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Formation and multinuclear magnetic resonance investigation of silylammonium tetracarbonylcobaltate contact ion pairs

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Abstract: Silylcobalt tetracarbonyls were reacted with various amines (B) in non-polar solvents to form silylammonium tetracarbonylcobaltate contact ion pairs formulated as [$B\mathrm{SiR}_3^+$, $^-\mathrm{Co(CO)}_4$]. The compounds were characterized by IR and multinuclear magnetic resonance spectroscopy both in solution and in solid state. Their properties are analogous to the known ion pairs [$B\mathrm{H}^+$, $^-\mathrm{Co(CO)}_4$] and to amine adducts of halosilanes as well.

Keywords: Silyammonium tetracarbonylcobaltates, contact ion pairs, multinuclear magnetic resonance, ^{29}*Si CP/MAS*

1 Introduction

Several carbonylmetallate salts exist in the form of contact ion pairs [1]. Among the carbonylcobaltates, the ion pairing phenomenon is well documented. The changes in the structure and reactivity of alkali metal tetracarbonylcobaltate salts were explained by the pairing or separation of the ions depending on the solvents and or ligands added [2–5]. The properties of variously substituted ammonium salts of tertacarbonylcobaltate were investigated and discussed exhaustively. The contact ion pair character of their $\mathrm{Me_3NH^+}$ and $\mathrm{Et_3NH^+}$ salts both in non-polar solvents and in solid state has been

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demonstrated [6]. Analogous results were obtained for a number of amine adducts of $HCo(CO)_3L$ (L = CO, triaryl phosphine) complexes [7, 8]. Ion pairing was found also in the case of $R_3PH^+[Co(CO)_4]^-$ complexes, the intermediates of the phosphine substitution of $HCo(CO)_4$ [9].

The interaction of silylcobalt tetracarbonyls and amines was initially reported by Aylett [10] and then followed by MacDiarmid [11]. $B_2SiH_3^+[Co(CO)_4]^-$ (B = py, NMe_3) was formed from $H_3SiCo(CO)_4$ [10] while $R_3SiCo(CO)_4$ gave $BSiR_3^+[Co(CO)_4]^-$ (R = Me, Et, Cl) type ion pairs with $B = NMe_3$ [11]. The compounds formed were characterized by their IR spectra recorded either in polar solvents, or in the solid state. The authors concluded that the separated $[Co(CO)_4]^-$ ion was present in the compounds [10, 11]. We described earlier that $R_3SiCo(CO)_4$ (R = alkyl or aryl) complexes formed contact ion pairs with nitrogen bases in some non-polar solvents [12–14]. The $\nu(CO)$ infrared spectra of these species were in accordance with a C_{3v} symmetry analogous to the ammonium tetracarbonylcobaltates mentioned above (*cf.* ref. [6]). Such compounds may also appear as intermediates in catalytic reactions [15–17]. Till now, however, no contact ion pairs with a silicon–cobalt interaction have been isolated. In this paper we describe our preparative, kinetic and spectroscopic results concerning silylammonium tetracarbonylcobaltates.

2 Results

2.1 Synthesis and IR spectra

Silylcobalt tetracarbonyls (**1**) were reacted with an excess of various amines (B) in toluene or dichloromethane generally at -15 to +20 °C to form contact ion pairs **2** according to eq. (1) (Chart 1).

$$\underset{\mathbf{1}}{R_3SiCo(CO)_4 + B} \xrightarrow[\text{toluene or } CH_2Cl_2]{} \underset{\mathbf{2}}{[BSiR_3^{+},{}^{-}Co(CO)_4]} \qquad (1)$$

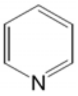
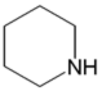
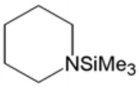
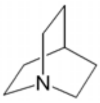
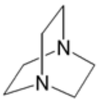
B R$_3$ (symbol)	–	 (py)	Et_3N	Et_2NH	 (pip)	 (tmspip)	 (quinuclidine)	 (dabco)
Me$_3$	**1A**				**2a**	**2b**		
Me$_2$Cl	**1B**		**2c**					
Et$_3$	**1C**		**2d**				**2e**	
Ph$_3$	**1D**	**2f**	**2g**	**2h**	**2i**		**2j**	**2k**
(OSiMe$_3$)$_3$	**1E**						**2l**	

Chart 1

We propose the formulation [BY$^+$, $^-$Co(CO)$_4$] (Y = H, SiR$_3$) for the contact ion pairs instead of BY$^+$[Co(CO)$_4$]$^-$ which will be used for solvent-separated ion pairs.

The solvents used in this study were aprotic and slightly polar ($\varepsilon_{20°C} < 10$). Oxygen-containing aprotic solvents like ethers were inapplicable since they react with silylcobalt complexes [13, 15, 16].

Reaction (1) was usually monitored by IR spectroscopy but conductivity measurements have been made as well. Adding one equivalent of quinuclidine to a 0.001 M solution of **1C** in CH$_2$Cl$_2$, increased the conductivity by about one order of magnitude. For **2e**, however, proved unambiguously as a non-electrolyte on the basis of its molar conductivity of $\Lambda_{\mathbf{2e}} = 1.55\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$ (25.0 °C, $c = 0.001$ M in CH$_2$Cl$_2$; for comparison: $\Lambda_{\mathrm{Bu4NClO4}} = 61.0\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^-$ under the same conditions, *cf.* refs. [18, 19]).

The IR spectra of [BSiR$_3^+$, $^-$Co(CO)$_4$] and those of the mentioned [BH$^+$, $^-$Co(CO)$_4$] ion pairs (*cf.* refs. [3, 4]) were very similar in the ν(CO) region concerning position of the bands and their relative intensities (Table 1).

Table 1 IR spectral data of **2** and some related complexes in the ν(CO) region.

Complex	ν(CO)/cm^{-1}	Ref.
2a	2020w 1924s 1898vs,br [a]	
2b	2018w 1924s 1900vs,br [a]	
[(tmspip)H$^+$, $^-$Co(CO)$_4$]	2018w 1922s 1898vs,br [a]	
2c	2014w 2020sh 1892vs,br [a]	
2d	2019w 1934s 1895vs [b]	[12]
2e	2020w 1931s 1897vs,br [b]	
2f	2010w 1930sh 1890vs,br [a]	
[pyH$^+$, $^-$Co(CO)$_4$]	2016w 1936s 1903vs [b]	[17]
2g	2016w 1921s 1895vs,br [a]	
2g	2016vw 1890vs,br [a,c]	
Ph$_4$P$^+$[Co(CO)$_4$]$^-$	1891vs, br [a]	[20]
2h	2010w 1930sh 1890vs,br [a]	
2i	2014w 1920s 1896vs,br [a]	
2j	2014w 1920s 1898vs,br [a]	
2k	2020w 1933s 1898vs [b]	
[(quinuclidine)H$^+$, $^-$Co(CO)$_4$]	2020w, 1931s, 1896vs [b]	[7]
2l	2019w 1925s 1896vs,br[a]	

[a] In dichloromethane;
[b] In toluene;
[c] A 20-fold excess of triethylamine was added.

The conversion of **1** depended on the properties of R, B and the solvent. In the case of the sterically less favorable amines (*e.g.* triethylamine), a higher excess is needed (up to 20-fold) to convert **1** to near quantitative yields of **2**. If at least a ten-fold excess of amine was used, the polarity of the reaction medium was enhanced which resulted in the appearance of the solvent-separated ion pair especially in dichloromethane (*cf.* refs. [8, 20], see Table 1). Quinuclidine and dabco gave the most stable complexes, thus, the products **2j**, **2k**, and **2l** could be isolated, but no crystals suitable for an X-ray structure determination could be obtained till now. After dissolving **2j, 2k** or **2l** in toluene or dichloromethane, the formation of **1D** or **1E**, respectively, could not be detected.

The ν(CO) region IR spectra of the reaction mixture of **1C** and quinuclidine recorded at different temperatures are shown in Fig. 1. Beside **1C** and **2e**, absorptions of a third component can be seen in the spectrum at –30 °C (Fig. 1b, indicated by arrows), however, its concentration was very low at room temperature (Fig. 1c).

The complexes $[B\mathrm{SiR}_3^+, {}^-\mathrm{Co(CO)}_4]$ are very sensitive to air and humidity. They should be stored below –30 °C. The silylpyridinium tetracarbonylcobaltate contact ion pair (**2f**) is particularly unstable thermally. Its decomposition to $Co_2(CO)_8$ and other products could be observed by IR spectroscopy at 0 °C (*cf.* ref. [21]). Blue-violet decomposition products containing Co(II) precipitated also from the solutions of other **2** complexes when standing at room temperature for several hours (*cf.* ref. [22]). These properties limited the methods and the time for examinations of these complexes.

2.2 Kinetics

The initial rate of the reaction

$$\mathbf{1D} + \mathrm{NEt}_3 \longrightarrow \mathbf{2Db} \tag{2}$$

was measured by IR spectroscopy at 20 °C in dichloromethane solution. Clear first order dependences were found for both of the starting materials, and the rate was independent of carbon monoxide (Table 2).

Table 2 The effects of the concentrations of $Ph_3SiCo(CO)_4$, triethylamine and carbon monoxide on the initial rate of reaction (2)[a]

$[Ph_3SiCo(CO)_4]$/M	[triethylamine]/M	10^5r/Ms^{-1}	10^3k/M^{-1}s^{-1} [b]
0.008	0.039	1.13	3.62
0.019	0.038	3.42	4.74
0.027	0.038	4.53	4.41
0.035	0.039	6.80	4.98
0.019	0.078	7.85	5.30
0.019	0.117	11.00	4.95
0.020[c]	0.113	9.75	4.31
0.019	0.150	12.60	4.42

[a] 20.0 °C, in dichloromethane, under Ar;
[b] $k = r[Ph_3SiCo(CO)_4]^1[\text{triethylamine}]^1$;
[c] PCO = 98.4 kPa.

2.3 NMR spectra

NMR data of several compounds [$B\mathrm{SiR}_3^+$, $^-\mathrm{Co(CO)}_4$] and of some precursors are compiled in Table 3. The complexes **2b** and **2e** were prepared and investigated *in situ*. The spectra of the isolated complexes **2j**, **2k**, and **2l** were recorded both in solution and in solid state.

The effect of the ion-pairing on the ^{1}H and ^{13}C NMR spectra is similar to that found in the case of [$B\mathrm{H}^+$, $^-\mathrm{Co(CO)}_4$] [7, 8]. Although the signals of the substituents of free and *N*-bound silicon atom differentiate from each other, no real tendency could be found concerning the chemical shift changes. Both the ^{1}H and ^{13}C signals are, however, solvent-dependent (Table 3). In contrast, ^{1}H and ^{13}C NMR resonances of the free amine could not be distinguished from those that were bound, only a broadening of the signals was observed (*vide infra*). At the same time, ^{13}C signals for CO ligands were found only in the *in situ* prepared concentrated probes of **2e** (compare with the related results for [$B\mathrm{H}^+$, $^-\mathrm{Co(CO)}_4$], see refs. [7, 8]).

The ^{13}C{^{1}H} spectra of **1C**-quinuclidine system recorded at several temperatures are shown in Fig. 2. We observed three pairs of Si-ethyl signals, the intensive high-frequency pair belongs to the free (not *N*-bound) SiEt_3 group (*cf.* ref. [23]). Based on the chemical shift values, the two low-frequency pairs were assigned to the *N*-bound SiEt_3 group**,** the ratio of these latter ones was clearly temperature-dependent. Interestingly enough, signals of quinuclidine showed the same temperature dependence as one of the *N*-bound SiEt_3 pair indicating that this pair and the quinuclidine take part in the same exchange process (*vide infra*).

By increasing the temperature of the sample ([quinuclidine]:[**1C**] = 1:1) stepwise to 358 K and then cooling it to 303 K resulted in the near disappearance of the signals for the free SiEt_3 groups. At the same time, the intensity of the *N*-bound SiEt_3 signals which were not involved in the exchange grew simultaneously (see Fig. 2a-d). The IR analysis of the sample showed the formation of **2e**.

In the ^{13}C{^{1}H} spectra recorded in $\mathrm{CD_2Cl_2}$, the signals of the *ortho*- and either the *meta*- (**2j**), or the *para*-carbon (**2k**) were split with an intensity ratio of ≈1:2 at 298 K (Table 3).

A striking difference (a –37 to –50 ppm low-frequency shift) was observed in the position of the ^{29}Si resonances of the **1** complexes, and those of the relevant ion pairs **2**. ^{29}Si CP/MAS spectra of **2j** and **2k** are shown in Fig 3.

The ^{59}Co spectra of **2e** and **2j**, recorded in toluene-d_8 and $\mathrm{CD_2Cl_2}$, respectively, exhibited intensive narrow resonances near to that of the solvated $[\mathrm{Co(CO)}_4]^-$ ion [26], but they were definitely broader ($\Delta\nu_{1/2}$ = 180 and 325 Hz, respectively) (see Table 3). The ion pair [(quinuclidine)H$^+$, $^-\mathrm{Co(CO)}_4$] [7] was measured in $\mathrm{CD_2Cl_2}$ and it showed a ^{59}Co resonance at –3078 ppm with a broadening similar to that of observed in the case of **2j**.

Table 3 NMR spectroscopic data of some complexes **2** and their precursors at 298 K.

Compound	^{1}H-NMR, δ/ppm	^{13}C-NMR, δ/ppm	^{29}Si-NMR, δ/ppm	^{59}Co-NMR, δ/ppm
1A	0.02 ^{a}	8.3 (CoSiCH$_3$)^{a}	44.36 ^{a,b}	
2b	–0.03 (s, ≈9H, CoSiCH$_3$); 0.04 (s,≈ 9H, NSiCH$_3$); 1.35 (m, br 6H, CH$_2$-γ, CH$_2$-β); 2.53 (m, br 4H, CH$_2$-α)^{a}	–0.2 (NSiCH$_3$); 2.9 (CoSiCH$_3$); 26.9 (CH$_2-\gamma$); 28.1 (CH$_2-\beta$); 47.5 (CH$_2$-α)^{a}	-5.8 (CoSi); 3.7 (NSi)^{a}	
1C	0.58 (q, 6H, SiCH$_2$); 1.08 (t, 9H, CH$_3$)^{c,d}	8.8 (CH$_3$); 12.5 (SiCH$_2$); 200.1 (CO)^{c,e}	54.9 ^{c,e}	
2e	0.57 (m, 6H, SiCH$_2$); 0.99 (m, 9H, CH$_3$); 1.17 (m, br 6H, CH_2CH); 1.38 (m, br 1H, CH); 2.51 (m, br 6H, NCH$_2$)^{d}	6.8 (SiCH$_2$)^{f}; 7.0 (CH$_3$); ≈20.6 (CH)^{g}; 23.8 (br, CH$_2$CH); 46.7 (br, NCH$_2$); 201.0 (CO) ^{d,e,h}	9.2 ^{e}	-3082 br^{e,n} ($\Delta\nu\frac{1}{2}$= 180 Hz)
1D	7.1-7.8 (m, C$_6$H$_5$)^{a,c}	128.7 (C$_m$); 130.3 (C$_p$); 136.2 (C$_o$); 139.1 (C$_{ipso}$), 199.6 (CO)^{a,c}	26.5^{d}	
	7.2-7.7 (m, C$_6$H$_5$)^{c,d}	127.9 (C$_m$); 129.6 (C$_p$); 135.4 (C$_o$); 138.2 (C$_{ipso}$); 198.8 (CO)^{c,i}	26.5^{j}	
Quinuclidine	1.28 (m, 6H, CH_2CH); 1.49 (m, 1H, CH); 2.75 (m, 6H, NCH$_2$)^{a}	21.4 (CH); 27.2 (CH$_2$CH); 48.2 (NCH$_2$)^{a}		
2j	1.01 (m, 6H, CH_2CH); 1.23 (m, 1H, CH); 2.52 (m, 6H, NCH$_2$); 7.0-8.0 (m, 15H, C$_6$H$_5$)^{a}	20.6 (CH); 25.4 (CH$_2$CH); 47.4 (NCH$_2$); ≈128.7 (C$_m$)^{k}; 130.2 (C$_p$); 136.0 (C$_o$); 138.1 (C$_{ipso}$)^{a,l}	-12.8 ^{d}	-3080 br^{d,n} ($\Delta\nu\frac{1}{2}$ = 325 Hz)
	1.82 (m, 6H, CH_2CH); 2.06 (m, 1H, CH); 3.10 (m, 6H, NCH$_2$); 7.1-7.7 (m, 15H, C$_6$H$_5$)^{d}	20.0 (CH); 24.2 (CH$_2$CH); 47.6 (NCH$_2$); 128.3 (C$_m$, minor) ^{m}; 128.4 (C$_m$, major) 130.4 (C$_p$); 135.4 (C$_o$, minor); 135.6 (C$_o$, major);136.5 (C$_{ipso}$)^{d,l}	-13.0 ^{j}	

[a] In C$_6$D$_6$; [b] Cf. ref. [23]; [c] Cf. ref. [24]; [d] In CD$_2$Cl$_2$; [e] In C$_7$D$_8$; [f] See Text and Fig. 2; [g] Covered by signals of C$_7$D$_8$; [h] At 303 K; [i] In CDCl$_3$; [j] 59Si CP/MAS; cf. ref. [25], [k] Covered by signals of C$_6$D$_6$; [l] No signals of CO ligands were found; [m] See text; [n] Cf. ref. [26].

Table 3 (continued) NMR spectroscopic data of some complexes **2** and their precursors at 298 K.

Compound	^{1}H-NMR, δ/ppm	^{13}C-NMR, δ/ppm	^{29}Si-NMR, δ/ppm	^{59}Co-NMR, δ/ppm
2k	2.84 (s,br 12H, CH_2); 7.1-7.7 (m, 15H, C_6H_5)^d	46.6 (br, CH_2); 128.3 (C_m); 130.2 (C_p, minor); 130.5 (C_p, major); 135.5 (C_o, minor); 135.6 (C_o, major);136.0 (C_{ipso})^{a,l}	–19.6 ^{d} –18.4 ^{j}	
1E	0.09 (s, 27 H, $Si(CH_3)_3^g$	1.3 ($OSi(CH_3)_3$); 198.6 (CO)^g	–56.8 (CoSi); 11.0 ($OSi(CH_3)_3$)^d	
2l	0.10); 1.79 (m,br 6H, CH_2CH_2CH); 2.02 (m,br, 1H, CH); 3.06 (m,br 6H, NCH_2)^d	1.7 ($OSi(CH_3)_3$); 20.3 (CH); 24.8 (CH_2CH_2CH); 47.8 (NCH_2)^{d,l}	-94.2 (CoSi); 11.3 ($OSi(CH_3)_3$)^d	

^{a} In C_6D_6; ^{b} Cf. ref. [23]; ^{c} Cf. ref. [24]; ^{d} In CD_2Cl_2; ^{e} In C_7D_8; ^{f} See Text and Fig. 2; ^{g} Covered by signals of C_7D_8; ^{h} At 303 K; ^{i} In $CDCl_3$; ^{j} 59Si CP/MAS; cf. ref. [25], ^{k} Covered by signals of C_6D_6; ^{l} No signals of CO ligands were found; ^{m} See text; ^{n} Cf. ref. [26].

3 Discussion

3.1 Kinetics and spectroscopic properties

The present kinetic results are analogous to those obtained earlier for ethyloxirane [27] and isobutyraldehyde [28] as nucleophiles. A contact ion pair intermediate similar to **2** was suggested for the reaction of oxiranes with silylcobalt tetracarbonyls [27, 29, 30]. Furthermore, formation and properties of the ion pairs **2** are remarkably analogous to those of some known neutral pentacoordinated organosilicon compounds. Since tetracarbonylcobaltate is regarded as a pseudohalide [31], the similarity of **2** and amine adducts of halosilanes is plausible. The latter species were supposed as intermediates in amine catalyzed nucleophilic substitution as well as in racemisation of silanes, $SiClR^1R^2R^3$ [32]. Corriu and coworkers found a substitution rate law of first order both for chlorosilane and for the catalyst. Our kinetic results led to analogous conclusion, *i.e.* a nucleophilic attack of the amine on the Si-atom of **1** took place in reactions (1) and (2).

In contrast to the majority of neutral pentacoordinated organosilanes, no evidence was obtained that **2** would be formed reversibly. The temperature-dependent IR (Fig. 1) and $^{13}C\{^1H\}$ spectra (Fig. 2) recorded from the reaction mixtures of **1C** and quinuclidine in toluene indicated, however, some fluxionality of the system. Note, that the observed temperature-dependence of the $^{13}C\{^1H\}$ spectra is unusual in the sense that narrowing of the signals is detected at lower temperatures as if the system were already below the coalescence, but the signal of the other exchange site is still not seen. A likely explanation can be given by assuming a small intensity short-lived "silent" exchange partner whose broad signal is buried in the noise [33].

We concluded from the temperature-dependent ^{13}C spectra (Fig. 2a-c) that quinuclidine and one of the N-bound SiEt$_3$ pairs participate in an exchange process, whilst the other one does not. The former may be a transient species. Similar result could be inferred from the IR spectra demonstrated in Fig. 1, *i.e.* an intermediate detectable at low temperature is transformed into **2e**. The unstable species may be described by the structure **3** (see Scheme 1). The IR spectra of **2e** (and the other **2** complexes) – which indicates a C_{3v} symmetry of the Co(CO)$_4$ moiety – as well as the ^{29}Si and ^{59}Co resonances are in accordance with a contact ion-paired form (Scheme 1) taking into consideration the analogy of **2** and the compounds [BH$^+$, $^-$Co(CO)$_4$] (*cf.* refs. [7, 8]) . Cobalt and silicon have a distorted trigonal bipyramidal coordination sphere in **2**, *i.e.* amine and Co(CO)$_4$ are axially coordinated to silicon. The slow formation of **2** from **3** — which is in fast equilibrium with **1** and the amine (B) — is consistent with our kinetic results. By assuming a reversible dissociation of **2** to the isolated ion pair **5** (this equilibrium is far on the side of **2**) the ^{59}Co spectra can be interpreted as well (*vide infra*).

The similarity of the ^{29}Si chemical shifts of **2** observed in solution and in the solid state supports the existence of a Co–Si interaction in both phases. The change of the ^{29}Si resonance in the pairs **1A-2b**, **1C-2e**, **1D-2j, 1D-2k**, and **1E-2l** (see Table 3) is analogous to that observed in amine adducts of organosilanes in which the increase of the coordination number from four to five resulted in a considerable (generally –10 to –50 ppm) low-frequency shift of the ^{29}Si signals [32, 34].

In order to prove unambiguously the presence of contact ion pairs in the solid state, we have recorded ^{29}Si CP/MAS spectra of **2j** and **2k**. It is known that the presence of scalar and dipolar coupling between a spin-1/2 and a quadrupolar nuclei can be reflected in the line shape of the spin-1/2 nucleus [25, 35]. Several examples of the so called second order quadrupolar or residual dipolar effect concerning the ^{29}Si–^{59}Co spin-pair have already been reported [35]. However, we are not aware of any report concerning the line of a ^{29}Si nucleus coupled to two different quadrupolar nuclei (^{14}N and ^{59}Co). Basically, the overall splitting pattern may be considered as the convolution of the different splittings. For **2j**, the CP/MAS spectrum exhibits a complicated pattern indeed (see Fig. 3), however, only the effect of the spin-7/2 ^{59}Co nucleus can be proved unambiguously. Eight unequally distanced lines are expected if only the cobalt nucleus were "seen" by the ^{29}Si [25]. Although the observed transitions are not sufficiently resolved, deconvolution of the experimental lineshape supports the existence of eight resonances. As far as it can be judged from the width of the whole pattern ($\approx$ 300 Hz), the absolute value of the one-bond ^{29}Si–^{59}Co coupling is about 40-50 Hz. Coupling to the ^{14}N nucleus could not be confirmed here, probably due to the fast ^{14}N relaxation or reduced dipolar coupling *i.e.* the larger distance between the two nuclei (*vide infra*).

For **2k**, the observed pattern is even more complicated (see Fig. 3), due to the fact that in this case even coupling to the other quadrupole, the ^{14}N nucleus is also mediated to the ^{29}Si by the residual dipolar effects. Apart from the sign of the quadrupolar shift, the ^{29}Si–^{14}N spin-pair is believed to behave analogously to the ^{13}C–^{14}N pair, at least in the sense that an unsymmetrical doublet is expected due to the identical effects of the m = +/−1 states of the ^{14}N spin (I = 1) on the ^{29}Si signal and to the opposite shift caused by the m = 0 ^{14}N state [25]. Indeed, the observed pattern can be interpreted this way qualitatively. The two parts of the pattern are separated by more 150 Hz, which is definitely larger than the expected ^{29}Si–^{59}Co coupling or quadrupolar shift values, *i.e.* the whole pattern cannot be caused by the simple cross-overs of the J-coupled ^{29}Si–^{59}Co transitions. Concerning the whole width of the two parts of the pattern (≈300 and 265 Hz) the absolute value of the one-bond ^{29}Si–^{59}Co coupling is about 40-45 Hz.

The ^{59}Co-^{14}N distances observed in analogous [BH$^+$, $^-$Co(CO)$_4$] (B = quinuclidine or dabco) complexes are different by 0.13 Å (they are 3.576 and 3.446 Å, respectively [7]) which confirms the possibility of a rather different residual dipolar coupling in **2j** and **2k**, too. This could explain, in part at least, the presence of the transferred quadrupolar effect of the ^{14}N nucleus in the dabco complex, **2k** and its absence from the ^{29}Si CP/MAS spectrum of the quinuclidine complex, **2j**.

It is known from the literature that both **1D** [21], and HCo(CO)$_4$[36] have ^{59}Co signals in the low-frequency region characteristic for the Co(−1) oxidation state [37]. The ^{59}Co shifts of **2e** and **2j** are also in this region. The ^{59}Co resonances are generally very broad unless there is tetrahedral, cubic or higher symmetry around the Co nucleus that cancels the quadrupolar relaxation contribution [37]. Note that in the case of equilibrium between a high and low symmetry species the line width will be heavily affected. Consequently, the position and line widths of the ^{59}Co signals of **2e** and **2j** are explainable with a structure like **2** and with the equilibrium **2** $\rightleftarrows$ **5** which is far on the side of **2**.

4 Conclusions

We have found that silylammonium tetracarbonylcobaltate contact ion pairs, [BSiR$_3^+$, $^-$Co(CO)$_4$] (**2**) are formed by the nucleophilic attack of amines on the Si-atom of silylcobalt tetracarbonyls (**1**). The IR and NMR spectra of the complexes **2** are in accordance with a C_{3v} symmetry of the Co(CO)$_4$ moiety and a distorted trigonal bipyramidal coordination sphere of Co and Si, *i.e.* amine and Co(CO)$_4$ are axially coordinated to silicon. To our knowledge, the complexes **2** are the first examples which may be regarded to have pentacoordinated silicon in a bonding interaction with a transition metal atom. Their properties are analogous to the known ion pairs [BH$^+$, $^-$Co(CO)$_4$] and to amine adducts of halosilanes as well.

5 Experimental

5.1 General

All manipulations involving air-sensitive compounds were carried out by the usual Schlenk technique using deoxygenated, dry solvents and gases as well as reaction vessels with magnetic stirring. Conductivity measurements have been performed using a Radelkis OK-102/0 type conductivity meter and an electrode of the type K-902 with a cell constant of 0.68 cm^{-1} (Radelkis). Infrared spectra were recorded by using a 0.06-0.12 mm CaF_2 cuvette on Specord IR 75, Specord M 80 (Carl Zeiss, Germany) or Avatar 330 FT-IR (Thermo Nicolet, USA) spectrometers, which were calibrated with benzene (1959.6 cm^{-1}) and polystyrene (1601.4 cm^{-1}).

Silylcobalt tetracarbonyls [12, 23, 38] and *N*-trimethylsilyl-piperidine [39] were prepared by literature methods. Other amines were commercially available compounds which were dried by standard techniques [40] and distilled before use.

5.2 Synthesis of 2

To a solution of **1** (0.2 mmol) in toluene or dichloromethane (5 ml), a 1.1 to 20-fold excess of the amine was added dropwise at –15 to +20 °C. Probe(s) for IR spectroscopic analysis was taken from the reaction mixture.

In the cases of preparative runs, a 1.1-fold excess of quinuclidine or dabco was added in small portions to a solution of **1D** or **1E** (2.0 mmol) in dichloromethane (20 ml) at –15 °C. The solution was allowed to warm up to 0 °C after the addition was complete, stirred for 2 hours and stored in a refrigerator overnight. Then the mixture was filtered and the mother liquor was cooled to –78 °C for crystallization. **2j**, **2k** and **2l** gave white microcrystals. **2l** was also obtained from the hexane solution of **1E** from the addition of quinuclidine dissolved in hexane. The precipitate formed was recrystallized from toluene-dichloromethane (3:1).

2j: Yield: 64%. Anal. Calc. for $C_{29}H_{28}CoNO_4Si$: C, 64.31; H, 5.21; N, 2.59; Co, 10.88. Found: C, 64.0; H, 5.1; N, 2.5; Co, 10.6%.

2k. Yield: 73%. Anal. Calc. for $C_{28}H_{27}CoN_2O_4Si$: C, 61.70; H, 5.00; N, 5.14; Co, 11.00. Found: C, 62.1; H, 5.2; N, 5.3; Co, 10.5%.

2l: Yield: 86%. Anal. Calc. for $C_{20}H_{40}CoNO_7Si_4$: C, 41.57; H, 6.97; N, 2.42; Co, 10.20; Si, 19.44. Found: C, 41.2; H, 7.0; N, 2.5; Co, 10.1; Si, 19.8%.

5.3 Kinetics

Kinetic measurements were performed as described previously [33, 41]. The reaction was started by injecting triethylamine stock solution into the vigorously stirred solution of **1D** in dichloromethane. Samples for IR analysis were taken by a gas-tight syringe and filled through a three-way Hamilton valve and Teflon tubing into the 0.06-0.12 mm

CaF_2 cuvette. Molar absorbance of **1D** in dichloromethane at 2087 cm^{-1}, ε_M 1708 cm^2 $mmol^{-1}$.

5.4 NMR techniques

The NMR spectra were recorded on a Varian UNITY 300 spectrometer operating at 7.04 Tesla. For ^1H (300 MHz), ^{13}C (75.4 MHz), ^{29}Si (59.59 MHz) spectra, we used a 5 mm Varian Broad Band probe and standard Varian software. Chemical shifts are shown and given relative to external TMS. In the case of ^{59}Co (70.84 MHz), $K_3Co(CN)_6$ was used as external reference. The solution state ^{29}Si NMR spectra were obtained either by direct measurement or by the DEPT technique making use of the two-bond ^1H-^{29}Si scalar couplings. Line widths of 2-3 Hz were common. The solid state ^{29}Si MAS spectra were recorded on a Doty XC5 probe using 5 mm o.d. zirkonia rotors. Chemical shifts were obtained by the substitution method, the proper ^1H : ^{29}Si cross polarization and ^1H decoupling conditions were checked with crystalline tetrakis(trimethylsilyl)silane. Samples were spun between 3000 and 8000 Hz. The 90° pulse width was 6 micros, the acquisition time 50 msecs. Relaxation delays of 30 and 5 sec were used in the direct MAS and CPMAS experiments, respectively. In the latter contact times of 3-4 msecs were applied.

^1H and ^{13}C NMR data of the amines used were taken mostly from the literature [42].

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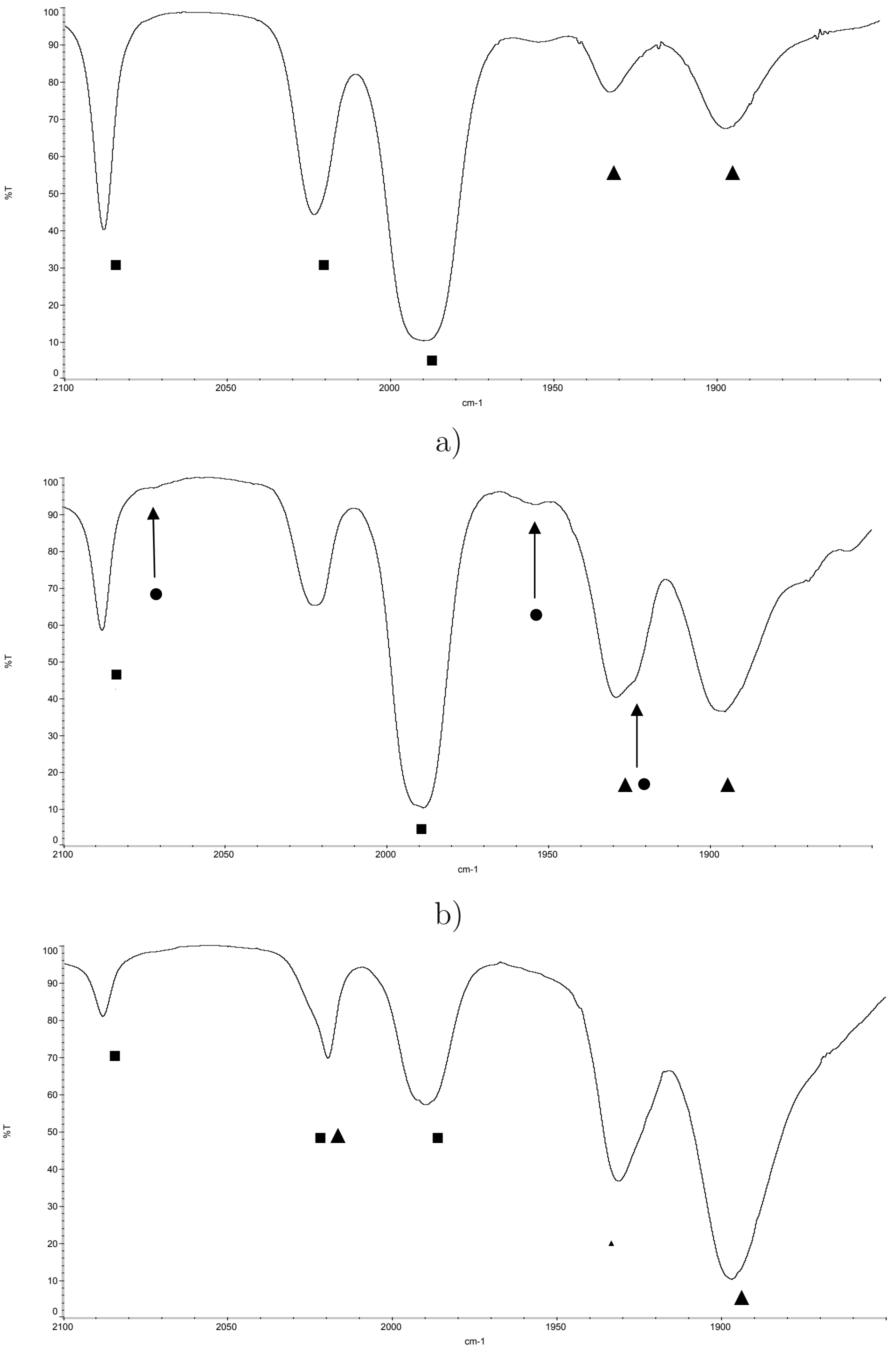
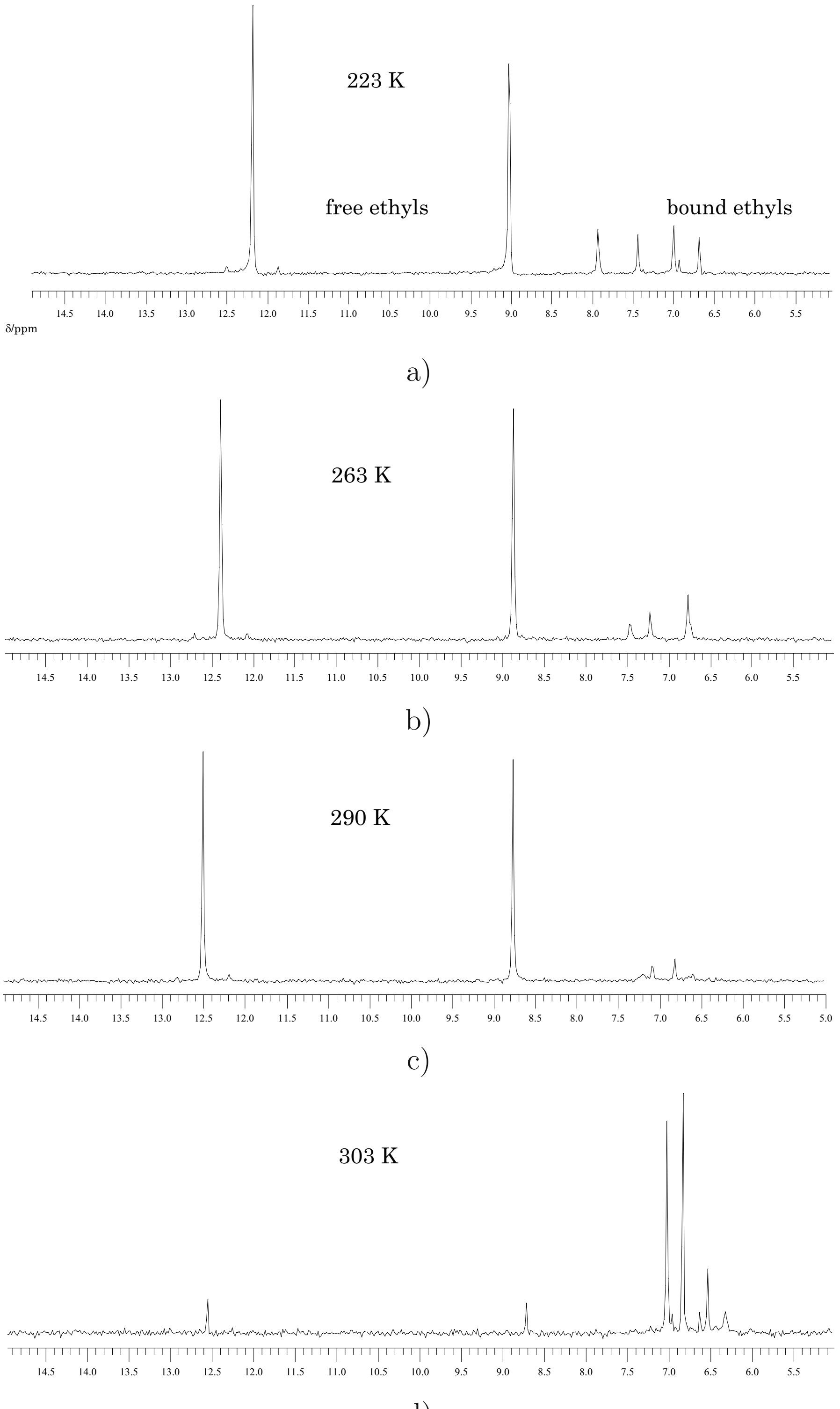


Fig. 1 IR spectra of the reaction mixture of 1C and quinuclidine in toluene (molar ratio = 1:1, [1C] = 0.1 M) in the ν(CO) region after 10 min (recorded at 25 °C) (a), after 30 min (recorded at - 30 °C) (b), and after 60 min stirring at 25 °C (recorded at 25 °C) (c). Symbols: **1C** ■, **2e** ▲, intermediate •.



a)

b)

c)

d)

Fig. 2 Temperature-dependent $^{13}C\{^1H\}$ spectra of the reaction mixture of **1C** and quinuclidine recorded in toluene-d_8. [**1C**] = 0.5 M, molar ratio = 2:1 (**a-c**) or 1:1 (**d**), magnetic field = 7.04 T. Only signals of the $SiEt_3$ moiety (free (high-frequency) and bound (low-frequency)) are shown (see Text).

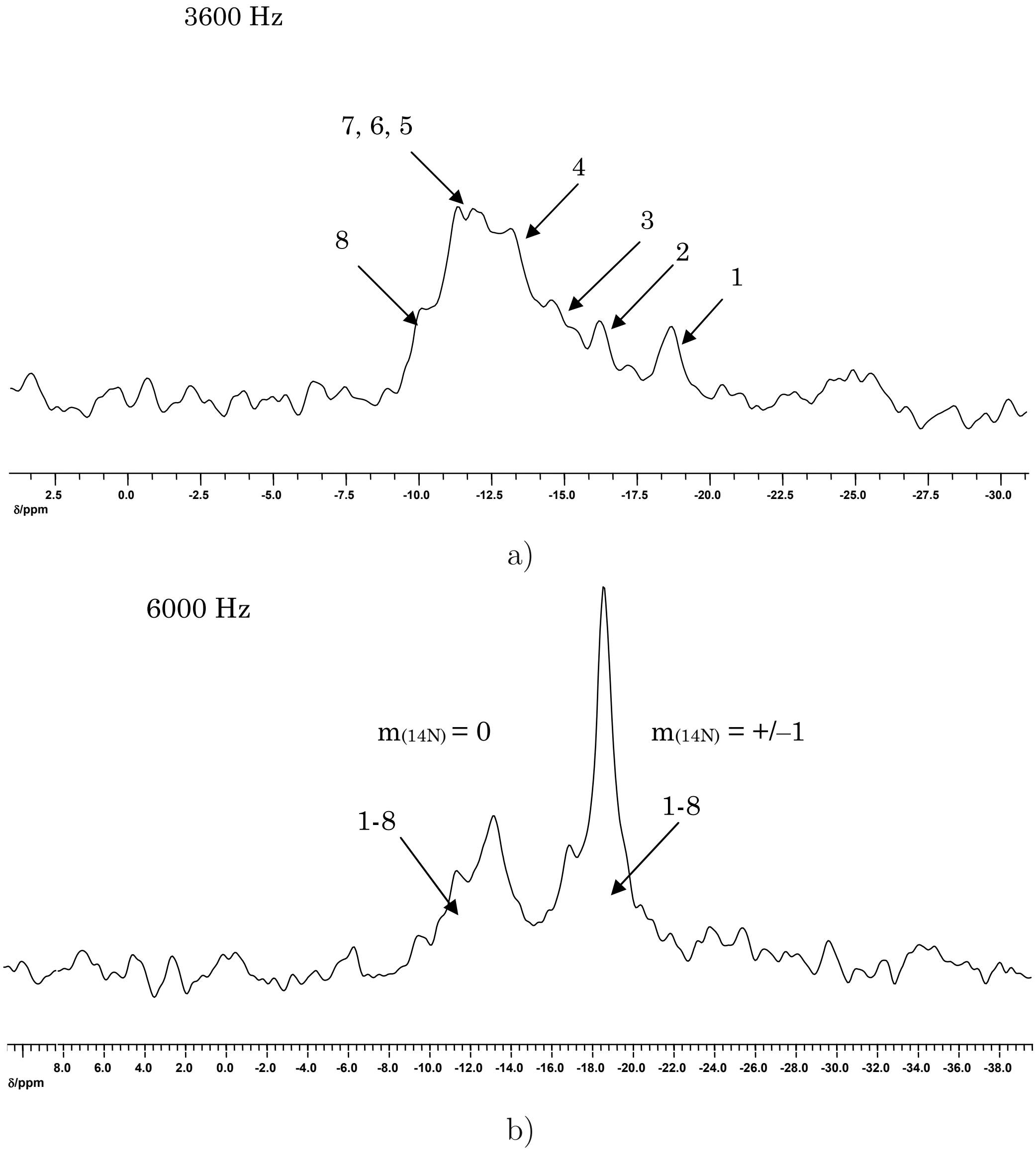
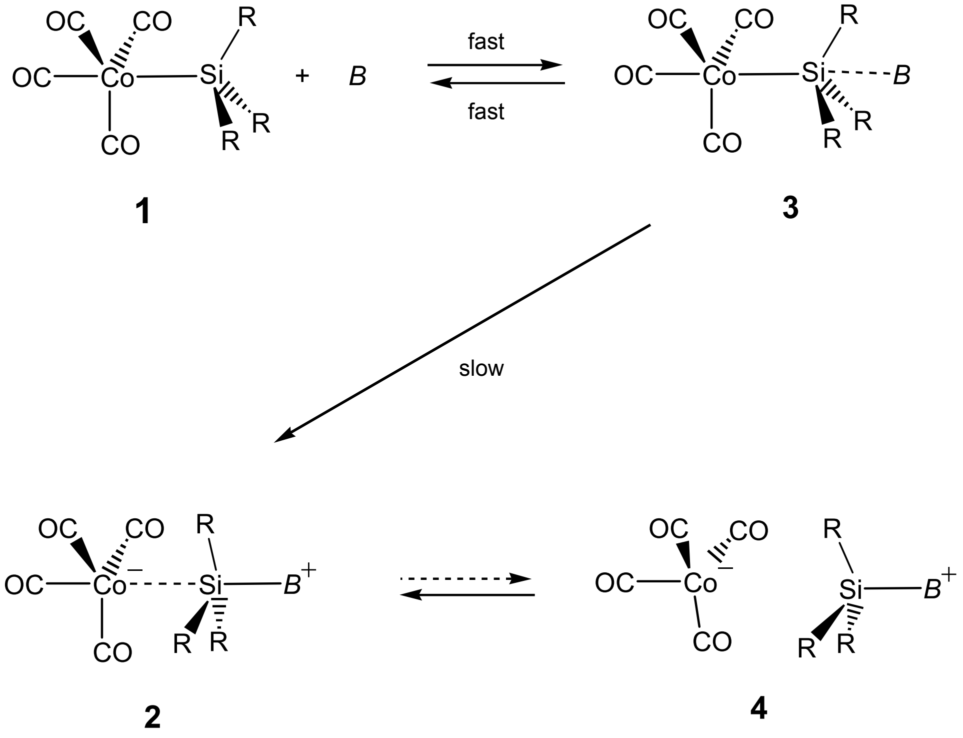


Fig. 3 ^{29}Si CP/MAS spectra of [(quinuclidine)SiPh$_3^+$, $^-$Co(CO)$_4$],**2j** (**a**), and [(dabco)SiPh$_3^+$, $^-$Co(CO)$_4$], **2k**(**b**). Magnetic field = 7 T, temperature = 293 K. 5 mm ZrO$_2$ rotors. Rotation speeds as indicated.



Scheme 1 Possible transformations in the silylcobalt tetracarbonyl/tertiary amine systems.