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Rhenium(I)-Catalyzed Cyclization of Silyl Enol Ethers Containing a Propargyl Carboxylate Moiety: Versatile Access to Highly Substituted Phenols

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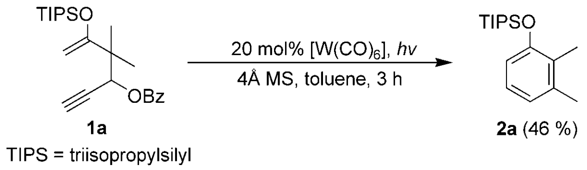
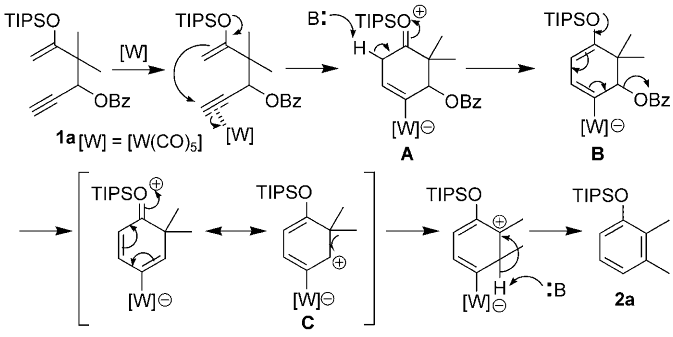
The use of propargyl carboxylates as substrates for the electrophilic activation of alkynes has been studied extensively and a variety of useful transformations have been developed utilizing intermediates generated by 1,2- or 1,3-acyloxy migration of the carboxylates.[1] As part of our ongoing research into the $[W(CO)_5(L)]$- and $[ReCl(CO)_4(L)]$-catalyzed cyclization of acetylenic silyl enol ethers through electrophilic activation of the alkyne moiety,[2] we have developed an interest in the reactions of silyl enol ethers containing a propargyl carboxylate moiety. In this case, two possibilities exist concerning the electrophilically activated alkyne moiety; these are attack of the silyl enol ether and 1,2- or 1,3-acyloxy migration[3] and further reaction pathways of the produced intermediates are another focus of our interest. In this communication, we report the regioselective preparation of highly substituted phenols by using 2-siloxy-1-en-5-ynes with an acyloxy substituent at the propargylic position.

When a silyl enol ether containing a propargyl benzoate moiety **1a** was treated with 20 mol% of $[W(CO)_6]$ in toluene in the presence of 4 Å molecular sieves (MS) under photoirradiation from a high-pressure Hg lamp, at ambient temperature the starting material was consumed within 3 h and 2,3-disubstituted phenol **2a** was obtained in 46% yield (Scheme 1). The proposed mechanism for the formation of **2a** is shown in Scheme 2. A 6-*endo* nucleophilic attack of the silyl enol ether moiety onto the alkyne, which is electrophilically activated by $[W(CO)_5]$, occurs to give the zwitterionic six-membered cyclic intermediate **A** in which the benzoate moiety remains intact.[4] This is followed by deprotonation of the silyloxonium to give cyclohexadiene derivative **B**, from which elimination of the benzoate occurs by electron donation from the silyl dienol ether moiety to give the cationic pentadienyl intermediate **C**. Finally, migration of the methyl substituent occurs along with protonation of the C–W bond to afford the final product **2a** and regenerate the catalyst. It should be noted that there are very few examples[5] of the alkyne part of the propargyl carboxylate being electrophilically activated for attack by nucleophiles without an accompanying acyloxy migration and the carboxylate moiety then utilized for further manipulation. As the unique transformation of silyl enol ether **1a** into a synthetically useful, substituted phenol was found to proceed catalytically,[6] we decided to optimize the reaction conditions.



Scheme 1. The reaction of **1a** with $[W(CO)_6]$.



Scheme 2. The proposed reaction mechanism.

Examination of the effect of other typical electrophilic metal complexes, such as Pt^{II}, Au^{I}, and Re^{I}, on the reaction revealed that, although the commonly employed Pt^{II} or Au^{I}

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catalysts did not give good results, the yield was improved by using $[Re(CO)_5Br]$[7,8] under photoirradiation (Table 1, entries 1–6).[9] As the deprotonation from the silyloxonium intermediate **A** is thought to be a crucial step, the effect of bases on this reaction was examined. Whereas addition of Et_3N completely suppressed the reaction, the yield of **2a** was improved to 84% by the addition of $NaHCO_3$ as a base (Table 1, entry 7). Furthermore, this reaction was found to proceed with only 10 mol% $[Re(CO)_5Br]$ in toluene at 110 °C without the need for photoirradiation(Table 1, entry 11).[10] With optimal conditions in hand, the generality of the reaction was examined.

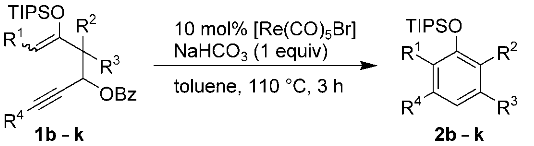
Table 1. Examination of the reaction conditions for phenol synthesis.

	Metal catalyst[a]	Additives	Conditions[b]	Yield [%] **2a**
1	$[W(CO)_6]$	4 Å MS	*hv*, RT, 3 h	46
2	$PtCl_2$	4 Å MS	110 °C, 8 h	17
3	AuCl	4 Å MS	RT, 1 d	trace
4	AuCl, AgOTf	none	RT, 1 d	3
5	$[PPh_3AuCl]$, AgOTf	none	RT, 1 d	trace
6	$[Re(CO)_5Br]$	4 Å MS	*hv*, RT, 3 h	76
7	$[Re(CO)_5Br]$	$NaHCO_3$	*hv*, RT, 3 h	84
8	$[Re(CO)_5Br]$	NEt_3	*hv*, RT, 3 h	N.R.[e]
9	$[Re(CO)_5Br]$	none	*hv*, RT, 3 h	66
10	$[Re(CO)_5Br]$[c]	$NaHCO_3$	*hv*, RT, 12 h[d]	83
11	$[Re(CO)_5Br]$[c]	$NaHCO_3$	110 °C, 3 h[d]	80

[a] 20 mol% of metal catalysts were used. [b] The substrate concentration was 0.05 M. [c] 10 mol% of metal catalysts were used. [d] The substrate concentration was 0.1 M. [e] N.R. = no reaction.

As summarized in Table 2, the catalytic reaction at 110 °C in toluene proceeded smoothly with cyclic substrates **1b**–**d** to give the corresponding phenols fused with a ring-expanded, six- or seven-membered ring in good yields. Examination of substrates containing different substituents at the tether (R^2 and R^3) revealed that selective migration is mostly achieved in this reaction. Thus, Me- and Et- or Me- and Bn-substituted (Bn = benzyl) substrates **1e** and **1f** were converted to the corresponding phenols **2e** and **2f**, respectively, in which the Et or Bn group migrated selectively, in good yield.[11] Me- and CO_2Et-substituted **1g** was also converted to the corresponding phenol with selective migration of the CO_2Et substituent. Although internal alkyne substrates required a higher temperature (150 °C in xylene) and an increased amount of rhenium catalyst (20 mol%), these reactions proceeded successfully with various substituents at the alkyne terminus, such as methyl (**1h**), phenyl (**1i**), and ethoxycarbonyl (**1j**), and the corresponding 2,3,5-trisubstituted phenols were obtained in reasonable yield. Finally, the substituted silyl enol ether **1k** was cleanly converted to the corresponding 2,3,6-trisubstituted phenol using 10 mol% $[Re(CO)_5Br]$ in toluene at 110 °C. Thus, we have succeeded in developing an efficient method for the synthesis of various types of substituted phenols by a $[Re(CO)_5Br]$-catalyzed reaction of 2-siloxy-1-en-5-ynes that have an acyloxy substituent at the propargylic position.

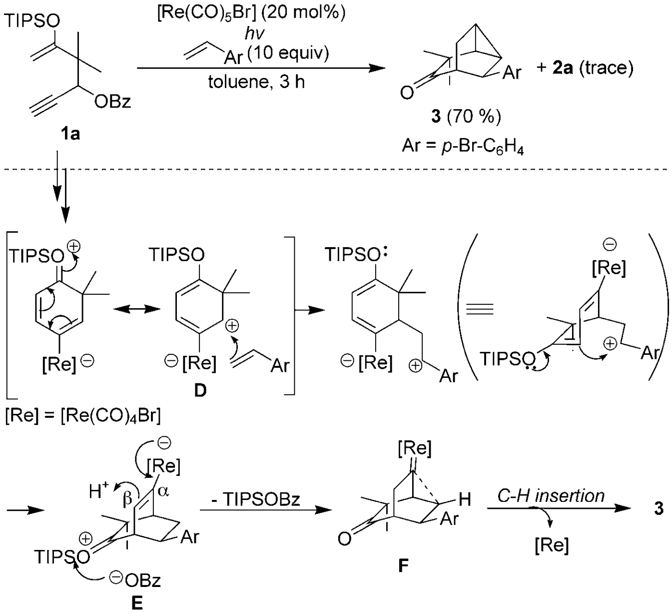
Table 2. Generality of the Re-catalyzed phenol synthesis using acyclic substrates.



Starting material	R^1	R^2	R^3	R^4	Yield [%]
1b	H	$-(CH_2)_4-$		H	90 (**2b**)
1c	H	$-(CH_2)_5-$		H	70 (**2c**)
1d	H	$-CH_2-(1,2-C_6H_4)-CH_2-$		H	88 (**2d**)
1e	H	Me	Et	H	81 (**2e**)[a]
1f[b]	H	Me	Bn	H	60 (**2f**)[c]
1g	H	Me	CO_2Et	H	74 (**2g**)
1h[d]	H	Me	Me	Me	76 (**2h**)
1i[d]	H	Me	Me	Ph	51 (**2i**)
1j[d]	H	Me	Me	CO_2Et	58 (**2j**)
1k	Me	Me	Me	H	78 (**2k**)

[a] It contained a small amount (ca. 5%) of an unidentified product, which could be Et migrated product. [b] Photoirradiation conditions by using high-pressure Hg lamp at room temperature. [c] The yield of desilylated product. [d] 20 mol% of $[Re(CO)_5Br]$ was used in xylene at 150 °C.

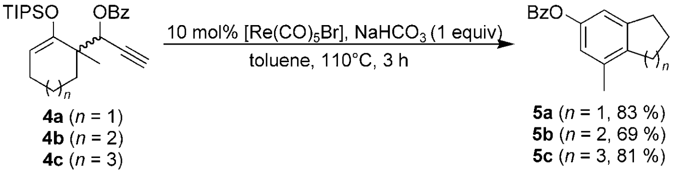
To support the proposed mechanism of the reaction, several attempts to trap the reactive intermediates were carried out. When the rhenium-catalyzed reaction was carried out in the presence of *p*-bromostyrene, a unique product (**3**) was obtained. The photochemical reaction of substrate **1a** with 20 mol% rhenium complex in the presence of *p*-bromostyrene gave cyclopropane-containing polycyclic compound **3**[12] in 70% yield.[13] This product is thought to be produced as shown in Scheme 3. Following the mechanism described in Scheme 2, the Re-containing cationic pentadienyl intermediate **D** was generated. Then *p*-bromostyrene nucleophilically



Scheme 3. The reaction of **1a** with rhenium catalysts in the presence of *p*-bromostyrene.

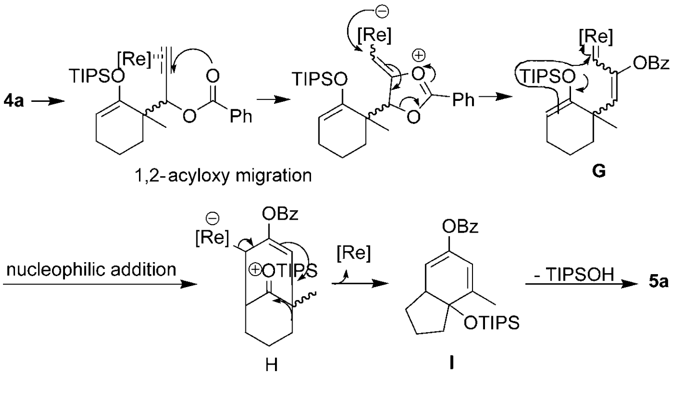
attacks the cation at the terminal position; this is followed by attack, in a formal [4+2] cycloaddition, of the silyl enol ether moiety on the benzylic cation produced, to give the zwitterionic cycloadduct **E**. Protonation of the alkenyl rhenium moiety at the β-position to the metal generates rhenium–carbene complex **F**,[14] which undergoes insertion into the neighboring C–H bond to give the final product **3** and regenerate the catalyst. This result supports the proposed mechanism of the substituted phenol synthesis (Scheme 2) and, in addition, suggests that the rhenium metal is retained in the substrate even after the generation of the cationic pentadienyl intermediate.

Next we examined the reaction using substrate **4a**, which contains a six-membered cyclic silyl enol ether moiety. In addition, it was found that treatment of **4a** under the optimized conditions gave a different type of substituted phenol **5a**, which has a fused five-membered ring, in 83 % yield (Scheme 4). Seven- and eight-membered cyclic silyl enol ethers also gave the corresponding ring-contracted fused phenols in good yield. Unfortunately, internal alkynes were not susceptible to reaction with this type of silyl enol ether.[15]



Scheme 4. The reaction of **4a–c** with $[Re(CO)_5Br]$.

The proposed mechanism for the formation of phenol **5a** is shown in Scheme 5. In this case, activation of the alkyne part of substrate **4a** occurs by rhenium-promoted 1,2-acyloxy migration of the propargyl carboxylate unit,[3] which leads to the formation of rhenium–carbene complex intermediate **G**. Then, intramolecular nucleophilic attack of the silyl enol ether on the rhenium–carbene complex occurs, which results in the formation of zwitterionic intermediate **H**. Electron donation from the allyl–rhenium moiety promotes alkyl migration to give the intermediate **I**,[16] which, finally, eliminates the silyl ether to aromatize and afford the product **5a**.[17] Thus, this reaction gives another useful method for the construction of phenols containing a fused ring by using this rhenium-catalyzed tandem reaction.



Scheme 5. The proposed reaction mechanism.

In conclusion, we have developed a rhenium-catalyzed synthesis of substituted phenols using 2-siloxy-1-en-5-ynes that have an acyloxy substituent at the propargylic position. The characteristic features of this reaction are: 1) depending on the structure of the silyl enol ether moiety, either nucleophilic addition of the silyl enol ether moiety, or 1,2-acyloxy migration occurs, 2) regioselective synthesis of substituted phenols is achieved by the selective migration of the tether substituents, and 3) a rhenium(I)–carbonyl complex, which is rarely used in organic synthesis, gives specifically good results.

Experimental Section

Example procedure for the cyclization reaction: Compound **1a** (40.0 mg, 0.1 mmol) was added to a mixture of $[Re(CO)_5Br]$ (4.0 mg, 0.01 mmol, 10 mol %) and $NaHCO_3$ (8.4 mg, 0.1 mmol) in degassed toluene (1 mL). After the mixture was heated at 110 °C for 3 h, the solvent was removed under reduced pressure to give the crude product, which was purified by preparative thin layer chromatography (5 % ethyl acetate in hexane) to give 22.2 mg of **2a** (0.08 mmol, 80 %) as a colorless oil.

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Keywords: alkynes · cycloaddition · elimination · phenols · rhenium

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[2] For the reaction of alkynes containing a silyl enol ether moiety promoted by a tungsten(0) carbonyl complex, see: a) K. Maeyama, N. Iwasawa, *J. Am. Chem. Soc.* **1998**, *120*, 1928–1929; b) N. Iwasawa, K. Maeyama, H. Kusama, *Org. Lett.* **2001**, *3*, 3871–3873; c) H. Kusama, H. Yamabe, N. Iwasawa, *Org. Lett.* **2002**, *4*, 2569–2571; d) N. Iwasawa, T. Miura, K. Kiyota, H. Kusama, K. Lee, P. H. Lee, *Org. Lett.* **2002**, *4*, 4463–4466; e) H. Kusama, Y. Onizawa, N. Iwasawa, *J. Am. Chem. Soc.* **2006**, *128*, 16500–16501; for the reaction promoted by rhenium(I) carbonyl complexes, see: f) H. Kusama, H. Yamabe, Y. Onizawa, T. Hoshino, N. Iwasawa, *Angew. Chem.* **2005**, *117*, 472–474; *Angew. Chem. Int. Ed.* **2005**, *44*, 468–470; for contributions from other groups on the reactions of alkynes containing a silyl enol ether moiety, see:g) K. Lee, P. H. Lee, *Adv. Synth. Catal.* **2007**, *349*, 2092–2096; h) B. K. Corkey, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 2764–2765; i) T. Godet, P. Belmont, *Synlett* **2008**,

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[3] For 1,2-acyloxy-migration, see: a) K. Miki, K. Ohe, S. Uemura, *J. Org. Chem.* **2003**, *68*, 8505–8513; b) K. Miki, T. Yokoi, F. Nishino, Y. Kato, Y. Washitake, K. Ohe, S. Uemura, *J. Org. Chem.* **2004**, *69*, 1557–1564; c) B. G. Pujanauski, B. A. B. Prasad, R. Sarpong, *J. Am. Chem. Soc.* **2006**, *128*, 6786–6787; d) X. Shi, D. J. Gorin, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 5802–5803; e) Y. Zou, D. Garayalde, Q. Wang, C. Nevado, A. Goeke, *Angew. Chem.* **2008**, *120*, 10264–10267; *Angew. Chem. Int. Ed.* **2008**, *47*, 10110–10113; f) X. Moreau, J.-P. Goddard, M. Bernard, G. Lemière, J. M. López-Romero, E. Mainetti, N. Marion, V. Mouriès, S. Thorimbert, L. Fensterbank, M. Malacria, *Adv. Synth. Catal.* **2008**, *350*, 43–48; g) A. Fürstner, P. Hannen, *Chem. Eur. J.* **2006**, *12*, 3006–3019; h) A. W. Sromek, A. V. Kel'in, V. Govergyan, *Angew. Chem.* **2004**, *116*, 2330–2332; *Angew. Chem. Int. Ed.* **2004**, *43*, 2280–2282; for 1,3-acyloxy migration, see: i) S. Anjum, J. Marco-Contelles, *Tetrahedron* **2005**, *61*, 4793–4803; j) K. Cariou, E. Mainetti, L. Fensterbank, M. Malacria, *Tetrahedron* **2004**, *60*, 9745–9755; k) L. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 16804–16805; l) S. Wang, L. Zhang, *Org. Lett.* **2006**, *8*, 4585–4587; m) P. Mauleón, J. L. Krinsky, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 4513–4520; n) A. S. Dudnik, T. Schwier, V. Gevorgyan, *Org. Lett.* **2008**, *10*, 1465–1468; o) T. Schwier, A. W. Sromek, D. M. L. Yap, D. Chernyak, V. Gevorgyan, *J. Am. Chem. Soc.* **2007**, *129*, 9868–9878.

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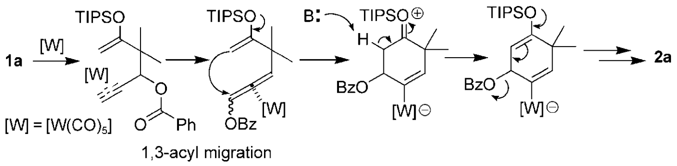

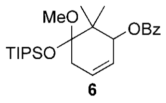

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[7] Use of $[\mathrm{Re(CO)_5Br}]$ as a Lewis acid catalyst in the Friedel–Crafts acylation was reported, see: H. Kusama, K. Narasaka, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2379–2383; therefore, in the reaction of **1a** with $[\mathrm{Re(CO)_5Br}]$, $[\mathrm{ReX(CO)_4(L)}]$ might have promoted elimination of the BzO group.

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[10] It is known that the generation of coordinatively unsaturated species $[\mathrm{ReBr(CO)_4(L)}]$ requires photoirradiation or heating to high temperatures.[8]

[11] In case of Me and Bn substituted substrate, 2,6-disubstituted phenol was also obtained in 20% yield. 2,3- and 2,6-disubstituted phenols were separated after desilylation (TBAF, THF, 0 °C). For similar migration of a Bn-group in a cyclohexadienone intermediate, see: B. Miller, *J. Am. Chem. Soc.* **1970**, *92*, 432–433.

[12] The structure of **3** was determined by X-ray crystallography. CCDC-752714 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] Compound **3** was also obtained without photoirradiation by using a catalytic amount of $[\{\mathrm{Re(CO)_3(thf)Br}\}_2]$ in toluene at room temperature for 1 day in 63% yield. Additionally, the protonated product of the cycloadduct **E** was obtained.

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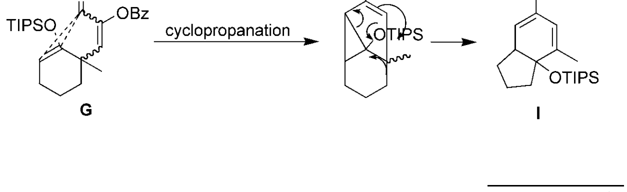
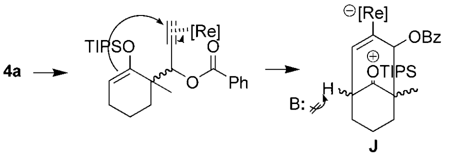
[15] If an internal alkyne substrate was employed under these reaction conditions, a complex mixture of products was obtained.

[16] Phenol **5a** could also be formed via cyclopropanation of the silyl enol ether by the rhenium carbene complex **G**, followed by alkyl migration as shown below to give the intermediate **I**:



[17] In this case, direct addition of the silyl enol ether to the electrophilically activated alkyne would give silyloxonium intermediate **J**, which cannot undergo further deprotonation. An equilibrium probably exists between the alkyne-π complex and the intermediate **J** and 1,2-acyloxy migration occurs from the π complex as another possible reaction pathway.



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