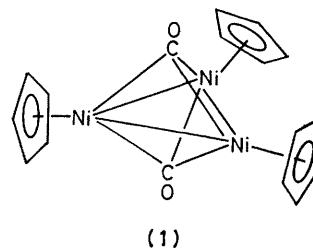


Di- μ -carbonyl-tris(cyclopentadienylnickel) as a Cluster Precursor to a Highly Active Ethylene Oligomerization Catalyst

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Summary The first example of the use of a cyclopentadienylnickel cluster to effect catalytic oligomerization of an olefin is reported; when a benzene solution of di- μ -carbonyl-tris(cyclopentadienylnickel) is allowed to react with silica-alumina and subsequently heated to 150 °C, a highly active catalyst is formed which oligomerizes ethylene to higher olefins with turnover frequencies greater than 10^5 mol ethylene per mol $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ per h.



THERE has been much recent interest in polynuclear metal complexes because they have potential applications in homogeneous catalysis and metal-surface modelling.¹ Frequently the catalytic properties of transition metal clusters are substantially altered when supported on inorganic oxides such as silica or alumina containing reactive surface hydroxy-groups.^{2,3}

We report a highly active catalyst for the oligomerization of ethylene to higher olefins formed by the interaction of the 49-electron⁴ trinickel cluster, $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ (**1**)⁵ with a silica-alumina surface, followed by thermal activation. This system represents the first use of a cyclopentadienylnickel cluster to effect the catalytic oligomerization of an olefin.

When a benzene solution containing 2.34×10^{-5} mol of (**1**) is stirred with 2 g of silica-alumina support,[†] a gradual decrease in the intense yellow-brown colour [from (**1**)] of the solution is observed. After 1 h the solution becomes colourless and the silica-alumina changes colour from white to yellow-brown, indicating the complete adsorption of (**1**) on to the support. Transfer of this supported nickel cluster, under argon, to a pressure reactor and subsequent thermal activation at 150 °C followed by the introduction of ethylene (3.45 MPa) produces $\text{C}_4\text{--C}_{20}$ olefins (reaction time generally 1 h; catalyst system active at lower pressures). Turnover frequencies of *ca.* 1.5×10^5 mol ethylene per mol $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ per h have been consistently observed. After 1 h the reaction mixture was

[†] The silica-alumina used was 87% SiO_2 , 12% Al_2O_3 , surface area 450 m^2/g and was calcined under purified argon flow at 550 °C for *ca.* 18 h. We found the silica:alumina ratio to be a critical variable in this catalyst system, with pure silica or alumina supports giving very low or no activity. In addition, control experiments with the $\text{SiO}_2\text{--Al}_2\text{O}_3$ support itself and with homogeneous hydrocarbon solutions of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ prove that both components are essential for catalytic activity.

rapidly cooled to 5 °C and the gases vented through a sampling bulb for analysis by mass spectrometry †. The remaining materials were filtered and the liquid products analysed by gas chromatography. The olefin products were identified using known standards and also by g.c.-m.s. experiments (Table 1).

TABLE 1 Product distribution obtained from the reaction of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ on silica-alumina with ethylene ^a

Olefin	Selectivity/% ^b
But-1-ene	3.8
But- <i>trans</i> -2-ene	18.3
But- <i>cis</i> -2-ene	12.4
(Total butenes)	(34.5)
C ₆	36.0
C ₈	17.0
C ₁₀	8.7
C ₁₂	3.3
C ₁₄	0.5
C ₁₆ —C ₂₀	trace
Total	100.0

^a 2.34×10^{-5} mol $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$, 3.45 MPa ethylene, 150 °C, 1 h. ^b Calculated as $[(\text{mol product olefin}) \times (\text{mol ethylene reacted})] / \Sigma[(\text{mol product olefins}) \times (\text{mol ethylene reacted})]$

Although C₄—C₁₄ olefins accounted for 95% of the reaction products, injection of larger sample sizes revealed the presence of small amounts of C₁₆—C₂₀ olefins as well. Capillary column g.c. analysis of the C₆ products (Table 2) indicates the presence of relatively large amounts of internal olefins. Under the reaction conditions used, the

TABLE 2 Results of the capillary column g.c. analysis of C₆ products

Compound	Selectivity/%
Hex-1-ene	6.56
2-Ethylbut-1-ene	16.69
<i>cis, trans</i> -Hex-3-ene	
<i>trans</i> -Hex-2-ene	
n-Hexane	2.53
<i>cis</i> -Hex-2-ene	21.91
3-Methyl- <i>cis</i> -pent-2-ene	
3-Methyl- <i>trans</i> -pent-2-ene	
Unidentified C ₆	2.83
Total	100.00

† Mass spectrometry revealed the presence of argon, benzene (solvent), ethylene and butenes.

§ s-Butylbenzene (5%), arising from the alkylation of the solvent with butene was also detected by g.c.-m.s. and by comparison of the retention time and fragmentation patterns with those of the authentic material.

¹ E. L. Muettterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91 and references therein.

² A. K. Smith, A. Theolier, J. M. Basset, R. Ugo, D. Commereuc, and Y. Chauvin, *J. Am. Chem. Soc.* 1978, **100**, 2590.

³ J. L. Bilhou, V. Bilhou-Bougnol, W. F. Graydon, J. M. Basset, A. K. Smith, and G. M. Zanderighi, *J. Organomet. Chem.*, 1978, **153**, 73.

⁴ H. C. Longuet-Higgins and A. J. Stone, *Mol. Phys.*, 1962, **5**, 417.

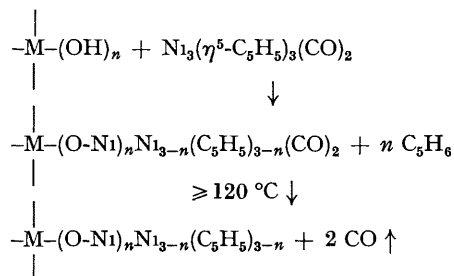
⁵ E. O. Fischer and C. Palm, *Chem. Ber.*, 1958, **91**, 1725.

⁶ The reaction of a cyclopentadienylmetal compound with surface hydroxy-groups has ample precedent. H. P. Boehm, *Adv. Catal.*, 1966, **16**, 179; J. J. Fripiat and J. Utyerrhoeven, *J. Phys. Chem.*, 1962, **66**, 800; F. J. Karol, G. L. Karapinka, C. Wu, A. W. Dow, R. N. Johnson, and W. L. Carrick, *J. Polym. Sci., Part A*, 1972, **10**, 2621.

⁷ M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1976, 26.

distribution of the butenes observed (Table 1) and independent subsequent experiments with hex-1-ene established that the system was effective as an olefin isomerization catalyst.

The nature of the interaction of (1) with the silica-alumina surface may be *via* reactions of the cyclopentadienyl ligand(s) with surface hydroxy-groups, liberating cyclopentadiene (Scheme 6). When the system is exposed



SCHEME. M = Si or Al

to ethylene at room temperature without prior thermal treatment, little, if any, reaction is observed. Gradual heating results in a rapid exothermic reaction commencing at ca. 120 °C and we suggest that this temperature represents the point at which removal of the carbon monoxide ligands is achieved, creating vacant co-ordination sites for ethylene complexation. This temperature is in agreement with that reported by Ichikawa in a related system.⁷

Ichikawa has demonstrated, *via* i.r. and e.s.r. experiments, that when (1) is allowed to react with a silica surface and heated to $\geq 120^\circ\text{C}$, a reversible signal is obtained upon removal and addition of CO, supporting the retention of the nickel triangular array. We are continuing our study of this system, including experiments designed to achieve a more detailed understanding of the nickel cluster-support interaction.

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