Preliminary communication

CARBON DIOXIDE FIXATION BY LANTHANIDE COMPLEXES

M.N. BOCHKAREV*, E.A. FEDOROVA, Yu.F. RADKOV, S.Ya. KHORSHEV,
G.S. KALININA and G.A. RAZUVAEV

Institute of Chemistry, U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)

Summary

The lanthanide compounds $[(Me_3Si)_2N]_m Ln[Sn(CH_2SiMe_3)_3]_{3-m} \cdot DME$ (Ln =
Pr, Nd; m = 0, 2, 3) add two molecules of carbon dioxide per lanthanide atom in
1,2-dimethoxyethane (DME) at room temperature and atmospheric pressure.
According to the IR spectroscopic data the molecules of CO_2 in the complexes
obtained are retained in their original form. One equivalent of CO_2 was evolved
on heating $[(Me_3SiCH_2)_3Sn]_3Pr \cdot 2CO_2 \cdot DME$ at 130—140°C in the absence
of a solvent. The other complexes did not evolve CO_2 on heating. The hydrol-
ysis of the complexes in the open system leads to the evolution of both CO_2
molecules. Upon hydrolysis in the closed system carbon dioxide remains in
the product containing praseodymium $(Me_3SiCH_2)_3SnPr(OH)_2 \cdot 2CO_2$.

The catalytic activation of small molecules is known to be an important
problem of modern chemistry. One of the most difficult tasks in this field is the
selection of catalysts for the activation of carbon dioxide. Upon interaction with
a potential catalyst CO_2 is often transformed into bound inactive carbonate and
carboxylate forms [1,2] or it disproportionates [3]. However, the CO_2 molecule
remains in its intact form while being fixed by complexes of nickel [4] or upon
formation of reversible complexes with cobalt compounds [5]. However, in
these cases the O—C—O angle is decreased to 132°, and fixation occurs as a result
of concerted interactions Co→C and O→M (where M is an alkali metal in the
molecule of the starting compound). In the IR spectra of such complexes there
are usually three strong bands in the following ranges: 1700—1650, 1300—1250,
and 1250—1200 cm^{-1} characteristic of CO_2 bound as a bent molecule in a re-
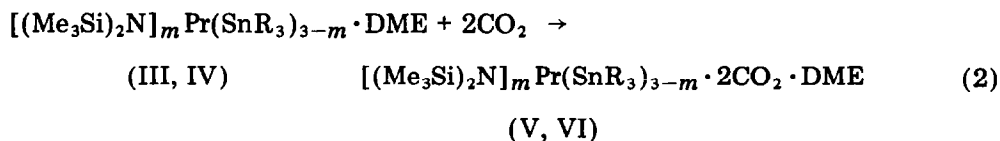duced form [5].
While studying the properties of lanthanide compounds we have found that
the amido derivatives $[(Me_3Si)_2N]_3Ln$ (Ln = Pr, Nd) react exothermally with
carbon dioxide in DME at room temperature and atmospheric pressure to add

two molecules of CO_2 per lanthanide atom. In this reaction the yellow-green solution of the praseodymium complex becomes green, while the pale blue colour of the solution of the neodymium compound practically does not change. The $[(Me_3Si)_2N]_3Ln \cdot 2CO_2$ complexes were isolated in 85% yield by precipitation with hexane from DME solutions as crystalline solids that decompose without melting, above 200°C.

$$[(Me_3Si)_2N]_3Ln + 2CO_2 \xrightarrow[\text{20°C, 1 atm}]{\text{DME}} [(Me_3Si)_2N]_3Ln \cdot 2CO_2 \qquad (1)$$
$$(I, II)$$
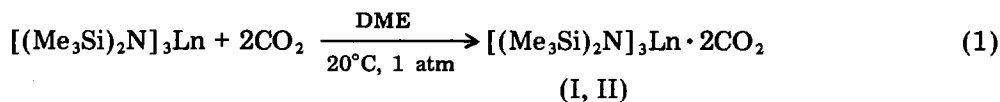
(I, Ln = Pr; II, Ln = Nd)

In the IR spectra of I and II are two strong bands at 2180 and 1520 cm^{-1} due to the presence of CO_2 molecules in addition to the signals of the starting compounds. The hydrolysis of the complexes proceeds with evolution of CO_2 in 95—100% yield. The stannylpraseodymium compounds $[(Me_3Si)_2N]_2Pr$-$Sn(CH_2SiMe_3)_3 \cdot DME$ (III) and $[(Me_3SiCH_2)_3Sn]_3Pr \cdot DME$ (IV) also add two equivalents of CO_2 per lanthanide atom (eq. 2).

$$[(Me_3Si)_2N]_m Pr(SnR_3)_{3-m} \cdot DME + 2CO_2 \rightarrow$$
$$(III, IV) \qquad\qquad [(Me_3Si)_2N]_m Pr(SnR_3)_{3-m} \cdot 2CO_2 \cdot DME \qquad (2)$$
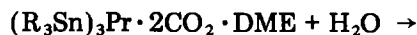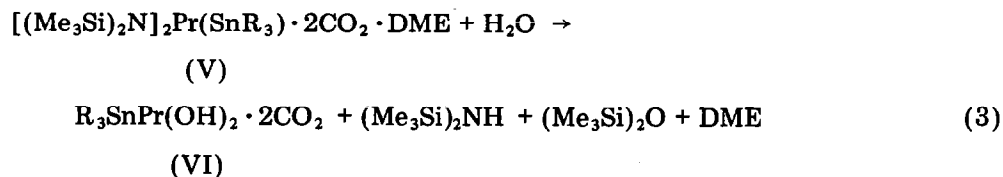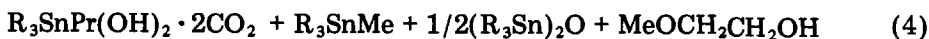$$(V, VI)$$

(V, m = 2; VI, m = 0; R = CH_2SiMe_3)

Product V precipitates as a green solid during carbonation of a DME solution of III.

Complex IV is practically insoluble in DME and other solvents, therefore a suspension in DME was used in the reaction with CO_2. In the course of the reaction the volume of the precipitate was increased and its green colour deepened visibly. Products V and VI are practically insoluble in DME, THF and toluene. On heating VI at 130—135°C in the absence of solvent, one mole of CO_2 was evolved. The second mole of CO_2 was not evolved even on complete decomposition of VI above 190°C. Complex V decomposes above 140°C without any evolution of CO_2.

The hydrolysis of V and VI in the open system at 20°C in THF is accompanied by evolution of both CO_2 molecules, but hydrolysis of V and VI in the closed system (without removal of the gaseous products) under the same conditions occurs without evolution of CO_2. In this case all CO_2 remains bound to the praseodymium containing residue $R_3SnPr(OH)_2 \cdot 2CO_2$ (VII).

$$[(Me_3Si)_2N]_2Pr(SnR_3) \cdot 2CO_2 \cdot DME + H_2O \rightarrow$$
$$(V)$$
$$R_3SnPr(OH)_2 \cdot 2CO_2 + (Me_3Si)_2NH + (Me_3Si)_2O + DME \qquad (3)$$
$$(VI)$$

$$(R_3Sn)_3Pr \cdot 2CO_2 \cdot DME + H_2O \rightarrow$$
$$(VII)$$
$$R_3SnPr(OH)_2 \cdot 2CO_2 + R_3SnMe + 1/2(R_3Sn)_2O + MeOCH_2CH_2OH \qquad (4)$$

Complex VII is stable in air, insoluble in organic solvents and it decomposes above 300°C. In vacuo at 50°C partial or complete removal of CO_2 from VII is observed.

Tri-n-butoxy-praseodymium and -neodymium add three moles of CO_2 per lanthanide atom in hexane. In this case, according to the IR spectrum (1580, 1370 and 1250 cm^{-1}, Fig. 1) the insertion of CO_2 into the O—Ln bond occurs with formation of carbonate derivatives (n-BuOCO$_2$)$_3$Ln.
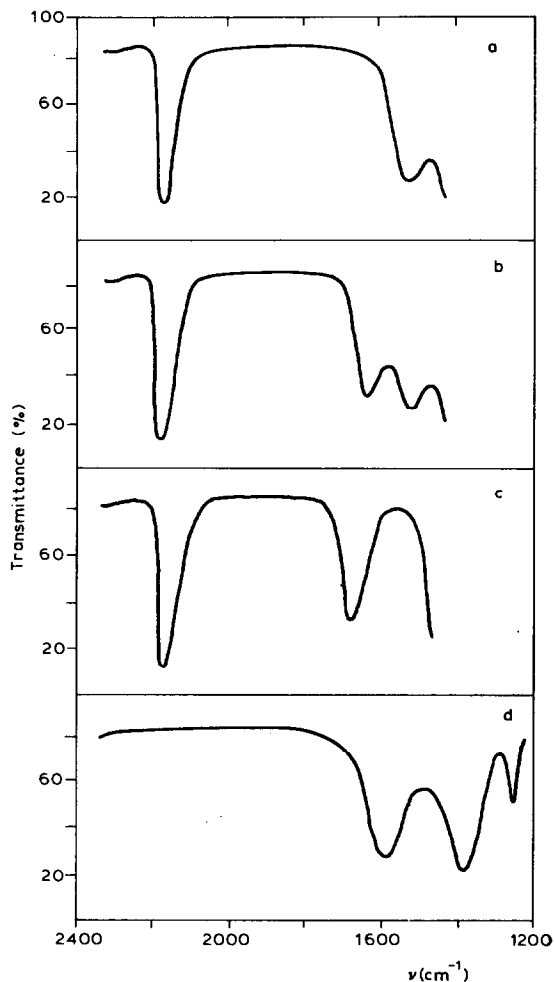

Fig. 1. IR spectra of the lanthanide complexes: (a) [(Me$_3$Si)$_2$N]$_3$Pr·2CO$_2$, (b) [(Me$_3$SiCH$_2$)$_3$Sn]$_3$Pr·2CO$_2$· DME and [(Me$_3$Si)$_2$N]$_2$PrSn(CH$_2$SiMe$_3$)$_3$·2CO$_2$·DME, (c) (Me$_3$SiCH$_2$)$_3$SnPr(OH)$_2$·2CO$_2$, (d) (n-BuOCO$_2$)$_3$Ln.

In the IR spectra of V and VI there are three strong bands at 2180, 1620 and 1520 cm^{-1} which are absent in the IR spectra of the starting compounds. The IR spectrum of VII contains two bands at 2180 and 1680 cm^{-1} in addition to absorption bands characteristic of (Me$_3$SiCH$_2$)$_3$Sn groupings and a wide band of stretching modes of OH groups at 3400 cm^{-1}. In our opinion the presence of the additional bands in the IR spectra of V, VI, and VII is due to the presence of

coordinated CO_2. From comparison of the IR spectra of the complexes obtained and the IR spectra of gaseous CO_2 ($2349\ cm^{-1}$), CO_2 in solution ($2340\ cm^{-1}$) [6], and adsorbed CO_2 (1640, 1560, 1390 and $1330\ cm^{-1}$) [7], fixed by the nickel and cobalt complexes (1700—1650, 1300—1250 and $1250—1200\ cm^{-1}$) [4,5] and also with the IR spectra of the carbonate complex of dicyclopentadienyltitanium (1475, $1425\ cm^{-1}$) [3], other carbonate (1780, 1260, $1020\ cm^{-1}$) and carboxylate (1640, 1300 and $1020\ cm^{-1}$) groupings [7], it may be concluded that the CO_2 molecules in complexes I, II and V—VII are in a linear intact form and bound by a coordination bond: $C=O:\rightarrow M$. It is presumed that the presence of three $\nu(C=O)$ bands in the spectra of V and VI is due to the presence of two coordination centres in these complexes (Sn and Pr atoms). The high frequency band at $2180\ cm^{-1}$ does not depend on the nature of the coordination centre; therefore there are only three bands instead of four.

From comparison of the spectra of I, II, V and VI (Fig. 1) it may be concluded that the band at $1520\ cm^{-1}$ corresponds to the mode of CO_2 coordinated to the praseodymium atom and the band at $1620\ cm^{-1}$ to CO_2 coordinated to the tin atom. Apparently the Pr atom loses its acceptor ability when two OH groups are bound to it. Therefore in complex VII CO_2 is coordinated to the tin atom and the low-frequency $\nu(C=O)$ band is found at $1680\ cm^{-1}$.

The data obtained allow one to assume that most of the lanthanide compounds are capable of fixing carbon dioxide, but the researches are being continued.

Experimental

All reactions were carried out under dry CO_2 or argon atmosphere. In all experiments a volume of CO_2 dissolved in DME or hexane was taken into consideration.

[(Me₃SiCH₂)₃Sn]₃Pr·2CO₂·DME (VI). A suspension of 1.73 g (1.26 mmol) of [(Me₃SiCH₂)₃Sn]₃Pr·DME (IV) in 15 ml of DME was placed in an ampoule linked to a gas burette which was filled with CO_2. The absorption of two moles of CO_2 per mole of IV (60 ml, 2.67 mmol) occurred at room temperature in 10—15 min. The ampoule was sealed and allowed to stand at room temperature overnight. The colour of the reaction mixture changed from yellow to green. The precipitate was separated by decanting the solvent after centrifuging the reaction mixture. The precipitate was washed with hexane and dried in vacuo to give 1.55 g (83%) of VI, dec. > 200°C. (Found: Pr, 10.14. $C_{42}H_{109}O_6PrSi_9Sn_3$ calcd.: Pr, 9.65%). As the elemental analysis of VI was difficult and gave lower results (C was 2.5% lower and H was 1% lower), fragmentation analysis of VI was additionally carried out. (Found: (Me₃SiCH₂)₃Sn, 78.33. [(Me₃SiCH₂)₃Sn]₃Pr·2CO₂·DME calcd.: (Me₃SiCH₂)₃Sn, 78.13%.) Difficulties in the elemental analyses of lanthanide compounds were also noted by other authors.

[(Me₃Si)₂N]₂PrSn(CH₂SiMe₃)₃·2CO₂·DME (V). Following the above procedure, 0.88 g (0.9 mmol) of III in 10 ml of DME absorbed 45 ml (2 mmol) of CO_2 to afford 0.81 g (84%) of V, dec. > 140°C. (Found: Pr, 14.25. $C_{30}H_{79}N_2O_6PrSi_7Sn$ calcd.: Pr, 13.82%.) Fragmentation analysis: Found: (Me₃SiCH₂)₃Sn, 37.20; (Me₃Si)₂N, 30.93. [(Me₃Si)₂N]₂PrSn(CH₂SiMe₃)₃·2CO₂·DME calcd.: (Me₃SiCH₂)₃Sn, 37.30; (Me₃Si)₂N, 31.45%.

Hydrolysis of VI in the open system. 1.04 g (0.7 mmol) of VI in 5 ml of hexane was placed in an ampoule linked to a gas burette. When 1 ml (excess) of

oxygen-free water was added immediately 30 ml (94%) of CO_2 was evolved. The IR spectrum of the gaseous products does not show the presence of CO. The organic layer was decanted from the precipitate, which was dried in vacuo to give 0.40 g (100%) of $(Me_3SiCH_2)_3SnPr(OH)_2$ (VIII), dec. > 300°C. Fragmentation analysis of VIII: Found: $(Me_3SiCH_2)_3Sn$, 69.20; Pr, 26.44. $(Me_3SiCH_2)_3SnPr(OH)_2$ calcd.: $(Me_3SiCH_2)_3Sn$, 68.50; Pr, 25.38%. GLC analysis of the organic layer showed the presence of $(Me_3SiCH_2)_3SnMe$ (0.24 g, 86%), $[(Me_3SiCH_2)_3Sn]_2O$ (0.22 g, 79%), methyl cellosolve (0.05 g, 96%) and traces of DME.

Hydrolysis of VI in the closed system. A mixture of 0.86 g (0.58 mmol) of VI in 5 ml of hexane and 1 ml (excess) of oxygen-free water was placed in an evacuated ampoule, after the ampoule was sealed and allowed to stand overnight. The organic layer was decanted from the precipitate which was dried in air to give 0.36 g (95%) of $(Me_3SiCH_2)_3SnPr(OH)_2 \cdot 2CO_2$ (VII), dec. > 300°C. Fragmentation analysis of VII: Found: $(Me_3SiCH_2)_3Sn$, 58.72; Pr, 20.85. $(Me_3SiCH_2)_3SnPr(OH)_2 \cdot 2CO_2$ calcd.: $(Me_3SiCH_2)_3Sn$, 59.12; Pr, 21.90%. GLC analysis of the organic layer gave $(Me_3SiCH_2)_3SnMe$ (0.2 g, 87%), $[(Me_3SiCH_2)_3Sn]_2O$ (0.17 g, 77%), methyl cellosolve (0.04 g, 91%) and traces of DME.

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