Bis(benzene)chromium: a pre-catalyst for the hydrosilation of ketones and aldehydes, and for the dehydrocoupling of triphenylsilane with primary alcohols†

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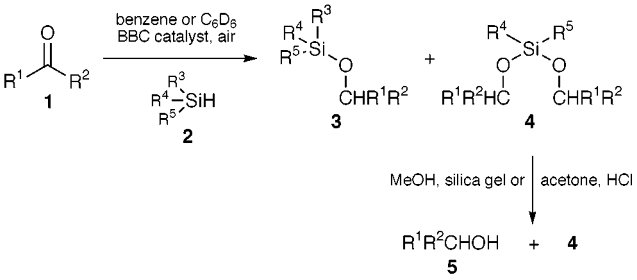
Bis(benzene)chromium is a valuable pre-catalyst for the hydrosilation of α-aryl carbonyl compounds as well as for the dehydrocoupling between primary alcohols and triphenylsilane.

For a number of years, the catalytic hydrosilation of ketones and aldehydes has been a widely used reaction in organic synthesis, known to be catalysed by a large number of transition metal compounds.[1–6] However, to our knowledge, bis(benzene)chromium (BBC) has never been used for this purpose, and moreover its known catalytic properties have been mentioned only in a very few instances.[7–10]

In this work, we show that under certain conditions, BBC is an active homogeneous catalyst for the hydrosilation of ketones and aldehydes as well as for the dehydrocoupling of primary alcohols with triphenylsilane.

The catalytic reaction was examined using different substrates **1** and a number of silanes **2** (**2**/**1** = 1.2 equiv.) in the presence of neutral BBC (6% mol) in benzene (or benzene-d_6) and under aerobic conditions (Scheme 1). With diphenylsilane and methylphenylsilane, compounds **3** were not stable on silica gel and were converted spontaneously to the corresponding alcohols **5** (MeOH, silica gel or acetone, HCl). The results are summarized in Table 1. It is of note that the hydrosilation reactions were generally clean as judged by the ^{1}H NMR spectra of the crude reaction mixtures. Thus silylenol ether, the main by-product resulting from dehydrogenative silylation, occasionally encountered with other catalysts,[1] was not detected in this case. The formation of polymers was accompanied by an increase in the aromatic signal intensity and the appearance of singlets (corresponding to SiH) in the range δ 5.5–6.0 was observed to a small extent.



Scheme 1

Saturated ketones are not reactive under these conditions. For instance, acetone gave only traces of compound **3** after 24 h at 40 °C in benzene (Table 1, entry 2). On the other hand, and as judged from the ^{1}H NMR spectra of the crude reaction mixtures, with excess acetone (both as solvent and reactant), reaction occurs with total conversion of the silane. We have also attempted the reduction of carbon–carbon multiple bonds but without success, with hydrosilation of 2-cyclopenten-1-one occurring exclusively on the carbonyl function (Table 1, entry 4).

Different silanes were used in the hydrosilation of *para*-anisaldehyde (Table 1, entries 5–8). Ph$_3$SiH, Me$_2$PhSiH and Et$_3$SiH are not effective in this reaction, probably owing to steric hindrance. This can also explain the poor yields for compound **4** obtained with Ph$_2$SiH$_2$ (Table 1, entries 1–5). With a less hindered silane (Table 1, entry 6 *vs.* 5), **4** is obtained in 21% yield. Two ethoxysilanes were also examined (Table 1, entries 7 and 8) with success. The formation of **4** is attributed to a redistribution reaction of the silane prior to hydrosilation.[11,12]

In order to gain information about the nature of the species responsible for the catalytic process, *para*-anisaldehyde was reacted with dimethylethoxysilane under argon in the presence of freshly sublimed BBC, by saturating the solution of the aldehyde and the silane in benzene with argon prior to the addition of the arene complex (Scheme 2). No reaction occured after 18 h at room temperature. It follows that although BBC is

Table 1 Hydrosilation of ketones and aldehydes by BBC‡

		2			Yield (%)			
Entry	**1**	R^3	R^4	R^5	**3**	**4**	**5**	Conditions
1	Acetophenone	H	Ph	Ph	—	< 5	90	*a–c*
2	Acetone	H	Ph	Ph	tr.[d]	—	—	*b, e–g*
3	Piperonal	H	Ph	Ph		< 5	65	*a–c*
4	2-Cyclopenten-1-one	H	Ph	Ph	47	—	—	*a, e, g, h*
5	*p*-Anisaldehyde	H	Ph	Ph	—	< 5	95	*a–c*
6	*p*-Anisaldehyde	H	Me	Ph	—	21	72	*a*
7	*p*-Anisaldehyde	OEt	Me	Me	50	24	—	*a, f, i*
8	*p*-Anisaldehyde	OEt	OEt	Me	39	18	—	*a, f, h, i*

[a] Isolated yields after flash chromatography. [b] **4** and **5** were characterized by ^{1}H NMR. [c] 70 °C, 3 h. [d] tr = trace. [e] Yields are calculated by ^{1}H NMR with ferrocene as reference. [f] 40 °C, 24 h. [g] **4** was not detected [h] 25% starting material left. [i] Products **3** and **4** have been fully characterized.

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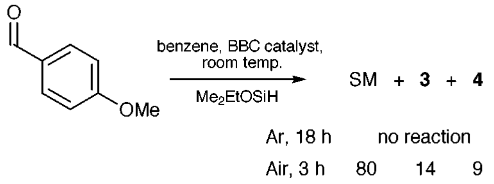
† Metal π complexes of benzene derivatives, part 54. Part 53: *Z. Anorg. Allg. Chem.*, 1999, **625**, 875.



Scheme 2 (SM = starting material)

the catalytic precursor, hydrosilation is thought to proceed by the transient formation of a species generated by the reaction of O_2 with BBC in the presence of trace amounts of water.[13] The mechanism seems therefore to be completely different from the well established Chalk and Harrod oxidative addition process in the case of late transition metal catalyst complexes. Instead it may involve primary electron transfer to yield the radical pair $BBC^+\ O_2^{-\cdot}$ and subsequent hydrogen atom abstraction from the silane by the hydroperoxide anion, thereby triggering a radical path for the hydrosilation. This option is currently being tested by means of EPR spectroscopy.

Under the same experimental conditions, primary alcohols led to fast dehydrocoupling in the presence of Ph_3SiH (Scheme 3) with vigorous gas evolution. Yields are of the same order as those reported in the literature for numerous other known catalysts.[14] Propargyl alcohol was thus converted to the corresponding silyl compound with the triple bond remaining intact. This reaction is an alternative, in the case of primary alcohols, to the protection method using bromotriphenylsilane in pyridine.[15]

$$\mathrm{ROH} \xrightarrow{\text{BBC catalyst, Air, Ph}_3\text{SiH}} \mathrm{ROSiPh_3}$$

Scheme 3

It has been demonstrated that BBC can behave as an efficient spin trap[16] and reactions described above provide further support to the hitherto unsuspected usefulness of this well known sandwich compound in organic synthesis.

Notes and references

‡ *Typical procedure* (Table 1, entry 7): Dimethylethoxysilane (1.2 mmol) was added, at room temperature, to a solution of *p*-anisaldehyde (1 mmol) and BBC (0.06 mmol) in benzene (1 mL). After 3 h at 40 °C in the presence of air, the reaction mixture was concentrated. The residue was flash chromatographed affording **3** [light petroleum–diethyl ether (90:10]) and then **4** (dichloromethane).

3 : ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27 (2H, d, *J* 8.0 Hz), 6.88 (2H, d, *J* 8.0 Hz), 4.72 (2H, s), 3.81 (3H, s), 3.75 (2H, q, *J* 7.2 Hz), 1.21 (3H, t, *J* 7.2 Hz), 0.16 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.8, 132.5, 128.2, 113.6, 64.2, 58.1, 55.1, 18.1, −7.0; IR (neat) : 2966, 2930, 2860, 2840, 1613, 1514, 1465, 1256, 1077, 1037, 867, 841 cm^{-1}, MS (*m/z*) 240, 225, 195, 179, 121, 77; Anal. Calc. for $C_{12}H_{20}O_3Si$: C, 60.00; H, 8.32. Found : C, 59.11; H, 8.25%.

4 : ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (4H, d, *J* 8.7 Hz), 6.87 (4H, d, *J* 8.7 Hz), 4.69 (4H, s), 3.81 (6H, s), 0.18 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.8, 132.6, 128.1, 113.6, 64.1, 55.1, −2.9; IR (neat) : 2960, 2930, 2860, 2840, 1613, 1513, 1464, 1260, 1065, 1036, 860, 800 cm^{-1}; MS (*m/z*) 332, 211, 121, 91; Anal. Calc. for $C_{18}H_{24}O_4Si$: C, 65.02; H, 4.27. Found : C, 63.85; H, 7.40%.

1 I. Ojima, in *The Chemistry of Organic Silicon Compounds, Part 2,* ed. Z. Rappoport, Wiley, New York, 1983, p. 1479.
2 W. P. Weber, in *Silicon Reagents for Organic Synthesis,* Springer-Verlag, Berlin–Heidelberg–New York, 1983, p. 288.
3 I. Itsuno *Org. React.*, 1998, **52**, 440.
4 H. Brunner, H. Nishiyama and K. Itoh, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, New York, 1993, p. 303.
5 B. Marciniec and J. Gulinski *J. Organomet. Chem,* 1993, **446**, 15.
6 B. Marciniec, J. Gulinski, W. Urbaniak and Z. W. Kornetka, in *Comprehensive Handbook on Hydrosilylation,* ed. B. Marciniec, Pergamon, Oxford, 1992.
7 B. G. Gribov, D. D. Mozzhukhin, B. I. Kozyrkin and A. S. Strizhkova, *J. Gen. Chem. USSR,* 1972, **42**, 2521
8 Y. Tazima and S. Yuguchi, *Bull. Chem. Soc. Jpn.,* 1966, **39**, 2534.
9 Y.-Z. Huang and J. Q. Zhou *J. Organomet. Chem,* 1988, **348**, 235.
10 G. Fochi, *Organometallics*, 1988, **7**, 2255.
11 M. D. Curtis and P. S. Epstein, *Adv. in Organomet. Chem.,* 1981, **19**, 213.
12 S. Xin, C. Aitken, J. F. Harrod, Y. Mu and E. Samuel, *Can. J. Chem.,* 1990, **68**, 471.
13 The oxidation potential of the couple BBC–BBC^+ is −0.68 V *vs.* SCE. For oxidation of BBC, see ref. 7.
14 C. Lorentz and U. Schubert, *Chem. Ber.*, 1995, **128**, 1267.
15 T. W. Greene and P. G. M. Wutz, in *Protective Groups in Organic Synthesis*, Wiley, 2nd edn, New York, 1991, p. 50.
16 E. Samuel, D. Caurant, D. Gourier, Ch. Elschenbroich and K. Agbaria *J. Am. Chem. Soc.,* 1988, **120**, 8088.

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