

Trigonal Pyramidal Five-co-ordinated Ni⁰ Complex

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Summary An X-ray investigation of the complex NiN(C₂H₄PPh₂)₃ shows that it is the first known complex to have trigonal pyramidal co-ordination.

THE diamagnetic compound tris-(2-diphenylphosphinoethyl)aminenickel(0) is precipitated as red crystals which are fairly stable in air when sodium tetrahydroborate is added to an ethanol-acetone solution containing nickel(II)

The compound is unstable in dichloroethane or THF solution even under dry nitrogen.

An X-ray analysis of this compound has been undertaken. *Crystal data:* C₄₂H₄₂NNiP₃, monoclinic, space group *C2/c*, *a* = 24.370(7), *b* = 11.242(4), *c* = 27.693(7) Å, β = 107.65(16)°, *Z* = 8.

Intensity measurements were collected on a Hilger diffractometer, and structure determination and refinement were carried out using 1864 independent reflections with *I* > 3σ to an *R* = 0.059.

Bond lengths and angles about the nickel are: Ni-N, 2.178(7); Ni-P(1), 2.117(3); Ni-P(2), 2.121(3); Ni-P(3), 2.118(3) Å; P(1)-Ni-P(2), 120.05(12)°; P(1)-Ni-P(3), 124.54(12)°; P(2)-Ni-P(3), 115.39(12)°; P(1)-Ni-N, 90.11(22)°; P(2)-Ni-N, 89.35(22)°; P(3)-Ni-N, 90.62(20)°.

No hydrogen atom of the phenyl group approaches the nickel atom at a distance shorter than 3.30 Å, and intermolecular contacts are never shorter than 3.6 Å.

The unique molecular shape of this complex, where, in particular, the N-Ni-P angles are practically equal to 90°, suggests the following comments concerning the electronic structure of the central nickel atom: (a) the EAN is equal to 36; (b) five localized electron-pairs are present in the valence shell of the nickel atom. These are directed from the central atom to the vertices of a trigonal bipyramid. Four of these pairs, the three occupying the equatorial positions and the fourth which occupies one of the axial positions, are σ-bonding. The fifth is a non-bonding pair which occupies the other axial position.

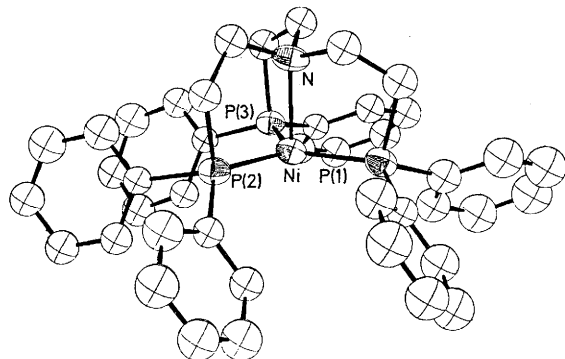


FIGURE. Molecular structure of NiN(C₂H₄PPh₂)₃.

nitrate, and tris-(2-diphenylphosphinoethyl)amine under nitrogen. That the compound contains no hydridic hydrogen has been shown by reaction with iodine when no hydrogen is evolved, and also by reaction with 2 mol. equiv. of hydrogen chloride to produce 1 mol. equiv. of hydrogen and nickel(II); also there is no Ni-H band in the i.r. spectrum. The electronic spectrum shows bands at 450 and 515 nm.

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