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Five-Coordinate Ni(II) Complexes of 1,2-Bis(diphenylphosphino)-*o*-carborane

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Tetraalkylammonium tetrahalonickelates have proven useful as reagents in the synthesis of four-coordinate nickel complexes via a non-aqueous chelation reaction [1, 2]. While attempting to utilize this scheme in the synthesis of square-planar nickel(II) complexes of 1,2-bis(diphenylphosphino)-*o*-carborane [3, 4] (dpc) we have discovered a facile preparation of five-coordinate nickel–dpc derivatives as illustrated in equation (1) (X = Cl or Br)*:

$$(Et_4N)_2NiX_4 + dpc \xrightarrow[\text{reflux}]{CH_3CN} (Et_4N)[Ni(dpc)X_3] + Et_4NX \qquad (1)$$

The iodo analog was synthesized from $(Et_4N)[Ni(dpc)Cl_3]$ via a metathesis using KI in ethanol. These appear to be the first examples of 5-coordinate nickelate derivatives containing Ni(II) in a P PX_3 environment.

Analogous reactions using the monodentate ligand triphenylphosphine and the bidentate ligand 1,2-bisdiphenylphosphinoethane (diphos) yielded the tetrahedral complexes $[(C_6H_5)_3P]_2NiX_2$ and $[(C_2H_5)_4N][(C_6H_5)_3PNiX_3]$ and the square planar complexes Ni(diphos)X_2 and [Ni(diphos)$_2$]X_2 respectively (depending on reaction conditions). Under no conditions were we able to isolate NiP_2X_3 complexes using these non-carborane based ligands.

The complexes are diamagnetic, insoluble in water, hydrocarbons and CCl_4, but dissolve readily in most common polar organic solvents. In 1,2-dichloroethane the molecular weight (by vapor phase osmometry on 10^{-3} *M* solutions) of the chloro derivative indicated that the complex was dissociated in this solvent to the extent expected for a 1:1 electrolyte (calcd. 806, found 433). Conductivity measurements (using Et_4NBr as a reference) were in agreement with literature data [5] for 1:1 electrolytes in 1,2-dichloroethane. As expected, 1:1 electrolytic behavior was also observed in acetonitrile.

The electronic spectra, measured in 1,2-dichloroethane and acetonitrile, exhibited principle d–d absorptions at 540–470 mμ (ϵ = 1000–1500) consistent with the spectrochemical series ($I < Br < Cl$). A second slightly weaker d–d absorption appeared at higher energies (390–330 mμ) in all three complexes. The spectra did not allow an unequivocal prediction of geometry. However, the positions, intensities and general shapes of the bands were consistent with reported data for known square-pyramidal complexes [6]. The colors (Cl, red; Br, maroon; I, purple) also suggest square-pyramidal geometry.

The ^1H nmr spectra revealed the characteristic quartet–triplet resonances of the tetraethylammonium cation [7] centered at approximately $\tau 6.9$ and $\tau 8.9$ respectively in all three complexes. The phenyl region showed 1:1:3 multiplet patterns which were insensitive to variable temperature experiments, (DMSO solutions, 20°–150 °C), suggesting free rotation of the phenyl rings. The nmr data are supportive of a square-pyramidal geometry in which the ortho hydrogen atoms on one of the two phenyl groups attached to each phosphorus experiences a deshielding due to the out-of-plane halogen atom. The ligand, dpc, and other phenylphosphines exhibit a 2:3 multiplet pattern.

A reaction analogous to (1) apparently occurs with the ligand 1,2-bis(chlorophenylphosphino)-*o*-carborane and $(Et_4N)_2NiX_4$ in acetonitrile. However, the highly colored solid products have not been satisfactorily characterized.

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*Satisfactory elemental analyses were obtained for all complexes.