

Reaction of ynolate anions derived from silylketenes with electrophiles: a facile preparation of silyl ynol ethers and functionalized silylketenes

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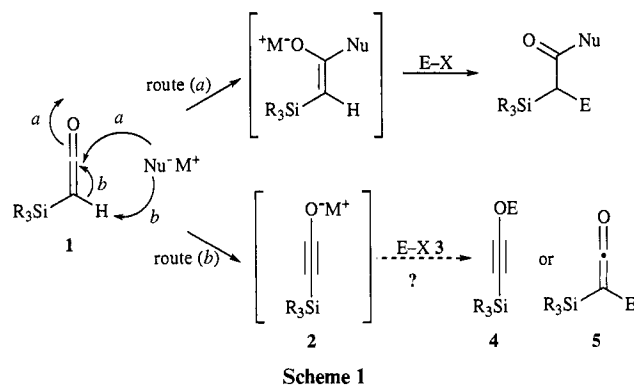
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Reaction of the ynolate anions **2a,b**, generated from the silylketenes **1a,b**, with a variety of electrophiles **3** is investigated. The reaction with bulky and/or hard silyl chlorides, such as Bu^tMe₂SiCl, Pr^t₃SiCl, (T_{hexyl})Me₂SiCl and Bu^tPh₂SiCl, exclusively gives the silyl ynol ethers **4**, while that with small or soft silyl chlorides and stannyl chlorides gives only the functionalized silylketenes **5** in modest to high yields, respectively. In the case of the reaction with small and hard Me₃SiCl, initial formation of the *O*-trimethylsilyl ynol ether **4b** and the subsequent rapid isomerization to the bis-silylketene **5a** are proposed by the trapping of **4b** as a cobalt complex **7b**.

Silylketenes **1** have attracted much attention because of their unique characteristics, such as easy handling, stability as monomers and storage for extended periods without polymerization, which are remarkable when contrasted with the parental ketene and alkylketenes.¹⁻⁴ In order to develop a useful methodology to utilize **1** as a silicon-containing C₂ synthon, we were interested in the reaction of **1** with anion nucleophiles (Nu⁻).^{1,3} In this case, two competitive reactions, addition of Nu⁻ to the carbonyl carbon of **1** to give the β-silyl enolate anion [Scheme 1, route (a)] and the proton abstraction by Nu⁻ to give the β-silyl ynolate anion **2** [route (b)] may take place. By using soft nucleophiles, we have selectively achieved the route (a) reactions and developed one-pot coupling of **1**, Nu⁻ and electrophiles (E⁺), giving silicon-containing reactive compounds.^{1,3} On the other hand, the route (b) reaction was first reported by Rathke and co-workers in the reaction of (trimethylsilyl)ketene **1a** and BuLi. The only successful reaction of **2a** was that with Me₃SiCl to give bis(trimethylsilyl)ketene as a single product.⁴ Although the ynolate anion **2** may react with electrophiles **3** at either the oxygen or the β-carbon atom, giving ynol derivatives **4** and substituted ketenes **5** respectively, the ambident nature of **2** has never been elucidated (Scheme 1).[†] Because the preparation and reaction of **2** seems to be the simplest and easiest way to prepare synthetically useful silylated ynol ethers⁶ and functionalized silylketenes⁷ and is also interesting in comparison to the well known ketone-enolate chemistry,[‡] we investigated the reaction of the ynolate anions **2a,b** with a variety of electrophiles **3**. Here we report that reaction with bulky and/or hard silyl chlorides exclusively gave the silyl ynol ethers **4**, while that with small or soft silyl chlorides and stannyl chlorides gave only the ketenes **5** in modest to high



yields, respectively. The initial formation of the *O*-trimethylsilyl ynol ether **4b** by the reaction of **2b** with small and hard Me₃SiCl and the subsequent rapid isomerization to the ketene **5a** is also proposed by the trapping of **4b** as a cobalt complex **7b**.

Results and discussion

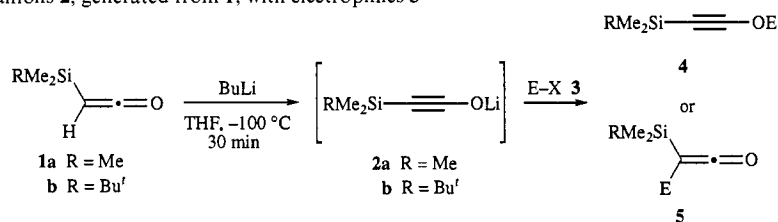
Similarly to Rathke's method,⁴ we first examined the ynolate anion formation from (*tert*-butyldimethylsilyl)ketene **1b** and its reaction with Me₃SiCl. A THF solution of **1b** was slowly added to a THF solution of BuLi at -100 °C, and the reaction mixture was stirred for 30 min. A THF solution of Me₃SiCl was added at the same temperature and the mixture was allowed to reach -70 °C over 3 h, then was quickly quenched with aqueous NaHCO₃ after dilution of the reaction mixture with hexane. IR and ¹H NMR analyses of the crude product showed the selective formation of the ketene **5a** [$\nu_{\max}(\text{CHCl}_3)$ 2078 cm⁻¹] in almost quantitative yield (entry 2, Table 1). On the other hand, similar treatment with Bu^tMe₂SiCl and rapid work-up at -50 °C provided the silyl ynol ether **4d** [$\nu_{\max}(\text{CHCl}_3)$ 2182 cm⁻¹] exclusively (entry 4). However, when the same reaction mixture was warmed to room temperature, **4d** completely isomerized to the ketene **5d** [$\nu_{\max}(\text{CHCl}_3)$ 2074 cm⁻¹] with some decomposition of **4d** (entry 5).§ We then

[†] Generation and reaction of ynolate anions is a field of growing interest in this decade.⁵ Several methods for the generation of the alkyl- or aryl-ynolate anions were recently developed based on rearrangement of α -keto dianions,^{5b,d,f,h} ring cleavage of heterocycles,^{5a,e} reaction of alkyn-1-yl toluene-*p*-sulfonate with MeLi,^{5c} and hydroxylation of alkyn-1-yl lithium.^{5g} Their reaction with limited electrophiles was also reported to provide ynol derivatives and/or substituted ketenes. However, studies of their ambident nature are rare.

[‡] Preparation of ynolate anions from ketene itself or alkylketenes has, to the best of our knowledge, never been reported, possibly due to the instability of such ketenes.

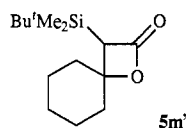
§ Preparation and a similar isomerization of the same ynol ether **4d** was previously reported for the reaction of dilithioynolate and Bu^tMe₂SiCl, but formation of **4d** was not reproducible.^{5e}

Table 1 Reaction of ynolate anions **2**, generated from **1**, with electrophiles **3**



Entry	1	3	Reaction conditions ^a	Products (yield, %)	
				4	5
1	1a	Bu ^t Me ₂ SiCl	-70 °C, 1.5 h	4a	50 ^b 5a —
2	1b	Me ₃ SiCl	-70 °C, 3 h	4b	— 5a 96 ^{b,c}
3	1b	Et ₃ SiCl	-70 °C, 3 h	4c	— 5c 85 ^b (33 ^e)
4	1b	Bu ^t Me ₂ SiCl	-50 °C, 6 h	4d	65 ^b 5d —
5	1b	Bu ^t Me ₂ SiCl	Room temp., 24 h	4d	— 5d (24 ^e)
6	1b	Bu ^t Me ₂ SiCl	-70 °C, HMPA (1 equiv.), 3 h	4d	— 5d 55 ^d (38 ^e)
7	1b	Pr ⁱ ₃ SiCl	-50 °C, 6 h	4e	50 ^b 5e —
8	1b	Pr ⁱ ₃ SiCl	-70 °C, HMPA (1 equiv.), 3 h	4e	— 5e 30 ^d (6 ^e)
9	1b	(Thexyl)Me ₂ SiCl	-50 °C, 6 h	4f	45 ^b 5f —
10	1b	PhMe ₂ SiCl	-70 °C, 3 h	4g	— 5g 90 ^b (22 ^e)
11	1b	Ph ₂ MeSiCl	-70 °C, 3 h	4h	— 5h 50 ^d (30 ^e)
12	1b	Ph ₃ SiCl	-70 °C, 3 h	4i	— 5i 75 ^d (40 ^e)
13	1b	Bu ^t Ph ₂ SiCl	Room temp., 24 h	4j	— 5j —
14	1b	Bu ^t Ph ₂ SiCl	-70 °C, HMPA (1 equiv.), 3 h	4j	35 ^b 5j —
15	1b	Bu ₃ SnCl	-70 °C, 3 h	4k	— 5k 95 ^{b,c}
16	1b	Ph ₃ SnCl	-70 °C, 3 h	4l	— 5l 85 ^b
17	1b	Cyclohexanone	-50 °C, 5 h	4m	— 5m ^f 52 ^f

^a All reactions at -100 °C for 1 h, then as shown in table. ^b Yields estimated by ¹H NMR data of the crude product. ^c Briefly reported in our previous paper.^{3c} ^d Yields estimated by those of the corresponding esters obtained by treatment of the reaction mixture with acidic EtOH (see Experimental section). ^e Isolated yields of analytically pure **5** by SiO₂ flash column chromatography. ^f A 52% yield of the silyllactone **5m'** was isolated as a single identified product.



examined the reaction of ynolate anions **2a,b** derived from **1a,b** with a variety of electrophiles **3** at low temperature. The results are shown in Table 1. Reactions with bulky silyl chlorides gave the ynone ethers **4a,e** and **f** in moderate yields without formation of the ketenes **5** (entries 1, 7 and 9), whereas those with relatively small Et₃SiCl (entry 3) or with silyl chlorides possessing phenyl groups (entries 10, 11 and 12) gave only ketenes **5c** and **g-i**. Addition of 1 equiv. of HMPA to the reaction with bulky Bu^tMe₂SiCl or Prⁱ₃SiCl completely changed the products from the ynone ethers **4d,e** to the ketenes **5d,e** (entries 6 and 8).⁸ However, it is interesting that in the reaction with Bu^tPh₂SiCl, the ynone ether **4j** was obtained for the first time using HMPA (entries 13 and 14). Stannylation using Bu₃SnCl or Ph₃SnCl also provided the ketenes **5k,l** in high yields (entries 15 and 16). Similarly, the reaction with cyclohexanone gave a 52% yield of the product **5m'** derived through the reaction at the carbon atoms (entry 17), however, those with PhCOCl, Ac₂O, PhCHO, MeI, (EtO)₂POCl, (PhO)₂POCl, PhSSO₂Ph and Br₂ gave neither **4** nor **5**.

The above results show that the reaction sites of the ynolates **2** are dependent on the hardness⁹ and bulkiness of the electrophiles. Thus, hard and bulky silyl chlorides reacted at the oxygen atom to give **4**, while soft silyl and stannyl chlorides gave the products **5** by the reaction at the carbon atom. The reason why Bu^tPh₂SiCl gave the ynone ether **4j** (entry 14) is probably that its bulkiness exceeded its softness. On the other hand, in the case of hard but relatively small Me₃SiCl (entry 2), exclusive formation of the C-silylated product **5a** must be due to rapid isomerization of the kinetically controlled product, trimethylsilyl ynone ether **4b**, similarly to but faster than the case with Bu^tMe₂SiCl. Therefore, we tried to trap **4b** as a cobalt complex.

Before trapping **4b**, we first examined the reaction of *O*-tert-butyltrimethylsilyl ynone ethers **4a,d** with Co₂(CO)₈. The ynone ether-cobalt complexes **6a,b** were formed at room temperature for 1.5 h and were isolated in good yields after flash column chromatography on SiO₂. However, they were very unstable and readily converted to the clusters **7a,b**¶ by treatment with 0.01 mol dm⁻³ NaOH or trifluoroacetic acid, and even on SiO₂. The structures of **6** and **7** were unambiguously confirmed by IR, ¹H NMR, ¹³C NMR, high resolution mass spectroscopies and/or elemental analysis, and finally by X-ray analysis (for **7b**) (Fig. 1). Next, into the reaction mixture of **1b**, BuLi and Me₃SiCl (the same conditions as entry 2 in Table 1) was added 1.2 equiv. of Co₂(CO)₈ at -78 °C, and the mixture was allowed to warm to room temperature to give the same cluster **7b** (3%) as a pure cobalt complex. Silylation of **1b** using Me₃SiOTf and Et₃N¹² in the presence of Co₂(CO)₈ at -30 to 10 °C also gave a 12% yield of **7b** (Scheme 2). Because treatment of the ketene **1b** or **5a** with Co₂(CO)₈ did not provide any cobalt complexes, these results suggest the initial formation of the ynone ether **4b**.

In conclusion, we have found that ynolate anions **2**,

¶ Although preparation of R₃SiCo₃(CO)₉ was reported by reaction of R₃SiCCl₃ and Co₂(CO)₈^{10a} or R₃SiH and HCCO₃(CO)₉,^{10b} this is the first formation of similar clusters from alkyne-cobalt complexes. Related conversion of the cobalt complexes of terminal alkynes **i** to the clusters **ii** is known.¹¹



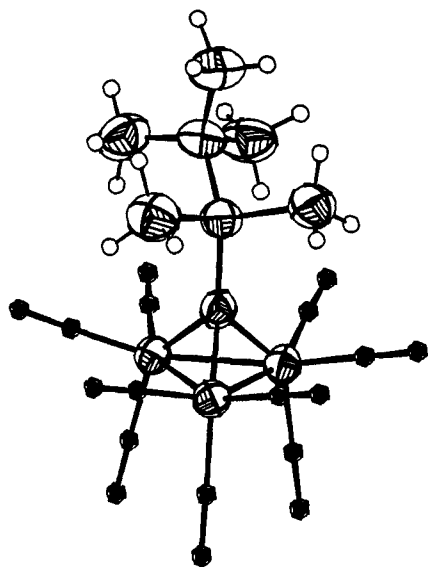
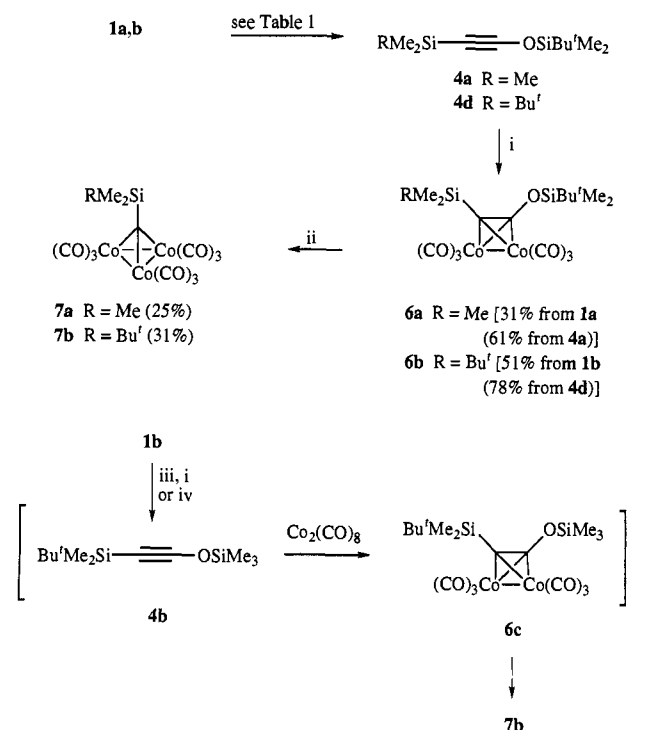


Fig. 1 X-Ray crystallographic structure of 7b. The CO groups are reduced for clarity.



Scheme 2 Reagents: i, $\text{Co}_2(\text{CO})_8$; ii, $0.01 \text{ mol dm}^{-3} \text{ NaOH}$; iii, BuLi then Me_3SiCl ; iv, Me_3SiOTf , Et_3N , $\text{Co}_2(\text{CO})_8$

generated by the reaction of silylketenes **1** and BuLi, reacted with various silyl and stannyl chlorides to give silyl ynol ethers **4** or functionalized silylketenes **5** depending on the electrophiles and the reaction conditions. Application of these products to organic syntheses is currently under investigation.

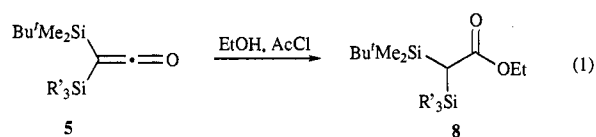
Experimental

All boiling and melting points are uncorrected. IR spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^1H and ^{13}C NMR spectra were measured on Varian-VXR200 (200 MHz), Hitachi R-250HT (250 MHz), JEOL JNM-EX270 (270 MHz) and JEOL JNM-GX500 (500 MHz) spectrometers with CHCl_3 as an internal standard. J Values are given in Hz. High-resolution mass spectra (HRMS) were recorded at 70 or 20 eV with a direct inlet system on JEOL JMS-D300 and JEOL JMS-HX100 spectrometers. E. Merck Silica gel 60 (230–400 mesh

ASTM) was used for flash column chromatography. Anhydrous THF was obtained by distillation from sodium benzophenone ketyl. Anhydrous EtOH was distilled over sodium. Dry CH_2Cl_2 was distilled over phosphorus pentoxide. Organic layers were dried with anhydrous Na_2SO_4 . Silylketenes (**1a,b**) were prepared according to the reported method.¹³ All other compounds are commercially available. Experimental data for compounds **5a** and **5k** were reported in ref. 2(c).

General procedure for the reaction of ynolate anion **2** derived from **1** with electrophiles **3**

Under a nitrogen atmosphere, a solution of BuLi (1.6 mol dm^{-3} ; 0.63 cm^3 , 1.0 mmol) in anhydrous THF (10 cm^3) was cooled to -100°C . A solution of **1** (1.0 mmol) in anhydrous THF (2 cm^3) was added over 10 min. The reaction mixture was stirred at the same temperature for 30 min, and a solution of **3** (1.0 mmol) in anhydrous THF (1 cm^3) was added over 5 min. The whole was stirred at -100°C for 1 h and then at the temperature and for the time shown in Table 1. Hexane (40 cm^3) was added at -70°C and the reaction mixture was poured into a mixture of hexane (60 cm^3), saturated aqueous NaHCO_3 (30 cm^3) and crushed ice (30 g). The whole mixture was vigorously stirred for 20 s, and the organic layer was separated, washed with ice water (60 cm^3) for 20 s, dried and concentrated under reduced pressure to give **4** or **5**. For entries 6, 8 and 14, hexamethylphosphoramide (HMPA) (1.0 mmol) was added just before addition of **3**. The ynol ethers **4a,d-f** (ca. 45–75% pure) were obtained as almost inseparable mixtures with silanol derivatives. The yields (see Table 1) were estimated by ^1H NMR spectral data of crude products with 3-methylanisole as an internal standard. Similarly, ca. 40% pure **4j** was obtained. The ketenes **5** (ca. 50–90% pure) were obtained as mixtures with silanols and analytically pure **5c-e,g-i** were obtained by SiO_2 flash column chromatography (hexane or hexane-ethyl acetate), although their yields were reduced owing to partial decomposition. Yields of **5** were estimated by ^1H NMR spectral data for the crude products (for **5a,c,g,k** and **l**) or conversion of the crude products to the corresponding esters **8** by treatment with acidic ethanol [eqn. (1)] as follows



(for **5d,e,h** and **i**). The lactone **5m'** was isolated by SiO_2 flash column chromatography (hexane-ethyl acetate). The physical state, boiling or melting point, IR, ^1H NMR, HRMS and elemental analysis data for products **4** and **5** are summarized in Table 2.

General procedure for the conversion of **5** to ethyl 2-(*tert*-butyldimethylsilyl)-2-substituted acetates **8**

Under a nitrogen atmosphere, a mixture of anhydrous EtOH (5 cm^3) and acetyl chloride (1 cm^3) was stirred for 30 min at room temperature. The crude product **5** obtained as above was added dropwise at 0°C , and the mixture was stirred overnight at room temperature. Diethyl ether and water were added and the aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine, dried and concentrated. The residue was purified by SiO_2 column chromatography (hexane-ethyl acetate) to afford pure **8** as a colourless oil. Spectral data and elemental analysis data for **8** are listed below.

8d ($\text{R}'_3 = \text{Bu}'\text{Me}_2$): $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1701; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 0.08 (6 H, s), 0.16 (6 H, s), 0.89 (18 H, s), 1.24 (3 H, t, J 7.5), 1.85 (1 H, s), 4.00 (2 H, q, J 7.5) [Found: M^+ , 316.2238. $\text{C}_{16}\text{H}_{36}\text{O}_2\text{Si}_2$ requires M , 316.2251].

8e ($\text{R}'_3 = \text{Pr}^i_3$): $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1688; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3)$ 0.11 (3 H, s), 0.24 (3 H, s), 0.90 (9 H, s), 1.03–1.26 (21 H, m), 1.23 (3 H, t, J 8), 2.17 (1 H, s), 3.96–4.06 (2 H, m) [Found: M^+ , 358.2723. $\text{C}_{19}\text{H}_{42}\text{O}_2\text{Si}_2$ requires M , 358.2723].

Table 2 Physical and spectral data for silyl ynol ethers **4** and substituted silylketenes **5**

Compound	Physical state [Bp/°C (mmHg) or mp/°C]	$\nu_{\max}(\text{CHCl}_3)/$ cm^{-1}	$\delta_{\text{H}}(\text{CDCl}_3)$	Formula	HRMS or analysis (%)	
					Found	Required
4a	Pale yellow oil 90–100 (0.2) ^a	2182	0.11 (9 H, s), 0.27 (6 H, s), 0.97 (9 H, s)	C ₁₁ H ₂₄ OSi ₂	228.1352	228.1363
4d	Pale yellow oil	2182	0.04 (6 H, s), 0.27 (6 H, s), 0.90 (9 H, s), 0.97 (9 H, s)	C ₁₄ H ₃₀ OSi ₂	270.1831	270.1832
4e	Yellow oil	2186	0.04 (6 H, s), 0.91 (9 H, s), 1.11 (18 H, d, J 7), 1.21–1.30 (3 H, m)	C ₁₇ H ₃₆ OSi ₂	312.2304	312.2304
4f	Yellow oil	2180	0.05 (6 H, s), 0.32 (6 H, s), 0.86–1.00 (21 H, m), 1.6–1.8 (1 H, m)	C ₁₆ H ₃₄ OSi ₂	298.2152	298.2147
4j	Yellow oil	2184	–0.03 (6 H, s), 0.79 (9 H, s), 1.16 (9 H, s), 7.37–7.47 (6 H, m), 7.71–7.76 (4 H, m)	C ₂₄ H ₃₄ OSi ₂	337.1428	337.1441 (M ⁺ – Bu ^t)
5c	Colourless oil	2074	0.13 (6 H, s), 0.67 (6 H, q, J 7.5), 0.95 (9 H, s), 0.98 (9 H, t, J 7.5)	C ₁₄ H ₃₀ OSi ₂	C 61.85 H 10.95	C 62.15 H 11.18
5d	Colourless oil	2072	0.16 (12 H, s), 0.94 (18 H, s)	C ₁₄ H ₃₀ OSi ₂	C 61.95 H 10.9	C 62.15 H 11.18
5e	Colourless oil	2068	0.18 (6 H, s), 0.99 (9 H, s), 1.07–1.18 (21 H, m)	C ₁₇ H ₃₆ OSi ₂	312.2300	312.2304
5g	Colourless oil	2080	0.00 (6 H, s), 0.47 (6 H, s), 0.89 (9 H, s), 7.35–7.38 (3 H, m), 7.55–7.58 (2 H, m)	C ₁₆ H ₂₆ OSi ₂	C 66.15 H 9.05	C 66.14 H 9.02
5h	Colourless oil	2081	–0.01 (6 H, s), 0.74 (3 H, s), 0.91 (9 H, s), 7.35–7.41 (6 H, m), 7.56–7.59 (4 H, m)	C ₂₁ H ₂₈ OSi ₂	C 71.8 H 7.8	C 71.53 H 8.00
5i	White crystals 134–135 ^b	2080	–0.10 (6 H, s), 0.88 (9 H, s), 7.36–7.43 (9 H, m), 7.67 (6 H, dd, J 1.5, 7.5)	C ₂₆ H ₃₀ OSi ₂	C 75.3 H 7.2	C 75.31 H 7.29
5l	White crystals 93–94 ^c	2066	–0.05 (6 H, s), 0.88 (9 H, s), 7.40–7.44 (9 H, m), 7.60–7.64 (6 H, m)	C ₂₆ H ₃₀ OSiSn	449.0390	449.0385 (M ⁺ – Bu ^t)
5m	White crystals 83–84 ^c	1802	0.14 (3 H, s), 0.20 (3 H, s), 0.94 (9 H, s), 1.58–2.06 (10 H, m), 2.94 (1 H, s)	C ₁₄ H ₂₆ O ₂ Si	254.1697	254.1699

^a Bath temperature. ^b Recrystallized from hexane–CH₂Cl₂. ^c Recrystallized from hexane.

8h (R'₃ = Ph₂Me): $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1690; δ_{H} (250 MHz; CDCl₃) –0.30 (3 H, s), 0.06 (3 H, s), 0.80 (3 H, s), 0.86 (9 H, s), 0.96 (3 H, t, J 7.5), 2.47 (1 H, s), 3.74 (2 H, q, J 7.5), 7.31–7.62 (10 H, m) [Found: M⁺, 398.2106. C₂₃H₃₄O₂Si₂ requires *M*, 398.2098].

8i (R'₃ = Ph₃): $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1692; δ_{H} (250 MHz; CDCl₃) –0.23 (3 H, s), –0.21 (3 H, s), 0.91 (9 H, s), 0.98 (3 H, t, J 7), 2.91 (1 H, s), 3.73 (2 H, q, J 7), 7.29–7.68 (15 H, m) [Found: M⁺, 460.2259. C₂₈H₃₆O₂Si₂ requires *M*, 460.2254].

The ynol ether–dicobalt hexacarbonyl complexes **6a** and **6b**

Into a solution of the crude ynol ether **4a**, obtained from **1a** (122 mg, 1.07 mmol) as above, in CH₂Cl₂ (6 cm³) was added Co₂(CO)₈ (365 mg, 1.07 mmol) at 0 °C, and the reaction mixture was stirred in the dark at room temperature for 1.5 h and then concentrated. The residue was purified by SiO₂ flash column chromatography (hexane) to afford pure **6a** (170 mg, 31% from **1a**) as a dark brown oil; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2087, 2047 and 2024; δ_{H} (250 MHz; CDCl₃) 0.27 (6 H, br s), 0.29 (9 H, br s), 0.93 (9 H, br s) [Found: M⁺, 513.9719. C₁₇H₂₄O₇Si₂Co₂ requires *M*, 513.9721].

Similarly to the preparation of **6a**, **6b** (1.39 g, 51% from **1b**) was obtained from the crude ynol ether **4d**, obtained from **1b** (4.9 mmol) as a dark brown gum; $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2087, 2047 and 2024; δ_{H} (250 MHz; CDCl₃) 0.23 (6 H, br s), 0.28 (6 H, br s), 0.93 (9 H, br s), 1.04 (9 H, br s); δ_{C} (67.5 MHz; CDCl₃) 200.7–199.5, 146.2, 54.8, 26.8, 25.3, 18.6, 17.9, –3.0, –5.4 [Found: M⁺, 556.0194. C₂₀H₃₀O₇Si₂Co₂ requires *M*, 556.0194].

The cobalt clusters **7a** and **7b**

NaOH (0.1 mol dm^{–3}; 0.5 cm³) was added to **6a** (100 mg, 0.194 mmol) in THF (5 cm³) at 0 °C and stirred for 10 min. After hexane (5 cm³) was added, the mixture was poured into a mixture of pH 7.0 phosphate buffer and hexane. The organic layer was separated, washed with brine, dried and concentrated. The residue was purified by SiO₂ column chromatography (hexane) to afford pure **7a** (25 mg, 25%) as purple crystals, mp 76 °C (decomp.) (from hexane–EtOH); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2103, 2053, 2037 and 2020; δ_{H} (270 MHz; CDCl₃) 0.36 (9 H, s); δ_{C} (67.5 MHz; CDCl₃) 199.9–199.7, 29.7, 3.3 (Found: C, 30.35; H, 1.95;

M⁺, 513.8017. C₁₃H₉O₉SiCo₃ requires C, 30.35; H, 1.75%; *M*, 513.8012).

Similarly to the preparation of **7a**, **7b** (11.5 mg, 31%) was obtained from **6b** (37.4 mg, 0.067 mmol) and NaOH (0.01 mol dm^{–3}; 0.2 cm³) as purple needles, mp 58 °C (decomp.) (from hexane–EtOH); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2101, 2053, 2037 and 2020; δ_{H} (270 MHz; CDCl₃) 0.33 (6 H, s), 1.07 (9 H, s); δ_{C} (67.5 MHz; CDCl₃) 199.5–200.1, 29.7, 27.7, 18.9, 0.8 (Found: C, 34.5; H, 2.85; M⁺, 555.8472. C₁₆H₁₅O₉SiCo₃ requires C, 34.55; H, 2.7%; *M*, 555.8478).

Trapping of **4b** as a cobalt complex

By reaction of **1b, BuLi, Me₃SiCl and Co₂(CO)₈.** According to the general procedure, compound **1b** (156 mg, 1.00 mmol) was treated with BuLi (0.61 cm³, 1.0 mmol) and then Me₃SiCl (0.14 cm³, 1.1 mmol) at –100 °C for 1 h and at –78 °C for 1 h. Co₂(CO)₈ (410 mg, 1.2 mmol) was added and the whole was stirred in the dark at –78 °C for 1 h and allowed to reach room temperature overnight. After hexane was added, the mixture was filtered and concentrated. The residue was purified by SiO₂ flash column chromatography (hexane) to afford **7b** (18 mg, 3%).

By reaction of **1b, Et₃N, Me₃SiOTf and Co₂(CO)₈.** Under a nitrogen atmosphere, Co₂(CO)₈ (342 mg, 1.0 mmol), Et₃N (0.17 cm³, 1.3 mmol) and Me₃SiOTf (0.23 cm³, 1.3 mmol) were successively added into a solution of **1b** (156 mg, 1.00 mmol) in CH₂Cl₂ (10 ml) at –30 °C, and the mixture was stirred overnight at room temperature. The reaction mixture was poured into a mixture of hexane and water and the aqueous layer was extracted with hexane. The combined organic layer was dried and concentrated. The residue was purified by SiO₂ flash column chromatography (hexane) to afford **7b** (67 mg, 12%).

Crystal structure determination

Single crystals of compound **7b** suitable for X-ray diffraction study were obtained from hexane–EtOH at 253 K. All measurements were carried out with a Mac Science MXC 18 four-circle automated diffractometer with graphite monochromated Cu-K α radiation and an 18 kW rotating anode

generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement. The data were collected at 288 K using the ω - 2θ scan technique to an above maximum 2θ value of 130° . All intensities were corrected for Lorentz and polarization effects. An analytical function for absorption correction was applied to the data.¹⁴ The structure was solved by direct methods using SHELXS86.¹⁵ The non-hydrogen atoms were refined anisotropically, while only coordinates of hydrogen atoms were refined. All calculations were performed using the CRYSTAN-G crystallographic software package from Mac Science. Atomic coordinates, bond lengths and bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/31.

Crystal data for 7b. $C_{16}H_{15}O_9SiCo_3$, M 556.00, crystal size $0.50 \times 0.50 \times 0.10$ mm³, triclinic, space group $P\bar{1}$, $a = 8.754(1)$, $b = 16.433(3)$, $c = 8.633(2)$ Å, $\alpha = 100.56(2)$, $\beta = 114.91(2)$, $\gamma = 84.83(2)^\circ$, $V = 1107.1(4)$ Å³, $Z = 2$, $D_c = 1.67$ g cm⁻³, $\lambda(\text{Cu-K}\alpha) = 1.54178$ Å, $\mu = 0.11$ cm⁻¹, $w = 1/[\sigma^2(F_o) + (0.047F_o)^2]$, $\Delta\rho_{\text{max}} = 1.01$ e Å⁻³ (0.398, 0.282, -0.139), $\Delta\rho_{\text{min}} = -0.70$ e Å⁻³ (0.815, 0.676, 0.359), $R = 0.065$ for 3251 independent reflections.

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