

Reactions of Propargyl Metallic Species Generated by the Addition of Alkynyllithiums to Fischer-Type Carbene Complexes

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The 1,2-addition reaction of highly nucleophilic organometallics such as alkylolithiums or Grignard reagents to Fischer-type carbene complexes would produce carbon-elongated group 6 organometallic intermediates, which could be employed for further manipulations.¹ However, most such reactions reported so far have been confined to additions to phenyl-substituted carbene complexes, and the addition intermediates have not been employed for further carbon–carbon bond formation.² Furthermore, carbene complexes having a primary or secondary alkyl substituent on the carbene carbon have never been successfully employed in this type of reaction, because deprotonation of the α -proton has taken place preferentially.³ In this paper we would like to report that a new type of propargyl metallic species is generated by the addition reaction of *alkynyllithiums* to Fischer-type carbene complexes including those having α -hydrogens, and that these species can be employed for several useful carbon–carbon bond-forming reactions.⁴

When phenylethyneyllithium was added to pentacarbonyl[1-methoxy-2-methyl-1-propylidene]tungsten(0) (**1a**; R¹ = *i*-Pr) at -78 °C in THF, a smooth addition reaction to the carbene complex **1a** was observed, and the complete consumption of **1a** indicated that deprotonation of α -proton did not occur under these conditions. Furthermore, neutral aqueous workup with pH 7 phosphate buffer at -78 °C followed by mild acid treatment gave the α,β -unsaturated ketone **2a** (R¹ = *i*-Pr, R² = Ph) in 86% yield,⁵ while acidic workup such as quenching with 2 M HCl or CF₃COOH at -78 °C gave the enyne **3a** (R² = Ph, R' = R'' = Me) with no detectable formation of **2a**.

The difference in reaction pathway depending on the quenching conditions can be explained as follows: The addition reaction of phenylethyneyllithium to **1a** occurs at -78 °C to give the addition intermediate **4a**. When strong acid is added to **4a**, elimination of methanol occurs to produce an unstable carbene

Scheme 1

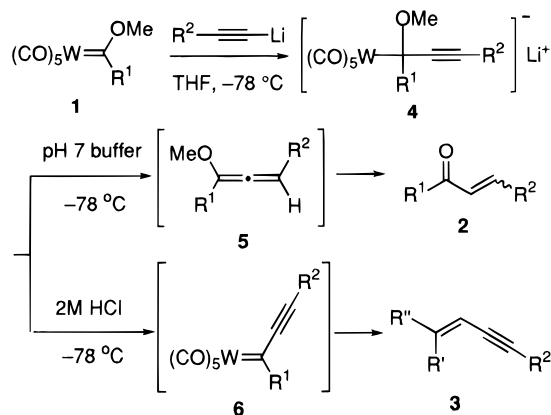


Table 1. The Addition Reactions of Alkynyllithiums to Tungsten Carbene Complexes

R ¹	R ²	conditions A ^{a,b} (yield of 2 /%)	conditions B ^d (yield of 3 /%)
<i>i</i> -Pr (1a)	Ph	86 (2a)	85 (R' = R'' = Me) (3a)
<i>i</i> -Pr	<i>n</i> -Hex	80	59 (R' = R'' = Me)
<i>n</i> -Bu (1b)	Ph	79	68 (R' = <i>n</i> -Pr, R'' = H) ^c
<i>n</i> -Bu	<i>n</i> -Hex	51	34 (R' = <i>n</i> -Pr, R'' = H) ^c
Ph (1c)	Ph	97	<i>d</i>
Ph	<i>n</i> -Hex	78 (2c)	<i>d</i>

^a Conditions A: The reaction is quenched with pH 7 buffer at -78 °C and then 2 M HCl is added to hydrolyze the vinyl ether completely. Conditions B: The reaction is quenched with 2 M HCl or CF₃COOH at -78 °C. ^b Obtained as a mixture of (*E*) and (*Z*) isomers. ^c (*Z*)-Enynes were obtained in about 10:1 ratio in these cases. ^d Enones **2** were obtained as major products.

intermediate **6a**, which gives the enyne **3a** by 1,2-hydrogen migration. On the other hand, when the reaction is quenched with pH 7 buffer, the addition intermediate **4a** behaves like a propargyl metallic species to give, on γ -protonation, a methyl 1,2-propadienyl ether **5a**, which is hydrolyzed to give enone **2a**.⁶ The results of the reaction of various tungsten carbene complexes and alkynyllithiums are summarized in Table 1. Even in the reactions of the primary alkyl-substituted carbene complex **1b**, the addition reaction occurs preferentially to the deprotonation reaction, and the products are obtained in moderate to good yields. It should be emphasized that in control experiments reaction of **1b** with *n*-octyllithium or phenyllithium gave none of the corresponding addition product and **1b** was recovered. Thus the use of *alkynyllithiums* is essential for the success of the addition reaction.

The production of α,β -unsaturated ketones indicates that the one-carbon homologation of alkynyllithiums to propargyl metallic species can be achieved by using the Fischer-type carbene complexes. Hence, it was expected that the propargylic metallic species could be applied to further carbon–carbon bond formation reactions.⁷ Most of the previously known types of propargyl metallic species are in equilibrium with allenyl metallic species, and in their reaction with aldehydes, a mixture of acetylenic and allenic alcohols is usually obtained,⁸ selective preparation of allenyl products being limited to several specific combinations of substrates and metals.⁹

(6) Casey and Brunsvold reported that the reaction of vinylolithium and phenylmethoxycarbene complex, followed by treatment with anhydrous HCl, gave 1-methoxy-1-phenylpropene as a major product instead of the desired vinylphenylcarbene complex. They proposed that protonation occurred at the γ -position of the addition intermediate.^{2a}

(7) For reactions of propargyl transition metal species, see for example: Shu, H.-G.; Shiu, L.-H.; Wang, S.-H.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 530 and references cited therein.

(8) Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 2, Chapter 9.2.

(1) For reviews on the chemistry of Fischer-type carbene complexes, see: (a) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, Chapter 5.3. (b) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, Chapter 5.4. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, Chapter 9.2. (d) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(2) For examples, see: (a) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1974**, *77*, 345. (b) Fischer, E. O.; Held, W. *J. Organomet. Chem.* **1976**, *112*, C59. (c) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (d) Iwasawa, N.; Saitou, M. *Chem. Lett.* **1994**, 231. (e) Barluenga, J.; Bernad, P. L., Jr.; Concellón, J. M. *Tetrahedron Lett.* **1994**, *50*, 9471. Several other examples are cited therein.

(3) For examples, see: (a) Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390. (b) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230. (c) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503. (d) Wulff, W. D.; Anderson, B. A.; Toole, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5485 and references cited therein.

(4) A similar type of propargylic species is proposed to be formed in the following examples: (a) Fischer, H.; Meisner, T.; Hofmann, J. *Chem. Ber.* **1990**, *123*, 1799. (b) Dötz, K. H.; Christoffers, C.; Knochel, P. J. *Organomet. Chem.* **1995**, *489*, C84.

(5) Formation of dienyl ethers and α,β -unsaturated ketones was reported by the thermal reaction of Fischer-type carbene complexes and alkynes via metallacyclobutene intermediates. (a) Macomber, D. W. *Organometallics* **1984**, *3*, 1589. (b) Harvey, D. F.; Neil, D. A. *Tetrahedron* **1993**, *49*, 2145 and references cited therein.

Table 2. Preparation of Various Furans and Pyrroles

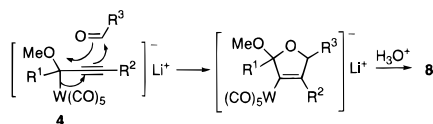
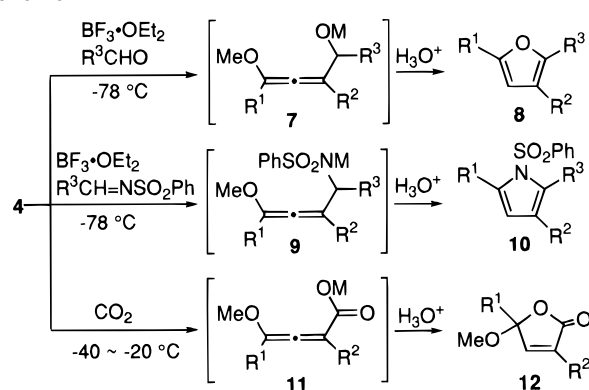
R ¹	R ²	R ³	yield of 8 /%	yield of 10 /%
Ph	<i>n</i> -Hex	Ph	86 (8m)	75
Ph	<i>n</i> -Hex	<i>i</i> -Pr	72 (8n)	
Ph	<i>n</i> -Hex	PhCH=CH	67	64
Ph	<i>n</i> -Hex	COOEt	80	
<i>i</i> -Pr	<i>n</i> -Hex	Ph	82	85 ^a
<i>n</i> -Bu	Ph	Ph	62	

^a The molybdenum complex was employed in this case, better yield being obtained than with the corresponding tungsten complex.

In the first place, we examined the reactions of the addition intermediates **4** with various aldehydes. When benzaldehyde was added to the addition intermediate derived from phenyl carbene complex **1c** and *n*-octynyllithium, the reaction proceeded at $-78\text{ }^{\circ}\text{C}$ and a furan derivative **8m** ($R^1 = R^3 = \text{Ph}$, $R^2 = n\text{-Hex}$), which was thought to be formed by cyclization of the allenyl intermediate **7m**,¹⁰ was obtained in 82% yield after aqueous workup. However, the corresponding reaction with isobutyraldehyde induced extensive self-condensation of the aldehyde, and the furan **8n** ($R^1 = \text{Ph}$, $R^2 = n\text{-Hex}$, $R^3 = i\text{-Pr}$) was obtained in only 12% yield together with the enone **2c** in 59% yield. We next examined the addition of Lewis acids to **4** to activate the aldehyde. Among several Lewis acids examined, $\text{BF}_3 \cdot \text{OEt}_2$ was the most effective and the desired furan **8n** was obtained in 72% yield. We also examined the possibility of preparing pyrrole derivatives by employing aldimines instead of aldehydes. After several trials, the intermediate propargyl metallic species were found to react with imines, in particular sulfonyl imines, in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ giving pyrrole derivatives **10** in good yields. As summarized in Table 2, a variety of 2,3,5-trisubstituted furans or pyrroles are obtained in which three substituents on the furans or pyrroles are derived from the substituents of the carbene complexes, alkynes, and aldehydes or imines, respectively. This reaction affords a unique three-component coupling approach to substituted furans or pyrroles. It should be noted that formation of the regioisomeric acetylenic product was not observed in these reactions. Carbon dioxide also reacts with these propargyl metallic species to give

(9) See for examples: (a) Daniels, R. G.; Paquette, L. A. *Tetrahedron Lett.* **1981**, 22, 1579. (b) Ishiguro, M.; Ikeda, N.; Yamamoto, H. *Chem. Lett.* **1982**, 1029. (c) Kobayashi, S.; Nishino, K. *J. Am. Chem. Soc.* **1995**, 117, 6392 and references cited therein.

(10) There is another possible mechanism where 1,2-migration of the pentacarbonylmetal portion occurs during the reaction as shown below. See the following references for related mechanisms: (a) Barluenga, J.; Tomás, M.; Rubio, E.; López-Peegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, 118, 695. (b) Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; Carbajo, R. J.; López-Ortiz, F.; García-Granda, S.; Pertierra, P. *Chem. Eur. J.* **1996**, 2, 88. See also ref 4.

**Scheme 2****Table 3.** Preparation of Various Butenolides

R ¹	R ²	yield of 12 /%	R ¹	R ²	yield of 12 /%
<i>i</i> -Pr	Ph	64	<i>n</i> -Bu	Ph	63
<i>i</i> -Pr	<i>n</i> -Hex	75	Ph	Ph	63
<i>i</i> -Pr	SiMe_3	66	Ph	<i>n</i> -Hex	72

the carboxylated compounds in good yields.¹¹ Thus, after the addition of alkynyllithiums to the carbene complexes, gaseous carbon dioxide was introduced to the reaction mixture. After acidic workup, butenolides **12** were obtained in good yield.¹² As shown in Table 3, this carboxylation reaction shows wide generality and various butenolides can be synthesized by this procedure.

In conclusion, a new type of propargyl metallic intermediate is generated by the addition reaction of alkynyllithiums with Fischer-type carbene complexes. This intermediate reacts regioselectively and in good yields with aldehydes, imines, and CO_2 to give respectively furans, pyrroles, and butenolides containing various substituents.

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Supporting Information Available: Experimental procedures and spectral data for compounds **2**, **3**, **8**, **10**, and **12** (12 pages). See any current masthead page for ordering and Internet access instructions.

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(11) There are a few examples of a CO_2 insertion reaction involving anionic tungsten-carbon derivatives: (a) Darensbourg, D. J.; Rokicki, A. *J. Am. Chem. Soc.* **1982**, 104, 349. (b) Darensbourg, D. J.; Grottsch, G. *J. Am. Chem. Soc.* **1985**, 107, 7473.

(12) Formation of butenolides as a minor product was reported on the thermal reaction of Fischer-type carbene complex and alkynes under a CO atmosphere. (a) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challenger, C. A.; Hylldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, 334, 9. (b) Bao, J.; Wulff, W. D.; Dragsich, V.; Wenglowksy, S.; Ball, R. G. *J. Am. Chem. Soc.* **1994**, 116, 7616. See also: Hoye, T. R.; Rehberg, G. *M. J. Am. Chem. Soc.* **1990**, 112, 2841.