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Catalytic Dimerisation of Norbornadiene Using Cobalt Carbonyl Clusters

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A recent communication by Manning *et al.* [1] prompts us to report our more extensive studies on the use of cobalt carbonyl catalysts in the dimerisation of norbornadiene.

It has been known since the work of Schrauzer [2] that various dinuclear cobalt carbonyl complexes are capable of catalytic, stereospecific dimerisation of norbornadiene to endo, endo-heptacyclo$[5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.0^{3,5}.0^{8,10}]$tetradecane (Binor-S). A mechanism involving a "π-complex multicentre" intermediate has been proposed, although later work [3, 4] has demonstrated that some mononuclear complexes catalyse the same reaction. We have now found that this reaction is also catalysed by a wide variety of neutral, anionic, and heterometallic cobalt carbonyl clusters. In view of the recent interest [5] in the use of transition metal carbonyl clusters in organic catalysis, this reaction thus provides an ideal system for evaluation of the influence on catalytic activity of several parameters associated with the metal cluster, in particular, cluster size, cluster substituent, and electron density in the cluster framework.

The catalyst systems used and the relative initial rates of dimerisation under a standard set of conditions (production of Binor-S in mmol/minute) are shown in Table 1.

Hexane was used as solvent (acetone for the ionic complexes), and in all cases, a co-catalyst in the form of a Lewis acid was required; $BF_3 \cdot Et_2O$, which yields homogeneous solutions, was used throughout (catalyst concentration = 0.01*M*; Lewis acid in 5:1 molar excess, NBD in 30:1 excess). In the absence of Lewis acid, dimerisation occurred only under forcing conditions to give dimers other than Binor-S, together with ketonic materials. The reaction is solvent dependent, however, and several of the clusters act as catalysts in dichloromethane in the absence of Lewis acid.

TABLE 1. Relative Rates for the Dimerisation of Norbornadiene to Binor-S (T = 46 °C).

Catalyst	Rate × 10^3 (mmol/min)
$[NMe_4][Co_6(CO)_{15}]$	~25
$[NMe_4][FeCo_3(CO)_{12}]$	73.1 ± 5.7
$HFeCo_3(CO)_{12}$	27.2 ± 2.4
$Co_4(CO)_{12}$	4.96 ± 0.85
$Co_2(CO)_8$	16.44 ± 0.18
$(NBD)_2Co_2(CO)_4$	16.23 ± 0.16
$Rh_4(CO)_{12}$	30.5 ± 2.8
$BrCCo_3(CO)_9$	23.20 ± 0.48
$ClCCo_3(CO)_9$	21.1 ± 2.5
$HCCo_3(CO)_9$	8.7 ± 1.4
$CH_3CCo_3(CO)_9$	1.07 ± 0.23
$PhCCo_3(CO)_9$	0.28 ± 0.09
$CF_3CCo_3(CO)_9$	0
$CH_3CCo_3(CO)_8(PPh_3)$	2.94 ± 0.61
$CH_3CCo_3(CO)_8(PBu^n_3)$	3.14 ± 0.41
$CH_3CCo_3(CO)_7(PBu^n_3)_2$	26.4 ± 5.0

The results indicate several points of importance:
(a) For both the binary neutral and anionic cobalt clusters, a decrease in catalytic efficiency is observed with an increase in cluster size, consistent with a decrease in the number of sites available per metal atom for substrate coordination.
(b) The order found for the $RCCo_3(CO)_9$ complexes ($H > Me > Ph > CF_3$) indicates that electronegativity, rather than size of the substituent, is the overriding factor. Results for the halo-clusters seem anomalous, but there is some kinetic evidence that these may proceed via a different mechanism [6].
c) Anionic clusters such as $[FeCo_3(CO)_{12}]^-$ and $[Co_6(CO)_{15}]^-$ show a greater catalytic activity than would be expected from neutral clusters of the same size. Thus, availability of electron density in the cluster framework appears to be an important factor. Similarly, progressive substitution of carbon monoxide by phosphine increases the catalytic activity of the cluster, although the effect seems to be roughly independent of the phosphine used. A similar increase in the catalytic activity of $Ir_4(CO)_{12}$ on phosphine substitution has been noted by Muetterties [7].

We have thus been able to show that it is possible to finely tune complexes of this potentially important group of catalysts by variation in cluster substituent. Further studies on both these and related systems are continuing.

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