2g, 135733-86-7; **2h**, 135733-87-8; **2i**, 135733-88-9; **2j**, 135733-89-0; **4**, 933-52-8; **5**, 135733-90-3; **6**, 135733-91-4; **9**, 95599-70-5; **10a**, 135733-92-5; **10b**, 135733-93-6; **10c**, 132724-77-7; **11**, 135733-94-7; **13**, 135733-95-8; RR'C=O (R = R' = Me), 67-64-1; RR'C=O (R = R' = Et), 96-22-0; RR'C=O (R = R' = *i*-Pr), 565-80-0; RR'C=O (R = R' = Ph), 119-61-9; RR'C=O (R = Pr, R' = H), 123-72-8; RR'C=O (R = Ph, R' = H), 100-52-7; RR'C=O (R = $CH{=}CH_2$, R' = H), 107-02-8; RR'C=O (R = $CH{=}CH_2$, R' = Me), 78-94-4; RR'C=O (R = $CH{=}CH_2$, R' = Et), 1629-58-9; tetraphenylcyclopentadienone, 479-33-4; methyl 2-furoate, 611-13-2.

Alkene and Alkyne Insertion Reactions of Cationic $Cp_2Zr(\eta^2\text{-pyridyl})(L)^+$ Complexes. Zirconium-Mediated Functionalization of Pyridines

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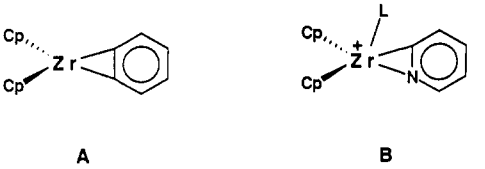
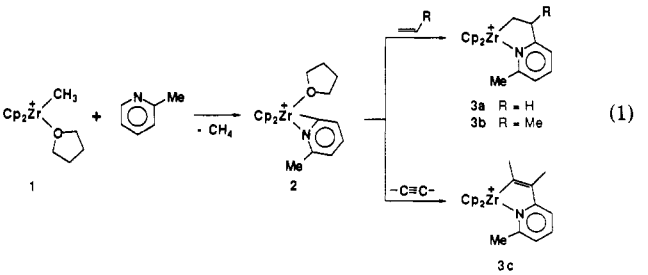
Cationic $Cp_2Zr(\eta^2\text{-pyridyl})(L)^+$ complexes (L = THF, py), which are available via ortho C–H activation reactions of pyridines with $Cp_2Zr(Me)(THF)^+$, undergo insertion of alkenes and alkynes to yield new five-membered azazirconacycles. Normal 1,2-insertion leading to β-substituted azametallacycles is observed for α-olefins $H_2C{=}CHR$ containing electron-donating substituents (R = alkyl, CH_2SiMe_3, CH_2OR), while 2,1-insertion leading to α-substituted products is observed for styrene, 2-vinylpyridine, and vinyltrimethylsilane. The regioselectivity of these reactions is rationalized on the basis of electronic effects in the insertion transition states and products. Terminal alkynes insert regioselectively to yield α-substituted unsaturated five-membered metallacycles, but the unsymmetrical internal alkyne 2-hexyne affords a mixture of regioisomers. Steric effects appear to determine the regioselectivity in these cases. The silylacetylene $MeC{\equiv}CSiMe_3$ inserts selectively, yielding an α-$SiMe_3$ substituted metallacycle as a result of steric and Si electronic effects. The overall sequence of pyridine ortho C–H activation and alkene/alkyne insertion provides a powerful zirconium-mediated approach to substituted/functionalized pyridines.

Introduction

Zirconocene aryne species, e.g. Cp_2Zr(benzyne) (A, Chart I), exhibit facile insertion reactions with olefins, acetylenes, nitriles, CO_2, and other substrates,[1-3] Buchwald and coworkers have developed elegant syntheses of aromatic and heterocyclic compounds based on this chemistry.[3] We are exploring the insertion chemistry of cationic pyridyl complexes $Cp_2Zr(pyridyl)(L)^+$ (B, L = labile ligand, Chart I), which in their ligand-free form are isoelectronic with Cp_2Zr(benzyne), with the aim of developing general Zr-mediated routes to substituted pyridine-based heterocycles. The cationic zirconium(IV) alkyl complex $Cp_2Zr(CH_3)(THF)^+$ (**1**)[4,5] reacts selectively with a variety of pyridines, pyrazines, and related substrates via ortho C–H activation to yield new, three-membered azametallacycles, as illustrated for 2-picoline in eq 1.[6,7] The cationic pyridyl complex Cp_2Zr(6-Me-pyridyl)$(THF)^+$ (**2**) reacts readily with ethylene, propene, and 2-butyne to afford five-membered azametallacycles **3a–c** (eq 1).[8] These reactions involve initial displacement of THF by substrate, followed by insertion into the Zr–C bond. The functionalized heterocyclic ligands of **3a–c** can be removed by hydrogenolysis in a catalytic process (**3a,b**)[9] or by β-H elimina-

Chart I





(1)

(1) For a recent review, see: Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.
(2) (a) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (b) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246.
(3) (a) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137. (c) Buchwald, S. L.; Lucas, E. A.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4396. (d) Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397. (e) Buchwald, S. L.; Fang, Q. *J. Org. Chem.* **1989**, *54*, 2793. (f) Buchwald, S. L.; King, S. M. *J. Am. Chem. Soc.* **1991**, *113*, 258.
(4) For general chemistry of $Cp_2Zr(R)(L)^+$ complexes, see: (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Soctt, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (d) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. (e) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. C. *Organometallics* **1989**, *8*, 2892. (f) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289. (g) Jordan, R. F.; LaPointe, R. E.; Baenziger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539. (h) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268.
(5) For reviews, see: (a) Jordan, R. F.; Bradley, P. K.; LaPointe, R. E.; Taylor, D. F. *New J. Chem.* **1990**, *14*, 505. (b) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (c) Jordan, R. F. *Adv. Organomet. Chem.*, in press.
(6) Jordan, R. F.; Guram, A. S. *Organometallics* **1990**, *9*, 2116.
(7) If both ortho sites are blocked, more remote C–H bonds are activated. See ref 6 and: Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833.
(8) (a) Jordan, R. F. Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546. (b) Taylor, D. F.; Guram, A. S.; Jordan, R. F. Unpublished results.

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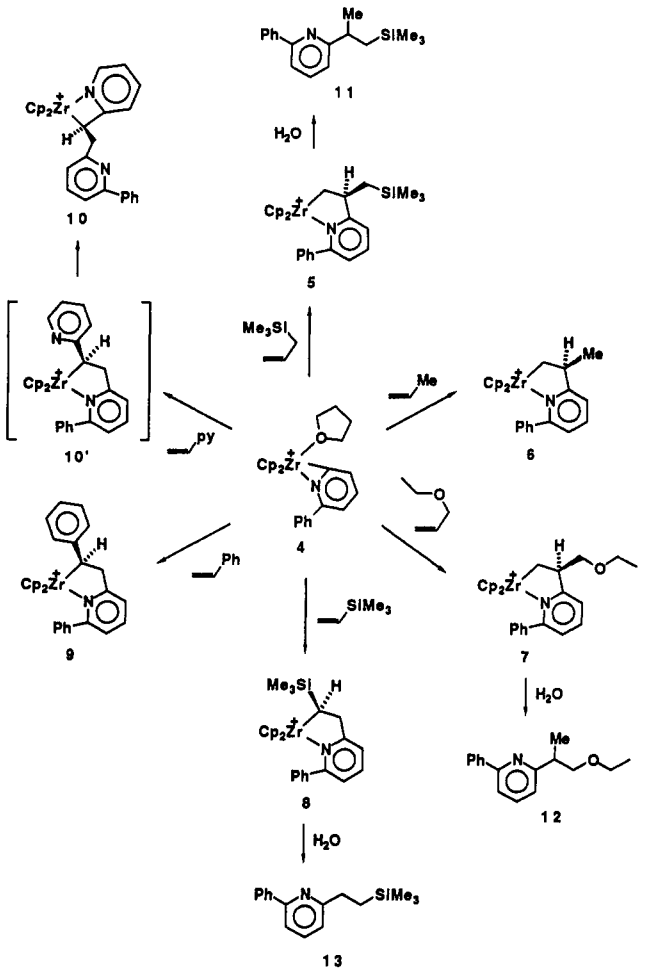
Scheme I



tion (**3a,b**) or hydrolysis in stoichiometric reactions. These overall reaction sequences provide a novel approach to alkylation/functionalization of pyridine-based heterocycles. In the present contribution we describe a more general study of the scope and regioselectivity of alkene and alkyne insertion reactions of the representative pyridyl complex $Cp_2Zr(\eta^2(C,N)$-{6-phenylpyridyl}$)(L)^+$ (**4**) and several analogues.[10]

Results

Olefin Insertion Reactions of $Cp_2Zr(\eta^2(C,N)$-{6-R-pyrid-2-yl}$)(THF)^+$ Complexes. The cationic phenylpyridyl complex $Cp_2Zr(\eta^2(C,N)$-{6-phenylpyrid-2-yl}$)(THF)^+$ (**4**),[11] which is available from the reaction of **1** with 2-phenylpyridine,[6] reacts efficiently with a variety of α-olefins at 23 °C (CH_2Cl_2, approximately 24 h) or at 60 °C ($ClCH_2CH_2Cl$, 2.5 h) to afford the five-membered metallacycles **5–10** as summarized in Scheme I.

Allyltrimethylsilane, propene, and allyl ethyl ether react with **4** via *1,2-insertion* to afford the β-substituted five-membered metallacycles **5–7** respectively (Scheme I). The ^1H NMR spectra of **5–7** each contain a multiplet at ca. δ 3.6 for the β-CH and a triplet (ca. δ 2.3, J = ca. 12.6 Hz) and doublet of doublets (ca. δ 0.8–1.0, J = ca. 12.6, 3.5 Hz) for the diastereotopic α-CH's. This pattern is similar to that observed previously for **3b** and is consistent with a near-planar metallacyclic structure in which the α-H–C–C–β-H dihedral angles are ca. 0 and 110°.[12] An X-ray diffraction analysis of **3a** revealed that the ring is only slightly puckered.[8a] The ^{13}C NMR spectra of **5–7** each exhibit a methylene carbon resonance (confirmed by DEPT) in the region δ 67.0–57.0. Additionally, the ^1H and ^{13}C NMR spectra of **5–7** each exhibit resonances for two inequivalent Cp ligands as expected for cyclic/chelated structures due to the presence of substituent at the β-position. For **5** and **7**, the insertion regiochemistry was confirmed by hydrolysis, which afforded 2-phenyl-6-(1-methyl-2-(trimethylsilyl)ethyl)pyridine (**11**)[10] and 2-phenyl-6-(1-methyl-2-ethoxyethyl)pyridine (**12**), respectively, as the sole organic products (Scheme I). Key data for **12** include ^1H NMR resonances at δ 1.34 (d, 3 H) and 3.32 (sextet, 1 H) and a ^{13}C NMR methine resonance at δ 42.7 (confirmed by DEPT) for the py-$CH(Me)CH_2$ fragment. Data for **11** are similar.[10]

In contrast, **4** reacts with vinyltrimethylsilane via *2,1-insertion* to afford the α-substituted five-membered metallacycle **8** (Scheme I).[10] The regiochemistry of **8** was unambigiously established by hydrolysis which gave 2-phenyl-6-(2-(trimethylsilyl)ethyl)pyridine (**13**) as the sole organic product.[10] The ^1H NMR spectrum of **8** is quite different from those of the 1,2-insertion products **3b** and **5–7** and exhibits three doublet of doublets at δ 3.72, 3.40, and 3.32 for β-CH's and α-CH respectively.[10,13] In this case, steric interactions between a Cp ligand and the α-$SiMe_3$ group probably severely distort the ring from planarity.

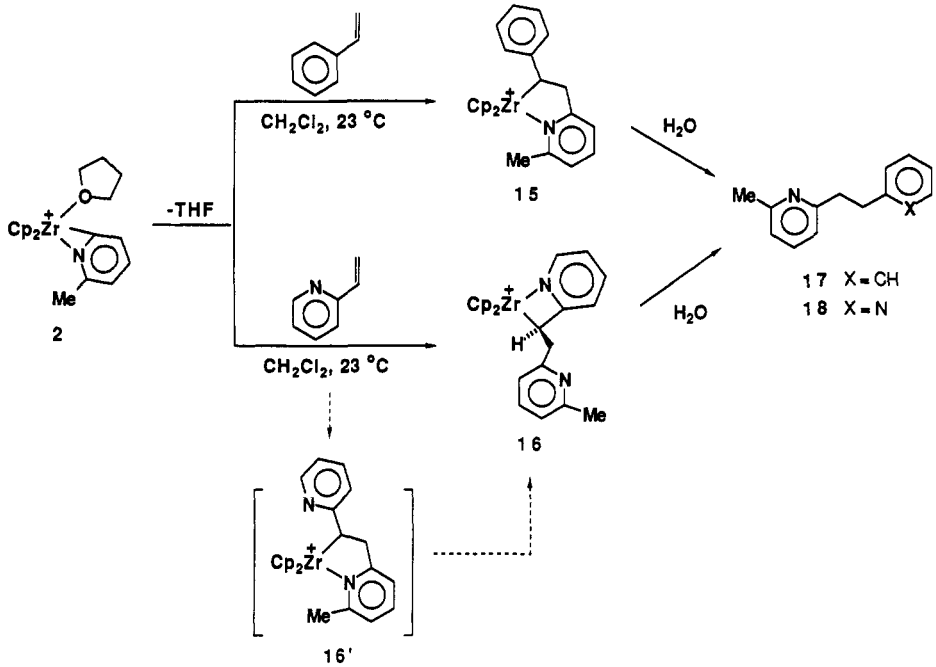
Complex **4** reacts with styrene to yield metallacycle **9** (Scheme I), which could not be completely characterized due to its poor solubility. The ^1H NMR spectrum of **9** (obtained from the reaction mixture containing unreacted **4** and styrene) is very similar to that of **8** and strongly suggests the 2,1-insertion regiochemistry shown.[14] Conspicuously absent from this spectrum is the triplet and doublet of doublets pattern characteristic of 1,2-insertion complexes **3b** and **5–7**.

To verify the structure of **9**, the synthesis of more soluble analogues amenable to complete characterization was investigated. The cationic methylpyridyl complex **2** reacts with styrene at 23 °C (CH_2Cl_2, approximately 14 h) via 2,1-insertion to afford metallacycle **15** (Scheme II), which is soluble to some extent in CD_2Cl_2 and is unambiguously characterized by NMR spectroscopy, elemental analysis, and hydrolysis experiments. The ^1H NMR spectrum of **15** exhibits three doublet of doublets at δ 4.56, 3.81, and 3.62 for the α-CH and β-CH's. This pattern is similar to that observed for **8**. The chelated structure is confirmed by the presence of two resonances for the inequivalent Cp's and a py–CH_3 resonance at δ 1.61, which is shifted upfield from that of free 2,6-dimethylpyridine (δ 2.46). The ^{13}C NMR spectrum of **15** exhibits resonances at δ 65.0 and 38.9 for Zr–CH– and $ZrCH(Ph)CH_2$–, respectively (assignments confirmed by DEPT), and two Cp resonances. The regiochemistry of **15** was confirmed by hydrolysis, which gave 6-methyl-2-(2-phenethyl)pyridine (**17**) as the only organic product. Key data for **17** include a ^1H NMR resonance at δ 3.0 (s, 4 H), and ^{13}C NMR resonances at δ 40.5 and

(9) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778.
(10) Guram, A. S.; Jordan, R. F. *Organometallics* **1990**, *9*, 2190.
(11) The counterion is BPh_4^- in all cases.

(12) For the Karplus correlation between dihedral angle and vicinal coupling constants, see: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981; pp 208–210.
(13) The assignment of ^1H NMR resonances for α-CH and β-CH's are based on coupling constants. In general, geminal couplings are larger than vicinal couplings. See ref 12.
(14) Key ^1H NMR data for **9** (from a mixture of unreacted **4** and styrene) ($ClCD_2CD_2Cl$, 300 MHz): δ 6.11 (s, 5 H, Cp), 5.67 (s, 5 H, Cp), 4.47 (dd, J = 13.4 Hz, J = 4.0 Hz, 1 H, $ZrCH(Ph)$), 3.86 (dd, J = 17.8 Hz, J = 13.4 Hz, 1 H, $ZrCH(Ph)CH_2$–), 3.61 (dd, J = 17.8 Hz, J = 4.0 Hz, 1 H, $ZrCH(Ph)CH_2$–).

Scheme II



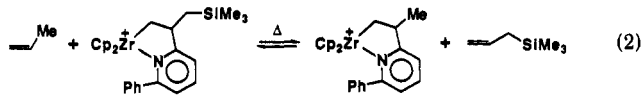
36.2 for the $-CH_2CH_2-$ group (^{13}C assignments confirmed by DEPT).

Complex **2** also reacts with 2-vinylpyridine via 2,1-insertion followed by rearrangement to yield four-membered metallacycle **16**, as shown in Scheme II. The ^1H NMR spectrum of **16** is similar to those of five-membered metallacycles **8**, **9**, and **15** and includes three doublet of doublets at δ 4.04, 3.48, and 3.19 for the β-CH's and α-CH, respectively. However, the py–CH_3 resonance (δ 2.59) appears far downfield from the corresponding resonances of **3a,b** (δ 1.51, 1.39), which contain chelated 6-Me-pyridyl groups, and near that of free 2,6-dimethylpyridine. This indicates that the disubstituted pyridine of **16** is not coordinated to Zr. The Zr*C*H– ^{13}C NMR resonance of **16** appears at δ 36.2 (assignment confirmed by DEPT), considerably upfield of the Zr–C resonances of five-membered metallacycles **3**, **5–8**, and **15** (δ 76.0–57.0) but close to the Zr–C ^{13}C resonance of the recently characterized four-membered metallacycle $Cp_2Zr(\eta^2(C,N)\text{-}CH_2\{6\text{-Me-pyrid-2-yl}\})^+$ (δ 38.9).[6,7] On the basis of these NMR data, **16** is assigned the four-membered metallacyclic structure shown in Scheme II. Hydrolysis of **16** yields 6-methyl-2-(2-(2′-pyridyl)ethyl)pyridine (**18**), which confirms the "2-1" regiochemistry of the reaction of **2** with 2-vinylpyridine. Key data for **18** include a ^1H NMR resonance at δ 3.15 (m, 4 H), and ^{13}C NMR resonances at δ 38.4 and 38.3 for the $-CH_2CH_2-$ group (^{13}C assignments conformed by DEPT). The formation of **16** likely proceeds via the initial five-membered metallacycle **16′**, which undergoes an intramolecular ligand substitution. Presumably the relative steric bulk (*o*-Me group) of the displaced pyridine ligand is responsible for this rearrangement. ^1H NMR monitoring of the reaction did not provide any evidence for **16′**, indicating that the rearrangement occurs rapidly.

Phenylpyridyl complex **4** reacts with 2-vinylpyridine to yield **10**, which, like **9**, is insoluble (Scheme I). The ^1H NMR data for **10** are similar to those of **16**,[15] and on this basis, **10** is assigned the analogous four-membered metallacyclic structure shown.

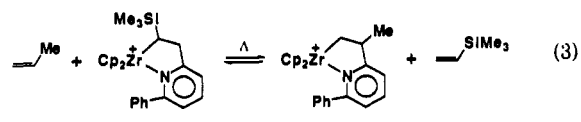
Complex **4** failed to react with the representative disubstituted olefins isobutylene, *trans*-2-butene, *cis*-2-butene, and cyclohexene under similar reaction conditions. Complex **4** reacts readily with conjugated dienes such as butadiene, 1,3-pentadiene, and 2-methyl-1,3-pentadiene to afford mixtures of products that remain to be characterized.[8b]

Origin of Regioselectivity in Alkene Insertion Reactions. Several experiments were performed to probe whether the regioselectivity observed in the olefin insertion reactions of **4** in Scheme I is kinetic or/and thermodynamic in origin. ^1H NMR monitoring of the reactions leading to **5**, **6**, and **8** (23 °C) does not reveal formation of the alternate regioisomers as transient intermediates. These insertions are reversible at higher temperatures. For example, the reaction of **5** with excess propene at 23 °C (CD_2Cl_2, 8 h) yields a trace of **6** and allyltrimethylsilane; at 65 °C ($ClCD_2CD_2Cl$, 1.5 h) a significant amount of **6** and allyltrimethylsilane is formed (eq 2). This reaction pre-



(2)

sumably involves deinsertion of **5** followed by propene insertion. The reverse reaction occurs at 80 °C but not at 23 °C (eq 2). Complex **8** does not react with excess propene or trimethylsilylacetylene at 65 °C ($ClCD_2CD_2Cl$, 1.5 h). However, thermolysis of **8** in presence of excess propene at 110 °C (C_6D_5Cl, sealed tube, 3.0 h) affords a mixture of vinyltrimethylsilane, **8**, and **6** (eq 3). The

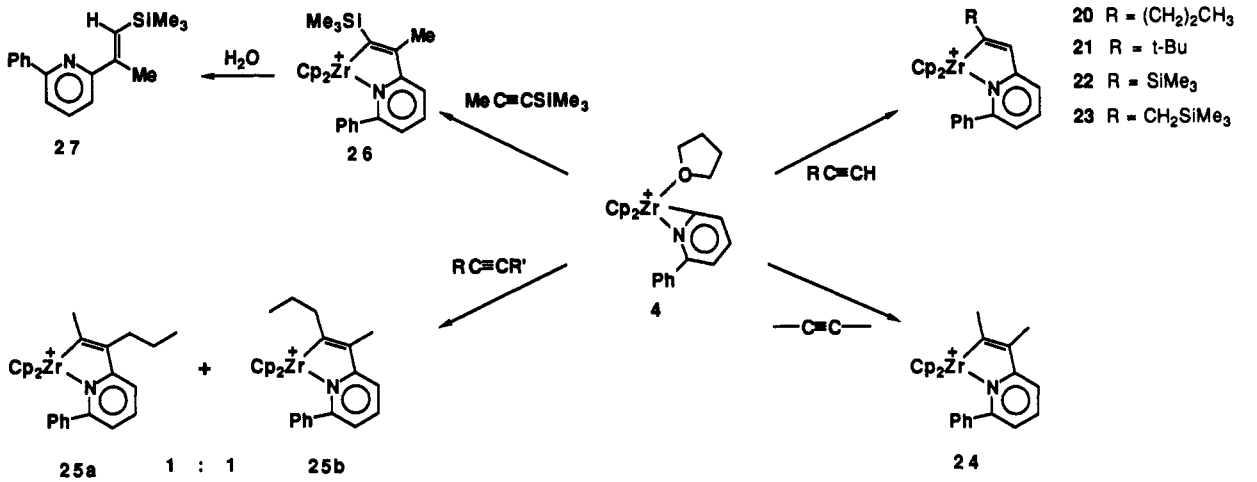


(3)

reverse reaction occurs at 80 °C (eq 3). No isomerization of **5**, **6**, or **8** is observed under conditions where olefin exchange experiments establish that deinsertion occurs

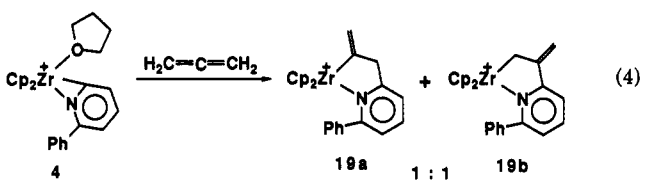
(15) Key ^1H NMR data for **10** (from a mixture of unreacted **4** and 2-vinylpyridine) (CD_2Cl_2, 300 MHz): δ 5.70 (s, 5 H, Cp), 5.56 (s, 5 H, Cp), 4.20 (dd, J = 17.7 Hz, J = 5.7 Hz, 1 H, ZrCH(py)C*H*$_2$–), 3.71 (dd, J = 17.8 Hz, J = 11.5 Hz, 1 H, ZrC*H*(py)–), 3.11 (dd, J = 11.8 Hz, J = 5.9 Hz, 1 H, ZrCH(py)C*H*$_2$–).

Scheme III

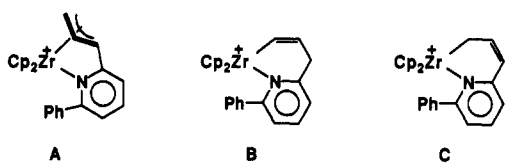


(120 °C, C_6D_5Cl, sealed tube). These observations establish that the observed products **5**, **6**, and **8** are thermodynamically favored and suggest that they are kinetically favored as well.[16] The situation is presumed to be the same for the other metallacycles.

Reaction of 4 with Allene. The reaction of the phenylpyridyl complex **4** with excess allene at 65 °C ($ClCH_2CH_2Cl$, 1.5 h) affords a 1/1 mixture of regioisomers **19a** and **19b** (eq 4), which differ in position of the exocyclic



(4)



double bond and could not be separated by recrystallization.[17] The ^1H NMR spectrum of **19a**/**19b** exhibits two Cp resonances at δ 5.92 and 5.45 and broad singlets at δ 4.08 and 2.46 assigned to the β-CH_2 of **19a** and the α-CH_2 of **19b**, respectively. The ^{13}C NMR exhibits Cp resonances at δ 114.5 and 114.2, resonances for the quaternary vinyl carbons at δ 190.8 (**19a**) and 149.9 (**19b**), and resonances at δ 126.7 and 112.5 for the exocyclic methylene carbons of the two isomers. The ^{13}C NMR assignments were confirmed by DEPT experiments. These ^1H and ^{13}C NMR data are inconsistent with η^3-allyl structure A and isomeric structures B and C (eq 4).

Alkyne Insertion Reactions of 4. Terminal and internal alkynes insert efficiently into the Zr–C bond of **4** under mild conditions (CH_2Cl_2, 23 °C, minutes), as summarized in Scheme III. The reactions of **4** with 1-pentyne, *tert*-butylacetylene, (trimethylsilyl)acetylene, and propargyltrimethylsilane afford metallacycles **20–23**, respectively, in which the alkyne substituent is located on the α-carbon. This regiochemistry is established by the ^{13}C NMR spectra of **20–23**, each of which exhibit a low-field quaternary carbon resonance (δ 226–240 region) for Zr—*C*(R)=CH– (assignments confirmed by DEPT). For comparison, the α-carbon resonances of the related metallacycle **3c** and the alkenyl complex $(C_5H_4Me)_2Zr$-({Me}*C*=CH{Me})(THF)$^+$ appear at δ 210.6 and 208.6, respectively.[4e,8a] The ^1H NMR spectra for **20–23** each exhibit a single resonance (δ 6.7–7.3) for the vinyl H, a Cp resonance, and the expected pattern for the aromatic H's and the aliphatic side chains.

Complex **4** reacts with 2-butyne to afford metallacycle **24** (Scheme III), which is analogous to complex **3c**. Poor regioselectivity is observed in reactions of **4** with unsymmetrical internal alkynes. For example, the reaction of **4** with 2-hexyne affords an inseparable, 1/1 mixture of regioisomers **25a** and **25b**. The NMR spectrum of this mixture exhibits two complete sets of resonances, including two characteristic low-field quaternary ^{13}C resonances at δ 217.8 and 212.7 for the Zr–*C*(vinyl) carbons. In contrast, **4** reacts regioselectively with 1-(trimethylsilyl)prop-1-yne (CH_2Cl_2, 1.0 h) to yield metallacycle **26**. The ^1H and ^{13}C NMR data unambigously establish the formation of a single isomer of **26**. The quaternary carbon resonance at δ 230.0 in the ^{13}C NMR spectrum of **26** suggests that the $SiMe_3$ substituent is located on the α-carbon. This is confirmed by hydrolysis which affords 2-phenyl-6-(1-methyl-2-(trimethylsilyl)ethenyl)pyridine (**27**) as the sole organic product (Scheme III). The small coupling (J = 0.9 Hz) between the vinyl H (δ 6.62) and the vinyl CH_3 (δ 2.36) in the ^1H NMR spectrum of **27** establishes that the CH_3 group is vicinal to the vinyl H.[18] The assigned trans geometry is based on the assumption of cis insertion and retention of configuration in the hydrolysis step.

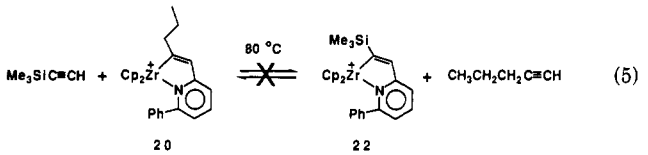
Origin of Regioselectivity in Alkyne Insertion Reactions. The rapidity of the alkyne insertion reactions leading to **20–26** (minutes at 23 °C) precludes ^1H NMR monitoring experiments to determine if alternate regioisomers are formed as transient intermediates. However, several observations establish that these reactions, unlike analogous alkene insertion reactions, are *irreversible* under the reaction conditions and more extreme conditions. ^1H NMR monitoring experiments reveal that no reaction occurs between metallacycle **20** and excess (trimethylsilyl)acetylene at 23 °C (CD_2Cl_2, 24 h) or even at 80 °C

(16) It is conceivable but unlikely that insertion in the sense opposite to that observed occurs rapidly and reversibly. This possibility cannot be rigorously ruled out as the alternate regioisomers are unavailable.

(17) A white fiber presumed to be polymeric allene was also isolated from the reaction mixture. Sorensen, W. R.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*, 2nd ed.; Interscience Publishers: New York, 1968; p 328.

(18) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: Braunschweig, Germany, 1969; p 316.

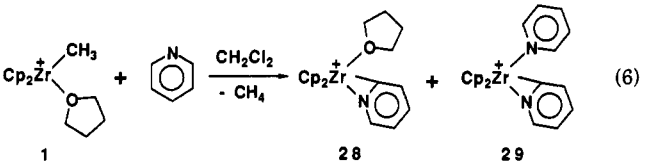
(sealed tube, 12 h), nor between metallacycle **22** and excess 1-pentyne under similar conditions (eq 5). Thermolysis



(5)

of $ClCD_2CD_2Cl$ solution of the 1/1 mixture of **25a** and **25b** at 65 °C (under vacuum, sealed tube, 24 h) does not change the isomer ratio. Independent thermolysis of **22** and of **23** at 110 °C ($ClCD_2CD_2Cl$, sealed tube) also does not induce isomerization of these complexes. These observations suggest but do not prove that the observed alkyne insertion products in Scheme III are kinetically favored.

Insertion Chemistry of $Cp_2Zr(pyridyl)(L)^+$ Complexes. Earlier we reported that the reaction of $Cp_2Zr(Me)(THF)^+$ (**1**) with pyridine yields a mixture of $Cp_2Zr(pyridyl)(THF)^+$ (**28**) and $Cp_2Zr(pyridyl)(pyridine)^+$ (**29**) (eq 6).[19] While the THF complex **28** reacts readily with

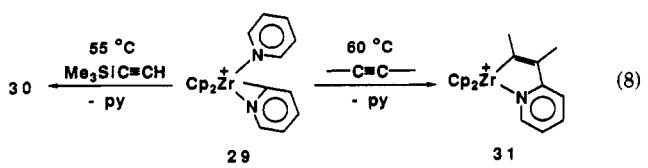


(6)

ethylene and 2-butyne at 23 °C, **29** does not due to strong binding of the sterically unencumbered pyridine ligand.[20] As **28** could not be separated from **29**, this appeared to preclude Zr-mediated coupling of pyridine itself with unsaturated substrates. To circumvent this problem, we investigated the reaction of **1** with pyridine in the presence of several representative alkynes at 50 °C, with the hope that **28** (or the ligand-free species $Cp_2Zr(pyridyl)^+$) would be competitively trapped by the unsaturated substrate and/or that **29**, if formed, would undergo pyridine dissociation and substrate insertion at the elevated temperature. Indeed, **1** reacts with pyridine in presence of (trimethylsilyl)acetylene at 55 °C (CH_2Cl_2, sealed tube, 5 h) to yield metallacycle **30** in a high yield (eq 7). There is no evidence

(7)

(^1H NMR) for **29** in the final reaction mixture. The spectroscopic properties of **30** are similar to those of analogous α-substituted metallacycles **20–23**. Additionally, the reaction of preformed **29** with (trimethylsilyl)acetylene at 55 °C ($ClCD_2CD_2Cl$) also yields **30** (eq 8). Similarly,



(8)

reaction of **29** with 2-butyne at 60 °C ($ClCD_2CD_2Cl$, 16 h) affords metallacycle **31** in good yield (eq 8). The spectroscopic properties of **31** are similar to those of **3c** and **24**.

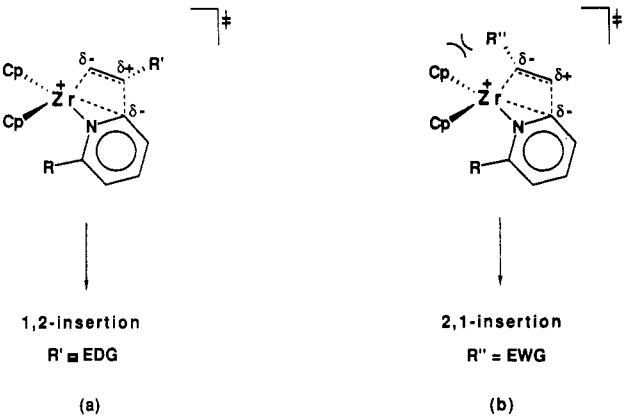


Figure 1. Proposed transition states for α-olefin insertion reactions of $Cp_2Zr(\eta^2\text{-pyridyl})^+$ complexes.

Discussion

Cationic pyridyl complexes $Cp_2Zr(\eta^2(C,N)\text{-}\{6\text{-R-pyridyl}\})(L)^+$ (R = H, Me, Ph; L = THF, py) react efficiently with a variety of α-olefins and alkynes via insertion into the Zr–C bond to yield five-membered metallacycles. The elaborated pyridyl ligand can be removed as a new substituted pyridine by hydrolysis and, presumably, as a functionalized pyridine by other standard Zr–C cleavage reactions.[21]

Alkenes $H_2C{=}CHR$ containing electron-donating substituents (R = alkyl, CH_2SiMe_3, CH_2OR) react with **4** via 1,2-insertion to yield β-substituted metallacycles (Scheme I). This regiochemistry is analogous to that observed in related insertions of $Cp_2Zr(benzyne)$[1-3] and related zirconocene metallacycles,[22-24] as well as for early-metal hydrides and alkyls.[25] Available evidence suggests that the 1,2-insertion products derived from **4** are both kinetically and thermodynamically favored, and the regioselectivity can be rationalized in terms of steric and electronic effects in the insertion transition states (Figure 1)[26] and the products. Cp/alkene substituent steric interactions disfavor the transition states leading to, and the products of, 1,2-insertion (Figure 1b). Additionally, electron-donating

(19) Complexes of the type **29** are not formed in reactions of **1** with ortho-substituted pyridines because these more crowded ligands are displayed by THF.

(20) Analogous complexes of 3- and 4-methylpyridine are unreactive with olefins for the same reason. Taylor, D. F.; Jordan, R. F. Unpublished results.

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(26) A polar transition state with a partial positive charge located β to the metal center has been implicated for insertions of α-olefins into M–H and M–R bonds.[26a-e] The two α-carbons in Figure 1 are likely to be partially negatively charged (developing and breaking Zr–C bonds). (a) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (b) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134. (c) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566. (d) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53.

Figure 2. Steric effects in alkyne insertion reactions of $Cp_2Zr(\eta^2$-pyridyl$)^+$ complexes.

alkyl substituents stabilize the developing positive charge on the β-carbon of the 1,2-insertion transition state (Figure 1a). This electronic effect is expected to be much more pronounced in the transition state leading to **5** because the $SiMe_3$ substituent is β to the developing positive charge (β-effect).[27] Similarly, for allyl ethyl ether, the OR substituent may provide anchimeric assistance for the 1,2-insertion leading to **7**.[28] The 1,2-insertion products are also electronically more stable than the 2,1-isomers (primary vs secondary metal alkyl).

$Cp_2Zr(pyridyl)^+$ complexes **4** and **2** react with several alkenes H_2C=CHR (R = $SiMe_3$, Ph, pyridine) via 2,1-insertion to give rare examples of stable secondary Cp_2Zr^{IV} alkyls (Schemes I and II).[2b,29] The 2,1-insertion regiochemistry observed for the reaction of **4** with vinyltrimethylsilane is opposite to that expected on basis of steric effects (destabilizing Cp/$SiMe_3$ interactions) and was rationalized on the basis of electronic effects originating from the $SiMe_3$ group; i.e., SiR_3 stabilizes the α negative charge and β positive charge in the polar transition state (Figure 1b) and the product (electron-rich Zr–alkyl carbon).[10] The selective formation of α-substituted metallacycles **9**, **10′**, **15**, and **16′** from the insertion reactions of $Cp_2Zr(\eta^2(C,N)$-{6-R-pyridyl}$)(L)^+$ (**2**, R = Me; **4**, R = Ph) with styrene and 2-vinylpyridine is also electronic in origin. The substituents on these olefins are electron-withdrawing and stabilize the α-negative charge in the polar transition states (Figure 1b) and the products. This electronic stabilization overrides the destabilizing steric effects and controls the insertion regiochemistry. There are several previous reports of reactions of styrene with early-metal hydrides $(C_5R_5)_2Zr(H)Cl$ and small metallacycles Cp_2Zr(olefin) in which 2,1-insertion is a minor or major pathway.[24,30,31] Electronic effects of the type described above likely control the regiochemistry in these cases. In a related case, Buchwald observed that hydrozirconation of 2-vinylfuran with $Cp_2Zr(H)Cl$ occurs in a 2,1-fashion.[31] It was suggested that coordination of the furan oxygen to Zr may influence/direct the insertion regiochemistry. Such an effect is possible for the reactions of **2** and **4** with vinylpyridine. However, the 2,1-insertions observed for vinyltrimethylsilane and styrene, which lack additional donor functions, and the normal 1,2-insertion observed for H_2C=$CHCH_2OR$,[32] suggest that such precoordination is unimportant for these pyridyl systems.

Pyridyl complex **4** rapidly inserts alkynes to yield new unsaturated five-membered azametallacycles (Scheme III). Terminal alkynes react regioselectively yielding α-substituted products, as observed in analogous reactions of Cp_2Zr(benzyne) and related species.[1,22,33] This regiochemistry is rationalized on the basis of steric effects. As the alkyne substituent lies in the plane between the two Cp ligands, steric interactions involving the pyridyl group are more severe than those involving the Cp ligands and favor α-substituted products and the presumed initial adducts (Figure 2) and transition states leading thereto.[34] The unsymmetrical internal alkyne 2-hexyne, in which the steric bulk of the substituents differs only slightly, reacts with **4** to yield a mixture of regioisomers. However, the silyl acetylene MeC≡C$SiMe_3$ selectively yields the α-$SiMe_3$-substituted metallacycle. This reflects the greater steric bulk of the $SiMe_3$ group vs the Me group and the electronic effects associated with Si (Si stabilizes α-negative and β-positive charge). Analogous regioselectivity is observed for related insertion/coupling reactions of Si-substituted alkynes at early-transition-metal centers.[3e,22,33-35]

Conclusion

Cationic zirconocene pyridyl complexes $Cp_2Zr(\eta^2(C,N)$-{6-R-pyridyl}$)(L)^+$ are easily prepared via ortho C–H activation reactions of $Cp_2Zr(CH_3)(THF)^+$ with pyridines. Like their neutral, isoelectronic analogues Cp_2Zr(benzyne) and related species, $Cp_2Zr(pyridyl)^+$ species react efficiently with α-olefins and alkynes via insertion into the Zr–C bond. The alkene insertion reactions are predictably regioselective as a result of strong electronic effects in the transition states and products. Alkenes H_2C=CHR containing electron-donating substituents (R = alkyl, CH_2SiMe_3, CH_2OR) react via 1,2-insertion to yield β-substituted metallacycles. In contrast, alkenes containing electron-withdrawing (R = Ph, pyridine) or SiR_3 substituents undergo unusual 2,1-insertions yielding α-substituted products. The insertion reactions of terminal alkynes and internal silylalkynes are also predictably regioselective. For terminal alkyne insertions, steric effects favor the formation of α-substituted products. Similarly, silylacetylenes $R_3SiC{\equiv}CR$ selectively yield α-SiR_3 substituted products as a result of steric and electronic effects. However, unsymmetrical internal alkynes containing sterically similar substituents do not insert regioselectively. This Zr-mediated ortho C–H activation/insertion chemistry represents an attractive method for the regio- and stereoselective functionalization of pyridine-based heterocycles. Subsequent reports from this laboratory will focus on synthetic organic applications.

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Experimental Section

All manipulations were performed under inert atmosphere or vacuum, using a Vacuum Atmospheres drybox, Schlenk techniques, or a high-vacuum line. $ClCH_2CH_2Cl$ and CH_2Cl_2 were distilled from CaH_2. CD_2Cl_2 and $ClCD_2CD_2Cl$ were purchased from MSD Isotopes and distilled from P_2O_5. All solvents were stored in evacuated bulbs and vacuum transferred into reaction flasks or NMR tubes. Alkenes and alkynes were purchased from Aldrich Chemical Co. Alkenes were stirred over, and vacuum transferred from, CaH_2 prior to use. Alkynes were dried with molecular sieves. NMR spectra were recorded on a Bruker 300- or 360-MHz spectrometer 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. The anion in all cases is BPh_4^-. All spectra of cationic complexes exhibited 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. FTIR spectra were recorded on a Mattson Cygnus 25 spectrometer. FTIR $\nu_{C=C}$ assignments for **20**, **21**, **23–25**, and **31** are based on comparison to that for **6**. For the alkyne insertion products **22**, **26**, and **30**, $\nu_{C=C}$ could not be assigned due to overlapping BPh_4^- and phenylpyridyl absorbances. Mass spectral analyses were performed on a VG Trio-1 benchtop GC–MS and a VG ZAB-HF high-resolution mass spectrometer. For GCMS, the relative intensities are reported in parentheses. Elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany, or E & R Microanalytical Laboratory, New York, NY.

$Cp_2Zr(Me)(THF)^+$ (**1**), $Cp_2Zr(\eta^2(C,N)$-{6-Me-pyridyl}$)(THF)^+$ (**2**) and $Cp_2Zr(\eta^2(C,N)$-{6-Me-pyridyl}$)$(pyridine)$^+$ (**29**) were prepared as described previously.[4d,h,6,8a] The procedure described for **5** was used in the preparation of alkene insertion complexes **6–10**, **15**, **16**, and **19ab**. The procedure described for **20** was used for the preparation of alkyne insertion complexes **21–26**.

Preparation of [$Cp_2Zr(\eta^2(C,N)$-{6-phenylpyridyl}$)$-(THF)][BPh_4] (4). This complex was prepared by the following procedure, which is a scaled-up version of that reported earlier.[6] Complete characterization data were reported earlier.[6] 2-Phenylpyridine (594 mg, 3.82 mmol) was added to a slurry of [$Cp_2Zr(Me)(THF)$][BPh_4] (**1**) (2.00 g, 3.18 mmol) in 30 mL of CH_2Cl_2. After stirring of the mixture at 23 °C for 15 min, all material dissolved and a clear solution was obtained. The solution was stirred for 3.0 h at room temperature. Hexane (50 mL) was added to the reaction solution to induce precipitation of the product. The solid was separated by filtration, washed with hexane (5 × 20 mL), and dried in vacuo. The crude product was recrystallized from CH_2Cl_2/hexane to give 2.40 g (99%) of **4** as a white solid.

[$Cp_2Zr(\eta^2(C,N)$-CH_2CH{CH_2SiMe_3}{6-phenylpyrid-2-yl}$)$][BPh_4] (5). A solution of **4** (900 mg, 1.18 mmol) and allyltrimethylsilane (803 mg, 7.05 mmol) in 20 mL of $ClCH_2CH_2Cl$ was heated at 60–65 °C under N_2 for 2.5 h. The resulting yellow solution was cooled to room temperature, and hexane (20–25 mL) was added to induce precipitation (the product may precipitate as a yellow oil). The precipitated product was washed with hexane (5 × 15 mL) and dried in vacuo. The crude product was recrystallized from CH_2Cl_2/hexane, yielding 694 mg (73%) of **8** as a yellow solid.

^1H NMR (360 MHz, CD_2Cl_2): δ 7.93 (t, J = 7.8 Hz, 1 H, Ar H), 7.8 (t, J = 7.6 Hz, 1 H, Ar H), 7.69 (t, J = 7.6 Hz, 2 H, Ar H), 7.57 (d, J = 8.1 Hz, 1 H, Ar H), 7.4 (d, J = 8.1 Hz, 1 H, Ar H), 7.08 (obscured by BPh_4^-, 2 H, Ar H), 6.39 (s, 5 H, Cp), 5.36 (s, 5 H, Cp), 3.60 (m, 1 H β-CH), 2.35 (t, J = 12.6 Hz, 1 H, α-CH), 1.6 (dd, J = 14.0 Hz, J = 3.8 Hz, 1 H, CH_2Si), 1.03 (dd, J = 12.6 Hz, J = 3.7 Hz, 1 H, α-CH), 0.74 (dd, J = 14.0 Hz, J = 10.2 Hz, 1 H, CH_2Si), 0.22 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 175.5, 158.6, 142.8, 139.7, 134.5, 133.3, 123.1, 122.3, 121.2, 113.3 (Cp), 112.7 (Cp), 57.1, 44.8, 26.0, 0.1.

Anal. Calcd for $C_{51}H_{52}BNSiZr$: C, 75.71; H, 6.48; N, 1.73; Zr, 11.27. Found: C, 75.41; H, 6.46; N, 1.62; Zr, 11.10.

[$Cp_2Zr(\eta^2(C,N)$-CH_2CH{CH_3}{6-phenylpyrid-2-yl}$)$][BPh_4] (6). This complex was isolated as a yellow solid from the reaction of **4** with propene (yield: 343 mg, 90%).

^1H NMR (300 MHz, CD_2Cl_2): δ 7.94 (t, J = 7.9 Hz, 1 H, Ar H), 7.80 (tt, J = 7.5 Hz, J = 1.2 Hz, 1 H, Ar H), 7.70 (t, J = 7.4 Hz, 2 H, Ar H), 7.41 (d, J = 7.7 Hz, 2 H, Ar H), 7.05 (obscured by BPh_4^-, 2 H, Ar H), 6.37 (s, 5 H, Cp), 5.37 (s, 5 H, Cp), 3.58 (m, 1 H, $ZrCH_2CH$–), 2.37 (t, J = 12.6 Hz, 1 H, $ZrCH_2$–), 1.43 (d, J = 6.4 Hz, 3 H, Me), 0.96 (dd, J = 12.6 Hz, J = 3.7 Hz, 1 H, $ZrCH_2$–).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 172.9, 158.8, 143.0, 139.8, 134.4, 133.3, 123.1, 121.9, 121.4, 113.3 (Cp), 112.9 (Cp), 57.5 ($ZrCH_2$–), 42.6 ($ZrCH_2CH$–), 23.2 (Me).

Anal. Calcd for $C_{48}H_{44}BNZr$: C, 78.24; H, 6.02; N, 1.90; Zr, 12.38. Found: C, 77.92; H, 6.19, N, 1.82; Zr, 12.50.

[$Cp_2Zr(\eta^2(C,N)$-CH_2CH{$CH_2OCH_2CH_3$}{6-phenylpyrid-2-yl}$)$][BPh_4] (7). This complex was isolated as a yellow solid from the reaction of **4** with allyl ethyl ether (yield: 361 mg, 71%).

^1H NMR (300 MHz, CD_2Cl_2): δ 7.97 (t, J = 7.8 Hz, 1 H, Ar H), 7.82 (m, 2 H, Ar H), 7.71 (t, J = 7.4 Hz, 2 H, Ar H), 7.44 (d, J = 7.5 Hz, 1 H, Ar H), 7.09 (obscured by BPh_4^-, 2 H, Ar H), 6.40 (s, 5 H, Cp), 5.38 (s, 5 H, Cp), 3.75–3.57 (m, 5 H, $-CHCH_2OCH_2$–), 2.28 (t, J = 12.8 Hz, 1 H, $ZrCH_2$–), 1.31 (t, J = 6.9 Hz, 3 H, Me), 0.79 (dd, J = 12.5 Hz, J = 3.3 Hz, 1 H, $ZrCH_2$–).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 171.2, 158.7, 143.1, 140.0, 134.5, 133.3, 123.3, 123.0, 121.2, 113.4 (Cp), 113.0 (Cp), 76.2, 67.0, 49.4, 48.4, 15.4 (Me).

Anal. Calcd for $C_{50}H_{48}BNOZr$: C, 76.90; H, 6.19; N, 1.79; Zr, 11.68. Found: C, 76.78; H, 6.17; N, 1.69; Zr, 11.55.

[$Cp_2Zr(\eta^2(C,N)$-CH{$SiMe_3$}CH_2{6-phenylpyrid-2-yl}$)$][BPh_4] (8). This complex was isolated as a yellow solid from the reaction of **4** with vinyltrimethylsilane (yield: 357 mg, 69%).

^1H NMR (360 MHz, CD_2Cl_2): δ 7.87 (t, J = 7.8 Hz, 1 H, Ar H), 7.76 (t, J = 7.5 Hz, 1 H, Ar H), 7.64 (t, J = 7.8 Hz, 2 H, Ar H), 7.31 (obscured by BPh_4^-, 2 H, Ar H), 7.13 (d, J = 7.0 Hz, 2 H, Ar H), 6.54 (s, 5 H, Cp), 5.64 (s, 5 H, Cp), 3.72 (dd, J = 18.7 Hz, J = 12.9 Hz, 1 H, β-CH), 3.40 (dd, J = 18.7 Hz, J = 3.0 Hz, 1 H, β-CH), 3.32 (dd, J = 12.9 Hz, J = 3.0 Hz, 1 H, α-CH), 0.09 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 169.1, 160.4, 143.1, 137.9, 132.7, 131.4, 126.8, 124.9, 124.4, 115.4 (Cp), 114.1 (Cp), 69.2, 38.6, 0.8.

Anal. Calcd for $C_{50}H_{50}BNSiZr$: C, 75.53; H, 6.34; N, 1.76; Zr 11.47. Found: C, 75.27; H, 6.33; N, 1.62; Zr, 11.25.

2-Phenyl-6-(1-methyl-2-(trimethylsilyl)ethyl)pyridine (11). A solution of **4** (100 mg, 0.13 mmol) and allyltrimethylsilane (118 mg, 1.04 mmol) in 7 mL of $ClCH_2CH_2Cl$ was heated at 60–65 °C under N_2 for 2.0 h. The yellow reaction solution was cooled to room temperature, and 5 mL of H_2O (N_2 purged and degassed) was added. The resulting colorless slurry was stirred at room temperature for 5.0 h. The organics were extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with saturated $NaHCO_3$ solution (10 mL) and then saturated NaCl solution (10 mL), dried with $MgSO_4$, and filtered. The solvents were removed by vacuum evaporation, and the crude yellowish oil was purified by column chromatography (alumina) with 8/1 hexane/CH_2Cl_2 as the eluent to yield 24 mg (73%) of **11** as a colorless oil.

^1H NMR (360 MHz, CD_2Cl_2): δ 8.05 (d, J = 6.9 Hz, 2 H, Ar H), 7.67 (t, J = 7.7 Hz, 1 H, Ar H), 7.55 (d, J = 7.8 Hz, 1 H, Ar H), 7.49–7.39 (m, 3 H, Ar H), 7.12 (d, J = 7.6 Hz, 1 H, Ar H), 3.15 (m, 1 H, $CH(Me)CH_2Si$), 1.37 (d, J = 6.8 Hz, 3 H, Me), 1.22 (dd, J = 14.5 Hz, J = 8.1 Hz, 1 H), 0.94 (dd, J = 14.5 Hz, J = 6.8 Hz, 1 H), –0.10 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 168.2, 156.4, 140.2, 137.3, 129.0, 128.9, 127.2, 119.9, 117.8, 39.0, 25.8, 25.0, –0.9 ($SiMe_3$).

GCMS (EI, 70 eV): m/e 269 (7) {molecular ion}, 254 (38) {M – Me}, 238 (14), 226 (6), 197 (11), 196 (100) {M – $SiMe_3$}, 73 (13) {$SiMe_3$}.

HRMS (EI): calcd for $C_{17}H_{23}NSi$, m/e 269.1600; obsd, m/e 269.1616.

6-(1-Methyl-2-ethoxyethyl)-2-phenylpyridine (12). To a solution of 17 mg (0.016 mmol) of **7** in CH_2Cl_2 (2.5 mL) was added 1 drop of H_2O. The two-phase reaction mixture was stirred for 10 min at 23 °C and then filtered through on alumina plug. The solvent was removed under vacuum, and the crude product was purified by column chromatography (alumina, CH_2Cl_2 eluent) to give 4.3 mg (86%) of **12** as a colorless liquid.

^1H NMR (300 MHz, CD_2Cl_2): δ 8.06 (br d, 2 H), 7.69 (t, J = 7.7 Hz, 1 H), 7.59 (d, J = 7.9 Hz, 1 H), 7.52–7.38 (m, 3 H), 7.14

(d, J = 7.6 Hz, 1 H), 3.80 (dd, J = 9.3 Hz, J = 7.0 Hz, 1 H, $-CH(Me)CH_2O-$), 3.61 (dd, J = 9.3 Hz, J = 6.7 Hz, 1 H, $-CH(Me)CH_2O-$), 3.47 (q, J = 7.0 Hz, 1 H, $-OCH_2CH_3$), 3.47 (q, J = 7.0 Hz, 1 H, $-OCH_2CH_3$), 3.22 (sextet, J = 6.9 Hz, 1 H, $-CH(Me)-$), 1.34 (d, J = 7.0 Hz, 3 H, $-CH(CH_3)-$), 1.13 (t, J = 7.0 Hz, 3 H, $-CH_2CH_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 165.8 (py α-C), 156.6 (py α-C), 140.1, 137.3, 129.1, 128.9, 127.2, 121.1, 118.2, 75.6 ($-CH_2O-$), 66.6 ($-CH_2O-$), 42.7 (py-CH(Me)-), 17.6 (Me), 15.4 (Me). Assignments were confirmed by DEPT.

GCMS (EI, 70 eV): m/e 241 (0.8) {molecular ion}, 226 (6) {M - Me}, 213 (14), 212 (100), 210 (2), 198 (2), 196 (36), 194 (8), 184 (11), 183 (17), 182 (37), 180 (5), 169 (8), 167 (3), 155 (4), 154 (12), 152 (3), 128 (4), 127 (7), 126 (2), 115 (2), 78 (3), 77 (8), 59 (4), 51 (3).

HRMS (EI): calcd for $C_{16}H_{19}NO$, m/e 241.1467; obsd, m/e 241.1476.

2-Phenyl-6-(2-(trimethylsilyl)ethyl)pyridine (13). This compound was prepared by hydrolysis of a $ClCH_2CH_2Cl$ solution of **8** (prepared by reaction of **4** with vinyltrimethylsilane) by using the procedure described for **11**: colorless oil; yield 28 mg, 80%.

^1H NMR (360 MHz, CD_2Cl_2): δ 8.04 (d, J = 6.9 Hz, 2 H, Ar H), 7.65 (t, J = 7.7 Hz, 1 H, Ar H), 7.55 (d, J = 7.2 Hz, 1 H, Ar H), 7.49–7.37 (m, 3 H, Ar H), 7.13 (d, J = 7.6 Hz, 1 H, Ar H), 2.86 (m, AA′XX′ pattern, 2 H), 1.03 (m, AA′XX′ pattern, 2 H), 0.05 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 164.7, 156.6, 140.1, 137.3, 129.0, 128.9, 127.2, 120.7, 117.6, 33.1, 17.1, -1.7.

GCMS (EI, 70 eV): m/e 255 (20) {molecular ion}, 240 (56) {M - Me}, 183 (16), 182 (100) {M - $SiMe_3$}, 73 (25) {$SiMe_3$}.

HRMS (EI): calcd for $C_{16}H_{21}NSi$, m/e 255.1443; obsd, m/e 255.1439.

$[Cp_2Zr(\eta^2(C,N)$-CH{Ph}CH_2{6-Me-pyrid-2-yl})$][BPh_4]$ (15). This five-membered metallacycle was isolated as a purple solid from the reaction of **2** with styrene (CH_2Cl_2, 23 °C, 14 h) in 78% yield (126 mg). The isolated product contains trace amounts of hexane.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.85 (t, J = 7.8 Hz, 1 H, py H), 7.33–6.85 (obscured by BPh_4^-, 7 H, py H and Ph H), 6.58 (s, 5 H, Cp), 6.21 (s, 5 H, Cp), 4.59 (dd, J = 11.9 Hz, J = 4.9 Hz, 1 H, α-CH), 3.84 (dd, J = 18.0 Hz, J = 11.9 Hz, 1 H, β-CH), 3.65 (dd, J = 17.9 Hz, J = 5.1 Hz, β-CH), 1.61 (s, 3 H, py-Me).

^{13}C NMR (75 MHz, CD_2Cl_2) (poor solubility precluded complete ^{13}C analysis and only key data are reported): δ 117.4 (Cp), 117.1 (Cp), 64.9 (Zr-CH(Ph)-), 38.9 (Zr-CH(Ph)-CH_2), 23.3 (Me).

Anal. Calcd for $C_{48}H_{44}BNZr$: C, 78.24; H, 6.02; N, 1.90. Found: C, 78.22; H, 6.10; N, 1.79.

$[Cp_2Zr(\eta^2(C,N)$-CH{CH_2-(6-Me-pyrid-2-yl)}{pyrid-2-yl})$][BPh_4]$ (16). This four-membered metallacycle was isolated as a yellow solid from the reaction of **2** with 2-vinylpyridine (CH_2Cl_2, 23 °C, 16 h) in 89% yield (247 mg). The isolated product contains 0.5 equiv of CH_2Cl_2, which is accounted for in the reported yield.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.92 (d, J = 5.3 Hz, 1 H, py H), 7.83 (t, J = 7.8 Hz, 1 H, py H), 7.70 (t, J = 7.5 H, 1 H, py H), 7.29 (obscured by BPh_4^-, 2 H, py H), 7.19 (m, 2 H, py H), 7.00 (obscured by BPh_4^-, 1 H, py H), 6.29 (s, 5 H, Cp), 5.56 (s, 5 H, Cp), 4.04 (dd, J = 17.3 Hz, J = 5.7 Hz, 1 H, Zr-CH(py)CH_2-), 3.48 (dd, J = 17.2 Hz, J = 11.7 Hz, 1 H, Zr-CH(py)CH_2-), 3.19 (dd, J = 11.8 Hz, J = 5.8 Hz, 1 H, Zr-CH), 2.59 (s, 3 H, Me).

^{13}C NMR (75 MHz, CD_2Cl_2): δ 169.9, 164.3, 160.1, 149.3, 141.1, 140.0, 125.8, 122.7, 120.7, 120.4, 113.1 (Cp), 112.6 (Cp), 41.7 (CH_2-{6-Me-py}), 36.2 (Zr-CH(py)-), 27.1 (Me).

Anal. Calcd for $C_{47}H_{43}BN_2Zr \cdot 0.5CH_2Cl_2$: C, 73.11; H, 5.68; N, 3.59. Found: C, 72.85; H, 5.72; N, 3.59.

6-Methyl-2-(2-phenethyl)pyridine (17). To a solution of 12 mg (0.016 mmol) of **15** in CH_2Cl_2 (2.5 mL) was added 1 drop of H_2O. The two-phase mixture was stirred for 10 min at 23 °C and then filtered through an alumina plug. The solvent was removed under vacuum and the crude product purified by column chromatography (alumina, CH_2Cl_2 eluent) to give 2.7 mg (84%) of **17** as a colorless liquid following solvent removal.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.44 (t, J = 7.68 Hz, 1 H, py H), 7.20 (m, 5 H, Ar H), 6.96 (d, J = 7.68 Hz, 1 H, py H), 6.88 (d, J = 7.68 Hz, 1 H, py H), 3.00 (s, 4 H, $-CH_2CH_2-$), 2.49 (s, 3 H, Me).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 161.0, 158.2, 142.4, 136.6, 128.8, 128.6, 126.2, 120.8, 119.9, 40.5 ($-CH_2-$), 36.2 ($-CH_2-$), 24.6 (Me). Assignments were confirmed by DEPT.

GCMS (EI, 70 eV): m/e 198 (8), 197 (63) {molecular ion}, 196 (100), 181 (11), 120 (39), 93 (16), 91 (19), 65 (10).

HRMS (EI): Calcd for $C_{14}H_{15}N$, m/e 197.1204; obsd, m/e 197.1178.

6-Methyl-2-(2-(pyrid-2-yl)ethyl)pyridine (18). This compound was isolated as a colorless oil from the hydrolysis of complex **16**·$0.5CH_2Cl_2$ (yield: 3.8 mg, 88%) by using the procedure described for **17**.

^1H NMR (300 MHz, CD_2Cl_2): δ 8.50 (br d, J = 4.1 Hz, 1 H, α-py H), 7.56 (dt, J = 7.7 Hz, J = 1.9 Hz, 1 H, py H), 7.44 (t, J = 7.7 Hz, 1 H, py H), 7.13 (d, J = 8.0 Hz, 1 H, py H), 7.10 (obscured, 1 H, py H), 6.96 (d, J = 7.7 Hz, 1 H, py H), 6.92 (d, J = 7.6 Hz, 1 H, py H), 3.15 (m, 4 H, $-CH_2CH_2-$), 2.49 (s, 3 H, Me).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 161.9, 161.0, 158.2, 149.6, 136.7, 136.4, 123.2, 121.3, 120.7, 119.9, 38.4 ($-CH_2-$), 38.3 ($-CH_2-$), 24.6 (Me).

GCMS (EI, 70 eV): m/e 199 (7), 198 (64) {molecular ion}, 197 (44), 195 (7), 121 (9), 120 (100), 106 (66), 93 (9), 92 (10), 79 (12), 78 (14), 77 (15), 66 (7), 65 (20), 52 (7), 51 (11).

HRMS (EI): calcd for $C_{14}H_{15}N$, m/e 198.1157; obsd, m/e 198.1161.

$[Cp_2Zr(\eta^2(C,N)$-C{=CH_2}CH_2{6-phenylpyrid-2-yl})$][BPh_4]$ (19a) and $[Cp_2Zr(\eta^2(C,N)$-CH_2C{=CH_2}{6-phenylpyrid-2-yl})$][BPh_4]$ (19b). An inseparable mixture of these regioisomers was isolated from the reaction of **4** with allene (yield: 155 mg, 82% yellow solid).

^1H NMR (360 MHz, CD_2Cl_2) (both isomers): δ 7.95–7.66 (m, 10 H, Ar H), 7.38 (obscured by BPh_4^-, 2 H, Ar H), 7.12 (d, J = 6.9 Hz, 2 H, Ar H), 7.02 (obscured by BPh_4^-, 2 H, Ar H), 5.99 (s, 10 H, Cp), 5.97 (br s, 1 H, $=CH_2$), 5.92 (s, 10 H, Cp), 5.45 (br s, 1 H, $=CH_2$), 5.23 (br s, 1 H, $=CH_2$), 4.76 (br s, 1 H, $=CH_2$), 4.08 (br s, 2 H, ZrC{=CH_2}CH_2-), 2.46 (br s, 2 H, ZrCH_2-).

^{13}C NMR (90 MHz, CD_2Cl_2) (both isomers): δ 190.8 (ZrC{=CH_2}-), 166.3, 165.5, 159.2, 159.0, 149.9 (Zr-CH-C=CH_2), 143.5, 143.4, 140.0, 138.4, 134.0, 133.5, 133.3, 133.2, 132.8, 126.7 (=CH_2), 124.5, 123.8, 123.4, 122.0, 121.9, 114.5 (Cp), 114.2 (Cp), 112.5 (=CH_2), 57.2 ($ZrCH_2$-), 50.4 (ZrC(=CH_2)CH_2-). Assignments were confirmed by DEPT.

Anal. Calcd for $C_{48}H_{42}BNZr$: C, 78.45; H, 5.76; N, 1.91; Zr, 12.41. Found: C, 78.29; H, 5.79; N, 1.79; Zr, 12.65.

$[Cp_2Zr(\eta^2(C,N)$-C{$CH_2CH_2CH_3$}=CH{6-phenylpyrid-2-yl})$][BPh_4]$ (20). To a solution of 225 mg (0.29 mmol) of **4** in 5 mL of CH_2Cl_2 was added 60 mg (0.88 mmol) of 1-pentyne. The solution was stirred for 1.5 h at room temperature and then filtered through a glass-wool plug. Hexane (10 mL) was added to the filtrate to induce precipitation of the product. The crude product was separated by filtration, recrystallized from CH_2Cl_2/hexane, washed with hexane (5 × 10 mL), and dried in vacuo to give 193 mg (87%) of **20** as a yellow solid.

^1H NMR (360 MHz, CD_2Cl_2): δ 7.88 (t, J = 7.8 Hz, 1 H, Ar H), 7.77 (tt, J = 7.5 Hz, J = 1.3 Hz, 1 H, Ar H), 7.67 (t, J = 7.7 Hz, 2 H, Ar H), 7.27 (dd, J = 8.0 Hz, J = 1.0 Hz, 1 H, Ar H), 7.15 (d, J = 6.8 Hz, 2 H, Ar H), 7.10 (dd, J = 7.7 Hz, J = 1.0 Hz, 1 H, Ar H), 6.77 (t, J = 1.7 Hz, 1 H, vinyl, H), 6.00 (s, 10 H, Cp), 2.28 (td, J = 7.8 Hz, J = 1.7 Hz, 2 H, Zr-C(CH_2CH_2-)=), 1.68 (hextet, J = 7.4 Hz, 2 H, Zr-C($CH_2CH_2CH_3$)=), 1.07 (t, J = 7.3 Hz, 3 H, $-CH_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 226.2 (Zr-C), 161.0, 159.1, 143.1, 137.4, 132.7, 132.4, 124.5, 123.6, 122.8, 120.9, 114.3 (Cp), 43.8, 22.2, 14.3.

FTIR (KBr pellet, cm^{-1}): $\nu_{C=C}$ 1527.7.

Anal. Calcd for $C_{50}H_{46}BNZr$: C, 78.71; H, 6.08; N, 1.84; Zr, 11.96. Found: C, 78.56; H, 6.08; N, 1.79; Zr, 11.75.

$[Cp_2Zr(\eta^2(C,N)$-C{t-Bu}=CH{6-phenylpyrid-2-yl})$][BPh_4]$ (21). This complex was isolated as a yellow solid from the reaction of **4** with *tert*-butylacetylene (yield: 169 mg, 84%).

^1H NMR (360 MHz, CD_2Cl_2): δ 7.85 (t, J = 7.9 Hz, 1 H, Ar H), 7.74 (t, J = 7.5 Hz, 1 H, Ar H), 7.64 (t, J = 7.9 Hz, 2 H, Ar H), 7.22 (m, 3 H, Ar H), 7.06 (1 H, obscured by BPh_4^-, Ar H), 6.81 (s, 1 H, vinyl H), 6.20 (s, 10 H, Cp), 1.19 (s, 9 H, t-Bu).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 237.1 (Zr–C), 160.2, 154.3, 142.9, 136.2 (obscured by BPh_4^-), 131.8, 130.0, 128.4, 124.8, 123.1, 121.6, 115.5 (Cp), 44.3 ($C(CH_3)_3$), 32.9 ($C(CH_3)_3$).

FTIR (KBr pellet, cm^{-1}): $\nu_{C=C}$ 1517.8.

Anal. Calcd for $C_{51}H_{48}BNZr$: C, 78.84; H, 6.23; N, 1.80; Zr, 11.74. Found: C, 78.58; H, 6.18; N, 1.74; Zr, 11.50.

[$Cp_2Zr(\eta^2(C,N)$-C{SiMe$_3$}=CH{6-phenylpyrid-2-yl})][BPh_4] (22). This complex was isolated as a yellow solid from the reaction of **4** with (trimethylsilyl)acetylene (yield: 400 mg, 96%). The isolated material contains trace amounts of hexane, which could not be removed under vacuum.

^1H NMR (360 MHz, CD_2Cl_2): δ 7.92 (t, J = 7.9 Hz, 1 H, Ar H), 7.76 (tt, J = 7.5 Hz, J = 1.3 Hz, 1 H, Ar H), 7.64 (t, J = 7.8 Hz, 2 H, Ar H), 7.29 (1 H, obscured by BPh_4^-, Ar H), 7.22 (s, 1 H, vinyl H), 7.17 (m, 3 H, Ar H), 6.09 (s, 10 H, Cp), 0.27 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 239.3 (Zr–C), 160.2, 157.1, 143.6, 136.4, 134.4, 132.4, 131.1, 126.7, 124.3, 123.1, 115.2, (Cp), 1.08 ($SiMe_3$).

Anal. Calcd for $C_{50}H_{48}BNSiZr$: C, 75.73; H, 6.10; N, 1.77; Zr, 11.50. Found: C, 75.60; H, 5.98; N, 1.74; Zr, 11.65.

[$Cp_2Zr(\eta^2(C,N)$-C{CH_2SiMe_3}=CH{6-phenylpyrid-2-yl})][BPh_4] (23). This complex was isolated as a yellow solid from the reaction of **4** with propargyltrimethylsilane (yield: 258 mg, 98%).

^1H NMR (360 MHz, CD_2Cl_2): δ 7.86 (t, J = 7.8 Hz, 1 H, Ar H), 7.76 (t, J = 7.6 Hz, 1 H, Ar H), 7.66 (t, J = 7.6 Hz, 2 H, Ar H), 7.21 (d, J = 8.1 Hz, 1 H, Ar H), 7.15 (d, J = 7.7 Hz, 2 H, Ar H), 7.06 (1 H, obscured by BPh_4^-, Ar H), 6.72 (t, J = 1.3 Hz, 1 H, vinyl H), 6.01 (s, 10 H, Cp), 1.93 (t, J = 1.3 Hz, 2 H, $-CH_2Si-$), 0.25 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 227.1 (Zr–C), 160.9, 159.0, 142.9, 137.5, 132.6, 132.3, 124.9, 124.6, 122.4, 120.4, 114.4 (Cp), 33.0 ($-CH_2Si-$), 0.17 ($SiMe_3$).

FTIR (KBr pellet, cm^{-1}): $\nu_{C=C}$ 1518.4.

Anal. Calcd for $C_{51}H_{50}BNSiZr$: C, 75.90; H, 6.24; N, 1.74; Zr, 11.30. Found: C, 75.80; H, 6.16; N, 1.79; Zr, 11.20.

[$Cp_2Zr(\eta^2(C,N)$-C{Me}=C{Me}{6-phenylpyrid-2-yl})][BPh_4] (24). This complex was isolated as a yellow solid from the reaction of **4** with 2-butyne (yield: 154 mg, 88%). The isolated material contains trace amounts of hexane, which could not be removed under vacuum.

^1H NMR (360 MHz, CD_2Cl_2): δ 7.93 (t, J = 7.9 Hz, 1 H, Ar H), 7.78 (t, J = 7.6 Hz, 1 H, Ar H), 7.68 (t, J = 7.7 Hz, 2 H, Ar H), 7.44 (d, J = 8.3 Hz, 1 H, Ar H), 7.16 (d, J = 6.7 Hz, 2 H, Ar H), 7.10 (d, J = 7.5 Hz, 1 H, Ar H), 5.94 (s, 10 H, Cp), 1.99 (s, 3 H, Me), 1.93 (s, 3 H, Me).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 212.1 (Zr–C), 164.4, 158.8, 143.1, 137.6, 133.2, 133.0, 131.9, 123.4, 121.0, 119.9, 113.7 (Cp), 24.4 (Me), 15.0 (Me).

FTIR (KBr pellet, cm^{-1}): $\nu_{C=C}$ 1528.7.

Anal. Calcd for $C_{49}H_{44}BNZr$: C, 78.58; H, 5.92; N, 1.87; Zr, 12.18. Found: C, 78.45; H, 5.79; N, 1.80; Zr, 11.95.

[$Cp_2Zr(\eta^2(C,N)$-C{$CH_2CH_2CH_3$}=C{Me}{6-phenylpyrid-2-yl})][BPh_4] (25a) and [$Cp_2Zr(\eta^2(C,N)$-C{Me}=C-{$CH_2CH_2CH_3$}{6-phenylpyrid-2-yl})][BPh_4] (25b). These complexes were isolated as an inseparable mixture of regioisomers from the reaction of **4** with 2-hexyne (yield: 211 mg, 91%, yellow solid).

^1H NMR (360 MHz, CD_2Cl_2) (both isomers): δ 7.93 (t, J = 7.9 Hz, 2 H, Ar H), 7.77 (m, 2 H, Ar H), 7.68 (m, 4 H, Ar H), 7.44 (d, J = 8.3 Hz, 2 H, Ar H), 7.16 (d, J = 7.7 Hz, 4 H, Ar H), 7.08 (m, 2 H, Ar H), 6.01 (s, 10 H, Cp), 5.93 (s, 10 H, Cp), 2.45 (t, J = 7.9 Hz, 2 H), 2.12 (m, 2 H), 2.01 (s, 3 H, Me), 1.94 (s, 3 H, Me), 1.64–1.53 (m, 4 H), 1.11–1.04 (m, 6 H, CH_2CH_3).

^{13}C NMR (90 MHz, CD_2Cl_2) (both isomers, partial): δ 217.8 (Zr–C), 212.7 (Zr–C), 113.9 (Cp), 113.8 (Cp).

FTIR (KBr pellet, cm^{-1}) (both isomers): $\nu_{C=C}$ 1526.7.

Anal. Calcd for $C_{51}H_{48}BNZr$: C, 78.84; H, 6.23; N, 1.80; Zr, 11.74. Found: C, 78.69, H, 6.09; N, 1.70; Zr, 11.95.

[$Cp_2Zr(\eta^2(C,N)$-C{$SiMe_3$}=C{Me}{6-phenylpyrid-2-yl})][BPh_4] (26). This complex was isolated as a yellow solid from the reaction of **4** with 1-(trimethylsilyl)propyne (yield: 193 mg, 92%).

^1H NMR (360 MHz, CD_2Cl_2): δ 7.98 (t, J = 8.0 Hz, 1 H, Ar H), 7.75 (tt, J = 7.5 Hz, J = 1.3 Hz, 1 H, Ar H), 7.64 (t, J = 7.5 Hz, 2 H, Ar H), 7.57 (dd, J = 8.4 Hz, J = 1.0 Hz, 1 H, Ar H), 7.18 (m, 3 H, Ar H), 6.13 (s, 10 H, Cp), 2.23 (s, 3 H, Me), 0.28 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2) (one quaternary carbon is overlapped by BPh_4^- resonances): δ 230.0 (Zr–C), 159.9, 159.7, 143.6, 140.9, 132.6, 131.1, 127.1, 124.3, 121.2, 115.5 (Cp), 24.3 (Me), 2.9 ($SiMe_3$).

Anal. Calcd for $C_{51}H_{50}BNSiZr$: C, 75.90; H, 6.24; N, 1.74; Zr, 11.30. Found: C, 75.70; H, 6.17; N, 1.74; Zr, 11.20.

2-Phenyl-6-(1-methyl-2-(trimethylsilyl)ethenyl)pyridine (27). To a solution of 99 mg (0.12 mmol) of **22** in CH_2Cl_2 (10 mL) was added 3.0 mL of H_2O under N_2. The two-phase mixture was stirred for 8.0 h at 25 °C. H_2O (20 mL) was added, and the organics were extracted with CH_2Cl_2 (3 × 10 mL). The combined organic fractions were washed with $NaHCO_3$ (saturated solution, 20 mL) and then NaCl (saturated solution, 20 mL), dried with $MgSO_4$, and filtered. The solvents were removed under vacuum, and the crude product was purified by column chromatography on alumina using 8/1 pentane/EtOAc as the eluent to give 32 mg (97%) of **27** as a colorless oil.

^1H NMR (300 MHz, CD_2Cl_2): δ 8.09 (br d, J = 6.9 Hz, 2 H, Ar H), 7.74 (t, J = 7.8 Hz, 1 H, Ar H), 7.65 (d, J = 6.8 Hz, 1 H, Ar H), 7.51–7.41 (m, 4 H, Ar H), 6.62 (q, J = 0.9 Hz, 1 H, vinyl H), 2.36 (d, J = 0.9 Hz, 3 H, Me), 0.25 (s, 9 H, $SiMe_3$).

^{13}C NMR (75 MHz, CD_2Cl_2): δ 159.8, 155.9, 151.8, 140.0, 137.4, 130.3, 129.2, 129.0, 127.2, 118.8, 118.4, 19.7 (Me), –0.02 ($SiMe_3$).

GCMS (EI, 70 eV): m/z 267 (17) {molecular ion}, 266 (15), 253 (19), 252 (100 {M – Me}, 236 (12), 222 (7), 220 (9), 194 (32) {M – $SiMe_3$}, 154 (6), 111 (7), 97 (6), 77 (5), 73 (31) {$SiMe_3$}, 59 (12), 58 (15), 51 (5).

HRMS (EI): Calcd for $C_{17}H_{21}NSi$, m/e 267.1443, obsd, m/e 267.1453.

[$Cp_2Zr(\eta^2(C,N)$-C{$SiMe_3$}=CH{pyrid-2-yl})][BPh_4] (30). A slurry of **1** (500 mg, 0.80 mmol), pyridine (69 mg, 0.88 mmol), and (trimethylsilyl)acetylene (234 mg, 2.39 mmol) in $ClCH_2CH_2Cl$ (15 mL) was heated under vacuum at 50 °C for 6.0 h. The resulting clear yellow solution was filtered through a glass-wool plug. Hexane was added dropwise to the filtrate until precipitation was complete. The solid was collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give 451 mg (79% yield) of **30** as a yellow solid. The isolated product contained 1.0 equiv of $ClCH_2CH_2Cl$, which could not be removed under vacuum. The presence of $ClCH_2CH_2Cl$ is accounted for in the reported yield.

Alternatively, **30** was prepared from the reaction of **29** (20 mg, 0.03 mmol) with (trimethylsilyl)acetylene (14 mg, 0.14 mmol) by using the procedure described for **31** (vide infra). Yield: ca. 95% by NMR spectroscopy.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.85 (td, J = 7.8 Hz, J = 1.6 Hz, 1 H, py H), 7.26 (br d, J = 8.0 Hz, 1 H, py H), 7.17 (s, 1 H, vinyl H), 6.99 (obscured by BPh_4^-, 1 H, py H), 6.73 (br d, J = 5.4 Hz, 1 H, py H), 6.43 (s, 10 H, Cp), 0.16 (s, 9 H, $SiMe_3$).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 243.5 (Zr–C–), 155.3, 147.3, 142.8, 136.8, 125.5, 122.4, 117.1 (Cp), 0.5 ($SiMe_3$).

Anal. Calcd for $C_{44}H_{44}BNSiZr{\cdot}ClCH_2CH_2Cl$: C, 67.72; H, 5.93; N, 1.72. Found: C, 67.66; H, 5.87; N, 1.68.

[$Cp_2Zr(\eta^2(C,N)$-C{Me}=CMe{pyrid-2-yl})][BPh_4] (31). A solution of **29** (289 mg, 0.41 mmol) and 2-butyne (89 mg, 1.64 mmol) in $ClCH_2CH_2Cl$ was heated under N_2 at 60 °C for 16 h. The resulting yellow solution was filtered through a glass-wool plug. Hexane was added dropwise to the filtrate until precipitation was complete. The solid was collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum to give 226 mg (81% yield) of **31** as a yellow solid. The isolated product contains trace amounts of hexane.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.85 (td, J = 7.9 Hz, J = 1.5 Hz, 1 H, py H), 7.42 (obscured by BPh_4^-, 1 H, py H), 6.96 (obscured by BPh_4^-, 1 H, py H), 6.65 (br d, J = 5.1 Hz, 1 H, py H), 6.35 (s, 10 H, Cp), 1.94 (s, 3 H, Me), 1.77 (s, 3 H, Me).

^{13}C NMR (90 MHz, CD_2Cl_2): δ 213.1 (Zr–C–), 161.5, 145.4, 142.6, 134.4, 121.6, 120.9, 116.5 (Cp), 21.4 (Me), 14.6 (Me).
FTIR (KBr pellet, cm^{-1}): $\nu_{C=C}$ 1534.9.

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Studies of the Oxidatively Promoted Carbonylation of η-Cp(CO)(L)FeMe in Methylene Chloride. Applications of the Quantitative Analysis of Ligand Effects

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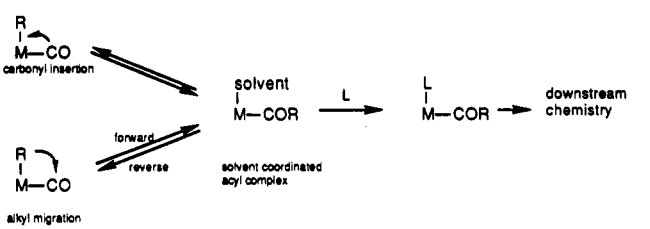
The carbonylation of η-Cp(CO)(L)$FeMe^+$ (L = $PPhMe_2$, PEt_3, PPh_2Me, PEt_2Ph, PPh_2Et, P(*p*-MeOPh)$_3$, P(*p*-MePh)$_3$, PPh_3, P(*p*-FPh)$_3$, P(*p*-ClPh)$_3$, P(*p*-CF_3Ph)$_3$, PPh_2Cy, $PPhCy_2$, PCy_3) in methylene chloride has been studied by a combination of kinetic, stereochemical, isotopic labeling, ligand effect, and electrochemical experiments. Redox-catalyzed (ferrocenium tetrafluoroborate) carbonylation of (+)-η-Cp(CO)(PPh_3)FeMe gives racemic η-Cp(CO)(PPh_3)FeCOMe. The results of control experiments suggest that the racemization is attributable to the configurational instability of η-Cp(CO)(PPh_3)$FeMe^+$. The redox-catalyzed carbonylation of η-Cp(CO)(PPh_3)FeMe under 1 atm of ^{13}CO affords η-Cp(^{13}CO)(PPh_3)FeCOMe. The rate of the electrochemically promoted carbonylation of η-Cp(CO)(L)FeMe is independent of the concentration of the starting complex, carbon monoxide, and the supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH). Kinetic data for the carbonylation of η-Cp(CO)(L)$FeMe^+$, which is first order in complex and zero order in carbon monoxide, were obtained by computer simulation analysis of cyclic and square-wave voltammetry data. Analysis of the data for L = P(*p*-ClPh)$_3$ and P(*p*-CF_3Ph)$_3$ reveals enthalpies of activation ($\Delta H^\ddagger$ = 7.8 ± 2.0, 6.7 ± 0.8 kcal/mol) and entropies of activation ($\Delta S^\ddagger$ = −23 ± 7, −25 ± 3 eu), respectively. Quantitative analysis of the ligand effect (QALE) data shows that the carbonylation of η-Cp(CO)(L)$FeMe^+$ is accelerated by poorer electron-donor ligands; the steric profile shows a region of steric inhibition for small ligands with a steric threshold at 150° after which the rate of reaction rises rapidly. Analysis of the $E°$ values for the η-Cp(CO)(L)FeMe/η-Cp(CO)(L)$FeMe^+$ couple also reveals a steric threshold at 150°.

Introduction

Because of its crucial position in the chemistry of carbon monoxide, the alkyl to acyl migratory insertion reaction is among the most studied of chemical processes.[1] The current view of this reaction is a composite picture derived from the results of studies of a number of systems (Scheme I). In particular, the kinetics, the nature of the carbonylation step (alkyl migration versus carbonyl insertion),[2] stereochemistry at both the metal[2] and the α-carbon of the alkyl group,[3] and the effect of the electron-donor capacity of the alkyl group[4] have received attention. It is now widely believed that many of the alkyl to acyl migratory insertions reactions are assisted by concomitant incorporation of a nucleophilic solute or solvent.[5] The role of oxidation state of the central metal has been little studied, however, although it is known that the oxidation[6,7] or reduction[8,9] of alkylmetal carbonyls greatly accelerates the carbonylation of the metal–alkyl bond.

A number of years ago we reported that the iron(III) complex η-Cp(CO)(PPh_3)$FeMe^+$ undergoes carbonylation at least 1 million times faster than the analogous iron(II) complex.[6c] The origins of this high reactivity have been of interest for a number of years.[10] Predicated by studies of the pyridine-induced rearrangement of η-Cp(CO)-

Scheme I



(PPh_3)$FeMe^+$, Trogler[10b] concluded that nucleophilic assistance might be important and that the heptacoordinate

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