Observation and Iodine Oxidation of the Protonated Anionic Propargyltungsten Species Formed in the Reaction of Fischer-Type Carbene Complexes with Alkynyllithiums

Nobuharu Iwasawa,* Takashi Ochiai, and Katsuya Maeyama

Department of Chemistry, Graduate School of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

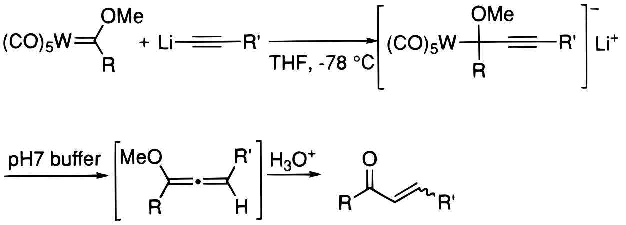
Received September 22, 1997[⊗]

Summary: Variable-temperature NMR studies of the reaction of anionic propargyltungsten species with methanol were carried out. On protonation, 1,2-migration of the metal group occurred to generate a vinylmetal species, which was stable up to 0 °C. Furthermore, iodine oxidation of the reaction intermediates gave one of several types of oxidized products, depending on the procedure used.

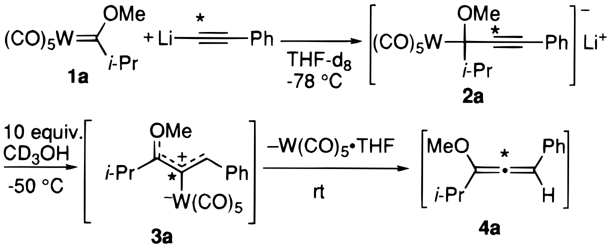
In previous papers we reported that alkynyllithiums add to Fischer-type carbene complexes to generate anionic propargylmetal species, which in turn react selectively with various electrophiles at the position γ to the metal.[1] For example, neutral aqueous workup of the addition reactions produces α,β-unsaturated ketones after hydrolysis of the intermediate allenyl ethers (Scheme 1). Furthermore, these propargylmetal species display high reactivity toward carbon electrophiles and react with aldehydes, sulfonylimines, and carbon dioxide to give furans, pyrroles, and 5-alkoxybutenolides, respectively, in good yields.

There have been a considerable number of examples reported of the reaction of *neutral* transition-metal propargyl species with highly reactive electrophiles such as SO$_2$, TCNE, tosyl isocyanate, and so on. These reactions are known to proceed via a [3 + 2] cycloaddition pathway with a concomitant 1,2-migration of the metal group.[2] On the other hand, reactions of *anionic* transition-metal propargyl species with electrophiles are rare, and their reaction mechanism has not been studied in detail.[3] We have noted in our studies the high nucleophilicity of anionic propargylmetal species, which makes them attractive as reactive intermediates, and we decided to study the behavior of these anionic propargyltungsten species when they react with electrophiles. In this paper we wish to report, on the basis of variable-temperature NMR studies, that the protonation of the anionic propargylmetal species with methanol proceeds with 1,2-migration of the metal group to generate a vinylmetal species, which is stable up to 0 °C in solution. Furthermore, iodine oxidation of the reaction intermediates is shown to give one of several types of oxidized products depending on the exact procedure used.

Scheme 1



Scheme 2[a]



[a] Asterisks indicate the ^{13}C-labeled position.

We first carried out variable-temperaure ^{1}H NMR experiments to obtain information on the structure of the intermediates produced on protonation of the addition intermediate **2a**, derived from (phenylethynyl)lithium and isopropylcarbene complex **1a**. Addition of (phenylethynyl)lithium to isopropylcarbene complex **1a** in THF-d_8 occurred smoothly at −78 °C to generate the addition intermediate **2a** (Scheme 2); in the ^{1}H NMR spectrum of **2a** the characteristic methine proton signal of the isopropyl carbene complex (δ 4.5 ppm) is replaced by a new methine proton signal at δ 2.3 ppm. Addition of about 10 mol equiv of CD$_3$OH at −78 °C brought about no change to the addition intermediate at this temperature, but when the temperature was raised to about −50 °C, the addition intermediate signals gradually disappeared and formation of a new species was observed. This new species remained unchanged until the mixture was warmed up further to 0 °C. At room temperature, new peaks grew in, which were assigned as those of the allenyl ether **4a** by comparison with an authentic sample, and after 12 h at room temperature, complete transformation to **4a** was observed. To further obtain information on the structure of the intermediate obtained on protonation, ^{13}C NMR measurements were

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) (a) Iwasawa, N.; Maeyama, K.; Saitou, M.; *J. Am. Chem. Soc.* **1997**, *119*, 1486. (b) Iwasawa, N.; Maeyama, K. *J. Org. Chem.* **1997**, *62*, 1918.

(2) (a) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523. (b) Welker, M. E. *Chem. Rev.* **1992**, *92*, 97 and references cited therein.

(3) A similar type of anionic 1,2-migration of pentacarbonyltungsten was also observed 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. (c) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695. (d) 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.

S0276-7333(97)00835-2 CCC: $14.00

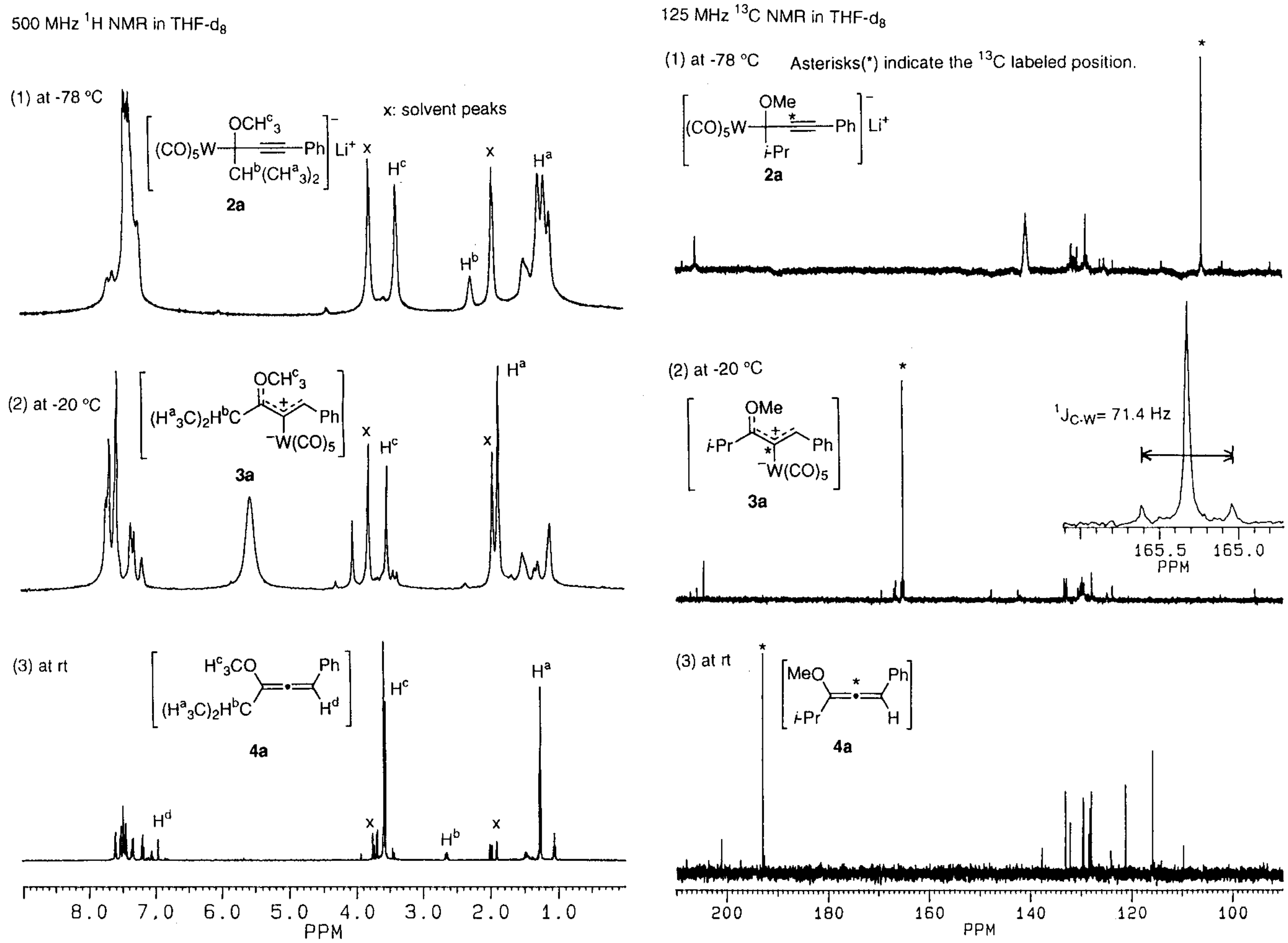


Figure 1. Variable-temperature ^{1}H and ^{13}C NMR studies of the protonation reaction of the anionic propargyltungsten species.

carried out by employing ^{13}C-labeled phenylacetylene-2-^{13}C (20% abundance). For addition intermediate **2a** a strong peak was observed at 106.1 ppm, corresponding to the signal of the asterisked acetylenic carbon. When CD_3OH was added and the temperature was raised to −50 °C, this peak gradually disappeared and another strong peak at 165.3 ppm started to grow. Importantly, this new signal has a set of satellite peaks due to coupling with tungsten-183 (natural abundance 14.3%) with a coupling constant of 71.4 Hz ($^1J_{C-W}$). The size of this coupling indicates that the labeled carbon is directly connected to tungsten via a single bond.[4] This peak persisted until the mixture was warmed to room temperature, and at room temperature, another new strong peak appeared at 193.0 ppm, corresponding to the central carbon of the allenyl ether **4a** (Figure 1).

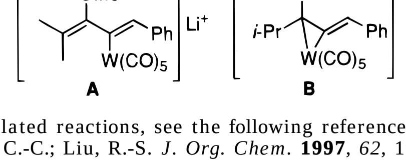
These observations strongly suggest that protonation occurs with 1,2-migration of tungsten to generate the vinylmetal intermediate **3a**,[5] which is stable up to 0 °C, and that elimination of pentacarbonyltungsten occurs slowly at room temperature to give the decomplexed allenyl ether **4a** (Scheme 2). Thus, the anionic propargyltungsten species has been shown to behave in a similar manner to the neutral ones.

We next investigated the iodine oxidation of these intermediates[6] (Scheme 3). In the first place, the addition intermediate **2a** (R = *i*-Pr, R′ = Ph) derived from (phenylethynyl)lithium and isopropylcarbene complex **1a** was directly treated with 2 mol equiv of iodine at −78 °C in the presence of triethylamine, followed by the addition of methanol (method A). Workup of the reaction mixture at room temperature gave the vinyl ether **7a** ($R^1 = R^2$ = Me, R′ = Ph) in 72% yield. This compound was probably produced by direct oxidation of the carbon−tungsten bond of **2a** to give the unstable iodo−methoxy intermediate **5a**, which eliminates hydrogen iodide to give the vinyl ether **7a**. On the other hand, when the addition intermediate **2a** was first treated with a large excess of methanol at −78 °C,[7] followed by oxidation with iodine (2 mol equiv) at −78

---

[4] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981.

[5] Although it is certain there is direct σ bonding between tungsten and the labeled carbon, we have not yet ruled out several other possibilities such as **A** and **B** for the exact structure of this intermediate.

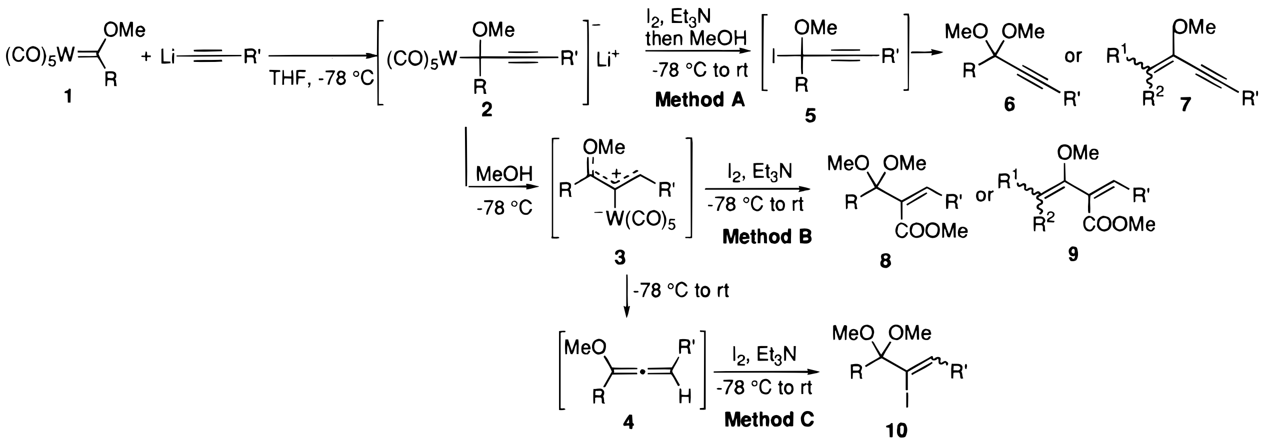


A **B**

[6] For related reactions, see the following references: (a) Shieh, S.-J.; Chen, C.-C.; Liu, R.-S. *J. Org. Chem.* **1997**, *62*, 1986. (b) 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. See also ref 2b.

[7] For the simplicity of the reaction procedure, addition of a large excess of MeOH at −78 °C was employed instead of adding 10 mol equiv of MeOH and raising the temperature to −50 °C. Protonation occurs completely under these conditions.

Scheme 3



°C to room temperature (method B), the dienyl ester **9a**, which contains an ester group on the carbon corresponding to the β-position of the original propargylmetal intermediate, was obtained in 85% yield with high geometrical purity (Z:E = >95:5). Formation of ester **9a** also suggests the intermediate formed on protonation has a structure such as **3a**. Furthermore, when the iodine oxidation was carried out after the protonated mixture had been warmed to room temperature (method C), the iodide **10a**, which was produced by the direct iodination of the decomplexed allenyl ether **4a**, was obtained in 86% yield as a mixture of geometrical isomers. In each of these three experiments, the product was obtained selectively without formation of the other two possible products. The results for the reactions of several alkynyllithiums and carbene complexes are summarized in Table 1. By appropriate choice of reaction conditions, the three types of synthetically useful products can be prepared selectively in good yield.

In conclusion, we have shown that the anionic propargyltungsten species prepared by the addition reaction of alkynyllithiums to Fischer-type carbene complexes are protonated with 1,2-migration of pentacarbonyltungsten to give vinyltungsten species which are stable up to room temperature. Furthermore, iodine oxidation of the reaction intermediates gives one of several types of oxidized products depending on the procedure used.

Acknowledgment. We are grateful to Professor Koichi Narasaka (the University of Tokyo) for helpful discussions and encouragement during this work. We also thank Professor Michio Murata (the University of Tokyo) for discussions on the interpretation of the NMR spectra. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from the Ministry of Education, Science, Sports and Culture, Government of Japan.

Table 1. Iodine Oxidation of the Addition Intermediates and their Protonated Species[a]

		yield/%		
R	R′	method A (**6** or **7**)	method B (**8** or **9**)	method C (**10**)
i-Pr	Ph	72 (**7**, $R^1 = R^2 = Me$)	85 (**9**)[b,c]	86[d,e]
i-Pr	*n*-Hex	68 (**7**, $R^1 = R^2 = Me$)	74 (**9**)[b,c]	74[f,g]
n-Bu	Ph	66[h] (**7**, $R^1 = n$-Pr, $R^2 = H$)	44 (**8**),[b] 22 (**9**)[i]	52[d,j]
Ph	*n*-Hex	95 (**6**)	86 (**8**)[b]	94[f,g]
Ph	Ph	85 (**6**)	84 (**8**)[b]	96[d,j]
Ph	CH_2CH_2OTBS	90 (**6**)	78 (**8**)[b]	93[f,g]

[a] Carbene complex:alkynyllithium:I_2 = 1:2:2. [b] (Z) isomer was obtained in ≥95:5 ratio. [c] Less than 5% yield of acetal ester **8** was also obtained. [d] A 5 equiv amount of I_2 employed. [e] Obtained as a 6:1 mixture of geometrical isomers. A small amount of dienyl iodide was also obtained. [f] One isomer was obtained in ≥95:5 ratio. Its geometry was not determined. [g] The reaction was quenched with 10% aqueous $Na_2S_2O_3$ solution at −78 °C. [h] Obtained as a mixture of geometrical isomers. [i] One isomer was obtained in ≥95:5 ratio. The geometry of its vinyl ether part was not determined. [j] Obtained as a 4:1 mixture of geometrical isomers.

Supporting Information Available: Text giving experimental procedures and spectral data for compounds **6**−**10** (8 pages). Ordering information is given on any current masthead page.

OM970835R