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Generation and Reaction of Tungsten-Containing Carbonyl Ylides: [3 + 2]-Cycloaddition Reaction with Electron-Rich Alkenes

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Abstract: Novel tungsten-containing carbonyl ylides **7**, generated by the reaction of the *o*-alkynylphenyl carbonyl derivatives **1** with a catalytic amount of $W(CO)_5$(thf), reacted with alkenes to give polycyclic compounds **5** through [3 + 2]-cycloaddition reaction followed by intramolecular C−H insertion of the produced nonstabilized carbene complex intermediates **8**. In the presence of triethylsilane, these tungsten-containing carbene intermediates **8** were smoothly trapped intermolecularly by triethylsilane to give silicon-containing cycloadducts **17** with regeneration of the $W(CO)_5$ species. By this procedure, the scope of alkenes employable for this reaction was clarified. The presence of the tungsten-containing carbonyl ylide **7c** was confirmed by direct observation of the mixture of *o*-ethynylphenyl ketone **1c** and $W(CO)_5$(thf-d_8). Careful analysis of the intermediate by 2D NMR, along with the observation of the direct coupling with tungsten-183 employing the ^{13}C-labeled substrate, confirmed the structure of the ylide **7c**. Examination using (*E*)- or (*Z*)- vinyl ether revealed that the [3 + 2]-cycloaddition reaction proceeded in a concerted manner and that the facial selectivity of the reaction differed considerably depending on the presence or absence of triethylsilane. These results clarified the reversible nature of this [3 + 2]-cycloaddition reaction.

Introduction

Transition-metal-catalyzed electrophilic activation of alkynes toward intramolecular addition of heteronucleophiles has attracted much attention as a useful method for the preparation of heterocyclic compounds.[1] In particular, construction of heteroaromatic compounds by cyclization of *o*-alkynylphenyl derivatives has emerged as a highly useful method for the preparation of compounds such as indoles,[2] isoquinolines,[3] benzofurans,[2g,4] isocoumarins, [2g,5] etc. Most extensively studied is the formation of an indole nucleus by the reaction of *o*-alkynylaniline derivatives through 5-*endo* cyclization. A variety of transition-metal catalysts such as palladium,[2a−e,3,4,5c] copper,[2e,f] silver,[5a] gold,[2a] mercury,[2g,5b] and so on have been employed for this purpose and applied for the synthesis of several natural products.[2f,3a,4b]

In these reactions, it is supposed that vinyl transition-metal intermediates **I** and **II** are generated by the nucleophilic addition of heteronucleophiles toward the transition-metal-activated alkyne moiety (Scheme 1). However, the produced vinylmetallic intermediates have been simply protonated in most cases and have rarely been employed for further carbon−carbon bond formation. One exception is the palladium-catalyzed reaction originally reported by Utimoto[2a] and developed extensively by Cacchi and co-workers,[2b,c] where cyclization−coupling reaction of *o*-alkynylaniline derivatives with aryl halides occurs through the electrophilic activation of the alkyne moiety by the arylpalladium(II) species. By this procedure, a substituent could be introduced on the 3-position of the indole nucleus. In recent reports, similar tandem cyclization−Heck reactions to prepare 4-substituted isoquinolines from *o*-alkynylbenzaldimines have been reported by Larock and co-workers.[3c] In these reactions, the produced vinylpalladium species behaves as a vinylmetallic species; that is, Heck-type coupling reaction with alkenes occurs at the position α to the metal.

As a heteronucleophile, the amino group of aniline derivatives has most frequently been employed along with the imino nitrogen of benzaldimine derivatives. On the contrary, the hydroxy or alkoxy group of phenol or benzyl alcohol derivatives[6] has been studied less commonly, and the use of the

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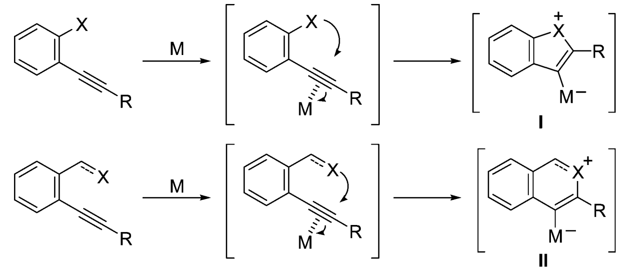
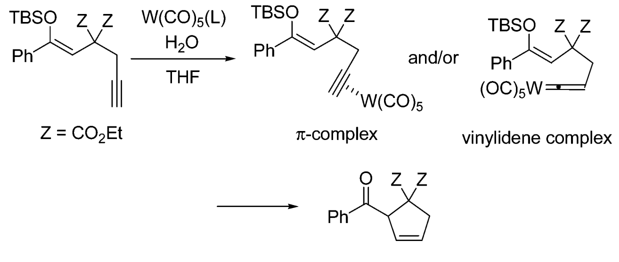
10.1021/ja044194k CCC: $30.25

Scheme 1



Scheme 2

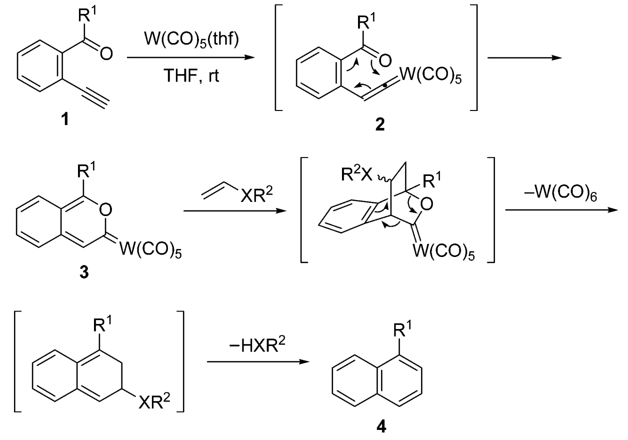


carbonyl oxygen of aryl aldehydes or aryl ketones has rarely been studied. Yamamoto reported one of these few examples, say, the cyclization of *o*-alkynylbenzaldehydes to 1-alkoxy-1*H*-isochromenes catalyzed by $Pd(OAc)_2$, which behaved both as a Lewis acid and as a transition metal,[7] and also developed a synthesis of substituted naphthalene derivatives through Lewis acid-catalyzed benzannulation between *o*-alkynylphenyl carbonyl derivatives and alkynes.[8] As a related reaction, iodine-promoted cyclization of *o*-alkynylphenyl carbonyl derivatives has recently been reported to give 1*H*-isochromenes.[9]

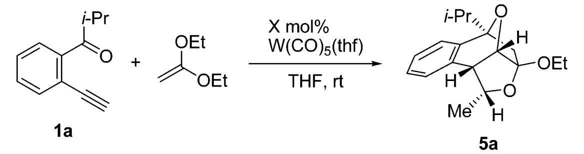
We have recently been developing synthetic reactions utilizing the electrophilic nature of pentacarbonyltungsten ($W(CO)_5$) species for the effective activation of alkynes through the formation of an alkyne−*π*-complex or its isomerized vinylidene complex (Scheme 2).[10] For example, *endo*-selective cyclization of 6-siloxy-5-en-1-ynes or 5-siloxy-5-en-1-ynes and solvent-dependent *exo*- or *endo*-selective cyclization of 7-siloxy-6-en-1-ynes have been developed utilizing this electrophilic property.

We also reported that benzopyranylidene complexes **3** can be prepared by the treatment of *o*-ethynylphenyl ketone derivatives **1** with $W(CO)_5(thf)$ through the electrocyclization of vinylidene intermediates **2** (Scheme 3).[11,12] These complexes undergo a Diels−Alder reaction with electron-rich alkenes such as vinyl ethers, ketene acetals, and enamines to give substituted naphthalenes **4** in good yield. To carry out these two reactions by a one-pot procedure, we examined the same complexation reaction in the presence of a ketene acetal, which led us to the discovery of the novel reaction pathways described below.[13]

Scheme 3



Scheme 4



100 mol% 73% yield[a]
20 mol% 76%,[a] 86%[b] yield
10 mol% 75% yield[b]

[a] 4 equiv. of 1,1-diethoxyethene was used.
[b] 3 equiv. of 1,1-diethoxyethene was used.

Results and Discussion

Generation and Reaction of Tungsten-Containing Carbonyl Ylides and Their Tandem [3 + 2]-Cycloaddition−Carbene Insertion, Leading to Novel Polycyclic Compounds. As mentioned in the Introduction, we examined the complexation reaction of an *o*-ethynylphenyl carbonyl compound in the presence of a ketene acetal to carry out both the formation of the benzopyranylidene complex and the successive Diels−Alder reaction by a one-pot procedure. When *o*-ethynylphenyl isopropyl ketone (**1a**) was treated with a stoichiometric amount of $W(CO)_5(thf)$ in the presence of 4 equiv of 1,1-diethoxyethene, the starting material was consumed within 2 h at room temperature. Surprisingly, purification of the crude product revealed that the expected 3-ethoxy-1-isopropylnaphthalene, the product of the Diels−Alder reaction between benzopyranylidene complex **3** and 1,1-diethoxyethene, had not been formed at all, but that a novel compound, **5a**, had been obtained in 73% yield as a single stereoisomer (Scheme 4).[13] Furthermore, the same product was obtained in nearly the same yield even with 10

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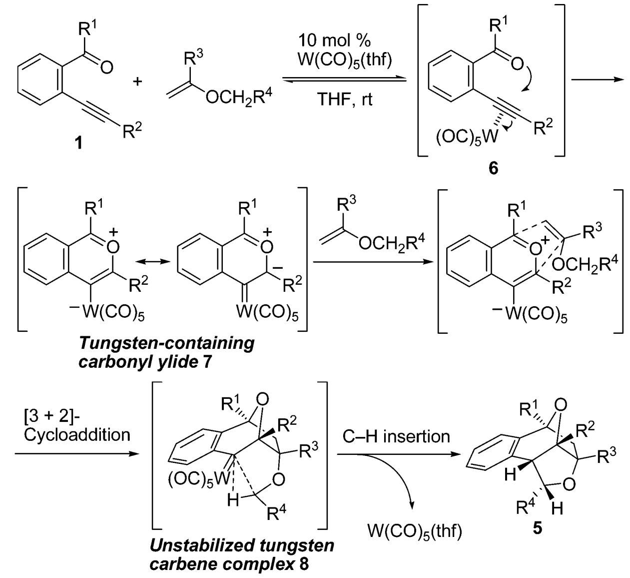
Scheme 5



mol % $W(CO)_5(thf)$ by carrying out the reaction in the presence of a smaller amount (3 equiv) of 1,1-diethoxyethene. The structure, including the relative stereochemistry, of this compound was confirmed to be as shown in Scheme 4 by X-ray analysis.[14]

The mechanism of this reaction is considered to be the following (Scheme 5). The alkyne moiety of *o*-ethynylphenyl ketone **1** is activated by $W(CO)_5$ electrophilically through π-complex formation.[15] The 6-*endo*-mode of the nucleophilic attack of the carbonyl oxygen onto the activated alkyne moiety generates a zwitterionic intermediate, **7**,[16–18] which readily undergoes [3 + 2]-cycloaddition with the electron-rich alkene to give an unstabilized tungsten carbene complex, **8**. Finally, the tungsten carbene moiety thus generated inserts into a carbon−hydrogen bond of the neighboring ethoxy group[19] to give the product **5** with regeneration of the $W(CO)_5$ species. The noteworthy feature of this reaction is that the alkenyltungsten species, produced by the addition of the carbonyl oxygen onto the tungsten-activated alkyne moiety, reacts with electrophiles at the β-position of the metal, generating the nonstabilized carbene complex, which further undergoes typical carbene reaction such as C−H bond insertion. Thus, the zwitterionic intermediate **7** could be regarded as a tungsten-containing carbonyl ylide, a novel bifunctional metal-containing reactive species, and behaves both as a carbonyl ylide and as a carbene complex to realize construction of a polycyclic carbon skeleton in a single operation.

The scope of this reaction was examined employing several *o*-(1-alkynyl)phenyl ketone derivatives and electron-rich alkenes (Table 1). Not only ketene acetal but also *n*-butyl vinyl ether can be employed as an electron-rich alkene component to give the corresponding polycyclic products in good yield even with 10 mol % $W(CO)_5(thf)$. Several kinds of aryl ketones including an aryl aldehyde are suitable for this reaction. Furthermore, an aryl aldehyde derivative, **1e**, containing an internal alkyne moiety also reacts smoothly with the vinyl ether (entry 8).[20] In most cases, a single diastereomer is obtained, whose relative stereochemistry is assigned to be the same as that of **5a** on the basis of the similarity of the coupling constants in its ^{1}H NMR spectrum.

Interestingly, when *o*-ethynylphenyl methyl ketone (**1b**) (R^1 = Me) was treated with $W(CO)_5(thf)$ in the presence of 5 equiv of water, 1,2-bis(acetyl)benzene (**13b**) was isolated in about 50% yield. Direct observation of the reaction mixture in THF-d_8 clearly showed the formation of a methyleneisobenzofuran derivative, **12b**, at room temperature. This compound is produced by the *exo*-mode of attack of the carbonyl oxygen[21] onto the $W(CO)_5-\pi$-complexed alkyne to give **11b**, followed by deprotonation from the methyl group and protonation of the tungsten−carbon bond (Scheme 6).

Furthermore, Ohe, Uemura, and their co-workers succeeded in isolating complexes **15** which were generated by reaction of cyclohexene derivative **14** with $M(CO)_5(L)$ (M = Cr, W) in THF (Scheme 7).[11d]

To account for these phenomena, we propose the following overall picture of the dynamic equilibria involved in this reaction, which can be partially controlled by the order of addition of the reagents (Scheme 8). The reaction of *o*-ethynylphenyl ketones with $W(CO)_5(thf)$ can proceed through the following three pathways: (i) *exo*-attack of the carbonyl oxygen on the π-complexed alkyne to give **11**, which might be in equilibrium with its tautomer **16**, (ii) *endo*-attack of the carbonyl oxygen on the π-complexed alkyne to give carbonyl ylide **7**, and (iii) 1,2-hydrogen shift to give vinylidene complex **2**. We currently suppose that reactions i and ii are faster than reaction iii, but that pathways i and ii are under rapid equilibrium. Thus, in the presence of a reagent capable of trapping intermediate **11** or **7** such as water or alkenes, the reaction proceeds through either pathway i or pathway ii to give the corresponding product **12** (path i) or tungsten−carbene

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(14) See the Supporting Information.

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(20) The same reaction of **1d** with ketene acetal did not give the corresponding cycloadduct, but aldol-type products **9** and **10** were produced in 85% yield.

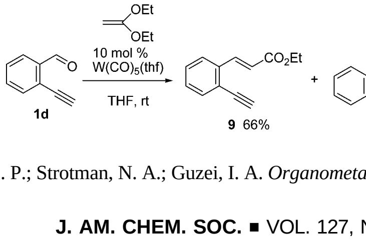

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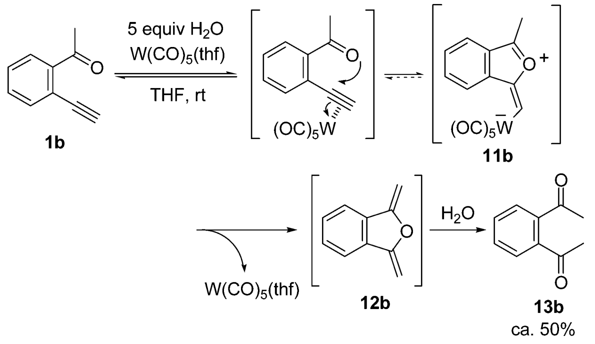
Table 1. Reaction of Various *o*-(1-Alkynyl)phenyl Ketones with Electron-Rich Alkenes[a]

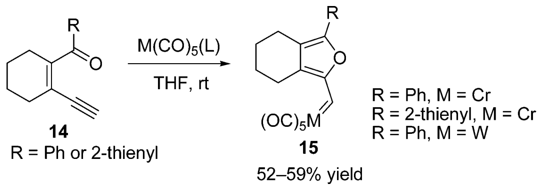
entry	R^1	R^2		R^3	R^4		time	yield/%
1	*i*-Pr	H	**1a**	OC_2H_5	CH_3	**5a**	23 h	75
2	*i*-Pr	H	**1a**	H	*n*-C_3H_7	**5b**	1 week	50
3	Me	H	**1b**	OC_2H_5	CH_3	**5c**	4 days	84
4	Me	H	**1b**	H	*n*-C_3H_7	**5d**	2 days	74
5	*n*-Pr	H	**1c**	OC_2H_5	CH_3	**5e**	2 days	81
6	*n*-Pr	H	**1c**	H	*n*-C_3H_7	**5f**	8 h	77
7[b]	H	H	**1d**	H	*n*-C_3H_7	**5g**	4 h	94
8	H	Me	**1e**	H	*n*-C_3H_7	**5h**	16 h	69

[a] 10 equiv of *n*-butyl vinyl ether and 3 equiv of 1,1-diethoxyethene were used. [b] Including an about 5% yield of an isomeric product concerning the substituent R^4.

Scheme 6



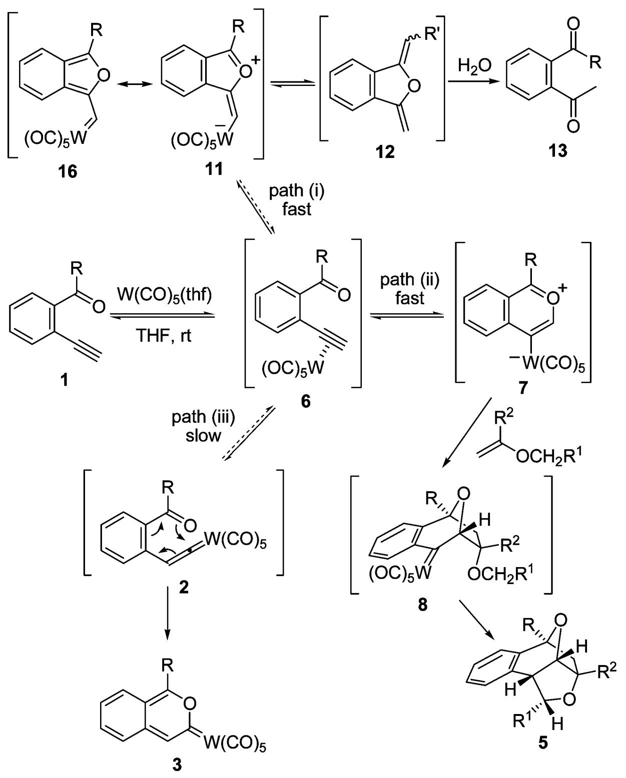
Scheme 7



intermediate **8** (path ii). However, in the absence of such trapping reagents, an equilibrium exists among **11**, **7**, and the π-complex **6**, and formation of vinylidene complex **2** occurs from the π-complex **6** as a relatively slower process, which gives a benzopyranylidene complex, **3**, through an irreversible unimolecular electrocyclization. It should be noted that in this *o*-ethynylphenyl ketone−$W(CO)_5(L)$ system exist three different reaction pathways, which are under rapid equilibrium through the π-complex, and that these pathways could be controlled with appropriate choice of the reaction parameters to give three different types of carbon frameworks.

Investigation with Various Alkenes: Reaction in the Presence of Silanes as Trapping Agents of Tungsten−Carbene Complex Intermediates. Since it had become clear that the reactions of several *o*-(1-alkynyl)phenyl ketone derivatives with a ketene acetal or a vinyl ether proceeded smoothly, we further continued our study to extend the scope of the reaction using various alkenes. Since all alkenes do not have a suitable insertable carbon−hydrogen bond and since carbene intermediate **8** is not stable, we needed to develop a method to trap intermediate **8** to allow the study of the reactivity with different alkenes. It is well-known that metal carbenoids or free carbenes can readily insert into a silicon−hydrogen bond of silanes.[22] Therefore, we decided to examine a reaction in the presence of 10 equiv of triethylsilane under the same conditions to capture the intermediates **8** intermolecularly. Thus, a mixture of *o*-ethynylbenzaldehyde (**1d**) and *n*-butyl vinyl ether was treated with 10 mol % $W(CO)_5$(thf) in the presence of triethylsilane in THF at room temperature, and the reaction was found to proceed as expected, giving the desired silicon-containing compound **17a** in 78% yield with a small amount of polycyclic compound **5g** (17% yield) (Scheme 9). The formation of this silicon-containing product **17a** clearly proved the existence of the tungsten−carbene intermediate **8d**. This major product **17a** was obtained as a single stereoisomer, the

Scheme 8



Scheme 9

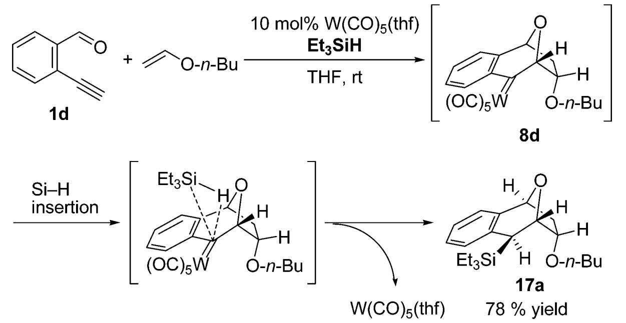


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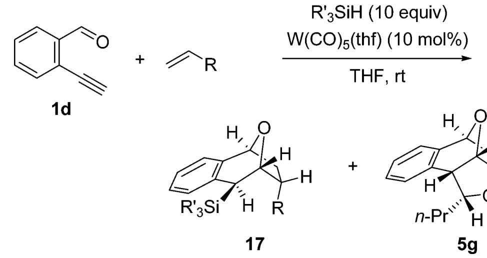
Table 2. Reaction of **1d** with Various Alkenes in the Presence of Silanes[a]



entry	R	R′$_3$SiH	yield/% 17	5g	ratio **17**:**5g**
1	O-*n*-Bu	Et$_3$SiH	78, **17a**	17	82:18
2		*t*-BuMe$_2$SiH	40, **17b**	53	43:57
3		Ph$_3$SiH	4, **17c**	84	5:95
4		*i*-Pr$_3$SiH	<3 **17d**	93	<3:>97
5		EtMe$_2$SiH	85, **17e**	6	93:7
6	O-*t*-Bu	Et$_3$SiH	74, **17f**		
7	OSiMe$_3$	Et$_3$SiH	70, **17g**		
8	CH$_2$SiMe$_3$	Et$_3$SiH	59, **17h**		
9	Ph	Et$_3$SiH	44, **17i**		

[a] Except **17i**, all products were obtained as a single stereoisomer, the structure of which was confirmed to be as shown above by the measurement of NOE. In the case of entry 9, a diastereomer concerning the substituent R was produced in a ratio of 98:2.

structure of which was confirmed to be as shown in Scheme 9 by measurement of the nuclear Overhauser effect (NOE).[14]

Although the tungsten-containing carbene intermediate was found to be easily trapped intermolecularly by triethylsilane, intramolecular insertion of the carbene part into the neighboring carbon−hydrogen bond slightly competes with the insertion into a silicon−hydrogen bond (Scheme 9). Thus, we further examined reactions employing various silanes to improve the efficiency of the carbene-trapping reaction.

The influence of the substituents on silicon for one chosen peculiar reaction is summarized in Table 2 (entries 1−5). The use of *tert*-butyldimethylsilane gave **17b** in lower yield than triethylsilane (93%, ratio **17b**:**5g** = 43:57, entry 2). Furthermore, the reactions in the presence of triphenylsilane or triisopropylsilane gave the corresponding silylated product **17c** or **17d** in very low yield, and intramolecular insertion of the carbene moiety into the neighboring C−H bond occurred predominantly (entries 3 and 4). As the larger size of the substituent of silane strongly hindered Si−H insertion of the carbene intermediate, we expected that a smaller silane would effectively trap the carbene intermediate. Indeed, by the use of ethyldimethylsilane, the ratio of the products **17e** and **5g** was improved to 93:7 (entry 5). All cycloadducts **17a**−**e** were obtained as a single stereoisomer, the structure of which was confirmed to be the same as that of compound **17a** by the similarity of the coupling pattern of their ^{1}H NMR spectra.

Since an efficient method for capturing the nonstabilized carbene intermediate had been established, we next investigated the reaction with various alkenes for [3 + 2]-cycloaddition with the tungsten-containing carbonyl ylide **7** by carrying out the reaction in the presence of triethylsilane (Table 2, entries 6−9). By this procedure, we can examine the reaction with alkenes containing no reactive C−H bond for intramolecular carbene insertion.[23] For example, when *tert*-butyl vinyl ether was employed in this reaction, the corresponding silicon-containing compound **17f** was obtained in high yield as a single stereoisomer (entry 6). This reaction could also be carried out with silyl enol ether and allylsilane to give the corresponding silylated product in good yield (entries 7 and 8). Furthermore, even styrene could be employed successfully (entry 9); however, 1-octene and methyl acrylate could not be reacted. Thus, by carrying out the reaction in the presence of silane, the scope of the alkenes employable for this [3 + 2]-cycloaddition was expanded to a great extent, and not only electron-rich alkenes such as ketene acetal and vinyl ethers but even styrene could be employed for this reaction.

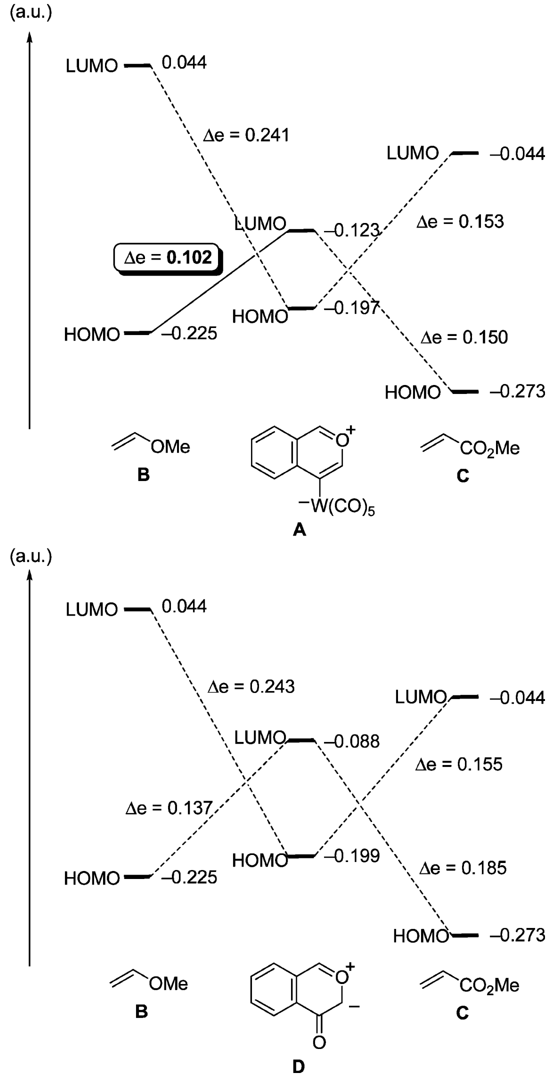


Figure 1. Energy level of the HOMO and LUMO of carbonyl ylides **A** and **D** (calculated by B3LYP/6-31G*).

To gain insight into the reactivity of the tungsten-containing carbonyl ylide, we searched the energy levels of the HOMO and LUMO of the tungsten-containing carbonyl ylide **A** and of a simple carbonyl ylide, **D**, by ab initio calculations as shown in Figure 1.[24] The LUMO of the ylide **A** is considerably lower

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[23] It is well-known that C−H insertion is facilitated by the electron donation from α-oxygen. For the electronic factor of carbene insertion into C−H bonds, see: (a) Seyferth, D.; Mai, V. A.; Gordon, M. E. *J. Org. Chem.* **1970**, *35*, 1993. (b) Adams, J.; Poupart, M.-A.; Grenier, L.; Schaller, C.; Ouimet, N.; Frenette, R. *Tetrahedron Lett.* **1989**, *30*, 1749.

[24] The calculations were performed with Gaussian 03 using the B3LYP hybrid density functional method. The lanl2dz basis set was used for the W atom, and the 6-31G* basis sets were used for the other atoms.

than that of ylide **D**, which suggests that a strong interaction between the LUMO of ylide **A** and the HOMO of an electron-rich alkene is more favorable than with ylide **D**. The normal carbonyl ylides react in general preferentially with electron-deficient alkenes such as methyl acrylate,[17] and there are few examples for the reaction with electron-rich alkenes.[25] On the contrary, the reactivity of the tungsten-containing ylide **A** is reversed and readily reacts with electron-rich alkenes. These results are in good agreement with the above calculation, and such a unique property of the metal-containing ylide **A** is thought to be derived from the strong electron-withdrawing nature of the tungsten carbonyl moiety.

Observation of the Tungsten-Containing Carbonyl Ylide. In this reaction, the tungsten-containing carbonyl ylide **7** was thought to be the key intermediate generated by treatment of $W(CO)_5(thf)$ with *o*-(1-alkynyl)phenyl carbonyl compound **1** (Scheme 5). Commonly, carbonyl ylides are unstable and highly reactive species, and thus, it was expected to be difficult to isolate the ylide **7**.[26] Therefore, we first tried to detect such species directly by NMR measurements. For that matter, 1-(2-ethynylphenyl)butan-1-one (**1c**) was treated with 1.7 equiv of $W(CO)_5(thf\text{-}d_8)$ in THF-d_8, and changes in the ^1H NMR spectra at 300 K with time were observed *in the absence of vinyl ether* (Figure 2). At $t = 5$ min, the formation of a set of signals derived from a new species (*, compound **X**) was observed at δ 8.92, 8.67, 8.56, 8.30, and 7.88 ppm. The signal at δ 8.92 was a singlet, and the coupling pattern of the latter four signals indicated that compound **X** was an *ortho*-disubstituted aryl compound with much lower electron density than the starting ketone **1c** as deduced from the explicit lower field shift of these signals. It could be considered that the singlet at 8.92 ppm could be assigned to be the hydrogen of the terminal alkyne. Furthermore, three new signals derived from the propyl group were also observed at higher field. At $t = 1.5$ h, these signals still appear with a weak intensity, and another set of signals (▲, compound **Y**) was observed, which coincided with those of the isolated benzopyranylidene complex **3c**.[11a] Finally, at $t = 3.5$ h, the signals corresponding to compound **X** mostly disappeared and the benzopyranylidene complex **3c** became the major product.

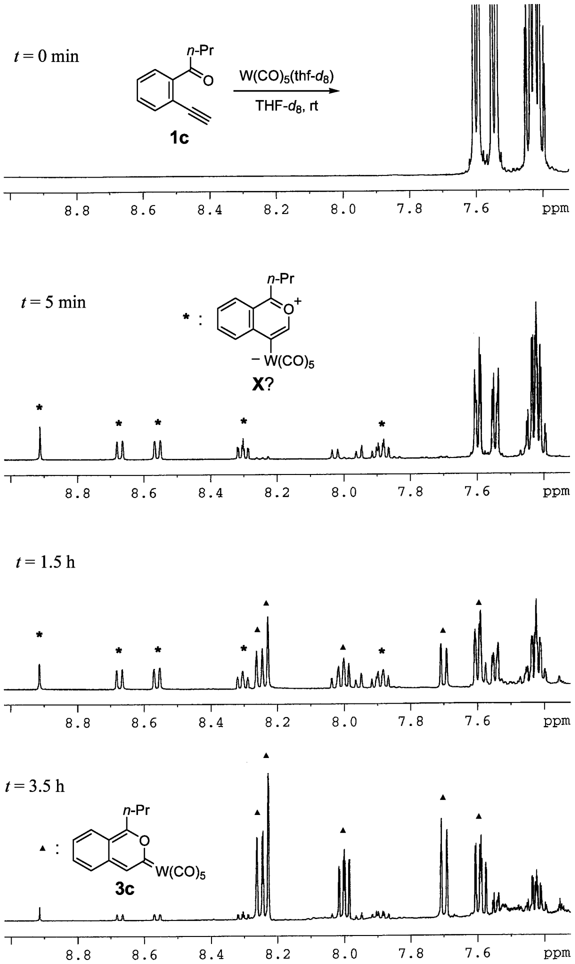

Figure 2. Change of the ^1H NMR spectra at 300 K.

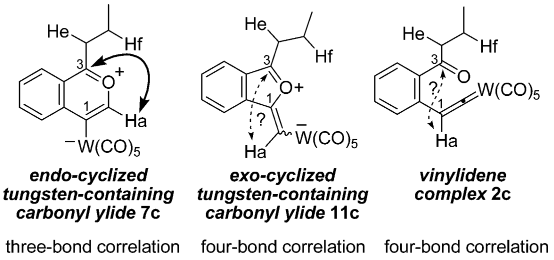

Figure 3. *endo*- and *exo*-cyclized carbonyl ylide **7c**, **11c**, and vinylidene complex **2c**.

As already mentioned, the reaction of *o*-ethynylphenyl ketones and $W(CO)_5(thf)$ in the absence of alkenes is thought to proceed through the following three pathways: (i) π-complex **6** undergoes a reversible *endo*-mode of attack of the carbonyl oxygen onto the π-complexed alkyne to give the tungsten-containing carbonyl ylide **7**, (ii) *exo*-attack of the carbonyl oxygen onto the π-complexed alkyne to give **11**, and (iii) 1,2-migration of the hydrogen of the π-complex **6** to give the vinylidene intermediate **2**, which then undergoes irreversible 6π-electrocyclization to give the pyranylidene complex **3c** (Scheme 8). Thus, at this point, intermediate **X** could be the *endo*-cyclized tungsten-containing carbonyl ylide **7c**, the *exo*-cyclized ylide **11c**, or the vinylidene complex **2c**. To obtain further information on the structure of the compound **X**, the same reaction was carried out at room temperature for 30 min and then cooled to 233 K to hinder advancement of the reaction during the measurement of the HMBC spectrum. As the ^{13}C signal at δ 184.6 ppm was found to have a correlation with H(e) and H(f) of the propyl group, this signal was assigned as C(3) derived from the carbonyl carbon. A noteworthy correlation was observed between C(3) and the singlet at δ 8.92 derived from the hydrogen of the alkyne (H(a)), which strongly suggests that this intermediate is neither the *exo*-cyclized tungsten-containing ylide **11c** nor the vinylidene complex **2c** but the *endo*-cyclized carbonyl ylide **7c** (Figure 3).

Since it was suggested that the intermediate **X** could be identified as the ylide **7c**, we next tried to confirm the presence of the direct bonding between tungsten and C(1) by carrying out the reaction employing ^{13}C-labeled **1c**[27] (Scheme 10). As

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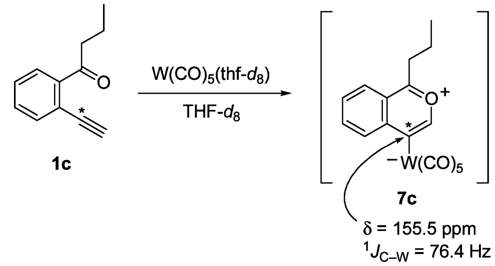
(25) (a) Savinov, S. N.; Austin, D. J. *Chem. Commun.* **1999**, 1813. (b) Kotera, M.; Ishii, K.; Tamura, O.; Sakamoto, M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 313. (c) Koyama, H.; Ball, R. G.; Berger, G. D. *Tetrahedron Lett.* **1994**, *35*, 9185.

(26) (a) Dörwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999; p 75. (b) Winter, M. J. *Comprehensive Organometallic Chemistry II*; Pergamon: New York, 1995; p 168. For isolation of carbonyl ylides, see: (c) Hamaguchi, M.; Ibata, T. *Tetrahedron Lett.* **1974**, *15*, 4475. (d) Janulis, E. P., Jr.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1983**, *105*, 5929.

Scheme 10 [a]



[a] The asterisk indicates the ^{13}C-labeled position.

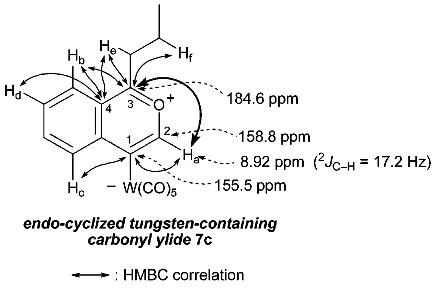
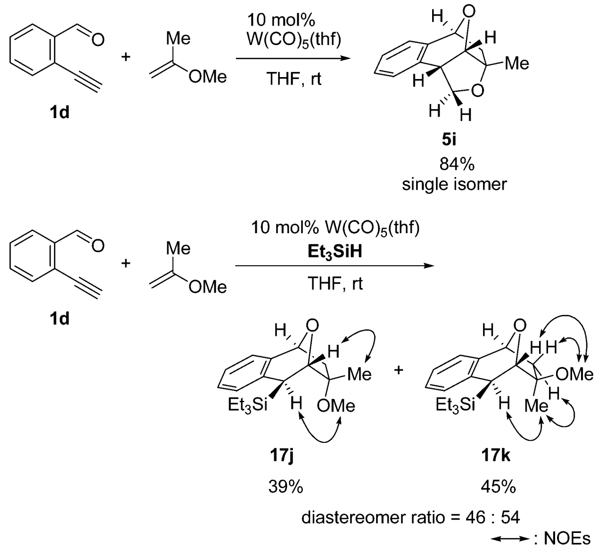


Figure 4. Selected correlations in the HMBC spectrum.

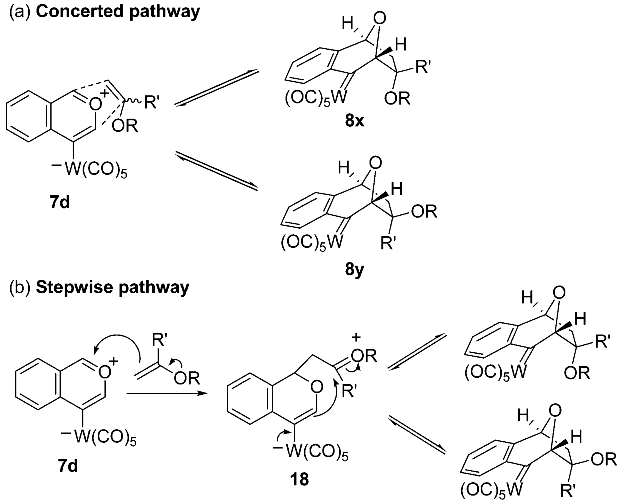
tungsten-183 (natural abundance 14.3%) has 1/2 nuclear spin while other isotopes of tungsten have no nuclear spin, a set of satellite peaks should be observed in the ^{13}C NMR spectrum at the carbon directly bonded to tungsten due to the coupling with tungsten-183.[28] Although a peak at δ 155.5 ppm was observed as a very weak signal in the case of the nonlabeled substrate, by using the ^{13}C-enriched substrate **1c** (20% ^{13}C), this peak had medium strength. In the HMBC spectrum, this carbon has a correlation with an *ortho* proton, H(c), of the benzene ring, which suggests that this carbon is surely C(1). Most importantly, this peak had a set of satellite peaks with a coupling constant of 76.4 Hz ($^{1}J_{\mathrm{C-W}}$).[29,30] This result indicates that the labeled C(1) is indeed directly connected to the tungsten. Additionally, the singlet at δ 8.92 in the ^{1}H NMR spectra showed a set of satellite peaks due to the $^{2}J_{\mathrm{C-H}}$ coupling ($^{2}J_{\mathrm{C-H}} = 17.2$ Hz) with the labeled carbon. Other correlations of compound **X** in the HMBC spectrum also agreed well with the structure of tungsten-containing carbonyl ylide **7c** (Figure 4). Thus, we have succeeded in observing directly the key reactive species, tungsten-containing carbonyl ylide **7**, which exists in a small amount during the reaction and is slowly converted to the benzopyranylidene complex **3** through the π-complex **6**, when the electron-rich alkene is not added to the mixture.

Concerted and Reversible Nature of the [3 + 2]-Cycloaddition Reaction. Since the above results clearly indicate that the tungsten-containing carbonyl ylide is indeed generated, we next studied the mechanism of [3 + 2]-cycloaddition reaction of the carbonyl ylide with alkenes. When 2-methoxypropene, a 1,1-disubstituted vinyl ether, was employed, we found an intriguing phenomenom concerning the stereoselectivity of the cycloadducts. The reaction of **1d** and 2-methoxypropene with a catalytic amount of W(CO)$_5$(thf) proceeded smoothly to afford the corresponding polycyclic compound **5i** as a single diastereoisomer in 84% yield (Scheme 11). On the other hand, the same reaction carried out in the presence of triethylsilane gave a mixture of two diastereomers, **17j** and **17k**, in nearly equal amounts in 84% yield. The stereochemistry of cycloadducts **17j** and **17k** was confirmed to be as shown in Scheme 11 by NOEs.

Scheme 11



Scheme 12



Thus, facial selectivity of these two reactions differs dramatically depending on the presence or absence of the carbene-trapping reagent, and these results clearly indicate the presence of an equilibrium in the [3 + 2]-cycloaddition reaction step. Two mechanisms may explain these phenomena, that is, (i) a concerted and reversible cycloaddition of the carbonyl ylide **7d** with the alkene (Scheme 12a) and (ii) a stepwise cycloaddition via a zwitterionic intermediate, **18**, and equilibrium existing through ring opening and reclosing of the carbene intermediates (Scheme 12b).[16b]

To discriminate between these two possibilities, we further examined the reaction with stereochemically well-defined trisubstituted vinyl ethers. The reaction of **1d** with (*E*)- or (*Z*)-2-methoxybut-2-ene in the presence of triethylsilane was carried out using a catalytic amount of W(CO)$_5$(thf) in THF at room temperature. As shown in Scheme 13, both reactions gave a mixture of two diastereomeric silylated compounds, which differ in the facial selectivity of [3 + 2]-cycloaddition. All products

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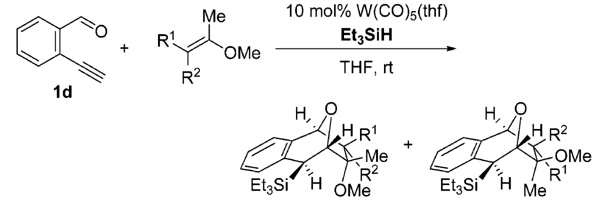
(27) For the preparation of **1c**, see the Supporting Information.

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

(29) (a) Iwasawa, N.; Ochiai, T.; Maeyama, K. *J. Org. Chem.* **1998**, *63*, 3164. (b) Iwasawa, N.; Ochiai, T.; Maeyama, K. *Organometallics* **1997**, *16*, 5137.

(30) For NMR charts, see the Supporting Information.

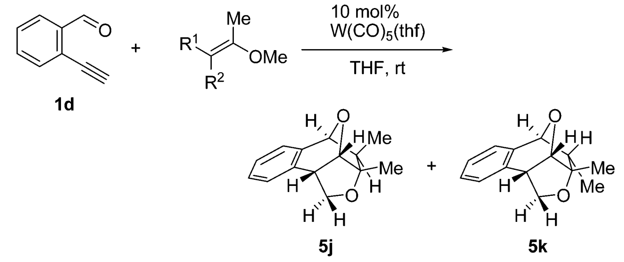
Scheme 13



(*E*)-2-methoxybut-2-ene (R^1 = Me, R^2 = H) **17l** : 71% **17m** : 8% **17l** : **17m** = 90 :10

(*Z*)-2-methoxybut-2-ene (R^1 = H, R^2 = Me) **17n** : 27% **17o** : 58% **17n** : **17o** = 32 : 68

Scheme 14



(*E*)-2-methoxybut-2-ene (R^1 = Me, R^2 = H) 94% **5j** : **5k** = **98** : 2

(*Z*)-2-methoxybut-2-ene (R^1 = H, R^2 = Me) 93% **5j** : **5k** = 17 : **83**

17l−o retained the stereochemistry of the vinyl ethers employed, which clearly suggested that the [3 + 2]-cycloaddition proceeded in a concerted manner. The stereochemistry of the cycloadducts **17l−o** was confirmed by NOEs.[14]

Next, we examined reactions in the absence of triethylsilane under similar conditions (Scheme 14). When the reaction using (*E*)-2-methoxybut-2-ene was carried out, two isomeric insertion products, **5j** and **5k**, were obtained in a ratio of 98:2, while the reaction with (*Z*)-isomer gave the same mixture in a ratio of 17:83. Thus, in these cases, the minor products did not retain the geometrical integrity of the vinyl ethers employed. Direct observation of the ^{1}H NMR spectra of both vinyl ethers in the presence of W(CO)$_5$(thf-d_8) in THF-d_8 revealed that isomerization of the geometry of the double bond hardly occurred in the presence of triethylsilane, while considerable isomerization was observed in the absence of triethylsilane, in particular, in the case of the (*Z*)-alkene. These results suggest that diastereomers **5k** (in the case of (*E*)-alkene) and **5j** (in the case of (*Z*)-alkene) were obtained from the reaction between substrate **1d** and in situ isomerized starting alkenes (in the absence of triethylsilane) through a still concerted mechanism in these cases also.

Comparison of the facial selectivity of the reactions in the presence or absence of triethylsilane clearly indicates that the selectivity differs considerably from one case to the other, and in particular, the selectivity is reversed for the reaction using the (*Z*)-alkene. Thus, there should be a rapid equilibrium at room temperature between the two cycloadducts **8x** and **8y** through the carbonyl ylide **7d** in a concerted [3 + 2]-cycloaddition−retrocycloaddition pathway (Scheme 12a). In the presence of triethylsilane, each of the two isomeric carbene intermediates was readily trapped to give diastereomeric silicon-containing cycloadducts, while in the case of the reaction without the silane, the polycyclic compound was obtained only from the isomer suitable for intramolecular C−H insertion by the equilibration of the two isomeric carbene intermediates.

It is known that [3 + 2]-cycloaddition of carbonyl ylides with alkenes is usually irreversible, and only a few specific cases were reported for the retrocycloaddition reactions.[31] Therefore, the facile equilibrium observed here is a very rare example of the retro-[3 + 2]-cycloaddition reaction of carbonyl ylide species and is the characteristic feature of the tungsten-containing carbonyl ylide.

Conclusion

In conclusion, a new type of bifunctional reactive species, tungsten-containing carbonyl ylide, is generated by the reaction of *o*-alkynylphenyl carbonyl compounds **1** with W(CO)$_5$(thf). This novel species undergoes [3 + 2]-cycloaddition reaction with electron-rich alkenes to give tungsten-containing carbene complex intermediates **8**, the carbene moiety of which inserts into a neighboring C−H bond intramolecularly to give the polycyclic compounds **5**. In the presence of triethylsilane, the same reaction provides the silicon-containing compounds **17**, intermolecular insertion products, in good yields. All these reactions proceed with a catalytic amount of W(CO)$_5$(thf) as the catalyst is regenerated at the insertion steps. The presence of the tungsten-containing carbonyl ylide **7c** is directly confirmed by NMR measurement using a ^{13}C-labeled substrate. The concerted and reversible nature of this [3 + 2]-cycloaddition reaction between tungsten-containing carbonyl ylide **7** and alkenes is disclosed by these studies. We believe the concept of the metal-containing 1,3-dipoles will find abundant application in organic chemistry and provide new opportunities to develop useful synthetic methods of various heterocyclic compounds.

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Supporting Information Available: Preparative methods and spectral and analytical data of compounds **5** and **17**, ^{13}C NMR spectra for the reaction shown in Scheme 10, and X-ray data for **5a** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA044194K

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(31) For examples, see: (a) Hamaguchi, M.; Ibata, T. *Chem. Lett.* **1975**, *4*, 499. (b) González, R.; Knight, B, W.; Wudl, F.; Semones, M. A.; Padwa, A. *J. Org. Chem.* **1994**, *59*, 7949.