Journal of Organometallic Chemistry, *451* (1993) 53–57

JOM 23344

Reaction of silylcobalt tetracarbonyls with oxiranes. Kinetics and mechanism *

József Kreisz, Attila Sisak and László Markó

Research Group for Petrochemistry of the Hungarian Academy of Sciences, P.O. Box 158, H-8201 Veszprém (Hungary)

Ferenc Ungváry

Institute of Organic Chemistry, University of Veszprém, P.O. Box 158, H-8201 Veszprém (Hungary)

(Received September 29, 1992)

Abstract

It has been shown that (β-silyloxyacyl)cobalt tetracarbonyls are formed in the reaction between silylcobalt tetracarbonyl, terminal oxirane, and carbon monoxide. The linear acyl isomer is obtained with a regioselectivity of about 80%, which is practically independent of the nature of the substituents in the silyl group. Kinetic studies have revealed a first order dependence on $Ph_3SiCo(CO)_4$, an increasing order with respect to ethyloxirane, and zero order with respect to $[Co(CO)_4]^-$ and CO. A mechanism involving a rapid formation of a tight ion pair, rate-determining internal S_N2 type substitution, and fast insertion of CO is suggested.

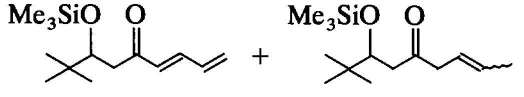
1. Introduction

The silyloxymethylative ring opening of cyclic ethers by the catalytic system $R_3SiH/CO/Co_2(CO)_8$ at 1 bar CO was found to be a useful synthetic method for the preparation of 1,3-bis-silyloxy compounds, such as **A** and **B** [1].

$$\mathrm{R'\underline{CHCH_2O}} + \mathrm{R_3SiH} + \mathrm{CO} \xrightarrow{\mathrm{Co_2(CO)_8}} \underset{\textbf{(A)}}{\mathrm{R_3SiOCHR'CH_2CH_2OSiR_3}} + \underset{\textbf{(B)}}{\mathrm{R_3SiOCH_2CHR'CH_2OSiR_3}} \quad (1)$$

Indirect evidence for the participation of an acylcobalt tetracarbonyl intermediate in the reactions was obtained by trapping such a complex with butadiene in the reaction of *tert*-butyloxirane and $Me_3SiCo(CO)_4$ [1].

$$\mathrm{{}^tBu\underline{CHCH_2O}} + \mathrm{Me_3SiCo(CO)_4} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow$$



(2)

(31%) (10%)

We have now shown that the reaction of oxiranes with silylcobalt tetracarbonyls affords (β-silyloxyacyl)cobalt tetracarbonyl complexes, thus confirming the occurrence of a reaction proposed as one step in the above siloxymethylative ring opening of oxiranes. The kinetics and mechanism of the reaction have been studied.

2. Results

2.1. *Preparation of (β-silyloxyacyl)cobalt tetracarbonyls*

These complexes were generally prepared from the corresponding oxirane (in > 10-fold molar excess) and

---

Correspondence to: Professor F. Ungváry.

* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry and its application in organic synthesis.

0022-328X/93/$6.00

TABLE 1. IR spectra of various β-$R_3SiO(C_3H_6)C(O)Co(CO)_4$ complexes (mixture of isomers **1** and **2** formed from methyloxirane) in the ν(CO) region [a]

R_3	ν(CO) (cm^{-1})					
Me_3	2103m	2043s	2023vs	2003vs	1712m	
Me_3 [b]	2103m	2043s	2025vs	2005vs	1736w	1700m
Et_2Me	2103m	2043s	2024vs	2003vs	1712m	
Et_3	2103m	2043s	2024vs	2003vs	1715m	
Me_2Ph	2103m	2043s	2024vs	2003vs	1714m	
Ph_3	2103m	2045s	2024vs	2004vs	1714m	
Me_2Cl	2107m	2047s	2026vs	2006vs	1714m	

[a] In pentane. [b] $R_3SiOCH_2CH_2C(O)Co(CO)_4$.

$R_3SiCo(CO)_4$ in pentane (when R = Ph in dichloromethane) solution under 650–850 mmHg of carbon monoxide at 0°C.

$$R_3SiCo(CO)_4 + R'\underline{CHCH_2O} + CO \longrightarrow R_3SiOCHR'CH_2C(O)Co(CO)_4$$

(**1**, major product)

$$+ R_3SiOCH_2CHR'C(O)Co(CO)_4 \quad (3)$$

(**2**, minor product)

For R' = H, reactions were performed at −15°C. After evaporation of the solvent *in vacuo*, the products were obtained as light brown oils in good yields. They are stable at room temperature for a few hours. Their infrared spectral data are listed in Table 1.

The actual isomer composition was determined by GLC-MS analysis of the corresponding methyl esters prepared by the reaction of the above acyl complex isomer mixture with NaOMe. The GC-MS analysis showed unequivocally that the complexes have the structures **1** and **2**. Table 2 illustrates that the regioselectivity of reaction (3) was practically independent of the identity of R_3 for R' = Me. One of the complexes formed from ethylene oxide, $Me_3SiOCH_2CH_2C(O)Co(CO)_4$, was also characterized by ^1H NMR spectroscopy.

TABLE 2. The effect of substituents in the R_3Si group on the regioselectivity of reaction (3) [a]

R_3	$R_3SiOCHMeCH_2$-$C(O)Co(CO)_4$ (%)	R_3SiOCH_2CHMe-$C(O)Co(CO)_4$ (%)
Me_3	79	21
Et_2Me	78	22
Et_3	78	22
Me_2Ph	81	19
Ph_3 [b]	80	20
Me_2Cl	78	22

[a] From GLC-MS analysis of the methyl esters formed from the isomer mixture of the complexes by the reaction with NaOMe (see text); $[R_3SiCo(CO)_4]$ = 0.5 M; [methyloxirane] = 10 M; P_{CO} = 860 mmHg, 0°C; in pentane. [b] In CH_2Cl_2.

TABLE 3. The effects of the concentrations of $Ph_3SiCo(CO)_4$ and ethyloxirane on the rate of reaction (3) [a]

$[Ph_3SiCo(CO)_4]$ (M)	[ethyloxirane] (M)	10^5r (Ms^{-1})	$10^5r/[Ph_3SiCo(CO)_4]$ (s^{-1})
0.025	1.16	0.51	20.4
0.050	1.16	1.06	21.2
0.100	1.16	2.10	21.0
0.250	1.16	5.30	21.2
0.025	0.58	0.20	
0.025	1.16	0.51	
0.025	2.32	2.10	
0.025	3.48	6.02	
0.025	4.64	13.10	
0.025 [b]	2.32	1.21	
0.025 [c]	2.32	3.36	
0.025 [d]	0.35	3.20	
0.025 [d,e]	0.35	3.40	
0.025 [d,f]	0.35	3.45	

[a] 20.0°C, in benzene, P_{CO} = 700±40 mmHg. [b] 0.0°C, in toluene. [c] 40.0°C, in toluene; [d] In Bu_2O/THF = 2/1 (v/v). [e] $[NaCo(CO)_4]$ = 0.025 M. [f] $[NaCo(CO)_4]$ = 0.075 M.

2.2. *Kinetics of reaction (3)*

Reaction (3) was studied for interaction of ethyl oxirane and $Ph_3SiCo(CO)_4$ in benzene. The reaction was monitored by gas volumetric measurement of the carbon monoxide uptake, or, in some cases, by observing the decrease in the highest frequency ν(CO) band of silylcobalt tetracarbonyl by IR spectroscopy. The kinetic data are listed in Table 3.

We observed a clear first order dependence for $[Ph_3SiCo(CO)_4]$. It was much more difficult to assign a definite order to ethyloxirane. The order seemed to increase from about 1.3 to 2.7 in the concentration range examined. To check the potential role of tetracarbonylcobaltate we added $NaCo(CO)_4$ to the reaction mixture [2*], but this caused no change in the rate within experimental error. Similarly, zero order was assigned to carbon monoxide since variation of P_{CO} between 860 and 430 mmHg had no influence on the rate. Polar solvents, such as dibutyl ether or tetrahydrofuran, were found to accelerate the reaction by approximately an order of magnitude compared with benzene. We should note, however, that these solvents

---

* Reference number with an asterisk indicates a note in the list of references.

TABLE 4. Some features of the kinetics of reactions (3) and (5)

Feature	Reaction (5) ($Y = H$, ref. 11)	Reaction (3) ($Y = SiPh_3$)
Reaction rate [a]	2.05×10^{-4}	3.2×10^{-5}
Order in $YCo(CO)_4$	1	1
Order in oxirane [b]	$\gg 1$	> 1
Effect of P_{CO}	none	none
Effect of solvent polarity	rate increases with rising polarity	rate increases with rising polarity
$\Delta H^{\ddagger}$ (kJ mol^{-1}) [c]	-2.3 ± 4.3 [d]	15.8 ± 1.6 [e]
$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1}) [c]	-277 ± 18 [d]	-258 ± 10 [e]

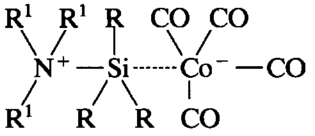
[a] [butyloxirane] = 0.427 M; [$YCo(CO)_4$] = 0.0256 M; in Bu_2O/THF = 4.7 (v/v), 20°C; $P_{CO} = 740$ mmHg; Y = H, or SiR_3, resp. [b] In hydrocarbon solvent. [c] Ethyloxirane was used. [d] The n-octane solvent contained methyl isobutyl ketone in 2.5 M concentration, at 0°C. [e] Benzene solvent, at 20°C.

are not inert towards silylcobalt carbonyls (*cf.* refs. 1, 3, 4) although they are much less reactive than oxiranes.

We examined the influence of temperature on rate over the range 0–40°C (Table 3). The temperature coefficient for reaction (3) was remarkably low. The calculated activation parameters are shown in Table 4.

3. Discussion

The reactions of various bases with the compounds $R_3SiM(CO)_n$ (M = Co, Mn and $n = 4$, 5, respectively) resulting in a heterolytic silicon–metal bond cleavage were studied previously [5,6]. Complexes of the types $[R_3SiNR^1_3][Co(CO)_4]$ (**3**) and $[R_3SiPR^2_3][Co(CO)_4]$ (**4**) were isolated [5]. The complexes **3** were suggested to exist as tight ion pairs [6] on the basis of the analogy



(**3a**)

between the IR spectra of $[HNR^1_3][Co(CO)_4]$ (**5**) [7] and **3**. Although nucleophilic attack of an oxygen base on silicon bonded to cobalt [1,3,8] (or to manganese [9]) has been postulated several times,

$$\mathrm{{>}O + R_3SiCo(CO)_4 \longrightarrow \left[{>}O^{+}SiR_3\right][Co(CO)_4]^{-}} \quad (4)$$

(**6**)

no oxonium salt of the type **6** has yet been detected, probably because of the high reactivity of such species. We reported previously [10] that the rate of the reaction of $Me_3SiCo(CO)_4$ with isobutyraldehyde does not depend on P_{CO}, which is consistent with ionic interaction between the reactants. Recently we investigated the kinetics of the ring opening carbonylation of oxiranes with $HCo(CO)_4$ [11]:

$$\mathrm{HCo(CO)_4 + Et\underline{CHCH_2O} + CO \longrightarrow HOCHEtCH_2C(O)Co(CO)_4} \quad (5)$$

(major product)

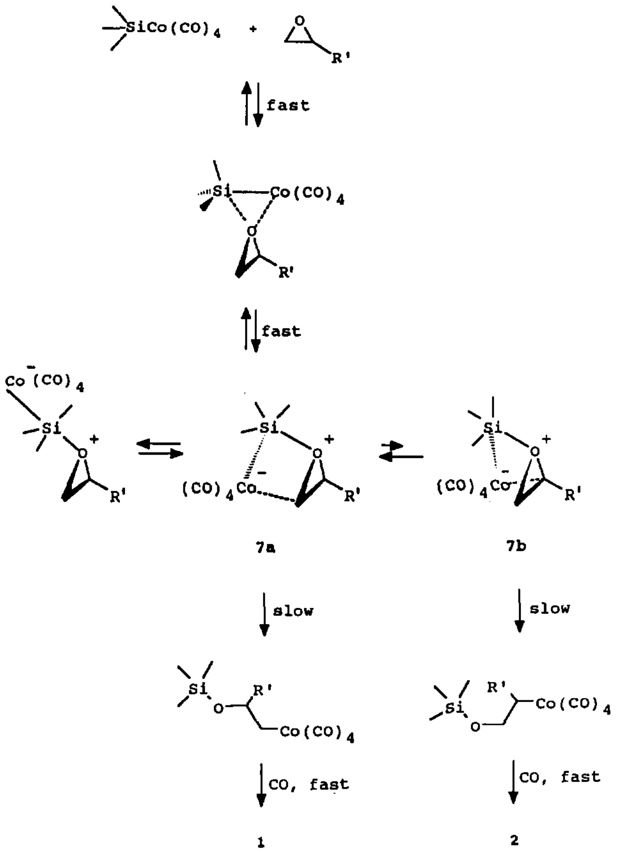
The results were interpreted in terms of formation of a preequilibrium ion pair and a subsequent rate determining S_N2 type substitution followed by fast CO insertion.

Hydrido- and silyl-metal species often show analogous reactivity (see *e.g.* refs. 3, 6, 12–13). Our present kinetic results suggest that the analogy between the processes formulated in eqns. (3) and (5) are not only formal. Table 4 summarizes some related features of these two reactions. The fairly low value of $\Delta H^{\ddagger}$ in both reactions together with the independence of rates on the CO concentration exclude the possibility of a fast preequilibrium step leading to a tricarbonyl cobalt intermediate [14*–16]. An ionic pathway presumably involving the step represented by eqn. (4) is also supported by the observed solvent effect and the very high negative activation entropy.

It is reasonable to assume that the ion pair **6** recombines by an S_N2 step. The selectivity data obtained for methyloxirane (Table 2) show that the carbon–cobalt bond could be formed predominantly at the more accessible carbon of the oxirane ring. A similar regioselectivity was observed when monosubstituted oxiranes reacted with (i) HCl in anhydrous solvents [17]; (ii) Me_3SiX (X = Cl, Br, I) in the presence or absence of catalyst (see *e.g.* refs. 18–21); (iii) $Me_3SiSePh$ in the presence of ZnI_2 catalyst [22]; (iv) $Me_3SiOSO_2CF_3$ in the presence of nitrogen bases [23].

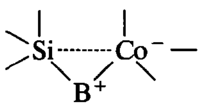
In (ii), the nucleophilicity of the halide "entering group" was found [19] to influence the product distribution. In all of the cases (i–iv), cycloalkene oxides gave *trans*-disubstituted cycloalkanes with high stereoselectivity. These features were interpreted generally with the formation of an oxonium salt followed by a S_N2 type attack of the halide or pseudohalide. The ion $[Co(CO)_4]^-$ has also been regarded as a pseudohalide [24], and the similarity of its behaviour in reactions (3) and (5) to that of halides supports this suggestion. A tight ion pair character of the oxonium–halide (-pseudohalide) pairs was suggested for reaction (5) and for the case (i). This property may be also responsible for the highly negative $\Delta S^{\ddagger}$ found, and it accounts for the fact that $NaCo(CO)_4$ added had no influence on the reaction rate.

The effect of ion-pairing in carbonyl metallates has been much discussed [24–26], and large differences were found between the reactivity of ion-paired and



Scheme 1.

solvent-separated alkali metal salts. In contrast to the situation for reactions of alkali carbonyl cobaltates, no systematic analysis of the effect on ion pairing on the reactivity of the tight ion-paired form of **3**, **5**, or **6** type complexes has yet been made [27*,28]. We assume that ion pairs of these types can exist not only in the *trans*-form such as **3a** but also in a *cis*-form, such as



which is probably more favoured for oxygen bases [29*,30].

The suggested route for reaction 3 is shown in Scheme 1. This route may also apply to reaction 5, (*cf.* ref. 11), since it is consistent with the common and different features of these two reactions (see Table 4). In both cases a fast formation of an oxonium tetracarbonylcobaltate ion pair followed by a slow S_N2 type substitution seems reasonable. The higher selectivity of the linear product, $YOCHR'CH_2C(O)Co(CO)_4$, in the case of $Y = H$ ($> 95\%$ as compared with $\approx 80\%$ obtained for $Y = SiR_3$) can be attributed to the greater steric hindrance in the **7b** type conformer, because of the shorter length of the $H-O^+$ bond compared with that of the $Si-O^+$ bond [31]. Furthermore, the activation entropy is higher for $Y = H$, than for $Y = SiR_3$ showing the greater rigidity of the assumed 4-centre transition state in the former case. Both reactions are also similar in respect of the fact that no $YOCHR'CH_2Co(CO)_4$ could be detected by IR spectroscopy, which is in accordance with the generally very unfavourable position of the alkyl–acyl equilibrium.

4. Experimental section

4.1. General

All manipulations were carried out by Schlenk techniques [32]. Materials were mainly commercial products. Gases (carbon monoxide, argon) were deoxygenated (BTS catalyst, BASF) and dried. Hydrosilanes and chlorosilanes (Fluka) were used without purification, solvents (Reanal) and epoxides (Fluka) were dried by standard methods, distilled, and stored under CO or Ar. Authentic samples of silylated methyl β-hydroxybutyrate and methyl β-hydroxy-isobutyrate were prepared by treating β-hydroxy-acid esters (Aldrich) with the corresponding chlorosilane in the presence of pyridine.

Crude $Co_2(CO)_8$ was prepared by the known method [33] and recrystallized from dichloromethane and pentane. $R_3SiCo(CO)_4$ [34] and $NaCo(CO)_4$ [35] were obtained as described previously.

GLC-analyses were performed with a HP Model 5830 A gas chromatograph and on a JEOL JMS 1-SG-2 GLC-MS system fitted with a 25 m OV-1 capillary column. IR spectra were recorded on a Specord IR 75 (Carl Zeiss, Jena) spectrophotometer using 0.01 cm CaF_2 cuvettes, the spectra were calibrated with benzene (1960) and polystyrene (1601 cm^{-1}). NMR spectra were recorded on Tesla Model BS 787 C (80 MHz, ^1H), Varian CFT 20 (80 MHz, ^1H; 20 MHz, $^{13}C\{^1H\}$) spectrometers.

4.2. Kinetic measurements

Thermostatted reaction vessels with magnetic stirring and a gasometric apparatus fitted with a mercury-filled gas burette were used for kinetic studies. The reaction was started by injecting an approximate volume of the $Ph_3SiCo(CO)_4$ stock solution into the vigorously stirred solution of ethyloxirane. Initial rates of CO uptake were determined from readings of the gas burette during the first few minutes of the reaction. Usually 3–5 readings per minute were made, and the initial rate was calculated from the tangent to these points. Reproducibility of the rates varied between ±1 and ±6%.

4.3. Preparation of $Me_3SiOCH_2CH_2C(O)Co(CO)_4$

To a vigorously stirred solution of oxirane (2 ml, ≈ 40 mmol) in hexane (10 ml) a solution of $Me_3SiCo(CO)_4$ (0.286 g, 1.16 mmol) in hexane (8 ml) was added dropwise from a syringe at −15°C, under a CO atmosphere maintained at a total pressure of 860 mmHg. At the end of the addition (*ca.* 10 min) the reaction was complete, as shown by the IR spectrum (see Table 1) of a 0.1 ml sample diluted with hexane (0.2 ml). $Me_3SiOCH_2CH_2C(O)Co(CO)_4$ (see Table 1) was formed with a selectivity of 86% along with a small amount of $Co_2(CO)_8$. The reaction mixture was evaporated *in vacuo* to leave a reddish brown oil. ^1H NMR (80 MHz, benzene-d_6, RT) δ 0.40 (s, 3H, CH_3), 3.34 (t, $J = 12$ Hz, 2H, CH_2CO), 3.80 (t, $J = 12$ Hz, 2H, CH_2O).

4.4. Preparation of the isomer mixture 1, 2 with R = Ph and R′ = Me

The procedure was the same as described above except that it was performed at 20°C and $Ph_3SiCo(CO)_4$ (0.5 g, 1.16 mmol) and methyloxirane (3 ml, 42.8 mmol) were used. The **1**, **2** mixture was obtained without any by-products as a yellowish brown oil.

4.5. Determination of the isomer ratio 1 : 2

Isomer mixtures prepared (*ca.* 2 mmol complex in 10 ml heptane) as described above were treated with an equimolar amount of NaOMe in methanol (5 ml) at room temperature. The reaction took place immediately to give the methyl esters. GLC-MS data for the esters were identical with those for the authentic samples of methyl β-silyloxybutyrates and methyl β-silyloxyisobutyrates, respectively (see Table 2).

References and notes

1 T. Murai, F. Yasui, S. Kato, Y. Hatayama, S. Suzuki, Y. Yamasaki, N. Sonoda, H. Kurosawa, Y. Kawasaki and S. Murai, *J. Am. Chem. Soc., 111* (1989) 7938.

2 $NaCo(CO)_4$ reacted neither with $Ph_3SiCo(CO)_4$ nor with the product complexes.

3 S. Murai and N. Sonoda, *Angew. Chem. Int. Ed. Eng., 18* (1979) 837.

4 A. Sisak *et al.*, unpublished results.

5 C. S. Candy, B. M. Kingston and M. F. Lappert, *Adv. Organomet. Chem., 11* (1973) 253 and refs. therein.

6 A. Sisak, F. Ungváry and L. Markó, *Organometallics, 5* (1986) 1019.

7 G. Fachinetti, L. Balocchi, F. Secco and M. Venturini, *Angew. Chem. Int. Ed. Eng., 20* (1981); F. Calderazzo, G. Fachinetti and F. Marchetti, *J. Chem. Soc., Chem. Commun.*, (1981) 181.

8 (a) N. Chatani, T. Sano, K. One, Y. Kawasaki and S. Murai, *J. Org. Chem., 55* (1990) 5924; (b) N. Chatani, Y. Karikawa, H. Nishimura and S. Murai, *Organometallics, 10* (1991) 21.

9 K. C. Brinkman and J. A. Gladysz, *Organometallics, 3* (1984) 147.

10 I. Kovács, A. Sisak, F. Ungváry and L. Markó, *Organometallics, 7* (1988) 1025.

11 J. Kreisz, F. Ungváry, A. Sisak and L. Markó, *J. Organomet. Chem., 417* (1991) 89.

12 F. Seitz and M. S. Wrighton, *Angew. Chem. Int. Ed. Eng., 27* (1988).

13 A. Sisak, E. Sámpár-Szerencsés, V. Galamb, L. Németh, F. Ungváry and G. Pályi, *Organometallics, 8* (1989) 1096.

14 $\Delta H^{\ddagger}$ values of CO-dissociation from alkyl- and acylcobalt tetracarbonyls were found to be in the range 82–105 kJ mol^{-1} (see ref. 15). The CO-dissociation energy calculated for $HCo(CO)_4$ is 184 kJ mol^{-1} (see ref. 16).

15 D. C. Roe, *Organometallics, 6* (1987) 942.

16 L. Versluis, C. Ziegler, F. J. Bearends and W. Ravenek, *J. Am. Chem. Soc., 111* (1989) 2018.

17 G. Lamaty, R. Maloq, C. Selve, A. Sivade and J. Wilde, *J. Chem. Soc., Perkin Trans., II* (1975) 1119.

18 R. C. Mehrotra and P. Bajaj, *J. Organomet. Chem., 22* (1970) 41.

19 M. R. Detty and M. D. Seidler, *J. Org. Chem., 46* (1981) 1283.

20 G. C. Andrews, T. C. Crawford and L. G. Contillo, Jr., *Tetrahedron Lett., 22* (1981) 3803.

21 H. R. Kricheldorf, G. Morber and W. Regel, *Synthesis*, (1981) 383.

22 N. Miyoshi, K. Kondo, S. Murai and N. Sonoda, *Chem. Lett.*, (1979) 909.

23 S. Murata, M. Suzuki and R. Noyori, *J. Am. Chem. Soc., 101* (1979) 2739.

24 J. E. Ellis, *J. Organomet. Chem., 86* (1975) 1.

25 M. Y. Darensbourg, *Progr. Inorg. Chem., 33* (1985) 221, and refs. therein; C. A. Ash, T. Delord, D. Simmons and M. Y. Darensbourg, *Organometallics, 5* (1986) 17.

26 F. Ungváry and A. Wojcicki, *J. Am. Chem. Soc., 109* (1987) 6848.

27 For example, $HCo(CO)_4$ was found to be unreactive in pure acrylonitrile, but it reacted easily with this olefin in the form of an ion-paired pyridinium salt in dichloromethane (see ref. 28).

28 A. Sisak, F. Ungváry and L. Markó, *J. Org. Chem., 55* (1990) 2508.

29 The attack of a base leading to *trans* and *cis* tight ion pairs corresponds to the known "S_N2-Si and S_Ni-Si mechanisms", respectively (see ref. 30). Experiments with silylcobalt carbonyls containing chiral Si may clarify this stereochemical problem.

30 L. H. Sommer, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill, New York, 1965.

31 R. C. Weast (ed.), *CRC Handbook of Chemistry and Physics*, 58th ed., CRC Press, Palm Beach, 1977, p. F-217.

32 D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley-Interscience, New York, 1986.

33 P. Szabó, L. Markó and G. Bor, *Chem. Techn. (Berlin), 13* (1961) 549.

34 A. C. Chalk and J. F. Harrod, *J. Am. Chem. Soc., 89* (1967) 1640; N. Sakurai, K. Miyoshi and Y. Nakadaira, *Tetrahedron Lett.*, (1977) 2671.

35 W. F. Edgell and J. Lyford, IV., *Inorg. Chem., 9* (1970) 1932.