Carbene Complexes

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Useful Reactions of Silylated Propargyltungsten or Propargylmolybdenum Species**

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The generation of silylated organometallic species is of high importance because of their unique reactivity, caused by the synergistic effects of the silyl group.[1] During studies into the addition reaction of Fischer-type carbene complexes of Group 6 metals,[2] we thought of generating silylated propargyltungsten or -molybdenum species[3] from the addition of an alkynyl lithium to a carbene complex in which the carbene carbon atom was substituted with a silyl group.[4]

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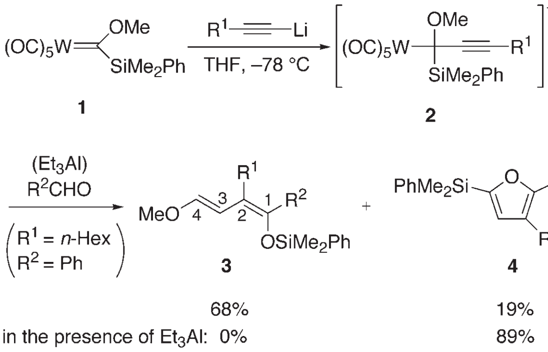
Herein, we describe the unique behavior of these silylated propargyl metal species in their reaction with electrophiles which enabled the preparation of a variety of synthetically useful compounds.

The dimethylphenylsilyl-substituted tungsten carbene complex **1** was treated with octynyllithium in THF at −78 °C (Scheme 1). The addition reaction occurred smoothly to give the silylated propargyltungsten species **2**. Further reaction with PhCHO afforded (*Z*,*E*)-1,4-dioxy-1,3-diene **3** ($R^1 = n$-Hex, $R^2 = Ph$), a useful electron-rich diene, in 68 % yield, along with a small amount (19 %) of another useful synthetic intermediate **4**. Alternatively, silylated furan derivative **4**, could be selectively obtained by carrying out the reaction in the presence of Et_3Al (Scheme 1).[5] Thus, the two types of addition product are available by selecting the reaction conditions.



Scheme 1. Reaction of silylated propargyltungsten species.

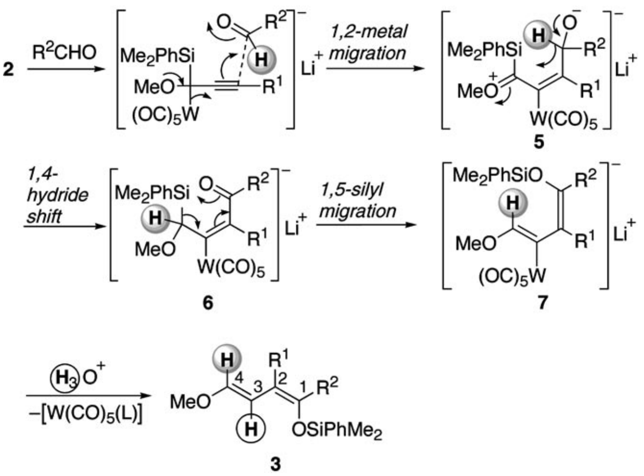
The scope of the reaction for the selective preparation of 1,4-dioxy-1,3-diene and furan derivatives is summarized in Table 1. The reaction was carried out without Et_3Al but using various combinations of aldehydes and alkyl- or aryl-substituted alkynyl lithium reagents to give the corresponding 1,4-dioxy-1,3-dienes **3** in reasonable yields (conditions A, Table 1). In particular, alkyl-substituted alkynyl lithium reagents generally gave the products in higher yields. In all cases, the geometrical isomer **3** was obtained with high selectivity (99:1 to 96:4). In contrast, the reaction in the presence of Et_3Al selectively gave the corresponding silylated furan products **4** in high yield (conditions B, Table 1).

Table 1: Scope of the reaction between **1**, alkynyl lithium reagents, and aldehydes.

Entry	R^1	R^2	Cond. A:[a] Yield **3**[c] (**4**) [%]	Cond. B:[b] Yield **4** [%]
1	*n*-Hex	Ph	68 (19)	89
2	*n*-Hex	*i*Pr	68 (16)	84
3	*n*-Hex	*c*-Hex	84 (5)	90
4	Ph	Ph	43 (45)	92
5	Ph	*i*Pr	49 (43)	85
6	$-(CH_2)_2OTBS$	*i*Pr	70 (17)	75

[a] Without Et_3Al. [b] In the presence of Et_3Al. [c] Obtained as a single geometrical isomer (>95:5). *c*-Hex = cyclohexyl, TBS = *tert*-butyldimethylsilyl.

We propose the reaction pathway shown in Scheme 2 to explain the formation of the 1,4-dioxy-1,3-dienes **3**. Reaction of the silylated propargyltungsten species **2** with aldehydes would proceed with 1,2-migration of $W(CO)_5$ to give zwitterionic addition intermediates **5**.[6] Rather than undergoing nucleophilic attack of the oxyanion on the oxonium moiety to give dihydrofuran derivatives,[2d] intermediates **5** would instead undergo an intramolecular 1,4-hydride shift[7] to give γ-silyl-α,β-unsaturated ketones **6**. These ketones would then undergo a 1,5-silyl migration[8] to give the dienyltungsten intermediates **7**.[9,10] Finally protonation of these intermediates on workup gives the 1,4-dioxy-1,3-dienes **3**. The fact that the reaction in the presence of Et_3Al gave the corresponding furans can be explained by considering the coordination of the oxyanion to Et_3Al, which prevents the 1,4-hydride shift.

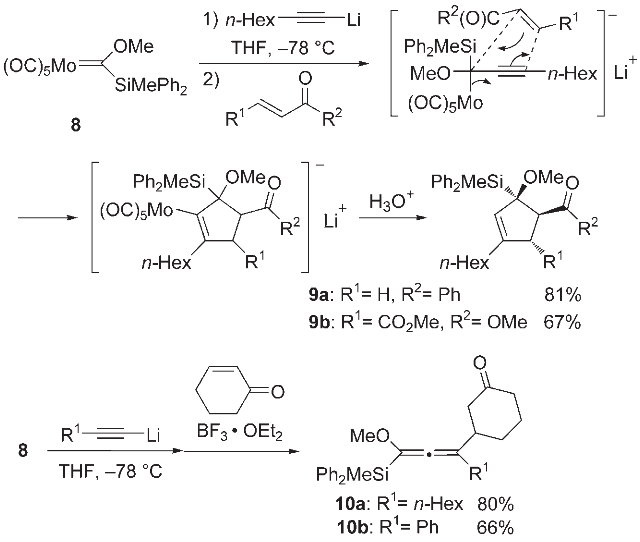


Scheme 2. Proposed mechanism for the addition reaction.

A series of deuteration experiments were carried out to confirm these suppositions. Thus, on quenching the reaction with D_2O, around 60 % of the hydrogen atoms on C3 (see Scheme 2, compound **3**) were exchanged with deuterium atoms. Furthermore, when the reaction was carried out using deuterated benzaldehyde (PhCDO), the product **3** was obtained in which nearly all the hydrogen atoms on C4 had been exchanged with deuterium atoms. Therefore, the hydrogen atom on C3 arises from protonation of the carbon–tungsten bond and the hydrogen atom on C4 is derived from the aldehyde through a 1,4-hydride shift.

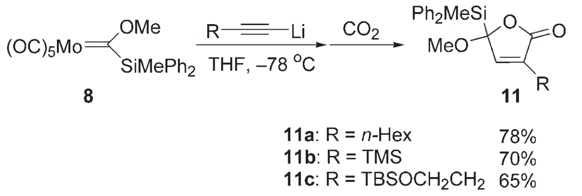
The enhanced reactivity of the silylated propargyl metal species is demonstrated by the following reaction with α,β-unsaturated carbonyl compounds. We found that neither propargyltungsten nor -molybdenum species derived from alkyl or aryl carbene complexes reacted well with α,β-unsaturated carbonyl compounds. However, the silylated propargylmolybdenum species reacted smoothly to give the corresponding [3+2] cycloaddition products **9** or 1,4-addition products **10** in good yields (Scheme 3).[11,12]

Furthermore, we investigated the reaction between the silylated propargyl metal species and CO_2. Again, the molybdenum complex **8** gave better results than the non-silylated derivatives, and after a mild acidic workup led to the



Scheme 3. Reaction with α,β-unsaturated carbonyl compounds.

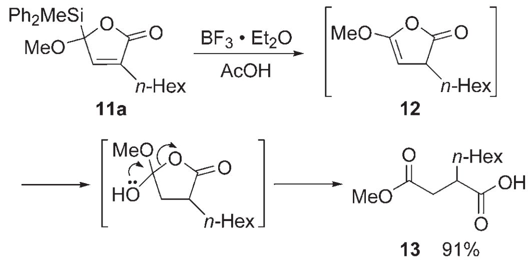
silylated methoxybutenolide products **11** in good yield (Scheme 4).



Scheme 4. Reaction with carbon dioxide. TMS = trimethylsilyl.

Finally, regioselective synthesis of succinic acid mono ester **13** was achieved by treatment of the silyl-substituted butenolide **11a** with $BF_3{\cdot}Et_2O$ in acetic acid at room temperature. Protonation of the allylsilane moiety of **11a** by acetic acid proceeded to give lactone **12**, which was then hydrolyzed to give **13** in 91% yield (Scheme 5). This method provides a concise preparation of succinic acid mono esters, which are not necessarily simple to synthesize.[13]

In conclusion, propargyltungsten or -molybdenum species with a synergic effect of a silyl substituent show enhanced and unique reactivity on reaction with electrophiles. A range of synthetically useful compounds were prepared by using these reactions.



Scheme 5. Synthesis of succinic acid mono ester.

Experimental Section

A typical procedure for the preparation of **3**: A solution of *n*-butyllithium (1.54 M, 0.24 mL, 0.37 mmol) in hexane was added dropwise to a solution of 1-octyne (62 mg, 0.55 mmol) in THF (0.5 mL) at −78 °C. After 30 minutes, a solution of the silyl carbene complex **1** (90 mg, 0.18 mmol) in THF (5 mL) was added. The red color of the carbene complex **1** changed to yellow within a few minutes. After 30 minutes, benzaldehyde (47 μL, 0.46 mmol) was added and the reaction mixture was stirred for a further 4 h at this temperature. Then pH 7 phosphate buffer (15 mL) was added and the mixture was extracted three times with EtOAc. The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 100:1) under argon to give 1-(dimethylphenylsiloxy)-2-hexyl-4-methoxy-1-phenylbuta-1,3-diene **3a** (48 mg, 0.12 mmol) in 68% yield as a bright yellow oil.

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[5] In previous reactions in which alkyl carbene complexes were employed, $BF_3{\cdot}OEt_2$ was required to promote the addition reaction with aldehydes. However, the corresponding reaction of the silylated propargyltungsten **2** proceeded smoothly without needing a Lewis acid, thus demonstrating its enhanced reactivity.

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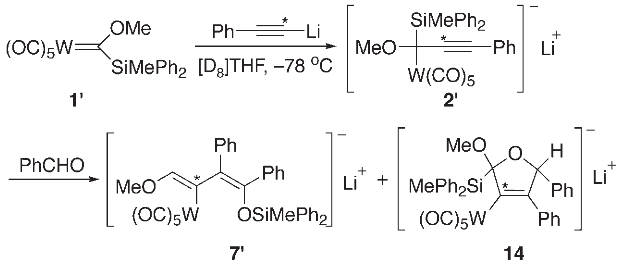
[9] A variable-temperature NMR study was carried out into the reaction of diphenylmethylsilyl-substituted propargyl metal species derived from tungsten complex **1'** and phenylacetylene labeled with ^{13}C at the terminal carbon atom. After addition of



PhCHO, formation of a dienyltungsten intermediate **7′** and a dihydrofuranyltungsten intermediate **14** were observed at −78 °C. Further details will be reported in due course.

[10] It is possible that an anionic pentacoordinate silicate intermediate is generated for species **5**, in which the formation of dihydrofuran intermediate may be suppressed (Scheme 2). We would like to thank one of the referees for suggesting this possibility.

[11] In general, propargylmolybdenum species are more reactive than propargyltungsten species. However, the tungsten silyl carbene complex is more stable than the corresponding molybdenum complex. Thus, we employed the tungsten complex in most of our studies, but for the reaction with CO_2 and electrophiles with lower activity, such as α,β-unsaturated carbonyl compounds, the use of the molybdenum complex gave better results.

[12] **9a**,**b** were obtained as single stereoisomers as shown, while **10a**,**b** were obtained as mixtures of isomers.

[13] R. Ballini, G. Bosica, A. Palmieri, M. Petrini, C. Pierantozzi, *Tetrahedron* **2003**, *59*, 7283, and references therein.