

Preliminary communication

SYNTHESIS AND CRYSTAL STRUCTURE OF THE *dihapto*-BONDED PHENYLISOTHIOCYANATE COMPLEX [(triphos)Ni(η^2 -SCNPh)] · 0.5 CH₂Cl₂

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Summary

The complex [(triphos)Ni(η^2 -SCNPh)] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) is obtained from the reaction of the nickel(0) complex [(triphos)Ni(η^2 -CS₂)] with phenylisothiocyanate. An X-ray crystal structure determination has shown that the nickel atom is five-coordinated by the three phosphorus atoms of triphos and the carbon and sulfur atoms of a SNCPh molecule.

Very few organoisothoncyanate complexes of transition metals are described in the literature [1]. In most instances, even though the SCNR appears initially to form a 1/1 complex with the organometallic fragment, degradation of the heteroallene to isonitrile follows. In other cases the coordination to the metal takes place with dimerization of SCNR. While some *dihapto*-bonded organoisothoncyanate complexes are known, in no case has a crystal structure been reported.

We have found that when a methylene chloride solution of [(triphos)-Ni(η^2 -CS₂)] (1) [2] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) is treated at room temperature under an inert atmosphere with an equivalent amount of phenylisothiocyanate, red crystals of [(triphos)Ni(η^2 -SCNPh)] · 0.5-CH₂Cl₂ (2) separate in 60% yield. Complex 2 is diamagnetic, and air-stable in the solid state. It is soluble in chlorinated solvents, in which it behaves as a non-electrolyte. The IR spectrum (Nujol mull) exhibits bands at 1640 and 645 cm⁻¹ attributable, respectively, to the C=N stretching vibration and the MSC vibration of a *dihapto*-bonded SCNPh group [1]. Strong phenyl vibrations appear at 1625, 1580, and 1485 cm⁻¹.

The crystals of 2 are orthorhombic, space group *Pbac*, *a* 23.142(7), *b* 21.429(7), *c* 17.204(6) Å, *Z* = 8. The intensities of 1499 reflections with

$I \geq 3\sigma(I)$ were measured on a Philips PW 1100 diffractometer using Mo- K_{α} radiation. The structure was solved by direct methods [3] and refined by least-squares routines [4] to a conventional R factor of 0.072.

The structure consists of isolated (triphos)Ni(SCNPh) molecules (see Fig. 1). The stereochemistry about the nickel atom is essentially that found in [(triphos)Co(η^2 -CS₂)] (3) [5] and 1 [6], with metal coordinated by the three phosphorus atoms of the triphos ligand and a CS linkage of the heteroallene molecule. It is noteworthy that 1 and 3 are practically superimposable molecules although their total electron counts differ by one unit.

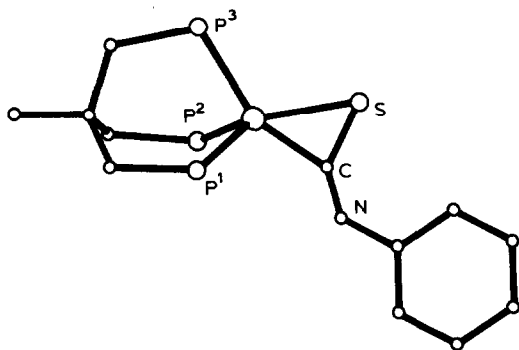


Fig. 1. Structure of the complex [(triphos)Ni(η^2 -SCNPh)]. For sake of clarity the phenyl rings of the triphos ligand are not shown.

The skeleton of 2, in spite of having the same primary geometry as that of 1 and 3, shows remarkable differences in some secondary parameters. In particular, coordination of SCNPh induces an unprecedented distortion of the usually rigid (triphos)M fragment. Determination of many crystal structures of complexes containing this fragment has in no case shown any P—M—P angles deviating by more than 5° from 90° [7] and the symmetry of the fragment was always approximately C_3 . In 2 the P¹—Ni—P² angles has a value of 101.2(2)°, while the other P—M—P angles remain close to 90°. There are some other parameters which clearly reflect the constrained coordination of 2. Thus, while in 1 and 3 the MSC plane is almost coplanar with the plane formed by the metal, a phosphorus atom, and the line of the L₃M threefold axis, here the dihedral angle between the two planes is 19°. Moreover the three Ni—P distances are spread over a range (2.157(6)—2.257(6) Å) which is noticeably wider than that in 1 and 3. The Ni—S distance is 2.259(6) Å, significantly longer than in 1 (2.206(4) Å), whereas no significant differences are found for the Ni—C and C—S distances, which in 2 have values of 1.88(2) and 1.68(2) Å, respectively. Finally a dihedral angle of 23° between the phenyl ring and the SCN plane rules out the possibility of substantial SCNPh plane.

A theoretical study of the bonding abilities of coordinated heteroallene molecules is in progress [8]. The present structure determination has important implications for assessing the electronic effects which variation in the nature of the heteroallene can exercise on the coordination to the metal.

References

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