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Preliminary communication

CATIONIC METAL NITROSYL COMPOUNDS

II CATALYTIC BEHAVIOUR OF CATIONIC COMPLEXES OF IRON

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Summary

Cationic nitrosyl compounds obtained by chloride abstraction from $[Fe(NO)_2Cl]_2$ are catalysts for the polymerisation of acrylonitrile and styrene and the dimerisation of norbornadiene

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We report below the radical, cationic and coordinating propagating abilities of $[Fe(NO)_2Cl]_2$ and related dinitrosyliron compounds in the oligomerisation of acrylonitrile, styrene and norbornadiene, respectively.

The catalytic species were prepared by two methods In method (a) $[Fe(NO)_2Cl]_2$ is mixed with $AgPF_6$, $AgBF_4$, $AgClO_4$ or $NaBPh_4$ and the pure or dilute substrate added In method (b) the compound $[Fe(NO)_2L_n]Y$ (L = acetonitrile, acrylonitrile, triphenylphosphine; Y = PF_6, BF_4, ClO_4, BPh_4) is formed before the addition of the reacting olefin. Results of catalyses are reported in Table 1 Blank tests for reactions of silver salts, sodium tetraphenylborate, nitric oxide with neat olefins were negative.

Acrylonitrile is polymerised to the same extent by type (a) and (b) catalysts (L = MeCN) No light oligomers were detected The infrared spectra of the solutions before the reaction show a difference in ν(NO) and ν(CN) frequencies for the BPh_4^- system compared to the others (BPh_4^- ν(NO) 1770, 1705 cm^{-1}, ν(CN) 2255 cm^{-1}, ClO_4^-, PF_6^-, BF_4^- ν(NO) 1815, 1730 cm^{-1}, ν(CN) 2275 cm^{-1}) The acrylonitrile coordination is not exactly the same which can account for the counter-anion dependence of the activity [1, 2, 3]. The compound $[Fe(NO)_2L_n]BPh_4$ is active when L is acetonitrile and inactive when L is triphenylphosphine. Radical scavengers such as hydroquinone and diphenylpicrylhydrazyl radical inhibits the polymerisation. Paramagnetic species in the case of the most active system are the monomeric iron cation and the phenyl radicals produced by tetra-

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TABLE 1

CATALYTIC ACTIVITY OF CATIONIC IRON(I) COMPOUNDS

Complex	Catalyst[a]	Unsaturated substrate	(Fe)[b] (%)	Reaction parameters		Conversion	Selectivities
				T (°C)	t (h)		
$[Fe(NO)_2Cl]_2$	(a)	C_3H_3N	2.1	78	22	0	—
1/2 $[Fe(NO)_2Cl]_2$ + $NaBPh_4$	(a)	C_3H_3N	2.2	78	22	100	100 (polymer)
1/2 $[Fe(NO)_2Cl]_2$ + $AgClO_4$	(a)	C_3H_3N	2.1	78	22	19	100
1/2 $[Fe(NO)_2Cl]_2$ + $AgPF_6$	(a)	C_3H_3N	2.3	78	22	2.5	100
1/2 $[Fe(NO)_2Cl]_2$ + $AgBF_4$	(a)	C_3H_3N	2.2	78	22	0	—
$[Fe(NO)_2(MeCN)_n]BPh_4$[c]	(b)	C_3H_3N	2.4	78	22	90	100
$[Fe(NO)_2(an)_n]BPh_4$[d]	(b)	C_3H_3N	2.3	78	22	89	100
$[Fe(NO)_2(PPh_3)_n]BPh_4$	(b)	C_3H_3N	2.0	78	22	0	—
$[Fe(NO)_2Cl]_2$	(a)	PhC_2H_3	2.3	20	22	1	100 (polymer)
1/2 $[Fe(NO)_2Cl]_2$ + $AgBF_4$ + CH_2Cl_2[e]	(a)	PhC_2H_3	1.0	0	22	74	100
1/2 $[Fe(NO)_2Cl]_2$ + $AgPF_6$ + CH_2Cl_2[e]	(a)	PhC_2H_3	1.0	0	22	70	100
1/2 $[Fe(NO)_2Cl]_2$ + $AgClO_4$ + CH_2Cl_2[e]	(a)	PhC_2H_3	1.0	0	22	8	100
1/2 $[Fe(NO)_2Cl]_2$ + $NaBPh_4$ + CH_2Cl_2[e]	(a)	PhC_2H_3	1.0	0	22	0.4	100
$[Fe(NO)_2(MeCN)_n]PF_6$	(b)	PhC_2H_3	2.0	0	22	36	100
$[Fe(NO)_2(PPh_3)_2]PF_6$	(b)	PhC_2H_3	2.0	0	22	0	—
$[Fe(NO)_2Cl]_2$ + CH_2Cl_2	(a)	C_7H_8	1.0	40	22	32	88 (*exo trans exo* dimer)
1/2 $[Fe(NO)_2Cl]_2$ + $AgBF_4$ + CH_2Cl_2	(a)	C_7H_8	1.0	40	22	76	94
1/2 $[Fe(NO)_2Cl]_2$ + $AgPF_6$ + CH_2Cl_2	(a)	C_7H_8	1.0	40	22	37	95
1/2 $[Fe(NO)_2Cl]_2$ + $NaBPh_4$ + CH_2Cl_2	(a)	C_7H_8	1.0	40	22	13	95
1/2 $[Fe(NO)_2Cl]_2$ + $AgClO_4$ + CH_2Cl_2	(a)	C_7H_8	1.0	40	22	7	95
$[Fe(NO)_2(MeCN)_n]PF_6$ + CH_2Cl_2	(b)	C_7H_8	1.0	40	22	0	

[a] See text. [b] Iron complex concentration (mol %) [c] MeCN = acetonitrile [d] an = acrylonitrile [e] CH_2Cl_2/styrene = 0.5 [f] CH_2Cl_2/norbornadiene = 5

phenylborate decomposition [4] However, the latter are more commonly transfer agents [5] and $[Fe(NO)_2Cl]_2$ + Ph_2Hg does not catalyse the reaction. Thus we assume that the metallic centre, by coordination of acrylonitrile, induces a radical which leads to polyacrylonitrile through a propagating step

Styrene is polymerised at low temperature when mixed with type (a) catalysts The loss of activity for type (b) catalysts may arise from the competing coordination between styrene and ligand L The results reported in Table 1 were obtained at 0°C, but the polymerising activity is observed even at –20°C and increases with the polarity of the medium. Moreover (i) the radical diphenylpicrylhydrazyl has no effect, (ii) acrylonitrile-styrene copolymerisation does not occur and (iii) isobutene is also polymerised. According to polymerisation data on polystyrene [5] these results indicate a cationic propagating step, the cationic iron moiety being the effective catalytic precursor. The counter-anion effect observed on the activity has to be related to the tightness of the ion-pairs formed [6—8]

Finally, norbornadiene is dimerised selectively to the *exo-trans-exo* dimer (95 %) The starting material $[Fe(NO)_2Cl]_2$ is active as a type (a) catalyst whereas $[Fe(NO)_2(MeCN)_n]PF_6$ is not Kinetic studies have shown that the catalytic activity parallels the appearance of the ESR signal attributed to the iron(I) moiety. The inactivity of $[Fe(NO)_2(MeCN)_n]PF_6$ is attributed to the strength of the iron—acetonitrile bond. A similar trend has already been observed with the cobalt homologues [1]. In this latter case, changing the counter-anion modifies the activity and the selectivity, whereas with the iron systems coordinating as well as non-coordinating anions exhibit the same selectivity. Only the activity is altered A mechanistic study of the norbornadiene dimerisation is being carried out

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References

1 D. Ballivet and I. Tkatchenko, J Molecular Cat., I (1976) 319
2 G.N. Schrauzer, J Amer. Chem. Soc., 81 (1959) 5310.
3 C A. Tolman and W C Seidel, J Amer. Chem. Soc , 96 (1974) 2774·
C.A. Tolman, J Amer Chem. Soc., 96 (1974) 2780.
4 L. Sacconi, P. Dapporto and P. Stoppioni, Inorg. Chem., 15 (1976) 325.
5 G. Odian, Principles of Polymerization, McGraw Hill, New York, 1970
6 P H. Plesch, Br. Polym J , 5 (1973) 1
7 D C. Pepper, Makromol. Chem., 175 (1974) 1077.
8 T. Higashimura, O. Kishiro K. Matsuzaki and T Uryu, J. Polym Sci., 13 (1975) 1393