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Hydroformylation of olefins using dispersed molecular catalysts on solid supports

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A new method for heterogenization of metal complex catalysts by precipitation of its water–soluble analogue as a Gr.2 metals (Ca, Sr or Ba) salt on porous supports has been proposed. This technique yields a highly dispersed catalyst having a significantly higher activity (TOF) for hydroformylation of olefins compared to other known heterogenized catalysts. The catalyst can be recycled with ease.

KEY WORDS: hydroformylation; heterogenization; rhodium; olefins; carbon support.

1. Introduction

The difficulties in catalyst-reaction product separation and catalyst recycle have been a major bottleneck in practical application of homogeneous catalysts [1]. The issue of catalyst-product separation is even more critical in fine chemicals and pharmaceutical products that are thermally sensitive and high boiling compounds [2]. In this context, numerous efforts have been made to heterogenize the metal complex catalysts using techniques like biphasic catalysis [3] and anchoring [4], encapsulation [5] or tethering [6] to solid supports. The precipitation of ruthenium and rhodium complexes of phosphonated BINAPs as the zirconate species has resulted in providing a heterogenized catalyst for chiral hydrogenation of aromatic ketones and β-keto esters [7]. The use of water–soluble catalyst in a two-phase system has been commercially successful for hydroformylation of propylene and 1-butene; however this technique has limitations due to the poor solubility of a majority of substrates in water [3]. Discovery of catalyst heterogenization methodologies without leaching of the expensive metals still constitutes a major challenge [8].

In this paper, we describe a simple method for synthesis of highly dispersed organometallic complexes heterogenized on inert supports. This method of immobilization is generic in nature and can be applied to a variety of supports, catalysts and catalytic reactions. We demonstrate here as an illustration the use of a carbon supported Ba salt of HRh(CO)(TPPTS)$_3$ [Catalyst C-I (see figure 1)], as a highly active and stable hydroformylation catalyst. The catalyst is formed by interaction of a carbon supported barium nitrate with an aqueous solution of HRh(CO)(TPPTS)$_3$ and NaTPPTS [1:6], [TPPTS = triphenylphosphine trisulfonate] to form a precipitated Ba^{+2} salt of HRh(CO)(TPPTS)$_3$ and free TPPTS-Ba$_{3/2}$ where Ba^{+2} is adsorbed on the carbon surface by physical adsorption. HRh(CO)(TPPTS)$_3$ is well known as an aqueous phase hydroformylation catalyst however the Ba^{+2} salt of the complex HRh(CO)(TPPTS)$_3$ [Catalyst C-II], is insoluble not only in water but also in organic solvents. Further, precipitation onto a support using a pre-adsorbed Ba^{+2} species provides a highly dispersed, active and stable form of catalyst C-I with a much larger surface area. Here, a significantly enhanced activity of catalyst C-I has been demonstrated for the hydroformylation of higher olefins. A schematic representation of the catalyst is shown in figure 1, which could exist in the polymeric form as shown or as a dimer.

2. Experimental

2.1. Preparation of catalyst

The dispersed heterogenized catalyst was synthesized from a water–soluble metal complex prepared by known methods [9] and then precipitating it as its barium salt on a porous support. In a typical case, aqueous solution of 20% Ba(NO$_3$)$_2$ (2 gm 8.51 mmol) was added to 10 g of activated charcoal. The mixture was refluxed for 4–5 h and evaporated to dryness to get barium nitrate impregnated carbon.

The carbon supported barium salt of HRhCO(TPPTS)$_3$ was prepared by taking 1.5 g of above prepared Ba(NO$_3$)$_2$ impregnated carbon in a small two-neck round bottom flask. An aqueous solution of HRhCO(TPPTS)$_3$ 131.5 mg (0.07 mmol) and

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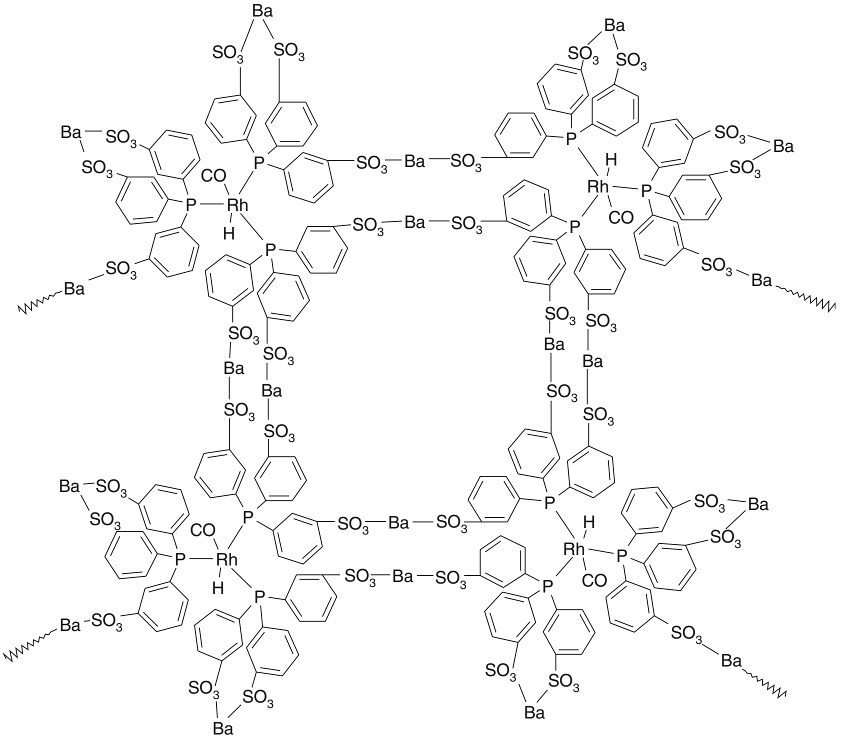

Figure 1. Schematic presentation of the precipitated catalytic complex C-II.

TPPTS 240.5 mg (0.42 mmol) Rh:P = 1:6) was added under constant stirring in a positive flow of argon. The stirring was continued for 4–5 h. The mixture was filtered; the precipitate was washed 2–3 times with cold and hot water respectively followed by water and toluene for 12 h each with soxhlet apparatus, to remove the unreacted catalyst. The precipitate was dried under vacuum (yield = 1.73 g).

2.2. *Experimental procedure for hydroformylation reaction*

In a typical experiment, known quantity of olefin with degassed solvent was charged in an autoclave. To this solution, a known quantity of catalyst was added. The contents were flushed with nitrogen and then with a mixture of CO and H_2. The reactor was heated to a desired temperature and then a mixture of CO and H_2(1:1) was introduced up to the desired pressure. A sample of the liquid phase mixture was withdrawn, and the reaction started by switching the stirrer on. The reaction was then continued at a constant pressure of syngas. The progress of the reaction was monitored by the pressure drop in reservoir with respect to time. When the gas absorption was complete, as per stoichiometry, the reaction was stopped, the reactor was cooled and the gas phase vented. A final sample of liquid was taken for analysis. The products were analyzed by gas chromatography on a HP-5 capillary column, 30 m (HP6890 series GC) in flame ionization detector.

2.3. *Characterization of catalyst*

The catalysts, C-I and C-II were characterized by FTIR, Solid state ^{31}P NMR, powder XRD, TEM, SEM and XPS [10]. Since catalyst C-I had absorbance in the total IR region, a similar catalyst was prepared on silica support [catalyst C-III] and was characterized using DRIFT-IR. Weak bands for νCO and νRh–H were observed at 1865 and 1990 cm^{-1}, whereas the corresponding values for the HRh(CO)(NaTPPTS)$_3$ and catalyst C-II were 1926 and 2007 cm^{-1} and 1987and 2061 cm^{-1}, respectively. The shift to lower frequencies as compared to the water–soluble complex could be due to support-catalyst interaction. The weak bands observed are probably due to the lower loading of the complex on support.

Solid-state ^{31}P NMR of C-I showed a signal at 2.51δ and a multiplet at 23.89δ [11]. The signal at 2.51δ is due to free TPPTS-Ba$_{3/2}$ as an excess of TPPTS is used in the preparation of the supported complex. The multiplet may arise from the mixing of the signals from the coordinated phosphine and phosphine oxide. The shift in the signals as compared to catalyst C-II could be a result of interaction of the catalyst with support.

The powder X-Ray Diffraction pattern of the catalyst C-I, C-II and C-III were identical indicating that the catalyst species was the same even when supported on carbon and silica. The surface area of catalyst C-I showed a reduction as compared to the virgin support C (36.43 and 158.3 m^2/g, respectively). As expected the pore volume also dropped to 0.066 cc/g for C-I as compared to 0.133 cc/g for the support. The catalyst was found to block smaller pores with diameters below 35 Å and the pores with size of 35 Å were in maximum number. For the support, the average pore diameter was 33 Å [10]. The TEM analysis of C-I shows a HRh(CO)(TPPTS-Ba$_x$)$_3$ particle size of 150–200 nm (as against ~300 nm for catalyst I). SEM studies showed that the catalyst particles are unevenly distributed on the support.The X-ray photoelectron spectra (XPS) shows a typical Rh^{+1} oxidation state (Rh 3 d$_{5/2}$ = 309.3 eV, 3 d$_{3/2}$ = 314.1 eV) as expected [10].

3. Results and discussion

The catalyst C-I (% Rh = 0.37 wt/wt), carbon supported barium salt of HRhCO(TPPTS)$_3$ was tested for the hydroformylation of 1-decene at 100 °C and a syngas pressure of 4.14 MPa, in toluene solvent. 95.1% conversion of 1-decene with 89.5% aldehyde selectivity was observed. The final *n*/*i* ratio was 0.51. This low *n*/*i* is observed because isomerization of olefins also occurs and hydroformylation of the internal olefins yields only branched products as seen from the concentration time profile in figure 2. The initial *n*/*i* ratio (for the first 15 min) wherein the major reaction is hydroformylation of 1-decene is 2.8 as seen in figure 3. The TOF (turnover frequency: mol aldehyde formed/mol catalyst/h) was 880 h^{-1}. The catalyst C-III, a silica supported barium salt of HRhCO(TPPTS)$_3$ also gave high TOF for decene hydroformylation, but appreciable amount of leaching (~3–4% Rh) was observed. When the catalyst C-II, (unsupported barium salt of HRhCO(TPPTS)$_3$) was used, a TOF of 84.9 h^{-1} was obtained (Bar B in figure 2). Although, the precipitation of the barium salt of HRh(CO)(TPPTS)$_3$ provides a heterogeneous catalyst for hydroformylation, only the complex on the surface of the particle is available for the reaction, which explains the lower TOF observed. When the catalyst is dispersed on a support [catalyst C-I and C-III], a larger quantity of rhodium is available for the reaction and hence a better performance is achieved. The rate for the dispersed catalyst, although lower by a third compared to the homogeneous catalyst [12a] (TOF 2750 h^{-1}), was improved over the aqueous biphasic catalyst [12b] (TOF 156 h^{-1}) by almost 5 fold.

On comparison with other heterogenized catalysts, the carbon-supported catalyst was more active over the anchored (Bar C, figure 4) [13], encapsulated [5b] (Bar D, figure 2) or tethered HRh(CO)(PPh$_3$)$_3$ catalysts [6d] (Bar E, figure 2) for hydroformylation of 1-decene as

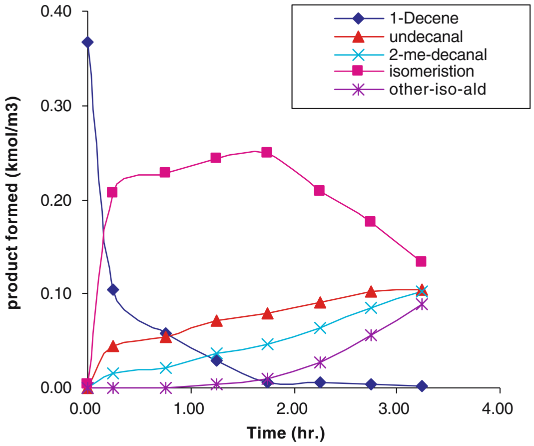

Figure 2. C.T. profile for decene hydroformylation at 100 °C. *Reaction conditions*: Catalyst: 0.100 g (0.37 wt/wt % Rh), 1-Decene: 0.391 kmol/m^3, Stirring speed: 1000 rpm, pCO + H$_2$(1:1): 4.14 MPa, Total charge: 2.7 × 10^{-5}m^3, Solvent: Toluene.

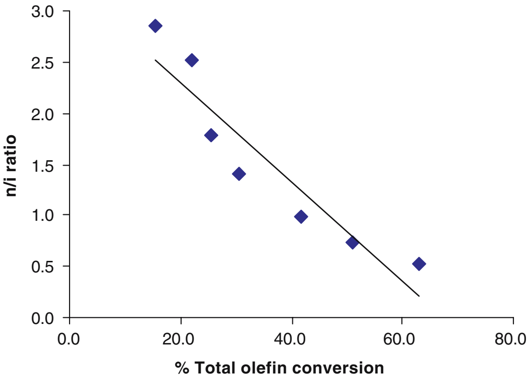

Figure 3. Conversion versus *n*/*i* ratio at 100 °C. *Reaction conditions: Catalyst*: 0.100 g (0.37 wt/wt % Rh), 1-Decene: 0.391 kmol/m^3, Stirring speed: 1000 rpm, pCO + H$_2$(1:1): 4.14 MPa, Total charge: 2.7 × 10^{-5}m^3, Solvent: Toluene.

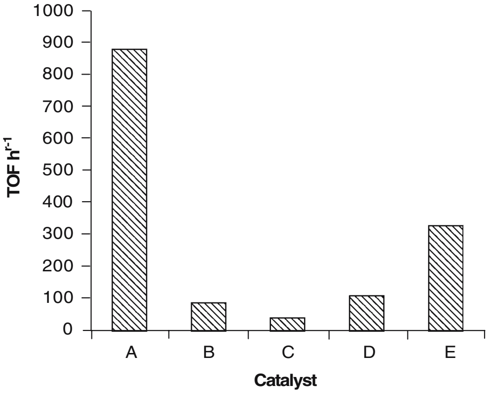

Figure 4. Comparison of activity for hydroformylation of 1-decene using different heterogenized catalysts. A: Catalyst C-I: 0.1 g (0.37 wt/wt % Rh), 1-decene: 0.391 kmol/m^3, *T*: 100 °C, pCO + H$_2$(1:1): 4.14 MPa, Stirring speed: 1000 rpm, Total charge: 2.7 × 10^{-5}m^3, Solvent: Toluene, Time: 2.83 h. B: Catalyst C-II: 0.1 gm (1.68 × 10^{-3} kmol/m^3), 1-decene: 0.394 kmol/m^3, *T*: 100 °C, Stirring speed: 1000 rpm, pCO + H$_2$ (1:1): 4.14 MPa, Total charge: 2.7 × 10^{-5} m^3, Solvent : Toluene, Time: 2.3 h. C: Anchored catalyst, Rh$_2$-MCM-41 [12]. D: Encapsulated catalyst, wk-MCM48 [5b] E: Tethered catalyst, wk-PTA-Y [6d].

shown in figure 4. It was also observed that *n*/*i* ratio for the anchored catalyst was 1.5 at 80% olefin conversion [13]. In case of the Na-Y encapsulated catalyst [5b] the *n*/*i* ratio was 0.44, whereas for the tethered catalyst it was 1.5 [6d]. Considerable leaching was observed in case of the anchored and encapsulated catalyst. The catalyst C-I was thus found to be superior to the earlier reported heterogenized catalyst with respect to its activity, selectivity and stability.

The catalyst C-I was also found to be equally effective for the hydroformylation of other olefins as shown in table 1. The important feature of this catalyst was the high activity observed for higher olefins like 1-decene and 1-dodecene where the availability of true heterogeneous catalysts has been a challenge. Isomerization of the terminal olefin was also observed leading to low *n*/*i* due to the hydroformylation of internal olefin.

The catalyst C-I was tested for its activity on recycle. For these studies, a known amount of 1-decene wa s added to the reactor at theend of each reaction and the reaction continued further. The results in figure 5 show that the catalyst is stable and the activity and selectivity of the catalyst was maintained during several recycles. The ICP analysis shows negligible leaching (~0.6% of rhodium metal taken) in the organic phase. No activity was observed when the organic phase was recycled without any catalyst. This shows that the activity is solely due to the carbon supported catalyst. The spectroscopic study of the catalyst before and after the reaction showed that the catalyst was intact [10].

In order to reduce the isomerization of olefins and improve the *n*/*i* ratio the hydroformylation was conducted at 80 °C. Figure 6 shows a concentration time profile for the hydroformylation of 1-decene at 80 °C using the catalyst C-I. In this case the isomerization of olefins was reduced and correspondingly the aldehyde *n*/*i* ratio (figure 7) also enhanced to 1.57 at an olefin conversion of 78.6%.

The role of solvent in the activity and selectivity of the hydroformylation of 1-decene using catalyst C-I was investigated at 80 °C and results are presented in

Table 1
Hydroformylation of terminal olefins using C-I catalyst

Sr. no	Substrate	% Conv-ersion	% Aldehyde selectivity.	*n*/*i*	TOF/h	Time (h)
1	1-Hexene	99.4	95.8	0.64	1261	2.22
2	1-Octene	97.3	92.4	0.56	1089	2.42
3	1-Decene	95.1	89.5	0.51	880	2.83
4	1-Dodecene	99.3	88.0	0.49	748	3.42
5	Styrene	99.1	97.6	1.14	1578	1.80
6	Camphene	66.1	98.3	1.18*	298	6.42
7	VAM	33.8	96.6	1.00	240	3.92
8	Cyclohexene	76.7	100	–	752	3.00

Reaction conditions: Catalyst: 0.100 g (0.37 wt/wt % Rh), Substrate: 0.391 kmol/m^3, *T*: 100 °C, Stirring speed: 1000 rpm, pCO + H$_2$(1:1): 4.14 MPa, Total charge: 2.7 × 10^{-5}m^3, Solvent: Toluene; *endo/exo.

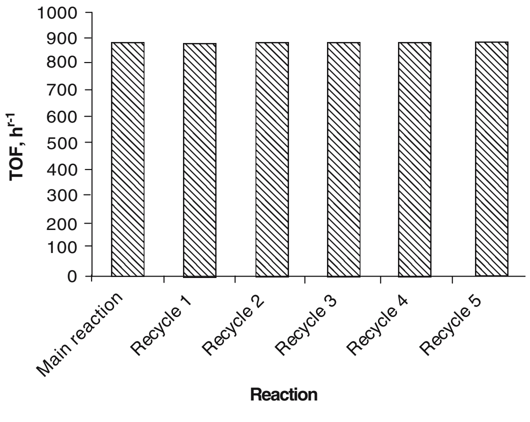

Figure 5. Recycle studies on hydroformylation of decene using C-I catalyst. *Reaction conditions*: Catalyst C-I: 0.100 g (0.37 wt/wt % Rh), 1-decene: 0.391 kmol/m^3, *T*: 100 °C, Stirring speed: 1000 rpm, pCO + H$_2$(1:1): 4.14 MPa, Total charge: 2.7 × 10^{-5}m^3, Solvent : Toluene, Time: 2.83 h.

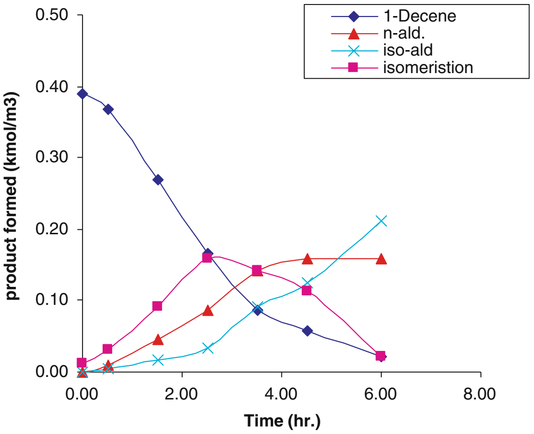

Figure 6. C.T. Profile for decene hydroformylation at 80 °C. *Reaction conditions*: Catalyst: 0.100 g (0.37 wt/wt % Rh), 1-decene: 0.391 kmol/m^3, Stirring speed: 1000 rpm, pCO + H$_2$(1:1): 4.14 MPa, Total charge: 2.7 × 10^{-5}m^3, Solvent: Toluene.

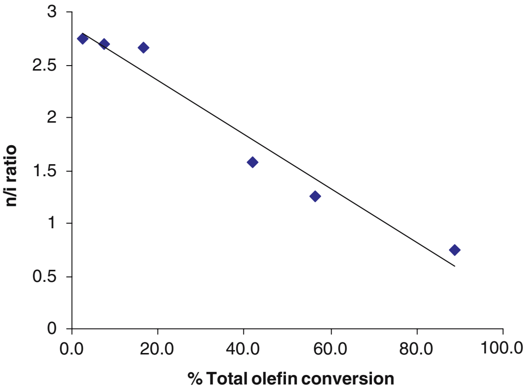

Figure 7. Conversion versus *n*/*i* ratio at 80 °C. *Reaction conditions*: Catalyst: 0.100 g (0.37 wt/wt % Rh), 1-Decene: 0.391 kmol/m^3, Stirring speed: 1000 rpm, pCO + H$_2$(1:1): 4.14 MPa, Total charge: 2.7 × 10^{-5}m^3, Solvent: Toluene.

Table 2
Solvent screening studies for hydroformylation of 1-decene

Sr. no	Solvent	Time (h)	% Conversion	% Aldehyde selectivity	*n*/*i*	TOF/h
1	Methanol	10.3	80.1	44.6	3.9	29
2	Ethanol	24.4	92.6	61.2	1.8	68
3	MEK	9.8	97.9	49.5	3.1	147
4	Octanol	17.9	96.9	100	0.93	168
5	Xylene	10.0	98.4	100	0.90	309
6	Toluene	5.9	98.5	100	0.73	460
7	Cyclohexane	10.25	98.8	97	0. 86	227
8	*n*-Hexane	9.9	96.8	100	0.92	305

Reaction conditions: Catalyst: 0.500 g (0.37 wt/wt % Rh), 1-decene: 0.62 kmol/m^3, *T*: 80 °C, Stirring speed: 1000 rpm, $pCO + H_2$(1:1): 4.14 MPa, Total charge: 8.5×10^{-5}m^3.

table 2. Polar solvents like alcohols lead to high isomerization activity. The highest hydroformylation activity was observed in relatively polar solvents, but *n*/*i* ratio was poor. This observation is contradictory to homogeneous hydroformylation wherein higher activity is observed in polar solvents like alcohols [14].

4. Conclusions

A methodology for immobilization of Rh complex catalysts for hydroformylation of olefins has been described which gives molecularly dispersed heterogeneous catalyst. The method involves conversion of a water–soluble Rh complex catalyst to its heterogeneous form as a barium salt on solid support. Such a catalyst showed significant improvement of catalytic activity and stability during hydroformylation of olefins. Although the Isomerization activity is high for this catalyst (similar to $HRhCO(TPPTS)_3$ catalyst) the concept can be applied to other catalysts which yield high *n*/*i* ratio. This approach is generic and can easily be extended to other catalytic systems. It is possible to heterogenize numerous organometallic complex catalysts by this technique, on to a variety of supports inclusive of carbon.

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[11] The ^{31}P nmr signal for $Ba_{3/2}$TPPTS and carbon supported $Ba_{3/2}$TPPTS is observed at -2.78 and 3.43δ. For C-II the δ value is 29.14 (doublet) for the coordinated P nuclei. The corresponding phosphine oxide appears in the same range as a part of the signal.

[12] (a) Reaction conditions: $HRhCO(PPh_3)_3$: 2.18×10^{-3} kmol/m^3, Rh:PPh_3 = 1:6 (excess), 1-decene : 0.4224 kmol/m^3, *T*: 100^{0}C, $pCO + H_2$(1:1): 4.14 MPa, Stirring speed : 1000 rpm, Solvent : Toluene, Total charge: 2.5×10^{-5}m^3, Time : 0.9 h. (b) $[Rh(COD)Cl]_2$: 1.48×10^{-3} kmol/m^3 (aq.), Rh:TPPTS = 1:6 (excess) 1-decene: 0.704 kmol/m^3 (org.), *T*: 100 °C, Stirring speed : 1000 rpm, $pCO + H_2$ (1:1): 4.14 MPa, Solvent : Toluene + Water (aqueous phase hold up = 0.4), Total charge : 2.5×10^{-5} m^3, Time: 6.6 h.

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