# Crystal Structures of Transition-metal Aryls. Part V.[1] *trans*-Bis[methyldiphenylphosphine]bis($\sigma$-pentafluorophenyl)nickel(II)

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The title compound crystallizes in the centrosymmetric orthorhombic space-group *Pbca* ($D_{2h}^{15}$, No. 61) with $a$ = 17·827(20), $b$ = 9·163(10), $c$ = 21·206(27) Å and $Z$ = 4. A single-crystal *X*-ray diffraction study has led to the accurate location of all atoms including hydrogens. The structure was refined, by the method of least-squares, to $R$ 3·8% for 1806 independent non-zero reflections. The molecule has precise $C_i$ symmetry, the $Ni^{II}$ centre being in square-planar co-ordination to two phosphine and two pentafluorophenyl ligands with Ni–$\sigma$-$C_6F_5$ 1·939(3) and Ni–$PPh_2Me$ 2·206(1) Å. These values are discussed and compared with results for *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$.

We have previously reported[1,2] an *X*-ray structural analysis of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$ in which the nickel–$\sigma$-perchlorophenyl bond distance is significantly (0·073 ± 0·014 Å) shorter than the nickel–$\sigma$-perfluorophenyl linkage. Our studies have now been extended to the species *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$.[3]

## EXPERIMENTAL

*Crystal Data.*—$C_{38}H_{26}F_{10}NiP_2$, $M = 793·29$, Orthorhombic, $a = 17·827(20)$, $b = 9·163(10)$, $c = 21·206(27)$ Å, $U = 3464·7$ Å$^3$, $D_m = 1·48(3)$ (by flotation), $Z = 4$, $D_c = 1·510$, $F(000) = 1608$. Space-group *Pbca* ($D_{2h}^{15}$, No. 61). Intensity data were collected with Cu-$K_\alpha$ radiation, $\lambda = 1·5418$ Å; $\mu(\text{Cu-}K_\alpha) = 23·64$ cm$^{-1}$.

*Collection and Reduction of Data.*—Diffraction data were collected with a 0·01° incrementing Supper–Pace automated diffractometer using a ' stationary-background, $\omega$-scan, stationary-background ' counting sequence and equi-inclination Weissenberg geometry. Two crystals were used in the analysis: crystal (C) (0·50 × 0·34 × 0·19 mm) mounted on its $c$ axis and used in collecting 1834 reflections from levels $hk0$—15 ($\sin\theta_{max.}$ 0·80); and crystal (B) (0·36 × 0·76 × 0·22 mm) mounted on its $b$ axis and used in the collection of 2079 reflections from levels $h0$—$9l$.

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[1] Part IV, M. R. Churchill and M. V. Veidis, *J. Chem. Soc.* (*A*), 1971, **3463**.

[2] M. R. Churchill and M. V. Veidis, *Chem. Comm.*, 1970, 1099.

[3] M. D. Rausch and F. E. Tibbetts, *Inorg. Chem.*, 1970, **9**, 512.

Details of the experimental procedure (*cf.* ref. 4) were: $\omega(hkl) = [1{\cdot}7 + 0{\cdot}8/L(hkl)]$; $d\omega/dt = 2$ deg min$^{-1}$; $t(B_1) = t(B_2) = 0{\cdot}25t(C)$; $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$.

Standard deviations were assigned according to the scheme: $I(hkl) \geqslant 4900$, $\sigma[I(hkl)] = 0{\cdot}1[I(hkl)]$; $I(hkl) < 4900$, $\sigma[I(hkl)] = 7{\cdot}0[I(hkl)]^{\frac{1}{2}}$.

Reflections were not included in the subsequent analysis if $<3\sigma$ above background or if their backgrounds ($B_1$ and $B_2$) were asymmetric with a ratio $>3{\cdot}0$. The remaining data were corrected for Lorentz and polarization effects. An absorption correction was applied and transmission coefficients were found to have the ranges 0·323—0·649 for crystal (C) and 0·410—0·613 for crystal (B). Data for the 26 Weissenberg levels were merged to a common scale using a least-squares procedure. The resulting 1806 independent non-zero reflections were used in a Wilson plot, from which were determined the approximate absolute scale-factor and the overall isotropic thermal parameter.

All calculations relative to the subsequent structural analysis were performed on the Harvard University IBM 360/65 computer using the CRYM crystallographic system written under the direction of Dr. R. E. Marsh at the California Institute of Technology. Scattering factors for neutral nickel and phosphorus were taken from ref. 5 while those for all other (neutral) atoms were taken from ref. 6. Dispersion corrections were made for nickel ($\Delta f' = -3{\cdot}1$, $\Delta f'' = +0{\cdot}6$e) and for phosphorus ($\Delta f' = +0{\cdot}2$, $\Delta f'' = +0{\cdot}5$e).[7] The residual minimized during refinement processes was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = \{\sigma[F^2(hkl)]\}^{-2}$ and $\sigma[F^2(hkl)]$ is derived from $\sigma[I(hkl)]$ by appropriate correction for Lorentz, polarization, absorption, and scale-factors.

*Solution and Refinement of Structure.*—With $Z = 4$ in space-group *Pbca*, the nickel atoms must (in the absence of disorder) occupy the four-fold positions *a* or *b* (Wyckoff notation),[8] with the molecule having $C_i$ symmetry. The nickel atom was arbitrarily assigned to the position $0,0,\frac{1}{2}$ (Wyckoff position *b*). The general phosphorus position was then quickly obtained from a study of a three-dimensional Patterson map which had been sharpened such that the average intensity was no longer θ-dependent and in which the origin peak had been removed. All non-hydrogen atoms were then located routinely from a three-dimensional Fourier synthesis phased by nickel and phosphorus contributions only. Three cycles of full-matrix refinement of positional and isotropic thermal parameters led to convergence at *R* 14·9%. Three cycles of anisotropic refinement reduced the discrepancy index to *R* 8·0%. At this point real and imaginary anomalous scattering contributions were applied to the nickel and phosphorus scattering curves; three more cycles of refinement reduced *R* to 7·1%. Hydrogen atoms on the phenyl rings were located from a difference Fourier synthesis; these were included in observed positions, but not refined. A one-parameter secondary extinction correction, based on the model of Zachariasen [9] was now included in the refinement. The secondary extinction factor (χ) modifies the structure-factor amplitudes according to the expression:

$$F_c^2(\text{corr.}) = F_c^2(\text{uncorr.})/[1 + \chi\beta F_c^2(\text{uncorr.})],$$

where $\beta = (1 + \cos^4 2\theta)/[\sin 2\theta\,(1 + \cos^2 2\theta)]$.

In two cycles of refinement *R* was reduced to 4·7%. At this stage hydrogen atoms of the methyl group were readily located from a difference Fourier synthesis; one cycle of refinement of all non-hydrogen parameters, with all hydrogen-atom parameters fixed led to $R = 3{\cdot}9\%$.

Finally, all parameters were refined: positional parameters for all atoms save nickel (fixed at $0,0,\frac{1}{2}$), anisotropic parameters for all non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms, an overall scale-factor, and the secondary extinction factor. Two cycles of full-matrix refinement led to convergence at *R* 3·8%, at which stage refinement was judged to be complete, since $(\Delta/\sigma) \sim 0{\cdot}1$ for hydrogen-atom thermal parameters and $(\Delta/\sigma) < 0{\cdot}05$ for all other parameters. The final value for the secondary extinction factor, χ, was $2{\cdot}474 \times 10^{-5}$.

TABLE 1

Atomic positions, with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ni | 0 | 0 | $\frac{1}{2}$ |
| P | 0·08656(4) | 0·13192(8) | 0·45225(3) |
| C(1) | −0·07849(16) | 0·08281(33) | 0·44781(13) |
| C(2) | −0·10180(18) | 0·02477(35) | 0·39117(15) |
| C(3) | −0·15262(20) | 0·09275(47) | 0·35200(15) |
| C(4) | −0·18276(21) | 0·22355(46) | 0·36955(19) |
| C(5) | −0·16137(20) | 0·28530(38) | 0·42424(20) |
| C(6) | −0·11061(18) | 0·21438(34) | 0·46211(15) |
| C(7) | 0·14783(18) | 0·01985(31) | 0·40382(14) |
| C(8) | 0·22388(20) | 0·04519(44) | 0·39883(18) |
| C(9) | 0·26771(23) | −0·03601(49) | 0·35751(20) |
| C(10) | 0·23571(27) | −0·14056(49) | 0·32178(21) |
| C(11) | 0·16061(25) | −0·17032(46) | 0·32595(20) |
| C(12) | 0·11646(22) | −0·09040(40) | 0·36791(16) |
| C(13) | 0·05460(17) | 0·27310(30) | 0·39756(14) |
| C(14) | 0·03616(21) | 0·41061(37) | 0·42030(18) |
| C(15) | 0·00763(23) | 0·51534(44) | 0·38054(25) |
| C(16) | −0·00176(26) | 0·48686(46) | 0·31823(26) |
| C(17) | 0·01690(34) | 0·35259(51) | 0·29470(26) |
| C(18) | 0·04519(26) | 0·24590(42) | 0·33420(18) |
| C(19) | 0·14895(25) | 0·23250(49) | 0·50450(19) |
| F(2) | −0·07310(12) | −0·10477(23) | 0·37127(8) |
| F(3) | −0·17103(15) | 0·03124(30) | 0·29614(9) |
| F(4) | −0·23308(16) | 0·28904(35) | 0·33182(15) |
| F(5) | −0·18891(14) | 0·41756(24) | 0·44124(13) |
| F(6) | −0·09006(13) | 0·28481(22) | 0·51544(10) |
| H(8) | 0·2457(20) | 0·1109(37) | 0·4222(15) |
| H(9) | 0·3195(23) | −0·0132(38) | 0·3581(17) |
| H(10) | 0·2641(28) | −0·1980(51) | 0·2940(20) |
| H(11) | 0·1346(26) | −0·2477(47) | 0·3006(18) |
| H(12) | 0·0635(21) | −0·1055(37) | 0·3724(15) |
| H(14) | 0·0463(18) | 0·4308(34) | 0·4703(17) |
| H(15) | −0·0044(24) | 0·6116(60) | 0·3901(22) |
| H(16) | −0·0161(28) | 0·5625(58) | 0·2863(26) |
| H(17) | 0·0122(30) | 0·3295(68) | 0·2518(32) |
| H(18) | 0·0694(25) | 0·1536(52) | 0·3133(21) |
| H(19A) | 0·1221(25) | 0·2895(44) | 0·5317(19) |
| H(19B) | 0·1769(21) | 0·2836(38) | 0·4808(16) |
| H(19C) | 0·1809(24) | 0·1636(46) | 0·5244(19) |

A final difference Fourier synthesis revealed no features greater than 0·2e Å$^{-3}$, thus providing independent verification of the determined structure. Final observed and calculated structure-factor amplitudes are listed in Supplementary Publication No. SUP 20295 (4 pp., 1 microfiche).*

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* See note concerning Supplementary Publications in Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full-size copies).

[4] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1968, **7**, 1123.

[5] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[6] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, pp. 202—203.

[7] Ref. 6, p. 214.

[8] Ref. 6, vol. 1, 1965 edn., p. 150.

[9] W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139; see also A. Larson, *ibid.*, 1967, **23**, 664.

Atomic positions, with estimated standard deviations are listed in Table 1; thermal parameters, with estimated standard deviations and their appropriate vibration ellipsoids are collected in Table 2.

## RESULTS AND DISCUSSION

*Description of the Structure.*—The crystal consists of discrete molecular units of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$ which are separated by normal van der Waals' distances.

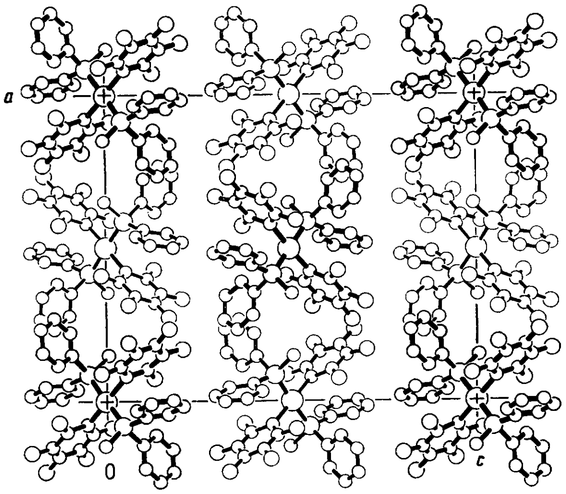

FIGURE 1 Packing of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$ molecules in the unit cell, viewed down *b*. Hydrogen atoms are omitted for clarity

The packing of molecules in the unit cell (viewed down *b*) is shown in Figure 1; there are no abnormally short intermolecular contacts. Each molecule has crystallographically required $C_i$ ($\bar{1}$) symmetry. Atoms in the basic asymmetric unit are labelled without superscripts; those in the remaining half of the molecule,

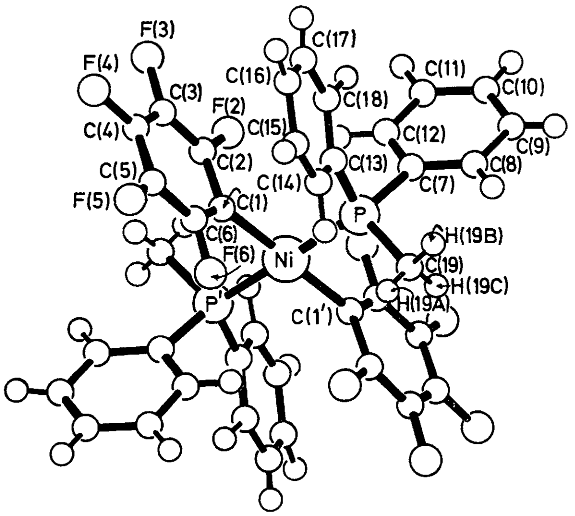

FIGURE 2 Numbering of atoms and molecular geometry

which is related to the basic unit by the transformation: $x', y', z' = -x, -y, 1 - z$, are labelled with a prime, as shown in Figure 2.

Bond distances with estimated standard deviations (and including mean values) are compiled in Table 3. Analogous angular information is available in Table 4.

The central nickel(II) atom has the expected[3] *trans*-planar co-ordination geometry. The $NiP_2C_2$ core of

TABLE 2

Atomic thermal parameters

*a*) Anisotropic thermal parameters * ($\times 10^5$)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ni | 244(3) | 933(12) | 151(2) | −10(7) | −28(3) | 37(5) |
| P | 254(3) | 1044(13) | 169(2) | −61(8) | −11(4) | 56(7) |
| C(1) | 256(11) | 1095(38) | 184(8) | −94(33) | −12(15) | 176(29) |
| C(2) | 311(12) | 1340(42) | 178(8) | −111(38) | −5(16) | 94(32) |
| C(3) | 355(14) | 2254(65) | 188(9) | −484(54) | −180(18) | 308(40) |
| C(4) | 352(14) | 1945(61) | 324(11) | 226(51) | −152(21) | 686(46) |
| C(5) | 310(13) | 1451(48) | 389(12) | 258(44) | 61(21) | 417(41) |
| C(6) | 293(11) | 1257(45) | 245(9) | −59(39) | 16(17) | 211(34) |
| C(7) | 275(12) | 1165(38) | 190(8) | 43(34) | 36(15) | 157(30) |
| C(8) | 312(13) | 1514(49) | 277(10) | 15(45) | 55(19) | 241(41) |
| C(9) | 309(16) | 1973(63) | 335(11) | 356(53) | 159(21) | 382(48) |
| C(10) | 522(21) | 1773(63) | 312(11) | 714(62) | 247(25) | 228(47) |
| C(11) | 498(18) | 1638(53) | 300(11) | 264(55) | 72(23) | −194(43) |
| C(12) | 345(14) | 1523(48) | 284(10) | 3(45) | 42(20) | −112(39) |
| C(13) | 285(11) | 1078(40) | 194(9) | −158(35) | −1(14) | 142(30) |
| C(14) | 420(14) | 1263(46) | 260(10) | 83(43) | 57(19) | 104(37) |
| C(15) | 511(18) | 1178(54) | 379(15) | 172(48) | 22(23) | 265(44) |
| C(16) | 613(23) | 1650(71) | 354(15) | 4(55) | −228(24) | 539(50) |
| C(17) | 950(29) | 1636(67) | 284(14) | −9(65) | −334(30) | 210(48) |
| C(18) | 658(20) | 1276(48) | 218(10) | 47(50) | −147(22) | 26(37) |
| C(19) | 353(14) | 1471(55) | 225(10) | −390(55) | −61(21) | 55(42) |
| F(2) | 471(9) | 1720(29) | 217(5) | −32(26) | −50(10) | −249(19) |
| F(3) | 637(12) | 3118(47) | 245(6) | −462(38) | −335(13) | 274(26) |
| F(4) | 592(12) | 3544(59) | 539(9) | 691(44) | −426(18) | 992(42) |
| F(5) | 515(10) | 1651(33) | 576(9) | 703(31) | 126(15) | 438(28) |
| F(6) | 542(10) | 1385(29) | 290(6) | 39(26) | 0(12) | −175(21) |

* The anisotropic thermal parameter is defined by: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}hl)]$.

TABLE 2 (*Continued*)

(*b*) Isotropic thermal parameters (Å$^2$) for hydrogen atoms

| | $B$/Å$^2$ | | $B$/Å$^2$ | | $B$/Å$^2$ | | $B$/Å$^2$ |
|---|---|---|---|---|---|---|---|
| H(8) | 1·6(8) | H(12) | 2·2(7) | H(16) | 6·5(13) | H(19A) | 3·4(9) |
| H(9) | 3·2(9) | H(14) | 2·2(7) | H(17) | 7·4(15) | H(19B) | 1·8(8) |
| H(10) | 5·1(11) | H(15) | 5·0(11) | H(18) | 5·2(11) | H(19C) | 3·6(9) |
| H(11) | 4·5(10) | | | | | | |

(*c*) Root-mean-square amplitudes and direction cosines for the axes of the atomic vibration ellipsoids

| Atom | $(\overline{U^2}_{\text{min.}})^{\frac{1}{2}}$/Å | $(\overline{U^2}_{\text{med.}})^{\frac{1}{2}}$/Å | $(\overline{U^2}_{\text{maj.}})^{\frac{1}{2}}$/Å |
|---|---|---|---|
| Ni | 0·181<br>(−0·382, 0·156, −0·911) | 0·200<br>(−0·862, −0·416, 0·290) | 0·207<br>(0·334, −0·896, −0·293) |
| P | 0·193<br>(−0·039, 0·351, −0·936) | 0·199<br>(−0·904, −0·411, −0·116) | 0·216<br>(0·425, −0·842, −0·333) |
| C(1) | 0·187<br>(−0·251, −0·630, 0·735) | 0·201<br>(−0·926, −0·066, −0·373) | 0·233<br>(0·284, −0·774, −0·567) |
| C(2) | 0·199<br>(0·061, 0·269, −0·961) | 0·219<br>(0·908, 0·385, 0·165) | 0·246<br>(−0·415, 0·883, 0·221) |
| C(3) | 0·176<br>(−0·539, 0·030, −0·842) | 0·232<br>(−0·732, −0·511, 0·451) | 0·333<br>(0·417, −0·859, −0·298) |
| C(4) | 0·179<br>(−0·575, 0·525, −0·628) | 0·262<br>(0·817, 0·415, −0·401) | 0·335<br>(−0·050, 0·743, 0·668) |
| C(5) | 0·206<br>(−0·765, 0·619, −0·178) | 0·236<br>(0·613, 0·616, −0·495) | 0·319<br>(0·196, 0·488, 0·851) |
| C(6) | 0·206<br>(−0·521, −0·643, 0·561) | 0·221<br>(−0·853, 0·370, −0·368) | 0·255<br>(0·029, −0·670, −0·742) |
| C(7) | 0·194<br>(−0·286, −0·488, 0·825) | 0·210<br>(−0·914, 0·396, −0·083) | 0·236<br>(−0·286, −0·778, −0·560) |
| C(8) | 0·217<br>(−0·801, −0·320, 0·506) | 0·233<br>(0·578, −0·637, 0·511) | 0·276<br>(−0·159, −0·702, −0·695) |
| C(9) | 0·205<br>(0·933, −0·188, −0·308) | 0·247<br>(−0·106, 0·674, −0·731) | 0·327<br>(0·345, 0·714, 0·609) |
| C(10) | 0·216<br>(−0·710, 0·560, 0·428) | 0·248<br>(0·014, 0·618, −0·786) | 0·349<br>(0·705, 0·552, 0·446) |
| C(11) | 0·231<br>(−0·429, 0·658, 0·619) | 0·279<br>(−0·280, 0·555, −0·783) | 0·295<br>(0·859, 0·509, 0·054) |
| C(12) | 0·232<br>(−0·878, 0·220, 0·425) | 0·246<br>(−0·442, −0·714, −0·543) | 0·266<br>(0·184, −0·664, 0·725) |
| C(13) | 0·189<br>(−0·444, −0·691, 0·571) | 0·212<br>(−0·732, −0·089, −0·676) | 0·235<br>(0·518, −0·718, −0·466) |
| C(14) | 0·225<br>(0·012, −0·864, 0·503) | 0·241<br>(0·556, −0·412, −0·722) | 0·268<br>(−0·831, −0·288, −0·476) |
| C(15) | 0·212<br>(−0·163, 0·943, −0·289) | 0·285<br>(0·895, 0·018, −0·445 | 0·304<br>(0·415, 0·331, 0·848) |
| C(16) | 0·211<br>(−0·273, 0·690, −0·670) | 0·294<br>(0·670, 0·636, 0·382) | 0·345<br>(0·690, −0·345, −0·637) |
| C(17) | 0·223<br>(−0·265, 0·437, −0·860) | 0·272<br>(0·169, 0·899, 0·404) | 0·404<br>(0·949, −0·039, −0·312) |
| C(18) | 0·214<br>(0·232, −0·198, 0·952) | 0·234<br>(0·018, 0·980, 0·199) | 0·330<br>(0·973, 0·029, −0·231) |
| C(19) | 0·205<br>(−0·759, −0·558, −0·336) | 0·226<br>(0·123, 0·383, −0·915) | 0·278<br>(0·640, −0·736, −0·222) |
| F(2) | 0·208<br>(0·154, 0·383, 0·911) | 0·276<br>(0·938, −0·345, −0·013) | 0·280<br>(0·310, 0·857, −0·412) |
| F(3) | 0·198<br>(0·444, −0·038, 0·896) | 0·319<br>(0·729, 0·597, −0·336) | 0·387<br>(−0·522, 0·801, 0·293) |
| F(4) | 0·201<br>(−0·674, 0·438, −0·595) | 0·382<br>(−0·739, −0·428, 0·521) | 0·433<br>(−0·027, 0·790, 0·612) |
| F(5) | 0·214<br>(−0·587, 0·810, −0·119) | 0·305<br>(−0·734, −0·464, 0·496) | 0·382<br>(−0·342, −0·378, −0·860) |
| F(6) | 0·230<br>(−0·038, 0·830, 0·556) | 0·268<br>(−0·059. 0·554. −0·831) | 0·296<br>(0·998, 0·065, −0·028) |

the molecule has precise $C_i$ symmetry, with the angles P–Ni–P′ and C(1)–Ni–C(1′) both 180°; other angles in the co-ordination sphere are: P–Ni–C(1) and P′–Ni–C(1′) 91·63(9)°, and P–Ni–C(1′) and P′–Ni–C(1) 88·37(9)°. These small irregularities from a truly 'square-planar' geometry presumably reflect some slight intramolecular repulsions.

*The Methyldiphenylphosphine Ligands.*—The two $PPh_2Me$ ligands are interrelated by a crystallographic inversion centre and are therefore equivalent. The

TABLE 3

Interatomic distances (Å) with estimated standard deviations in parentheses

(*a*) Distances from nickel atom

| | | | |
|---|---|---|---|
| Ni–C(1) | 1·939(3) | Ni–P | 2·206(1) |

(*b*) Distances within $\sigma$-$C_6F_5$ ligand

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·378(4) | | |
| C(2)–C(3) | 1·378(5) | C(2)–F(2) | 1·360(4) |
| C(3)–C(4) | 1·365(6) | C(3)–F(3) | 1·352(4) |
| C(4)–C(5) | 1·346(6) | C(4)–F(4) | 1·344(5) |
| C(5)–C(6) | 1·373(5) | C(5)–F(5) | 1·356(4) |
| C(6)–C(1) | 1·369(4) | C(6)–F(6) | 1·353(4) |
| Mean | 1·368(12) * | Mean | 1·353(6) * |

(*c*) Phosphorus–carbon distances within the $PPh_2Me$ ligand

| | | | |
|---|---|---|---|
| P–C(7) | 1·817(3) | | |
| P–C(13) | 1·828(3) | P–C(19) | 1·821(4) |
| Mean | 1·823(8) * | | |

(*d*) Carbon–carbon distances within the $PPh_2Me$ ligand

| | | | |
|---|---|---|---|
| C(7)–C(8) | 1·380(5) | C(13)–C(14) | 1·389(5) |
| C(8)–C(9) | 1·390(6) | C(14)–C(15) | 1·375(6) |
| C(9)–C(10) | 1·348(6) | C(15)–C(16) | 1·357(8) |
| C(10)–C(11) | 1·369(7) | C(16)–C(17) | 1·369(7) |
| C(11)–C(12) | 1·396(6) | C(17)–C(18) | 1·383(7) |
| C(12)–C(7) | 1·383(5) | C(18)–C(13) | 1·377(5) |
| | | Mean | 1·376(14)* |

(*e*) Carbon–hydrogen distances in phenyl rings

| | | | |
|---|---|---|---|
| C(8)–H(8) | 0·87(3) | C(14)–H(14) | 1·09(4) |
| C(9)–H(9) | 0·95(4) | C(15)–H(15) | 0·93(5) |
| C(10)–H(10) | 0·94(5) | C(16)–H(16) | 1·00(5) |
| C(11)–H(11) | 1·00(4) | C(17)–H(17) | 0·94(7) |
| C(12)–H(12) | 0·96(4) | C(18)–H(18) | 1·05(5) |
| | | Mean | 0·97(6) * |

(*f*) Carbon–hydrogen distances in methyl group

| | | | |
|---|---|---|---|
| C(19)–H(19A) | 0·91(4) | | |
| C(19)–H(19B) | 0·85(4) | C(19)–H(19C) | 0·95(4) |
| | | Mean | 0·90(5) * |

* Estimated standard deviations for mean distances are calculated from the formula: $\sigma = \left[\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2/(N-1)\right]^{\frac{1}{2}}$ where $\chi_i$ is the *i*th bond length and $\bar{\chi}$ is the mean of the *N* 'equivalent' bond lengths.

nickel–phosphine distance of 2·206(1) Å is shorter than that predicted from the sum of the covalent radii [1·10 for P (ref. 10) and somewhere in the range 1·18—1·39 Å for Ni$^{II}$ (ref. 11)] and is also significantly shorter than that of 2·230(1) Å found in *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$, *vide infra.*

Phosphorus–phenyl distances are P–C(7) 1·817(3) and P–C(13) 1·828(3) Å [mean 1·823(8) Å], while the phosphorus–methyl distance, P–C(19), is 1·821(4) Å. The two phenyl rings are planar within the limits of experimental error. The root-mean-square deviations of carbon atoms from their least-squares planes are 0·008 Å for C(7)–C(12) [Plane (III) of Table 5] and 0·005 Å for C(13)–C(18) [Plane (IV) of Table 5]. Individual carbon–carbon distances within these phenyl rings range from 1·348(6) to 1·396(6) Å, mean 1·376(14) Å. Carbon–hydrogen distances range from 0·87(3) to 1·09(4) Å [mean 0·97(6) Å] for phenyl hydrogens and

TABLE 4

Interatomic angles (°), with estimated standard deviations in parentheses

(*a*) Around nickel atom

| | | | |
|---|---|---|---|
| P–Ni–C(1) | 91·63(9) | P–Ni–P′ | 180·00(–) |
| P–Ni–C(1′) | 88·37(9) | C(1)–Ni–C(1′) | 180·00(–) |

(*b*) Within $C_6F_5$ ring

| | | | |
|---|---|---|---|
| C(6)–C(1)–C(2) | 114·0(3) | C(3)–C(4)–C(5) | 119·5(4) |
| C(1)–C(2)–C(3) | 123·3(3) | C(4)–C(5)–C(6) | 119·5(4) |
| C(2)–C(3)–C(4) | 119·4(3) | C(5)–C(6)–C(1) | 124·2(3) |

(*c*) Involving substituents of $C_6F_5$ ring

| | | | |
|---|---|---|---|
| C(6)–C(1)–Ni | 121·3(2) | C(3)–C(4)–F(4) | 119·5(4) |
| C(2)–C(1)–Ni | 124·4(2) | C(5)–C(4)–F(4) | 121·0(4) |
| C(1)–C(2)–F(2) | 119·6(3) | C(4)–C(5)–F(5) | 120·2(3) |
| C(3)–C(2)–F(2) | 117·0(3) | C(6)–C(5)–F(5) | 120·4(3) |
| C(2)–C(3)–F(3) | 120·0(3) | C(5)–C(6)–F(6) | 116·2(3) |
| C(4)–C(3)–F(3) | 120·6(3) | C(1)–C(6)–F(6) | 119·5(3) |

(*d*) Angles at phosphorus atom

| | | | |
|---|---|---|---|
| Ni–P–C(7) | 111·7(1) | C(7)–P–C(13) | 103·2(1) |
| Ni–P–C(13) | 117·4(1) | C(7)–P–C(19) | 105·2(2) |
| Ni–P–C(19) | 115·2(1) | C(13)–P–C(19) | 102·6(2) |

(*e*) Within phenyl groups

| | | | |
|---|---|---|---|
| C(12)–C(7)–C(8) | 118·6(3) | C(18)–C(13)–C(14) | 118·3(3) |
| C(7)–C(8)–C(9) | 120·7(4) | C(13)–C(14)–C(15) | 120·5(3) |
| C(8)–C(9)–C(10) | 119·8(4) | C(14)–C(15)–C(16) | 120·6(4) |
| C(9)–C(10)–C(11) | 121·3(4) | C(15)–C(16)–C(17) | 119·9(5) |
| C(10)–C(11)–C(12) | 119·2(4) | C(16)–C(17)–C(18) | 120·2(5) |
| C(11)–C(12)–C(7) | 120·4(3) | C(17)–C(18)–C(13) | 120·5(4) |

(*f*) Involving substituents on phenyl rings

| | | | |
|---|---|---|---|
| C(12)–C(7)–P | 122·6(3) | C(18)–C(13)–P | 121·9(3) |
| C(8)–C(7)–P | 118·7(2) | C(14)–C(13)–P | 119·7(2) |
| C(7)–C(8)–H(8) | 121(2) | C(13)–C(14)–H(14) | 117(2) |
| C(9)–C(8)–H(8) | 119(2) | C(15)–C(14)–H(14) | 123(2) |
| C(8)–C(9)–H(9) | 115(2) | C(14)–C(15)–H(15) | 128(3) |
| C(10)–C(9)–H(9) | 125(2) | C(16)–C(15)–H(15) | 111(3) |
| C(9)–C(10)–H(10) | 122(3) | C(15)–C(16)–H(16) | 124(3) |
| C(11)–C(10)–H(10) | 117(3) | C(17)–C(16)–H(16) | 116(3) |
| C(10)–C(11)–H(11) | 124(2) | C(16)–C(17)–H(17) | 122(4) |
| C(12)–C(11)–H(11) | 117(2) | C(18)–C(17)–H(17) | 117(4) |
| C(11)–C(12)–H(12) | 123(2) | C(17)–C(18)–H(18) | 118(3) |
| C(7)–C(12)–H(12) | 117(2) | C(13)–C(18)–H(18) | 121(3) |

(*g*) Within methyl group

| | | | |
|---|---|---|---|
| P–C(19)–H(19A) | 111(3) | H(19A)–C(19)–H(19B) | 111(4) |
| P–C(19)–H(19B) | 106(2) | H(19A)–C(19)–H(19C) | 114(4) |
| P–C(19)–H(19C) | 107(3) | H(19B)–C(19)–H(19C) | 106(4) |

TABLE 5

Equations of least-squares planes * showing the distances (Å), in square brackets, of atoms from the plane

Plane (I): $-0{\cdot}1332X + 0{\cdot}7308Y + 0{\cdot}6694Z - 7{\cdot}098 = 0$

[Ni 0·000, P 0·000, P′ 0·000, C(1), 0·000, C(1′) 0·000]

Plane (II): $-0{\cdot}7475X - 0{\cdot}4720Y + 0{\cdot}4673Z - 5{\cdot}125 = 0$

[C(1) 0·000, C(2) 0·001, C(3) −0·004, C(4) 0·006, C(5) −0·004, C(6) 0·001, F(2) † −0·018, F(3) † −0·046, F(4) † 0·019, F(5) † −0·041, F(6) † −0·049]

Plane (III): $0{\cdot}1806X - 0{\cdot}6666Y + 0{\cdot}7232Z - 6{\cdot}558 = 0$

[C(7) −0·011, C(8) 0·003, C(9) 0·006, C(10) −0·006, C(11) −0·002, C(12) 0·011, H(8) † 0·030, H(9) † 0·042, H(10) † 0·010, H(11) † −0·003, H(12) † 0·001]

Plane (IV): $0{\cdot}9289X + 0{\cdot}3224Y - 0{\cdot}1822Z - 0{\cdot}181 = 0$

[C(13) −0·006, C(14) 0·007, C(15) −0·003, C(16) −0·001, C(17) 0·002, C(18) 0·002, H(14) † 0·041, H(15) † 0·045, H(16) † 0·109, H(17) † 0·022, H(18) † 0·211]

* The Cartesian co-ordinates (*X*, *Y*, *Z*) are related to the fractional cell co-ordinates (*x*, *y*, *z*) by the transformation: [*X*, *Y*, *Z*] = [*xa*, *yb*, *zc*]. † These atoms given zero weight in calculating least-squares plane. All other listed atoms were given unit weight.

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[10] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 246.

[11] M. R. Churchill, *Perspectives in Structural Chem.*, 1970, **3**, 91; see, especially, pp. 147—148 and references therein.

0·85(4) to 0·95(4) [mean 0·90(5) Å] for methyl hydrogens. These distances are, of course, systematically decreased from the true carbon–hydrogen bond length of *ca.* 1·08 Å owing to the non-spherical electron distribution about each hydrogen atom.

Angles within the phenyl rings of the $PPh_2Me$ ligands show an interesting abnormality. While ten of the twelve independent values lie in the range 119·2(4)—121·3(4)°, the two smallest angles, C(12)–C(7)–C(8) 118·6(3)° and C(18)–C(13)–C(14) 118·3(3)°, involve carbon atoms directly bonded to phosphorus. It would appear that these two phenyl groups deviate significantly from *quasi*-$D_{6h}$ symmetry. [The corresponding angles in *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$ are also less than the ideal trigonal value, being 119·1(7) and 118·5(7)°. In this case, however, the result is significant only at the 2σ level.]

As is customary in both the tertiary phosphines and their complexes,[12] the C–P–C angles are each significantly lower than the ideal $sp^3$ angle and range from 102·6(2) to 105·2(2)° while the Ni–P–C angles are each greater than 109·47°, varying from 111·7(1) to 117·4(1)°.

*The Perfluorophenyl Ligands.*—The six carbon atoms of the $C_6F_5$ ligand have a root-mean-square deviation of only 0·004 Å from their least-squares plane [Plane (II) of Table 5]. The fluorine atoms deviate slightly (but, nevertheless, significantly) from the plane, their individual deviations, (Å) being: F(2) —0·018, F(3) —0·046, F(4) 0·019, F(5) —0·041, and F(6) —0·049.

Carbon–carbon distances within this ligand range from 1·346(6) to 1·378(5), mean 1·368(12) Å, while carbon–fluorine distances vary from 1·344(5) to 1·360(4), mean 1·353(6) Å.

Angles within the carbon skeleton of the perfluorophenyl ligand show the customary marked deviation from ideal $D_{6h}$ symmetry, which appears to be general for transition-metal aryls (see Table 6 of ref. 1). The angle at the nickel-bonded carbon atom [C(6)–C(1)–C(2)] is 114·0(3°) while angles at the adjacent (*ortho*) carbon atoms are: C(1)–C(2)–C(3) 123·3(3) and C(5)–C(6)–C(1) 124·2(3)°. These values are 20, 11, and 14σ (respectively) from the ideal $sp^2$ angle of 120·0°.

Each of the σ-$C_6F_5$ ligands lies at an angle of 86·13° to the nickel co-ordination plane defined by Ni, P, P′, C(1), and C(1′) [Plane (I) of Table 5].

*Comparison of the Structures of* trans-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$ *and* trans-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$.—Since these two species crystallize in different space-groups, there is no expectation that rotationally-free groups will take up the same conformation. However, in each case the perhalogenoaryl ligands are approximately perpendicular to the nickel co-ordination plane [79·42° for the σ-$C_6F_5$ and 85·02° for the σ-$C_6Cl_5$ group in *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)(\sigma\text{-}C_6Cl_5)$ and 86·13° for each of the σ-$C_6F_5$ ligands in *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)$]. Parameters essentially unaffected by rotational changes are listed in Table 6; the last column provides an excellent criterion as to the meaningfulness of differences in bond length or bond angle between the two species. There are only three parameters which change significantly in the *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)X$ framework as X is changed from σ-$C_6F_5$ to σ-$C_6Cl_5$. These are: (i) an increase of 0·039 Å (3·7σ) in the Ni–σ-$C_6F_5$ bond; (ii) an increase of 0·024 Å (17σ) in each of the Ni–$PPh_2Me$ bond lengths; and (iii) a decrease of 2·0° (3·0σ) in the C–C–C angle at the nickel-bonded carbon atom of the σ-$C_6F_5$ ligand.

TABLE 6

Comparison of bond lengths and angles in *trans*-$(PPh_2Me)_2Ni(C_6F_5)_2$ and *trans*-$(PPh_2Me)_2Ni(C_6F_5)(C_6Cl_5)$ *

| Parameter | $(PPh_2Me)_2Ni(C_6F_5)_2$ | $(PPh_2Me)_2Ni(C_6F_5)(C_6Cl_5)$ * | $\Delta/(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}$ |
|---|---|---|---|
| (*a*) Distances involving perhalogenoaryl ligands | | | |
| Ni–$C_6F_5$ | 1·939(3) | 1·978(10) | 3·7σ |
| Ni–$C_6Cl_5$ | | 1·905(10) | |
| C–C($C_6F_5$) | 1·368(12) † | 1·375(2) † | 0·6σ |
| C–F($C_6F_5$) | 1·353(6) † | 1·347(18) † | 0·3σ |
| (*b*) Distances involving $PPh_2Me$ ligands | | | |
| Ni–$PPh_2Me$ | 2·206(1) | 2·230(1) | 17·0σ |
| P–Ph | 1·823(8) † | 1·823(2) † | 0·0σ |
| P–Me | 1·821(4) | 1·853(7) ‡ | |
| C–C(Ph) | 1·376(14) † | 1·384(14) † | 0·4σ |
| (*c*) C–C–C Angles within $C_6F_5$ ligand(s) | | | |
| At Ni | 114·0(3) | 112·0(5) | 3·0σ |
| *ortho* | 123·8(6) † | 125·8(7) | 2·2σ |
| *meta* | 119·5(1) † | 118·4(8) | 1·4σ |
| *para* | 119·5(4) | 119·6(7) | 0·1σ |

* See ref. 1. † These are average values; the estimated standard deviations are calculated by use of the formula given as a footnote to Table 3. ‡ Hydrogen atoms of this methyl group were not located; this value may, therefore, have some systematic error associated with it.

We presently offer no explanation for the angular change noted in (iii). However, changes noted in (i) and (ii) show that substitution of σ-$C_6F_5$ by σ-$C_6Cl_5$ results not only in a short Ni–(σ-$C_6Cl_5$) bond [1·905(10) Å (ref. 1)] but also in the lengthening of all other nickel–ligand bonds. This essentially isotropic expansion of bond lengths in the nickel co-ordination sphere can be explained most satisfactorily by the σ-$C_6Cl_5$ ligand donating more charge to the central $Ni^{II}$ ion than does a σ-$C_6F_5$ ligand. It would appear, then, that a σ-$C_6Cl_5$ ligand is inherently a better σ donor than is a σ $C_6F_5$ ligand.

We hope that current structural studies involving such species as $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$ and $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Cl$ will help to provide further information on the nature of metal–σ-aryl bonding.

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[12] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.* (*A*), 1968, 2970; see, especially, Table 7, p. 2976.