Finally we may note that the dihedral angle between the bridging systems Fe1-S-Fe2 and Fe1-C11-Fe2 is 158.3° in molecule A and 157.4° in molecule B. This may be compared with an angle of 154.7° between the two Fe-(CO)-Fe bridges in (azulene)$_2$Fe$_4$(CO)$_{10}$.[25]

Registry No. cis-(π-C$_5$H$_5$)$_2$Fe$_2$(CO)$_3$(SO$_2$), 39797-02-9.

Crystal Structures of Transition Metal Aryls. VI.[1-6] Molecular Geometry of trans-Bromobis(methyldiphenylphosphine)(o-pentafluorophenyl)nickel(II), Including the Location and Refinement of Hydrogen Atoms

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The complex trans-bromobis(methyldiphenylphosphine)(o-pentafluorophenyl)nickel(II), trans-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)Br, crystallizes in the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15) with a = 27.434 (4), b = 11.543 (2), c = 21.433 (3) Å; and β = 114.13 (1)°. The observed density (1.49 (2) g cm^{-3}) is consistent with that calculated for M = 706.21, V = 6194.3 Å^3, and Z = 8 (ρ_{calcd} = 1.514 g cm^{-3}). X-Ray diffraction data were collected with a Picker FACS-1 automated diffractometer and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located, the final discrepancy indices being R_F = 6.16% and R_{wF} = 4.28% for the 3459 independent reflections representing data complete to 2θ = 42.5° (Mo Kα radiation). The central nickel(II) atom is in (slightly distorted) square-planar coordination with Ni-PPh$_2$Me = 2.215 (1) and 2.216 (1) Å, Ni-Br = 2.325 (1) Å, and Ni-o-C$_6$F$_5$ = 1.880 (4) Å. This last value is compared with Ni-o-C$_6$F$_5$ distances of 1.939 (3) Å in trans-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)$_2$ and 1.978 (10) Å in trans-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)(o-C$_6$Cl$_5$).

Introduction

For some years we have been interested in the structural characterization of the transition metal-carbon σ bond and have demonstrated conclusively that a metal-perfluoroalkyl σ bond is shorter than the analogous metal-alkyl bond,[7] that a metal-σ-vinyl linkage is shorter than the corresponding metal-alkyl bond,[8] and that a metal-σ-acyl bond is contracted relative to a metal-alkyl bond.[9]

Structural characterization of the metal-σ-aryl linkage has proved rather more difficult. Thus, studies on the species (π-C$_5$H$_5$)Ni(PPh$_3$)(o-C$_6$H$_5$)[5] and (π-C$_5$H$_5$)Ni(PPh$_3$)(o-C$_6$F$_5$)[6] revealed the distances Ni-o-C$_6$H$_5$ = 1.904 (7) Å and Ni-o-C$_6$F$_5$ = 1.914 (14) Å, but these results are inconclusive insofar as no analogous nickel-alkyl distance has been measured. The molybdenum complex, (π-C$_7$H$_7$)Mo(CO)$_2$-(o-C$_6$F$_5$)[4] was found to have a Mo-o-C$_6$F$_5$ distance of 2.244 (9) Å as compared to molybdenum-alkyl distances of 2.397 (19) Å in (π-C$_5$H$_5$)Mo(CO)$_3$C$_2$H$_5$,[10] 2.36 (2) Å in (π-C$_5$H$_5$)-

Mo(CO)$_3$CH$_2$CO$_2$H,[11] and 2.383 (10) Å in [(azulene)Mo-(CO)$_3$CH$_3$]$_2$.[12] There are thus some indications that a metal-σ-aryl distance is typically ~0.1 Å shorter than the analogous metal-alkyl distance (see also ref 13).

[It may be noted here that Parshall and Mrowca state[14] (in our opinion, erroneously) that "for σ-alkyl *and aryl* [our italics] compounds, C-M bond lengths are almost exactly those predicted by addition of the covalent radii for carbon and for the transition metal in the appropriate valence state."]

We have recently begun a series of systematic studies on trans-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)(X) species with a view toward ascertaining how changes in the nature of X affect the trans Ni-o-C$_6$F$_5$ bond. Previous parts of this series have involved accurate structural reports of trans-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)-(o-C$_6$Cl$_5$)[3] and trans-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)$_2$;[2] herewithin we describe the results of an X-ray diffraction study of trans-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)Br.

Collection and Correction of the X-Ray Diffraction Data

Yellow crystals of the complex were supplied by Professor M. D. Rausch.[15] Preliminary h(0-3)l Weissenberg photographs, a b-axis rotation photograph, (0-3)kl and hk(0-3) precession photographs, and a and c cone-axis photographs yielded approximate cell dimensions, demonstrated the C_{2h} (2/m) Laue symmetry of the diffraction

(1) For previous parts in the series, see ref 2-6.

(2) Part V: M. R. Churchill and M. V. Veidis, *J. Chem. Soc., Dalton Trans.*, 670 (1972).

(3) Part IV: M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 3463 (1971).

(4) Part III: M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 1110 (1969).

(5) Part II: M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 266 (1969).

(6) Part I: M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).

(7) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 6, 1213 (1967); see also M. R. Churchill, *ibid.*, 4, 1734 (1965); 6, 185 (1967) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 161 (1970).

(8) M. R. Churchill and J. Wormald, *Inorg. Chem.*, 8, 1936 (1969); *J. Amer. Chem. Soc.*, 93, 354 (1971).

(9) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 7, 953 (1968).

(10) M. J. Bennett and R. Mason, *Proc. Chem. Soc., London*, 273 (1963); M. J. Bennett, Ph.D. Thesis, Sheffield University, England, 1965, pp 38-74.

(11) J. K. P. Ariyaratne, A. M. Bjerrum, M. L. H. Green, M. Ishaq, C. K. Prout, and M. G. Swanick, *J. Chem. Soc. A*, 1309 (1969).

(12) P. H. Bird and M. R. Churchill, *Inorg. Chem.*, 7, 349 (1968).

(13) M. R. Churchill, *Perspect. Struct. Chem.*, 3, 91 (1970); see, especially, Table II on p 155.

(14) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, 7, 157 (1968); see, especially, p 174, section III-B-3, lines 11-14.

(15) See M. D. Rausch and F. E. Tibbetts, *Inorg. Chem.*, 9, 512 (1970).

pattern, and indicated the following systematic absences: hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$.

These extinctions are compatible with the noncentrosymmetric space group Cc (C_s^4; No. 9) or with the centrosymmetric space group $C2/c$ (C_{2h}^6; No. 15). (The successful solution of the structure, *vide infra*, indicates the latter centrosymmetric possibility to be the true space group.)

The crystal selected for data collection was approximately cylindrical in shape, being elongated along b with well-formed (010) and (0$\bar{1}$0) faces [(010) → (0$\bar{1}$0) = 0.30 mm] and with a radius of 0.08 mm. (The sides consisted of small but distinct $\{101\}$ and $\{201\}$ faces.)

The crystal was centered on a Picker FACS-1 automated diffractometer. The apparatus and *modus operandi* have been described in detail previously.[16a]

Under "high resolution" conditions the 2θ, ω, and χ settings of the resolved Mo $K\alpha_1$ peaks ($\lambda = 0.70926$ Å) of 12 high-angle reflections, which were well dispersed in reciprocal space, were determined. These values were used in a least-squares refinement of the cell and orientation parameters.[17]

The resulting unit cell parameters (measured at 25°) are $a = 27.4342$ (41), $b = 11.5432$ (19), $c = 21.4329$ (27) Å; $\beta = 114.13$ (1)°. The unit cell volume is 6194.3 Å³. The observed density ($\rho_{obsd} = 1.49$ (2) g cm⁻³ by neutral buoyancy in aqueous barium iodide solution) is consistent with that calculated for $M = 706.21$ and $Z = 8$ ($\rho_{calcd} = 1.514$ g cm⁻³). No crystallographic symmetry is imposed upon the molecule.

Intensity data were measured by executing a coupled θ-2θ (crystal:counter) scan from 0.65° in 2θ below the Mo $K\alpha_1$ peak to 0.65° in 2θ above the Mo $K\alpha_2$ peak at a scan speed of 1.0 deg min⁻¹, thereby accumulating C counts in t_c seconds. Background counts (with stationary crystal and stationary counter), each 40 sec in duration, were measured at the low- and high-angle limits of the θ-2θ scan, yielding B_1 and B_2 counts (respectively) in a total background counting time (t_B) of 80 sec. Copper-foil attenuators, whose transmission factors for Mo $K\alpha$ radiation had previously been accurately determined experimentally (and which decreased the diffracted beam by successive factors of ~3.0-3.5), were automatically inserted when required to keep the maximum counting rate below ~8500 counts/sec, thereby minimizing possible coincidence losses.

A take-off angle of 4.0° was employed; the detector aperture was 6.0 × 6.0 mm in size and was 330 mm distant from the crystal. Prior to collecting intensity data, a strong axial reflection (040) was measured by a θ-2θ scan at $\chi = 90°$ and at 10° intervals of ϕ from $\phi = 0°$ to $\phi = 350°$ (see ref 18). Even though μ(Mo $K\alpha$) = 21.50 cm⁻¹, the intensity of the axial reflection varied from the mean value by only 2%. An absorption correction was therefore deemed unnecessary.

Data for the octants hkl and $hk\bar{l}$ and having $0° < 2\theta < 42.5°$ were collected, using Mo $K\alpha$ radiation (*i.e.*, Mo radiation filtered through Nb foil). The intensities of three standard reflections were collected after each batch of 50 reflections; root-mean-square deviations from the mean intensity were 1.24% for the 420, 1.15% for the 024, and 1.35% for the 204 reflection; these deviations were reduced to 0.53, 0.48, and 0.61% (respectively) upon applying a linear decay correction to the entire data set.[16b]

The integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated from the following expressions.[16b]

$$I = q[(C + 4.5) - (t_c/t_B)(B_1 + B_2 + 9.0)]$$

$$\sigma(I) = q[(C + 4.5) + (t_c/t_B)^2(B_1 + B_2 + 9.0) + 24.75 + q^{-2}p^2I^2]^{1/2}$$

The "ignorance factor," p, was defined as 0.04; q is the combined correction for attenuator used and the "linear decay correction," and the numerical terms are introduced to compensate for the truncation of the last digit of C, B_1, and B_2 on the punched-tape output from the diffractometer.

Any negative I was redefined as zero; no data were rejected as "not significantly above background."

The unscaled structure-factor amplitudes, F^*, and their standard deviations, $\sigma(F^*)$, were calculated[16b] from the expressions

$$F^* = (I/Lp)^{1/2}$$

$$\sigma(F^*) = [\sigma(I)/Lp]^{1/2} \text{ for } \sigma(I) \geqslant I$$

$$\sigma(F^*) = \{F^* - [(F^*)^2 - \sigma(I)/Lp]^{1/2}\} \text{ for } \sigma(I) < I$$

Here, $1/Lp$ is the multiplicative Lorentz-polarization factor, given by $(2 \sin 2\theta)/(1 + \cos^2 2\theta)$.

Finally, equivalent $0kl$ and $0k\bar{l}$ data were averaged and their intensity replaced by their σ^{-2}-weighted average, with appropriately modified standard deviations. A total of 3459 independent reflections was available for the subsequent structural analysis.

Solution and Refinement of the Structure

Programs used during the elucidation of the structure include FORDAP (Fourier synthesis, by A. Zalkin), SFIX (structure-factor calculation with full-matrix least-squares refinement, adapted from SFLS5, by C. T. Prewitt), STAN1 (distances, angles, and their esd's by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral nickel, bromine, phosphorus, fluorine, and carbon were taken from the compilation of Cromer and Waber;[19] for hydrogen, the scattering factors of Mason and Robertson[20] were used. The nickel, bromine, phosphorus, fluorine, and carbon values were corrected for both the real and the imaginary component of anomalous dispersion.[21]

The function minimized in least-squares refinement processes was $\Sigma w(|F_o| - |F_c|)^2$ where $w(hkl) = \sigma^{-2}[F_o(hkl)]$ and $\sigma[F_o(hkl)] = \sigma[F^*(hkl)] \cdot |F_o(hkl)|/|F^*(hkl)|$.

Discrepancy indices referred to below are

$$R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

The positions of the nickel, the bromine, and the two phosphorus atoms were obtained from a three-dimensional Patterson synthesis. A Fourier synthesis, phased by these four "heavy" atoms, led rapidly to the location of all remaining nonhydrogen atoms. Full-matrix least-squares refinement of individual positional and isotropic thermal parameters for all nonhydrogen atoms converged at $R_F = 11.8\%$ and $R_{wF} = 12.5\%$. Refinement was continued now using anisotropic thermal parameters for the 41 nonhydrogen atoms, leading to convergence with $R_F = 7.3\%$ and $R_{wF} = 5.9\%$. (Due to a limitation in the number of parameters that could be refined simultaneously, parameters for Ni, Br, the C_6F_5 group, one PPh₂Me ligand, and the other P atom were refined at one time; the same atoms, save for substituting the second for the first PPh₂Me group, were refined in the next cycle. This process was repeated until convergence was reached.)

A difference-Fourier synthesis now led to the unambiguous location of all hydrogen atoms, including those of the two methyl groups. Peak heights for methyl hydrogen ranged from 0.37 to 0.53 e Å⁻³ and for phenyl hydrogens ranged from 0.35 to 0.53 e Å⁻³. Refinement was continued (now in *three* blocks) using anisotropic thermal parameters for all nonhydrogen atoms, isotropic thermal parameters for hydrogen atoms, and allowing the variation of all positional parameters, including those of the hydrogen atoms. Convergence (*i.e.*, $(\Delta/\sigma)_{max} < 0.1$) was reached with $R_F = 6.16\%$ and $R_{wF} = 4.28\%$.

Finally, all positional parameters were refined simultaneously, while thermal parameters were held constant. The discrepancy indices remained unchanged ($R_F = 6.16\%$ and $R_{wF} = 4.28\%$) and no significant shifts occurred; the correlation matrix from this refinement was used for determining the estimated standard deviations on interatomic distances and angles (see footnote to Table III). A final difference-Fourier synthesis revealed no significant features, thus confirming the correctness of the determined structure. [The highest peaks, in order, were 0.52 e Å⁻³ at 0.09, 0.14, 0.05 (~1.0 Å from Br), 0.49 e Å⁻³ at 0.09, 0.28, 0.13 (~0.9 Å from Ni), 0.47 e Å⁻³ at 0.16, 0.26, 0.11 (~1.0 Å from Ni), 0.40 e Å⁻³ at 0.14, 0.32, 0.16 (~0.9 Å from Ni), and 0.38 e Å⁻³ at 0.19, 0.16, 0.08 (~1.7 Å from Br); all other features were below 0.35 e Å⁻³.]

(16) (a) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 525 (1973). (b) All data reduction, linear decay corrections, etc., were performed using the program REDUCE by B. G. DeBoer.

(17) All diffractometer routines were performed using programs described by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967), and adapted by the Picker Corporation to the DEC PDP8/I computer which forms an integral part of the FACS-1 system.

(18) This is easily accomplished by decoupling the ϕ drive and setting ϕ manually while the θ-2θ scan routine program is in operation.

(19) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(20) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, 2, 57 (1966).

(21) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, 53, 1891 (1970).

Table I. Positional and Isotropic Thermal Parameters[a] for *trans*-(PPh₂Me)₂Ni(σ-C₆F₅)Br

Atom	x	y	z	B, Å²
Ni	0.127203 (22)	0.278984 (48)	0.128759 (26)	3.66
Br	0.133010 (27)	0.127937 (47)	0.060395 (29)	6.33
P(1)	0.12702 (5)	0.15002 (10)	0.20528 (6)	3.76
P(2)	0.13477 (5)	0.40478 (10)	0.05519 (6)	3.81
F(2)	0.02665 (10)	0.41051 (24)	0.11457 (13)	5.82
F(3)	0.01298 (12)	0.58131 (27)	0.19026 (15)	7.44
F(4)	0.09658 (14)	0.66170 (28)	0.30093 (16)	8.49
F(5)	0.19576 (13)	0.57210 (32)	0.33310 (16)	9.19
F(6)	0.21055 (11)	0.40322 (26)	0.25730 (14)	6.71
C(1)	0.11891 (17)	0.39995 (35)	0.18234 (20)	3.73
C(2)	0.07061 (18)	0.44900 (38)	0.16930 (20)	4.01
C(3)	0.06172 (19)	0.53580 (42)	0.20663 (24)	4.78
C(4)	0.10340 (22)	0.57687 (42)	0.26191 (26)	5.52
C(5)	0.15311 (20)	0.53249 (43)	0.27822 (23)	5.48
C(6)	0.16016 (19)	0.44534 (39)	0.23892 (23)	4.63
C(11)	0.12772 (19)	0.19947 (37)	0.28620 (22)	4.25
C(12)	0.08154 (25)	0.23168 (55)	0.29030 (29)	7.03
C(13)	0.08068 (32)	0.27452 (64)	0.35070 (37)	8.80
C(14)	0.12763 (38)	0.27876 (67)	0.40665 (34)	9.15
C(15)	0.17317 (36)	0.24924 (70)	0.40419 (31)	10.11
C(16)	0.17425 (25)	0.20837 (59)	0.34394 (28)	7.69
C(11')	0.06961 (17)	0.05609 (37)	0.17342 (21)	3.94
C(12')	0.06766 (23)	−0.04388 (49)	0.20844 (30)	6.46
C(13')	0.02254 (32)	−0.11345 (55)	0.18273 (40)	8.46
C(14')	−0.01960 (31)	−0.08336 (64)	0.12512 (44)	8.83
C(15')	−0.01851 (27)	0.01510 (70)	0.09139 (35)	9.29
C(16')	0.02659 (22)	0.08259 (49)	0.11499 (30)	6.53
C(1'')	0.18550 (26)	0.05693 (57)	0.23155 (31)	6.31
C(21)	0.12518 (17)	0.55864 (38)	0.06732 (21)	4.03
C(22)	0.07604 (21)	0.60836 (47)	0.04014 (26)	5.29
C(23)	0.06728 (26)	0.72244 (53)	0.04960 (31)	6.79
C(24)	0.10910 (28)	0.79106 (53)	0.08698 (33)	7.27
C(25)	0.15894 (28)	0.74359 (52)	0.11539 (35)	8.29
C(26)	0.16696 (22)	0.62687 (44)	0.10599 (28)	5.96
C(21')	0.20059 (19)	0.40005 (39)	0.05677 (23)	4.63
C(22')	0.24201 (22)	0.34875 (45)	0.11142 (27)	5.46
C(23')	0.29334 (26)	0.34996 (52)	0.11457 (33)	6.83
C(24')	0.30301 (26)	0.39597 (66)	0.06357 (40)	8.23
C(25')	0.26334 (29)	0.44434 (77)	0.00868 (37)	9.63
C(26')	0.21246 (25)	0.44781 (61)	0.00580 (31)	7.53
C(2'')	0.08921 (26)	0.38026 (57)	−0.03391 (27)	5.99
H(12)	0.0514 (21)	0.2130 (45)	0.2516 (29)	9.0 (17)
H(13)	0.0480 (23)	0.3022 (49)	0.3524 (28)	9.6 (21)
H(14)	0.1217 (20)	0.3103 (44)	0.4365 (26)	7.6 (24)
H(15)	0.2102 (25)	0.2602 (51)	0.4332 (31)	10.4 (33)
H(16)	0.2068 (25)	0.1905 (55)	0.3394 (30)	11.1 (27)
H(12')	0.0970 (18)	−0.0552 (38)	0.2498 (23)	6.5 (19)
H(13')	0.0272 (21)	−0.1783 (48)	0.2107 (26)	8.9 (22)
H(14')	−0.0451 (24)	−0.1280 (54)	0.1127 (31)	10.5 (28)
H(15')	−0.0404 (22)	0.0287 (49)	0.0531 (28)	9.0 (26)
H(16')	0.0276 (18)	0.1491 (40)	0.0952 (23)	6.9 (18)
H(1A'')	0.1869 (21)	0.0097 (49)	0.2675 (29)	9.3 (19)
H(1B'')	0.1849 (18)	0.0211 (40)	0.1980 (24)	6.6 (16)
H(1C'')	0.2240 (25)	0.1027 (49)	0.2495 (29)	10.3 (21)
H(22)	0.0515 (11)	0.5721 (23)	0.0193 (13)	1.1 (21)
H(23)	0.0354 (17)	0.7509 (35)	0.0363 (20)	5.2 (21)
H(24)	0.1019 (18)	0.8742 (43)	0.0894 (23)	6.9 (13)
H(25)	0.1940 (25)	0.7898 (52)	0.1399 (30)	11.0 (26)
H(26)	0.2039 (18)	0.5970 (39)	0.1259 (22)	6.8 (20)
H(22')	0.2351 (16)	0.3214 (36)	0.1492 (21)	5.9 (13)
H(23')	0.3126 (22)	0.3180 (49)	0.1492 (27)	8.7 (23)
H(24')	0.3334 (19)	0.3962 (40)	0.0629 (24)	6.9 (17)
H(25')	0.2653 (27)	0.4797 (58)	−0.0283 (33)	12.4 (25)
H(26')	0.1857 (23)	0.4805 (52)	−0.0342 (29)	10.1 (25)
H(2A'')	0.0998 (21)	0.3195 (50)	−0.0493 (29)	8.8 (20)
H(2B'')	0.0922 (20)	0.4367 (45)	−0.0654 (27)	7.9 (15)
H(2C'')	0.0558 (21)	0.3689 (42)	−0.0399 (25)	7.5 (16)

[a] "Equivalent isotropic thermal parameters" provided for nonhydrogen atoms correspond to the average mean-square displacement along the three principal axes of the vibration ellipsoid.

The observed structure-factor amplitudes were inspected for evidence of extinction; none was found. The final (corrected for true n) "goodness-of-fit," defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.23 where the number of reflections (m) was 3459 and the number of parameters (n) was 474. (The ratio $m{:}n$ was 7.30:1.)

The $w\Delta^2$ values did not show any appreciable variation either as a function of (sin θ/λ) or as a function of $|F_o|$, thereby indicating the validity of the applied weighting scheme.

A table of observed and calculated structure-factor amplitudes is available;[22] positional and isotropic thermal parameters are shown in Table I, while anisotropic thermal parameters are collected in Table II.

Table II. Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^b$
Ni	4.12 (3)	3.56 (3)	3.18 (2)	−0.44 (2)	1.36 (2)	−0.58 (2)	(0.24,0.22,0.19)
Br	9.84 (4)	4.64 (3)	5.61 (3)	−0.85 (3)	4.28 (3)	−1.38 (2)	(0.36,0.27,0.21)
P(1)	3.87 (6)	3.81 (6)	3.32 (6)	0.13 (5)	1.20 (5)	−0.15 (4)	(0.23,0.22,0.20)
P(2)	4.23 (6)	3.90 (6)	3.03 (6)	−0.27 (5)	1.19 (5)	−0.34 (4)	(0.24,0.22,0.19)
F(2)	4.59 (14)	7.09 (16)	4.60 (13)	0.15 (12)	0.67 (12)	−0.76 (12)	(0.31,0.28,0.22)
F(3)	6.68 (18)	8.07 (20)	7.62 (19)	2.20 (16)	3.00 (15)	−0.69 (15)	(0.36,0.31,0.24)
F(4)	10.08 (23)	7.75 (19)	7.91 (19)	0.29 (17)	3.97 (17)	−3.55 (16)	(0.39,0.36,0.22)
F(5)	8.07 (20)	10.11 (22)	7.07 (18)	−1.35 (18)	0.73 (16)	−4.77 (17)	(0.43,0.35,0.20)
F(6)	4.34 (15)	8.10 (18)	6.39 (16)	−0.57 (14)	0.86 (12)	−2.27 (14)	(0.36,0.28,0.22)
C(1)	4.23 (26)	3.67 (22)	3.19 (22)	−0.37 (20)	1.41 (20)	−0.17 (18)	(0.24,0.21,0.20)
C(2)	4.55 (27)	4.39 (24)	3.07 (22)	−0.22 (21)	1.54 (21)	−0.45 (18)	(0.24,0.24,0.19)
C(3)	4.65 (28)	5.25 (28)	4.55 (27)	0.72 (24)	1.99 (23)	0.20 (22)	(0.27,0.24,0.23)
C(4)	6.75 (35)	4.69 (27)	5.61 (30)	0.04 (26)	3.03 (28)	−1.64 (23)	(0.30,0.29,0.20)
C(5)	5.61 (32)	5.79 (30)	3.91 (25)	−1.77 (26)	0.79 (24)	−2.35 (23)	(0.31,0.30,0.16)
C(6)	4.26 (28)	4.67 (25)	4.55 (26)	−0.11 (22)	1.37 (22)	−0.60 (21)	(0.26,0.24,0.22)
C(11)	4.82 (27)	3.95 (25)	3.87 (24)	−0.19 (20)	1.65 (23)	0.06 (18)	(0.25,0.22,0.22)
C(12)	6.56 (40)	9.53 (43)	5.58 (35)	−1.06 (35)	3.06 (32)	−2.58 (32)	(0.37,0.28,0.23)
C(13)	9.47 (55)	10.43 (51)	8.44 (49)	−1.24 (43)	5.62 (45)	−2.92 (40)	(0.40,0.33,0.25)
C(14)	13.74 (85)	8.98 (48)	5.81 (46)	−0.41 (50)	5.11 (54)	−1.80 (39)	(0.42,0.35,0.23)
C(15)	10.39 (73)	12.20 (62)	4.82 (39)	2.21 (55)	0.15 (47)	−1.98 (37)	(0.46,0.35,0.23)
C(16)	6.98 (41)	9.49 (45)	4.64 (32)	2.11 (35)	0.37 (30)	−1.88 (29)	(0.41,0.28,0.22)
C(11')	4.30 (26)	3.60 (23)	3.77 (24)	−0.13 (19)	1.51 (22)	−0.40 (18)	(0.24,0.23,0.20)
C(12')	6.42 (38)	5.82 (34)	6.40 (35)	−1.59 (30)	1.88 (31)	0.59 (28)	(0.34,0.28,0.24)
C(13')	9.93 (60)	5.81 (42)	10.40 (60)	−1.67 (44)	4.92 (50)	0.66 (42)	(0.37,0.36,0.24)
C(14')	8.88 (57)	7.35 (51)	11.17 (63)	−4.20 (48)	5.04 (50)	−3.67 (48)	(0.42,0.33,0.21)
C(15')	7.14 (48)	9.45 (53)	8.09 (50)	−2.78 (43)	−0.13 (40)	−0.27 (44)	(0.42,0.34,0.24)
C(16')	4.85 (33)	6.09 (37)	6.81 (37)	−1.78 (30)	0.53 (28)	−0.06 (31)	(0.35,0.29,0.21)
C(1'')	6.35 (39)	6.97 (39)	5.34 (37)	2.22 (31)	2.13 (31)	0.54 (33)	(0.34,0.26,0.24)
C(21)	4.11 (26)	4.27 (25)	3.36 (22)	0.51 (23)	1.20 (20)	0.49 (19)	(0.24,0.23,0.20)
C(22)	5.15 (38)	5.13 (36)	5.00 (30)	−0.21 (32)	1.46 (27)	0.39 (26)	(0.28,0.25,0.24)
C(23)	6.99 (48)	6.04 (44)	7.70 (40)	2.63 (41)	3.36 (37)	1.78 (33)	(0.35,0.30,0.22)
C(24)	9.35 (53)	4.73 (37)	7.75 (39)	0.37 (39)	3.51 (37)	−0.62 (31)	(0.35,0.32,0.24)
C(25)	7.22 (48)	6.00 (43)	9.55 (47)	−1.17 (38)	1.29 (38)	−2.94 (34)	(0.41,0.32,0.22)
C(26)	5.10 (33)	4.47 (32)	6.76 (33)	−0.15 (27)	0.85 (28)	−1.53 (26)	(0.34,0.25,0.21)
C(21')	5.83 (29)	4.35 (25)	4.07 (23)	0.15 (22)	2.38 (24)	−0.02 (20)	(0.27,0.23,0.22)
C(22')	5.68 (35)	5.40 (31)	5.47 (33)	−0.37 (25)	2.43 (29)	−0.43 (24)	(0.28,0.26,0.25)
C(23')	6.71 (47)	6.37 (39)	7.39 (47)	0.63 (33)	2.85 (40)	−0.17 (34)	(0.31,0.30,0.27)
C(24')	5.37 (44)	10.70 (52)	10.26 (60)	0.49 (38)	4.88 (47)	−0.49 (46)	(0.37,0.36,0.21)
C(25')	7.67 (55)	14.93 (63)	8.34 (55)	1.71 (46)	5.38 (47)	2.76 (46)	(0.45,0.33,0.23)
C(26')	6.76 (41)	10.44 (47)	6.39 (38)	10.08 (35)	3.69 (33)	2.08 (34)	(0.38,0.29,0.24)
C(2'')	6.70 (44)	6.35 (38)	3.72 (29)	−0.47 (33)	0.90 (28)	−0.87 (27)	(0.32,0.29,0.21)

[a] These anisotropic thermal parameters have units of Å^2 and are analogous to the normal isotropic thermal parameters, entering the expression for the structure factor in the form $\exp[-0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes of its vibration ellipsoid. For orientation, see Figure 1.

Description of the Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are collected in Table III; bond angles, with esd's, are summarized in Table IV. The molecular stereochemistry is illustrated in Figure 1. Hydrogen atoms, omitted from this diagram for the sake of clarity, are labeled similarly to their attached carbon atoms.

The crystal consists of discrete molecular units of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$ which are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts.

The central d^8 Ni(II) ion has a slightly distorted square-planar coordination environment. Trans angles are P(1)–Ni–P(2) = 175.10 (05)° and Br–Ni–C(1) = 177.22 (14)°, while the cis angles are Br–Ni–P(1) = 89.09 (04)°, Br–Ni–P(2) = 89.57 (04)°, C(1)–Ni–P(1) = 90.54 (13)° and C(1)–Ni–P(2) = 91.02 (13)°. The deviations of trans angles from 180° and cis angles from 90° are thus small, but are significant, and presumably result from slight intramolecular repulsions.

(22) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1656.
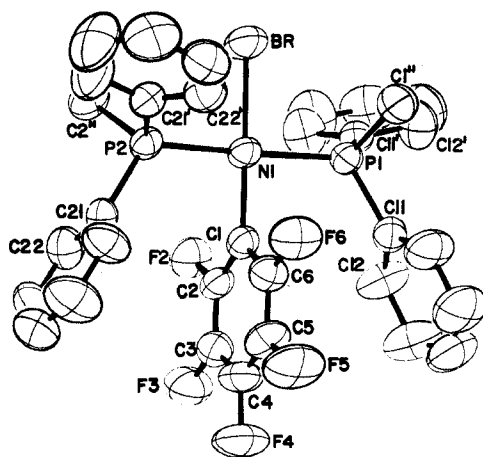
Figure 1. Labeling of atoms in the *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$ molecule. This ORTEP diagram shows the 50% probability envelopes for the vibration ellipsoids of nonhydrogen atoms. Hydrogen atoms have been omitted for the sake of clarity.

Methyldiphenylphosphine Ligands. The two PPh₂Me ligands are equivalent within the limits of experimental error. The nickel–phosphorus bond lengths are Ni–P(1) = 2.2164 (13) Å and Ni–P(2) = 2.2148 (13) Å, the mean value being 2.2156 Å. The phosphorus–phenyl bonds, P(1)–C(11) =

Table III. Interatomic Distances (in Å) with Estimated Standard Deviations for *trans*-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)Br[a,b]

Atoms	Distance	Atoms	Distance
(a) Distances from Nickel Atom			
Ni–Br	2.3245 (08)	Ni· · ·F(2)	3.0531 (27)
Ni–P(1)	2.2164 (13)	Ni· · ·F(6)	3.1186 (26)
Ni–P(2)	2.2148 (13)	Ni· · ·H(16')	2.937 (46)
Ni–C(1)	1.8800 (41)	Ni· · ·H(22')	2.851 (41)
(b) Distances from Phosphorus Atom			
P(1)–C(11)	1.818 (4)	P(2)–C(21)	1.829 (5)
P(1)–C(11')	1.801 (5)	P(2)–C(21')	1.793 (5)
P(1)–C(1'')	1.819 (6)	P(2)–C(2'')	1.827 (5)
P(1)· · ·Br	3.186 (1)	P(2)· · ·Br	3.199 (1)
(c) Distances within (o-C$_6$F$_5$) Ligand			
C(1)–C(2)	1.361 (5)		
C(2)–C(3)	1.365 (6)	C(2)–F(2)	1.368 (5)
C(3)–C(4)	1.352 (6)	C(3)–F(3)	1.343 (5)
C(4)–C(5)	1.362 (6)	C(4)–F(4)	1.350 (5)
C(5)–C(6)	1.376 (7)	C(5)–F(5)	1.355 (5)
C(6)–C(1)	1.380 (6)	C(6)–F(6)	1.363 (5)
F(2)· · ·F(3)	2.675 (4)	F(4)· · ·F(5)	2.723 (5)
F(3)· · ·F(4)	2.702 (4)	F(5)· · ·F(6)	2.673 (4)
(d) Carbon–Carbon Distances within PPh$_2$Me Ligands			
C(11)–C(12)	1.357 (7)	C(11')–C(12')	1.389 (7)
C(12)–C(13)	1.395 (8)	C(12')–C(13')	1.387 (8)
C(13)–C(14)	1.355 (10)	C(13')–C(14')	1.347 (9)
C(14)–C(15)	1.317 (10)	C(14')–C(15')	1.354 (9)
C(15)–C(16)	1.387 (9)	C(15')–C(16')	1.372 (8)
C(16)–C(11)	1.371 (7)	C(16')–C(11')	1.359 (6)
C(21)–C(22)	1.358 (6)	C(21')–C(22')	1.388 (7)
C(22)–C(23)	1.368 (7)	C(22')–C(23')	1.382 (9)
C(23)–C(24)	1.354 (9)	C(23')–C(24')	1.336 (9)
C(24)–C(25)	1.364 (8)	C(24')–C(25')	1.354 (10)
C(25)–C(26)	1.393 (7)	C(25')–C(26')	1.372 (10)
C(26)–C(21)	1.358 (6)	C(26')–C(21')	1.376 (7)
(e) Carbon–Hydrogen Distances in Phenyl Groups			
C(12)–H(12)	0.93 (5)	C(12')–H(12')	0.93 (4)
C(13)–H(13)	0.97 (5)	C(13')–H(13')	0.93 (5)
C(14)–H(14)	0.81 (5)	C(14')–H(14')	0.82 (6)
C(15)–H(15)	0.96 (6)	C(15')–H(15')	0.81 (5)
C(16)–H(16)	0.96 (6)	C(16')–H(16')	0.88 (4)
C(22)–H(22)	0.76 (2)	C(22')–H(22')	0.96 (4)
C(23)–H(23)	0.87 (4)	C(23')–H(23')	0.80 (5)
C(24)–H(24)	0.99 (5)	C(24')–H(24')	0.84 (4)
C(25)–H(25)	1.04 (6)	C(25')–H(25')	0.91 (6)
C(26)–H(26)	0.99 (4)	C(26')–H(26')	0.95 (6)
(f) Carbon–Hydrogen Distances in Methyl Groups			
C(1'')–H(1A'')	0.93 (5)	C(2'')–H(2A'')	0.87 (5)
C(1'')–H(1B'')	0.82 (5)	C(2'')–H(2B'')	0.96 (5)
C(1'')–H(1C'')	1.10 (6)	C(2'')–H(2C'')	0.88 (5)

[a] Esd's were calculated by considering those elements of the full positional correlation matrix (see text) whose magnitudes were greater than 0.10. The calculation was performed using the FORTRAN IV program STAN1 by B. D. DeBoer. Contributions from errors in the unit cell dimensions are included. [b] Bond lengths are not corrected for the effects of thermal motion.

1.818 (4) Å, P(1)–C(11') = 1.801 (5) Å, P(2)–C(21) = 1.829 (5) Å, and P(2)–C(21') = 1.793 (5) Å, average 1.810 Å in length, as compared to values (in Å) of 1.821 (6) and 1.824 (6) in *trans*-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)(o-C$_6$Cl$_5$),[3] 1.817 (3) and 1.828 (3) in *trans*-(PPh$_2$Me)Ni(o-C$_6$F$_5$)$_2$,[2] 1.826 (av) in (π-C$_5$H$_5$)Ni(PPh$_3$)(o-C$_6$H$_5$),[5] and 1.827 (av) in (π-C$_5$H$_5$)Ni-(PPh$_3$)(o-C$_6$F$_5$).[6]

The phosphorus–methyl distances, P(1)–C(1'') = 1.819 (6) Å and P(2)–C(2'') = 1.827 (5) Å, appear to be about normal [*cf.* 1.853 (7) Å in *trans*-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)(o-C$_6$Cl$_5$)[3] and 1.821 (4) Å in *trans*-(PPh$_2$Me)$_2$Ni(o-C$_6$F$_5$)$_2$[2]].

Individual carbon–carbon bond distances within the four phenyl groups range from C(14)–C(15) = 1.317 (10) Å to C(12)–C(13) = 1.395 (8) Å, the average of the 24 values being 1.366 ± 0.019 Å. (N. B., esd's on average values in the

text are calculated using the "scatter formula" given in footnote *a* to Table VI and are prefaced by "±" rather than being enclosed in parentheses as are individual esd's.)

There appear to be some systematic variations in carbon–carbon distance around the phenyl rings. Thus, C(P-bonded)–C(ortho) = 1.357 (7)–1.389 (7) Å (average 1.370 ± 0.014 Å); C(ortho)–C(meta) = 1.368 (7)–1.395 (8) Å (av 1.382 ± 0.010 Å); C(meta)–C(para) = 1.317 (9)–1.364 (8) Å (average 1.348 ± 0.015 Å). However, differences in mean distances are small, with C(ortho)–C(meta) > C(P-bonded)–C(ortho) > C(meta)–C(para), by successive increments of 0.012 (1.0 σ) and 0.022 Å (1.6 σ). The mean C-(ortho)–C(meta) distance is approximately 2.6 σ greater than the average C(meta)–C(para) distance. We interpret these figures not in terms of any real differences in the C–C bond order but as an artifact resulting from a "swinging" rigid body motion of the phenyl groups relative to their P–C bonds.

Carbon–carbon–carbon angles within the four phenyl groups range from C(26)–C(21)–C(22) = 117.3 (5) to C(21)–C(22)–C(23) = 123.2 (5)°, averaging 120.0°. Internal angles at the P-bonded carbon are all significantly (*i.e.*, >3 σ) less than the ideal trigonal value; thus, C(16)–C(11)–C(12) = 118.1 (5)°, C(16')–C(11')–C(12') = 118.3 (5)°, C(26)–C(21)–C(22) = 117.3 (5)°, and C(26')–C(21')–C(22') = 117.6 (5)° (mean = 117.8°).

This phenomenon has previously been noted by Churchill and Veidis.[23] We may also note that internal angles at the ortho carbons range from 119.4 (6) to 123.2 (5)° (av 121.0°), at the meta carbons range from 117.6 (8) to 120.9 (6)° (av 119.8°), and at the para carbons range from 118.8 (5) to 122.0 (7)° (av 120.6°).

Carbon–hydrogen distances within the phenyl rings range from C(22)–H(22) = 0.76 (2) Å to C(25)–H(25) = 1.04 (6) Å, the average of the 20 independent values being 0.91 Å. This value is, of course, systematically reduced from the accepted internuclear C–H distance of 1.08 Å,[24] due to the centroid of the electron density associated with the hydrogen atom not being coincident with the position of the hydrogen nucleus, but, rather, being displaced in the direction of the H–C σ bond.

External angles to the phenyl rings are of two varieties; those of the type C–C–P range from 120.0 (4) to 122.4 (4)° (averaging 121.9°), while those of the type C–C–H are inherently less precisely determined and range from 103 (4) to 135 (4)°, the mean of the 40 independent values being 120°—the angle expected as the external bisector of a planar regular hexagon.

Within the two methyl groups P–C–H angles range from 109 (3) to 115 (3)° (averaging 112°), while H–C–H angles vary from 98 (5) to 114 (5)° (averaging 107°). Carbon–hydrogen distances within the methyl groups range from C(1'')–H(1B'') = 0.82 (5) Å to C(1'')–H(1C'') = 1.10 (6) Å, the average value being 0.93 Å, *i.e.*, indistinguishable from the mean value for the C(phenyl)–H bonds (*vide supra*).

As is typical both of tertiary phosphines and their complexes,[25] angles about the phosphorus atoms deviate from the ideal tetrahedral value of 109° 28'. Thus Ni–P–C angles range from 110.69 (16) to 119.51 (15)° (averaging 114.54°), while C–P–C angles range from 102.55 (21) to 106.61 (27)° (averaging 103.98°).

Bromide Ligand. The observed nickel(II)–bromide distance

(23) See ref 2, especially lines 6–17, left hand column, p 675.

(24) L. E. Sutton, *Chem. Soc., Spec. Publ., Suppl.*, No. 18, S18s (1965).

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

Table IV. Bond Angles (in degrees) for *trans*-(PPh₂Me)₂Ni(σ-C₆F₅)Br

Atoms	Angle	Atoms	Angle
		(a) Around Nickel Atom	
Br–Ni–P(1)	89.09 (04)	P(1)–Ni–P(2)	175.10 (05)
Br–Ni–P(2)	89.57 (04)	P(1)–Ni–C(1)	90.54 (13)
Br–Ni–C(1)	177.22 (14)	P(2)–Ni–C(1)	91.02 (13)
		(b) Around Phosphorus Atoms	
Ni–P(1)–C(11)	119.51 (15)	Ni–P(2)–C(21)	118.34 (14)
Ni–P(1)–C(11′)	112.96 (15)	Ni–P(2)–C(21′)	110.69 (16)
Ni–P(1)–C(1″)	110.94 (22)	Ni–P(2)–C(2″)	114.79 (23)
C(11)–P(1)–C(11′)	102.55 (21)	C(21)–P(2)–C(21′)	103.24 (21)
C(11)–P(1)–C(1″)	103.06 (24)	C(21)–P(2)–C(2″)	102.84 (25)
C(11′)–P(1)–C(1″)	106.61 (27)	C(21′)–P(2)–C(2″)	105.57 (27)
		(c) Angles in (σ-C₆F₅) Ligand	
C(6)–C(1)–C(2)	113.7 (4)	C(3)–C(4)–C(5)	119.5 (4)
C(1)–C(2)–C(3)	125.3 (4)	C(4)–C(5)–C(6)	119.7 (4)
C(2)–C(3)–C(4)	118.8 (4)	C(5)–C(6)–C(1)	123.1 (4)
C(6)–C(1)–Ni	123.9 (3)	C(3)–C(4)–F(4)	121.0 (5)
C(2)–C(1)–Ni	122.3 (3)	C(5)–C(4)–F(4)	119.5 (5)
C(1)–C(2)–F(2)	119.0 (4)	C(4)–C(5)–F(5)	121.0 (4)
C(3)–C(2)–F(2)	115.8 (4)	C(6)–C(5)–F(5)	119.4 (5)
C(2)–C(3)–F(3)	122.1 (4)	C(5)–C(6)–F(6)	117.6 (4)
C(4)–C(3)–F(3)	119.1 (4)	C(1)–C(6)–F(6)	119.3 (4)
		(d) Angles within Phenyl Rings	
C(16)–C(11)–C(12)	118.1 (5)	C(16′)–C(11′)–C(12′)	118.3 (5)
C(11)–C(12)–C(13)	121.8 (6)	C(11′)–C(12′)–C(13′)	119.4 (6)
C(12)–C(13)–C(14)	117.6 (8)	C(12′)–C(13′)–C(14′)	120.5 (6)
C(13)–C(14)–C(15)	122.0 (7)	C(13′)–C(14′)–C(15′)	120.5 (6)
C(14)–C(15)–C(16)	120.5 (7)	C(14′)–C(15′)–C(16′)	119.6 (7)
C(15)–C(16)–C(11)	120.0 (6)	C(15′)–C(16′)–C(11′)	121.7 (6)
C(26)–C(21)–C(22)	117.3 (5)	C(26′)–C(21′)–C(22′)	117.6 (5)
C(21)–C(22)–C(23)	123.2 (5)	C(21′)–C(22′)–C(23′)	120.2 (6)
C(22)–C(23)–C(24)	119.5 (5)	C(22′)–C(23′)–C(24′)	120.2 (6)
C(23)–C(24)–C(25)	118.8 (5)	C(23′)–C(24′)–C(25′)	121.1 (6)
C(24)–C(25)–C(26)	120.9 (6)	C(24′)–C(25′)–C(26′)	119.5 (7)
C(25)–C(26)–C(21)	120.4 (5)	C(25′)–C(26′)–C(21′)	121.3 (6)
		(e) External Angles to Phenyl Rings	
C(16)–C(11)–P(1)	121.8 (4)	C(16′)–C(11′)–P(1)	120.6 (4)
C(12)–C(11)–P(1)	120.1 (4)	C(12′)–C(11′)–P(1)	121.1 (4)
C(11)–C(12)–H(12)	113 (4)	C(11′)–C(12′)–H(12′)	115 (3)
C(13)–C(12)–H(12)	125 (4)	C(13′)–C(12′)–H(12′)	126 (3)
C(12)–C(13)–H(13)	121 (4)	C(12′)–C(13′)–H(13′)	110 (4)
C(14)–C(13)–H(13)	121 (4)	C(14′)–C(13′)–H(13′)	129 (4)
C(13)–C(14)–H(14)	107 (4)	C(13′)–C(14′)–H(14′)	116 (5)
C(15)–C(14)–H(14)	131 (4)	C(15′)–C(14′)–H(14′)	124 (5)
C(14)–C(15)–H(15)	135 (4)	C(14′)–C(15′)–H(15′)	122 (4)
C(16)–C(15)–H(15)	103 (4)	C(16′)–C(15′)–H(15′)	117 (4)
C(15)–C(16)–H(16)	123 (4)	C(15′)–C(16′)–H(16′)	121 (3)
C(11)–C(16)–H(16)	117 (4)	C(11′)–C(16′)–H(16′)	117 (3)
C(26)–C(21)–P(2)	121.0 (4)	C(26′)–C(21′)–P(2)	122.4 (4)
C(22)–C(21)–P(2)	121.6 (4)	C(22′)–C(21′)–P(2)	120.0 (4)
C(21)–C(22)–H(22)	120 (2)	C(21′)–C(22′)–H(22′)	118 (3)
C(23)–C(22)–H(22)	117 (2)	C(23′)–C(22′)–H(22′)	121 (3)
C(22)–C(23)–H(23)	122 (3)	C(22′)–C(23′)–H(23′)	108 (4)
C(24)–C(23)–H(23)	118 (3)	C(24′)–C(23′)–H(23′)	132 (4)
C(23)–C(24)–H(24)	117 (3)	C(23′)–C(24′)–H(24′)	123 (4)
C(25)–C(24)–H(24)	124 (3)	C(25′)–C(24′)–H(24′)	116 (4)
C(24)–C(25)–H(25)	125 (4)	C(24′)–C(25′)–H(25′)	129 (5)
C(26)–C(25)–H(25)	114 (4)	C(26′)–C(25′)–H(25′)	112 (5)
C(25)–C(26)–H(26)	118 (3)	C(25′)–C(26′)–H(26′)	117 (4)
C(21)–C(26)–H(26)	122 (3)	C(21′)–C(26′)–H(26′)	122 (4)
		(f) Angles in Methyl Groups	
P(1)–C(1″)–H(1A″)	110 (4)	H(1A″)–C(1″)–H(1B″)	114 (5)
P(1)–C(1″)–H(1B″)	109 (3)	H(1A″)–C(1″)–H(1C″)	106 (4)
P(1)–C(1″)–H(1C″)	115 (3)	H(1B″)–C(1″)–H(1C″)	103 (5)
P(2)–C(2″)–H(2A″)	109 (4)	H(2A″)–C(2″)–H(2B″)	98 (5)
P(2)–C(2″)–H(2B″)	114 (3)	H(2A″)–C(2″)–H(2C″)	108 (5)
P(2)–C(2″)–H(2C″)	114 (3)	H(2B″)–C(2″)–H(2C″)	112 (5)

in the present *trans*-(PPh₂Me)₂Ni(σ-C₆F₅)Br molecule is 2.3245 (8) Å. While no dimensions are available for the molecule *trans*-(PPh₂Me)₂NiBr₂, data *are* available for certain other bis(*tert*-phosphine)dibromonickel(II) species[26–29] (see Table V). One can surmise, from this data, that the Ni–Br distances in a square-planar *trans*-(PPh₂Me)₂NiBr₂ molecule

(26) V. Scatturin and A. Turco, *J. Inorg. Nucl. Chem.*, **8**, 447 (1958).

(27) B. T. Kilbourn and H. M. Powell, *J. Chem. Soc. A*, 1688 (1970).

(28) J. A. Stalick and J. A. Ibers, *Inorg. Chem.*, **9**, 453 (1970).

(29) J. A. J. Jarvis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1473 (1968).

Table V. Distances (in Å) within Selected Four-Coordinate Phosphine–Nickel–Bromide Species

Complex	Ni–Br	Ni–P	Ref
(A) Square-Planar Species			
trans-[PEt₃]₂NiBr₂	2.30 (1)	2.26 (1)	26
trans-[PPh₂(CH₂Ph)]₂NiBr₂	2.305 (3)	2.263 (7)	27
trans-[PPhMe₂]₂NiBr₂	2.297 (2)	2.251 (3)	28
(B) Tetrahedral Species			
[PPh₃]₂NiBr₂	2.346 (3)	2.343 (5)	29
	2.329 (3)	2.323 (5)	
[PPh₂(CH₂Ph)]₂NiBr₂	2.359 (4)	2.316 (7)	27
	2.351 (5)	2.314 (8)	

should be ~2.30 Å in length. The observed Ni–Br distance of 2.3245 (8) Å in the present complex appears to be increased slightly (by about 0.025 Å) from the value expected for a bond of unit bond order. It is possible that the *trans*-(o-C₆F₅) ligand exerts some slight trans-lengthening influence upon this Ni–Br bond.

o-Pentafluorophenyl Ligand. The Ni-(o-C₆F₅) distance, Ni–C(1), is 1.8800 (41) Å, the angles Ni–C(1)–C(2) and Ni–C(1)–C(6) being 122.3 (3) and 123.9 (3)°, respectively.

Carbon–carbon distances within this ligand range from C(3)–C(4) = 1.352 (6) to C(6)–C(1) = 1.380 (6) Å, with a mean value of 1.366 Å; carbon–fluorine bond lengths range from C(3)–F(3) = 1.343 (5) Å to C(2)–F(2) = 1.368 (5) Å, the average distance being 1.356 Å.

Angles within the carbon skeleton of the perfluorophenyl ligand show the marked deviations from D_{6h} symmetry which are characteristic (*inter alia*) of σ-bonded transition metal aryls.[30] The internal angle at the nickel-bonded carbon, *i.e.*, ∠C(6)–C(1)–C(2), is 113.7 (4)°, or almost 16σ lower than the ideal trigonal angle of 120°. Angles at the adjacent (ortho) carbon atoms are *increased* from the ideal trigonal angle, with ∠C(1)–C(2)–C(3) = 125.3 (4)° and ∠C(5)–C(6)–C(1) = 123.1 (4)°. Angles at the meta carbon atoms [∠C(2)–C(3)–C(4) = 118.8 (4)° and ∠C(4)–C(5)–C(6) = 119.7 (4)°] and at the para carbon atom [∠C(3)–C(4)–C(5) = 119.5 (4)°] do not deviate so markedly from the regular hexagonal interior angle. The deviations of C–C–C angles from 120° also cause systematic variations in F· · ·F contacts within the C₆F₅ ligand. Thus, the ortho–meta distances, F(2)· · ·F(3) = 2.675 (4) Å and F(6)· · ·F(5) = 2.673 (4) Å, are similar but are significantly shorter than the meta–para distances, F(3)· · ·F(4) = 2.702 (4) Å and F(5)· · ·F(4) = 2.723 (5) Å.

Discussion

Parameters from structural studies on *trans*-(PPh₂Me)₂Ni-(o-C₆F₅)Br, *trans*-(PPh₂Me)₂Ni(o-C₆F₅)₂,[2] and *trans*-(PPh₂Me)₂Ni(o-C₆F₅)(o-C₆Cl₅)[3] are summarized in Table VI. We make the following observations.

(1) The length of the Ni–o-C₆F₅ bond is significantly affected by the ligand trans to it, varying from 1.8800 (41) (with trans Br) to 1.939 (3) (with trans o-C₆F₅) to 1.978 (10) Å (with trans o-C₆Cl₅). We assume that the "normal" value is 1.88 Å, since a Br ligand exerts no significant trans-lengthening influence. (Unfortunately the argument here tends to become slightly tortuous because the Br ligand could exert a "negative" trans-lengthening influence if the Ni–Br bond itself is appreciably lengthened by the trans influence of the o-C₆F₅ ligand! However, *vide supra*, the Ni–Br bond appears to be increased from its normal value by no more than 0.025 Å.)

(2) The average carbon–carbon bond length in the o-C₆F₅

(30) See ref 3, Table 6, on p 3468.

Table VI. Comparison of the Geometry of *trans*-[PPh₂Me]₂Ni(o-C₆F₅)X Species[a]

Parameter	X = Br	X = (o-C₆F₅)[b]	X = (o-C₆Cl₅)[c]
(A) Distances Involving the o-C₆F₅ Ligand			
Ni-(o-C₆F₅)	1.8800 (41)	1.939 (3)	1.978 (10)
C–C (av)	1.366 (10)*	1.368 (12)*	1.375 (2)*
C–F (av)	1.356 (10)*	1.353 (6)*	1.347 (18)*
(B) Distances Involving PPh₂Me Ligands			
Ni–PPh₂Me	2.2156 (11)*	2.206 (1)	2.230 (1)
P–Ph	1.810 (16)*	1.823 (8)*	1.823 (2)*
P–Me	1.823 (6)*	1.821 (4)	1.853 (7)
C–C(Ph)	1.366	1.376	1.384
C–H(Ph)	0.91	0.97	d
C–H(Me)	0.93	0.90	d
(C) C–C–C Angles within o-C₆F₅ Ligands			
At Ni	113.7 (4)	114.0 (3)	112.0 (5)
Ortho	125.3 (4)	123.2 (3)	125.8 (7)
	123.1 (4)	124.2 (3)	
Meta	118.8 (4)	119.4 (3)	118.4 (8)
	119.7 (4)	119.5 (4)	
Para	119.5 (4)	119.5 (4)	119.6 (7)

^{a} Esd's followed by an asterisk are calculated by the "scatter formula," *i.e.*, $\sigma(\text{mean}) = [\frac{1}{N}\sum_{i=1}^{i=N}(\chi_i - \overline{\chi})^2/(N-1)]^{1/2}$ where χ_i is the *i*th bond length and $\overline{\chi}$ is the mean of the N equivalent bond lengths. ^{b} See ref 2. ^{c} See ref 3. ^{d} Hydrogen atoms not located in this study.

ligands is 1.366 ± 0.010 Å in *trans*-(PPh₂Me)₂Ni(o-C₆F₅)Br, 1.368 ± 0.012 Å in *trans*-(PPh₂Me)₂Ni(o-C₆F₅)₂,[2] and 1.375 ± 0.002 Å in *trans*-(PPh₂Me)₂Ni(o-C₆F₅)(o-C₆Cl₅).[3] Other available data include 1.381 ± 0.007 Å in (π-C₇H₇)Mo(CO)₂-(o-C₆F₅)[4] and 1.383 ± 0.040 Å in (π-C₅H₅)Ni(PPh₃)(o-C₆F₅).[6] Although each of these values is below the accepted C–C(aromatic) distance of 1.394 ± 0.005 Å,[31] it is not possible unambiguously to attribute this shortening to a true electronic effect rather than to an artificial librational shortening.

(3) The average C(aromatic)–F distances are 1.356 ± 0.010 Å in *trans*-(PPh₂Me)₂Ni(o-C₆F₅)Br, 1.353 ± 0.006 Å in *trans*-(PPh₂Me)₂Ni(o-C₆F₅)₂,[2] and 1.347 ± 0.018 Å in *trans*-(PPh₂Me)₂Ni(o-C₆F₅)(o-C₆Cl₅);[3] other distances are 1.341 ± 0.013 Å in (π-C₇H₇)Mo(CO)₂(o-C₆F₅)[4] and 1.342 ± 0.019 Å in (π-C₅H₅)Ni(PPh₃)(o-C₆F₅).[6] (In each case the number following "±" is the "scatter" from the mean.) Again, we emphasize that none of these distances have been corrected for possible librational contraction. Nevertheless, we believe that the σ^{-2}-weighted average of 1.351 Å represents a value for the C(aromatic)–F distance which is superior to that provided in the standard compilation of interatomic distances.[32]

(4) Angles within the six-membered carbocyclic ring of each of the o-C₆F₅ ligands form a self-consistent pattern in agreement with features discussed previously (*cf.* Table VI, section C and ref 30).

(5) The Ni–PPh₂Me distances do vary significantly from one o-C₆F₅ derivative to another. The pattern of variation seems to defy any simple explanation.

(31) L. E. Sutton, *Chem. Soc., Spec. Publ., Suppl.*, No. 18, S16s (1965).

(32) The provided value [*Chem. Soc., Spec. Publ., Suppl.*, No. 18, S18s (1965)] is C(aromatic)–F = 1.328 ± 0.005 Å.