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

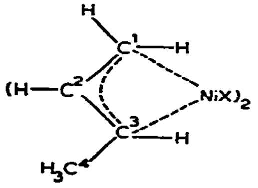
Preliminary communication

^{13}C nuclear magnetic resonance spectra of bis(π-crotylnickel halides)

L.A. CHURLYAEVA, M.I. LOBACH, G.P. KONDRATENKOV and V.A. KORMER
S. V. Lebedev Central Synthetic Rubber Research Institute, Leningrad (U.S.S.R.)

(Received April 4th, 1972)

^{1}H NMR spectroscopy has been widely applied to structural investigation of transition metal π-allylic complexes. ^{13}C NMR spectroscopy can also yield useful information. We report here some results of the study on bis(π-crotylnickel halides) (I) by ^{13}C NMR spectroscopy. The complexes under investigation are structurally related to the catalysts used in stereospecific diene polymerization[1].



(I)

Bis(π-crotylnickel halides) were prepared by treating the appropriate crotyl halide with nickel carbonyl[2]. The spectra of solutions in toluene-d_8 were measured at 22.63 MHz on a Bruker HX - 90 Spectrometer using Fouriers pulse method with random noise decoupling of the protons. C_6F_6 was used as external ^{19}F field/frequency lock. The chemical shifts were measured relative to hexamethyldisiloxane (HMDS).

The ^{13}C NMR spectra of the bis(π-crotylnickel halides) and of the corresponding crotyl halides $C^4H_3C^3H{=}C^2HC^1H_2X$ contained four singlets with the chemical shifts reported in Table 1. The C(1) chemical shift variation in the crotyl halides paralleled the decrease in electronegativity of the halogen atoms as previously reported for the alkyl halides[3].

The formation of the complex results in upfield shifts of the C(2) and C(3) resonances of ca. 24 and 53–57 ppm respectively in contrast to a downfield shift of the methylene carbon signal line (C(1)). These findings indicate a significant change in the local shielding of the allylic carbon atoms due probably to the partial contribution of the metal-to-ligand dative interaction. The metal-to-ligand electron transfer is accompanied by a charge variation in the π-allylic group. The central carbon atom is most screened as is also shown by ^1H NMR data[4,5]. The stronger shielding of C(1) and C(3) indicates a higher electron density at these atoms than at C(2), the C(1) atom of the π-allylic ligand being the most negative of the three. As can be seen from Table 1 the shielding of the C(1), C(2) and C(4) atoms in the crotyl compounds increase with *trans*-ligands in the order $I < Br < Cl$. The findings suggest greater lability of the π-allylic ligand in the iodine complex compared with the chlorine one.

TABLE 1

^{13}C NMR CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS J(C–H) OF BIS-(π-CROTYLNICKEL HALIDES) AND CROTYL HALIDES

Compounds	*^{13}C chemical shifts (ppm from external HMDS)*				*^1H–^{13}C coupling constants (Hz)*			
	C(1)	*C(2)*	*C(3)*	*C(4)*	*J(C(1)–H)*	*J(C(2)–H)*	*J(C(3)–H)*	*J(C(4)*
C_4H_7Cl	45.2	129.7	126.9	28.2	153	–	–	125
C_4H_7Br	34.0	130.9	128.2	18.6	154	–	–	125
C_4H_7I	19.5	129.7	129.7	8.4	–	–	–	–
$(C_4H_7NiCl)_2$	48.0	106.9	70.0	16.8	159	163	161	124
$(C_4H_7NiBr)_2$	49.6	105.6	71.2	18.0	161	165	161	124
$(C_4H_7NiI)_2$	52.4	105.5	76.3	19.6	162	161	161	–

The undecoupled ^{13}C NMR spectra revealed the spin–spin coupling constants for directly bonded ^1H–^{13}C since the values were great enough (120 through 270 Hz depending on the carbon atom hybridization[3]). The C(2) and C(3) resonances were split into doublets and C(1) and C(4) into a triplet and a quartet respectively. The values of the coupling constants of ^1H bound to C(1), C(2) or C(3) covered the range 159–165 Hz irrespective the nature of the halide bridge (*cf.* Table 1). The data are consistent with sp^2 hybridization of the allylic carbon atoms.

REFERENCES

1 V.A. Kormer, B.D. Babitskii and M.I. Lobach, *Advan. Chem. Ser.*, 91 (1969) 306.
2 E.O. Fischer and G. Burger, *Z. Naturforsch. B*, 16 (1961) 77.
3 J.W. Emsley, J. Feeney and L.H. Sutcliffe, *High Resolution NMR-Spectroscopy, Vol. 2*, Pergamon Press, Oxford, 1966.
4 M.I. Lobach, V.A. Kormer, I.Yu. Tseretely, G.P. Kondratenkov, B.D. Babitskii and V.I. Klepikova, *J. Polymer Sci., Part B*, (1971) 71.
5 T. Matsumoto and J. Furukawa, *J. Polymer Sci., Part B*, 5 (1967) 955.