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Reactions of Iodinated Vinylidene Complexes Generated from 1-Iodo-1-alkynes and $W(CO)_5(thf)$

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In this contribution, we report the first example of the generation of iodinated vinylidene complexes of pentacarbonyltungsten (0) by the reaction of 1-iodo-1-alkynes with $W(CO)_5(thf)$, and the use of these complexes in two types of synthetically useful reactions, that is, the 6π-electrocyclization of *o*-(iodoethynyl)styrenes and endo-selective cyclization of ω-iodoacetylenic silyl enol ethers.

Recently transition-metal vinylidene complexes have become the center of great interest in organic and organometallic chemistry, due, not only to their facile generation from terminal alkynes, but also to their unique reactivities.[1] Whereas several synthetically useful reactions utilizing the vinylidene complexes generated from terminal alkynes have been developed over the past decade,[2] reactions of vinylidene complexes derived from alkynes possessing a labile substituent at the terminus involving 1,2-migration of that substituent have hardly been studied.[3−5]

We have previously reported several synthetic reactions using vinylidene complexes of group 6 metals derived from terminal alkynes, that is, the $W(CO)_5(thf)$-catalyzed endo-selective cyclization of ω-acetylenic silyl enol ethers,[6] and the 6π-electrocyclization of *o*-ethynylstyrenes[7] and *o*-ethynylphenyl ketones.[8] However, it is not possible, by these procedures, to introduce a substituent onto the olefinic part derived from the terminal alkyne. The development of a method allowing us to manipulate this position effectively is highly desirable. For this purpose, we decided to examine the possibility of generating iodinated vinylidene complexes from 1-iodo-1-alkynes using $W(CO)_5(thf)$, expecting that cyclizations similar to those described above could be achieved along with introduction of an iodine atom into the olefinic part of the products. To our knowledge, only one example has been reported for the preparation of iodinated vinylidene complexes from 1-iodo-1-alkynes using $CpMn(CO)_2(thf)$, and no synthetic utility has been reported for such complexes.[5a]

First we examined 6π-electrocyclization of *o*-(iodoethynyl)styrenes[2h,7] using a stoichiometric amount of $W(CO)_5(thf)$. When 1-(iodoethynyl)-2-(1-methylethenyl)benzene **1** was treated with 1.0 M amount of preformed $W(CO)_5(thf)$ at room temperature, it was completely consumed within 4 h and 1-iodo-4-methylnaphthalene **2** was obtained in 95% yield. The position of the iodine atom is confirmed by the presence of two doublets at $\delta = 7.02$ and 7.96, corresponding to the H_a and H_b protons, respectively.[9] Furthermore, this reaction could be carried out successfully even with only a catalytic amount (as little as 0.1 M amount) of $W(CO)_5(thf)$ to give the same product in good yield. The reaction is thought to proceed as follows: treatment of **1** with $W(CO)_5(thf)$ would give an alkyne-$W(CO)_5$ π-complex, which gradually isomerizes to the iodinated vinylidene intermediate **A** via 1,2-migration of the iodo group; then 6π-electrocyclization occurs forming the carbene intermediate **B**, which affords the iodo-substituted naphthalene by 1,2-hydrogen migration with regeneration of $W(CO)_5(thf)$ (Scheme 1).[9,10]

Scheme 1

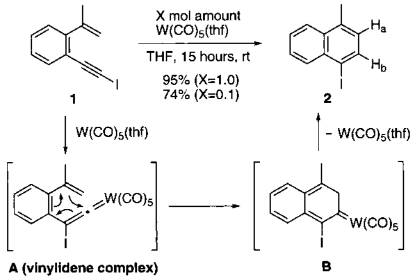
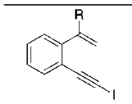
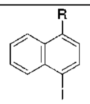
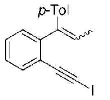
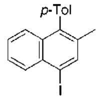
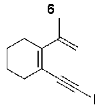
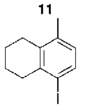


Table 1. Synthesis of Iodo-Substituted Naphthalene Derivatives

substrate	product	yield(%) Amount of $W(CO)_5(thf)$ 1.0 molar	 0.1–0.2 molar
			
3 R=*p*-Tol	**8**	93	81[a)]
4 R=OTBS	**9**	83	81[b)]
5 R=CO_2Me	**10**	84	26[b)]
			
6	**11**	42	32[b)]
			
7	**12**	67	34[b)]

[a] 0.1 M amount of $W(CO)_5(thf)$ was used. [b] 0.2 M amount of $W(CO)_5(thf)$ was used.

The scope of the reaction is summarized in Table 1. Not only iodo-substituted aromatic enynes **3**−**6** but also the nonaromatic dienyne derivative **7** were cyclized to afford the corresponding iodo-substituted naphthalene and benzene derivatives **8**−**12**. Use of a stoichiometric amount of $W(CO)_5(thf)$ generally gives the product in good yield, while the yield of the catalytic reaction varies depending on the structure and the substituents of the substrate. In particular, the difference in reactivity between α-siloxy derivative **4** and α-methoxycarbonyl derivative **5** suggests that this cyclization proceeds smoothly when the electron density at the β-position of the olefin is high.[11]

We next studied intramolecular nucleophilic attack of a silyl enol ether onto the iodinated vinylidene complex.[6] When an ω-iodoacetylenic silyl enol ether **13** was treated with a 1.0 M amount of $W(CO)_5(thf)$ in the presence of 3.0 M amounts of H_2O, the reaction again proceeded smoothly at room temperature to give an iodo-substituted cyclopentene derivative **14** in 65% yield. The position of iodine atom, confirmed by an NOE experiment, supports the hypothesis that this reaction also proceeds through the iodinated vinylidene complex **D**. The carbene carbon of the complex is expected to be highly electrophilic, and thus nucleophilic attack of the silyl enol ether occurs here to give the vinylmetallic species **E**, which is protonated by H_2O to give the corresponding iodo-substituted β,γ-unsaturated ketone **14** (Scheme 2). Reactions of

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Scheme 2

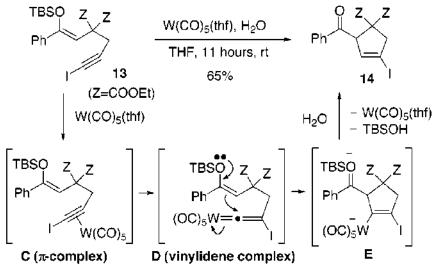
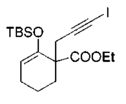
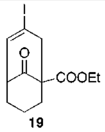
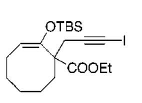
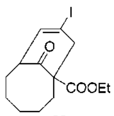
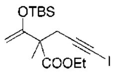
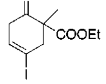
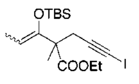
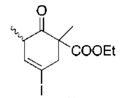
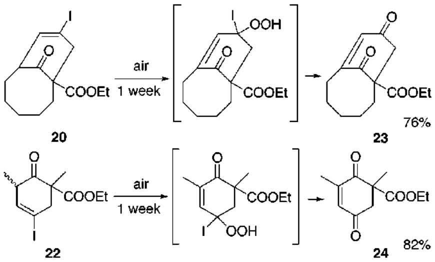


Table 2. Cyclization of ω-Iodoacetylenic Silyl Enol Ethers Using a Stoichiometric Amount of $W(CO)_5(thf)$

substrates	product	yield (%)
 **15**	 **19**	70
 **16**	 **20**	73
 **17**	 **21**	46
 **18**[a)]	 **22**[b)]	64

[a] **18** was a 3:2 mixture of *E* and *Z* isomers. [b] **22** was a 1:2 mixture of *syn* and *anti* isomers.

Scheme 3



some representative substrates are summarized in Table 2. In every case, the reaction proceeds readily at room temperature to give the iodo-substituted β,γ-unsaturated ketone, the endo-cyclized product, in good yield without formation of the alternative iodine positional isomer.[12,13] Although one would expect that the reaction should proceed with only a catalytic amount of $W(CO)_5(thf)$, in fact these conditions gave only a poor yield of the product.[14]

We also found that these cyclized products were gradually oxidized by air to provide α,β-unsaturated diketones in good yield. For example, when the bicyclic compound **20** was kept in an open vessel without solvent for 1 week at room temperature, the diketone derivative **23** was obtained in 76% yield. Under similar conditions the monocyclic compound **22** was also transformed to the corresponding product **24** in 82% yield. We assume that this reaction proceeds through allylic oxidation by molecular oxygen to give an α,β-unsaturated γ-peroxy ketone as the initial product, which is converted to the enedione.[15,16]

In conclusion, we have succeeded in generating iodinated tungsten vinylidene complexes from 1-iodo-1-alkynes, and have employed these complexes in two types of synthetically useful reaction. The iodine is retained in the products of these reactions, making them very versatile substrates for further coupling reactions. Further studies to expand the synthetic utility of iodinated vinylidene complexes are in progress in our laboratory.

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Supporting Information Available: Preparative methods and spectral and analytical data of compounds **1**−**33** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For a review on vinylidene complexes, see: (a) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.
(2) For recent synthetic use of vinylidene complexes, see: (a) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990. (b) McDonald, F. E.; Reddy, K. S.; Díaz, Y. *J. Am. Chem. Soc.* **2000**, *122*, 4304. (c) Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **1999**, *121*, 11680. (d) McDonald, F. E. *Chem. Eur. J.* **1999**, *5*, 3103. (e) Tokunaga, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 2867. (f) Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1997**, 507. (g) Ohe, K.; Kojima, M.; Yonehara, K.; Uemura, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1823. (h) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (i) Trost, B. M. *Chem. Ber.* **1996**, *129*, 1313. (j) Wang, Y.; Finn, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 8045.
(3) For examples of migration of a trialkylsilyl group, see: (a) Katayama, H.; Onitsuka, K.; Ozawa, F. *Organometallics* **1996**, *15*, 4642. (b) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35. (c) Connelly, N. G.; Geiger, W. E.; Lagunas, M. C.; Metz, B.; Rieger, A. L.; Rieger, P. H.; Shaw, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 12202. (d) Sakurai, H.; Fujii, T.; Sakamoto, K.; *Chem. Lett.* **1992**, 339. (e) Werner, H.; Schneider, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 700.
(4) For example of migration of alkylthio group, see: Miller, D. C.; Angelici, R. J. *Organometallics* **1991**, *10*, 79.
(5) For example of migration of the iodo group, see: (a) Löwe, C.; Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1989**, *371*, 311. For iodinated dinuclear vinylidene complexes, see: (b) Bruce, M. I. Koutsantonis, G. A.; Liddell, M. J.; Nicholson, B. K. *J. Organomet. Chem.* **1987**, *320*, 217. (c) Horváth, I. T.; Pályi, G.; Markó, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1054.
(6) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928.
(7) Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344.
(8) (a) Iwasawa, N.; Shido, M.; Maeyama, K.; Kusama, H *J. Am. Chem. Soc.* **2000**, *122*, 10226. See also: (b) Ohe, K.; Miki, K.; Yokoi, T.; Nishino, F.; Uemura, S. *Organometallics* **2000**, *19*, 5525.
(9) The signals corresponding to H_a and H_b were confirmed by the following deuterium experiment. When **1** deuterated at both positions of the alkene terminus was treated with $W(CO)_5(thf)$, the two doublets at $\delta = 7.02$ and 7.96 in the ^1H NMR spectra of the product **2** completely disappeared. This result also supports that 1,2-hydrogen migration occurs from the carbene intermediate **B** to give the product.
(10) We monitored the reaction of **1** with $W(CO)_5(thf)$-d_8 by NMR in THF-d_8. During the course of the reaction, only the starting material and the cyclized product were observed and none of the possible intermediates could be detected.
(11) The reaction time necessary for consumption of the starting material under the stoichiometric conditions was 1 h for **4** and 2 h for **5**. The reaction of **5** with 0.2 M amount of $W(CO)_5(thf)$ gave a substantial amount of polymerization products judging from the presence of broadened peaks in the ^1H NMR spectrum of the crude product.
(12) On the basis of deuterium exchange experiments we have previously proposed that for the similar reaction of terminal alkynes the cyclization takes place through both π-alkyne complexes (like **C**) and vinylidene complexes (like **D**).[6] In contrast, it is noted that this reaction for 1-iodo-1-alkynes occurs through the vinylidene complexes alone.
(13) For other recent examples of nucleophilic endo-selective cyclization onto alkynes, see: (a) Kim, K.; Okamoto, S.; Sato, F. *Org. Lett.* **2001**, *3*, 67. (b) Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 4081. (c) Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5339.
(14) Under the catalytic conditions, complex mixtures of products including the product starting material hydrolysis were obtained.
(15) Crabtree, R. H.; Habib, A. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 7, Chapter 1.1.
(16) It is noteworthy that the iodo-substituted products are easily oxidized by molecular oxygen, as the corresponding hydrogen-substituted products are air-stable for a longer period of time.

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