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Heterometallic catalysts. Cobalt carbonyl derivatives of lanthanides in catalysis of octene-1 hydroformylation *

I.P. Beletskaya,
Moscow State University, Chemical Department (U.S.S.R.)

G.K.-I. Magomedov, and A.Z. Voskoboinikov *
State Scientific-Research Institute of Chemistry and Technology of Organoelement Compounds,
111123 Moscow, Shosse Eutuziastov 38 (U.S.S.R.)

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Abstract

The results of an investigation involving the catalysis of octene-1 hydroformylation with heterobimetallic catalysts, cobalt carbonyl derivatives of lanthanides, are reported.

Introduction

The main difference between poly- and mono-nuclear complex systems is well known, and leaving aside general energy considerations, its essence lies in the possibility of binding one or more ligands with more than one metallic centre [1,2]. This statement was formulated for systems containing late transition metals with similar series. However, a more promising approach is based on application of "polar" metals from the coordination point of view (i.e. elements of the early and late transition metals together or transition and non-transition metals) in one catalytic system. There are a number of reasons for the unusual catalytic properties of such heterometallic systems:

1. Metals with different coordination abilities can take part in different stages of the catalytic cycle and can even cause consecutive catalytic conversions. Examples of such heterometallic systems include the bifunctional catalyst of hydroformylation-acetalization reactions, $Sn[Co(CO)_4]_4$ [3], as well as catalysts of the process of isomerization-amidocarbonylation of oxyranes based on compounds of cobalt with additives, such as Lewis-type acids, for example $Ti(OPr\text{-}i)_4$ and $Al(OPr\text{-}i)_3$ [4].

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* This paper marks the centenary of the discovery of metal carbonyls.

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2. Structures containing an early transition or a non-transition metal can be considered as a ligand with certain electronic properties relative to the neighbouring elements of triads. In this case, the catalytic cycle is carried out by the central elements of the triad and the role of the second metal reduces ease of generation, conversion or stabilization of the particular intermediate. Tin-containing catalysts of olefin carbonylation, $PtH(SnCl_3)(CO)(PPh_3)$ [5,6] and $M(CO)_5SnCl_2$ ($M =$ Cr, Mo, W) [7], are good examples. The authors [8–11] believe that the catalytic activity of zirconium- and hafnium-rhodium carbonyl systems in the process of hydroformylation has a similar nature. But in any case one should not forget the possible participation of hydride derivatives of early transition and non-transition elements in some stages of the catalytic cycle. The results of our work confirm this theory.

3. The difference in the coordination abilities of metals which constitute the catalytic system maintains the diversity of their binding to ligands which are the potential participants of the catalytic cycle. In this case, the diversity is often broader than that for traditional clusters of triad elements. For example, in the case of metal-carbonyl derivatives of lanthanides, which have been studied intensively in the last few years [12], a series of different types of CO interaction with the metallic skeleton has been found. Concurrent with terminal carbon monoxide binding in bimetallic clusters $ILnCo(CO)_4$, isocarbonyl binding, as, for example, in $(C_5H_5)_2Yb(\eta\text{-}OC)Co(CO)_3$ or $La[(\mu\text{-}OC)Mo(CO)_2(C_5H_5)]_3$, a semi-bridging carbonyl interaction, $Er[(\mu,\ \pi\text{-}OC)Mo(CO)_2(C_5H_5)]_3$, as well as more complex types of binding [13] have been found and the equilibrium of ionic states in solution of solvent-separated and contact (via CO) ion pairs was established for complexes with the composition $X_2LnCo(CO)_4$ ($X = Cl, C_5H_5$). This multinuclear interaction leads to loosening of the bond in the ligand and increases its reactivity relative to nucleophilic and electrophilic attack. This process of facilitation of the dissociation of small molecules resembles the activation of a substrate on the surface of a heterogeneous catalyst. There are no reliable data concerning homogeneous catalyst systems of this type. But the influence of Lewis acids which has a similar effect on the activity of transition metal complexes in the processes of activation of carbon monoxide and C–H bonds [14] should also be noted. The importance of this route for non-catalytic activation of the C–H bond on a thorium-ruthenium cluster was demonstrated recently [15].

The presence of a broad range of CO binding in metal carbonyl derivatives of lanthanides stimulated this work. We studied the catalytic activity of cobalt carbonyl derivatives in the hydroformylation of octene-1.

$$\text{n-}C_6H_{13}CH{=}CH_2 \xrightarrow[H_2+CO]{\text{Catalyst}} \underset{\text{(n-structure)}}{\text{n-}C_6H_{13}CH_2CH_2CHO} + \underset{\text{(iso-structure)}}{\text{n-}C_6H_{13}CH(CH_3)CHO} \qquad (1)$$

Practically any cobalt-containing system should be a catalyst for hydroformylation. The formation of an actual catalytic intermediate, cobalt hydridocarbonyl at elevated pressure of synthesis-gas and temperature, is responsible for this [16]. Therefore, one can expect cobalt-carbonyl complexes of lanthanides to be catalytically active in hydroformylation. First it was of interest to us to compare its activity with unmodified $Co_2(CO)_8$.

Results and discussion

The results of the effect of lanthanide-containing cobalt-carbonyl catalytic systems on the hydroformylation of octene-1 are shown in Table 1. For convenience, we chose conditions leading to 50% conversion of the olefin into a mixture of isomeric nonanal and methyloctanal for unmodified octacarbonyldicobalt. Individual cyclopentadienyl complexes of ytterbium and lutecium were not active even under more severe conditions. Therefore, there is no doubt that in the case of bimetallic systems the cobalt centres carry the catalytic cycle by the traditional route for $HCo(CO)_4$ [14]. However, when $(C_5H_5)_2YbOCCo(CO)_3$ or a mixture of ytterbocene/$Co_2(CO)_8$ (2/1) was used [12] as the catalyst, a considerably higher conversion of the starting olefin into isomeric aldehydes than that for $Co_2(CO)_8$ was achieved. The addition of a Lewis acid, $(C_5H_5)_3Lu$, to $Co_2(CO)_8$ did not give rise to a noticeable change of the process parameters, but IR spectral data showed the presence of effective coordination of lutetium atoms by the bridge carbonyl group of octacarbonyldicobalt, the stretching vibration frequency of which decreased by 57 cm^{-1} (1773 cm^{-1}).

The constant isomeric ratio of aldehyde in the products indicates that lanthanide particles can take part only in those stages which do not influence the regioselectivity of the process, i.e. they can take part in the initial and final stages [14]. Apparently, the catalytic intermediate, cobalt hydridocarbonyl, is formed as a result of hydrogenolysis (eq. 2) of the starting heterobimetallic complex. Ytterbium

$$(C_5H_5)_2YbOCCo(CO)_3 \xrightleftharpoons{H_2} (C_5H_5)_2YbH + HCo(CO)_4 \qquad (2)$$

hydride, $(C_5H_5)_2YbH$, which is sufficiently stable at elevated hydrogen pressure, is generated along with $HCo(CO)_4$ [17]. Conversion (eq. 2) proceeds with more difficulty than the traditional route of $HCo(CO)_4$ from $Co_2(CO)_8$ formation, but it does not cause a decrease in catalyst efficiency. On the contrary, the catalyst

Table 1

Results of the hydroformylation of octene-1 by lanthanide-containing cobalt-carbonyl catalysts (6.5 MPa $CO:H_2 = 3:2$; 135 °C; octene-1 concentration 0.87 mole/l, catalyst concentration by cobalt $1.1 \cdot 10^{-3}$ mole/l in a mixture of $(C_2H_5)_2O:THF = 4:1$ (vol.); 5 h)

Catalytic system	Octene-1 conversion (%) (±2%)	n-/iso-aldehydes in products
$(C_5H_5)_2YbOCCo(CO)_3$	75	1.10–1.15
$(C_5H_5)_2Yb/0.5Co_2(CO)_8$	75	1.10–1.15
$(C_5H_5)_2YbCl/NaCo(CO)_4$	60	1.15–1.20
$(C_5H_5)_2LuCl/NaCo(CO)_4$	60	1.15–1.20
$(C_5H_5)_3Lu/0.5Co_2(CO)_8$	50	1.10–1.15
$0.5Co_2(CO)_8$	50	1.10–1.15
$(C_2H_5)_4NCl/0.5Co_2(CO)_8$	35	1.20–1.25
$NaCo(CO)_4$	55	1.00–1.05
$(C_5H_5)_2Co$	45	1.00–1.05
$(C_5H_5)Co(CO)_2$	45	1.00–1.05
$(C_5H_5)_2Yb$[a]	<1	–
$(C_5H_5)_3Lu$[a]	<1	–

[a] 17.5 MPa $CO/H_2 = 7/5$; 150 °C; catalyst concentration 3.3×10^{-3} mol/l.

efficiency increases, and we relate this to the presence of lanthanide hydrides in the reaction mixture as well as to their participation in the hydrogenation of acylcobalt carbonyl particles.

Using the stoichiometric interaction of lutetium hydride with benzoylpentacarbonylrhenium as an example [18], we simulated the last stage of the catalytic cycle of hydroformylation in which the lanthanide hydrides take part. Benzaldehyde

$$[(\mathrm{C_5H_5})_2\mathrm{Lu}(\mu\text{-H})(\mathrm{THF})]_2 \xrightleftharpoons{\mathrm{THF}} 2(\mathrm{C_5H_5})_2\mathrm{LuH(THF)} \tag{3}$$

$$(\mathrm{C_5H_5})_2\mathrm{LuH(THF)} + \mathrm{C_6H_5CORe(CO)_5} \xrightarrow{\mathrm{THF}} \mathrm{C_6H_5CHO} + [(\mathrm{C_5H_5})_2\mathrm{Lu(THF)}]\mathrm{Re(CO)_5} \tag{4}$$

was isolated as 2,4-dinitrophenylhydrazone. Rheniumcarbonyl bimetallic complex, which was synthesized independently in a similar way (eq. 5), is formed as well [18].

$$(\mathrm{C_5H_5})_2\mathrm{LuCl(THF)} + \mathrm{NaRe(CO)_5} \xrightarrow{\mathrm{THF}} [(\mathrm{C_5H_5})_2\mathrm{Lu(THF)}]\mathrm{Re(CO)_5} + \mathrm{NaCl} \tag{5}$$

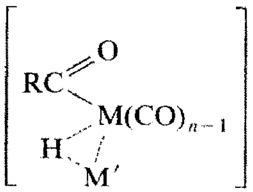
An intensive discussion arises from the last stage of hydroformylation, the hydrogenation of acylcobalt carbonyls (eq. 6). Concerning the traditional catalytic system, $\mathrm{Co_2(CO)_8}$, it is not clear which hydrogenating agent $\mathrm{H_2}$ (M = H) or $\mathrm{HCo(CO)_4}$ (M = $\mathrm{Co(CO)_4}$) is more important in the reaction shown in eq. 6 [14].

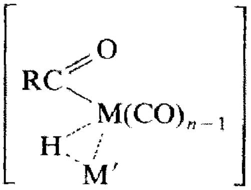
$$\mathrm{RCOCo(CO)_4 + HM} \longrightarrow \mathrm{RCHO + HCo(CO)_4} \tag{6}$$

It is believed that this phenomenon depends on specific hydroformylation conditions, i.e. $\mathrm{HCo(CO)_4}$ plays a decisive role at low partial hydrogen pressure and low temperature, but under other conditions preference is given to $\mathrm{H_2}$ [19–21]. The important preliminary ligand exchange of CO by the molecule of solvent S (eq. 7) is followed by oxidative addition of the hydride HM (eq. 8) and elimination of the aldehyde molecule (eq. 9) [14,21–25]. As to $\mathrm{HSnR_3}$, the overall rate of the reaction

$$\mathrm{RCOM(CO)}_n \underset{\mathrm{CO}}{\overset{\mathrm{S}}{\rightleftharpoons}} \mathrm{RCOM(CO)}_{n-1}\mathrm{(S)} \tag{7}$$

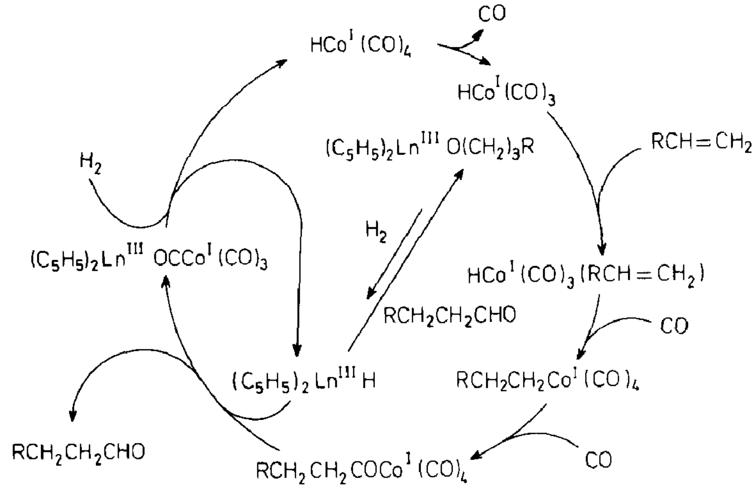
$$\mathrm{RCOM(CO)}_{n-1}\mathrm{(S)} + \mathrm{HM'} \rightleftharpoons \tag{8}$$





$$\xrightarrow{\mathrm{S}} \mathrm{RCHO + M'M(CO)}_{n-1}\mathrm{(S)} \tag{9}$$

with $\mathrm{CH_3COCo(CO)_3(PPh_3)}$ is determined by CO dissociation from the coordination sphere of the metal (eq. 7); however, in the case of $\mathrm{HSiR_3}$, oxidative addition of hydride (eq. 8) is the determining factor [26]. The lanthanide hydrides have greater hydride mobility than $\mathrm{HSnR_3}$. Therefore, the dissociation of carbon monoxide in



Scheme 1

$RCOM(CO)_{n-1}(S)$ (eq. 7) should be the limiting stage for them, but in the case of H_2 and $HCo(CO)_4$ the limiting stage is probably reaction 8.

The suggested scheme of the catalytic cycle of octene-1 hydroformylation on cobalt carbonyl complexes of lanthanides, in which hydrides of *f*-elements (along with H_2 and $HCo(CO)_4$) take part in the hydrogenation stage of acylcobalt carbonyls, is shown below. For simplicity, the route of formation of the second isomeric aldehyde is not shown.

The catalytic systems $(C_5H_5)_2YbCl/NaCo(CO)_4$ and $(C_5H_5)_2LuCl/NaCo(CO)_4$ lead to an increase in the conversion of the starting olefin by a factor of 1.2 only. Therefore, the nature of the lanthanide does not have a great influence on the result of catalysis (Scheme 1). The conversion is the same both for ytterbium, which has two stable oxidation states in organometallic compounds, which allows the secondary oxidation-reduction cycles $Yb^{3+} \rightleftarrows Yb^{2+}$, and for lutetium, which has a stable 3 + oxidation state.

The relatively lower activity of the last two systems compared to $(C_5H_5)_2YbOCCo(CO)_3$ can be explained as follows. We have shown earlier that the chlorides bis(cyclopentadienyl)lanthanides react with $NaCo(CO)_4$ in THF yielding ionic heterobimetallic complexes [12]. As this takes place, 50% of the halide is consumed to form the corresponding ate-complex. As a result, the actual concentration of the bimetallic complex in the catalytic mixture will be much lower than the

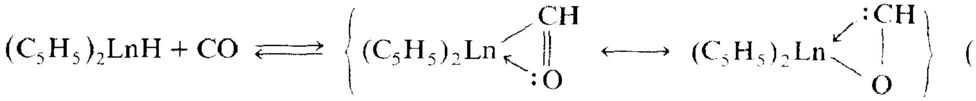
$$2(C_5H_5)_2LnCl + NaCo(CO)_4 \xrightarrow{THF} \left[(C_5H_5)_2LnCl_2\right]Na + \left[(C_5H_5)_2Ln(THF)_2\right]\left[Co(CO)_4\right] \quad (10)$$

concentration of the starting $NaCo(CO)_4$. However, in a weakly solvating solvent (the catalysis was studied in such a medium) and at elevated temperatures the ate-complex is not sufficiently stable and therefore the concentration of the heterobimetallic catalyst increases. Because of this, one should consider the inhibiting influence of chloride ions on the cobalt catalyst of hydroformylation as the main reason for some catalyst deactivation. It is clear from Table 1 that addition of

$(C_2H_5)_4NCl$ to octacarbonyldicobalt lowers its activity greatly and increases the n-/iso-aldehydes ratio in the products.

The considerably lower isomeric ratio of aldehydes in the products in the case of cobaltocene or $(C_5H_5)Co(CO)_2$ allows us to abandon the suggestion concerning the formation of cyclopentadienylcobalt carbonyl catalytic intermediates under the process conditions. In principle, there are no obstacles to the formation of similar particles and this has been shown by Crease and Legzdins [27].

The contribution of lanthanides to the hydrogenation of acylcobalt-carbonyl particles in the final stage of hydroformylation must ensure a considerable increase in catalyst efficiency. In practice, the conversion growth is at best 1.5. This phenomenon can be attributed only to deactivation of hydride particles during the process. $(C_5H_5)_2LnH$ are capable of forming formyl complexes during reaction with carbon monoxide; it is similar to the phenomenon known in the chemistry of actinides [28,29], which can undergo the following conversions:


(11)

We believe that the main route of deactivation of lanthanide hydrides is their reaction with aldehyde, which accumulates during the process. Lutetium hydride has been shown to react readily with benzaldehyde according to eq. 12.

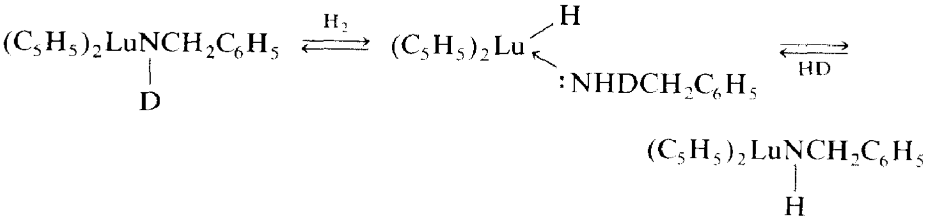
$$[(C_5H_5)_2Ln(\mu\text{-}H)(THF)]_2 + 2C_6H_5CHO \xrightarrow{THF} 2(THF)(C_5H_5)_2LnOCH_2C_6H_5 \quad (12)$$

The rate of reaction is comparable to that of processes 3–4. However, application of cobalt-carbonyl complexes instead of rhenium-carbonyl complexes as well as the use of aliphatic aldehydes instead of benzaldehyde should substantially change the rate ratio of processes 3–4 and 12 for hydrogenation of acylcarbonyls. Therefore, $(C_5H_5)_2LnH$ deactivation by reactions which are similar to 12 does not influence the first stage of hydroformylation, i.e. when the concentration of isomeric C_9-aldehydes is small. It is noted that the rate of the process drops greatly as the product accumulates; in this case, the drop is considerably larger than one would expect on the basis of kinetic relations assuming the absence of catalyst deactivation.

It may be supposed that lanthanide alcoholates are capable of undergoing hydrogenolysis (eq. 13) with regeneration of co-catalyst $(C_5H_5)_2LnH$ at an increased H_2 pressure as well as at elevated temperatures. We studied as similar reaction for the amide complex of lutetium [30] which undergoes 95% isotopic

$$(C_5H_5)_2LnOR \overset{H_2}{\rightleftharpoons} (C_5H_5)_2LnH + ROH \quad (13)$$

exchange of deuterium by protium at 20 °C and 5 MPa H_2, giving lutetium hydride as an intermediate product (eq. 14).


(14)

The process of co-catalyst regeneration (eq. 13) is designated in the general scheme of the catalytic cycle. However, at higher levels of octene-1 conversion to aldehydes it cannot compete with $(C_5H_5)_2LnH$ deactivation by eq. 12 in full measure. This is confirmed by the small amount of isomeric C_9-alcohols in the hydroformylation products, which at best reaches 3–5% and corresponds to the level which can be ensured by $HCo(CO)_4$ during aldehyde hydrogenation [14].

In spite of the deactivation of the co-catalyst, lanthanide hydrides, the increase in activity in the case of heterobimetallic systems is appreciable. It confirms once more the perspective of the approach described in the Introduction.

Experimental

The main methods and experimental conditions have been presented in a preliminary communication [31].

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