the National Science Foundation via the establishment of a Minority Research Center of Excellence in Materials Science at the University of Texas at El Paso.

Supplementary Material Available: Tables of crystal data, data collection, and refinement, complete bond lengths and bond angles, anisotropic thermal parameters, and H atom positional parameters (28 pages); listings of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Scope and Regiochemistry of Ligand C–H Activation Reactions of $Cp_2Zr(CH_3)(THF)^+$

Richard F. Jordan* and Anil S. Guram

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

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The cationic complex $Cp_2Zr(CH_3)(THF)^+$ (1) reacts with a series of N-heterocycles derived from pyridine via ligand substitution followed by ligand C–H activation (σ-bond metathesis). Complex 1 reacts with 2,5-dimethylpyrazine, 2-phenylpyridine, phenanthridine, and 7,8-benzoquinoline to yield cyclometalated products **5–8**, which contain three-membered Zr–N–C rings. The reaction of 1 with quinoline yields primarily the α-C–H activation product **9**, but a minor product **10**, resulting from activation of H-8, is also observed. Complex 1 also reacts with more remote C–H bonds of acridine, phenazine, and 2,6-dimethylpyridine (which lack α-hydrogens) to yield the four-membered-ring products **11**, **12**, and **14**. The general trend for ortho C–H activation and formation of three-membered-ring products exhibited by $Cp_2Zr(CH_3)^+$ contrasts with the preference for activation of more remote C–H bonds and formation of four- or five-membered-ring products exhibited by late-metal systems. No ligand C–H activation is observed for $Cp_2Zr(CH_3)$(*N*-methylimidazole)$^+$ (**16**), $Cp_2Zr(CH_3)$(*N*-methylimidazole)$_2^+$ (**17**), or $Cp_2Zr(CH_3)$(4,4′-Me_2bpy)$^+$ (**18**). The lack of reactivity in the latter two cases is ascribed to the lack of a low-lying Zr-based LUMO. Substrates that do not displace the THF ligand of 1, such as 2-phenylquinoline and 2-methylthiophene, do not undergo C–H activation.

Introduction

Several facile C–H activations involving counterion or ligand C–H bonds have been observed recently for cationic d^0 complexes $Cp^*_2ZrR^+$ and $Cp_2Zr(R)(L)^+$.[1,2] These reactions are believed to proceed by σ-bond metathesis mechanisms involving four-center transition states that are accessed by initial interaction/coordination of the C–H bond with/to the electrophilic metal center.[3-5] We are exploring the possibility of developing productive σ-bond metathesis reaction schemes by combining these reactions with insertion, β-H elimination, Zr–R bond hydrogenolysis, and ligand-exchange reactions.[6,7] We reported previously that $Cp_2Zr(Me)(THF)^+$ (1)[8] reacts with pyridine and 2-

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

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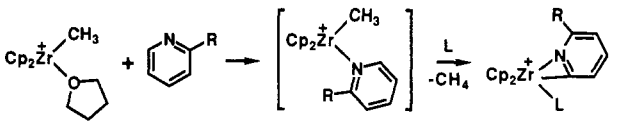
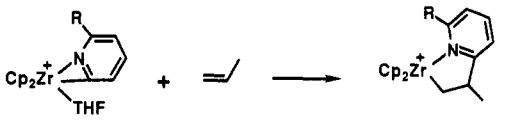
methylpyridine to yield the intermediate adducts **2**, which undergo CH_4 elimination under mild conditions to yield the cationic pyridyl complexes **3** (eq 1).[1a,c] These pyridyl



1 2 3 (1)



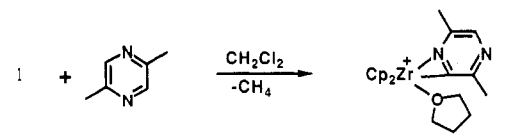
4 (2)

complexes undergo facile insertion of alkenes and acetylenes to afford ring-expanded complexes with chelated structures such as **4** (eq 2). The disubstituted pyridine groups of these ring-expanded complexes can be removed by β-H elimination in stoichiometric reactions[1c,d] or by hydrogenolysis in a catalytic process.[1a] In order to exploit this chemistry in both catalytic and stoichiometric organic syntheses, it is necessary to develop an understanding of the scope, selectivity, and mechanistic aspects of the key C–H activation step in eq 1. This paper describes the reactions of **1** with a variety of heterocyclic compounds. The results provide some insights to the requirements for and the regiochemical preferences of ligand C–H activations in this system.

Results

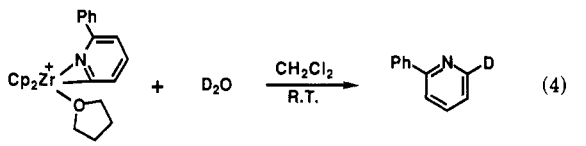
General Procedure. The reactions of **1** with a variety of nitrogen-, oxygen-, and sulfur-containing heterocyclic compounds were investigated. The standard reaction procedure involved addition of 1–2 equiv of the heterocycle to a slurry of **1** in CH_2Cl_2 at 23 °C followed by stirring for 2–4 h. The solvent, other volatiles, and excess heterocycle were removed under vacuum and by hexane washes, and the crude products were purified by recrystallization (CH_2Cl_2/hexane) and characterized by NMR spectroscopy, analysis, and deuteriolysis experiments. Methane is eliminated in cases where C–H activation occurs,[1] but in this work it was not quantified.

Activation of Aryl α-C–H Bonds. Complex **1** reacts with a variety of N-heterocycles derived from pyridine to yield CH_4 and cyclometalated products as summarized in Table I. A general preference for activation of the aryl C–H bond α to N and formation of cationic complexes containing three-membered Zr–N–C rings is observed. For example, **1** reacts readily with 2,5-dimethylpyrazine to yield complex **5** in high yield (entry 1 in Table I and eq 3). Similarly, orthometalated complexes **6** and **7** are



1 5 (3)

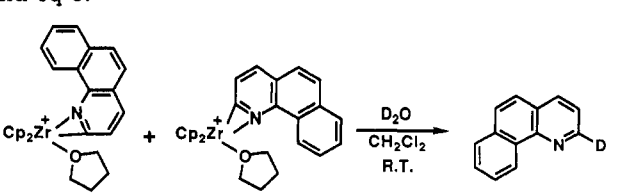
formed in the reactions of **1** with 2-phenylpyridine and phenanthridine (3,4-benzoquinoline), respectively (entries 2 and 3 in Table I). Structural assignments of complexes **5–7** are based on NMR spectroscopic data, which are similar to those of complex **3** and the PMe_3 analogue $Cp_2Zr\{\eta^2(N,C^2)\text{-}NC_5H_3(6\text{-}CH_3)\}(PMe_3)^+$, which were characterized previously.[1a,c,d] For the parent N-heterocycles, the ^1H NMR resonances for the hydrogens α to N are shifted significantly downfield (to δ 8.3–9.3)[9] compared to the other aromatic resonances. For **5** the α-^1H resonance appears at δ 8.34 and integrates for 1 H. For both **6** and **7** the characteristic downfield α-^1H resonance is absent. The ^{13}C NMR spectra of these complexes each exhibit a downfield Zr–C resonance (δ 220–190), characteristic of three-membered Zr–N–C ring complexes.[1a,c,d] In the case of complex **6**, α-C–H activation was confirmed by deuteriolysis, which gave 6-deuterio-2-phenylpyridine (eq 4). The presence of 1 equiv of coordinated THF in **5–7** is established by the observation of ^1H and ^{13}C NMR THF resonances that are shifted downfield from those of free THF.[10]



6 (4)

For complexes **5–7**, two isomers that differ in the position of coordinated THF (cis to C or N) are possible. The observation of single sets of Cp, metalated heterocycle, and THF resonances in the ^1H and ^{13}C NMR spectra of **5–7** indicates that these complexes exist as single isomers or that isomer interconversion is rapid. This question was addressed for **5**. The ^1H NMR spectrum of **5** at −90 °C is unchanged from that at ambient temperature, consistent with the presence of a single isomer. Also, the spectrum of **5** is unchanged in the presence of added THF and exhibits separate resonances for coordinated (1 equiv) and free THF, indicating that THF exchange, which is probably required for isomer interconversion, is slow. These observations, along with observations of slow isomer interconversion for **3** (L = PMe_3, THF, pyridine, 2-methylpyridine),[1a,c,d] and for **8** and **9** (vide infra), strongly suggest that **5–7** exist as single isomers. The structures listed in Table I and the equations are anticipated to be favored on the basis of steric considerations and the X-ray structure of $Cp_2Zr[\eta^2\text{-}(N,C^2)\text{-}NC_5H_4(CH_3)](PMe_3)^+$.[1d]

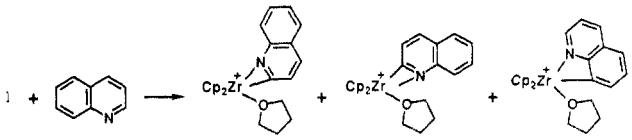
Complex **1** reacts with 7,8-benzoquinoline to yield the orthometalated complex **8**, which is isolated as a 1.5/1 mixture of two isomers (entry 4 in Table I). The ^1H and ^{13}C NMR spectra of this mixture exhibit, for each isomer, sharp singlets for the Cp ligands, resonances for coordinated THF (1 equiv), and low-field ^{13}C signals (δ 203.3, 190.8) characteristic of three-membered Zr–N–C rings. Deuteriolysis of the mixture gives 2-deuterio-7,8-benzoquinoline as the sole organic product (eq 5). These results are consistent with the existence of two isomers that contain three-membered Zr–N–C rings but differ in the position of the coordinated THF as illustrated in entry 4 and eq 5.



8a 8b (5)

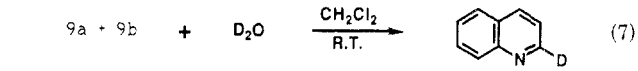
(9) ^1H NMR data (α-C–H, CD_2Cl_2): 2,5-dimethylpyrazine, δ 8.28 (s, 2 H); 2-phenylpyridine, δ 8.7 (m, 1 H); phenanthridine, δ 9.28 (s, 1 H).
(10) ^1H NMR of THF (CD_2Cl_2): δ 3.67 (m, 4 H), 1.81 (m, 4 H). ^{13}C NMR of THF (CD_2Cl_2): δ 68.22, 26.36.

The major product of the reaction of **1** with quinoline (entry 5 in Table I, eq 6) is three-membered-ring complex **9**, which is isolated as a 1/1 mixture of two isomers. The



9a,9b (6)

^{1}H NMR spectrum of **9** exhibits two Cp resonances and two sets of resonances for coordinated THF. The aromatic region is complicated, but low-field α-C–H resonances are conspicuously absent.[11] The ^{13}C NMR spectrum exhibits two complete sets of resonances, including Cp signals at δ 111.9 and 110.9 and signals for Zr–C at δ 208.8 and 192.5. Deuteriolysis of **9** affords only 2-deuterioquinoline (eq 7). These data establish that the isomers of **9** both contain three-membered Zr–C–N rings but differ in the distribution of ligands in the plane between the two Cp ligands.

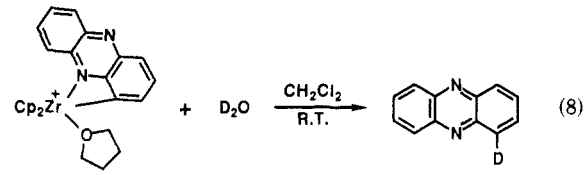


(7)

The minor product **10** (ca. 20%) is also produced in the reaction of **1** with quinoline (eq 6). However, because **10** could not be isolated free of **9** and is formed in low yield, this complex was characterized by ^{1}H NMR spectroscopy only.[12] The ^{1}H NMR spectrum of **10** displays a doublet at δ 9.2, which is assigned to the hydrogen α to N and which indicates that **10** does not have a three-membered-ring structure. The remaining pattern in the aromatic region, the presence of a set of Cp and coordinated THF resonances, and the absence of a high-field Zr–CH_3 resonance are consistent with the four-membered-ring structure shown, resulting from remote C–H activation.

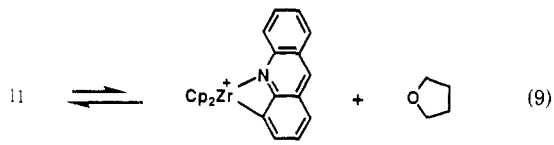
Activation of Remote Aryl C–H Bonds. The formation of **10** as a minor product in the reaction of **1** with quinoline establishes that activation of remote aryl C–H bonds is possible but is less favorable than α-C–H activation. The reactions of **1** with several N-heterocycles that lack α-hydrogens were studied to investigate the scope of remote C–H activation in this system. Complex **1** reacts with acridine (2,3-benzoquinoline) and phenazine (entries 6 and 7 in Table I) to yield the four-membered-ring complexes **11** and **12**, respectively. The ^{1}H NMR spectra of **11** and **12** exhibit singlets for the Cp ligands and complex aromatic patterns. In neither case is a high-field Zr–CH_3 resonance present. In the ^{13}C NMR spectra of **11** and **12**, the Zr–C(aryl) resonances appear at δ 171.2 and 170.2, respectively; for comparison the Zr–C resonances in $Cp_2Zr(Ph)(THF)^+$ and Cp_2ZrPh_2 appear at δ 184.9 and 183.1, respectively.[13] Deuteriolysis of **12** yields 1-deuteriophenazine (eq 8). The presence of 1 equiv of coordinated THF in both **11** and **12** is established by ^{1}H and ^{13}C NMR THF resonances, which are shifted downfield from those of free THF.[10]

The THF ligand of **11** is more labile than those in **5**–**9** and is extensively dissociated in CD_2Cl_2 solution. The ^{1}H



12 (8)

NMR spectrum of **11** (CD_2Cl_2, ambient temperature) in the presence of added THF (12 equiv) exhibits a single set of THF resonances, indicating that exchange of coordinated and free THF is rapid. Furthermore, under these conditions the Cp resonance is shifted upfield by 0.10 ppm and the aromatic resonance at δ 7.43 is shifted downfield by 0.20 ppm compared to the values observed in the absence of added THF. These spectral changes are ascribed to inhibition of THF dissociation by added THF and imply that **11** undergoes extensive THF dissociation in CD_2Cl_2 solution (eq 9). The existence of the equilibrium in eq



13 (9)

12 was confirmed by low-temperature spectroscopy. The ^{1}H NMR spectrum of **11** at −90 °C (CD_2Cl_2) exhibits two Cp resonances (δ 6.06, 6.39; ca. 6/4 ratio), two resonances for H-9 of the acridyl ligand (δ 9.01, 9.03, ca. 6/4 ratio; the remaining aromatic region is complicated), and resonances for coordinated and free THF, which are assigned to **11** and its THF dissociation product (**13**), respectively. Addition of excess THF (3.8 equiv) to the solution results in growth of the resonances for **11** and disappearance of the resonances for **13**, as expected as a result of mass action. The solution behavior of **12** was not studied but is expected to be similar to that of **11** due to the structural similarity of these complexes.

Activation of Side-Chain Aliphatic C–H Bonds. The observation of the remote C–H activation reactions described above, and our previous observation of H/D scrambling involving the CH_3 group of 2-methylpyridine in hydrogenolysis reactions of **3**,[1a] suggested that activation of side-chain aliphatic C–H bonds might be possible with suitable substrates. In fact, complex **1** reacts readily with 2,6-dimethylpyridine (lutidine), to yield after recrystallization the four-membered-ring complex **14**, resulting from activation of a methyl C–H bond (entry 8 in Table I). The ^{1}H NMR spectrum of **14** exhibits a single Cp resonance at δ 6.42, CH_2 and CH_3 resonances at δ 2.89 and 2.08, integrating for 2 and 3 H, respectively, and the expected pattern in the aryl region. The ^{13}C NMR spectrum exhibits a single Cp resonance at δ 117.0 and Zr–CH_2 and CH_3 resonances at δ 38.9 and 24.8.

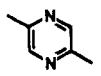
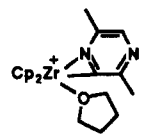
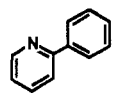
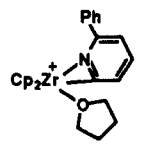
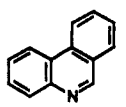
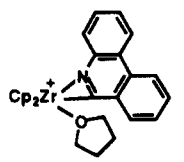
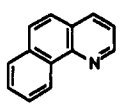
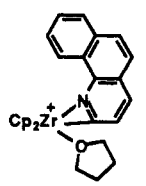
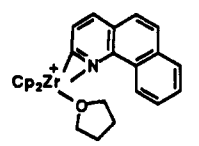
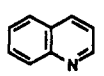
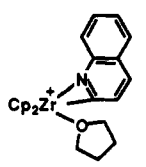
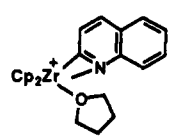
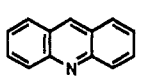
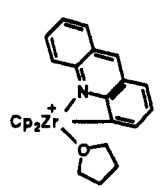
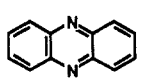
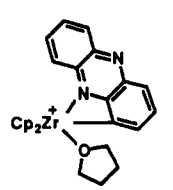
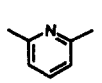
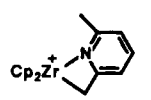
The isolation of **14** rather than the corresponding THF adduct $Cp_2Zr\{\eta^2(N,C)\text{-}CH_2NC_5H_3(6\text{-}Me)\}(THF)^+$ (**15**) indicates that the latter complex contains a labile THF ligand, consistent with the high lability observed for the THF ligand of the four-membered-ring complex **11**. Complex **15** is isolated, however, from the reaction of **14** with neat THF. The ^{1}H NMR spectrum of **15** (CD_2Cl_2) contains THF resonances at δ 3.67 (4 H) and 1.88 (4 H), which are shifted only slightly from those of free THF.[10] However, the Zr–CH_2 resonance at δ 2.29 is shifted significantly upfield from the corresponding resonance in **14**. The Cp and Zr–CH_2 resonances of **15** shift with changes in the concentration of **15** and upon addition of excess

(11) Partial ^{1}H NMR of quinoline (360 MHz, CD_2Cl_2): δ 8.9 (dd, J = 4.2, 1.7 Hz, 1 H, H-2), 8.15 (dd, J = 7.9, 1.6 Hz, 1 H, H-8).

(12) ^{1}H NMR of **10** (360 MHz, CD_2Cl_2): δ 9.2 (dd, J = 5.2, 1.6 Hz, α-H), 8.56 (d, J = 8.2 Hz, 1 H, Ar H), 8.34 (d, J = 7.6 Hz, 1 H, Ar H), 8.14 (m, 1 H, Ar H), 8.03 (d, J = 7.9 Hz, 1 H, Ar H), 7.53 (dd, J = 8.2, 5.2 Hz, 1 H, Ar H), 6.02 (s, 10 H, CpH), 3.70 (m, 4 H, THF), 1.82 (m, 4 H, THF).

(13) Jordan, R. F.; Wang, Y.; Borkowsky, S.; Bradley, P. K.; Echols, S. F. Manuscript in preparation.

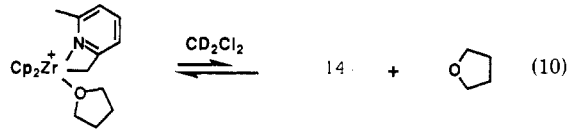
Table I. Reactions of $Cp_2Zr(CH_3)(THF)^+$ (1) with N-Heterocycles[a]

Entry	Substrate	Product(s)	Yield(%)[b]
1		 5	83
2		 6	97
3		 7	86
4		 8a  8b	90
5[c]		 9a  9b	75
6		 11	88
7		 12	77
8		 14	81

[a] Conditions: CH_2Cl_2, 23 °C, 2–4 h. [b] Isolated yields. [c] Complex **10** (ca. 20%) is also produced in this case.

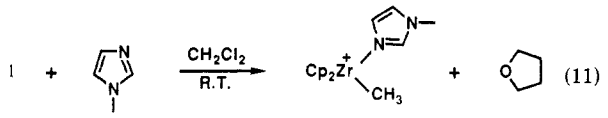
THF, and in the latter case a single set of THF resonances is observed. These observations confirm that, as expected, **15** undergoes extensive THF dissociation in CH_2Cl_2 solution and that exchange of free and coordinated THF is rapid (eq 10). Presumably interconversion of the two possible isomers of **15** is rapid (via **14**). Both **14** and **15**

decompose slowly in CH_2Cl_2 solution.



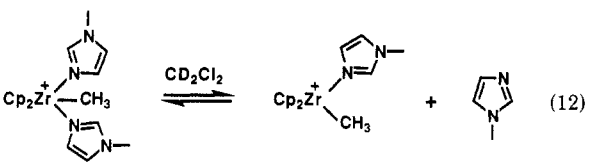
15

Formation of Unreactive Complexes. Complex 1 reacts with several substrates to form 16-electron $Cp_2Zr(CH_3)(L)^+$ or 18-electron $Cp_2Zr(Me)(L)_2^+$ complexes that are resistant to C–H activation. For example, ^1H NMR monitoring of the reaction of 1 with *N*-methylimidazole in CD_2Cl_2 at 23 °C reveals the formation of $Cp_2Zr(CH_3)$(*N*-methylimidazole)$^+$ (**16**) and the liberation of 1 equiv of free THF (eq 11).[14] Under these conditions no ligand C–H activation is observed.



16

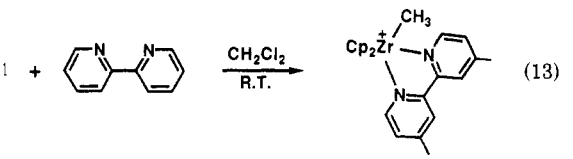
Complex 1 reacts with excess *N*-methylimidazole to yield the isolable bis(*N*-methylimidazole) adduct 17 (eq 12).



17 16

The −90 °C ^1H NMR spectrum of 17 contains single Cp and Zr–CH_3 resonances but two singlets for the N–CH_3 groups, indicating that the *N*-methylimidazole ligands are inequivalent. These results are consistent with either (i) a structure in which the Zr–CH_3 group is in an outer coordination site in the plane between the two Cp ligands or (ii) the structure shown in eq 12, in which the *N*-methylimidazole ligands are rotated such that the N–CH_3 groups are inequivalent. We have studied several related complexes previously, including $Cp_2Zr(H)(PMe_3)_2^+$ and $(C_5H_4Me)_2Zr(H)(PMe_3)_2^+$, $Cp_2Zr(Me)(PMe_3)_2^+$, and $Cp_2Zr(Me)(CH_3CN)_2^+$, and in each case the symmetric structure with the Zr–CH_3 group in the central coordination site is preferred.[6] On this basis **17** is assigned the structure shown in eq 12. However, it should be noted that the related actinide complex $(C_5Me_5)_2Th(Me)(THF)_2^+$ has an unsymmetrical structure with the Th–CH_3 group in an outer site.[15] ^1H NMR studies establish that 17 undergoes reversible dissociation of *N*-methylimidazole in CD_2Cl_2 solution at ambient temperature (eq 12). Thus, as the temperature is raised from −90 °C to ambient temperature, the Cp resonance shifts downfield toward that of the mono(*N*-methylimidazole) complex **16**, and the N–CH_3 resonances coalesce. Addition of 3 equiv of excess *N*-methylimidazole to a solution of 17 at ambient temperature causes the Cp and Zr–CH_3 resonances to shift upfield (by 0.10 and 0.24 ppm, respectively) from their values in the absence of excess ligand, and under these conditions a single N–CH_3 resonances is observed. The PMe_3 and CH_3CN ligands of $Cp_2Zr(CH_3)(PMe_3)_2^+$ and $Cp_2Zr(CH_3)(CH_3CN)_2^+$ are also labile at ambient temperature.[6] Thermolysis of 17, which is in equilibrium with the mono(*N*-methylimidazole) adduct **16**, at 70–80 °C (CD_2ClCD_2Cl) results in slow decomposition, and no C–H activation is observed.

Similarly, 1 reacts with 4,4′-dimethylbipyridine to yield the 18-electron complex **18** (eq 13).[6a] Thermolysis of 18 (70–80 °C, $ClCH_2CH_2Cl$) results only in slow decomposition, and no C–H activation is observed.



18

Unreactive Substrates. No reaction is observed between 1 and 2-phenylquinoline or 2-methylthiophene, under the standard reaction conditions (CH_2Cl_2, 4 h, 23 °C). In each case, 1 is recovered unchanged from the reaction mixture in high yield. ^1H NMR monitoring of CD_2Cl_2 solutions containing 1 and these substrates reveals that the resonances of 1 and the free heterocycle do not shift (even after a period of 5 h). This indicates that displacement of the coordinated THF of 1 by these heterocycles does not occur under these conditions.

Discussion

The cationic methyl complex $Cp_2Zr(CH_3)(THF)^+$ (1) reacts efficiently with a variety of N-heterocycles via C–H activation/CH_4 elimination to yield cyclometalated products. The results summarized in Table I and the equations establish two important requirements for substrate C–H bond activation in this system: (i) initial displacement of THF and coordination of the heterocyclic substrate to the $Cp_2Zr(CH_3)^+$ fragment must occur and (ii) an empty orbital must be available on Zr in the $Cp_2Zr(CH_3)$(substrate)$^+$ complex for coordination/activation of a substrate C–H bond. These results are consistent with the mechanism illustrated in eq 1. A variety of N-heterocycles derived from pyridine, entries 1–8 in Table I, meet these two requirements and undergo facile C–H activation chemistry. In contrast, the sterically crowded heterocycle 2-phenylquinoline and the weakly basic substrate 2-methylthiophene do not displace THF from 1 and do not undergo C–H activation. The five-membered heterocycle *N*-methylimidazole and the bidentate ligand 4,4′-dimethylbipyridine react with 1 to form the 18-electron complexes 17 and 18. Neither 17 nor 18 undergo CH_4 elimination because in both cases the low-lying Zr-based LUMO required for initial activation of the C–H bond is lacking. The 16-electron complex $Cp_2Zr(CH_3)$(*N*-methylimidazole)$^+$ (**16**), formed by reaction of 1 with 1 equiv of *N*-methylimidazole, or by ligand dissociation of 17, does not undergo C–H activation/CH_4 elimination under the mild conditions studied in this work. The reason for the lower reactivity in this case is not yet understood. Presumably interaction of the α-C–H bonds with the Zr(IV) center is less favored than for the six-membered N-heterocyclic ligands (vide

(14) ^1H NMR of **16** (CD_2Cl_2): δ 6.28 (s, 10 H, Cp), 3.35 (br s, 3 H, NCH_3), 0.63 (s, 3 H, $ZrCH_3$); the remaining resonances are broadened by exchange and obscured by BPh_4^-. Compare to ^1H NMR of 1 (CD_2Cl_2): δ 6.31 (s, 10 H, Cp), 3.44 (m, 4 H, THF), 1.80 (m, 4 H, THF), 0.74 (s, 3 H, $ZrCH_3$). Compare also to ^1H NMR of *N*-methylimidazole (CD_2Cl_2): δ 7.36 (s, 1 H), 6.95 (s, 1 H), 6.88 (s, 1 H), 3.63 (s, 3 H, NCH_3).

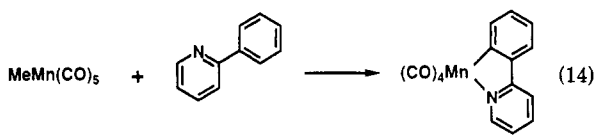
(15) Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.

(16) THF provides a reasonable compromise of stability and reactivity. $Cp_2Zr(R)(L)^+$ complexes containing more labile ligands (e.g. 2-Me-THF) react more rapidly with CH_2Cl_2 or BPh_4^-. Turner and Hlatky have shown that the use of C_6Me_6 ligands and other counterions allows the synthesis of base-free $(C_5Me_5)_2Zr(R)^+$ complexes.[1b]

infra). Further studies of this and related substrates are underway.[17]

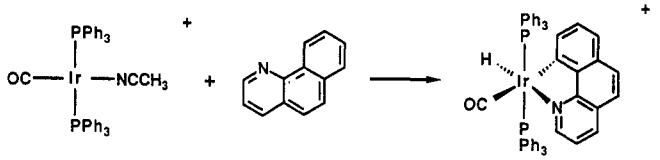
The present study has been limited to the ligand C–H activation chemistry of **1**. It should be possible to use other $Cp_2Zr(R)(L)^+$ complexes to circumvent the limitations of **1** noted above. In particular, $Cp_2Zr(R)(L)^+$ complexes with (i) ligands that are more labile than THF,[16] (ii) R groups that are more reactive than CH_3 (e.g. H, CH_2Ph), or (iii) R groups that are more bulky than CH_3 (to disfavor $Cp_2Zr(R)(L)_2^+$ complexes) are under study.[17]

A general preference for activation of C–H bonds that are α to N of the N-heterocycles is observed in the reactions of **1**. For example, three-membered-ring complexes **5–8** are formed in the reactions of **1** with 2,5-dimethylpyrazine, 2-phenylpyridine, phenanthridine, and 7,8-benzoquinoline, respectively. No evidence for activation of more remote aryl or aliphatic C–H bonds or for reduction of the heterocycle ring is observed.[18] Similarly, the major product of the reaction of **1** with quinoline is the orthometalated complex **9**. Teuben and co-workers reported similar results for the reactions of d^1 Cp_2TiR complexes with several substituted pyridines,[19] and orthometalations of pyridine itself have been reported for several other early-metal systems.[2a,e,f,20] This selectivity observed for the group 4 metallocene complexes is quite different from that exhibited by group 7–10 metal systems, which usually react with these substrates to yield five-membered metallacycles via activation of remote C–H bonds.[21] For example $MeMn(CO)_5$ reacts with 2-phenylpyridine via metalation of the ortho position of the Ph group, yielding **19** (eq 14),[22] and $Ir(CO)(CH_3CN)(PPh_3)_2^+$ reacts with 7,8-benzoquinoline via metalation at C-10 to yield **20** (eq 15).[23,24] These reactions also involve



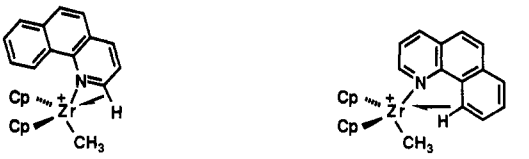
(14)

19



20

(15)



(A) (B)

Figure 1. Interaction of α and remote ligand C–H bonds with $Cp_2Zr(CH_3)^+$.

initial coordination of the substrate through N, followed by C–H activation. The latter step can occur by initial coordination of a C–H bond followed by oxidative addition.[25]

These selectivity trends may be due in part to the spatial properties of the metal frontier orbitals. In a 16-electron $Cp_2Zr(R)(L)^+$ complex, the Zr-based LUMO (which is localized in the plane between the two Cp ligands) has lobes ca. 45° from the Zr–L bond,[26] and Zr–H–C interactions with proximate α-C–H bonds, leading to C–H activation, may be favored as shown in A in Figure 1. Low-temperature NMR studies of related 2-methylpyridine complexes **2** provide some evidence for such agostic interactions involving α-C–H bonds.[1d] Also, spectroscopic and X-ray diffraction studies establish the presence of β-agostic interactions in $(C_5H_4Me)_2Zr(CH_2CH_2R)(PMe_3)^+$, $Cp_2Zr\{C(SiMe_3)=CHPh\}Cl$, and several other d^0 metallocene complexes.[1b,2e,f,3f,6g,i–k,27] Steric factors may also influence the regioselectivity of these C–H activation reactions. For example, species B in Figure 1 may be disfavored due to steric crowding involving the $Zr–CH_3$ group. The observed activation of the α-C–H bonds of 2,5-dimethylpyrazine (entry 1) and 2-methylpyridine[1a,c,d] rather than the more acidic Me C–H bonds[28] is consistent with the proposal that the orientation of the C–H bonds in the $Cp_2Zr(R)(substrate)^+$ complex is a major influence on the regioselectivity of the C–H activation.

In contrast, in the late-metal systems the $L_nM(substrate)$ intermediates have structures derived from square-planar or octahedral geometries. The metal-based LUMO's are ca. 90° from the M–N bond, and interaction of more remote C–H bonds leading to formation of five-membered-ring products is favored. For example, Crabtree has established by X-ray crystallography and NMR spectroscopy that the 8-Me group of 8-methylquinoline (mq) in IrH_2-

(17) Jordan, R. F.; Guram, A. Unpublished results.

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(20) (a) Dormond, A.; El Bouadili, A. A.; Moise, C. *J. Chem. Soc., Chem. Commun.* **1985**, 914. (b) Arnold, J.; Woo, H.-G.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 2045.

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(23) Neve, F.; Ghedini, M.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1989**, *28*, 3084.

(24) For other representative examples see: (a) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647. (b) Kasahara, A. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1272. (c) Cockburn, B. N.; Howe, D. V.; Keating, T.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 404. (d) Nonoyama, M. *J. Organomet. Chem.* **1974**, *74*, 115. (e) Trofimenko, S. *Inorg. Chem.* **1973**, *12*, 1215. (f) Tin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2091. (g) Hiraki, K.; Obayashi, Y.; Oki, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1372. (h) Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 687.

(25) For discussions see refs 3 and 5. Other pathways are available for high-oxidation-state systems.

(26) Leading references: (a) Green, J. C.; Green, M. L. H.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1972**, 421. (b) Green, M. L. H. *Pure Appl. Chem.* **1972**, *30*, 373. (c) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433. (d) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (e) Bruce, M. R. M.; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639. (f) Zhu, L.; Kostic, N. M. *J. Organomet. Chem.* **1987**, *335*, 395.

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$(PPh_3)_2(mq)^+$ adopts an agostic structure involving the vacant site cis to N.[3k] The 8-methylquinoline ligand in this complex is otherwise undistorted. Observation of H/D exchange involving this Me group shows that C–H activation occurs reversibly. The corresponding 7,8-benzoquinoline complex undergoes C–H oxidative addition to give $Ir(H)(PPh_3)_2(H_2O)(\eta^2\text{-}(N,C^{10})\text{-benzoquinolinato})^+$, which has a structure similar to that of **20**.[29] A variety of related square-planar and octahedral systems containing C–H–M interactions have been reported.[30] Deeming and Rothwell have provided evidence that, in the former case, in-plane rather than axial C–H–M interactions are required for C–H activation.[31,32]

When both α sites in the N-heterocycle are blocked, as in entries 6–8 of Table I, activation of remote alkyl or aryl C–H bonds can occur in the coordination sphere of $Cp_2Zr(CH_3)^+$. In these particular cases four-membered rings are formed. It is surprising that such crowded substrates react efficiently with **1**. However, assuming substrate coordination is not precluded, steric crowding can promote C–H activation in these systems by increasing the interaction of the C–H bond with the metal-centered LUMO. This well-known effect[33] has been noted by Teuben in studies of $Cp_2Ti(R)(L)$ complexes[19] and utilized by Buchwald to promote C–H abstraction in Cp_2ZrRR' complexes.[34] The lower steric requirements of the five-membered heterocycle *N*-methylimidazole (versus six-membered heterocycles derived from pyridine) may be a contributing factor to the low C–H activation reactivity of **16**.

The cyclometalated complexes **3** and **6** display efficient insertion chemistry with several alkenes and alkynes.[1,17] Subsequent reports from our laboratory will describe the insertion chemistry of **5**–**15** as well as efforts to develop synthetic applications of these complexes.[17]

Experimental Section

All manipulations were performed under inert atmosphere or vacuum, with use of a Vacuum Atmospheres Drybox, Schlenk techniques, or a high-vacuum line. Solvents were purified by distillation from appropriate drying/deoxygenating agents prior to use,[35] stored in evacuated bulbs, and vacuum-transferred into reaction flasks or NMR tubes. All nitrogen-containing heterocycles were purchased from Aldrich; those that are liquids at ambient temperature were stirred over KOH pellets and distilled from CaH_2 prior to use. NMR spectra were recorded on Bruker 300- or 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. ^2H NMR chemical shifts were assigned with use of CD_2Cl_2 as an external reference. All spectra of cationic complexes exhibited the expected 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 163.5 (q, J = 49 Hz), 135.4, 125.7, 121.7. Elemental analyses were performed by Analytische Laboratorien, West Germany, or Schwarzkopf Microanalytical Laboratory.

General Procedure for Reactions of $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (1) with N-Heterocycles. The procedure described below for **6** was utilized in the reactions of **1** with all heterocycles unless noted. The procedure described below for the deuteriolysis of **9** was used in all cases unless noted.

$[Cp_2Zr\{\eta^2(N,C^2)\text{-}N_2C_4(3,6\text{-}Me)_2\}(THF)][BPh_4]$ (5). This complex was isolated as an off-white solid from the reaction of **1** with 2,5-dimethylpyrazine (yield 118 mg, 83.0%). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.34 (s, 1 H, Ar H), 5.93 (s, 10 H, CpH), 3.90 (m, 4 H, THF), 2.77 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.02 (m, 4 H, THF). This spectrum is unchanged at −90 °C. ^{13}C NMR (90 MHz, CD_2Cl_2): δ 194.94 (C–Zr), 159.04, 149.65, 145.39, 110.78 (Cp), 78.47 (THF), 25.89 (THF), 23.28 (CH_3), 20.04 (CH_3). Anal. Calcd for $C_{44}H_{45}BN_2OZr$: C, 73.41; H, 6.30; N, 3.89; Zr, 12.67. Found: C, 73.32; H, 6.14; N, 3.83; Zr, 12.85.

$[Cp_2Zr\{\eta^2(N,C^2)NC_5H_3(6\text{-}Ph)\}(THF)][BPh_4]$ (6). To a slurry of **1** (239 mg, 0.381 mmol) in CH_2Cl_2 (15 mL) was added 2-phenylpyridine (71 mg, 0.46 mmol). After the mixture was stirred at 23 °C for 15 min, all material dissolved and a clear solution was obtained. The solution was stirred for 2.5 h at room temperature. Hexane (25–30 mL) was added to the reaction solution to induce precipitation of the product. The solid was separated by filtration, washed with hexane (5 × 10 mL), and dried in vacuo. The crude product was recrystallized from CH_2Cl_2/hexane (yield 269 mg, 92%). ^1H NMR (360 MHz, CD_2Cl_2): δ 7.90–7.88 (br m, 2 H, Ar H), 7.54–7.50 (br m, 6 H, Ar H), 6.00 (s, 10 H, CpH), 3.47 (m, 4 H, THF), 1.60 (m, 4 H, THF). ^{13}C NMR (90 MHz, CD_2Cl_2): δ 201.66 (C-2), 157.97 (C-6), 139.53, 137.55, 130.68, 130.03, 129.64, 127.73, 122.10, 110.91 (Cp), 77.50 (THF), 25.69 (THF). Anal. Calcd for $C_{49}H_{46}BNOZr$: C, 76.74; H, 6.04; N, 1.83; Zr, 11.89. Found: C, 76.23; H, 5.90; N, 1.76; Zr, 12.10.

Deuteriolysis of **6** gave 6-deuterio-2-phenylpyridine, which was characterized by comparison of its ^1H and ^2H NMR spectra to the ^1H NMR spectrum of 2-phenylpyridine.[9] ^2H NMR (45 MHz, CH_2Cl_2): δ 8.5 (br s, D-6).

$[Cp_2Zr\{\eta^2(N,C^2)\text{-}3,4\text{-benzoquinolinato}\}(THF)][BPh_4]$ (7). This complex was isolated as a white solid from the reaction of **1** with phenanthridine (yield 235 mg, 85.5%). ^1H NMR (360 MHz, CD_2Cl_2): δ 8.77 (d, J = 8.24 Hz, 1 H, Ar H), 8.72 (m, 1 H, Ar H), 8.36 (d, J = 7.72 Hz, 1 H, Ar H), 8.12 (t, J = 8.3 Hz, 1 H, Ar H), 8.0 (t, J = 7.5 Hz, 1 H, Ar H), 7.8 (m, 2 H, Ar H), 7.73 (m, 1 H, Ar H), 6.04 (s, 10 H, CpH), 4.07 (m, 4 H, THF), 2.11 (m, 4 H, THF). ^{13}C NMR (90 MHz, CD_2Cl_2): δ 215.32 (C–Zr), 140.28, 134.40, 133.23, 132.09, 130.22, 129.91, 129.87, 128.36, 127.32, 124.41, 124.33, 123.57, 110.71 (Cp), 78.45 (THF), 25.92 (THF). Anal. Calcd for $C_{51}H_{46}BNOZr$: C, 77.44; H, 5.86; N, 1.77; Zr, 11.53. Found: C, 77.19; H, 5.76; N, 1.74; Zr, 11.70.

$[Cp_2Zr\{\eta^2(N,C^2)\text{-}7,8\text{-benzoquinolinato}\}(THF)][BPh_4]$ (8). This complex (mixture of isomers) was isolated as an off-white solid from the reaction of **1** with 7,8-benzoquinoline (yield 227 mg, 90.0%). The isomer ratio was determined to be 1.5:1 integration of ^1H NMR Cp signals. ^1H NMR (360 MHz, CD_2Cl_2): major isomer δ 8.5–7.5 (m, 8 H, Ar H), 6.14 (s, 10 H, CpH), 4.06 (m, 4 H, THF), 2.05 (m, 4 H, THF); minor isomer δ 8.5–7.5 (m, 8 H, Ar H), 6.06 (s, 10 H, CpH), 3.76 (m, 4 H, THF), 1.91 (m, 4 H, THF). ^{13}C NMR (90 MHz, CD_2Cl_2): both isomers δ 203.30 (C–Zr), 190.83 (C–Zr), 153.57, 149.22, 144.32, 143.51, 139.06, 138.82, 135.26, 135.04, 131.59, 130.59, 129.89, 129.75, 129.68, 129.38, 129.08, 128.73, 128.10, 127.91, 127.69, 127.63, 126.50, 126.30, 123.34, 122.63, 112.58 (Cp), 111.16 (Cp), 78.54 (THF), 77.65 (THF), 26.37 (THF), 26.07 (THF). Anal. Calcd for $C_{51}H_{46}BNOZr$: C, 77.44; H, 5.86; N, 1.77; Zr, 11.53. Found: C, 77.27; H, 5.68; N, 1.79; Zr, 11.75.

Deuteriolysis of **8** (mixture of isomers) gave 2-deuterio-7,8-benzoquinoline (contaminated by BPh_3), which was characterized by comparison of its ^1H and ^2H NMR spectra with the ^1H NMR

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spectrum of 7,8-benzoquinoline.[36] ^2H NMR (45 MHz, CH_2Cl_2): δ 8.9 (br s, D-2).

$[Cp_2Zr(\eta^2(N,C^2)$-quinolinato)(THF)][BPh_4] (9). Reaction of **1** with quinoline gave a mixture of **9** and **10**. Complex **9** was isolated by recrystallization of this mixture from CH_2Cl_2/hexane and exists as a mixture of two isomers (yield 210 mg, 75.0%). The isomer ratio (1/1) was determined by integration of the ^1H Cp resonances. ^1H NMR (360 MHz, CD_2Cl_2): mixture of isomers δ 8.30–7.65 (m, 12 H, ArH), 6.08 (s, 10 H, CpH), 5.99 (s, 10 H, CpH), 4.12 (m, 8 H, THF), 2.15 (m, 4 H, THF), 2.10 (m, 4 H, THF). ^{13}C NMR (90 MHz, CD_2Cl_2): mixture of isomers, δ 208.82 (C–Zr), 192.54 (C–Zr), 145.22, 144.33, 138.98, 138.79, 132.67, 132.10, 130.62, 130.40, 130.11, 129.88, 129.12, 128.50, 127.75, 126.79, 123.48, 122.50, 111.86 (Cp), 110.87 (Cp), 78.93 (THF), 78.31 (THF), 26.49 (THF), 25.97 (THF). Anal. Calcd for $C_{47}H_{44}BNOZr$: C, 76.19; H, 5.99; N, 1.89; Zr, 12.31. Found: C, 76.06; H, 6.03; N, 1.95; Zr, 12.15.

Deuteriolysis of 9 (Mixture of Isomers). To a solution of a mixture of **9a** and **9b** (12 mg, 0.016 mmol) in CH_2Cl_2 (1 mL) was added D_2O (1 mL, degassed and N_2 purged) under a positive pressure of N_2. The resultant slurry was allowed to stand overnight with occasional stirring. The organics were extracted with several portions of CH_2Cl_2 (3 × 1 mL). The extracts were combined, dried with $MgSO_4$, and filtered. Concentration of the solution by vacuum evaporation of the solvent gave a pale yellow residue (2 mg) of 2-deuterioquinoline, which was characterized by comparison of its ^2H NMR spectrum with the ^1H NMR spectrum of quinoline.[11] ^2H NMR (45 MHz, CH_2Cl_2): δ 8.8 (br s, D-2).

$[Cp_2Zr(\eta^2(N,C^1)$acridinyl)(THF)][BPh_4] (11). This complex was isolated as a yellow powder from the reaction of **1** with acridine (yield 365 mg, 88.0%). ^1H NMR (360 MHz, CD_2Cl_2): δ 9.02 (s, 1 H, Ar H), 8.20 (d, J = 8.7 Hz, 1 H, Ar H), 8.10 (d, J = 6.5 Hz, 1 H, Ar H), 8.0–7.93 (m, 2 H, Ar H), 7.73 (t, J = 8.6 Hz, 1 H, Ar H), 7.76 (dd, J = 8.7, 6.5 Hz, 1 H, Ar H), 7.47 (d, J = 8.8 Hz, 1 H, Ar H, partially obscured by BPh_4^-), 6.26 (s, 10 H, CpH), 3.79 (m, 4 H, THF), 1.98 (m, 4 H, THF).[37] ^{13}C NMR (90 MHz, CD_2Cl_2): δ 171.17 (C–Zr), 145.17, 143.39, 142.09, 134.45, 130.92, 129.39, 128.96, 127.66, 127.01, 125.49, 123.93, 123.58, 115.03 (Cp), 74.24 (THF), 25.87 (THF). Anal. Calcd for $C_{51}H_{46}BNOZr$: C, 77.44; H, 5.86; N, 1.77; Zr, 11.53. Found: C, 77.24; H, 5.75; N, 1.79; Zr, 11.45.

$[Cp_2Zr(\eta^2(N,C^1)$-phenazinyl)(THF)][BPh_4] (12). This complex was isolated as a brown solid from the reaction of **1** with 1.5 equiv of phenazine for 6 h at 23 °C (yield 243 mg, 77.0%). Duplicate elemental analyses of a spectroscopically pure sample gave low C values. ^1H NMR (360 MHz, CD_2Cl_2): δ 8.43 (d, J = 7.5 Hz, 1 H, Ar H), 8.41–7.90 (m, 5 H, Ar H), 7.61 (d, J = 7.6 Hz, 1 H, Ar H), 6.17 (s, 10 H, Cp), 3.75 (m, 4 H, THF), 1.97 (m, 4 H, THF). ^{13}C NMR (90 MHz, CD_2Cl_2): δ 170.2 (C–Zr), 145.18, 143.37, 142.87, 138.84, 137.76, 133.73, 133.41, 132.37, 131.01, 127.70, 125.52, 113.56 (Cp), 74.97 (THF), 25.86 (THF). Anal. Calcd for $C_{50}H_{45}BN_2OZr$: C, 75.83; H, 5.73; N, 3.54; Zr, 11.52. Found: C, 71.36; H, 5.73; N, 3.52; Zr, 11.95.

Deuteriolysis of **12** gave 1-deuteriophenazine, which was characterized by comparison of its ^1H and ^2H NMR spectra with the ^1H NMR spectrum of phenazine.[38] ^1H NMR (300 MHz, CD_2Cl_2): δ 8.25 (m, 3 H), 7.85 (m, 4 H). ^2H NMR (45 MHz, CH_2Cl_2): δ 8.3 (br s).

$[Cp_2Zr\{\eta^2(N,C)$-$CH_2NC_5H_3(6$-$CH_3)\}][BPh_4]$ (14). This complex was isolated as a orange solid from the reaction of **1** with 2,6-dimethylpyridine (yield 71 mg, 56%). ^1H NMR (360 MHz, CD_2Cl_2): δ 7.79 (t, J = 7.8 Hz, 1 H, Ar H), 7.22 (d, J = 7.8 Hz, 1 H, Ar H), 7.13 (d, J = 7.8 Hz, 1 H, Ar H), 6.42 (s, 10 H, CpH), 2.89 (s, 2 H, CH_2Zr), 2.08 (s, 3 H, CH_3). ^{13}C NMR (90 MHz, CD_2Cl_2): δ 157.26, 142.11, 127.72, 124.78, 123.14, 116.98 (Cp), 38.92 (CH_2Zr), 24.75 (CH_3). Anal. Calcd for $C_{41}H_{38}BNZr$: C, 76.14; H, 5.92; N, 2.17; Zr, 14.10. Found: C, 75.86; H, 5.84; N, 2.00; Zr, 14.05.

$[Cp_2Zr\{\eta^2(N,C)$-$CH_2NC_5H_3(6$-$CH_3)\}(THF)][BPh_4]$ (15). Complex **14** was dissolved in THF. The solvent was evaporated, and the resulting white solid was washed with hexane and dried under vacuum (yield 105 mg, 100%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.70 (t, J = 7.75 Hz, 1 H, Ar H), 7.08–7.01 (2 H, obscured by BPh_4^-, Ar H), 6.22 (s, 10 H, CpH), 3.67 (m, 4 H, THF), 2.29 (s, 2 H, CH_2Zr), 2.27 (s, 3 H, CH_3), 1.88 (m, 4 H, THF). The Cp and $ZrCH_2$ resonances shift upfield for concentrated solutions or upon addition of excess THF, due to changes in the ratio of **14**/**15**, which are in rapid exchange. ^{13}C NMR (90 MHz, CD_2Cl_2, −50 °C) δ 156.2, 139.6, 125.6 (obscured by BPh_4^-), 122.4, 122.0, 113.0 (Cp), 74.1 (THF), 25.4 ($ZrCH_2$), 24.1 (THF), 22.4 (CH_3). The assignments of the $ZrCH_2$ and CH_3 resonances were confirmed by a DEPT experiment. Anal. Calcd for $C_{45}H_{46}BNOZr$: C, 75.18; H, 6.45; N, 1.95; Zr, 12.69. Found: C, 75.09; H, 6.37; N, 1.87; Zr, 12.85.

$[Cp_2Zr(CH_3)(N$-methylimidazole$)_2][BPh_4]$ (17). This complex was isolated as a white solid from the reaction of **1** with excess (>2.0 equiv) *N*-methylimidazole (yield 218 mg, 80.4%). ^1H NMR (360 MHz, CD_2Cl_2): δ 6.97 (br s, 2 H), 6.76 (br s, 2 H), 6.56 (br s, 2 H), 6.06 (s, 10 H, Cp), 3.8 (br s, 6 H, NCH_3), 0.27 (br s, 3 H, $ZrCH_3$); at −90 °C, δ 7.32 (1 H, obscured by BPh_4^-), 7.23 (s, 1 H), 6.70 (m, 3 H), 6.49 (s, 1 H), 5.92 (s, 10 H, Cp), 3.39 (s, 3 H, N–CH_3), 3.22 (s, 3 H, N–CH_3). ^{13}C NMR (90 MHz, CD_2Cl_2): δ 139.2 (C-2), 129.1 (C-3), 122.1 (C-4, obscured by BPh_4^-, confirmed by gated ^{13}C NMR), 112.9 (Cp), 38.4, 34.5. Anal. Calcd for $C_{43}H_{45}BN_4Zr$: C, 71.74; H, 6.30; N, 7.78; Zr, 12.67. Found: C, 71.59; H, 6.30; N, 7.66; Zr, 12.85.

$[Cp_2Zr(CH_3)(4,4'$-Me_2bpy)][BPh_4] (18). A slurry of **1** (1.07 g, 1.70 mmol) and 4,4′-dimethylbipyridine (0.334 g, 1.81 mmol) in 20 mL of CH_2Cl_2 was stirred at 23 °C for 40 min, during which time all the solid dissolved. Filtration gave a solution of **18**. Attempts to crystallize **18** failed due to the extremely high solubility of this complex. The solvent was removed under vacuum and the residue washed with hexane, yielding **18**·0.5C_6H_{14} as a pale pink solid (yield 1.26 g, 95%). An analytical sample of **18**·1.0$C_6H_5CH_3$ was obtained by precipitation of **18** from a CH_2Cl_2 solution with toluene. ^1H NMR (360 MHz, CD_2Cl_2): δ 8.45 (d, J = 5.9 Hz, 1 H), 8.43 (d, J = 5.8 Hz, 1 H) (H-6, H-6′), 7.89 (br s, 2 H, H-3, H-3′), 5.87 (s, 10 H, Cp), 2.52 (s), 2.50 (s) (total 6 H, bpy–CH_3), 0.48 (s, 3 H, Zr–CH_3), H-5, H-5′ obscured by BPh_4^-. ^{13}C NMR (90 MHz, CD_2Cl_2): δ 155.2 (d, J_{CH} = 10 Hz), 152.3 (d, J = 9 Hz) (C-2, C-2′), 154.7 (t, J = 6 Hz), 154.0 (t, J = 6 Hz) (C-4, C-4′), 152.2 (dm, J = 190 Hz), 151.0 (dd, J = 180 Hz, 4 H) (C-6, C-6′), 127.7, 127.6 (J_{CH} not determined due to interference by BPh_4^- resonances) (C-3, C-3′), 124.1, 123.9 (J_{CH} not determined due to interference by BPh_4^- resonances), 111.8 (d, J = 174 Hz, Cp), 35.9 (q, J = 121 Hz, Zr–CH_3), 21.5 (q of t, J = 129, 4 Hz), 21.4 (q of t, J = 128, 4 Hz) (bpy CH_3, CH_3'). Anal. Calcd for $C_{47}H_{45}BN_2Zr{\cdot}C_6H_5CH_3$: C, 77.95; H, 6.42; N, 3.36. Found: C, 77.75; H, 6.34; N, 3.56.

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(36) Partial ^1H NMR of 7,8-benzoquinoline (CD_2Cl_2): δ 9.3 (m, 1 H, H-10), 9.0 (dd, J = 4.4, 2.6 Hz, 1 H, H-2 α to N). The signal for H-10 is shifted downfield due to proximity to N. Jackman, L. M.; Sternhell, S. *Applications of NMR Spectroscopy in Organic Chemistry*; Pergamon: Oxford, 1969; p 214.

(37) The Cp resonance and the aromatic resonance at δ 7.43 shift with changes in the concentration of **11** and in the presence of added THF due to changes in the extent of THF dissociation from **11**. The −90 °C ^1H NMR spectrum exhibits resonances for **11** and its THF dissociation product, as described in the text.

(38) ^1H NMR of phenazine (300 MHz, CD_2Cl_2): δ 8.25 (m, 4 H, H-1), 7.85 (m, 4 H, H-2).