

Supramolecular Structures of Four-Coordinate Nickel Bis(Triphenylphosphine) Nitrosyl Complexes

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The multiple phenyl-phenyl edge-to-face (*ef*) C—H \cdots π attractive interactions of the concerted sextuple phenyl embrace (SPE) give a sum of interaction energy sufficient to make it a dominant supramolecular motif for triphenylphosphine (TPP) complexes (Dance & Scudder, *Chem. Comm.* 1995, 1039-40). The title complexes, NiX(NO)(P(C₆H₅)₃)₂, with X = NCS⁻, N₃⁻, or Cl⁻, while closely related have quite different supramolecular structures.

The primary extended interactions in the isothiocyanato complex are SPE between adjacent TPP occurring in parallel chains alternating; d[P-P] = 7.087 Å, colinearity = 176.9 ° and d[P-P] = 7.246 Å, colinearity = 173.0 ° SPE. Chains are joined by four phenyl ring regions to form layers dominated by *ef* C—H \cdots π interactions. Layers are bound by nitrosyl-phenyl and phenyl-phenyl interactions.

The chloro complex contains a benzene solvate which has one end inserted into the cleft of an Ni(bis-TPP) fragment located on a pseudo 2-fold axis utilizing one complex-to-benzene *ef* and one benzene-to-complex *ef* interaction to each of the TPP ligands. Eight additional *ef* interactions form the central region of the cavity and the chloro and nitrosyl ligands of another molecule cap the cavity. Thus, the benzene molecule, able to form considerably more C—H \cdots π interactions, becomes the major supramolecular link in the structure.

The shortest intermolecular P-P distances in the azido complex are 7.411 Å and 7.825 Å with colinearities of 86.9 ° and 117.7 °, thus not SPE. The strongest nonbond is a 2.493 Å *intramolecular* C—H \cdots N interaction to the lone pair on the N bonded to Ni destroying the pseudo three-fold symmetry of one TPP, while another strong *intramolecular* C—H \cdots N interaction to the azido ligand π cloud involves the other TPP, thus disrupting both possibilities to form SPEs. The azido ligand is also involved in intermolecular nonbonded interactions. Thus, as the strongest hydrogen bond acceptor, the azido ligand becomes the most important determiner of the supramolecular structure.