substitution proceeds smoothly even at −60 °C, *(2a)* being formed within 1 h in 92% yield. Analogously, from a series of substituted phenyl(trimethyl)silanes *(1a)—(1h)* and benzaldehyde, the benzhydrylsilyl ethers *(2a)—(2h)* or, after hydrolysis, the benzhydrols *(3)* were obtained (Table 1).

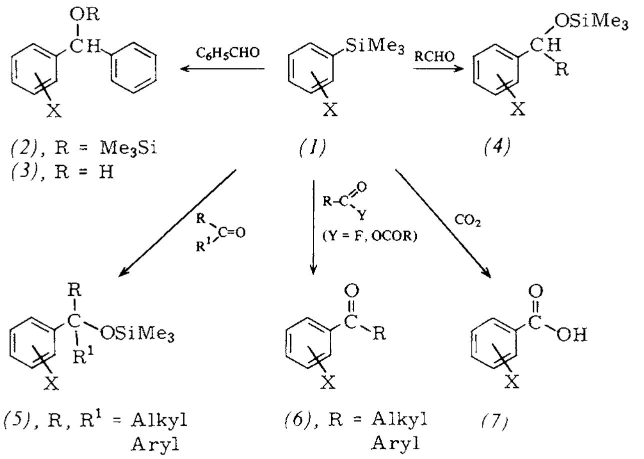

Table 1. Benzhydrylsilyl ethers *(2)* and benzhydrols *(3)* from mono-substituted phenyl(trimethyl)silanes *(1)* and benzaldehyde.

Educt	*(1)* X	$KOC(CH_3)_3$ [mol-%]	Conditions Solvent	[h]	[°C]	Product	Yield [%]
(1a)	*o*-NO_2	10	DMF	1	− 60	*(2a)*	92 [a]
(1b)	*o*-Cl	20	DMF	1	− 30	*(2b)*	80 [a]
(1c)	*o*-F	5	DMF	1	+ 20	*(2c)*	76 [b]
(1d)	*o*-C_6H_5O	14	DMF	2	+ 20	*(2d)*	68 [b]
(1e)	*o*-$C_6H_5SO_2$	7	DMF	1	+ 20	*(2e)*	97 [b]
(1f)	*o*-CH_3O	25	HMPT [c]	0.3	+ 20	*(2f)*	trace [a]
(1g)	*m*-Cl	30	HMPT [c]	4	+ 100	*(3g)*	78 [d]
(1h)	*p*-Cl	30	HMPT [c]	3	+ 100	*(3h)*	42 [d]

[a] Determined by gas chromatography. [b] Isolated. [c] Hexamethylphosphoric triamide. [d] Determined by gas chromatography after acid hydrolysis.

For the nitro- and chlorophenyl(trimethyl)silanes, the relative reactivity correlates well with the σ^I-substituent constants[7a], but diverges significantly from the order of stabilization of the phenyl anions which would be essential intermediates for a nucleophilic desilylation[7b]. The σ^I correlation holds also for the other arylsilyl substrates *(1c)—(1f)* in Table 1; the remarkable increase in reactivity from *(1d)* to *(1f)* is similarly mirrored in the substituent constants. This clearly indicates that the electrophile participates significantly in the rate-limiting step of the reactions reported here—in contrast to normal nucleophilic desilylation[7b]. Since "hard" bases have proven especially effective nucleophilic catalysts ($KOC(CH_3)_3$, KF, CsF, tetraalkylammonium fluoride, KOAc)[8], one must assume that interaction of the catalyst with the silicon is the decisive factor for the reaction.

We have also extended the reaction to substituted benzaldehydes and aliphatic aldehydes, to ketones, acyl fluorides and carboxylic acid anhydrides as well as to carbon dioxide; the respective products, secondary *(4)* and tertiary benzyl alcohols *(5)*, aryl ketones *(6)* and substituted benzoic acids *(7)*, are obtained, at least in part, in excellent yields.

The scope of the procedure can be further widened by variation of the arylsilyl substrate. From 2-trimethylsilylbenzthiazole and benzaldehyde, for instance, the substitution product is formed in 78% yield, only after heating to 160 °C for 40 h[6b]; in the presence of 1 mol-% of potassium *tert*-butanolate, 91% of the product is obtained after 15 min at −60 °C. Since the heteroaryl(trimethyl)silanes are readily accessible *via* cycloaddition reactions[3], this method allows the introduction of substituents into heterocyclic substrates with high regioselectivity[9].

The reaction will be of special preparative advantage in those cases where organometallic derivatives cannot be employed because of the presence of reactive functional groups in the molecule (nitro or carbonyl compounds) or because of secondary reactions, *e.g.* formation of dehydroarenes from halogen compounds or isomerization to more stable anions.

Experimental:

(2a): Potassium *tert*-butanolate (83 mg, 0.74 mmol) is added to a constantly stirred mixture of *(1a)*[10] (3.91 g, 20 mmol) and benzaldehyde (2.12 g, 20 mmol) in 25 cm³ DMF at room temperature. The solutions warms slightly and turns red; as indicated by GLC, the reaction is complete after 1 h. The catalyst is filtered off, and the DMF distilled off. Upon fractional distillation, the oily residue yields 4.81 g (80%) *(2a)*, b.p. 136—138 °C/0.1 torr. ¹H-NMR ($CDCl_3$): $\delta = 0.07$ (s, 9H), 6.57 (s, H), 7.20—8.00 (m, 9H).

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Nucleophilic Catalysis of Reactions of Tricarbonyl(trimethylsilylarene)chromium Complexes with Electrophiles[**]

By *Franz Effenberger* and *Klaus Schöllkopf*[*]

Dedicated to Professor Gerhard Pfleiderer on the occasion of his 60th birthday

Electrophilic substitution of aryl(trimethyl)silanes having electron-donating substituents, *e.g.* alkyl- or aminophenyl(trimethyl)silanes, is not amenable to nucleophilic catalysis[1]; Friedel-Crafts catalysts, on the other hand, specially facilitate reactions of such substrates with electrophiles. In this case, however, the directing influence of the substituents often overrides the tendency of the trimethylsilyl moiety to *ipso*-substitution, and regular H-substitution results[2]. Recent investigations have established the electron-withdrawing effect

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of the tricarbonylchromium group in arene(tricarbonyl)-chromium complexes and given many examples for their preparative application[3a]. Both the facile metalation of these complexes[3b] and the dissociation constants of the respective complexed benzoic acids[3c] clearly demonstrate the high inductive aryl anion stabilization potential of the $Cr(CO)_3$ group; thus, an electrophilic desilylation under nucleophilic catalysis[1] seems feasible.

Tricarbonylchromium complexes of mono- and bis(trimethylsilyl)benzenes [*(2)*, R = H, Me_3Si], which are readily obtainable in good yield from the respective benzene derivatives *(1)* by heating with hexacarbonylchromium[4], do not react with aldehydes and ketones even at elevated temperatures. Upon addition of nucleophilic catalysts such as potassium *tert*-butanolate or cesium fluoride, however, formation of *(3)* takes place, even at room temperature (Table 1).

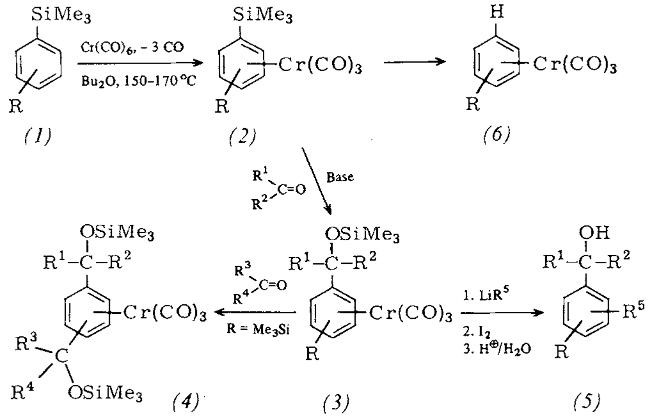

Table 1. Reaction of tricarbonyl(trimethylsilylarene)chromium complexes *(2)* with electrophiles in dimethylformamide (DMF) with addition of 10 mol-% CsF.

Educt	R	R^1	R^2	*t* [h]	Product	Yield [%]
(2a)	*o*-CH_3	H	C_6H_5	0.25	*(3a)*	81
(2b)	*m*-CH_3	H	C_6H_5	0.5	*(3b)*	83
(2c)	*p*-CH_3	H	C_6H_5	2.5	*(3c)*	81
(2d)	*o*-Cl	H	C_6H_5	0.75	*(3d)*	83
(2e)	*m*-Cl	H	C_6H_5	0.3	*(3e)*	70
(2f)	*p*-Cl	H	C_6H_5	2.0	*(3f)*	57
(2g)	H	H	C_6H_5	5.0	*(3g)*	88
(2g)	H	H	CH_3	5.0	*(3h)*	30 [a]
(2g)	H	H	C_3H_7	6.0	*(3i)*	43 [b]
(2g)	H	CH_3	CH_3	10.0	*(3k)*	50 [c]
(2g)	H	CH_3	C_6H_5	7.0	*(3l)*	29 [d]
(2g)	H	C_6H_5	C_6H_5	40.0	*(3m)*	75

[a] 32% *(6g)*. [b] 38% *(6g)*. [c] 28% *(6g)*. [d] 55% *(6g)*.

The position of R relative to the trimethylsilyl group does not greatly influence the rate of formation of *(3)* from *(2)*, as is to be expected from the dissociation constants of the substituted (tricarbonylchromium)benzoic acid complexes[3c]. This is in sharp contrast, though, to the nucleophilic catalysis of electrophilic substitutions where the rate is enhanced by electron-withdrawing groups in the substrate[1]. With enolizable carbonyl reagents, partial protodesilylation of the complexes *(2)* to *(6)* is unavoidable.

Products which still bear a trimethylsilyl group are susceptible to secondary reactions with another carbonyl compound to give *(4)*. Since the activating $Cr(CO)_3$ group is retained in formation of *(3)* or *(4)*, the respective benzene derivatives *(5)* can be obtained by subsequent addition of nucleophiles[3a] and oxidative work-up.

The introduction of many different types of substituents into easily accessible benzene derivatives *(1)*, can therefore be carried out using this method. Compared to the transformations *(2)*→*(3)* or *(3)*→*(4)* *via* organometallic derivatives, the procedure offers a much wider range of substituent variation[1]; at the same time, undesirable metalation processes, *e.g.* benzyl anion formation from alkylbenzenes[3b], are avoided.

Experimental:

(3g): Benzaldehyde (2.13 g, 20 mmol) is added dropwise to a stirred solution of *(2g)*[5] (5.73 g, 20 mmol) and CsF (0.30 g, 2 mmol) in 15 cm^3 DMF under an inert gas atmosphere. The completion of the reaction is monitored by GC. The reaction mixture is diluted with 150 cm^3 ether, the precipitated salt filtered off, and the ethereal phase washed with water and dried over sodium sulfate. The solvent is stripped off, and the residue recrystallized from *n*-hexane. Yield: 6.9 g (88%) *(3g)*, m.p. 90—91 °C.

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[5] *(2g)* was first characterized by *D. Seyferth* and *D. L. Alleston* [Inorg. Chem. *2*, 417 (1963)]; we have prepared *(2g)* in 95% yield, following a procedure described by *C. A. L. Mahaffy* and *P. L. Pauson* [Inorg. Synth. *19*, 154 (1979)].

Synthesis and ESR Characterization of the Triplet Species μ-(η^6:η^6-Biphenyl)-bis[(η^6-benzene)vanadium][**]

By *Christoph Elschenbroich* and *Jürgen Heck*[*]

While the individual electrons of the two radical centers in a real diradical are neither paired nor unpaired, but independent of each other so that no distinction can be made between a mono- and a diradical by ESR spectroscopy, a triplet radical can be recognized by its zero field splitting and by a characteristic hyperfine structure[1]. The transition between diradical and triplet radical is, however, gradual and it is therefore important to study the extent of spin-spin interaction as a function of the nature, separation, and charge of the radical centers. Such investigations have been carried out on coupled pairs of triphenylmethyl radicals *(1)*[2] and, *inter alia*, on bisnitroxides *(2)*[3].

Our interest focusses on paramagnetic intersandwich compounds of the type *(3)*[4]. We report here on the preparation and properties of the neutral complex μ-(η^6:η^6-biphenyl)-bis[(η^6-benzene)vanadium(0)] *(5)*$^{\cdot\cdot}$, which is isoelectronic with the dication {μ-(η^6:η^6-biphenyl)-bis[(η^6-benbenzene) chromium(I)]}$^{++}$ *(4)*$^{++}$[4b]. We obtained the novel in-

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