_o| - |F_c||$. ^{b} $[R_w]^2 = \sum w(\Delta F_H)^2/\sum w(F_{o,H})^2$. ^{c} SDOUW = standard deviation in observation of unit weight. ^{d} Killean and Lawrence weights = $1/(S^2 + (PF)^2 + Q)$, where S is the estimated standard deviation in F from counting statistics. If several octants are averaged, S is the larger of two estimates—one based on counting statistics, the other based on the agreement between equivalent reflections. (Killean, R. C. G.; Lawrence, J. L. *Acta. Crystallog., Sect. B* **1969**, *B25*, 1750).

described above, was 1.90 g (84%).

Variable-Temperature ^{1}H NMR Spectrum of 6. A solution of **6** (22.3 mg, 0.0356 mmol) in CD_2ClCD_2Cl (0.4 mL) was prepared in a sealed NMR tube. Spectra were recorded at various temperatures ranging from 23 to 77 °C. The Cp resonances of **6a** and **6b** were observed to coalesce at 66 °C. The experiment was repeated with a second sealed NMR tube that contained **6** (22.0 mg, 0.0350 mmol) and excess THF (0.9 equiv) in CD_2ClCD_2Cl, and the coalescence temperature was unchanged.

Thermolysis of 6 in CD_2Cl_2. A solution of **6** (16 mg, 0.023 mmol) in CD_2Cl_2 (0.4 mL) in a sealed NMR tube was maintained at 40 °C and periodically monitored by ^{1}H NMR over a period of 2 weeks. The resonances of **6** decreased in intensity, and resonances assignable to $Cp_2Zr[\eta^2$-N,C-NC_5H_3(6-Me)]Cl were observed. The same product was formed by reaction of **6** (33 mg, 0.047 mmol) and $[Et_3N(CH_2Ph)]Cl$ (12 mg, 0.053 mmol) in CD_2Cl_2 (0.4 mL).

$[Cp_2Zr(CH_3)$(picoline)$][BPh_4]$ (7a). Compound **1** (21.0 mg, 0.0335 mmol) was placed into an NMR tube. α-Picoline (3.6 μL, 0.036 mmol) was added via syringe, and the tube was quickly cooled to −196 °C and evacuated. The tube was warmed to −78 °C, and CH_2Cl_2 (0.6 mL) was added via vacuum transfer. Upon agitation of the tube at −78 °C, all solid material dissolved. The solvent was removed under vacuum at −78 °C, and the resulting solid was dried at −78 °C for 7 h and then dissolved in CD_2Cl_2 (0.4 mL) at that temperature. The sample was placed into a cold NMR probe (−35 °C), which was cooled further to −50 °C, and the ^{1}H and ^{13}C spectra were recorded. Complex **7b** was prepared from $[Cp'_2Zr(CH_3)(THF)][BPh_4]$[38] and characterized in a similar manner.

$[Cp_2Zr\{\eta^2$-N,C-NC_5H_3(6-Me)$\}(PMe_3)][BPh_4]$ (8). Trimethylphosphine (3.05 mmol) was added from a calibrated gas bulb to a solution of **6** (1.60 g, 2.27 mmol) in CH_2Cl_2 (30 mL). The solution was stirred for 45 h at room temperature, and the volume was reduced by half. Addition of hexane caused the precipitation of a white solid, which was collected by filtration, washed with cold CH_2Cl_2, and dried in vacuo overnight (yield 1.16 g, 72%). Anal. Calcd for $C_{43}H_{45}BNPZr$: C, 72.85; H, 6.41; N, 1.98; P, 4.37; Zr, 12.87. Found: C, 72.73; H, 6.33; N, 1.87; P, 4.15; Zr, 12.90.

9: A solution of **6** (2.43 g, 4.45 mmol) in CH_2Cl_2 (35 mL) was exposed to 1 atm of ethylene at 23 °C. Almost immediately an orange precipitate formed. The resulting slurry was stirred overnight at 23 °C and then concentrated to 15 mL. The orange solid was collected by filtration, washed with cold CH_2Cl_2, and dried in vacuo overnight at 23 °C (yield 2.07 g, 91%). Anal. Calcd for $C_{42}H_{40}BNZr$: C, 76.33; H, 6.11; N, 2.12; Zr, 13.80. Found: C, 76.84; H, 6.18; N, 2.09; Zr, 13.18.

10: A solution of **6** (5.74 g, 7.76 mmol) in CH_2Cl_2 (100 mL) was frozen at −196 °C, and propylene (30.6 mmol) was added from a calibrated gas bulb. Warming the reaction mixture to 23 °C produced a yellow solution, which was stirred overnight, after which time a precipitate was present. The solution was concentrated to 40 mL, and the yellow product was collected by filtration, washed twice with 5-mL portions of cold CH_2Cl_2, and dried overnight under vacuum at 23 °C (yield 4.77 g, 91%). Despite several recrystallization attempts it was not possible to obtain this compound free of solvent. Recrystallization from $ClCH_2CH_2Cl$ yielded a product containing 3.4% $ClCH_2CH_2Cl$ by ^{1}H NMR. Anal. Calcd for $C_{43}H_{42}BNZr\cdot0.034C_2H_4Cl_2$: C, 74.73; H, 6.22; Cl, 2.44; N, 2.01; Zr, 13.06. Found: C, 74.45; H, 6.06; Cl, 2.70; N, 1.91; Zr, 13.25.

11: A solution of **6** (1.84 g, 2.60 mmol) in CH_2Cl_2 (25 mL) was frozen at −196 °C, and 2-butyne (9.13 mmol) was added from a calibrated gas bulb. Warming produced a yellow solution, which

was stirred for 4 h at 23 °C, during which time a yellow precipitate formed. The slurry was concentrated to 18 mL, and the lemon-yellow product was collected by filtration, washed with CH_2Cl_2, and dried under vacuum at 23 °C overnight (yield 1.38 g, 77%). A second crop of product (0.21 g) was recovered from the filtrate, bringing the total yield to 88%. Anal. Calcd for $C_{44}H_{42}BNZr$: C, 76.93; H, 6.18; N, 2.04; Zr, 13.28. Found: C, 76.86; H, 6.00; N, 2.02; Zr, 13.25.

Reaction of 10 with CD_3CN. NMR Scale. A solution of **10** (13 mg, 0.019 mmol) in CD_3CN (0.4 mL) was prepared in a sealed NMR tube and monitored by ^1H NMR. The resonances for **10** were shifted as described in the text and decreased in intensity while resonances for **13**-d_3 and **14** grew in intensity. After 4.5 h at 23 °C the yield of both **13**-d_3 and **14** were 74%. After 19 h the yield of **14** was 100%.[51]

Preparative Scale. A solution of **10** was generated by reaction of a solution of **6** (5.15 g, 7.31 mmol) in CH_2Cl_2 (110 mL) with propylene (22.1 mmol) for 22 h at 23 °C. The CH_2Cl_2 and excess propylene were removed under vacuum, and CH_3CN (100 mL) was added. The CH_3CN solution was stirred for 3.5 days at 23 °C. The resulting slurry was exposed to air, diluted with 30 mL of ether, and filtered. The filtrate was extracted with 2 N HCl, and the aqueous portion was made basic by the addition of solid KOH and extracted with hexane. Evaporation of the hexane gave **14** (0.61 g, 63%) as a yellow liquid. Anal. Calcd for $C_9H_{11}N$: C, 81.14; H, 8.34; N, 10.52. Found: C, 80.50; H, 8.35, N, 10.24. MS calcd for $C_9H_{11}N$ 133.0891, found 133.0895.

(51) Complex **13** slowly decomposes under these conditions to unidentified products. After 19 h the yield of **13** was 56%.

Reaction of 10 with PMe_3. A solution of **10** (8.1 mg, 0.012 mmol) in CD_2Cl_2 (0.4 mL) was charged with PMe_3 (0.47 mmol) from a calibrated gas bulb and sealed in an NMR tube. The reaction was monitored by ^1H NMR at 23 °C. The resonances for **10** were shifted as described in the text and decreased in intensity, while resonances for **14** and **17** grew in intensity. After 78 h the yields of **14** and **17** were 60%. Cp_2ZrCl_2 (13%) and an unknown Cp_2Zr product or products (δ 6.32, 6.07 Cp) were also present.

X-ray Structure Determinations of 8 and 9. Suitable crystals of **8** were grown by slow evaporation of a CH_2Cl_2 solution, mounted in capillaries, and sealed under N_2. Suitable crystals of **9** were grown by cooling a concentrated CH_2Cl_2 solution and mounted in capillaries under N_2 in a drybox. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer as summarized in Table VI.

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Supplementary Material Available: For **8** and **9**, tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions (9 pages); listings of h, k, l, F_o, F_c, and $\sigma(F_o)$ for **8** and **9** (23 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Dynamics of (Organosilyl)anilides

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A series of (organosilyl)formanilides of the type $HCONPhSiR^1R^2R^3$, where $R^1R^2R^3$ = Me_2H, MePhH, Me_3, Et_3, $(n\text{-}Pr)_3$, $(i\text{-}Pr)_3$, $(n\text{-}Bu)_3$, $(OEt)_3$, $(OSiMe_3)_3$, Me_2OMe, Me_2Et, $Me_2CH{=}CH_2$, $Me_2\text{-}i\text{-}Pr$, $Me_2C_3H_6Cl$, $Me_2C_2H_4OAc$, $Me(n\text{-}Bu)_2$, Me_2Ph, and $Ph_2\text{-}t\text{-}Bu$, and a series of (organosilyl)acetanilides of the form $CH_3CON(p\text{-}R^4C_6H_4)SiMe_2H$, where R^4 = OMe, H, and Cl, were prepared by amination and transsilylation. Most of the (organosilyl)formanilides exist as rapidly equilibrating mixtures of amide and imidate tautomers and exhibit hindered rotation about the C–N bond in the amide tautomer. Bulky groups and alkoxy groups at silicon favor the imidate tautomer. The size of the silyl group has no effect on the barrier to either silyl tautomerism or hindered rotation, while electron-withdrawing alkoxy groups on the silicon lower both barriers. The effect of substituents on the rate of tautomerism is consistent with an intramolecular, concerted mechanism. The rotamer populations are relatively insensitive to variations in the silyl group. The more stable rotamer has the silyl moiety cis to the carbonyl. The (dimethylsilyl)acetanilides also exist as a dynamic mixture of amide and imidate tautomers. The attempted preparation of the $SiMe_2CHCl_2$ formanilide derivative led to substitution at carbon rather than silicon. The product, $(HCONPh)_2CHSiMe_2Cl$, was shown by X-ray crystallography to have distorted trigonal-bipyramidal geometry at Si, with two nonequivalent dative bonds from carbonyl oxygen atoms to silicon. For $C_{17}H_{19}ClN_2O_2Si$: monoclinic, $P2_1/c$, a = 10.420 (3) Å, b = 17.322 (5) Å, c = 10.561 (2) Å, β = 112.26 (2)°, V = 1764.3 (10) Å^3, Z = 4, $R(F)$ = 5.29% for 1796 reflections, $F_o \geq 3\sigma(F_o)$.

The ambident nature of the amide function makes it ideal for the study of bonding and tautomerism in organometallic congeners of carbon. Previous studies of trimethylsilyl-, germyl-, and stannylamides have demonstrated the unique position of silicon among the group IV elements. Only these derivatives undergo rapid amide/imidate silyl tautomerism, display fluxionality, and have severely lowered barriers to rotation about the C–N bond in the *N*-(trimethylsilyl)amide form. The strong Si–O bond is presumably responsible for the presence of the imidate tautomer, while the lower rotational barrier can be attributed to (p–d)π-bonding in the transition state.

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