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THERMALLY STABLE RIGID π-ALLYLNICKEL COMPOUNDS, (π-CHRCR'CH$_2$)Ni(PPhMe$_2$)C$_6$Cl$_5$

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Summary

The reaction of $C_6Cl_5Ni(PPhMe_2)_2Cl$ with $CHR{=}CR'CH_2MgX$ (X = Br or Cl) yields π-allylnickel compounds, (π-CHRCR'CH$_2$)Ni(PPhMe$_2$)C$_6$Cl$_5$ (Ia, R = R' = H; Ib, R = H, R' = CH_3; Ic, R = CH_3, R' = H), which are stable in the solid state below ca. 150°C and are fairly stable in solution in the absence of oxygen. The π-allyl group was found by PMR spectroscopy to be rigid even in the presence of an excess of $PPhMe_2$, $P(OEt)_3$ or $P(OMe)_3$.

Introduction

Much attention has been paid to the characterization of the intermediates involved in nickel-catalyzed organic reactions in order to elucidate the mechanisms of such processes [1-3]. Some π-allylnickel compounds of type (π-allyl)-NiRL (I) have been isolated mainly by Wilke and his co-workers [4,5]. These compounds, however, are relatively thermally unstable probably due to the ease of reductive elimination or β-hydrogen elimination. In order to carry out a detailed investigation of the properties of the π-allylnickel bond in I, we have attempted synthesis of more thermally stable π-allylnickel compounds of type I by the reactions of *trans*-chloro(pentachlorophenyl)bis(dimethylphenylphosphine)nickel, $C_6Cl_5Ni(PPhMe_2)_2Cl$, with some allylmagnesium halides. We have chosen pentachlorophenyl as a ligand because it possesses no β-hydrogen and because its nickel compounds have been reported to be thermally stable [6], in accord with its short nickel—carbon bond [7].

Experimental

PMR spectra were recorded on a JEOL model JNM-PS-100 operating at 100 MHz. IR spectra were recorded on a JASCO model IR-G. The starting material $C_6Cl_5Ni(PPhMe_2)_2Cl$ was prepared as previously reported [8]. The following reactions were carried out under nitrogen.

Preparation of (π-allyl)Ni($PPhMe_2$)C_6Cl_5 (Ia) and (π-2-methallyl)Ni($PPhMe_2$)C_6Cl_5 (Ib)

Allylmagnesium bromide, prepared from Mg turnings (490 mg, 0.02 mol) and allyl bromide (610 mg, 5 mmol) in dry ether (30 ml), were added to a solution of $C_6Cl_5Ni(PPhMe_2)_2Cl$ (630 mg, 1 mmol) in dry ether/benzene (20 ml/5 ml) at —10°C. After the mixture had been stirred for 24 h at 20°C, 50 ml of saturated aqueous NH_4Cl solution was added. The organic layer was separated and the solvent was removed under reduced pressure. Repeated recrystallization from n-hexane gave orange crystals of (π-allyl)Ni($PPhMe_2$)C_6Cl_5 (340 mg, 70%), m.p. 76°C (dec. 152°C). (Found: C, 41.73; H, 3.17. $C_{17}H_{16}Cl_5PNi$ calcd.: C, 41.91; H, 3.31%.) IR (KBr disc): 1490 w, 1020 w, 808 m (π-allyl), 1314 s, 1278 s, 1232 s, 666s, 616 s, (C_6Cl_5), 940 s, 912 s, 742 s, 488 m cm^{-1} ($PPhMe_2$).

Similarly, Ib was obtained from β-methallylmagnesium chloride. Yield of Ib, 300 mg (60%), m.p. 78°C (dec. 150°C). (Found: C, 43.37; H, 3.79. $C_{18}H_{18}Cl_5PNi$ calcd.: C, 43.13; H, 3.62%.) IR (KBr disc): 1490 w, 1028 w, 842 m (π-2-methallyl), 1316 s, 1286 s, 1232 s, 664 s, 616 m (C_6Cl_5), 950 s, 908 s, 742 s, 488 m cm^{-1} ($PPhMe_2$).

Preparation of (π-1-methallyl)Ni($PPhMe_2$)C_6Cl_5 (Ic)

An identical procedure was used with crotylmagnesium chloride excepting that the residual oil, obtained after evaporation of the solvent, was heated to 40-50°C at 10^{-3} Torr for 4 h to remove the white sublimate of by-product, C_6Cl_5H (12 mg, 5%). 1,3-Butadiene was trapped in liquid nitrogen after stirring the mixture of crotylmagnesium chloride and $C_6Cl_5Ni(PPhMe_2)_2Cl$. Yield of Ic, 310 mg (62%), m.p. 82°C (dec. 164°C). (Found: C, 42.69; H, 3.59. $C_{18}H_{18}Cl_5PNi$ calcd.: C, 43.13; H, 3.62%.) IR (KBr disc): 1486 w, 1028 w, 822 m (π-1-methallyl), 1312 s, 1278 s, 1226 s, 655 s, 607 s (C_6Cl_5), 936 m, 900 s, 730 s, 488 m cm^{-1} ($PPhMe_2$). C_6Cl_5H was identified by comparison with an authentic

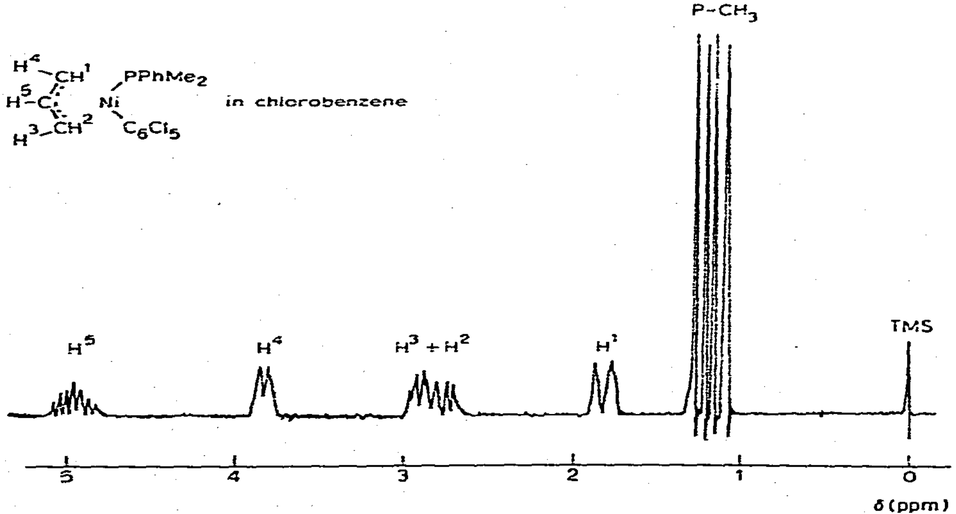


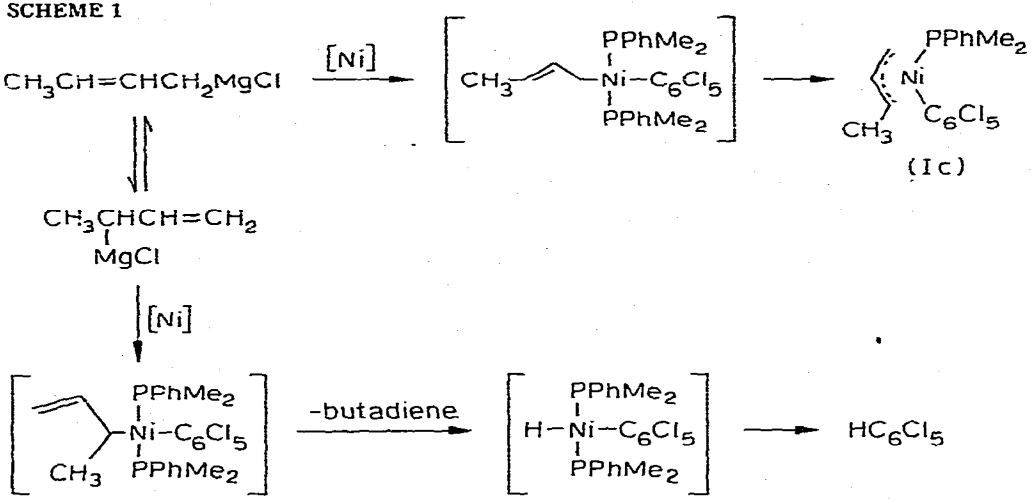
Fig. 1. PMR spectrum of (π-allyl)Ni($PPhMe_2$)C_6Cl_5.

specimen prepared from C_6Cl_5Li and ethanol (m.p. and IR spectrum). Butadiene was identified by gas chromatography. When the reaction was carried out in THF, the yield of C_6Cl_5H increased to 25% and the yield of Ic decreased to 40%.

Results and discussion

The reaction of $C_6Cl_5Ni(PPhMe_2)_2Cl$ with allyl- (or β-methallyl-)magnesium halide yields a π-allyl (or π-2-methallyl)nickel compound with release of one mole of dimethylphenylphosphine. It seems very probable that dimethylphenylphosphine is eliminated from a σ-allylnickel intermediate formed in the first step of the reaction. An analogous reaction with crotylmagnesium chloride gave π-1-methallyl compound and additional products, C_6Cl_5H and 1,3-butadiene, which probably resulted from the β-hydrogen elimination of another σ-intermediate followed by the reductive elimination as shown in Scheme 1. This route is enhanced in a reaction conducted in THF.

SCHEME 1



$[Ni] = C_6Cl_5Ni(PPhMe_2)_2Cl$

The decomposition temperatures of Ia-Ic are higher than those of (π-allyl)-$Ni(CH_3)L$ [4] and their ether, THF, benzene or n-hexane solutions are fairly stable in the absence of oxygen.

The PMR spectra of Ia-Ic show that these compounds have a rigid π-allyl group. Observation of two doublets for the phosphine methyl protons is due to the lack of a plane of symmetry. The spectrum of Ia (Fig. 1) is unchanged even at 80°C in the presence of an excess of free ligand such as dimethylphenylphosphine, triethyl phosphite or trimethyl phosphite. This observation is in contrast to the data reported for π-allyl compounds of the type (π-allyl)NiLX [9]. The lack of fluxional character in our compounds can be attributed to the presence of the pentachlorophenyl group, which may prevent the formation of intermediates A-C proposed to account for the fluxional character of π-allyl groups in

TABLE 1

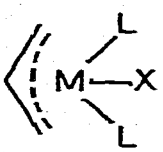
PMR DATA OF (π-CHRCR'CH$_2$)Ni(PPhMe$_2$)C$_6$Cl$_5$, MEASURED IN CHLOROBENZENE

The assignment is based on the results of spin decoupling measurements and the knowledge that the central proton (H^5) has the lowest chemical shift and that the *trans*-coupling constants, J_{15} and J_{25}, are larger than the *cis*-coupling constants, J_{35} and J_{45}.

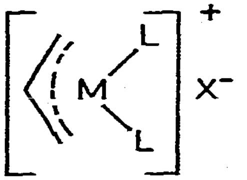
R	R'	$\delta(H^5)^a$	$\delta(H^4)$	$\delta(H^3)$	$\delta(H^2)$	$\delta(H^1)$	δ(P—CH$_3$)
H	H	4.94 m	3.53 d $J_{45} = 7$	2.84 m $J_{35} = 10$ $J_{3P} = 6^b$	2.66 m $J_{25} = 14$ $J_{2P} = 6^b$	1.79 d $J_{15} = 13$	1.20 d, 1.12 d $J_{PH} = 9$
H	CH$_3$	(1.76) s (—CH$_3$)	3.32 s	2.56 d $J_{3P} = 6^b$	2.51 d $J_{2P} = 6^b$	1.84 s	1.22 d, 1.14 d $J_{PH} = 9$
CH$_3$	H	4.68 m	2.54 m $J_{45} = 7$ $J_{4P} = 5$	(1.16) d (—CH$_3$) $J_{2\text{-}CH_3} = 6$	3.42 m $J_{25} = 12$ $J_{2P} = 6$ $J_{2\text{-}CH_3} = 6$	1.50 d $J_{15} = 14$	1.22 d, 1.14 d $J_{PH} = 9$

[a] For proton numbering scheme see Fig. 1. [b] Because of overlapping of H^2 and H^3 signals, the coupling constants, J_{2P} and J_{3P}, cannot be evaluated precisely.

(π-allyl)MLX (M = Pd or Ni) [10,11]. The compounds decompose above 80°C in solution, and an equilibrium between π- and σ-bonded allylic forms, proposed by Faller and Mattina [12], could not be studied.



(A)



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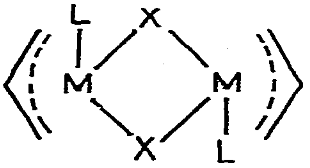

(C)

Theoretically four isomers are possible for Ic depending upon the position of the methyl group, i.e., *trans* or *cis* to phosphine and *anti* or *syn* to the central proton of the allyl group. The spectrum of Ic, however, shows the existence of the only one species. The PMR parameter in Table 1 can be assigned most satisfactorily to a conformation with the methyl group *syn* to the central proton and *trans* to the phosphine. Other PMR spectral details for Ia-Ic are given in Table 1.

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