Crystal and Molecular Structure of Tetrafluoroethylene-1,1,1-tris-(diphenylphosphinomethyl)ethane nickel

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Summary Crystal structure analysis of tetrafluoroethylene-1,1,1-tris(diphenylphosphinomethyl)ethanenickel has established that the phosphine ligand is tridentate through three phosphorus atoms; the co-ordinated C_2F_4 group is highly distorted, each CF_2 being bent away from the planar conformation by an average of 42°.

IN the course of studies of nickel d^{10} tetrafluoroethylene complexes[1] it was found that tetrafluoroethylene-1,1,1-tris(diphenylphosphinomethyl)ethanenickel was unreactive towards excess of tetrafluoroethylene (TFE). Thus the presumed three-membered ring system $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2}}$ is not converted into a five-membered ring system $\overline{\mathrm{Ni{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2{\cdot}CF_2}}$ as has been found in other reactions.[2] For a fuller understanding of the chemistry of this system and, in particular to establish whether this resistance to the formation of a five-membered ring could be related to the absence of a vacant co-ordination site it was necessary to determine by crystal structure analysis the manner of co-ordination of the phosphine which could function either as a bidentate or a tridentate ligand. Further, although the distinctive chemistry of metal complexes containing polytertiary phosphine ligands has been much studied[3] there is a paucity of quantitative molecular structural data.

Crystal data: $C_{43}H_{39}F_4NiP_3$, $M = 783$, monoclinic, space-group $P2_1/c$; $a = 10{\cdot}567(3)$, $b = 20{\cdot}510(3)$, $c = 18{\cdot}963(3)$ Å, $\beta = 114{\cdot}20(2)°$, ($\lambda = 0{\cdot}7107$ Å for Mo-K_α); $U = 3749$ Å^3; $Z = 4$, $D_c = 1{\cdot}39$ g cm^{-3}; $\mu = 6{\cdot}99$ cm^{-1} for Mo-K_α.

The structure was solved by conventional heavy-atom methods but with the phenyl rings treated as rigid groups. It was refined to $R = 0{\cdot}084$ using 1272 independent reflections ($2\theta \leqslant 40°$ and with $|F|^2 \geqslant 3\sigma|F|^2$) measured on a four-circle diffractometer and with Mo-K_α radiation.

The molecular structure is illustrated in the Figure which shows that all three phosphorus atoms are co-ordinated to nickel. There is therefore no vacant co-ordination site to facilitate addition of TFE. Bond distances are Ni–P(1) 2·28(1), Ni–P(2) 2·26(1), and Ni–P(3) 2·21(1) Å. The mean values of the angles P–Ni–P and P–Ni–(mid-point C–C) are 92·5 and 122·7°. The C_2F_4 molecule is symmetrically co-ordinated to nickel with Ni–C(6) 1·88(2) Å, Ni–C(7) 1·84(2) Å, and ∠ C(6)–Ni–C(7) 43(1)°. The C–C bond length of 1·37(3) Å is consistent with those observed in other TFE complexes but the departure from planarity of

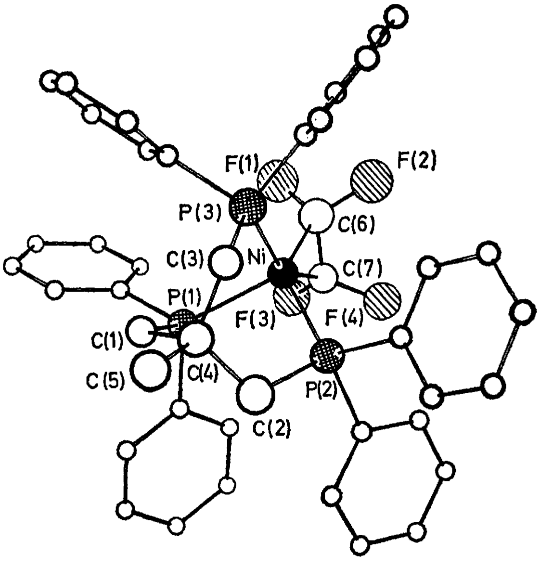

FIGURE. *A general view of the molecule.*

the C_2F_4 molecule is greater than hitherto observed.[4] Thus the angle α between the normals to the two CF_2 planes is 84° which means that each CF_2 plane has been bent away from the planar molecular conformation by an average of 42°.

If the TFE is regarded as a monodentate π-donor the co-ordination geometry is distorted tetrahedral and closely similar to that observed in the cation $[Ni\{MeC(CH_2PEt_2)_3\}(NO)]^+$[5] and the compound $\{MeC(CH_2PPh_2)_3\}NiI$,[6] the only other two authenticated examples of a triphosphine co-ordinating as a tridentate ligand through its phosphorus atoms.

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