Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

BIS(π-ALLYLNICKEL HALOACETATES)

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(Received September 16th, 1969)

SUMMARY

The synthesis and the physico-chemical properties of a series of bis(π-allylnickel haloacetates), which were found to be very efficient catalysts for the 1,4-stereospecific polymerization of 1,3-butadiene, are reported.

In the past few years a number of papers were published describing the synthesis of bis(π-allylnickel halides). Among other methods, E. O. Fischer reported the first synthesis of bis(π-allylnickel halides) by the reaction of tetracarbonylnickel with allyl halides[1]; π-allylic nickel complexes can also be obtained by the reaction of allyl halides with other complexes of nickel(0), such as bis(1,5-cyclooctadiene)nickel(0), as reported by Wilke and coll.[2].

This report describes the synthesis and the physico-chemical properties of a series of bis(π-allylnickel haloacetates). The new π-allylic type complexes were obtained in high yields by an oxidative addition reaction between the allylic ester of an haloacetic acid and a zerovalent nickel complex, *i.e.* bis(1,5-cyclooctadiene)nickel[3]:

$$(C_8H_{12})_2Ni + C_3H_5OCOCH_{3-n}X_n \rightarrow [\pi\text{-}C_3H_5\text{-}Ni\text{-}OCOCH_{3-n}X_n]_2 + 2\,C_8H_{12}$$

The reaction is carried out, under argon atmosphere, in the presence of benzene or ether as solvent, starting from equimolar amounts of nickel complex and allylic haloacetate and it is rapidly completed at room temperature. Depending on the reaction medium used, pure compounds, as shown in Table 1, were isolated either by precipitation, or by evaporation to dryness under low pressure followed by successive washings of the reaction product with cold pentane.

Bis(π-allylnickel haloacetates) are diamagnetic amorphous coloured solids (orange-brown), stable for several weeks at room temperature under inert atmosphere. All the complexes obtained are very soluble in diethyl ether. Cryoscopic determinations performed on cyclohexane solutions of the complexes have shown that the π-allylnickel trifluoroacetate is associated as a binuclear species like many π-allyl transition metal halide compounds: cryometric molecular weight was found equal to 415, a 426 value being calculated for the dimer. Their π-allylic structure was confirmed by nuclear magnetic resonance, carried out at 10° on deuterochloroform solutions of the complexes; as it appears from Table 2, the chemical shift as well as the relative intensity observed are in good agreement with the proposed structure.

TABLE 1

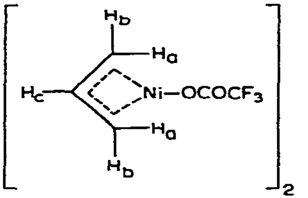
SYNTHESIS OF BIS(π-ALLYLNICKEL ACETATE) DERIVATIVES

Ni compounds	Conversion (%)	Elemental analysis[a] (%)					
			C	H	Hal	Ni	O
$C_3H_5NiOCOCH_3$	80	Calcd.:	38.0	5.0		36.8	20.2
		Found:	36.8	4.8		35.6	22.4
$C_3H_5NiOCOCH_2Cl$	90	Calcd.:	31.2	3.6	18.2	30.3	16.7
		Found:	30.8	3.1	18.6	29.5	17.6
$C_3H_5NiOCOCHCl_2$	92	Calcd.:	26.5	2.6	31.0	25.8	14.1
		Found:	26.1	2.3	31.1	24.9	15.5
$C_3H_5NiOCOCCl_3$	92	Calcd.:	23.0	2.0	40.0	23.0	12.0
		Found:	23.2	1.5	40.6	21.7	12.7
$C_3H_5NiOCOCF_3$	95	Calcd.:	28.3	2.3	27.0	27.3	15.1
		Found:	28.0	2.5	26.7	27.4	15.4[b]

[a] Performed by Dr. Alfred Bernhardt (mikroanalytisches laboratorium, Elbach über Engelskirchen, West-Germany). [b] Calculated by difference, the presence of fluorine in the complex preventing a direct determination.

TABLE 2

NMR DATA OF BIS(π-ALLYLNICKEL TRIFLUOROACETATE)



Chemical shift, δ (ppm)	Relative intensity	Assignment
2.35	2	H_a
2.55		
3.10	2	H_b
3.20		
6.00	1	H_c

The IR absorption spectra of the solid compounds, performed on KBr pellets prepared under argon atmosphere, show all the absorption bands characteristic of the substituted acetate groups, besides the absorption at 2930 and 2860 cm^{-1} due to the CH_2 and CH bonds of the π-allyl group. Moreover, as summarized in Table 3, variations of the elongation vibration frequencies for the carbonyl bonds were observed depending on the electronegativity of the acetate anions.

Bis(π-allylnickel haloacetates) were found to be very efficient catalysts for the 1,4 stereospecific polymerization of 1,3-butadiene, without the addition of any cocatalyst, and we have evidenced a definite correlation between the catalytic activity of the complexes and the electron-withdrawing properties of their coordinated counter-ions[5]. Furthermore, we succeeded to show by means of both cryometry and nuclear magnetic resonance, that the addition of 1,3-butadiene to bis(π-allylnickel trifluoro-

TABLE 3

VARIATIONS OF C=O GROUP STRETCHING VIBRATION FREQUENCIES IN ALLYLIC HALOACETATES AND THE CORRESPONDING NICKEL COMPLEXES

Esters	ν(C=O) (cm^{-1})[a]	Nickel complexes	ν(C=O) (cm^{-1})
$C_3H_5OCOCH_3$	1735	$C_3H_5NiOCOCH_3$	1560
$C_3H_5OCOCH_2Cl$	1735–1757	$C_3H_5NiOCOCH_2Cl$	1595
$C_3H_5OCOCHCl_2$	1745–1765	$C_3H_5NiOCOCHCl_2$	1620
$C_3H_5OCOCCl_3$	1762	$C_3H_5NiOCOCCl_3$	1650
$C_3H_5OCOCF_3$	1780	$C_3H_5NiOCOCF_3$	1670

[a] These values determined from neat compounds are completely comparable to those in solution and reported in ref. 4.

acetate) converts the binuclear complex into a mononuclear species on which butadiene is coordinated, with a formation constant evaluated to about 7 l/mole, to yield the complex presumably responsible for the stereospecific propagation reaction:

$$[\pi\text{-}C_3H_5\text{-}Ni\text{-}OCOCF_3]_2 + 2\,C_4H_6 \rightleftharpoons 2\,[\pi\text{-}C_3H_5\text{-}Ni\text{-}OCOCF_3\cdot C_4H_6]$$

ACKNOWLEDGEMENT

This work was done under contract with the "Délégation Générale à la Recherche Scientifique et Technique" (Convention no. 66.00.459). The authors are indebted to Mr. Aubin for his assistance with the experimental part of this work.

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