A Comparison of Nickel–Perfluorophenyl and Nickel–Perchlorophenyl Linkages, from an *X*-Ray Crystallographic Study of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$

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Summary A single-crystal *X*-ray diffraction study of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$ ($R = 4{\cdot}91\%$) shows the nickel–pentachlorophenyl distance of $1{\cdot}905 \pm 0{\cdot}010$ Å to be significantly ($5{\cdot}4\sigma$) shorter than the nickel–pentafluorophenyl distance of $1{\cdot}978 \pm 0{\cdot}009$ Å.

As with perfluoroalkyls,[1,2,3a] the greater stability‡ of transition-metal σ-aryls (relative to σ-alkyls) appears to be associated with a shorter metal–carbon bond distance.[3b,4] However, while σ-perfluoroaryls are demonstrably more stable than *non-fluorinated* σ-aryls, no significant difference was found between nickel–carbon distances in $(\pi\text{-}C_5H_5)Ni(PPh_3)(\sigma\text{-}C_6F_5)$ [$Ni\text{–}(\sigma\text{-}C_6F_5) = 1{\cdot}914 \pm 0{\cdot}014$ Å[5,6] and $(\pi\text{-}C_5H_5)Ni(PPh_3)(\sigma\text{-}C_6H_5)$ [$Ni\text{–}(\sigma\text{-}C_6H_5) = 1{\cdot}904 \pm 0{\cdot}007$ Å].[5,7]

We now report the results of a single-crystal *X*-ray diffraction study of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$.[8] The present structural study is the first on a σ-perchlorophenyl complex and the first on a molecule containing more than one type of simple metal–carbon σ-bond.§

Crystal data: $C_{38}H_{26}P_2F_5Cl_5Ni$, $M = 875{\cdot}56$, monoclinic, $a = 15{\cdot}822(13)$, $b = 16{\cdot}888(12)$, $c = 15{\cdot}375(19)$, $\beta = 114{\cdot}16 \pm 0{\cdot}03°$, $U = 3748{\cdot}4$ Å^3, $D_m = 1{\cdot}48 \pm 0{\cdot}05$, $D_c = 1{\cdot}551$ g cm^{-3}, $Z = 4$, space group $C2/c$ (C^6_{2h}; No. 15).

Diffraction data to $\sin\theta = 0{\cdot}38$ (Mo-K_α radiation, $\bar{\lambda} = 0{\cdot}7107$ Å) were collected on a Supper–Pace "Buerger Automated Diffractometer" using a 'stationary-background, ω-scan, stationary-background' counting sequence and equi-inclination Weissenberg geometry. Data for the levels $hk0$—16 and 0—$16kl$ were corrected for absorption ($\mu = 9{\cdot}78$ cm^{-1}) and merged to a common scale. Solution of the structure was accomplished *via* a combination of a Patterson map, Fourier syntheses, and full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms. All atoms other than methyl hydrogens have been located, the final discrepancy index R being $4{\cdot}91\%$ for the 1604 independent non-zero reflections.

The nickel atom lies at $0,0{\cdot}0362,1/4$ [*i.e.*, special position 4(e) of space group $C2/c$[9]]; the molecule thus has crystallographically-required C_2 symmetry (see Figure). While the NiP_2C_2 core of the molecule is required to be strictly planar, bond angles around the nickel atom centre are not perfectly regular, *viz.*,

$\angle[(Cl_5C_6)\text{–}Ni\text{–}(C_6F_5)] = 180{\cdot}0°$, $\angle[P\text{–}Ni\text{–}Pi] = 176{\cdot}7 \pm 0{\cdot}1°$, $\angle[P\text{–}Ni\text{–}(C_6F_5)] = \angle[P'\text{–}Ni\text{–}(C_6F_5)] = 91{\cdot}6 \pm 0{\cdot}2°$, $\angle[P\text{–}Ni\text{–}(C_6Cl_5)] = \angle[P'\text{–}Ni\text{–}(C_6Cl_5)] = 88{\cdot}4 \pm 0{\cdot}2°$.

The nickel–phosphorus bond lengths are each $2{\cdot}230 \pm 0{\cdot}003$ Å, mean distances within the diphenylmethylphosphine ligands being $P\text{–}C_6H_5 = 1{\cdot}823(6)$, $P\text{–}CH_3 = 1{\cdot}853(7)$, and $C\text{–}C = 1{\cdot}385(12)$ Å.

The nickel–pentafluorophenyl bond length is $1{\cdot}978 \pm 0{\cdot}009$ Å. The six carbon atoms of the $\sigma\text{-}C_6F_5$ ligand form a plane (root-mean-square deviation $0{\cdot}005$ Å) from which the fluorine atoms deviate by a maximum of only $0{\cdot}029$ Å. Mean distances within this ligand are $C\text{–}C = 1{\cdot}374(10)$ and $C\text{–}F = 1{\cdot}347(10)$ Å.

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‡ Throughout this text, the term "stability" should be taken to mean stability with respect to thermal decomposition and aerobic (or other chemical) oxidation.

§ Such ligands as CO, CN, RNC are not included by this statement since they are bonded to a transition metal both by a metal–carbon σ-bond and by a strong $d_\pi \rightarrow p_\pi$ (metal → ligand) π-bond.

The nickel–pentachlorophenyl distance is 1·905 ± 0·010 Å. While the six carbon atoms of this ligand are approximately coplanar (root-mean-square deviation 0·017 Å) the individual chlorine atoms lie +0·064, −0·108, 0·000, +0·108, −0·064 Å from this plane (distances given cyclically, starting with an *ortho*-chlorine). Presumably these deviations are a result of repulsions between adjacent chlorine atoms. Average bond lengths within this ligand are C–C = 1·395(10) and C–Cl = 1·722(10) Å.

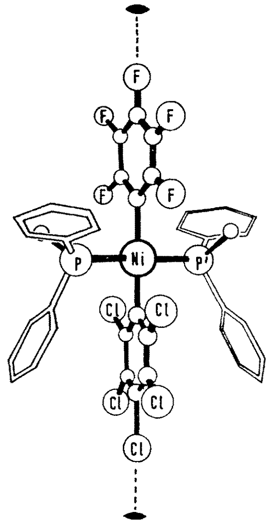

FIGURE. *The molecular geometry of* trans-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$, *showing the crystallographic* C_2 *axis.*

The σ-C_6F_5 ligand makes a dihedral angle of 79°25′ with the NiP_2C_2 co-ordination plane; other dihedral angles are $\angle[C_6Cl_5\text{–}NiP_2C_2] = 85°01'$ and $\angle[C_6Cl_5\text{–}C_6F_5] = 5°37'$.

The difference of 0·073 Å between Ni–(σ-C_6F_5) and Ni–(σ-C_6Cl_5) bond lengths is meaningful at the 5·4σ level. The Ni–(σ-C_6Cl_5) bond is thus significantly shorter (*and, therefore, stronger*) than the Ni–(σ-C_6F_5) linkage. Possible reasons for this include the following:

(i) the Ni–(σ-C_6Cl_5) bond is shortened relative to the Ni–(σ-C_6F_5) bond due either to increased d_π–p_π metal → ligand back-donation or to the Ni ← C_6Cl_5 σ-bond being stronger than the Ni ← C_6F_5 σ-bond.

(ii) the Ni–(σ-C_6F_5) bond is lengthened relative to the Ni–(σ-C_6Cl_5) bond due to the *trans*-effect of a C_6Cl_5 ligand being greater than that of a C_6F_5 ligand.

It is unlikely that the difference in nickel–carbon bond lengths is steric in origin since angular distortions of *ca.* 1·6° in the nickel co-ordination sphere involve far less energy than bond expansion by 0·073 Å.

It is hoped that the above picture will be clarified by accurate crystallographic studies on such species as *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$ and *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)X$ (X = Cl, Br, I).

We thank Professor M. D. Rausch for providing the sample; this work was generously supported by the National Science Foundation and the Advanced Research Projects Agency.

(*Received, July* 13*th*, 1970; *Com.* 1115.)

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