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Novel Synthesis of Pentacarbonylbenzopyranylidenetungsten(0) Complexes and Their Diels−Alder Reaction with Electron-Rich Alkenes

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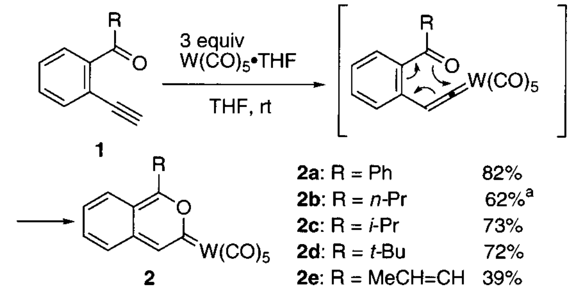
It is known that terminal alkynes and carbonyl complexes of low valent group 6 metals such as $M(CO)_5$·L (M = Cr, Mo, W; L = THF, Et_3N, etc.) are in equilibrium with their vinylidene complexes.[1] Although these complexes are expected to have unique characteristics, their use in synthetic reactions has been quite limited.[2,3] We previously reported the highly efficient $W(CO)_5$·THF-catalyzed electrocyclization of aromatic enynes via vinylidene intermediates.[4,5] This led us to expect that novel benzopyranylidene complexes[6,7] could be obtained from *o*-ethynylphenyl ketones by the dienone-electrocyclization[8,9] of the corresponding vinylidene intermediates. In this paper we describe the realization of this approach, and its application to the synthesis of substituted naphthalenes through a Diels−Alder reaction with electron-rich alkenes.

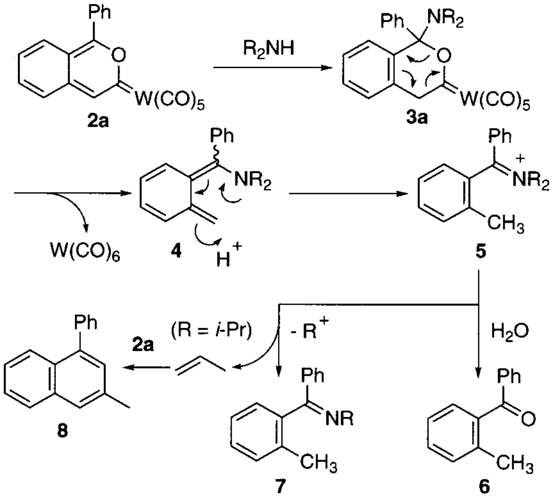
When *o*-ethynylbenzophenone **1a** (R = Ph) was treated with 1.5 M amounts of preformed $W(CO)_5$·THF at room temperature, a dark blue color gradually appeared. After the mixture had been stirred for 3 days, the crude product was purified by silica gel chromatography to give a dark-blue, air-stable, crystalline solid. The presence of a typical carbene carbon in the ^{13}C NMR spectra (δ = 230.9 ppm) and the elemental analysis both supported the conclusion that the expected benzopyranylidene complex **2a** had actually been produced by this procedure (75% yield). The yield of **2a** was further improved to 82% by carrying out the reaction using 3 M amounts of $W(CO)_5$·THF at room temperature for 1 day.

Scheme 1



[a] 5 M amounts of $W(CO)_5$·THF were employed.

Scheme 2



Various substituted benzopyranylidene complexes were obtained by this procedure as summarized in Scheme 1. Not only the benzophenone derivative **1a** but also alkyl phenyl ketone derivatives **1b**−**d** gave the corresponding complexes in good yield. Furthermore, a propenyl derivative **1e** gave the complex **2e** in moderate yield. However, when the *o*-ethynylbenzaldehyde **1f** (R = H) was employed, only unidentified polymerized products were obtained. Direct observation of the reaction mixture by ^1H NMR revealed that some of the desired complex **2f** was formed at first, but that it decomposed completely within 1 day.

We next examined the reactivity of these complexes. When **2a** was treated with Et_2NH,[10] the complex was consumed instantaneously at 0 °C, and *o*-methylbenzophenone **6** was isolated in 63% yield. Formation of **6** can be explained as follows: First, Et_2NH adds in a 1,6-manner to give aminal **3a** (R = Et). Then elimination of $W(CO)_6$ occurs to give enamine **4**, which is hydrolyzed to give **6**, via iminium salt **5** (Scheme 2). Unexpectedly, when the same reaction was carried out using *i*-Pr_2NH, imine **7** (R = *i*-Pr) and 3-methyl-1-phenylnaphthalene **8** were isolated in 9% and 14% yield, respectively, along with *o*-methylben-

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(1) (a) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739. (b) Szymanska-Buzar, T.; Downs, A. J.; Greene, T. M.; Marshall, A. S. *J. Organomet. Chem.* **1995**, *495*, 163.

(2) For the synthetic use of vinylidene intermediates containing group 6 metals, see: McDonald, F. E. *Chem. Eur. J.* **1999**, *5*, 3103 and references therein.

(3) 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, G. A. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(4) Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344. See also: Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928.

(5) For the first example of the transition-metal catalyzed electrocyclization of dienynes, see: Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319.

(6) Synthesis of an isomeric benzo[*e*]pyranylidene complex was reported using the aldol-type reaction of a methyl carbene complex with salicylaldehyde; however, synthesis of benzo[*d*]pyranylidene complexes of group 6 metals has not been reported before. Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537. See also: Licandro, E.; Maiorana, S.; Papagni, A.; Zanotti, G. A.; Cariati, F.; Bruni, S.; Moret, M.; Chiesi V. A. *Inorg. Chim. Acta* **1994**, *220*, 233.

(7) Several methods have been reported for the synthesis of pyranylidene complexes. All of them employ carbene complexes as precursors. Aumann, R.; Meyer, A. G.; Fröhlich, R. *J. Am. Chem. Soc.* **1996**, *118*, 10853. References are cited therein.

(8) For a general review, see: Okamura, W. H.; de Lera, A. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5, pp 699−750.

(9) Professor Berke and co-workers have mentioned in one of their papers the possibility of the formation of a benzopyranylidene complex by electrocyclization of vinylidene intermediate which is produced by the dimerization of propiolate on reaction with chromium carbonyl complex. However, they have proposed this possibility based only on the observation that the color of the solution of this vinylidene complex changed depending on the polarity of the solvent, and they neither detected nor isolated the pyranylidene complex at all. See: Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.* **1981**, *36b*, 929.

(10) Aumann et al. have reported that aminolysis of the 2*H*-pyran-2-ylidenetungsten complex affords amino-1-tungsta-1,3,5-hexatrienes having different structures depending on the reaction temperature, and the type of amine involved. See: Aumann, R.; Roths, K.; Jasper, B.; Fröhlich, R. *Organometallics* **1996**, *15*, 1257. See also: Yu, Z.; Aumann, R.; Fröhlich, R.; Roths, K.; Hecht, J. *J. Organomet. Chem.* **1997**, *541*, 187.

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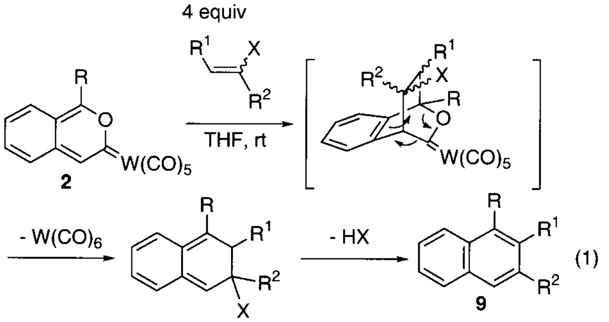
Table 1. Reaction of Benzopyranylidene Complexes with Electron-Rich Olefins



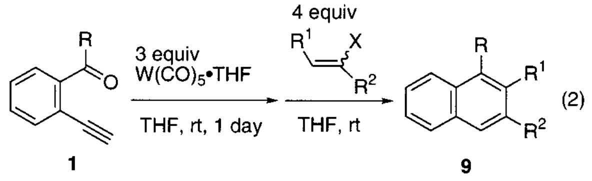
R	R^1, R^2, X	reaction time	yield (%)
Ph	$R^1 = R^2 = H$, X = O-*n*-Bu	10 h	95[a] (**9a**)
Ph	$R^1 = H$, $R^2 = X = OEt$	15 min	74[b] (**9b**)
Ph	$R^1 = R^2 = -(CH_2)_3-$, X = morpholine	instantaneous	79 (**9c**)
n-Pr	$R^1 = R^2 = H$, X = O-*n*-Bu	1 h	79 (**9d**)
n-Pr	$R^1 = R^2 = -(CH_2)_3-$, X = morpholine	instantaneous	73 (**9e**)
i-Pr	$R^1 = R^2 = H$, X = O-*n*-Bu	2.5 h	81 (**9f**)
t-Bu	$R^1 = R^2 = H$, X = O-*n*-Bu	overnight	88 (**9g**)

[a] A catalytic amount of *p*-toluenesulfonic acid monohydrate was added. [b] A catalytic amount of TMSCl was added.

zophenone **6** in 48% yield. Formation of **7** and **8** suggests that elimination of propene from iminium salt **5** occurs and that the propene formed reacts with the complex **2a** to give the Diels–Alder product, which undergoes elimination of $W(CO)_6$ followed by air-oxidation to give naphthalene **8** (see eq 1).[11]

From this result the reactivity of **2a** as a diene in the Diels–Alder reaction is expected to be high, and so we next tried to develop a method for the synthesis of substituted naphthalene derivatives by the reaction of various dienophiles with the benzopyranylidene complexes **2**.[12] When **2a** (R=Ph) was treated with 4 equiv of butyl vinyl ether ($R^1 = R^2 = H$, X = O-*n*-Bu) at room temperature in THF, the reaction was complete within 10 h giving 1-phenylnaphthalene **9a** in 95% yield (eq 1). In Table 1 is summarized the preparation of naphthalenes variously substituted at the 1-, 2-, and 3-positions by the reaction of various benzopyranylidene complexes **2** and typical electron-rich alkenes. All the reactions proceeded smoothly without the necessity of employing a large excess of the dienophiles,[12] and in particular, the reaction with an enamine proceeded instantaneously to give a 1,2,3-trisubstituted naphthalene in good yield.

Table 2. Synthesis of Various Naphthalene Derivatives



R	R^1, R^2, X	yield (%)
Ph	$R^1 = R^2 = H$, X = O-*n*-Bu	84[a] (**9a**)
Ph	$R^1 = H$, $R^2 = X = OEt$	58[b] (**9b**)
Ph	$R^1 = R^2 = -(CH_2)_3-$, X = morpholine	64 (**9c**)
i-Pr	$R^1 = R^2 = H$, X = O-*n*-Bu	66[a] (**9f**)
i-Pr	$R^1 = H$, $R^2 = X = OEt$	54 (**9h**)
t-Bu	$R^1 = R^2 = H$, X = O-*n*-Bu	65 (**9g**)
t-Bu	$R^1 = H$, $R^2 = X = OEt$	62 (**9i**)

[a] A catalytic amount of *p*-toluenesulfonic acid monohydrate was added. [b] This reaction was carried out at 0 °C.

This naphthalene synthesis could be carried out without isolating the intermediate complexes. Thus, on treatment of the *o*-ethynylphenyl ketone derivatives **1** with $W(CO)_5$•THF for 1 day followed by addition of a dienophile, we could obtain various substituted naphthalene derivatives in good overall yield without the necessity of isolating the intermediate complexes (eq 2, Table 2).

In summary, we have developed a novel method for the synthesis of benzopyranylidene complexes from *o*-ethynylphenyl ketones by electrocyclization of the vinylidene intermediates, and have applied this method to the synthesis of substituted naphthalenes by the Diels–Alder reaction with electron-rich alkenes. We are currently studying this naphthalene synthesis with a catalytic amount of $W(CO)_6$.

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Supporting Information Available: Preparative methods and spectral and analytical data of compounds **1**, **2**, and **6**–**9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] When we examined the reaction of 1-pentene with the benzopyranylidene complex **2a** in THF, the corresponding Diels–Alder product, 1-phenyl-3-propylnaphthalene, was obtained in 19% yield. It is also possible that an enamine, generated during the reaction by abstraction of an isopropyl methine proton by ortho quinodimethane intermediate **4**, is the reactive species, although we have not detected the expected amine ({(*o*-methylphenyl)methyl}-isopropylamine) in the crude product.

[12] Wulff et al. have reported that electron-rich olefins react with pyranylidene complexes to give dihydrobenzene derivatives. However, their reactivity is not very high, the dienophiles are usually employed as solvent, and it takes a long time for completion of the reaction. Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. Aumann et al. have also reported the same type of reactions using a stoichimetric amount of enamines as dienophiles. Aumann, R.; Meyer, A. G.; Fröhlich, R. *J. Am. Chem. Soc.* **1996**, *118*, 10853.