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CARBONYLATIONS MEDIATED BY DICYCLOPENTADIENYL SAMARIUM

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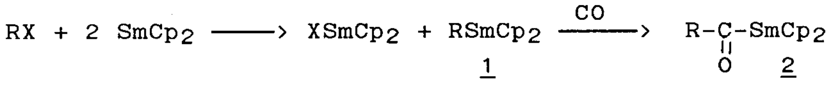
Summmary : Reaction of *t*-BuBr with $SmCp_2$ and CO leads to the formation of different carbonylation products according to experimental conditions. *t*-BuCHOHCHOH*t*-Bu is obtained if the reaction is followed by hydrolysis. *t*-$BuCOCHOHC_6H_{13}$ is produced if the carbonylation of *t*-BuBr is followed by addition of heptanal. The product *t*-BuCOCOCHOH*t*-Bu which has incorporated three CO units, has also been isolated in a low yield.

We have recently reported the reaction of benzylic halides with divalent dicyclopentadienyl samarium, which leads to benzylsamarium (III) complexes[1]. The organometallic structure of these compounds has been assigned by a study of their reactivity. We then undertook studies of carbonylation of halogenated compounds in the presence of $SmCp_2$ in the hope to detect the formation of transient organometallic derivatives. We wish to present now evidence of monocarbonylation and double carbonylation of *t*-butyl bromide mediated by $SmCp_2$.

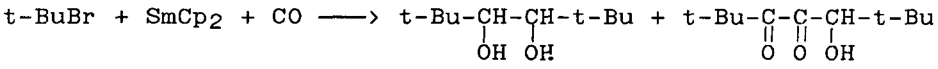
Our initial aim was to prepare organosamarium compounds 1 by adding an organic halide on $SmCp_2$, as previously described[1], and to trap 1 by CO with formation of the acyl complex 2 :



$$RX + 2\,SmCp_2 \longrightarrow XSmCp_2 + \underset{\underline{1}}{RSmCp_2} \xrightarrow{CO} R\text{-}\underset{\substack{\| \\ O}}{C}\text{-}SmCp_2 \quad \underline{2}$$

a: R = $PhCH_2$
b: R = *t*-Bu

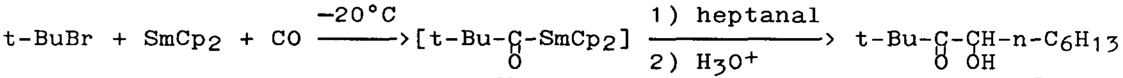
The benzyl samarium complex 1a, prepared from benzyl chloride as in[1], was submitted to a prolonged bubbling of CO or left overnight under CO pressure. After hydrolysis of the reaction mixture, only toluene was obtained, at the exclusion of any product indicative of a CO insertion. An attempt was then made to form dicyclopentadienyl *t*-butyl-acyl samarium 2b by the same route[2]. When *t*-butyl bromide was added to $SmCp_2$ while bubbling CO in THF solution at low temperature, two organic products, 3 [3] and 4 [5], could be isolated after hydrolysis. The 3/4 ratio depends on the reaction temperature and on the $SmCp_2$/*t*-BuBr ratio (isolated yields are expressed by respect to *t*-BuBr) :



$$t\text{-BuBr} + SmCp_2 + CO \longrightarrow t\text{-Bu-}\underset{OH}{CH}\text{-}\underset{OH}{CH}\text{-}t\text{-Bu} + t\text{-Bu-}\underset{O}{C}\text{-}\underset{O}{C}\text{-}\underset{OH}{CH}\text{-}t\text{-Bu}$$

				3	4
1	:	3.5	temp. -40°C	46%	0%
1	:	2.5	" -20°C	15%	12%

Compounds 3 and 4 are likely to involve formation of intermediate alkyl and acyl species 1b and 2b. When heptanal was added to the reaction mixture obtained by reacting *t*-BuBr with $SmCp_2$ at -20°C while bubbling CO, ketol 5 was obtained[6].

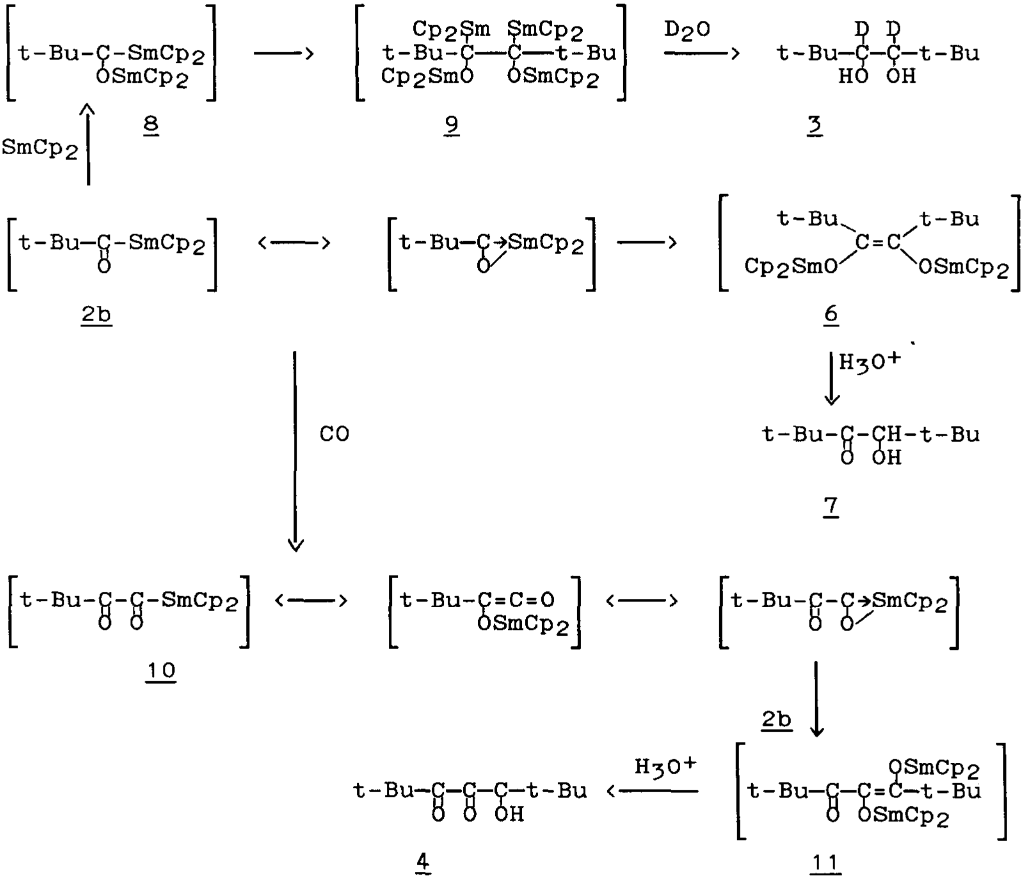


$$t\text{-BuBr} + SmCp_2 + CO \xrightarrow{-20°C} [t\text{-Bu-}\underset{O}{C}\text{-}SmCp_2] \xrightarrow[2)\ H_3O^+]{1)\ \text{heptanal}} t\text{-Bu-}\underset{O}{C}\text{-}\underset{OH}{CH}\text{-}n\text{-}C_6H_{13}$$

2b 5

Ketol 5 had already been obtained in a two step process by reacting pivaloyl choride with $SmCp_2$ at -20°C before adding heptanal[7]. This gives some evidence for the involvment of a common acyl intermediate 2b. Acylsamarium 2b has an alkoxycarbene mesomeric structure. Dimerization of this latter should lead to the enediolate complexe 6. Such a dimerization has been previously described by Evans[8] with formylsamarium complexes. In our system we observed formation of ketol 7 in fair amount only when the reaction mixture was allowed to reach room temperature. This could indicate that enolate 6 is not an intermediate in the formation of pinacol 3. When carbonylation of *t*-BuBr is performed at -40°C and followed by deuterolysis, incorporation of two deuterium atoms on carbon atoms in 3 was observed. We tentatively suggest that reduction of the acyl intermediate 2b preferentially occurs at low temperature, leading to radical 8, which gives species 9 before hydrolysis.

Double carbonylation reactions of alkyl complexes of lutetium and thorium, followed by dimerization, leading to enedione diolate complexes, have been reported[9,10]. Formation of the formally "triple CO incorporation" product 4 can be explained only by a double carbonylation reaction involving one samarium atom. We suggest that carbonylation of compound 2b leads to intermediate 10 which can have glyoxylic or ketene (as it has been proposed by Marks[11]) or α-keto-alkoxycarbene structures. Coupling of 10 and 2b as their carbenoid forms leads to 11 which after hydrolysis is transformed into 4. Product 4 was always obtained in low yield because of competive reactions on 2b : at low temperature, 9 is preferentially formed and at higher temperature, 6 is produced[12].



In conclusion, formation of pinacol 3 and ketol 4, during the reaction of *t*-BuBr with $SmCp_2$ and CO, gives good evidence for the occurence of an acylsamarium intermediate obtained by carbonylation of transient *t*-butyl samarium dicyclopentadienyl. A double carbonylation on the latter, although a minor pathway, has been also clearly revealed.

Acknowledgments

We thank CNRS for its financial support and Dr J.L.Namy for fruitful discussions.

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(1) J.Collin, J.L.Namy, C.Bied, H.B.Kagan, Inorganica Chimica Acta, **1987**, 140, 29.

(2) Reaction of *t*-butyl bromide at -40°C with $SmCp_2$ showed disappearance of the purple precipitate of $SmCp_2$ and transformation to an orange solution. Further addition of aldehyde or acid chloride to this solution did not lead to expected reaction products (alcohol or ketone). No evidence for the formation of a *t*-butylsamarium complex 1b has been obtained in this way. 1b is either not stable or not reactive enough towards aldehyde or acyl chloride.

(3) Synthesis of 3 : to a suspension of 14 mmol Cp_2Sm in 200 ml THF, prepared as previously described[4] and washed twice with THF, at -40°C was added 548 mg (4 mmol) *t*-BuBr in 20 ml THF within 1 hour, while CO was bubbled in the solution. At the end of the addition the purple precipitate of $SmCp_2$ had disappeared and the solution had become dark brown. Water was then added. After the usual workup[4] the crude material was purified by flash chromatography on a silica column and analysed with GC, GC/MS and ^1H NMR. 160 mg (46% yield) of 3 were isolated.

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(5) Synthesis of 4 : procedure was similar to that described above for preparation of 3 but 548 mg (4 mmol) *t*-BuBr were added to a suspension of 10 mmol $SmCp_2$ at -20°C while bubbling CO. After the end of the addition bubbling of CO was maintained during one hour before hydrolysis. After workup and flash chromatography on silica 52 mg (15%) of 3 and 48 mg (12%) of 4 were separated. Anal. : Calcd for $C_{11}H_{20}O_3$: C, 65.96 H, 10.07 ; Found : C, 66.21 ; H, 10.30.

Spectroscopic data of 4

^1H NMR ($CDCl_3$, 250 MHz) : ppm, 4.60 (s,1H) ; 2.87 (s, 1H) ; 1.30 (s,9H) ; 0.98 (s,9H). ^{13}C NMR ($CDCl_3$; 250 MHz) : ppm, 206.7 ; 204.0 ; 79.7 ; 36.4 ; 26.8 ; 26.6.

IR cm^{-1} : 1720,1695.

(6) Synthesis of 8 :

The procedure was the same as for 4 but at the end of addition of *t*-BuBr, when the reaction mixture had become brown, 456 mg (4 mmol) of heptanal were added. After the temperature of the reaction mixture had reached room temperature, hydrolysis was performed. After the usual workup and purification, 332 mg (42% yield) of ketol 6 was obtained.

Spectroscopic data of 8

^1H NMR ($CDCl_3$, 250MHz) ppm, 4.52 (m,1H) ; 3.22 (d,1H) ; 1.28 (m,10H) ; 1.21 (s,9H) ; 0.89 (t,3H).

IR cm^{-1} : 3475, 1699.

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(12) Small amounts of hydroxydiketone 4 are also observed when bubbling CO at -20°C through a solution of pivaloyl samarium dicyclopentadienyl, prepared from addition of *t*-BuCOCl on $SmCp_2$. This observation supports involvment of the same intermediate 2b in the two experiments.

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