Synthesis of (η^3-Allyl)(η^4-cyclo-octa-1,5-diene)nickel Cations: Valuable Catalysts for the Oligomerization of Alkenes

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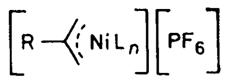
Summary η^3-Allylnickel cations stabilised by 'labile' ligands, obtained by metathetical exchange of η^3-allylnickel halides with non-complexing anions in the presence of dienes or donating solvents, are efficient catalysts for the oligomerization of unsaturated hydrocarbons and lead to unusual selectivities and to new η^3-allylnickel complexes which may be intermediates in these reactions.

Very few η^3-allylnickel cations have been reported in the literature, and these are generally associated with phosphorus(III) ligands.[1,2,3] These complexes, *i.e.* $[(\eta^3\text{-allyl})NiL_n]^+$ (**1**) where $n = 1$ or 2, have been reported to be active for alkene dimerization,[4] alkene–butadiene codimerization,[3] or butadiene polymerization.[5] Few examples of complexes (**1**) with ligands other than phosphorus(III) compounds have been reported. If labile ligands are used, we can anticipate a higher activity in the oligomerization of unsaturated hydrocarbons, similar to that already observed for 'naked' nickel.[1] We describe below a general procedure for the synthesis of such compounds, their high activity for the conversion of hydrocarbons, and some insight into the reaction mechanism.

$[\eta^3\text{-}RC_3H_4)NiL_n]^+$ $[(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_8H_{12})Ni][AlBr_4]$
(**1**) R = H, alkyl, or phenyl (**2**)

Walter[6] has reported that bis(allylnickel bromide) reacts with aluminium bromide in the presence of cyclo-octa-1,5-diene (cod) to give the ionic complex (**2**). A more general procedure consists of allowing tetrahydrofuran (THF) solutions of bis(allylnickel halides) to react with salts of so-called non-complexing ions, *e.g.* $AgBF_4$, $TlPF_6$, in the presence of an excess of cyclo-octa-1,5-diene. Elimination of the silver or thallium halides and subsequent work-up leads to complexes (**3**)—(**8**) in good yields (Table 1).†



	R	L	*n*
(**3**)	H	cod	1
(**4**)	Me	cod	1
(**5**)	Me	MeCN	2
(**6**)	Me	PhCN	2
(**7**)	Me	thf	2
(**8**)	Ph	cod	1

However, intractable products are obtained when anion exchange is performed with sodium tetraphenylborate. This may be explained by further reaction of the tetraphenylborate anion with the organonickel cation as has already been described.[7] Substitution of cyclo-octa-1,5-diene by dienes like cyclohexa-1,3-diene, cyclo-octa-1,3-diene, and bicyclo[2.2.1]heptadiene leads to polymerization of these ligands. Furthermore, if the reaction is performed in the presence of arenes (benzene, toluene, hexamethylbenzene), no (η^3-allyl)(η-arene)nickel cations are formed. This difficulty in preparing the hexafluorophosphate analogue of (**9**)[8] may be explained by the low solubility of $Tl[PF_6]$ in benzene compared with the solubility of $AlBr_3$ in this solvent.

$[(\eta^3\text{-}C_3H_5)(\eta\text{-}C_6H_6)Ni][AlBr_4]$
(**9**)

$[(\eta^3\text{-}C_4H_7)Ni\{P(OEt)_3\}_2][PF_6]$
(**10**)

$[(2\text{-}MeC_3H_4)(PPh_3)_2Ni][PF_6]$
(**11**)

Compound (**2**) was reported as being inactive for propylene oligomerization.[6] This contrasts with the behaviour of (**9**) and (**10**) in butadiene polymerization[5] as well as the codimerization of butadiene and ethylene with (**10**),[3] and in fact we have found (**2**) and some of the complexes listed in Table 1 to be efficient catalysts for the conversion of unsaturated hydrocarbons. Ethylene and propylene are found to produce, respectively, C_4, C_6, C_8 and C_6, C_9, C_{12} oligomers. Mainly (98%) *cis*-poly-1,4-butadiene is obtained under mild conditions. Hex-1-ene also polymerises in the presence of (**2**). So far, we have achieved turnover frequencies of up to 2000 h^{-1} in the case of ethylene and propylene. Table 2 shows the product selectivity and the influence of the starting complex on the activity. The product selectivity is clearly indicated by the use of the phosphine complex $[(2\text{-}MeC_3H_4)(PPh_3)_2Ni][PF_6]$ (**11**)[2,9] which mainly favours C_4 alkenes. With ethylene, linear hexenes (< 50%) and 3-methylpent-2-ene (> 50%) are produced. When (**4**) is used as the catalyst, an orange crystalline compound with different spectral properties is recovered at the end of the reaction (62% yield) and its structure was determined to be (**12**) by ^1H n.m.r. spectroscopy [$\delta(CDCl_3)$ 5·6 and 5·0 (4H,

Table 1. Isolated yield and ^1H n.m.r. data[a] associated with the cationic allylnickel complexes.

Complex	Yield/%	$\delta(H_{syn})$	$\delta(H_{anti})$	δ(*meso*-R)	δ(cod or other ligands)	Solvent
(**3**)	78	3·70(2H,m,br)	2·80(2H,m,br)	5·96(1H, t,*J* 10 Hz)	2·49(8H,s), 5·62(4H,m,br)	CD_3CN
(**4**)	70	4·30(2H,s)	3·20(2H,s)	2·30(3H,s)	2·60(4H,s,br), 2·70(4H,s,br), 5·95 (4H,m,br)	CD_2Cl_2
(**5**)	88	3·50(2H,s)	2·60(2H,s)	2·40(3H,s)	2·45(6H,s)	$CDCl_3$
(**6**)	70	3·70(2H,s)	2·90(2H,s)	2·50(3H,s)	7·75(10H,m)	$CDCl_3$
(**7**)	76	2·80(2H,s)	2·00	2·50(3H,s)	2·00(10H,m,br), 3·90(8H,s,br)	CD_2Cl_2
(**8**)	73	4·68(2H,s)	3·30(2H,s)	7·50(5H,s)	3·0—2·0(8H,m), 5·75(2H,m,br), 5·98(2H,m,br)	CD_2Cl_2

[a] Relative to external Me_4Si.

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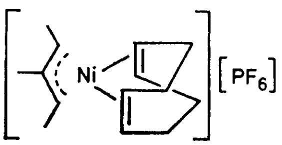
† Satisfactory analyses have been obtained for all the reported cationic complexes.

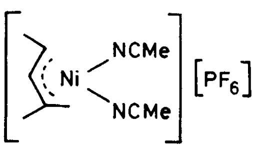
Table 2. Catalytic oligomerisation of ethylene at 25 °C.

Catalyst	Solvent	Turnover frequency/h^{-1}	Initial pressure/bar	Product selectivity (%)						
				C_4	C_6	C_8	C_{8+}	n-C_4	*cis*-2-C_4	*trans*-2-C_4
(**2**)	PhCl	510	10·0	40·5	42·4	13·4	3·6	2·6	69·4	28·0
(**4**)	CH_2Cl_2	2000	10·0	54·8	33·6	9·7	1·8	16·8	55·3	27·8
(**7**)	CH_2Cl_2	635	10·0	53·2	32·4	10·9	3·5	29·4	46·4	24·2
(**11**)	CH_2Cl_2	640	6·0	86·2	13·8	<0·2	—	3·5	61·7	34·8
(**12**)	CH_2Cl_2	570	4·0	70·9	26·8	2·3	<0·1	2·5	68·4	29·1

br m), 3·7 (2H, q, J 6·5 Hz), 2·7 and 2·5 (8H, br m), 2·1 (3H, s) and 1·3 (6H, d, J 6·5 Hz)]. This complex could not be formed from the initial reaction of the allyl ligand of (**2**) with ethylene. However, (**5**), which is not as efficient as (**2**) in the trimerization of ethylene, reacts with ethylene to give (**13**) [δ($CDCl_3$) 5·10 (1H, d, J 13 Hz), 3·40 (1H, d of q, J 13 and 6 Hz), 2·35 (6H, s), 1·10 (6H, s) and 1·00 (3H, d, J 6 Hz)].



(**12**)



(**13**)

Similar complexes are apparently formed during the oligomerization of other alkenes although no attempts to isolate them have been made. Oligomerization of hex-1-ene (50% C_{12}, 5% C_{18}), is accompanied by the isomerization of the starting alkene to *cis*- and *trans*-hex-2-ene (38%) and, more surprisingly, with the production of butenes (*ca.* 2%).

The evidence for a nickel hydride as the catalytic species is still lacking. However, nickel(II) hydrides have been already proposed as active species in the dimerization of alkenes.[4] The isolation of (**12**) suggests that cyclo-octa-1,5-diene is present in the active species.

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