Synthesis and Reactivity of $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)^+$. Regioselective Acetylation of Alkynes and Alkenes

Anil S. Guram and Richard F. Jordan*

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

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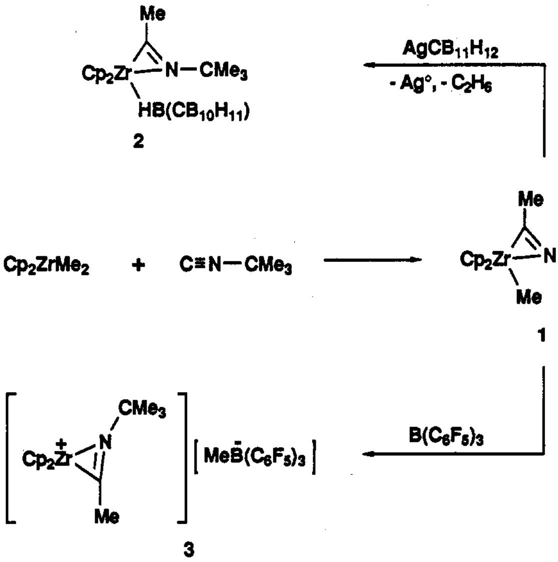
Summary: The cationic iminoacyl species $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)^+$, generated *in situ* from $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)(CH_3)$ and $B(C_6F_5)_3$, inserts alkynes and alkenes to yield metallacycles which can be hydrolyzed to ketones in high overall yield.

Neutral η^2-(iminoacyl) complexes of early transition metals exhibit a variety of interesting reactions including isocyanide deinsertion, 1,2-hydrogen shifts, and inter-/intramolecular addition and coupling reactions.[1] However, reactions with nonpolar unsaturated substrates have not been reported.[2] As a part of our effort to develop synthetic applications of $Cp_2Zr(R)(L)^+$ complexes,[3,4] we recently reported that $Cp_2Zr(\eta^2\text{-}C,O\text{-}C\{=O\}R)(L)^+$ η^2-acyl complexes undergo alternating multiple insertion of alkynes and carbon monoxide.[5] This result, and earlier insertion chemistry developed for $Cp_2Zr(\eta^2\text{-pyridyl})(L)^+$ complexes,[4] suggested that analogous cationic η^2-(iminoacyl) species $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=NR\}R)^+$ would exhibit enhanced reactivity. Here we report that $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)^+$ species undergo facile insertion reactions with alkynes and alkenes which offer an efficient method for the regioselective acetylation of these substrates.

$Cp_2Zr(CH_3)_2$ reacts irreversibly with *tert*-butyl isocyanide (23 °C, CH_2Cl_2, 5 min) to afford the air-stable η^2-(iminoacyl) complex $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)(CH_3)$ (**1**, 100%, eq 1).[6] The low-field $Zr\text{-}C\{=N^tBu\}$ ^{13}C NMR resonance (δ 235) and the IR $\nu_{C=N}$ absorbance at 1639.6 cm⁻¹ for **1** are consistent with the η^2-coordination mode.[1,7] The ^1H NMR spectrum of **1** in toluene-d_8 exhibits pairs of Cp, ^tBu, and CH_3 resonances, indicating that **1** exists as a 1/1 mixture of "N-inside" and "N-outside" isomers (resulting from different orientation of the η^2-(iminoacyl) functionality)[7j] in this solvent. However, these resonances appear as singlets in CD_2Cl_2, indicating that isomer interconversion is rapid in this solvent.



(1)

Several methods were explored for conversion of **1** into cationic $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)^+$ species. In an initial approach, $CB_{11}H_{12}^-$ was used as a weakly coordinating anion.[8] Complex **1** reacts with $AgCB_{11}H_{12}$ (23 °C, toluene, 5 min) via Ag^+ oxidative $Zr\text{-}CH_3$ bond cleavage to afford $Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)(CB_{11}H_{12})$ (**2**, 100%, eq 1). Spectroscopic data for **2** establish the η^2-(iminoacyl) structure (^{13}C NMR δ 229.3, $Zr\text{-}C\{=N^tBu\}\text{-}$; IR $\nu_{C=N}$ 1670.6 cm⁻¹).[1,7,9] The ^{11}B NMR spectrum of **2** consists of three doublets at δ −7.35 (1B, J = 117 Hz), −13.08 (5B, J = 135 Hz), and −15.37 (5B, J = 154 Hz). The lowered J_{BH} value for the unique B indicates that the $CB_{11}H_{12}^-$ anion is weakly coordinated to Zr via a Zr–H–B interaction involving the B–H para to the carborane C.[8b] The μ-H resonance is not observed in the ^1H NMR spectrum; presumably, it is broadened by anion exchange.[8] The IR spectrum of **1** (KBr pellet) exhibits three ν_{BH} bands (2560, 2283, 2204 cm⁻¹), consistent with the loss of symmetry due to coordination of $CB_{11}H_{12}^-$ to Zr.[8a] Initial experiments indicated that **2** is quite reactive with alkynes and alkenes due to the lability of the $CB_{11}H_{12}^-$ anion. However, because

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(1) For a recent review, see: Durfee, L. D.; Rothwell, I. P. *Chem Rev.* **1988**, *88*, 1059.

(2) The coupling of coordinated alkynes with η^2-(iminoacyl) and η^2-acyl ligands in $CpTa(Me)(ArCCAr)(\eta^2\text{-}C\{N\text{-}^tBu\}Me)$ and $CpTa(Me)(ArCCAr)(\eta^2\text{-}C\{O\}Me)$ has been reported. Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M. *Organometallics* **1990**, *9*, 66.

(3) For a review, see: Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(4) (a) Guram, A. S.; Jordan, R. F. *J. Org. Chem.* **1992**, *57*, 5994. (b) Guram, A. S.; Jordan, R. F. *Organometallics* **1991**, *10*, 3470. (c) Guram, A. S.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1992**, *114*, 8991. (d) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546.

(5) Guram, A. S.; Guo, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 4902.

(6) Detailed experimental procedures and complete characterization data for all organometallic and organic compounds are provided in the supplementary material.

(7) Group 4 metal η^2-iminoacyl complexes: (a) Lappert, M. F.; Luong-Thi, N. T.; Miline, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35. (b) Van Bolhuis, F.; DeBoer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *170*, 299. (c) Dormond, A.; Dachour, A. *J. Organomet. Chem.* **1980**, *193*, 321. (d) Klei, K.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297. (e) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462. (f) Reger, D. L.; Tarquin, M. E.; Lebioda, L. *Organometallics* **1983**, *2*, 1763. (g) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. (h) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (i) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390. (j) Lubben, T. V.; Plossi, K.; Norton, J. R.; Miller, M. M.; Anderson, O. P. *Organometallics* **1992**, *11*, 122.

(8) (a) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643 and references cited therein. (b) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897. (c) Borkowsky, S. L.; Baenziger, N. C.; Jordan, R. F. *Organometallics* **1993**, *12*, 486.

(9) By analogy to structurally characterized $Cp_2Zr(\eta^2\text{-}C\{=N\text{-}^tBu\}CH_3)(O_2CCF_3)$ and $Cp_2Ti(\eta^2\text{-}C\{=N\text{-}^tBu\})(CN\text{-}^tBu)^+$,[7h,j] it is likely that **2** adopts an "N-inside" structure; however, this was not conclusively established.

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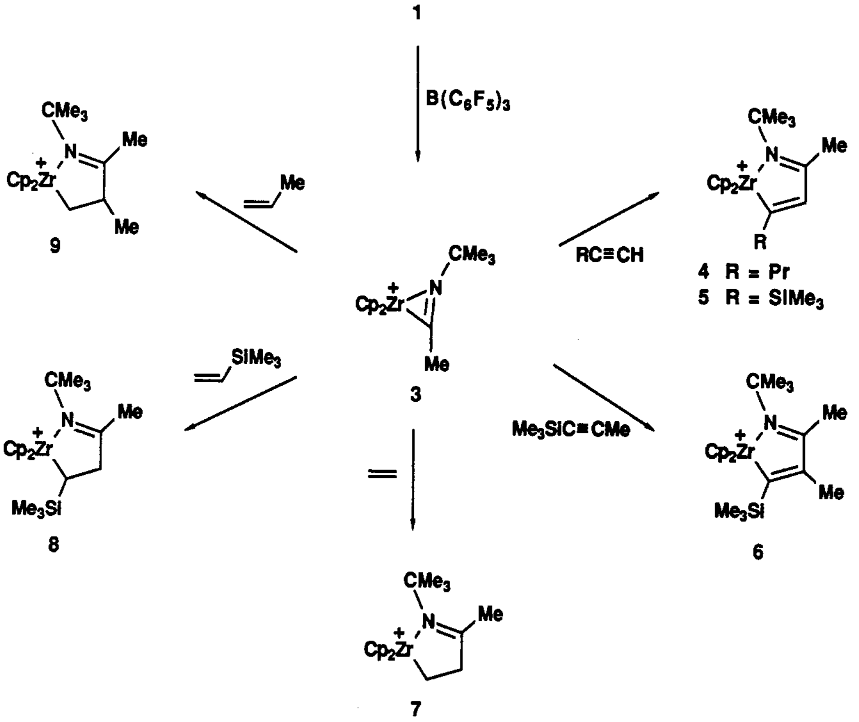
Scheme I



2 is thermally sensitive, air sensitive, and unstable in chlorinated solvents, a more robust reagent was sought.

A more stable cationic η^2-(iminoacyl) complex, $[Cp_2Zr(\eta^2\text{-}C,N\text{-}C\{=N^tBu\}CH_3)][CH_3B(C_6F_5)_3]$ (**3**), was prepared by CH_3^- abstraction from **1** using $B(C_6F_5)_3$ (23 °C, CH_2Cl_2, 2 min, 100%).[10] In contrast to **2**, complex **3** is stable at ambient temperature and in chlorinated solvents. Moreover, **3** is stable in air for at least 10 min at ambient temperature. The η^2-(iminoacyl) coordination mode is clearly evident from the spectroscopic data (^{13}C NMR δ 233, $Zr\mathit{C}\{=N^tBu\}$–; IR $\nu_{C=N}$ 1646.2 cm^{-1}), and NMR data are consistent with a noncoordinated $MeB(C_6F_5)_3^-$ anion.[11]

The reactivity of **3** (generated *in situ* from **1** and $B(C_6F_5)_3$) with alkynes was explored (Scheme I). **3** reacts rapidly with terminal alkynes such as 1-pentyne and (trimethylsilyl)acetylene (23 °C, CH_2Cl_2, 5 min, 100%) via insertion into the Zr–C(iminoacyl) bond to afford the five-membered unsaturated metallacycles **4** and **5**, respectively. Products resulting from alkyne C–H bond activation or multiple alkyne insertion are not observed. The ^{13}C NMR spectra of **4** and **5** exhibit low-field Zr–*C*(R) = resonances (δ 239.5 and 253.8, respectively; confirmed by DEPT for **4**), indicating that the alkyne substituent is α to Zr. The –*C*=N^{t}Bu resonance appears at δ 181.5 and 178.6 for **4** and **5**, respectively. These values are downfield from the values of organic imine analogues[12] and establish that the imine N is coordinated to Zr. The IR $\nu_{C=N}$ values (**4**, 1640.6; **5**, 1642.3 cm^{-1}) are also consistent with the imine N-coordination. The reaction of **3** with the internal alkyne 1-(trimethylsilyl)propyne (23 °C, CH_2Cl_2, 30–45 min) quantitatively affords the unsaturated metallacycle **6**, in which the –SiMe$_3$ substituent is α to Zr. The ^{13}C and IR data for **6** are similar to data for **4** and **5** and establish the chelated structure. The alkyne insertion regiochemistry was confirmed by hydrolysis (*vide infra*).

Complex **3** also reacts rapidly and quantitatively with olefins via insertion into the Zr–C(iminoacyl) bond (Scheme I). Reaction of **3** with ethylene (1 atm, <23 °C, CH_2Cl_2, <1 min) cleanly affords metallacycle **7**. Reaction of **3** with vinyltrimethylsilane (23 °C, CH_2Cl_2, <5 min) proceeds via 2,1-insertion to afford metallacycle **8**, in which the –SiMe$_3$ substituent is α to Zr. Hydrolysis of **8** affords 4-(trimethylsilyl)butan-2-one and unambiguously establishes the insertion regiochemistry. **3** reacts with propene (23 °C, CH_2Cl_2, <5 min) via 1,2-insertion to afford metallacycle **9**, in which the –Me substituent is β to Zr. Spectroscopic data for **7**–**9** are similar to data for unsaturated analogues **4**–**6** and are consistent with chelated structures.

The high reactivity of **3** and its ease of generation from air-stable **1**, make it an attractive reagent for acetylation of alkynes and alkenes. Thus, sequential addition of solutions of $B(C_6F_5)_3$ and the unsaturated substrate to **1** using Schlenk techniques, followed by hydrolysis, extraction, and purification affords ketones in excellent yields (84–92%, Scheme II).[13] Thus, *in situ* generated **3** reacts with (trimethylsilyl)propyne and a proton source to afford 4-(trimethylsilyl)-3-methylbut-3-en-2-one (**10**, 85%). The absence of coupling between the vinyl-H and vinyl-CH$_3$

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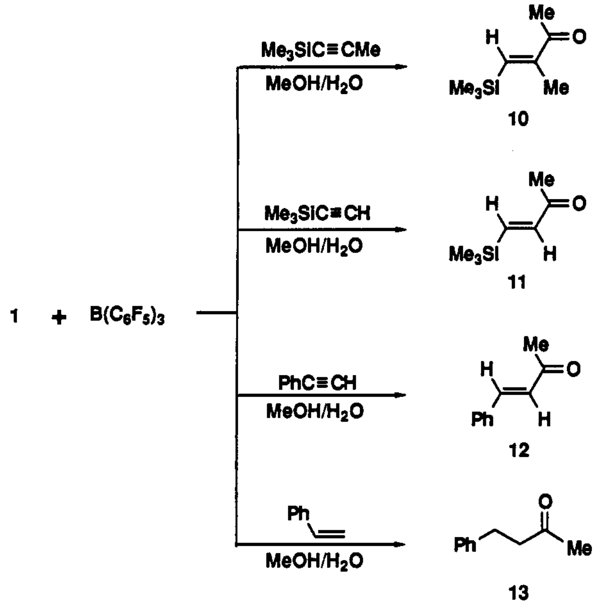
[10] (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (b) Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375.

[11] The NMR data for the $MeB(C_6F_5)^-$ anion in **3** are identical to data for **4**–**9**; coordination of the anion to Zr in the latter complexes is very unlikely due to steric constraints.

[12] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1979.

[13] Example experimental procedure: To solid **1** (500 mg, 1.49 mmol) was added a solution of $B(C_6F_5)_3$ (770 mg, 1.50 mmol) in CH_2Cl_2 (~5 mL) under N_2 with stirring at ambient temperature. After the colorless solution was stirred for 5 min, a solution of (trimethylsilyl)acetylene (200 mg, 2.04 mmol) in CH_2Cl_2 (~5 mL) was added resulting in a bright yellow solution. The reaction was stirred for an additional 45 min. The volatiles were removed on a rotary evaporator, and the residue was dissolved in MeOH (~5 mL). H_2O (10 mL) was added and the reaction mixture stirred for 15 min, yielding a colorless heterogenous (gel-like) mixture. The gel was extracted with CH_2Cl_2 (3 × 7 mL). The organic extract was washed with saturated NaCl solution (1 × 10 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic extracts were condensed to ~0.5 mL on a rotary evaporator and the residue column chromatographed on alumina using hexane and then hexane/CH_2Cl_2 (1:1) to afford **10** (R_f (CH_2Cl_2) 0.65) as a pale yellow oil (yield 199 mg, 85%).

Scheme II



in the ^{1}H NMR spectrum of 10 establishes the assigned regiochemistry. The (*E*)-alkenyl geometry for 10 is assigned by 2D-NOESY experiments and by analogy to 11 and 12 (*vide infra*) and the known cis insertion chemistry of $Cp_2Zr(pyridyl)^+$ and related complexes.[3-5] Similar reactions of *in situ* generated 3 with (trimethylsilyl)acetylene and phenylacetylene afford (*E*)-alkenyl ketones 11 and 12, respectively. The ^{1}H NMR spectra for 11 and 12 exhibit large coupling (J = 16–20 Hz) between the vinyl-H's consistent with the assigned *E* geometry. Ketone 13 was isolated after hydrolysis of the reaction of *in situ* generated 3 and styrene.

The enhanced reactivity of 3 relative to neutral early transition metal iminoacyl complexes is ascribed to high Lewis acidity of the cationic Zr(IV) center which promotes coordination and activation of unsaturated substrates. The regioselectivity observed in these reactions is similar to that observed for analogous reactions of $Cp_2Zr(\eta^2\text{-pyridyl})(L)^+$ and $Cp_2Zr(\eta^2\text{-acyl})(L)^+$ complexes and has been rationalized on the basis of steric/electronic effects.[4-6] The high yield syntheses of unsaturated and saturated carbonyl compounds 10–13 clearly demonstrate the synthetic potential of 3 as a novel acetyl anion equivalent for the acetylation of alkynes and alkenes.[14-16] The mild reaction conditions, moderate air stability of the reagents involved, and the use of normal alkynes/alkenes as electrophiles are especially noteworthy. For comparison, most reactions involving acyl anion equivalents reported to date use more vigorous reaction conditions, highly air-sensitive/pyrophoric strong bases, and/or elaborate workup procedures.[15,16] Furthermore, these reactions generally utilize electrophiles other than alkynes and alkenes. In the present study, a single iminoacyl complex (1) was used, and the intermediate cationic azazirconacycles were hydrolyzed to afford ketones. Presumably, the use of other iminoacyl complexes, and other electrophilic Zr–C cleavage reactions, could provide access to a wider variety of products.[17] Work is currently underway to broaden the scope of this chemistry.

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Supplementary Material Available: Detailed experimental procedures, spectroscopic and analytical data, and ^{13}C NMR spectra for compounds 1–13 (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Related "acyl anion equivalents" generated from acyl zirconocene chloride/$AlCl_3$ reagent systems and their reactions with CH_3COCl have been described. Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

(15) For comprehensive reviews on acyl anion equivalents, see: (a) Ager, D. J. In *Umpoled Synthons: A survey of Sources and Uses in Synthesis*; Hase, T. A., Ed.; Wiley: New York, 1987; p 19 and references cited therein. (b) Martin, S. F. *Synthesis* **1979**, 633. (c) Seebach, D. *Angew. Chem., Int Ed. Engl.* **1979**, *18*, 239. (c) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1.

(16) Key recent reports on acyl anion equivalents: (a) Seyferth, D.; Weinstein, R. M.; Hui, R. C.; Wang, W.-L.; Archer, C. M. *J. Org. Chem.* **1992**, *57*, 5620 and references cited therein. (b) Katritzky, A.; Yang, Z.; Lam, J. N. *J. Org. Chem.* **1991**, *56*, 6917 and references cited therein. (c) Sengupta, S.; Snieckus, V. *J. Org. Chem.* **1990**, *55*, 5680 and references cited therein.

(17) Leading references: (a) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (b) Negishi, E.; Takahashi, T. *Aldrichchim. Acta* **1985**, *18*, 31. (c) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. (d) Negishi, E.; Swanson, D. R.; Miller, S. R. *Tetrahedron Lett.* **1988**, *29*, 1631.