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SYNTHESIS AND STRUCTURE OF METAL CARBONYL DERIVATIVES OF LANTHANIUM, SAMARIUM AND YTTERBIUM

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Summary

It has been shown that the reaction of amalgamated lanthanides (Ln) with binuclear carbonyls $Co_2(CO)_8$ and $[CpMo(CO)_3]_2$ in THF at room temperature leads, depending on the reagent ratio, to tris-(I) or bis- metal carbonyl(II) complexes of lanthanides, $Ln[M(CO)_mL]_n$ (Ln = Sm, Yb; $M(CO)_mL = Co(CO)_4$, $Mo(CO)_3Cp$; $n = 2,3$). II (Ln = Sm, Yb) may also be obtained by reduction of the respective I with naphthalene radical anions in THF.

IR and UV spectroscopy proved that these compounds contain a transition metal–lanthanide bond.

Lanthanide metal carbonyl derivatives are of great interest from the viewpoint of studying their structure and investigating the possible existence of a metal–lanthanide bond. They are also of interest from a practical viewpoint for use as catalysts and for obtaining hard-to-get lanthanide compounds.

Earlier we had produced metal carbonyl derivatives of lanthanides at oxidation states +2 and +3.

Trivalent derivatives were obtained by reaction of binuclear metal carbonyls with amalgamated lanthanides, Ln/Hg [1] (eq 1), and divalent derivatives were synthesized by the reaction between Hg derivatives of cobalt carbonyl with 4(5)-fold excess of the respective lanthanide, eq. 2.

$$[M(CO)_mL]_2 + Ln/Hg \xrightarrow[\text{THF, 20°C}]{} Ln[M(CO)_mL]_3 \cdot n\text{THF} \qquad (1)$$

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$(M(CO)_mL = Co(CO)_4, Mo(CO)_3C_5H_5;\ Ln = Sm, La, Eu, Tm, Er, Yb;\ n = 2\text{–}4)$

$$Hg[Co(CO)_4]_2 + mLn^0 = Ln[Co(CO)_4]_2 \cdot nTHF \qquad (2)$$

$(Ln = Sm, Yb, Eu;\ m = 4(5);\ n = 2\text{–}4)$

A similar product was obtained also by the reaction between Tl salts of cobalt carbonyl and lanthanide diiodide [2,3], eq. 3.

$$2(OC)_4CoTl + LnI_2 \cdot nTHF \xrightarrow{THF} Ln[Co(CO)_4]_2 \cdot nTHF + 2TlI \qquad (3)$$

$(Ln = Sm, Eu, Yb)$

In this work, we have shown for Sm and Yb, that by reaction 1 it is also possible to produce divalent lanthanide derivatives, if one uses 10–14-fold excess of zero-valent lanthanide/metal, over cobalt or molybdenum carbonyls, eqs. 4 and 5.

$$mLn/Hg + Co_2(CO)_8 \xrightarrow{THF} Ln[Co(CO)_4]_2 \cdot nTHF \qquad (4)$$

$$mLn/Hg + [Mo(CO)_3C_5H_5]_2 \xrightarrow{THF} Ln[Mo(CO)_3C_5H_5]_2 \cdot nTHF \qquad (5)$$

$(m = 10\text{–}14;\ Ln = Sm, Yb)$

On the other hand, reaction 2 may be used to produce metal carbonyl derivatives of trivalent lanthanides, as in the case with the reaction of Er/Hg with $Hg[Co(CO)_4]_2$ [4], eq. 6.

$$3Hg[Co(CO)_4]_2 + 2Ln/Hg \rightarrow 2Ln[Co(CO)_4]_3 \cdot nTHF \qquad (6)$$

$(Ln = Sm, La, Eu, Tm, Yb;\ n = 4\text{–}5)$

It is known that trivalent derivatives of lanthanides of the type Cp_3Ln are reduced, in the case where Ln = Yb, Sm, to divalent derivatives Cp_2Ln under the action of various reductants [5].

We have shown that metal carbonyl derivatives of trivalent Sm and Yb, $[(CO)_4Co]_3Ln$, $[C_5H_5(CO)_3Mo]_3Ln$ (Ln = Sm, Yb), are also reduced under the action of Ln^0 or a naphthalene radical anion, eqs. 7 and 8.

$$[L(CO)_mM]_3Ln + Ln^0 \xrightarrow{THF} 2Ln[M(CO)_mL]_2 \cdot nTHF \qquad (7)$$

$$[L(CO)_mM]_3Ln + Na^+Naphthalene^- \rightarrow Ln[M(CO)_mL]_2 + NaM(CO)_mL \qquad (8)$$

$(L(CO)_mM = Co(CO)_4, Mo(CO)_3C_5H_5;\ Ln = Sm, Yb)$

The compounds obtained were characterized by IR spectroscopy. The fact that Ln^{III} compounds reduce to Ln^{II} derivatives together with the absence of the absorption lines of free anions $Co(CO)_4^-$ and $Mo(CO)_3C_5H_5^-$, in the IR spectra of compounds such as $Ln[Co(CO)_4]_3$ and $Ln[Mo(CO)_3C_5H_5]_3$, in our opinion proves the existence of direct interaction between Ln and a metal (particularly Co, Mo) (Table 1).

Alternatively it was shown that complexes, where the CO group was inserted, could not be reduced (in compounds of the type $Ln[OCCo(CO)_3]_3$ and Ln[OC-

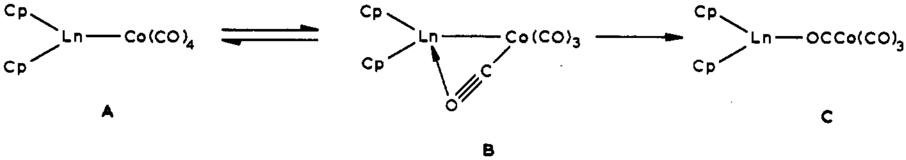
TABLE 1

IR SPECTRA OF METALCARBONYL DERIVATIVES OF DI- AND TRIVALENT LANTHANIUM, SAMARIUM AND YTTERBIUM IN THF SOLUTIONS (divalent derivatives were obtained by reduction with naphthalene radical anion or by a reaction with mercury compound)

Complex	ν(CO) (cm^{-1})
$Sm[Co(CO)_4]_3$	2060s, 2030wsh, 1980sh, 1960s, 1930sh, 1900sh, 1830sh, 1800sh, 1730sh.
$Yb[Co(CO)_4]_3$	2060s, 2025s, 1985sh, 1960sh, 1910sh, 1800sh, 1785sh.
$Sm[Co(CO)_4]_2$ [a]	2060m, 2048m, 2030s, 2010m, 1965s, 1930s, 1775s, 1765s.
$Sm[Co(CO)_4]_2$	2060s, 2048s, 2030sh, 2010sh, 1967sh, 1930s, 1770s, 1785sh.
$Yb[Co(CO)_4]_2$ [a]	2045w, 2030m, 2010m, 1915s, 1900s, 1805s, 1786s.
$Yb[Co(CO)_4]_2$	2045w, 2020s, 2010m, 1915s, 1998s, 1805s, 1785s.
$La[Mo(CO)_3Cp]_3$	2020s, 1900s, 1810m, 1780w, 1675s.
$Sm[Mo(CO)_3Cp]_2$	2020s, 1930s, 1820s, 1775sh.
$Yb[Mo(CO)_3Cp]_3$	2020s, 1910s, 1820s, 1770sh.
$Sm[Mo(CO)_3Cp]_2$ [a]	2020s, 1940s, 1910s, 1900s, 1798s, 1748sh.
$Sm[Mo(CO)_3Cp]_2$	2020s, 1953s, 1925s, 1900s, 1798s, 1748sh.
$Yb[Mo(CO)_3Cp]_2$	2025s, 1970w, 1960s, 1940s, 1915w, 1890sh, 1740m.
$Yb[Mo(CO)_3Cp]_2$ [a]	2020s, 1963w, 1953s, 1940s, 1910w, 1890sh, 1740m.
$Hg[Mo(CO)_3Cp]_2$	1990s, 1995s, 1862s.
$Hg[Co(CO)_4]_2$	2060s, 1995s.
$Na^+[Mo(CO)_3Cp]^-$	1970s, 1900s, 1750sh.
$Na^+ Co(CO)_4^-$	1970s, 1860sh.

[a] Obtained according to ref. 5.

$Mo(CO)_2Cp]_3$), but gave decomposition products. Thus, we may assume that the CO group insertion into the metal–lanthanide bond proceeds as follows:



Taking into account that frequencies of the terminal CO group in the compounds under study lie in the region of 1900–2000 cm^{-1} (for structure **A**), and that of the bridging group at 1580–1700 cm^{-1} (for structure **C**), then the bands at intermediate values of 1700–1800 cm^{-1}, which disappear in the final structure **C** can be ascribed to the CO group, coordinated with a lanthanide atom (as in structure **B**). This conclusion is consistent with the results presented in refs. 6, 7, where the frequency drop, for ν(CO) of metal carbonyls, from 1900–2100 to 1700–1800 cm^{-1} was observed when they formed adducts with Cp_3Ln. Moreover, X-ray analysis data confirmed the CO group intrusion for the following compounds: $Cp_2Yb{-}OCCo(CO)_3 \cdot THF$ [8], $Cp_2Yb{-}OCFe_3(CO)_{11}C{-}O{-}YbCp_2$ [9], $[Cp(CO)_2MoC{-}O{-}]_3La \cdot 6THF$ [10]. The ν(CO) bands of these compounds are in the region of 1580–1700 cm^{-1}. The bands at 220–280 cm^{-1} in the low-frequency range according to ref. 11 can be ascribed to Ln–O bond oscillations.

Complexes of the $Cl_2LnCo(CO)_4$ type (Ln = Sm, Tm, Eu, Yb) failed to show the CO group frequency drop to 1580–1700 cm^{-1}. This is in agreement with ref. 6, where Cp_2LnCl, in contrast to Cp_3Ln, did not form an adduct with metal carbonyl derivatives due to the dimeric structure of the former.

Therefore, one can assume that prior to CO group intrusion into the metal–lanthanide bond, an intramolecular coordination of one carbonyl group to the lanthanide atom takes place, structure **B**, (similar to that observed for metal-carbonyl derivatives of *d* elements [12,13]), and the bands at 1700–1800 cm^{-1} should probably be ascribed to valency oscillations of such CO groups.

UV spectroscopic data supplies further evidence in favour of CO group coordination to the lanthanide metal. A broad band with an absorption maximum at 520–540 nm is observed in the UV spectra of the $Cp_2Ln{-}Co(CO)_4$ complexes. Addition of one equivalent of PPh_3 caused the disappearance of this band and instead a narrow band with λ_{max} at 420 nm emerged (IR spectra of phosphine comlexes showed no migration of the CO group). The same phenomenon was observed in the UV spectrum of the $Hg[Co(CO)_4]_2$ complex, where the CO group was not coordinated with the mercury atom [14].

An interesting point is a very complex IR spectra for divalent lanthanide metalcarbonyl complexes at 1600–2100 cm^{-1} compared to that of the respective mercury derivatives for metal carbonyls. For example, the IR spectrum of $Hg[Co(CO)_4]_2$ has only two ν(co) bands at 2060 and 1995 cm^{-1} (this complies with the linear structure of the complex and local symmetry of the trigonal bipyramidal $Co(CO)_4$ fragments, close to C_{3v}). Spectra for samarium and ytterbium (cobalt tetracarbonyl) derivatives in the same region show up to five bands for Sm, and even six, for Yb. This increase in the number of the CO group valency oscillation bands for lanthanide compounds can be attributed to the lower general symmetry of the $Ln[Co(CO)_4]_2$ molecule (Ln = Sm, Yb) compared to the $Hg[Co(CO)_4]_2$ molecule due to a lack of molecule linearity, also because of lower local symmetry for $Co(CO)_4$ fragments due to bonding of the lanthanide atom with the carbonyl oxygen.

Table 1 shows that IR spectra of cobalt carbonyl complexes of samarium and ytterbium in solution after reduction are virtually the same as those for specially prepared samples of $Ln[Co(CO)_4]_2 \cdot n$THF.

However no formation of a divalent complex was observed when the aged $Sm[Co(CO)_4]_3 \cdot n$THF complex with CO bridging group (indicated by 1675 cm^{-1} in the IR spectrum) was reduced. Apparently the complex undergoes a complete decomposition which is reflected by sharp changes in the whole range of the IR spectrum and by color change.

A similar situation is observed by comparison of the IR-spectra for $Ln[Mo(CO)_3Cp]_3$complexes (Ln = Sm, Yb), where reduction yields $Ln[Mo(CO)_3Cp]_2$ complexes. However, for Ln = La we failed to observe an alteration, the IR spectra of the obtained compound always had a broad band, 1675 cm^{-1}, corresponding to a bridging structure. That is why reduction of this complex leads to its decomposition. Thus, it is clear that the nature of the metal affects the facility of CO group intrusion.

Experimental

All experiments were carried out in argon, solvents were dried and purified.

The synthesis of tris(tetracarbonylcobaltate)samarium tetrakis(tetrahydrofuranate), $Sm[Co(CO)_4]_3 \cdot nTHF$

0.32 g (2 mmol) of amalgamated Sm prepared according to ref. 4 were added to

0.98 g (1.72 mmol) of $Hg[Co(CO)_4]_2$ in 50 ml of THF. The reaction mixture was stirred for 6 h at room temperature. The resulting light-yellow solution was then decanted from the precipitate. The product is sedimentated from the solution by hexane at low temperature. After short vacuum drying $Sm[Co(CO)_4]_3 \cdot 4THF$, m.p. 100°C (decomp.), is obtained in the form of a yellow powder with 45% yield (0.64 g). Found: C, 36.15; H, 3.12; Co, 16.56. $C_{28}H_{32}Co_3SmO_{16}$ calcd.: C, 35.33; H, 3.36; Co, 18.6%.

Similarly tris(tetracarbonylcobaltate)ytterbium tristetrahydrofuranate, $Yb[Co(CO)_4]_3 \cdot 3THF$, was obtained in the form of a dark-yellow powder, m.p. 116°C (decomp.) with 57% yield. Found: C, 31.19; H, 2.58; Co, 18.83. $C_{24}H_{24}Co_3YbO_{15}$ calcd.: C, 31.93; H, 2.66; Co, 19.62%.

$Sm[Co(CO)_4]_3 \cdot n$THF reduction by Na^+Naph^- in THF

A dark-blue solution of 0.12 g (0.8 mmol) Na^+Naph^- in 25 ml THF was added to a yellow solution, 0.15 g(0.16 mmol) of $Sm[Co(CO)_4]_3 \cdot 4THF$ in 25ml THF at room temperature. During addition the blue color of the radical anion vanished and in 1 h the reaction mixture acquired a pale-violet color. IR spectra show the presence of $Na^+Co(CO)_4{}^-$ and $Sm[Co(CO)_4]_2$.

Reduction of $Yb[Co(CO)_4]_3 \cdot n$THF, $Sm[Mo(CO)_3Cp]_3 \cdot n$THF and $Yb[Mo(CO)_3Cp]_3 \cdot n$THF was performed in a similar way.

In an attempted reduction of $Sm[Mo(CO)_3Cp]_3 \cdot 4THF$ with sodium naphthalene (IR spectra of such compounds had a band at 1675 cm^{-1} indicating a bridged structure) neither the divalent derivative nor the corresponding anion could be detected.

Reduction of $La[Mo(CO)_3Cp]_3 \cdot 6THF$ with Na^+Naph^- in THF

0.12 g (0.8 mmol) Na^+Naph^- in 25 ml of THF was added to the solution of 0.15 g (0.12 mmol) $La[Mo(CO)_3Cp]_3 \cdot 6THF$ in 25 ml of THF. The brownish solution of the lanthanide complex does not in fact change its color with Na^+Naph^- addition. After 4 h the reaction mixture color changed to light brown and a precipitate was formed. IR spectra showed the absence of CO group absorption bands in the reaction products.

Synthesis of tris(cyclopentadienyltricarbonylmolybdenate)samarium tetrakis(tetrahydrofuranate), $Sm[Mo(CO)_3Cp]_3 \cdot 4THF$

0.11 g (0.73 mmol) Sm/Hg was added to 0.29 g (0.42 mmol) $Hg[Mo(CO)_3Cp]_2$ in 40 ml of THF. The reaction mixture being stirred for 3 h at room temperature, the yellowish solution was separated from the precipitate and 50 ml of hexane was added to the filtrate, the resulting solution cooled to −70°C. A dark-brown precipitate was separated, washed by cold hexane (3 × 25 ml) and after a short period of vacuum drying $Sm[Mo(CO)_3Cp]_3$ was obtained in the form of the THF complex, $Sm[Mo(CO)_3Cp]_3 \cdot 4THF$ with 71% (0.21 g) yield and m.p. 140°C (decomp.). Found: C, 40,43; H, 4.17. $C_{40}H_{47}Mo_3SmO_{13}$ calcd.: C, 40.92; H, 4.01; Sm, 12.79; Mo, 24.6%.

Similarly tris(cyclopentadienyltricarbonylmolybdenate)ytterbium tetrakis(tetrahydrofuranate), $Yb[Mo(CO)_3Cp]_3 \cdot 4THF$ was obtained in the form of yellow powder with 66% yield. Found: C, 39.80; H, 4.32. $C_{40}H_{47}Mo_3YbO_{13}$ calcd.: C, 40.13; H 3.93%. Tris(cyclopentadienyltricarbonylmolybdenate)lanthanum hexakis(tetrahydrofuranate), $La[Mo(CO)_3Cp]_3 \cdot 6THF$ was produced according to ref. 10.

Synthesis of bis(tetracarbonylcobaltate)samarium tetrakis(tetrahydrofuranate), $Sm[Co(CO)_4]_2 \cdot 4THF$ and related complexes

A solution of 0.34 g (1 mmol) $Co_2(CO)_8$ in 10 ml of THF was added dropwise to a suspension of 1.2 g (8 mmol) amalgamated samarium in 25 ml of THF over 5 h at room temperature. The cloudy solution was allowed to settle and the light-yellow solution was poured into 50 ml of hexane at −40°C and cooled further. $Sm[Co(CO)_4]_2$was precipitated in the form of THF complex, $Sm[Co(CO)_4]_2 \cdot 4THF$, with 72% yield and m.p. 60°C (decomp.) Found: C, 36.11; H, 3.82; Co, 14.35. $C_{24}H_{32}O_{12}Co_2Sm$ calcd.: C, 36.92; H, 4.10; Co, 15.12%. Bis(tetracarbonylcobaltate)ytterbium tris(tetrahydrofuranate), $Yb[Co(CO)_4]_2 \cdot 3THF$ was produced in a similar way with 79% yield, m.p. 105°C (decomp.) Found: C, 32.21; H, 3.15, Co, 15.89. $C_{20}H_{24}Co_2O_{11}Yb$ calcd.: C, 32.83; H, 3.28; Co, 16.14%.

2.4 g (16 mmol) Sm/Hg and 0.49 g (1 mmol) $[Mo(CO)_3Cp]_2$ in 25 ml of THF produced bis(cyclopentadienyltricarbonylmolybdenate)samarium tetrakis(tetrahydrofuranate), $Sm[Mo(CO)_3Cp]_2 \cdot 4THF$ with 62% yield, m.p. 120°C (decomp.), under the same conditions as in the preceding experiment: Found: C, 40.21, H, 4.27, Mo, 19.82. $C_{32}H_{42}H_{42}Mo_2SmO_{10}$. calcd.: C, 41.38; H, 4.53; Mo, 20.69%. Bis(cyclopentadienyltricarbonylmolybdenate)ytterbium tris(tetrahydrofuranate), $Yb[Mo(CO)_3Cp]_2 \cdot 3THF$ was produced similarly with 70% yield, m.p. 165°C (decomp.), Found: C, 37.11; H, 3.66; Mo, 20.95. $C_{28}H_{34}Mo_2YbO_9$. calcd.: C, 38.23; H, 3.87; Mo, 21.84%.

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