Trigonal Pyramidal Five-co-ordinated Ni^0 Complex

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Summary An *X*-ray investigation of the complex $NiN(C_2H_4PPh_2)_3$ 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) 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. The compound is unstable in dichloroethane or THF solution even under dry nitrogen.

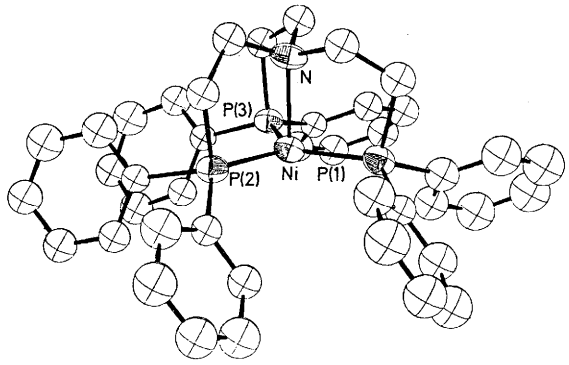

FIGURE. Molecular structure of $NiN(C_2H_4PPh_2)_3$.

An *X*-ray analysis of this compound has been undertaken. *Crystal data:* $C_{42}H_{42}NNiP_3$, monoclinic, space group $C2/c$, $a = 24{\cdot}370(7)$, $b = 11{\cdot}242(4)$, $c = 27{\cdot}693(7)$ Å, $\beta = 107{\cdot}65(16)°$, $Z = 8$.

Intensity measurements were collected on a Hilger diffractometer, and structure determination and refinement were carried out using 1864 independent reflections with $I > 3\sigma$ to an $R = 0{\cdot}059$.

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.

(*Received, 3rd August* 1973; *Com.* 1123.)