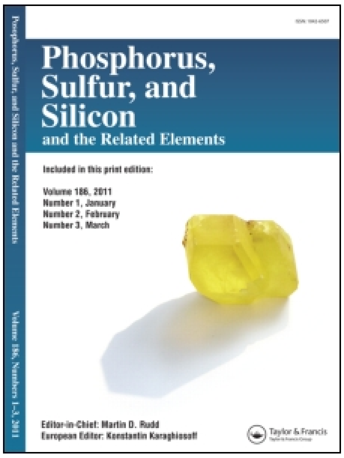

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UNEXPECTED REACTIVITY OF HYPERVALENT ANIONIC SPECIES AS ELECTRON ACCEPTORS

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UNEXPECTED REACTIVITY OF HYPERVALENT ANIONIC SPECIES AS ELECTRON ACCEPTORS

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(Received 28 December 1988)

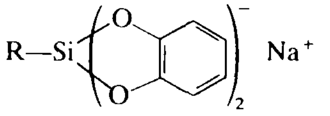
The unexpected behaviour of hypervalent anionic silicon (and germanium) species $[Si(o\text{-}O_2C_6H_3R')_3]^{2-}2M^+$, $[RSi(o\text{-}O_2C_6H_3R')_2]^-M^+$ and $[Ge(o\text{-}O_2C_6H_3R')_3]^{2-}2M^+$ ($R' = H, NO_2$) in the presence of some nucleophilic reagents involving a possible single electron transfer process is described. This capacity to accept electrons depends on both constituents of the complexes (ligand, central atom (Si or Ge), cation associated to the complex) and the nature of the reagents ($PhCH_2MgBr$, $Cp(CO)_2Fe\,Na$, $Li/Me_3SiCl/THF$ system).

Key words: Hypervalent; hexacoordinated anionic silicon; nucleophilic; electron transfer.

Recently we have reported the preparation of organosilanes avoiding the path through elemental silicon.[1] This process involves the depolymerisation of silica using catechol as a complexing agent under basic conditions, first reported by Rosenheim in water[2].

1 a M = Na
b M = K

Hexacoordinated complexes **1***a* and **1***b*, but also pentacoordinated **2**, and hexacoordinated germanium complexes **3** can undergo nucleophilic attack.[1,3,4]



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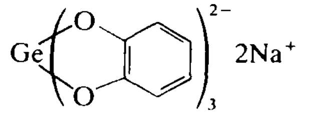

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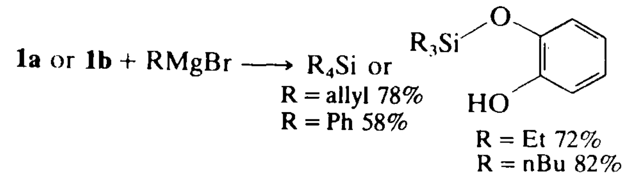
Reactions with Grignard or organolithium reagents lead to the formation of silicon (or germanium)–carbon bonds in good yields.



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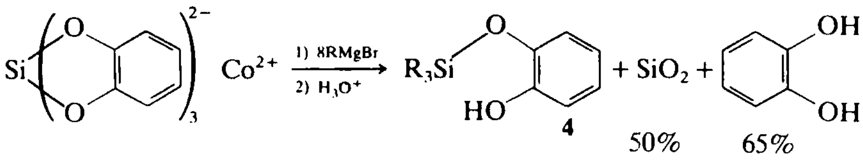
We report here the unexpected behaviour of these complexes in the presence of some nucleophilic reagents involving a possible single electron transfer process (SET).

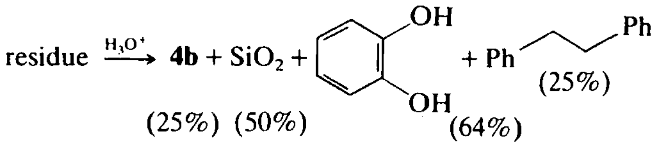
The reaction of an excess of Grignard reagent on the complex **1c** ($2M^+ = Co^{2+}$) in THF leads to a poor yield of organosilane **4** in opposition to the good yields obtained with **1a** or **1b**[1]. Surprisingly, a large excess of Grignard reagent is consumed during the reaction.



a R = nBu (17%)
b R = $PhCH_2$ (25%)
c R = nC_8H_{17} (20%)

Silica (50%) and catechol (65%) are partially† recovered in this process. The reaction mixture in the case of the benzyl Grignard was distilled before hydrolysis: 4.5 equivalents of toluene were recovered.

$$\mathbf{1c} + 8PhCH_2MgCl \longrightarrow 4.5\ PhCH_3 + \text{residue}$$



An acidic hydrolysis of the residue after distillation allowed the recovery of 25% of silane **4** ($R = PhCH_2$), 50% of silica, 64% of catechol based on **1c** and 25% of bibenzyl based on the benzyl Grignard. Two equivalents of toluene originate from the well known oxydation-reduction reaction of Grignard reagents with transition metal compounds.[5] We have checked that 2 equivalents of $PhCH_2MgCl$ are consumed in the reaction with $CoCl_2$ with the formation of toluene.

$$CoCl_2 + 2PhCH_2MgCl \longrightarrow 2PhCH_3$$

However, the reaction of $PhCH_2MgCl$, due to the presence of Co^{II}, cannot account for the formation of 4.5 eq. of toluene and 1.8 eq of bibenzyl. The formation of toluene and bibenzyl is indicative of a possible electron exchange between the Grignard reagent and the anionic part of the complex **1c** with the intermediate benzyl radical $PhCH_2\cdot$ giving either dimerization (formation of Ph$\diagup\!\!\diagdown\!\!\diagup$Ph) or abstraction of a hydrogen atom from the reaction mixture (formation of $PhCH_3$).

In the same way, we checked that the octyl Grignard reagent leads to a mixture of octane and octene before hydrolysis.

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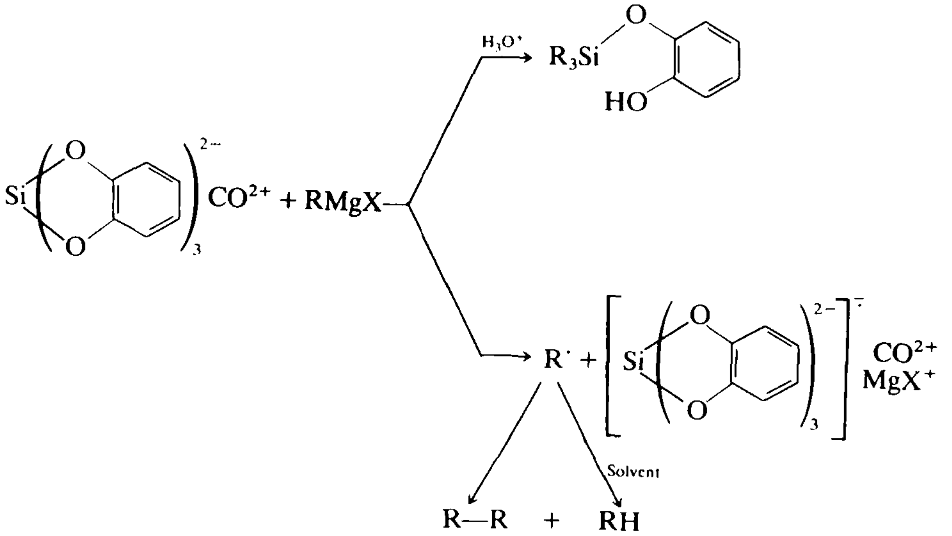
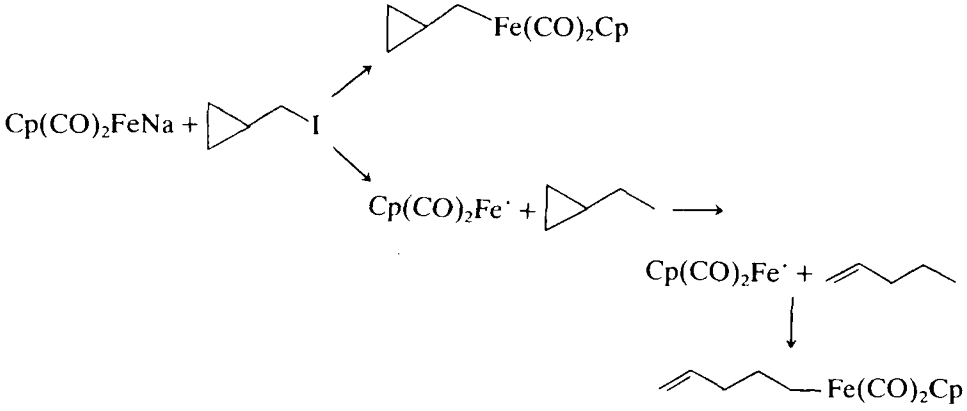
† In the case of the starting material **1a** or **1b**, it is possible to recover, quantitatively, SiO_2 and catechol after hydrolysis.



In order to support this hypothesis of an electron transfer process, we investigated the reactivity of the η^5-cyclopentadienyldicarbonyliron anion **5** towards complexes **1**, **2** and **3**. Indeed this anion **5** is known to be a versatile reagent. It can react either by nucleophilic substitution or by electron transfer towards alkyl halides[6].



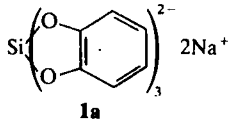
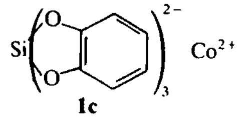
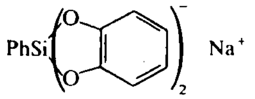
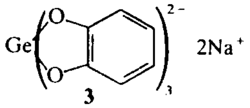
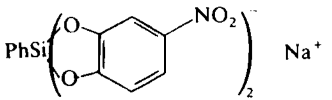
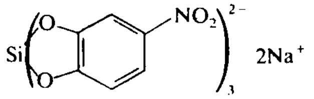
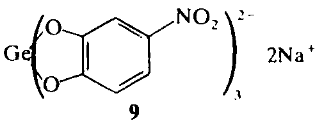
When complex **1a** was treated with **3** equivalents of $Cp(CO)_2FeNa$ **5**, only 1 equivalent of the dimer **6** was isolated and the excess of **5** was trapped with MeI[7] according to the reaction.

$$\underset{}{\mathbf{1a}} + \underset{\mathbf{5}}{3Cp(CO)_2FeNa} \xrightarrow[3\text{ days}, 25°C]{THF} \xrightarrow{MeI} \underset{\mathbf{6}}{1[Cp(CO)_2Fe]_2} + 1Cp(CO)_2FeMe$$

Apparently the anion **5** does not proceed by a nucleophilic attack at silicon since no Si–Fe bond is formed. In contrast, the formation of the dimer **6** seems to be in agreement with an electron transfer from **5** to complexes **1**, **2**, **3**, (Table I).

TABLE I

Comparative reactivities of $Cp(CO)_2FeNa$ **5** and the system $Li/Me_3SiCl/THF$ towards complexes

Complex	$Cp(CO)_2FeNa$ **5** (eq consumed)	$[Cp(CO)_2Fe]_2$ **6** (eq formed)	Eq Li (eq consumed)
 **1a**	2	1	1
 **1c**	4	2	6.6
 **2**	1	0.5	
 **3**	2	1	6
 **7**	6* (4)	3* (2)	
 **8**	9* (6)	4.5* (3)	9
 **9**	6* (3)	3* (1.5)	6

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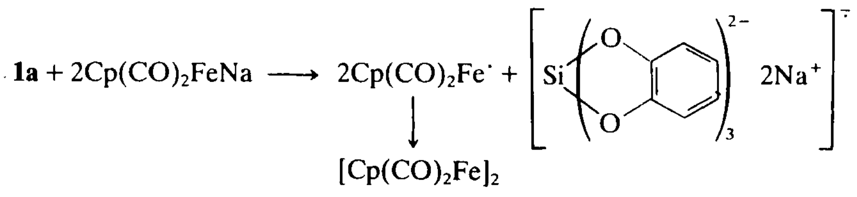
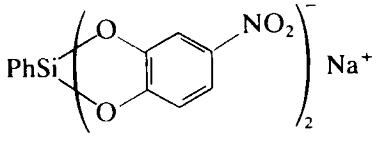
*We have checked that the nitro group reacted with 1 eq of **5** giving **6**.



In order to corroborate these unexpected results involving an electron transfer from a neutral entity to an anionic species, we have investigated the reactivity of the system Li/Me_3SiCl/THF towards complexes **1**, **2** and **3**. This system has a very good ability to transfer electrons.[8] Furthermore, we have extended the study of the reactivity of the anion $Cp(CO)_2FeNa$ **5** and of the system Li/Me_3SiCl/THF towards silicon and germanium complexes **7**, **8** and **9** having a nitro group as a substituent on the catechol. Nitro groups are well known for promoting the capacity of substrates to accept electrons when they are treated by Grignard reagents[9] or alcoholates.[10]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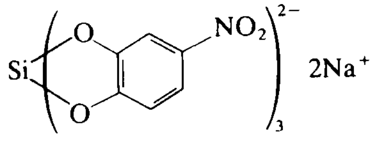
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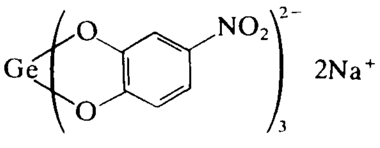
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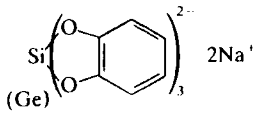
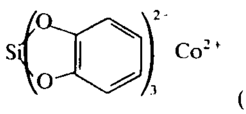
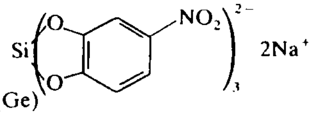
In the case of the system Li/Me_3SiCl/THF, the disappearance of lithium has been observed (Table II). No reaction occurs between Li and Me_3SiCl under the same conditions.

These results confirm the hypothesis of the possible electron transfer between the organometallic reagent and the anionic moiety of complexes **1**, **2**, **3**, **7**, **8**, **9**.

In conclusion, the experimental results reported here seem to be in agreement with a radical process. The reactions are summarized in Table II. It is important to point out that the reactivity of hypervalent silicon (or germanium) species with highly reducing agents able to react by an electron transfer process depends on the constituents of the complexes (the nature of the ligand, the central atom (Si or Ge), the cation associated with the complex) and also on the nature of the reagent.

TABLE II

			
RMgX	Substitution R_3Si, R_4Si	Substitution + electron transfer reaction	No substitution Side reaction on nitrogroup
$Cp(CO)_2Fe^-$	Electron transfer reaction	Electron transfer reaction	Electron transfer reaction
Li/Me_3SiCl/THF	Electron transfer reaction	Electron transfer reaction	Electron transfer reaction

Work is in progress in order to determine the nature of the silicon species formed during these reactions. Indeed, only silica has been partially isolated in reactions 3 and 4. We do not recover silicon metal.

EXPERIMENTAL

Reactions were carried out under nitrogen in Schlenk tubes on a vacuum line. Solvents were dried and deoxygenated. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer, ^{1}H NMR spectra with a Varian EM 360 spectrometer and ^{29}Si NMR spectra with a Bruker WP-200 SY. Chemical shifts, δ, are relative to Me_4Si. Starting materials were commercial products or were prepared by literature methods.

Cobalt tris(benzene-1,2 diolato)silicate **1c**. A solution of 1.52 g (40 mmoles) of MeOLi was added to a solution of 2.6 g (20 mmoles) of $CoCl_2$ in 30 ml of methanol. The solid obtained was filtered and washed with methanol in order to eliminate LiCl. Cobalt methoxide was obtained quantitatively and then suspended in 120 ml MeOH. A solution of 6.6 g (60 mmoles of catechol and 3.04 g (20 mmoles) of $Si(OMe)_4$ was added to this suspension. The reaction mixture was stirred 24 h under reflux. The solid formed was filtered and washed three times with methanol and twice with ether, then dried under vacuum at 120°C during 48 h. 6.2 g (75%) of complex **1c** were obtained as a pale pink powder. IR (KBr) ν (cm^{-1}): 1595 w, 1490 s, 1455 w, 1340 w, 1250 s, 1103 w, 1020 w, 870 w, 820 s, 740 s, 700 w.

Sodium tris(4-nitrobenzene-1,2 diolato)silicate **8**. A solution of 1.08 g (20 mmoles) of MeONa in 40 ml of MeOH was added to a solution of 4.65 g (30 mmoles) of 4-nitrocatechol and 1.52 g (10 mmoles) of $Si(OMe)_4$ in 20 ml of methanol. The mixture was stirred 2 hours, the solvent was then evaporated under vacuum and the residue washed with ether, filtered and dried under vacuum 24 h at 110C. 5.22 g (98%) of complex **8** were isolated as an orange powder. IR (KBr) ν (cm^{-1}): 1590 w, 1485 s, 1325 w, 1265 s, 1070 w, 945 w, 863 w, 835 w, 815 s, 750 w, 732 w, 700 s.
^{1}H NMR (CD_3CD): 6.4–6.6 (3H, multiplet, aromatics meta of NO_2); 7.4–7.6 (6H, multiplet, aromatics ortho of NO_2). ^{29}Si NMR (CD_3OD): −138,57.

Sodium bis(4-nitrobenzene-1,2 diolatophenyl)silicate **7**. **7** was prepared in the same way as **8** starting from $PhSi(OEt)_3$. IR (KBr), ν (cm^{-1}): 1592 w, 1480 s, 1363 w, 1325 s, 1275 s, 1238 w, 1112 w, 1065 w, 840 w, 821 s, 730 w, 740 w, 695 w.
^{1}H NMR (CD_3OD): 6.8–7.0 (2H, multiplet, aromatics meta of NO_2); 7.1–7.3 (4H, multiplet, aromatic ortho of NO_2); 7.6–7.8 (5H, multiplet, phenyl group). ^{29}Si NMR (CD_3OD): −83.21.

Reaction of benzylmagnesiumbromide with complex **1c**. Benzylmagnesiumbromide (1.05 M solution) was added equivalent by equivalent to 2.05 g (5 mmoles) of cobalt tris(benzene-1,2 diolato)silicate suspended in 40 ml of THF. When the test with Gilman's reagent (11) remained positive during 36 h after addition of Grignard, the reaction mixture was distilled under vacuum, the distilling fraction was trapped in liquid nitrogen. The residue of distillation was taken up with THF and distilled again in order to prevent any loss of product. This work-up was made twice. The fractions of distillation were put together and analysed by GC. Toluene (56%) was titrated by GC using cyclooctene as internal standard. The solid residue of the distillation was taken up with ether, hydrolysed with 10% H_2SO_4, and then extracted with ether. Silica (0.15 g; 50%) was filtered. The joined organic layers were washed with 10% NaOH, with water and dried over $MgSO_4$. They were analysed by GC. Bibenzyl (25%) was titrated using biphenyl as an internal standard. Tribenzyl (2-hydroxyphenoxy)silane was separated from bibenzyl and biphenyl by chromatography on silica using pentane and pentane/ether (90/10) as eluant. 0.510 g (25%) of **4** ($R = PhCH_2$) were recovered. The aqueous basic layers were acidified (pH = 3) with 25% H_2SO_4 and extracted with ether. Ether was washed with water and dried over $MgSO_4$. Solvent was evaporated and 1.05 g (64%) of catechol were recovered.

Reaction of $Cp(CO)_2FeNa$ with complex **1a** *is given as example.* 1.77 g (5 mmoles) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in solution in 55 ml of THF was stirred with an excess of sodium amalgam for 2 hours at room temperature. Mercury was decanted and the solution of anion (10 mmoles) was added dropwise to 1.33 g (3.33 mmoles) of **1a** in 20 ml of THF. The reaction was checked by IR spectroscopy. After 3 days at 60°C (no change in IR), the reaction mixture was treated with an excess of CH_3I (9 ml). IR spectroscopy indicated the transformation of the remaining anion **5** into $Cp(CO)_2FeCH_3$. The reaction mixture was evaporated and the residue taken up with CH_2Cl_2 and was chromatographed under nitrogen on acidic alumina. 0.72 g of $Cp(CO)_2FeCH_3$ (37%) yellow band eluted with light petroleum and 1.12 g of $[Cp(CO)_2Fe]_2$ (63%) red band eluted with CH_2Cl_2 were isolated and compared with authentic samples.[7] The yields cited are estimated gross yields, obtained by comparison with the chromatographic separation of a sample of known composition in a blank determination.

Reaction with Li/Me$_3$SiCl/THF with complex **3** *is given as example.* To 2.21 g (5 mmoles) of sodium tris (benzene-1,2 diolato)germanate **3** suspended in 25 ml of THF were added 0.245 g (35 mmoles) of lithium and 5 ml (40 mmoles) of Me_3SiCl. The reaction mixture became clear and then the color turned brown. It was stirred at room temperature for 16 h. The remaining lithium 0.035 g (5 mmoles) was isolated. The reaction mixture was filtered, 1.23 g of LiCl were isolated and compared by X-ray spectroscopy to an authentic sample. No silicon species could be isolated.

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