

Communications to the Editor

Trimerization of *tert*-Butylacetylene to 1,3,6-Tri(*tert*-butyl)fulvene Catalyzed by Titanium Aryloxy Compounds

Eric S. Johnson, Gary J. Balaich, Phillip E. Fanwick, and Ian P. Rothwell*

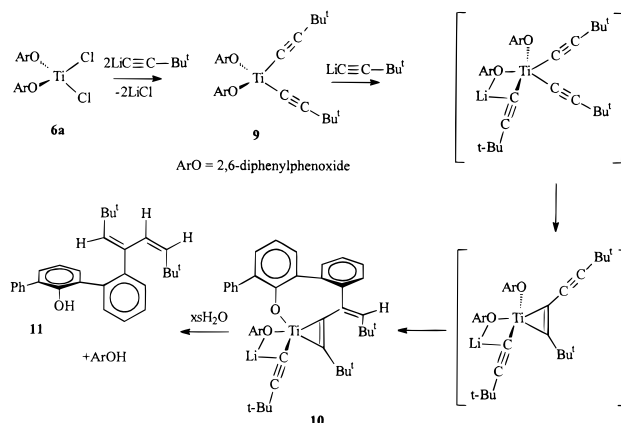
Department of Chemistry
1393 Brown Building, Purdue University
West Lafayette, Indiana 47907-1393

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The [2 + 2 + 2] cycloaddition of alkyne segments to produce the arene nucleus is one of the most ubiquitous and studied reactions in organo-transition-metal chemistry.^{1,2} In contrast there are only scattered reports of the stoichiometric conversion of three alkyne units into the fulvene nucleus via a formal [2+2+1] cycloaddition.^{3,4} In this paper, we report on our initial synthetic and mechanistic studies of a titanium aryloxy catalyst system which selectively converts *tert*-butylacetylene into the corresponding fulvene.

The titanacyclopentadiene compound [(2,6-Ph₂C₆H₃O)₂Ti-(C₄H₂Bu₂)₂] **1** (Table 1; 2,6-Ph₂C₆H₃O = 2,6-diphenylphenoxide) has been demonstrated to be a catalyst for the slow cyclotrimerization of *tert*-butylacetylene into 1,3,5-tri(*tert*-butyl)benzene (**2**).⁵ When one or more equivalents of LiC≡CBu^t is mixed with **1** in benzene solution the resulting system causes the catalytic production of 1,3,6-tri(*tert*-butyl)fulvene (**3**) along with dimer **4** and smaller amounts of an as yet unidentified alkyne oligomer (**5**) (Table 1).⁶ This catalysis can be more conveniently carried out without isolation of **1** by activating one of the dichlorides [(ArO)₂TiCl₂] **6** (ArO = 2,6-diphenylphenoxide,⁷ **a**; 2,6-diisopropylphenoxide,^{6,8} **b**; 2,6-dimethylphenoxide,⁶ **c**) with >2 equiv of LiC≡CBu^t (Table 1). The result of heating (100 °C sealed vessel) a mixture of these components with HC≡CBu^t in benzene can be monitored by GC to show the catalytic buildup of products over time (Figure 1). Although a small amount of arene **2** is initially produced, it is rapidly exceeded by fulvene **3**. The ratio of **3**:**4**:**5** produced throughout the reaction remains almost constant. The purification of dimer **4** can be achieved by vacuum distillation, while bright yellow fulvene **3** can be separated by chromatography. The potential utility of fulvene **3** is demonstrated by its reaction with alkylating

Scheme 1



Scheme 2

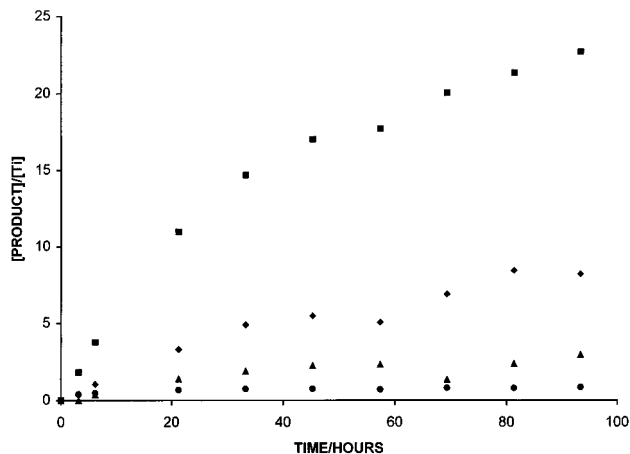
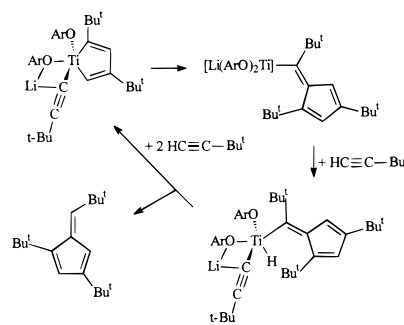


Figure 1. Plot showing the buildup with time of **2** (circle), fulvene **3** (square), **4** (diamond), and **5** (triangle) produced at 100 °C from HC≡CBu^t (30 mL, 244 mmol) using **6b** (1.00 g, 2.1 mmol) activated with LiC≡CBu^t (0.74 g, 8.40 mmol) in benzene (6 mL).

agents (eq 1) to produce (after workup) the corresponding bulky cyclopentadienes **7** and **8** (structurally characterized).^{6,9}

A variety of mechanistic pathways leading to fulvene formation can be envisaged including those involving vinylidene intermediates.^{3,4} The stoichiometric reaction of **6a** with 2 equiv of LiC≡CBu^t produces the bis(alkynyl) **9** which is then converted by an extra equivalent of LiC≡CBu^t to the mixed

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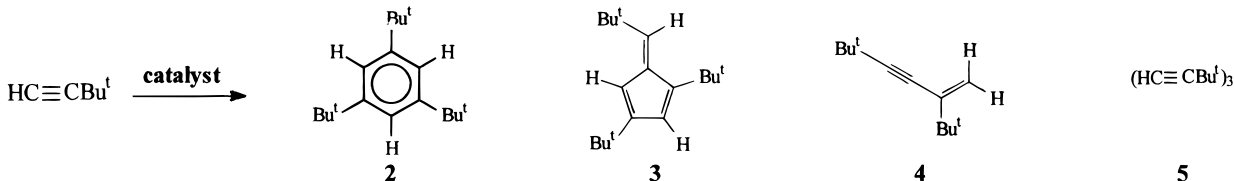
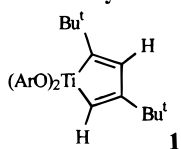
(6) Experimental details and characterization data are contained in the Supporting Information.

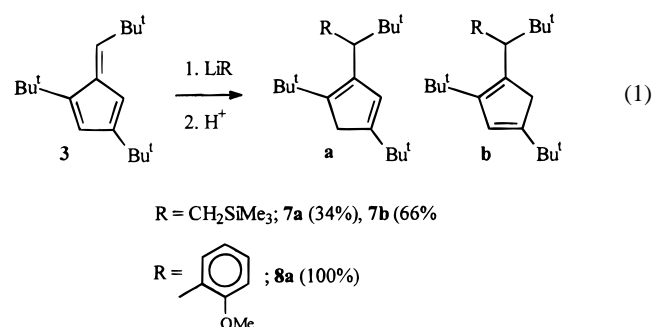
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(9) Crystallographic data for C₂₅H₃₈ **8a** at 296 K: *a* = 13.702(3), *b* = 10.326(1), and *c* = 17.255(3) Å, β = 111.74(2)°, *V* = 2267(1) Å³, *Z* = 4 in space group *P2₁/c*. Data for TiLiC₅₄O₂H₅₃ **10** at 296 K: *a* = 10.800(4), *b* = 40.398(9), and *c* = 11.646(4) Å, β = 117.41(3)°, *V* = 4510(5) Å³, *Z* = 4 in space group *P2₁/n*.

Table 1. Product Distribution (%) from the Oligomerization of HC≡CBu^t using Various Titanium Catalysts⁶

$\text{HC}\equiv\text{CBu}^t$  catalyst	2	3	4	5
 1	100	0	0	0
1 + LiC≡CBu ^t	5	75	16	4
[Ti(OC ₆ H ₃ Ph ₂ -2,6) ₂ Cl ₂] / 3LiC≡CBu ^t	6	65	19	10
[Ti(OC ₆ H ₃ Pr ⁱ -2,6) ₂ Cl ₂] / 3LiC≡CBu ^t	3	71	17	9
[Ti(OC ₆ H ₃ Me ₂ -2,6) ₂ Cl ₂] / 3LiC≡CBu ^t	3	63	22	12
10	10	78	8	4



lithium/titanium ate species **10** (Scheme 1).⁶ The formulation of **10** is based upon structural studies⁹ as well as its hydrolysis to yield the phenol **11**. The production of **10** may arise via initial coupling of acetylide units to a diyne followed by cyclometalation and reductive coupling. Compound **10** acts as a single component catalyst producing a similar blend of products as produced by [(ArO)₂TiCl₂]/LiC≡CBu^t mixtures.

These observations lead us to propose that the catalytic reaction proceeds via titanacyclopentadiene/acetylide coupling

followed by liberation of fulvene by CH bond activation (either σ -bond metathesis or insertion) on an alkyne unit (Scheme 2). In the case of the [(ArO)₂TiCl₂]/3LiC≡CBu^t systems, initial coupling of acetylides to a diyne precede titanacyclopentadiene formation. The production of dimer **4** can be similarly accounted for by η^2 -alkyne/acetylide coupling. Attempts to utilize less bulky terminal alkynes has been found to lead to oligomeric products. Further studies of this reactivity are underway.

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Supporting Information Available: Experimental details of the synthesis of new compounds, description of the experimental procedures for X-ray diffraction studies, ORTEP drawings and tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and multiplicities for **10** and **8a** (33 pages). See any current masthead page for ordering and Internet access instructions.

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