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Preliminary communication

THE STRUCTURE OF THE COMPLEX $[(\pi\text{-}C_6H_{11})Ni(PPh_3)_2]^+ZnCl_3^-$ CONTAINING A 1,1′,2-TRIMETHYLALLYL LIGAND

M. ZOCCHI and A. ALBINATI
Sezione Chimica Macromolecolare e Materiali, Istituto di Chimica Industriale del Politecnico, Piazza Leonardo da Vinci, 32, 20133 Milano (Italy)

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Summary

The structure of the title complex has been determined by X-ray diffraction methods; the conformation of the trimethylallyl ligand is discussed.

This investigation was undertaken as part of our study of structural changes occurring in unsaturated hydrocarbons on coordination to transition metals.

Single crystals suitable for X-ray diffraction work were chosen from a batch prepared by Vitulii et al. [1].

The crystal data are as follows: $a = 18.968(3)$, $b = 19.497(3)$, $c = 21.363(3)$ Å; space group *Pbca*; 8 units $C_6H_{11}Ni(PPh_3)_2 \cdot ZnCl_3$ per cell.

The intensities of 2321 non-zero independent Bragg reflections up to $2\theta = 50$ (graphite-monochromatized Mo-K_α radiation) were measured on a four-circle automated X-ray diffractometer by the ω-scanning technique and by averaging two background counts for each reflection. The intensity data were corrected for Lorentz and polarization factors, but not for absorption since the crystal was small and of regular shape. The structure was solved by Patterson and Fourier methods and refined by least squares with isotropic thermal parameters down to a value of 0.103 for R, the conventional disagreement factor. Any further refinement requires a rigid-body treatment of the phenyl rings of the triphenylphosphine ligands, due to the large number of parameters to be determined. Such a refinement, involving anisotropic thermal factors, is in progress.

The structure involves $[C_6H_{11}Ni(PPh_3)_2]^+$ cations and $Zn_2Cl_6^{2-}$ dimeric anions. In the anion the geometry about each zinc atom is approximately tetrahedral; two of the six chlorine atoms form bridges between the two halves of the dimeric unit, which are related to each other by a crystallographic symmetry center. In the cation (Fig. 1 and Table 1) the

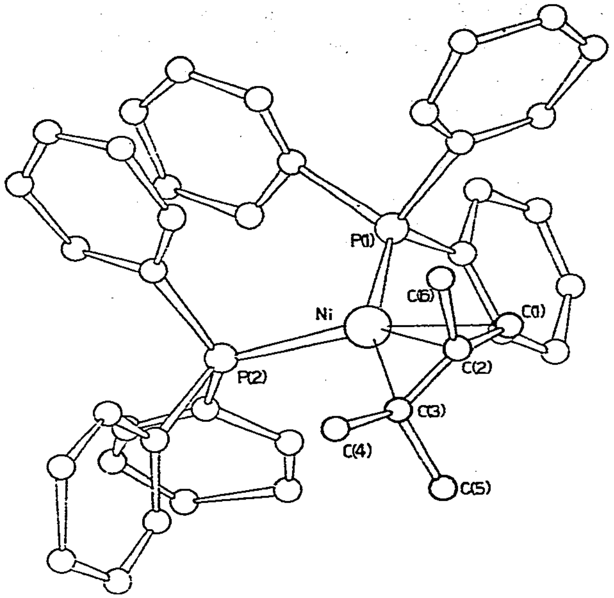

Fig.1. Structure of the complex cation $[(\pi\text{-}C_6H_{11})Ni(PPh_3)_2]^+$.

TABLE 1

INTERATOMIC DISTANCES (in Å) AND BOND ANGLES (degrees)

Ni—P(1)	2.235(4)	P(1)—Ni—P(2)	102.2(1)
Ni—P(2)	2.220(5)	C(1)—Ni—C(3)	71.2(5)
Ni—C(1)	2.04 (2)	C(1)—C(2)—C(3)	129 (1)
Ni—C(2)	1,98 (3)	C(2)—C(3)—C(4)	130 (1)
Ni—C(3)	2.13 (3)	C(1)—C(2)—C(6)	122 (1)
C(1)—C(2)	1.34 (3)	C(3)—C(2)—C(6)	108 (1)
C(2)—C(3)	1.36 (4)	C(2)—C(3)—C(5)	109 (1)
C(3)—C(4)	1.50 (4)	C(4)—C(3)—C(5)	115 (1)
C(3)—C(5)	1.68 (4)		
C(2)—C(6)	1.65 (4)		

coordination about the nickel atom is approximately square planar, if one considers the trimethylallyl group as a bidentate ligand. The geometry of the bonding of this group to the metal resembles the one already observed in similar complexes [2], and the values of the Ni—C bond distances are not significantly different from those found in other cases [3].

The conformation of the 1,1′,2-trimethylallyl ligand is close to that expected for 2,3-dimethyl-*trans*-butadiene, with carbon atoms C(1), C(2), C(3), and C(4) (methyl) approximately in the same plane. A notable feature of this ligand is that the angle C(1)—C(2)—C(3) is larger than that usually found (range 120—124°) in a coordinated allyl group [4,5]. It is also noteworthy that the methyl substituents C(5) and C(6) are at rather short distances (average 2.95 Å) from the metal. A similarly short metal—carbon (methylene) distance, in a cobalt complex which is a catalyst for the dimerization of butadiene, was taken by Allegra et al. [4] as an indication of a possible electronic interaction between the metal and one of the hydrogen atoms of a methylene group belonging to an unsaturated hydrocarbon ligand. Formation of a metal hydride may also be an intermediate step in the preparation of the complex we have studied.

Acknowledgements

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