

Cyclopentadienyl Activation via Reductive Elimination: An Old Ligand Learns Some New Tricks

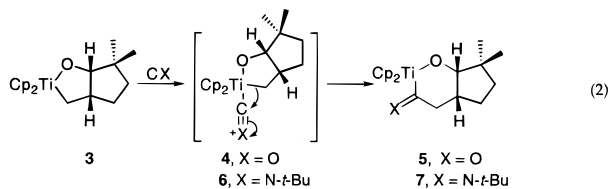
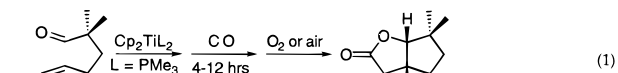
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Cyclopentadienyl (Cp) ligands are among the most extensively utilized ligands in organometallic chemistry. One reason for this is the great stability of the η^5 -Cp binding mode. In most organometallic reactions of transition metal complexes, the η^5 -Cp ligand plays the role of spectator, staying tightly bound η^5 to the metal center throughout the course of the reaction. In our studies of titanocene-mediated organic reactions, we have found that a titanium-bound η^5 -Cp ligand can be remarkably reactive. Herein we describe the ready participation of a titanocene η^5 -Cp ligand in a sequence of carbon–carbon bond forming reactions that completely removes the Cp ligand from the titanium coordination sphere.

We recently reported that γ -butyrolactones can be prepared from tethered enals or enones via the reaction sequence of reductive coupling,¹ carbonylation, and reductive elimination (eq 1).² The carbonylation step in this sequence is slow, taking 4–12 h at room temperature. We reasoned that replacing CO with an isoelectronic, but more Lewis-basic, isonitrile ligand might result in a more facile insertion reaction proceeding through the lower energy reactive intermediate **6** (eq 2).³ Consistent with this hypothesis, metallacycle **3** reacted rapidly with *t*-BuNC, but the product obtained was not the expected metallacycle **7**. Obtained instead was a complex, **8** (70% yield),⁴ where one of the η^5 -Cp ligands is converted to a group possessing five inequivalent protons (¹H NMR) and five inequivalent carbons (¹³C NMR). It appeared that one Cp ligand had adopted a lower hapticity binding mode.



X-ray quality crystals of the isonitrile insertion product **8** could be obtained by slow recrystallization from a cold toluene solution (2d, -33°C). The molecular structure, established by single-crystal X-ray analysis, is shown in Figure 1. Complex **8** possesses a single η^5 -Cp ligand and an η^4 -azadiene⁵ ligand linked to an alkoxide. The unusual azadiene ligand is derived from the coupling of the incoming *t*-BuNC ligand to both the metallacycle ring and one of the Cp ligands of **3**. The long–

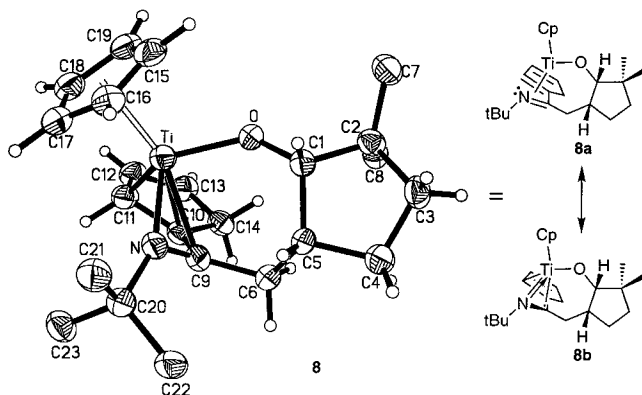
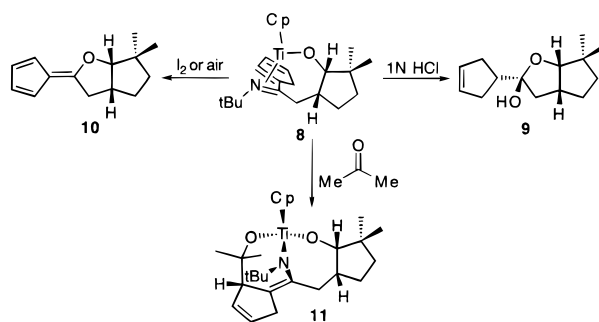


Figure 1. ORTEP drawing of *t*-BuNC insertion adduct **8** showing 30% probability thermal ellipsoids. Hydrogen atoms on C7–C8 and C21–C23 were omitted for clarity.

Scheme 1



short–long alternation of bond lengths in the bound N–C–C–C unit suggests that the azadiene is best described as a σ^2, π donor ligand bound to a d^0 Ti(IV) center. The short Ti–N bond distance (1.886(5) Å) and the planar nitrogen geometry (sum of subtended angles = $359.2(7)^\circ$) suggest significant p_π – d_π donation from the nitrogen lone pair making the azadiene a 6e donor ligand and **8** a 16e complex. Bonding of the azadiene ligand to the metal center is best described by resonance structure **8b**.

We briefly examined the reaction chemistry of complex **8**. Our preliminary findings are summarized in Scheme 1. Acid-mediated hydrolysis of **8** produced lactol **9** in 81% yield⁴ (8:1 mixture of diastereomers),⁶ and air oxidation of **8** produced fulvene **10** in 23% yield.⁴ Complex **8** reacted cleanly with acetone to give the insertion product **11** in 74% yield.⁴

The molecular structure of the acetone insertion product **11**, established by single-crystal X-ray analysis, is shown in Figure 2. Complex **11** possesses a single η^5 -Cp ligand and an enamide ligand linked to two alkoxides. The Ti...C₁₀ interatomic distance of 3.149 Å indicates an η^1 bonding mode for the Ti–enamide moiety; the close Ti...C₉ contact of 2.568(5) Å suggests, however, that there may be a weak interaction between the metal center and the enamide olefin. The short Ti–N bond distance (1.914(4) Å) and the planar nitrogen geometry (sum of subtended angles = $360.0(6)^\circ$) suggest significant p_π – d_π donation from the nitrogen lone pair making the enamide nitrogen a 3e donor and **11** a 14e complex (resonance structure **11b**).

Reaction of metallacycle **3** with the smaller isonitrile *n*-BuNC proceeded along a different pathway than that of the corresponding *t*-BuNC reaction described above (eq 3). Three equivalents of *n*-BuNC were required for complete conversion of **3**. Although the organometallic product(s) could not be isolated or positively identified in this case, treatment of the

(6) Major isomer stereochemistry (shown) was established by X-ray crystallography.

(1) Hewlett, D. F.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1684–1686.

(2) Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc.* **1996**, *118*, 1557–1558.

(3) For the use of isonitrile insertion in cyclopentenone synthesis, see: (a) Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803–5805. (b) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593–8601.

(4) Overall yield from 2,2-dimethyl-5-hexenal (**1**).

(5) (a) Davis, J. M.; Whitby, R. J.; Jaxachamiec, A. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1743–1745. (b) Scholz, J.; Nolte, M.; Kruger, C. *Chem. Ber.* **1993**, *126*, 803–809.

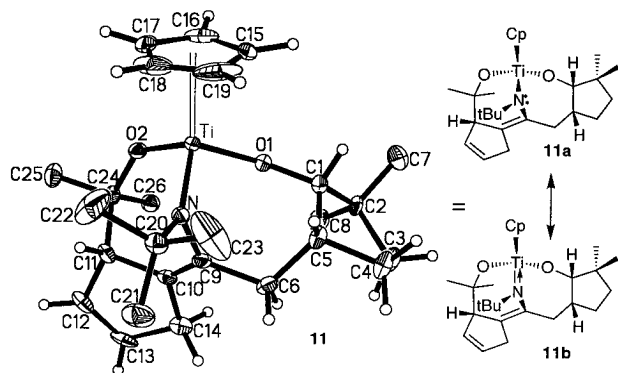
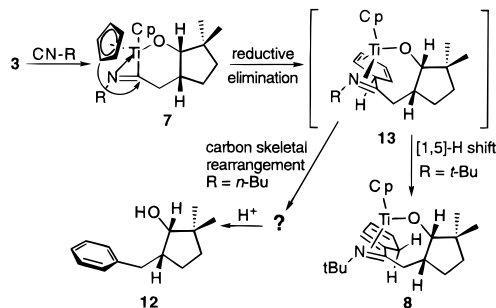
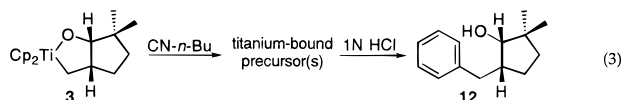


Figure 2. ORTEP drawing of acetone insertion adduct **11** showing 30% probability thermal ellipsoids. Hydrogen atoms on C7–C8, C21–C23, and C25–C26 were omitted for clarity.

Scheme 2



crude reaction mixture with 1 N HCl afforded the aromatic product **12** in 94% yield.⁴ Apparently the six carbons of the phenyl ring are derived from a Cp ligand and one molecule of *n*-BuNC.

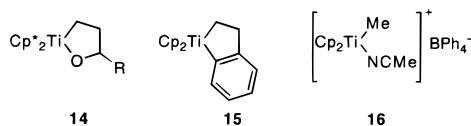


Proposed pathways for the formation of products **8** and **12** are shown in Scheme 2. When the reaction of **3** with *t*-BuNC was monitored by ¹H NMR, a transient set of proton signals consistent with intermediate **7** was observed at early stages of the reaction. Conversion of **7** to **8** or **12** can be envisioned to proceed through a common intermediate **13** formed via reductive elimination of the Cp and iminoacyl ligands (electrophilic attack of a Cp ligand by the iminoacyl carbon). The fate of intermediate **13** appears to be determined by the isonitrile-derived nitrogen substituent.⁷ When the nitrogen substituent is *t*-Bu, hydrogen atom migration on the substituted cyclopentadiene produces **8**. When the nitrogen substituent is *n*-Bu, a proton- or metal-assisted carbon skeletal rearrangement takes place producing **12**.⁸

Isonitrile insertion into metal–alkyl bonds has been observed for most of the d-block metals as well as numerous actinide and lanthanide elements.⁹ While the reactivity of group 4

(7) Preliminary investigation of a number of tethered enal substrates indicates that the observed divergent reactivity is completely general and that the reaction pathway is determined entirely by the nitrogen substituent.

metallocene alkyls with isonitriles has not been extensively studied, in the cases where it has been examined it proceeds uneventfully without cyclopentadienyl participation. For example, titanocene complexes **14**–**16** react cleanly with *t*-BuNC to afford the expected iminoacyl products.^{10,11}



Although lower hapticity Cp binding modes can form via ring slippage¹² to η^3 - or η^1 -C₅R₅ or reductive elimination¹³ to η^4 -C₅R₆, such reactions are usually reversible with equilibrium strongly favoring the η^5 binding mode. Irreversible ring slippage of η^5 -Cp ligands to η^3 and η^1 binding modes has been documented and several η^3 - and η^1 -C₅R₅ complexes have been structurally characterized.^{14,15} Complexes possessing the η^4 -C₅R₆ ligand have also been structurally characterized, but we know of no previous examples of irreversible reductive elimination of an η^5 -Cp ligand. The results reported here illustrate a unique mode of reactivity for titanocene complexes and demonstrate once again that η^5 -Cp ligands are not always the benign spectators they are often assumed to be.¹⁶

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Supporting Information Available: Experimental procedures, spectral data for all compounds, and listings of fractional atomic coordinates and anisotropic thermal parameters for compounds **8**–**11** (41 pages). Ordering information is given on any current masthead page.

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(8) Although it is premature at this stage to invoke a specific sequence of steps for the formation of **12**, the presence of a phenyl ring suggests a Wagner–Meerwein-type ring expansion. Carbocationic rearrangement of an intermediate derived from lactol **9** is unlikely since protonation of lactol **9** with 1 N HCl or concd AcOH did not lead to formation of **12**. Another possibility is that ring expansion takes place before protonation producing a mixture of intermediates of the type [CpTi(N-*n*-Bu)(OR)]_n which liberates **12** (ROH) upon protonation.

(9) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079.

(10) (a) Campora, J.; Buchwald, S. L.; Gutierrez-Puebla, E.; Monge, A. *Organometallics* **1995**, *14*, 2039–2046. (b) Mashima, K.; Haraguchi, H.; Oyoshi, A.; Sakai, N.; Takaya, H. *Organometallics* **1991**, *10*, 2731–2736. (c) Bochmann, M.; Wilson, L.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556–2563.

(11) Isonitrile insertion in zirconocene and hafnocene metallacycles: Kloppenburg, L.; Petersen, J. L. *Polyhedron* **1995**, *14*, 69–80 and references cited therein.

(12) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307–318.

(13) (a) Jones, W. D.; Maguire, J. A. *Organometallics* **1985**, *4*, 951–953. (b) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966–5968. (c) Werner, H.; Hoffmann, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 794–795. (d) Elmitt, K.; Green, M. L. H.; Forder, R. A.; Jefferson, I.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1974**, 747–748.

(14) (a) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejnen, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329–333. (b) van Raaij, E. U.; Brintzinger, H. H.; Zsolnai, L.; Huttner, G. *Z. Anorg. Allg. Chem.* **1989**, *577*, 217–222.

(15) Examples of structurally characterized η^1 -cyclopentadienyl complexes formed by ring slippage are cited in ref 12.

(16) Unexpected participation of an η^5 -Cp ligand was recently observed by Gleiter when pinacol coupling of ketones with Cp₂Ti(PMe₃)₂ was attempted. Fulvene products, resulting from reductive Cp–ketone coupling, were formed instead: Gleiter, R.; Wittwer, W. *Chem. Ber.* **1994**, *127*, 1797–1798.