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Crystal and Molecular Structure of Tris(triphenylphosphine)pentakis(pentafluorophenylethynyl)rhodiumdisilver

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The heteronuclear trimetallic complex tris(triphenylphosphine)pentakis(pentafluorophenylethynyl)rhodiumdisilver, $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$, has previously been prepared by the reaction of $RhCl(PPh_3)_3$ and $Ag(C{\equiv}CC_6F_5)$. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ [C_{2h}^5; No. 14] with a = 15.9023 (19) Å, b = 21.4974 (27) Å, c = 25.0411 (33) Å, and β = 102.00 (1)°. The observed density of 1.627 (5) g cm^{-3} is consistent with the value of 1.635 g cm^{-3} calculated for V = 8373.5 (18) Å^3, mol wt 2060.93, and Z = 4. No crystallographic symmetry is imposed upon the molecule. Single-crystal X-ray diffraction data, complete to 2θ = 40° (Mo Kα radiation), were collected with a Picker FACS-1 automated diffractometer and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The final discrepancy indices are R_F = 6.20% and R_{wF} = 6.21% for the 7820 symmetry-independent reflections (none rejected). All 125 nonhydrogen atoms have been accurately located. (Two phenyl groups of a triphenylphosphine ligand are subject to disorder and have been resolved.) The molecule contains three metal atoms in a bent arrangement $\angle$[Ag(1)···Rh···Ag(2)] = 110.55 (2)°. The central rhodium atom is in essentially regular octahedral coordination to one PPh_3 ligand (Rh–P(3) = 2.3431 (18) Å) and five σ-acetylide ligands (Rh–C(α) = 2.004 (7)–2.039 (6) Å). Each silver atom is in a tetrahedral coordination environment, being bonded to one PPh_3 ligand (Ag(1)–P(1) = 2.3877 (19) Å, Ag(2)–P(2) = 2.3903 (19) Å) and bonded asymmetrically to three acetylenic π bonds, such that Ag···C(α) = 2.334 (6)–2.636 (6) Å and Ag···C(β) = 2.600 (7)–3.117 (6) Å. The octahedral and tetrahedral coordination about rhodium and silver, the nonequivalence of the angles P(1)–Ag(1)···Rh = 175.83 (6)° and P(2)–Ag(2)···Rh = 155.56 (5)°, and the long metal–metal distances [Rh···Ag(1) = 3.1021 (8) Å, Rh···Ag(2) = 3.0871 (8) Å] militate against direct metal–metal bonds and in favor of a zwitterionic association of $[(PPh_3)Rh^{III}(C{\equiv}CC_6F_5)_5]^{2-}$ and $[(PPh_3)Ag^I]^+$ held together by silver–acetylene π bonding.

Introduction

We have been interested for some time in the heteronuclear metal complexes synthesized by the interaction of group 1B metal acetylides with transition metal complexes.[1] We have previously published the results of a structural study on $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$, a molecule prepared from $IrCl(CO)(PPh_3)_2$ and $[PhC{\equiv}CCu]_n$.[1,2]

The present study was undertaken in order to determine the molecular structure (especially the ligand–metal connectivity) of a species of formula $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ which had been synthesized by the reaction of Wilkinson's catalyst, $RhCl(PPh_3)_3$, and $Ag(C{\equiv}CC_6F_5)$. A report of this work (at an intermediate stage of refinement) has appeared previously.[3]

Collection of the X-Ray Diffraction Data

A sample of $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ was provided by Professor M. I. Bruce. The crystal selected for the X-ray diffraction study was a hexagonal plate between $\{10\bar{1}\}$ faces 0.098 mm apart bounded (cyclically) by $(10\bar{1})$, $(1\bar{1}0)$, $(0\bar{1}1)$ and $(\bar{1}\bar{1}0)$, $(\bar{1}01)$, (010), and $(01\bar{1})$. The plate face was of maximum dimensions 0.45 mm × 0.52 mm.

Preliminary photographic data on a number of crystals (including $h(0\text{-}2)l$ Weissenberg photographs and a b-axis rotation photograph—all taken with Cu Kα radiation; $hk0$ and $0kl$ precession photographs and cone-axis photographs about a and c—taken with Mo Kα radiation) indicated C_{2h} ($2/m$) Laue symmetry, provided approximate unit cell parameters, and revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the nonstandard centrosymmetric monoclinic space group $P2_1/n$ is thereby indicated.

The "data crystal" was transferred to a Picker FACS-1 automated diffractometer, was accurately centered, and was aligned with $[\bar{3}05]$ coincident with the ϕ axis. Unit cell measurement and data collection were carried out as described previously;[4] details specific to the present analysis are listed in Table I.

As a check on the severity of the absorption problem, the strong axial reflection $\bar{3}05$ was measured (by a θ–2θ scan) at χ = 90° and at 10° intervals from ϕ = 0° to ϕ = 350°. The variation in intensity as a function of ϕ [which we define as (maximum – minimum)/average] was 24.5%, indicating that an absorption correction was desirable. When these "ϕ-scan" data were later corrected for the effects of absorption (along with the primary data set), the variation of intensity with ϕ was reduced impressively to 1.7%. This confirms the validity of the absorption correction and suggests also that secondary extinction is unlikely to be of any major significance.

Solution and Refinement of the Structure

Computer programs used during the structural analysis include FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations and least-squares refinement, by B. G. DeBoer), STANI (distances and angles, with esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson). All calculations were performed on an IBM 370/158 computer.

Scattering factors for neutral silver, rhodium, phosphorus, fluorine, and carbon were taken from the compilation of Cromer and Waber;[5] for hydrogen, the "best floated spherical H atom" values of Stewart et al.[6] were used. Both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for *all* nonhydrogen atoms, using the values of Cromer and Liberman.[7]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(|F_o|)$. Discrepancy indices used below are defined as

$$R_F = \left[\frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o|^2 - |F_c|^2)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The analysis was begun using only those 3387 reflections for which $2\theta < 30°$. A three-dimensional Patterson map led, quickly and unambiguously, to the location of the three metal atoms. An "observed" Fourier synthesis provided the positions of the three phosphorus atoms; a difference-Fourier synthesis then showed the presence of all five $C{\equiv}CC_6F_5$ ligands. Three cycles of full-matrix least-squares refinement of the scale factor along with the coordinates and isotropic thermal parameters of the 71 atoms constituting the $RhAg_2(C{\equiv}CC_6F_5)_5(P)_3$ moiety (285 parameters in all) led to convergence with R_F = 30.1% and R_{wF} = 38.8%. A second difference-Fourier synthesis now led to the location of all 54 carbon atoms associated with the three PPh_3 ligands. Three "cycles" of refinement of all positional and thermal parameters, plus the scale factor (501 parameters in all), resulted in reduction of the discrepancy indices to R_F = 10.8% and R_{wF} = 12.8%. [It should be noted that each "cycle" consisted of two calculations—first, parameters for all atoms in the $RhAg_2(PPh_3)_3$ portion of the molecule were refined; second, parameters of the $RhAg_2(C{\equiv}CC_6F_5)_5(P)_3$ portion were refined.]

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Table I. Experimental Data for the X-Ray Diffraction Study of $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$

(A) Crystal Parameters at 21.0 ± 0.2°C[a]

$a = 15.9023\ (19)$ Å	Space group $P2_1/n$[b]
$b = 21.4974\ (27)$ Å	$Z = 4$
$c = 25.0411\ (33)$ Å	Mol wt 2060.93
$\cos\beta = -0.20787\ (15)$	ρ(calcd) = 1.635 g cm^{-3}
$\beta = 102.00\ (1)$	ρ(obsd)[c] = 1.627 (5) g cm^{-3}
$V = 8373.5\ (18)$ Å^3	

(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: Cu foil; used if I(peak) > 10^4 counts/sec
Takeoff angle: 3.0°
Detector aperture: 4.5 mm × 4.5 mm
Crystal-detector distance: 330 mm
Crystal orientation: ϕ axis = [$\bar{3}05$]
Reflection measured: $\pm h$, $+k$, $+l$[d]
Maximum 2θ: 40°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (0.90 + 0.692 \tan\theta)°$, starting 0.45° below the Mo Kα peak
Background measurement: stationary crystal, stationary counter; 20 sec each at beginning and end of 2θ scan
Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an anisotropic linear decay correction)[e] were 1.2% for $\bar{3}01$, 0.5% for 0,0,10, and 1.3% for 062
Reflections collected: 7820 independent measurements, 457 duplicate or equivalent measurements[d] (averaged into primary data set), and 338 systematic absences

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 4, using an "ignorance factor" of $p = 0.03$
Absorption coefficient: $\mu = 7.95$ cm^{-1}; maximum and minimum transmission factors[f] were 0.931 and 0.724, respectively

[a] Unit cell parameters are from a least-squares fit to the setting angles of the Mo Kα peaks (λ 0.710730 Å) of 12 reflections with $2\theta = 36.0$–40.7°. (A takeoff angle of 3.0° was used to ensure that Mo Kα_1 and Mo Kα_2 peaks were not resolved.) Maximum and root-mean-square disagreements were 0.020 and 0.011°, respectively. [b] $P2_1/n$ is a nonstandard setting of space group $P2_1/c$ [C_{2h}^5; No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$. [c] The density was measured by neutral buoyancy in aqueous KI. [d] Reflections with $2\theta \leqslant 15°$ were measured twice (at the beginning and at the end of the data-taking period) and averaged [$R(F^2) = 2.8\%$]. [e] Data reduction and analysis, including decay correction, were performed using the Fortran IV program **RDUS2**, by B. G. DeBoer. [f] Absorption corrections were applied using the program **DRABZ**, by B. G. DeBoer.

At this stage data with $30° \leq 2\theta < 40°$ became available and were added to the primary data set, yielding 7820 independent reflections.

It now became clear that refinement could only proceed at a reasonable rate if we made some drastic modifications to our approach. Accordingly, we stripped the least-squares program down to a "diagonal-elements-of-matrix-only" (DEMON) form. Four cycles of refinement of all positional parameters, anisotropic thermal parameters for Rh, Ag, P, and F atoms, isotropic thermal parameters for C atoms, and the scale factor (656 parameters in all) led to a reduction in the discrepancy indices from $R_F = 14.05\%$ and $R_{wF} = 13.81\%$ down to $R_F = 8.40\%$ and $R_{wF} = 8.23\%$. [During the use of the DEMON program a "damping factor" was used such that (applied shift) = 0.7(calculated shift). This prevented any divergence, but some oscillation of shifts did, nevertheless, occur.]

Inspection of the thermal parameters of all atoms showed huge values for some phenyl carbon atoms. Accordingly, a third difference-Fourier map was computed (omitting contributions from atoms C(71)–C(76) and C(91)–C(96)) and it was discovered that these two phenyl groups, both attached to P(3), were subjected to disorder about their C(P bonded)–C(para) axes. Atoms C(72), C(73), C(75), C(76), C(92), C(93), C(95), and C(96) were partitioned into their "starred" and "nonstarred" components (all "starred" atoms being required to occur in one molecular rotamer—using considerations of van der Waals contacts) and coupled occupancy factors of α and 1 − α were applied to the two sets.

Refinement was now continued with the parameters of a total of 133 atoms or part-atoms being allowed to vary and using anisotropic parameters for all atoms other than C or H. The analysis now consisted of the refinement of 689 parameters to fit 7820 reflections. A total of eight cycles under the DEMON approximation led to a state of convergence with $R_F = 6.32\%$ and $R_{wF} = 6.39\%$. During this process, hydrogen atoms were included in calculated positions, 0.95 Å[8] outward along the (centroid of phenyl ring)→(carbon atom) vectors, with $B(H) = [B(C) + 1.0]$ Å^2. Shifts of hydrogen atom parameters were set equal to those of their attached carbon atoms—i.e., each C–H moiety was treated as a rigid, nonrotating group.

The final phase of the refinement process involved a return to the full-matrix approach so as to compensate for any errors which might have arisen in the DEMON approximation and so that we could obtain correlation coefficients between atomic positional parameters. After repositioning hydrogen atoms according to the criteria stated above, refinement was continued in stages: (i) all thermal parameters, the scale factor, and α were refined; (ii) all positional parameters in the $RhAg_2(C{\equiv}CC_6F_5)_5(P)_3$ portion of the molecule were refined; (iii) all positional parameters in the $RhAg_2(PPh_3)_3$ portion of the molecule were refined; (iv) steps i–iii were repeated; (v) a "clean-up" cycle was run, which included parameters for each atom which was associated with a parameter for which $\Delta/\sigma > 0.2$ in the last cycle in which it was refined.

The resulting discrepancy indices were $R_F = 6.201\%$ and $R_{wF} = 6.212\%$. The final "goodness of fit", defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.827. The number of reflections (m) was 7820 and the number of refined parameters (n) was 689, yielding an $m{:}n$ ratio of 11.35:1. The function $\sum w(|F_o| - |F_c|)^2$ was essentially independent of either $|F_o|$ or $(\sin\theta)/\lambda$, thereby suggesting that the weighting scheme was reasonable. There was no evidence for secondary extinction. (This was checked by comparing $|F_o|$ vs. $|F_c|$ for strong low-angle reflections.)

The validity of the least-squares refinement was confirmed independently by means of a final difference-Fourier synthesis; the greatest peaks (in order) were of height 0.72 e Å^{-3} (at 0.396, 0.226, 0.320), 0.68 e Å^{-3} (at 0.252, 0.296, 0.290 and at 0.316, 0.262, 0.290 (all near carbon atoms of C_6F_5 group "E")), and 0.57 e Å^{-3} (at 0.284, 0.034, 0.170 (between atoms C(32) and C(33))). All other peaks were below 0.51 e Å^{-3} in height. The ten largest peaks all occur in positions which suggest anisotropy in the thermal motion of the carbon atoms. However, since anisotropic refinement of all 133 atoms would have required 1199 parameters (and would also have lowered the data:parameter ratio to an unacceptable value of 6.5:1), these features were ignored and the structural refinement was declared complete! [Note that the DEMON program (which is dimensioned to hold 300 atoms and vary 2000 parameters) required less than half of the core storage space of the full-matrix program LSHF (dimensioned for 200 atoms and 360 variables) and required approximately 20 min/cycle as compared to 143 min/"cycle" composed of stages i, ii, and iii (vide supra) of "full-matrix" refinement.]

A table of observed and calculated structure factor amplitudes is available (see paragraph at end of paper regarding supplementary material). Final positional parameters are listed in Table II; anisotropic thermal parameters appear in Table III.

Results and Discussion

Intramolecular distances and their estimated standard deviations (esd's) are collected in Table IV; interatomic angles and their esd's are listed in Table V. Least-squares planes through phenyl rings etc., along with deviations of atoms from those planes, are given in Table VI.

The central $RhAg_2(C{\equiv}C{-}C)_5(P)_3$ portion of the molecule is shown in Figure 1. The overall molecular geometry is illustrated in Figure 2, while Figure 3 shows the molecule (with some carbon atoms of the P(3) triphenylphosphine ligand omitted) viewed from a direction only slightly displaced from the P(3)–Rh–C(1A) axis. It has been possible to label only key atoms in the figures; however, the remaining atom designations may be determined unambiguously. The pentafluorophenylethynyl groups are labeled such that the α-carbon atoms are designated C(1x) [x = A, B, C, D, E], the β-carbon atoms are C(2x), and the phenyl carbon atoms are, cyclically,

Table II. Final Positional Parameters with Esd's^a for $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$

Atom	*x*	*y*	*z*	*B*,^{b} Å^2	Atom	*x*	*y*	*z*	*B*,^{b} Å^2
Rh	−0.063665 (32)	0.264704 (24)	0.091175 (21)	3.969	C(31)	−0.0227 (5)	0.0111 (3)	0.2312 (3)	6.0 (2)
Ag(1)	−0.084489 (40)	0.159439 (26)	0.172167 (24)	6.046	C(32)	0.0608 (5)	0.0248 (4)	0.2487 (3)	7.4 (2)
Ag(2)	0.045069 (37)	0.219436 (29)	0.009999 (24)	6.113	C(33)	0.1273 (6)	−0.0213 (4)	0.2539 (4)	9.0 (2)
P(1)	−0.10125 (14)	0.07320 (9)	0.22914 (8)	5.671	C(34)	0.0997 (7)	−0.0781 (5)	0.2374 (4)	9.9 (3)
P(2)	0.17087 (12)	0.18003 (9)	−0.01653 (7)	5.110	C(35)	0.0187 (7)	−0.0954 (5)	0.2200 (4)	11.0 (3)
P(3)	−0.12918 (11)	0.36283 (8)	0.08394 (7)	4.354	C(36)	−0.0473 (7)	−0.0487 (4)	0.2160 (4)	9.1 (2)
C(1A)	0.0048 (4)	0.1838 (3)	0.1023 (2)	4.3 (1)	H(32)	0.0761	0.0665	0.2590	8.4
C(2A)	0.0527 (4)	0.1396 (3)	0.1148 (3)	4.5 (1)	H(33)	0.1866	−0.0124	0.2667	10.0
C(3A)	0.1206 (4)	0.0959 (3)	0.1327 (3)	4.5 (1)	H(34)	0.1426	−0.1092	0.2393	10.9
C(4A)	0.1964 (5)	0.1146 (3)	0.1653 (3)	5.7 (2)	H(35)	0.0042	−0.1373	0.2100	12.0
C(5A)	0.2658 (6)	0.0739 (4)	0.1806 (4)	7.9 (2)	H(36)	−0.1064	−0.0583	0.2033	10.1
C(6A)	0.2581 (6)	0.0155 (4)	0.1623 (4)	8.0 (2)	C(41)	0.1765 (4)	0.1941 (3)	−0.0871 (3)	5.3 (2)
C(7A)	0.1867 (5)	−0.0072 (4)	0.1319 (3)	6.9 (2)	C(42)	0.2197 (5)	0.1542 (4)	−0.1166 (3)	6.7 (2)
C(8A)	0.1160 (5)	0.0345 (4)	0.1165 (3)	6.3 (2)	C(43)	0.2231 (5)	0.1688 (4)	−0.1705 (3)	7.6 (2)
F(4A)	0.2055 (3)	0.1720 (2)	0.1846 (2)	7.98	C(44)	0.1826 (6)	0.2204 (4)	−0.1937 (4)	8.7 (2)
F(5A)	0.3398 (3)	0.0957 (3)	0.2118 (2)	12.54	C(45)	0.1408 (6)	0.2594 (5)	−0.1667 (4)	9.1 (2)
F(6A)	0.3279 (4)	−0.0235 (3)	0.1764 (3)	14.70	C(46)	0.1384 (5)	0.2468 (4)	−0.1126 (4)	7.6 (2)
F(7A)	0.1771 (4)	−0.0657 (2)	0.1163 (2)	11.91	H(42)	0.2469	0.1178	−0.0997	7.7
F(8A)	0.0439 (3)	0.0123 (2)	0.0865 (2)	9.21	H(43)	0.2528	0.1422	−0.1905	8.6
C(1B)	−0.1725 (4)	0.2203 (3)	0.0964 (3)	4.6 (1)	H(44)	0.1843	0.2296	−0.2306	9.7
C(2B)	−0.2380 (4)	0.1933 (3)	0.1018 (3)	5.2 (2)	H(45)	0.1137	0.2954	−0.1843	10.2
C(3B)	−0.3211 (4)	0.1669 (3)	0.1056 (3)	4.9 (1)	H(46)	0.1092	0.2741	−0.0929	8.6
C(4B)	−0.3764 (5)	0.1412 (3)	0.0613 (3)	5.7 (2)	C(51)	0.2670 (4)	0.2148 (3)	0.0234 (3)	5.2 (2)
C(5B)	−0.4551 (5)	0.1150 (4)	0.0655 (3)	6.8 (2)	C(52)	0.2703 (5)	0.2238 (3)	0.0785 (3)	6.3 (2)
C(6B)	−0.4773 (5)	0.1163 (4)	0.1144 (3)	7.0 (2)	C(53)	0.3451 (5)	0.2448 (4)	0.1131 (4)	7.5 (2)
C(7B)	−0.4264 (5)	0.1404 (4)	0.1587 (3)	7.0 (2)	C(54)	0.4149 (6)	0.2587 (4)	0.0929 (4)	8.1 (2)
C(8B)	−0.3484 (5)	0.1668 (3)	0.1538 (3)	5.8 (2)	C(55)	0.4129 (6)	0.2530 (4)	0.0378 (4)	8.2 (2)
F(4B)	−0.3546 (3)	0.1396 (2)	0.0123 (2)	7.96	C(56)	0.3383 (5)	0.2301 (3)	0.0036 (3)	6.7 (2)
F(5B)	−0.5038 (3)	0.0896 (3)	0.0209 (2)	10.29	H(52)	0.2208	0.2142	0.0926	7.3
F(6B)	−0.5536 (3)	0.0894 (3)	0.1183 (2)	11.25	H(53)	0.3476	0.2498	0.1511	8.5
F(7B)	−0.4500 (3)	0.1424 (3)	0.2071 (2)	10.53	H(54)	0.4654	0.2733	0.1169	9.1
F(8B)	−0.2984 (3)	0.1901 (2)	0.1990 (2)	8.51	H(55)	0.4620	0.2637	0.0237	9.2
C(1C)	−0.0351 (4)	0.2702 (3)	0.1739 (3)	4.4 (1)	H(56)	0.3361	0.2248	−0.0343	7.7
C(2C)	−0.0188 (4)	0.2650 (3)	0.2225 (3)	4.8 (1)	C(61)	0.1915 (4)	0.0975 (3)	−0.0079 (3)	4.7 (1)
C(3C)	0.0042 (4)	0.2641 (3)	0.2814 (3)	4.9 (1)	C(62)	0.1250 (5)	0.0568 (4)	−0.0241 (3)	6.9 (2)
C(4C)	−0.0327 (5)	0.3049 (4)	0.3125 (3)	6.4 (2)	C(63)	0.1374 (6)	−0.0077 (4)	−0.0207 (3)	8.1 (2)
C(5C)	−0.0122 (6)	0.3047 (4)	0.3692 (4)	7.9 (2)	C(64)	0.2167 (5)	−0.0306 (4)	0.0005 (3)	7.2 (2)
C(6C)	0.0412 (6)	0.2628 (4)	0.3948 (4)	7.4 (2)	C(65)	0.2843 (5)	0.0084 (4)	0.0181 (3)	6.9 (2)
C(7C)	0.0797 (5)	0.2208 (4)	0.3683 (4)	7.3 (2)	C(66)	0.2715 (5)	0.0732 (4)	0.0144 (3)	6.2 (2)
C(8C)	0.0606 (5)	0.2218 (4)	0.3106 (3)	6.3 (2)	H(62)	0.0696	0.0734	−0.0386	7.9
F(4C)	−0.0884 (4)	0.3475 (2)	0.2869 (2)	10.12	H(63)	0.0912	−0.0358	−0.0328	9.1
F(5C)	−0.0520 (5)	0.3460 (3)	0.3971 (2)	13.12	H(64)	0.2253	−0.0743	0.0032	8.2
F(6C)	0.0592 (5)	0.2589 (3)	0.4507 (2)	12.75	H(65)	0.3394	−0.0086	0.0329	7.9
F(7C)	0.1349 (4)	0.1781 (3)	0.3931 (2)	11.35	H(66)	0.3179	0.1011	0.0266	7.2
F(8C)	0.0984 (3)	0.1804 (2)	0.2833 (2)	8.60	C(71)	−0.2340 (4)	0.3666 (3)	0.1024 (3)	5.1 (2)
C(1D)	0.0443 (4)	0.3089 (3)	0.0819 (2)	4.5 (1)	C(72*)^c	−0.3035 (9)	0.4025 (7)	0.0667 (6)	7.1 (4)
C(2D)	0.1063 (4)	0.3353 (3)	0.0718 (3)	5.3 (2)	C(72)^c	−0.3003 (11)	0.3318 (8)	0.0739 (7)	6.4 (5)
C(3D)	0.1788 (4)	0.3696 (3)	0.0602 (3)	4.8 (1)	C(73*)^c	−0.3847 (11)	0.4084 (8)	0.0845 (7)	8.9 (5)
C(4D)	0.2473 (5)	0.3857 (4)	0.1002 (3)	6.5 (2)	C(73)^c	−0.3807 (13)	0.3323 (9)	0.0887 (8)	8.2 (5)
C(5D)	0.3196 (6)	0.4169 (4)	0.0881 (4)	7.9 (2)	C(74)	−0.3892 (7)	0.3769 (5)	0.1351 (4)	10.2 (3)
C(6D)	0.3191 (5)	0.4316 (4)	0.0357 (4)	7.2 (2)	C(75*)^c	−0.3273 (11)	0.3534 (9)	0.1652 (7)	7.2 (5)
C(7D)	0.2527 (5)	0.4156 (3)	−0.0050 (3)	6.1 (2)	C(75)^c	−0.3140 (13)	0.3848 (10)	0.1738 (8)	7.0 (5)
C(8D)	0.1839 (4)	0.3846 (3)	0.0077 (3)	5.1 (2)	C(76*)^c	−0.2474 (9)	0.3453 (8)	0.1482 (6)	6.0 (3)
F(4D)	0.2482 (3)	0.3731 (3)	0.1523 (2)	10.81	C(76)^c	−0.2369 (11)	0.3845 (9)	0.1557 (7)	5.8 (4)
F(5D)	0.3864 (4)	0.4311 (4)	0.1277 (2)	14.79	H(72*)^c	−0.2960	0.4205	0.0333	8.1
F(6D)	0.3892 (3)	0.4605 (3)	0.0238 (2)	11.72	H(72)^c	−0.2943	0.3109	0.0415	7.4
F(7D)	0.2558 (3)	0.4285 (2)	−0.0571 (2)	9.19	H(73*)^c	−0.4313	0.4307	0.0630	9.9
F(8D)	0.1196 (3)	0.3702 (2)	−0.0340 (2)	8.08	H(73)^c	−0.4291	0.3123	0.0668	9.2
C(1E)	−0.0952 (4)	0.2516 (3)	0.0097 (3)	4.5 (1)	H(74)	−0.4414	0.3783	0.1479	11.2
C(2E)	−0.1120 (4)	0.2444 (3)	−0.0391 (3)	5.2 (2)	H(75*)^c	−0.3374	0.3369	0.1985	8.2
C(3E)	−0.1482 (5)	0.2378 (3)	−0.0973 (3)	5.9 (2)	H(75)^c	−0.3172	0.3986	0.2093	8.0
C(4E)	−0.1106 (7)	0.2679 (5)	−0.1359 (4)	8.2 (2)	H(76*)^c	−0.2001	0.3240	0.1700	7.0
C(5E)	−0.1478 (7)	0.2599 (5)	−0.1938 (4)	8.9 (2)	H(76)^c	−0.1864	0.3995	0.1794	6.8
C(6E)	−0.2109 (7)	0.2239 (4)	−0.2062 (4)	8.4 (2)	C(81)	−0.0716 (4)	0.4245 (3)	0.1266 (3)	4.8 (1)
C(7E)	−0.2537 (6)	0.1946 (5)	−0.1735 (4)	7.9 (2)	C(82)	−0.1083 (5)	0.4834 (4)	0.1225 (3)	7.3 (2)
C(8E)	−0.2176 (6)	0.2028 (4)	−0.1164 (4)	6.6 (2)	C(83)	−0.0677 (6)	0.5325 (5)	0.1540 (4)	8.8 (2)
F(4E)	−0.0443 (4)	0.3052 (3)	−0.1204 (2)	11.64	C(84)	0.0079 (6)	0.5221 (4)	0.1900 (3)	7.8 (2)
F(5E)	−0.1049 (6)	0.2906 (4)	−0.2275 (3)	17.04	C(85)	0.0452 (5)	0.4649 (4)	0.1951 (3)	7.1 (2)
F(6E)	−0.2446 (6)	0.2161 (3)	−0.2618 (2)	17.39	C(86)	0.0053 (4)	0.4158 (3)	0.1630 (3)	5.6 (2)
F(7E)	−0.3206 (4)	0.1587 (3)	−0.1883 (3)	13.46	H(82)	−0.1614	0.4899	0.0975	8.3
F(8E)	−0.2579 (3)	0.1737 (2)	−0.0821 (2)	8.25	H(83)	−0.0926	0.5729	0.1510	9.8
C(11)	−0.2037 (5)	0.0361 (3)	0.2079 (3)	5.7 (2)	H(84)	0.0352	0.5554	0.2118	8.8
C(12)	−0.2366 (5)	0.0262 (4)	0.1528 (3)	6.7 (2)	H(85)	0.0982	0.4588	0.2203	8.1
C(13)	−0.3135 (5)	−0.0012 (4)	0.1334 (4)	7.9 (2)	H(86)	0.0309	0.3756	0.1662	6.6
C(14)	−0.3662 (7)	−0.0191 (4)	0.1686 (4)	9.4 (2)	C(91)	−0.1442 (4)	0.3970 (3)	0.0156 (3)	4.9 (1)
C(15)	−0.3362 (7)	−0.0088 (5)	0.2236 (4)	10.0 (3)	C(92*)^c	−0.0808 (9)	0.4418 (7)	0.0071 (6)	5.8 (3)
C(16)	−0.2554 (5)	0.0166 (4)	0.2435 (4)	7.8 (2)	C(92)^c	−0.0827 (11)	0.4033 (8)	−0.0106 (7)	5.4 (4)

Table II (*Continued*)

Atom	*x*	*y*	*z*	B,[b] Å^2	Atom	*x*	*y*	*z*	B,[b] Å^2
H(12)	−0.2025	0.0388	0.1277	7.7	C(93*)[c]	−0.0844 (10)	0.4653 (9)	−0.0444 (7)	7.5 (4)
H(13)	−0.3329	−0.0078	0.0953	8.9	C(93)[c]	−0.0919 (13)	0.4314 (9)	−0.0635 (8)	6.4 (5)
H(14)	−0.4208	−0.0375	0.1553	10.4	C(94)	−0.1593 (6)	0.4470 (4)	−0.0867 (4)	8.4 (2)
H(15)	−0.3714	−0.0208	0.2482	11.0	C(95*)[c]	−0.2103 (10)	0.4028 (8)	−0.0814 (7)	7.5 (4)
H(16)	−0.2347	0.0224	0.2816	8.8	C(95)[c]	−0.2358 (13)	0.4397 (9)	−0.0637 (8)	7.0 (5)
C(21)	−0.0952 (4)	0.0935 (3)	0.2999 (3)	5.5 (2)	C(96*)[c]	−0.2032 (8)	0.3779 (7)	−0.0269 (5)	5.6 (3)
C(22)	−0.1368 (5)	0.1469 (4)	0.3119 (3)	6.5 (2)	C(96)[c]	−0.2306 (11)	0.4142 (8)	−0.0111 (6)	5.5 (4)
C(23)	−0.1338 (5)	0.1641 (4)	0.3655 (3)	7.0 (2)	H(92*)[c]	−0.0364	0.4554	0.0363	6.8
C(24)	−0.0888 (5)	0.1314 (4)	0.4070 (4)	7.8 (2)	H(92)[c]	−0.0278	0.3898	0.0087	6.4
C(25)	−0.0439 (6)	0.0778 (4)	0.3974 (4)	8.7 (2)	H(93*)[c]	−0.0420	0.4943	−0.0500	8.5
C(26)	−0.0500 (5)	0.0591 (4)	0.3433 (3)	7.5 (2)	H(93)[c]	−0.0468	0.4381	−0.0824	7.4
H(22)	−0.1681	0.1710	0.2826	7.5	H(94)	−0.1684	0.4646	−0.1223	9.4
H(23)	−0.1633	0.2003	0.3734	8.0	H(95*)[c]	−0.2523	0.3898	−0.1121	8.5
H(24)	−0.0869	0.1445	0.4435	8.8	H(95)[c]	−0.2911	0.4521	−0.0830	8.0
H(25)	−0.0116	0.0544	0.4269	9.7	H(96*)[c]	−0.2425	0.3470	−0.0203	6.6
H(26)	−0.0214	0.0223	0.3358	8.5	H(96)[c]	−0.2782	0.4086	0.0059	6.5

[a] Esd's, shown in parentheses, are right adjusted to the last digit of the preceding number. They are derived from the inverse of the least-squares matrix from the last cycle in which that particular parameter was varied. [b] For anisotropic thermal parameters of the heavier atoms (i.e., Rh, Ag, P, F), see Table III. [c] Two phenyl rings are subject to disorder about their C(P bonded)· · ·C(para) axes. Resulting occupancies: 0.5546 (79) for atoms C(72*), C(73*), C(75*), C(76*), H(72*), H(73*), H(75*), H(76*), C(92*), C(93*), C(95*), C(96*), H(92*), H(93*), H(95*), H(96*); 0.4454 (79) for the corresponding nonstarred atoms.

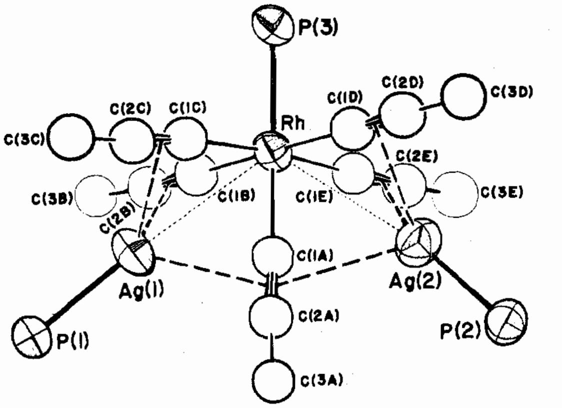

Figure 1. $RhAg_2(C{\equiv}C{-}C)_5(P)_3$ "core" of the molecule, showing the octahedral coordination about the rhodium atom and the tetrahedral coordination about the silver atoms [**ORTEP** diagram, 50% ellipsoids].

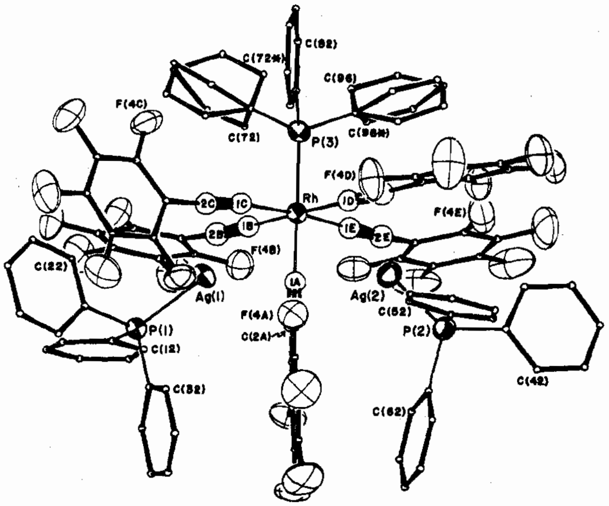

Figure 2. Entire $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ molecule [**ORTEP** diagram, 30% vibration ellipsoids for Rh, Ag, P, F, and alkynyl C atoms, with phenyl C atoms artificially reduced to spheres of radius 0.07 Å]. The six heavy atoms have been given a harlequinesque appearance so as to show clearly.

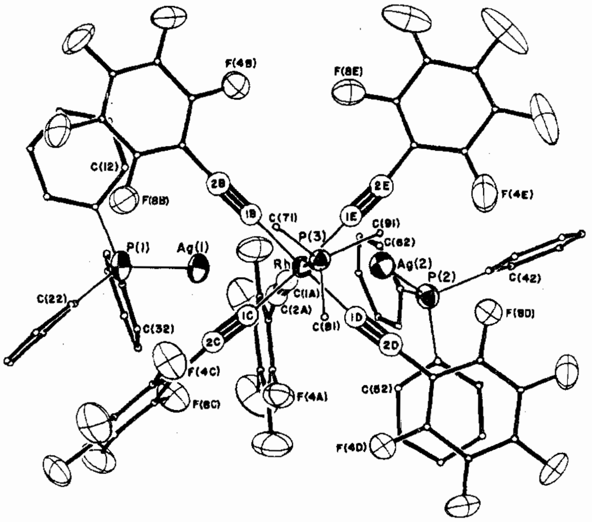

Figure 3. $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ molecule viewed from a direction slightly displaced from its pseudo-C_4 axis. Only the α-carbon atoms attached to P(3) are shown [**ORTEP** diagram, conditions as for Figure 2].

C(3x) through C(8x); fluorine atoms are numbered identically with their attached carbon atoms. Phenyl groups of the triphenylphosphine ligands are labeled cyclically as C(10*n* + 1) through C(10*n* + 6) (*n* = 1-9), where atom C(10*n* + 1) is linked to a phosphorus atom.

The three metal atoms are present in a bent arrangement such that ∠[Ag(1)···Rh···Ag(2)] is 110.55 (2)°. The central rhodium atom is bonded to one PPh_3 ligand and to five σ-($C{\equiv}CC_6F_5$) ligands. Each silver atom is linked to one PPh_3 ligand and participates in unsymmetrical π linkages [i.e., $d(\text{Ag–C}(1x)) \neq d(\text{Ag–C}(2x))$] to three acetylenic residues.

The metal atoms appear to be present in their most common oxidation states (i.e., Rh(III) and Ag(I)), there being no direct metal–metal bonds. Evidence favoring this description (rather than the alternative structure with metal–metal bonds, which would be based on Rh(V) and Ag(0)) is as follows.

(i) The rhodium–silver distances, Rh···Ag(1) = 3.1021 (8) Å and Rh···Ag(2) = 3.0871 (8) Å, are considerably longer than might be expected for rhodium–silver single bonds [ca. 2.790 Å, based upon $(\text{Rh–Rh})_{\text{min}}$ = 2.690 Å and $(\text{Ag–Ag})_{\text{min}}$ = 2.889 Å in the pure metals].[9]

(ii) In the absence of metal–metal bonding, the Rh(III) atom has its expected regular octahedral coordination geometry and the Ag(I) atoms each have a typical tetrahedral coordination geometry. This seems very reasonable.

(iii) If metal–metal bonding is assumed to be present, then the metal atoms each have both unusual oxidation states

Table III. Anisotropic Thermal Parameters[a,b] for the Heavier Atoms in $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
Rh	3.79 (3)	4.00 (3)	4.16 (3)	−0.07 (2)	0.91 (2)	0.57 (2)	0.208, 0.220, 0.243
Ag(1)	7.28 (4)	4.89 (3)	6.45 (3)	−0.05 (3)	2.55 (3)	1.77 (2)	0.208, 0.288, 0.322
Ag(2)	5.36 (3)	7.08 (4)	6.26 (3)	1.39 (3)	2.04 (3)	0.30 (3)	0.230, 0.280, 0.318
P(1)	8.01 (13)	4.31 (10)	5.55 (11)	0.73 (9)	3.36 (10)	0.99 (8)	0.211, 0.239, 0.337
P(2)	5.30 (10)	5.59 (10)	4.66 (10)	0.64 (8)	1.53 (8)	0.10 (8)	0.230, 0.252, 0.279
P(3)	4.21 (9)	4.09 (9)	4.70 (9)	−0.22 (7)	0.78 (7)	0.38 (7)	0.220, 0.231, 0.252
F(4A)	8.7 (3)	7.8 (3)	6.8 (2)	−1.1 (2)	0.1 (2)	−1.1 (2)	0.26, 0.33, 0.36
F(5A)	7.1 (3)	16.6 (5)	12.0 (4)	0.7 (3)	−2.2 (3)	−0.6 (4)	0.26, 0.44, 0.47
F(6A)	13.6 (5)	16.6 (5)	13.0 (4)	10.5 (4)	0.8 (4)	3.4 (4)	0.22, 0.43, 0.57
F(7A)	20.0 (6)	4.7 (3)	11.2 (4)	3.1 (3)	3.6 (4)	−0.1 (2)	0.23, 0.37, 0.51
F(8A)	9.2 (3)	6.0 (2)	11.2 (3)	−1.4 (2)	−0.8 (3)	−0.7 (2)	0.25, 0.33, 0.42
F(4B)	7.5 (3)	9.4 (3)	6.9 (2)	0.1 (2)	1.2 (2)	0.5 (2)	0.29, 0.31, 0.35
F(5B)	7.2 (3)	12.7 (4)	9.9 (3)	−2.4 (3)	−0.7 (2)	−1.5 (3)	0.26, 0.39, 0.42
F(6B)	5.7 (3)	13.6 (4)	15.2 (4)	−3.5 (3)	3.8 (3)	0.7 (3)	0.21, 0.43, 0.44
F(7B)	9.4 (3)	14.2 (4)	9.7 (3)	−1.4 (3)	5.8 (3)	−0.4 (3)	0.24, 0.39, 0.43
F(8B)	8.2 (3)	10.1 (3)	7.7 (3)	−1.4 (2)	2.7 (2)	−2.4 (2)	0.28, 0.31, 0.39
F(4C)	13.0 (4)	8.7 (3)	9.3 (3)	4.5 (3)	3.7 (3)	−0.4 (2)	0.25, 0.35, 0.45
F(5C)	18.3 (6)	13.1 (4)	9.1 (3)	1.7 (4)	5.6 (4)	−4.0 (3)	0.25, 0.44, 0.49
F(6C)	17.5 (5)	15.8 (5)	4.4 (2)	−5.7 (4)	1.0 (3)	−0.7 (3)	0.23, 0.38, 0.54
F(7C)	11.9 (4)	11.6 (4)	8.7 (3)	1.8 (3)	−2.2 (3)	3.2 (3)	0.24, 0.41, 0.45
F(8C)	9.3 (3)	8.3 (3)	7.9 (3)	3.4 (2)	1.0 (2)	0.1 (2)	0.26, 0.32, 0.40
F(4D)	9.7 (3)	16.3 (5)	6.1 (3)	−4.9 (3)	0.8 (2)	0.9 (3)	0.28, 0.30, 0.50
F(5D)	9.6 (4)	24.5 (7)	9.6 (4)	−9.1 (4)	0.4 (3)	−2.5 (4)	0.24, 0.37, 0.60
F(6D)	8.1 (3)	14.2 (4)	13.9 (4)	−5.0 (3)	4.8 (3)	1.4 (3)	0.21, 0.43, 0.47
F(7D)	8.3 (3)	11.7 (3)	8.5 (3)	1.3 (3)	3.8 (2)	3.7 (3)	0.25, 0.32, 0.43
F(8D)	7.0 (3)	10.6 (3)	6.5 (2)	−1.0 (2)	1.0 (2)	0.6 (2)	0.28, 0.29, 0.37
F(4E)	11.2 (4)	14.5 (5)	10.2 (4)	1.4 (4)	4.3 (3)	4.8 (3)	0.28, 0.37, 0.48
F(5E)	23.0 (8)	20.9 (7)	9.2 (4)	7.4 (6)	7.8 (5)	7.3 (4)	0.25, 0.44, 0.63
F(6E)	30.1 (9)	14.7 (5)	5.0 (3)	10.8 (6)	−1.9 (4)	−1.2 (3)	0.24, 0.34, 0.70
F(7E)	14.6 (5)	9.0 (4)	13.1 (5)	3.6 (3)	−5.7 (4)	−3.7 (3)	0.29, 0.30, 0.58
F(8E)	7.6 (3)	7.0 (3)	9.4 (3)	0.3 (2)	0.0 (2)	−1.0 (2)	0.29, 0.30, 0.38

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å². They enter the expression for the structure factor in the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] See footnote *a* to Table II. [c] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

[Rh(V) and Ag(0)] and unusual coordination geometries [cis bicapped octahedral for Rh(V) and monocapped tetrahedral, which could also be described as very distorted trigonal bipyramidal, for Ag(0)]. This seems unreasonable.

(iv) The angles P(1)–Ag(1)···Rh and P(2)–Ag(2)···Rh have values of 175.83 (6) and 155.56 (5)°. (This can be seen clearly in Figure 3.) If there were direct rhodium–silver linkages, one would expect these angles to be equivalent.

It seems, therefore, that the $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ molecule is zwitterionic and consists of $[(PPh_3)Rh^{III}(C{\equiv}CC_6F_5)_5]^{2-}$ and $[(PPh_3)Ag^{I}]^+$ ions, which are held together only by silver–acetylene π bonding.

The two independent silver–phosphorus bond lengths are Ag(1)–P(1) = 2.3877 (19) Å and Ag(2)–P(2) = 2.3903 (19) Å. These distances are each considerably shorter than the sum of the appropriate covalent radii (r(P) = 1.10 Å and r(Ag) = 1.52 Å,[10] suggesting Ag–P = 2.62 Å), presumably due to d_π–d_π M→P back-donation, and are at the low end of the range found previously for Ag(I)–P(sp^3) linkages—cf. Ag–P = 2.490 (4) Å in $[Ag(PMe_3)(C{\equiv}CPh)]_\infty$,[11] 2.465 (4)–2.492 (3) Å in $[Ag(PPh_3)_2]_3Al(O_2C_2S_2)_3$,[12] 2.455 (2)–2.480 (2) Å in $[Ag(PPh_3)_2]_3Fe(O_2C_2S_2)_3$,[12] 2.455 (5)–2.466 (5) Å in $[Ag(PPh_3)I]_4$,[13] 2.438 (2) Å in $[Ag(PEt_3)I]_4$,[14] 2.411 (3)–2.412 (3) Å in $[Ag[P(OMe)_3]_2NO_3]_2$,[15] and 2.372 (3)–2.386 (3) Å in $[Ag(PPh_3)Cl]_4$.[13]

The rhodium–phosphorus distance Rh–P(3) = 2.3431 (18) Å is again contracted from the expected single-bond distance (2.42 Å, based upon covalent radii of 1.32 Å for Rh(III),[16] and 1.10 Å for P(sp^3)[10]) and is similar to values found for other Rh(III)–P(sp^3) linkages—i.e., 2.350 (4) Å in $RhI_2Me(PPh_3)_2{\cdot}C_6H_6$[17] and 2.332 (4)–2.344 (4) Å in $RhHCl(SiCl_3)(PPh_3)_2{\cdot}xSiHCl_3$.[18]

For the purpose of subsequent discussion it is covenient now to define two symbols. The first, σ(ext), is an *external* estimate of the esd of any one individual measurement and is defined by eq 1, where χ_i is the *i*th of *N* "equivalent" measurements

$$\sigma(\text{ext}) = [\Sigma(\chi_i - \bar{\chi})^2/(N-1)]^{1/2} \tag{1}$$

and $\bar{\chi}$ is the average of the *N* measurements. The second, σ(aver), is an external estimate of the esd associated with the averaged value and is defined in eq 2. The former defines

$$\sigma(\text{aver}) = [\Sigma(\chi_i - \bar{\chi})^2/N(N-1)]^{1/2} \tag{2}$$

the width of the (presumed) gaussian distribution of independent values while the latter defines the precision with which the center of that distribution is known. The two quantities are, of course, related by $\sigma(\text{aver}) = N^{-1/2}\sigma(\text{ext})$.

The five rhodium–carbon σ-bond lengths are Rh–C(1A) = 2.039 (6) Å, Rh–C(1B) = 2.004 (7) Å, Rh–C(1C) = 2.030 (7) Å, Rh–C(1D) = 2.019 (6) Å, and Rh–C(1E) = 2.017 (7) Å. The average value is 2.022 Å (σ(ext) = 0.013 Å, σ(aver) = 0.006 Å) and is indistinguishable from the distance predicted as the sum of the appropriate covalent radii (2.01 Å, based on r(Rh(III)) = 1.32 Å[16] and r(C(sp)) = 0.69 Å[19]). Note that the rhodium atom has idealized local symmetry of C_{4v}. The Rh–C(1A) bond is thus group theoretically not equivalent to the other four Rh–C σ linkages. However, the axial Rh–C(1A) distance of 2.039 (6) Å is only 0.021 Å (i.e., ca. 2.5 σ) longer than the average value of 2.018 Å (σ(ext) = 0.011 Å, σ(aver) = 0.006 Å) for the four equatorial Rh–C σ bonds.

The rhodium atom is in a fairly regular octahedral coordination environment with angles between mutually cis ligands ranging from 84.9 (2) to 94.3 (3)° and angles between mutually trans ligands ranging from 173.8 (2) to 177.1 (3)°.

The silver–acetylene π linkages are highly asymmetric and interatomic distances vary widely with Ag–C(1x) = 2.334 (6)–2.636 (6) Å and Ag–C(2x) = 2.600 (7)–3.117 (6) Å. Even the silver–(midpoint of acetylene) distances show considerable variation, with Ag(1)–M(A)[20] = 2.642 Å,

Table IV. Interatomic Distances (Å) with Esd's[a] for $\mathrm{RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3}$

Atoms	Dist	Atoms	Dist
(A) Metal-Metal Distances			
Rh· · ·Ag(1)	3.1021 (8)	Ag(1)· · ·Ag(2)	5.0870 (12)
Rh· · ·Ag(2)	3.0871 (8)		
(B) Metal-Phosphorus Distances			
Rh-P(3)	2.3431 (18)	Ag(2)-P(2)	2.3903 (19)
Ag(1)-P(1)	2.3877 (19)		
(C) Rhodium-Carbon Distances			
Rh-C(1A)	2.039 (6)	Rh-C(1D)	2.019 (6)
Rh-C(1B)	2.004 (7)	Rh-C(1E)	2.017 (7)
Rh-C(1C)	2.030 (7)		
(D) Silver-Carbon Distances			
Ag(1)-C(1A)	2.528 (6)	Ag(2)-C(1A)	2.636 (6)
Ag(1)-C(2A)	2.882 (6)	Ag(2)-C(2A)	3.117 (6)
Ag(1)-C(1B)	2.484 (6)	Ag(2)-C(1D)	2.636 (6)
Ag(1)-C(2B)	2.794 (7)	Ag(2)-C(2D)	2.986 (7)
Ag(1)-C(1C)	2.505 (6)	Ag(2)-C(1E)	2.334 (6)
Ag(1)-C(2C)	2.698 (7)	Ag(2)-C(2E)	2.600 (7)
Ag(1)-M(A)[b]	2.642	Ag(2)-M(A)[b]	2.822
Ag(1)-M(B)[b]	2.572	Ag(2)-M(D)[b]	2.751
Ag(1)-M(C)[b]	2.534	Ag(2)-M(E)[b]	2.306
(E) Phosphorus-Carbon Distances			
P(1)-C(11)	1.793 (8)	P(2)-C(61)	1.809 (7)
P(1)-C(21)	1.808 (7)	P(3)-C(71)	1.821 (7)
P(1)-C(31)	1.822 (8)	P(3)-C(81)	1.824 (7)
P(2)-C(41)	1.814 (7)	P(3)-C(91)	1.832 (7)
P(2)-C(51)	1.806 (7)		
(F) Carbon-Fluorine Distances			
C(4A)-F(4A)	1.322 (8)	C(7C)-F(7C)	1.331 (9)
C(5A)-F(5A)	1.354 (10)	C(8C)-F(8C)	1.339 (8)
C(6A)-F(6A)	1.377 (10)	C(4D)-F(4D)	1.330 (8)
C(7A)-F(7A)	1.317 (10)	C(5D)-F(5D)	1.328 (9)
C(8A)-F(8A)	1.323 (9)	C(6D)-F(6D)	1.361 (9)
C(4B)-F(4B)	1.344 (8)	C(7D)-F(7D)	1.344 (8)
C(5B)-F(5B)	1.336 (8)	C(8D)-F(8D)	1.336 (7)
C(6B)-F(6B)	1.367 (9)	C(4E)-F(4E)	1.317 (10)
C(7B)-F(7B)	1.340 (9)	C(5E)-F(5E)	1.362 (11)
C(8B)-F(8B)	1.337 (8)	C(6E)-F(6E)	1.395 (11)
C(4C)-F(4C)	1.341 (8)	C(7E)-F(7E)	1.304 (10)
C(5C)-F(5C)	1.365 (9)	C(8E)-F(8E)	1.330 (8)
C(6C)-F(6C)	1.372 (9)		
(G) Acetylenic C≡C Distances			
C(1A)-C(2A)	1.218 (8)	C(1D)-C(2D)	1.206 (8)
C(1B)-C(2B)	1.225 (8)	C(1E)-C(2E)	1.204 (8)
C(1C)-C(2C)	1.196 (8)		
(H) C(sp)-C(sp^2) Distances			
C(2A)-C(3A)	1.430 (9)	C(2D)-C(3D)	1.450 (10)
C(2B)-C(3B)	1.460 (9)	C(2E)-C(3E)	1.460 (9)
C(2C)-C(3C)	1.444 (9)		
(I) C-C C_6F_5 Distances			
C(3A)-C(4A)	1.369 (9)	C(6A)-C(7A)	1.321 (13)
C(4A)-C(5A)	1.397 (11)	C(7A)-C(8A)	1.426 (12)
C(5A)-C(6A)	1.335 (11)	C(8A)-C(3A)	1.379 (11)
C(3B)-C(4B)	1.379 (9)	C(6B)-C(7B)	1.336 (10)
C(4B)-C(5B)	1.396 (10)	C(7B)-C(8B)	1.393 (10)
C(5B)-C(6B)	1.343 (10)	C(8B)-C(3B)	1.364 (9)
C(3C)-C(4C)	1.381 (9)	C(6C)-C(7C)	1.342 (11)
C(4C)-C(5C)	1.388 (10)	C(7C)-C(8C)	1.413 (10)
C(5C)-C(6C)	1.312 (10)	C(8C)-C(3C)	1.375 (9)
C(3D)-C(4D)	1.361 (9)	C(6D)-C(7D)	1.351 (9)
C(4D)-C(5D)	1.418 (10)	C(7D)-C(8D)	1.374 (9)
C(5D)-C(6D)	1.349 (10)	C(8D)-C(3D)	1.372 (9)
C(3E)-C(4E)	1.396 (12)	C(6E)-C(7E)	1.326 (12)
C(4E)-C(5E)	1.457 (12)	C(7E)-C(8E)	1.438 (11)
C(5E)-C(6E)	1.255 (11)	C(8E)-C(3E)	1.339 (10)
(J) C-C C_6H_5 Distances			
C(11)-C(12)	1.388 (9)	C(14)-C(15)	1.380 (12)
C(12)-C(13)	1.353 (10)	C(15)-C(16)	1.388 (11)
C(13)-C(14)	1.390 (11)	C(16)-C(11)	1.396 (10)
C(21)-C(22)	1.389 (9)	C(24)-C(25)	1.403 (12)
C(22)-C(23)	1.381 (9)	C(25)-C(26)	1.397 (10)
C(23)-C(24)	1.335 (10)	C(26)-C(21)	1.386 (10)
C(31)-C(32)	1.341 (9)	C(34)-C(35)	1.325 (12)
C(32)-C(33)	1.435 (11)	C(35)-C(36)	1.441 (13)
C(33)-C(34)	1.334 (12)	C(36)-C(31)	1.374 (10)
C(41)-C(42)	1.401 (10)	C(44)-C(45)	1.337 (12)
C(42)-C(43)	1.397 (10)	C(45)-C(46)	1.389 (11)
C(43)-C(44)	1.352 (11)	C(46)-C(41)	1.377 (10)
C(51)-C(52)	1.384 (9)	C(54)-C(55)	1.380 (11)
C(52)-C(53)	1.393 (10)	C(55)-C(56)	1.399 (10)
C(53)-C(54)	1.344 (11)	C(56)-C(51)	1.368 (9)
C(61)-C(62)	1.368 (9)	C(64)-C(65)	1.360 (10)
C(62)-C(63)	1.400 (10)	C(65)-C(66)	1.410 (10)
C(63)-C(64)	1.356 (10)	C(66)-C(61)	1.381 (9)
C(71)-C(72)	1.367 (18)	C(74)-C(75)	1.384 (23)
C(72)-C(73)	1.403 (24)	C(75)-C(76)	1.392 (24)
C(73)-C(74)	1.536 (21)	C(76)-C(71)	1.400 (18)
C(71)-C(72*)	1.484 (15)	C(74)-C(75*)	1.217 (18)
C(72*)-C(73*)	1.458 (20)	C(75*)-C(76*)	1.434 (21)
C(73*)-C(74)	1.451 (17)	C(76*)-C(71)	1.293 (15)
C(81)-C(82)	1.389 (10)	C(84)-C(85)	1.358 (10)
C(82)-C(83)	1.395 (11)	C(85)-C(86)	1.397 (10)
C(83)-C(84)	1.363 (10)	C(86)-C(81)	1.379 (9)
C(91)-C(92)	1.292 (17)	C(94)-C(95)	1.460 (22)
C(92)-C(93)	1.435 (22)	C(95)-C(96)	1.412 (23)
C(93)-C(94)	1.159 (18)	C(96)-C(91)	1.446 (18)
C(91)-C(92*)	1.440 (15)	C(94)-C(95*)	1.275 (16)
C(92*)-C(93*)	1.375 (18)	C(95*)-C(96*)	1.446 (19)
C(93*)-C(94)	1.473 (20)	C(96*)-C(91)	1.330 (14)
(K) Distances between Disordered Positions[c]			
C(72)· · ·C(72*)	1.53 (2)	C(75)· · ·C(75*)	0.73 (2)
C(73)· · ·C(73*)	1.64 (2)	C(76)· · ·C(76*)	0.87 (2)
C(92)· · ·C(92*)	0.94 (2)	C(95)· · ·C(95*)	1.03 (2)
C(93)· · ·C(93*)	0.86 (2)	C(96)· · ·C(96*)	1.01 (2)
C(72*)· · ·C(96)	2.48 (2)	C(72)· · ·C(96*)	3.37 (2)
C(72*)· · ·C(96*)	3.14 (2)	C(72)· · ·C(96)	3.14 (2)

[a] Esd's, shown in parentheses, are right adjusted to the last digit of the preceding number. Their calculation, using the Fortran IV program **STAN1** by B. G. DeBoer, included the effects of uncertainties in unit cell parameters, as well as all correlation coefficients of magnitude greater than 0.075. No corrections have been applied for the effects of thermal motion. [b] M(A) is the midpoint of the acetylenic linkage C(1A)-C(2A), M(B) is the midpoint of C(2A)-C(2B), etc. [c] Minimum distances of these positions to C(82) and C(86) are C(82)· · ·C(76) = 3.18 (2) Å and C(82)· · ·C(92*) = 3.14 (2) Å. All others are >3.5 Å.

Ag(1)–M(B) = 2.572 Å, Ag(1)–M(C) = 2.534 Å, Ag(2)–M(A) = 2.822 Å, Ag(2)–M(D) = 2.751 Å, and Ag(2)–M(E) = 2.396 Å.

Atom Ag(1) is in a fairly regular (but trigonally distorted) tetrahedral coordination environment with P(1)–Ag(1)–M(x) angles ranging from 123.34 to 129.62° and M(x)–Ag(1)–M(x') angles varying from 83.30 to 93.75°. The coordination geometry around Ag(2) is far less regular, with P(2)–Ag(2)–M(A) = 108.75°, P(2)–Ag(2)–M(D) = 113.76°, P(2)–Ag(2)–M(E) = 148.99°, M(A)–Ag(2)–M(D) = 81.77°, M(D)–Ag(2)–M(E) = 89.40°, and M(E)–Ag(2)–M(A) = 94.20°.

Table V. Interatomic Angles (deg) with Esd's[a] for $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$

Atoms	Angle	Atoms	Angle
(A) Angles at Rhodium			
P(3)-Rh-C(1B)	93.3 (2)	C(1A)-Rh-C(1B)	91.7 (3)
P(3)-Rh-C(1C)	91.6 (2)	C(1A)-Rh-C(1C)	84.9 (2)
P(3)-Rh-C(1D)	86.7 (2)	C(1A)-Rh-C(1D)	88.5 (3)
P(3)-Rh-C(1E)	92.0 (2)	C(1A)-Rh-C(1E)	91.9 (2)
P(3)-Rh-C(1A)	173.8 (2)	C(1B)-Rh-C(1C)	88.6 (3)
C(1B)-Rh-C(1D)	177.1 (3)	C(1C)-Rh-C(1D)	94.3 (3)
C(1C)-Rh-C(1E)	175.1 (3)	C(1D)-Rh-C(1E)	89.3 (3)
		C(1E)-Rh-C(1B)	87.9 (3)
Ag(1)-Rh-Ag(2)	110.55 (2)	P(3)-Rh-Ag(1)	126.95 (5)
		P(3)-Rh-Ag(2)	122.26 (5)
Ag(1)-Rh-C(1A)	54.3 (2)	Ag(2)-Rh-C(1A)	57.6 (2)
Ag(1)-Rh-C(1B)	53.1 (2)	Ag(2)-Rh-C(1D)	57.7 (2)
Ag(1)-Rh-C(1C)	53.6 (2)	Ag(2)-Rh-C(1E)	49.1 (2)
(B) Angles at Silver			
Rh-Ag(1)-P(1)	175.83 (6)	Rh-Ag(2)-P(2)	155.56 (5)
P(1)-Ag(1)-C(1A)	136.34 (15)	P(2)-Ag(2)-C(1A)	120.69 (14)
P(1)-Ag(1)-C(1B)	138.63 (16)	P(2)-Ag(2)-C(1D)	124.82 (15)
P(1)-Ag(1)-C(1C)	143.24 (16)	P(2)-Ag(2)-C(1E)	163.47 (17)
P(1)-Ag(1)-C(2A)	111.89 (14)	P(2)-Ag(2)-C(2A)	98.65 (13)
P(1)-Ag(1)-C(2B)	112.81 (15)	P(2)-Ag(2)-C(2D)	103.78 (14)
P(1)-Ag(1)-C(2C)	117.00 (15)	P(2)-Ag(2)-C(2E)	135.98 (17)
P(1)-Ag(1)-M(A)[b]	123.34	P(2)-Ag(2)-M(A)	108.75
P(1)-Ag(1)-M(B)	124.96	P(2)-Ag(2)-M(D)	113.76
P(1)-Ag(1)-M(C)	129.62	P(2)-Ag(2)-M(E)	148.99
M(A)-Ag(1)-M(B)	93.75	M(A)-Ag(2)-M(D)	81.77
M(B)-Ag(1)-M(C)	89.79	M(D)-Ag(2)-M(E)	89.40
M(C)-Ag(1)-M(A)	83.30	M(E)-Ag(2)-M(A)	94.20
(C) Angles at Phosphorus			
Ag(1)-P(1)-C(11)	112.1 (3)	Ag(2)-P(2)-C(41)	115.2 (2)
Ag(1)-P(1)-C(21)	114.1 (2)	Ag(2)-P(2)-C(51)	111.1 (2)
Ag(1)-P(1)-C(31)	115.1 (2)	Ag(2)-P(2)-C(61)	117.1 (2)
C(11)-P(1)-C(21)	104.9 (3)	C(41)-P(2)-C(51)	105.2 (3)
C(21)-P(1)-C(31)	104.9 (3)	C(51)-P(2)-C(61)	103.2 (3)
C(31)-P(1)-C(11)	104.6 (3)	C(61)-P(2)-C(41)	103.6 (3)
Rh-P(3)-C(71)	115.8 (2)	C(71)-P(3)-C(81)	101.2 (3)
Rh-P(3)-C(81)	116.6 (2)	C(81)-P(3)-C(91)	101.9 (3)
Rh-P(3)-C(91)	113.8 (2)	C(91)-P(3)-C(71)	105.7 (3)
(D) Angles at Acetylenic Carbon			
Rh-C(1A)-C(2A)	171.2 (6)	C(1A)-C(2A)-C(3A)	169.6 (7)
Rh-C(1B)-C(2B)	177.4 (7)	C(1B)-C(2B)-C(3B)	174.0 (8)
Rh-C(1C)-C(2C)	171.3 (6)	C(1C)-C(2C)-C(3C)	174.9 (7)
Rh-C(1D)-C(2D)	174.8 (6)	C(1D)-C(2D)-C(3D)	177.3 (9)
Rh-C(1E)-C(2E)	178.3 (8)	C(1E)-C(2E)-C(3E)	169.7 (8)
Ag(1)-C(1A)-Ag(2)	160.2 (3)	Ag(1)-C(2A)-Ag(2)	115.9 (2)
Ag(1)-M(A)-Ag(2)	137.2		
(E) Exterior Angles for C_6F_5 Groups			
C(2A)-C(3A)-C(4A)	120.6 (6)	C(2A)-C(3A)-C(8A)	120.8 (7)
C(2B)-C(3B)-C(4B)	122.4 (6)	C(2B)-C(3B)-C(8B)	121.1 (6)
C(2C)-C(3C)-C(4C)	121.4 (7)	C(2C)-C(3C)-C(8C)	123.3 (6)
C(2D)-C(3D)-C(4D)	122.0 (6)	C(2D)-C(3D)-C(8D)	121.3 (6)
C(2E)-C(3E)-C(4E)	120.7 (8)	C(2E)-C(3E)-C(8E)	122.4 (7)
C(3A)-C(4A)-F(4A)	120.5 (6)	C(3A)-C(8A)-F(8A)	120.0 (7)
C(3B)-C(4B)-F(4B)	120.3 (7)	C(3B)-C(8B)-F(8B)	120.4 (7)
C(3C)-C(4C)-F(4C)	118.6 (7)	C(3C)-C(8C)-F(8C)	118.8 (7)
C(3D)-C(4D)-F(4D)	120.9 (7)	C(3D)-C(8D)-F(8D)	120.4 (6)
C(3E)-C(4E)-F(4E)	120.6 (9)	C(3E)-C(8E)-F(8E)	120.5 (8)
C(5A)-C(4A)-F(4A)	117.6 (7)	C(7A)-C(8A)-F(8A)	117.9 (7)
C(5B)-C(4B)-F(4B)	117.6 (7)	C(7B)-C(8B)-F(8B)	117.5 (7)
C(5C)-C(4C)-F(4C)	118.8 (7)	C(7C)-C(8C)-F(8C)	119.1 (7)
C(5D)-C(4D)-F(4D)	117.5 (7)	C(7D)-C(8D)-F(8D)	116.6 (6)
C(5E)-C(4E)-F(4E)	119.9 (9)	C(7E)-C(8E)-F(8E)	116.0 (8)
C(4A)-C(5A)-F(5A)	119.0 (8)	C(8A)-C(7A)-F(7A)	119.0 (8)
C(4B)-C(5B)-F(5B)	118.4 (7)	C(8B)-C(7B)-F(7B)	119.3 (7)
C(4C)-C(5C)-F(5C)	119.2 (8)	C(8C)-C(7C)-F(7C)	118.1 (8)
C(4D)-C(5D)-F(5D)	120.5 (8)	C(8D)-C(7D)-F(7D)	121.1 (7)
C(4E)-C(5E)-F(5E)	114.1 (10)	C(8E)-C(7E)-F(7E)	119.2 (9)
C(6A)-C(5A)-F(5A)	122.0 (9)	C(6A)-C(7A)-F(7A)	123.7 (8)
(E) (*Continued*)			
C(6B)-C(5B)-F(5B)	123.6 (8)	C(6B)-C(7B)-F(7B)	121.9 (8)
C(6C)-C(5C)-F(5C)	121.2 (9)	C(6C)-C(7C)-F(7C)	123.8 (8)
C(6D)-C(5D)-F(5D)	120.9 (8)	C(6D)-C(7D)-F(7D)	119.9 (7)
C(6E)-C(5E)-F(5E)	128.6 (11)	C(6E)-C(7E)-F(7E)	126.8 (11)
C(5A)-C(6A)-F(6A)	118.2 (9)	C(7A)-C(6A)-F(6A)	118.3 (9)
C(5B)-C(6B)-F(6B)	117.5 (8)	C(7B)-C(6B)-F(6B)	119.9 (8)
C(5C)-C(6C)-F(6C)	121.2 (9)	C(7C)-C(6C)-F(6C)	116.4 (8)
C(5D)-C(6D)-F(6D)	118.7 (8)	C(7D)-C(6D)-F(6D)	119.9 (8)
C(5E)-C(6E)-F(6E)	116.3 (10)	C(7E)-C(6E)-F(6E)	114.7 (10)
(F) Interior Angles of C_6F_5 Groups			
C(4A)-C(3A)-C(8A)	116.2 (7)	C(5A)-C(6A)-C(7A)	123.5 (9)
C(4B)-C(3B)-C(8B)-	116.4 (7)	C(5B)-C(6B)-C(7B)	122.5 (8)
C(4C)-C(3C)-C(8C)	115.3 (7)	C(5C)-C(6C)-C(7C)	122.4 (9)
C(4D)-C(3D)-C(8D)	116.6 (7)	C(5D)-C(6D)-C(7D)	121.3 (8)
C(4E)-C(3E)-C(8E)	117.0 (8)	C(5E)-C(6E)-C(7E)	128.9 (12)
C(3A)-C(4A)-C(5A)	121.9 (7)	C(3A)-C(8A)-C(7A)	122.1 (7)
C(3B)-C(4B)-C(5B)	122.2 (7)	C(3B)-C(8B)-C(7B)	122.1 (7)
C(3C)-C(4C)-C(5C)	122.5 (8)	C(3C)-C(8C)-C(7C)	122.1 (7)
C(3D)-C(4D)-C(5D)	121.6 (7)	C(3D)-C(8D)-C(7D)	122.9 (6)
C(3E)-C(4E)-C(5E)	119.4 (10)	C(3E)-C(8E)-C(7E)	123.6 (8)
C(4A)-C(5A)-C(6A)	118.9 (9)	C(6A)-C(7A)-C(8A)	117.3 (8)
C(4B)-C(5B)-C(6B)	118.0 (7)	C(6B)-C(7B)-C(8B)	118.7 (8)
C(4C)-C(5C)-C(6C)	119.5 (9)	C(6C)-C(7C)-C(8C)	118.2 (8)
C(4D)-C(5D)-C(6D)	118.5 (8)	C(6D)-C(7D)-C(8D)	119.0 (7)
C(4E)-C(5E)-C(6E)	117.2 (11)	C(6E)-C(7E)-C(8E)	113.9 (10)
(G) Exterior Angles of C_6H_5 Groups			
P(1)-C(11)-C(12)	119.6 (6)	P(1)-C(11)-C(16)	124.3 (6)
P(1)-C(21)-C(22)	118.8 (5)	P(1)-C(21)-C(26)	123.6 (6)
P(1)-C(31)-C(32)	118.3 (6)	P(1)-C(31)-C(36)	121.6 (7)
P(2)-C(41)-C(42)	122.7 (6)	P(2)-C(41)-C(46)	118.9 (6)
P(2)-C(51)-C(52)	117.5 (5)	P(2)-C(51)-C(56)	124.7 (6)
P(2)-C(61)-C(62)	118.9 (5)	P(2)-C(61)-C(66)	123.2 (5)
P(3)-C(71)-C(72*)	118.5 (7)	P(3)-C(71)-C(76*)	122.5 (8)
P(3)-C(71)-C(72)	119.5 (9)	P(3)-C(71)-C(76)	117.8 (9)
P(3)-C(81)-C(82)	117.9 (6)	P(3)-C(81)-C(86)	123.8 (5)
P(3)-C(91)-C(92*)	116.6 (7)	P(3)-C(91)-C(96*)	123.9 (8)
P(3)-C(91)-C(92)	123.4 (9)	P(3)-C(91)-C(96)	117.4 (8)
(H) Interior Angles of C_6H_5 Groups			
C(12)-C(11)-C(16)	116.1 (7)	C(13)-C(14)-C(15)	117.4 (10)
C(22)-C(21)-C(26)	117.6 (7)	C(23)-C(24)-C(25)	120.6 (9)
C(32)-C(31)-C(36)	120.1 (8)	C(33)-C(34)-C(35)	126.5 (12)
C(42)-C(41)-C(46)	118.4 (7)	C(43)-C(44)-C(45)	122.6 (10)
C(52)-C(51)-C(56)	117.8 (7)	C(53)-C(54)-C(55)	120.4 (9)
C(62)-C(61)-C(66)	117.9 (7)	C(63)-C(64)-C(65)	120.8 (9)
C(72*)-C(71)-C(76*)	118.6 (10)	C(73*)-C(74)-C(75*)	123.6 (15)
C(72)-C(71)-C(76)	118.3 (12)	C(73)-C(74)-C(75)	114.0 (15)
C(82)-C(81)-C(86)	118.3 (7)	C(83)-C(84)-C(85)	121.3 (9)
C(92*)-C(91)-C(96*)	119.1 (10)	C(93*)-C(94)-C(95*)	124.0 (12)
C(92)-C(91)-C(96)	119.1 (11)	C(93)-C(94)-C(95)	121.9 (15)
C(11)-C(12)-C(13)	123.2 (8)	C(11)-C(16)-C(15)	120.8 (9)
C(21)-C(22)-C(23)	120.6 (7)	C(21)-C(26)-C(25)	121.9 (8)
C(31)-C(32)-C(33)	122.6 (8)	C(31)-C(36)-C(35)	118.2 (9)
C(41)-C(42)-C(43)	119.6 (8)	C(41)-C(46)-C(45)	121.0 (8)
C(51)-C(52)-C(53)	121.0 (0)	C(51)-C(56)-C(55)	121.6 (8)
C(61)-C(62)-C(63)	121.7 (8)	C(61)-C(66)-C(65)	120.6 (7)
C(71)-C(72*)-C(73*)	117.2 (13)	C(71)-C(76*)-C(75*)	122.7 (14)
C(71)-C(72)-C(73)	120.3 (16)	C(71)-C(76)-C(75)	121.1 (16)
C(81)-C(82)-C(83)	120.7 (8)	C(81)-C(86)-C(85)	120.8 (7)
C(91)-C(92*)-C(93*)	119.3 (13)	C(91)-C(96*)-C(95*)	123.0 (13)
C(91)-C(92)-C(93)	124.7 (15)	C(91)-C(96)-C(95)	113.3 (15)
C(12)-C(13)-C(14)	120.8 (9)	C(14)-C(15)-C(16)	121.6 (10)
C(22)-C(23)-C(24)	121.4 (8)	C(24)-C(25)-C(26)	117.8 (9)
C(32)-C(33)-C(34)	114.5 (9)	C(34)-C(35)-C(36)	118.0 (11)
C(42)-C(43)-C(44)	119.3 (9)	C(44)-C(45)-C(46)	119.2 (10)
C(52)-C(53)-C(54)	120.3 (9)	C(54)-C(55)-C(56)	118.9 (9)
C(62)-C(63)-C(64)	119.4 (9)	C(64)-C(65)-C(66)	119.6 (8)
C(72*)-C(73*)-C(74)	115.8 (14)	C(74)-C(75*)-C(76*)	121.3 (17)
C(72)-C(73)-C(74)	115.7 (16)	C(74)-C(75)-C(76)	117.7 (18)
C(82)-C(83)-C(84)	119.4 (9)	C(84)-C(85)-C(86)	119.5 (8)
C(92*)-C(93*)-C(94)	116.5 (14)	C(94)-C(95*)-C(96*)	116.7 (14)
C(92)-C(93)-C(94)	119.5 (18)	C(94)-C(95)-C(96)	121.3 (16)

[a] See footnote *a* of Table IV. [b] M(x) is the average position of C(1x) and C(2x), i.e., the midpoint of the acetylenic bond in the $C{\equiv}CC_6F_5$ ligand labeled x.

Table VI. Atomic Deviations from, and Angles between Least-Squares Planes in $RhAg_2(C\equiv CC_6F_5)_5(PPh_3)_3$[a]

Atom	Dev, Å	Atom	Dev, Å
Plane I: $-0.48080X + 0.87369Y - 0.07416Z = 5.4971$			
Rh*	0.0239 (5)	P(3)	2.363 (2)
C(1B)*	0.025 (7)	C(1D)*	0.023 (6)
C(2B)	0.024 (7)	C(2D)	0.037 (7)
C(3B)	0.165 (7)	C(3D)	0.119 (7)
C(1C)*	−0.035 (6)	C(1E)*	−0.036 (6)
C(2C)	−0.224 (7)	C(2E)	−0.077 (7)
C(3C)	−0.375 (7)	C(3E)	0.036 (8)
Ag(1)	−1.7384 (6)	Ag(2)	−1.7134 (6)
Plane II: $0.02879X + 0.12864Y + 0.99127Z = 2.9113$			
Rh*	−0.0083 (5)	C(1B)*	−0.056 (7)
P(3)*	0.059 (2)	C(2B)	−0.029 (7)
C(1A)*	0.067 (6)	C(3B)	−0.048 (7)
C(2A)	0.269 (7)	C(1D)*	−0.061 (6)
C(3A)	0.611 (6)	C(2D)	−0.202 (7)
Ag(1)	1.6454 (6)	C(3D)	−0.355 (7)
Ag(2)	−2.0425 (6)		
Plane III: $0.88675X + 0.45707Y - 0.06899Z = 1.1409$			
Rh*	−0.0127 (5)	C(1C)*	−0.077 (6)
P(3)*	0.073 (2)	C(2C)	−0.206 (7)
C(1A)*	0.089 (6)	C(3C)	−0.262 (7)
C(2A)	0.250 (7)	C(1E)*	−0.072 (6)
C(3A)	0.666 (6)	C(2E)	−0.072 (7)
Ag(1)	−1.8513 (6)	C(3E)	−0.280 (8)
Ag(2)	1.5877 (6)		
Plane IV: $0.71708X + 0.30912Y + 0.62469Z = 2.0878$			
Rh*	0.0000 (5)	P(3)	−0.179 (2)
Ag(1)*	0.0000 (6)	P(1)	−0.105 (2)
Ag(2)*	0.0000 (6)	P(2)	0.866 (2)
C(1A)	0.372 (6)	C(1B)	−1.476 (7)
C(2A)	0.769 (7)	C(1C)	1.320 (6)
C(3A)	1.460 (6)	C(1D)	1.418 (6)
F(6A)	3.536 (7)	C(1E)	−1.389 (6)

Dihedral Angles, Deg

I-II	88.57	II-III	89.09	II-IV	47.18
I-III	91.25	I-IV	96.95	III-IV	42.77

Atom	Dev, Å	Atom	Dev, Å
Plane A: $-0.50566X - 0.26273Y + 0.82176Z = 1.5430$			
C(4A)*	−0.006 (7)	F(4A)*	0.034 (5)
C(5A)*	0.013 (9)	F(5A)*	0.005 (6)
C(6A)*	−0.011 (10)	F(6A)*	−0.032 (7)
C(7A)*	−0.002 (8)	F(7A)*	0.050 (6)
C(8A)*	−0.019 (8)	F(8A)*	0.003 (5)
C(3A)*	−0.035 (6)	C(2A)	−0.142 (7)
Ag(1)	2.1544 (6)	C(1A)	−0.293 (6)
Ag(2)	−2.9173 (6)	Rh	−0.4510 (5)
Plane B: $-0.40689X + 0.88581Y - 0.22312Z = 4.9079$			
C(4B)*	0.011 (7)	F(4B)*	0.003 (5)
C(5B)*	0.009 (8)	F(5B)*	−0.011 (5)
C(6B)*	0.011 (8)	F(6B)*	−0.020 (6)
C(7B)*	−0.006 (8)	F(7B)*	0.023 (6)
C(8B)*	0.009 (7)	F(8B)*	−0.023 (5)
C(3B)*	−0.006 (7)	C(2B)	−0.027 (7)
Ag(1)	−1.9014 (6)	C(1B)	0.080 (7)
Ag(2)	−1.0543 (6)	Rh	0.2395 (5)
Plane C: $0.76979X + 0.63819Y + 0.01168Z = 2.6287$			
C(4C)*	−0.009 (8)	F(4C)*	−0.011 (5)
C(5C)*	0.028 (9)	F(5C)*	0.004 (7)
C(6C)*	0.012 (9)	F(6C)*	−0.029 (6)
C(7C)*	0.006 (9)	F(7C)*	0.003 (6)
C(8C)*	0.000 (8)	F(8C)*	−0.003 (5)
C(3C)*	−0.002 (7)	C(2C)	−0.052 (7)
Ag(1)	−2.1162 (6)	C(1C)	0.002 (6)
Ag(2)	0.8963 (6)	Rh	−0.1158 (5)
Plane D: $-0.46175X + 0.88131Y + 0.10043Z = 5.9787$			
C(4D)*	−0.000 (8)	F(4D)*	0.007 (6)
C(5D)*	0.001 (9)	F(5D)*	−0.028 (7)
C(6D)*	0.029 (9)	F(6D)*	0.004 (6)
C(7D)*	0.015 (8)	F(7D)*	−0.017 (5)
C(8D)*	−0.005 (7)	F(8D)*	−0.008 (5)
C(3D)*	0.003 (7)	C(2D)	−0.058 (7)
Ag(1)	−1.5003 (6)	C(1D)	−0.053 (6)
Ag(2)	−2.1036 (6)	Rh	−0.0528 (5)

Atom	Dev, Å	Atom	Dev, Å
Plane E: $-0.61501X + 0.78848Y + 0.00793Z = 5.1761$			
C(4E)*	−0.016 (10)	F(4E)*	0.021 (6)
C(5E)*	0.017 (11)	F(5E)*	0.004 (8)
C(6E)*	−0.019 (10)	F(6E)*	−0.010 (8)
C(7E)*	0.014 (10)	F(7E)*	0.010 (7)
C(8E)*	−0.006 (9)	F(8E)*	0.011 (5)
C(3E)*	−0.026 (8)	C(2E)	−0.071 (7)
Ag(1)	−1.0626 (6)	C(1E)	0.053 (6)
Ag(2)	−1.8634 (6)	Rh	0.2430 (5)
Plane Ph1: $-0.41872X + 0.90495Y - 0.07576Z = 2.1220$			
C(11)*	0.004 (7)	C(14)*	−0.001 (10)
C(12)*	0.014 (8)	C(15)*	0.018 (11)
C(13)*	−0.015 (9)	C(16)*	−0.019 (9)
P(1)	0.051 (2)	Ag(1)	1.5981 (6)
Plane Ph2: $0.83819X + 0.54481Y - 0.02490Z = -1.6667$			
C(21)*	0.001 (7)	C(24)*	−0.002 (9)
C(22)*	0.013 (8)	C(25)*	0.016 (10)
C(23)*	−0.012 (8)	C(26)*	−0.015 (8)
P(1)	0.035 (2)	Ag(1)	1.5517 (6)
Plane Ph3: $-0.28528X - 0.20308Y + 0.93668Z = 5.7013$			
C(31)*	0.001 (7)	C(34)*	−0.014 (11)
C(32)*	−0.009 (9)	C(35)*	0.006 (11)
C(33)*	0.015 (10)	C(36)*	0.001 (10)
P(1)	0.036 (2)	Ag(1)	−1.8083 (6)
Plane Ph4: $0.79605X + 0.51916Y + 0.31109Z = 4.1035$			
C(41)*	−0.005 (7)	C(44)*	−0.006 (10)
C(42)*	−0.006 (8)	C(45)*	−0.005 (10)
C(43)*	0.012 (9)	C(46)*	0.011 (9)
P(2)	0.011 (2)	Ag(2)	−1.0492 (6)
Plane Ph5: $-0.30435X + 0.93840Y - 0.16367Z = 2.9981$			
C(51)*	−0.013 (7)	C(54)*	−0.013 (9)
C(52)*	0.018 (8)	C(55)*	0.016 (9)
C(53)*	−0.004 (9)	C(56)*	−0.003 (8)
P(2)	−0.153 (2)	Ag(2)	1.1862 (6)
Plane Ph6: $-0.40781X + 0.01152Y + 0.91300Z = -1.3978$			
C(61)*	−0.014 (7)	C(64)*	−0.002 (8)
C(62)*	0.011 (8)	C(65)*	−0.001 (8)
C(63)*	−0.003 (9)	C(66)*	0.009 (8)
P(2)	−0.071 (2)	Ag(2)	1.4047 (6)
Plane Ph7*: $0.22388X + 0.85514Y + 0.46757Z = 6.9878$			
C(71)*	−0.029 (7)	C(74)*	−0.054 (11)
C(72*)*	0.016 (15)	C(75*)*	0.042 (19)
C(73*)*	0.020 (17)	C(76*)*	0.004 (15)
P(3)	0.086 (2)	Rh	−1.4104 (5)
Plane Ph7: $-0.08843X + 0.88070Y - 0.46534Z = 5.9739$			
C(71)*	0.176 (7)	C(74)*	0.232 (11)
C(72)*	−0.079 (18)	C(75)*	−0.147 (21)
C(73)*	−0.118 (20)	C(76)*	−0.064 (18)
P(3)	0.159 (2)	Rh	−1.8700 (5)
Plane Ph8: $-0.66114X - 0.23226Y + 0.71341Z = 1.2811$			
C(81)*	−0.001 (7)	C(84)*	0.003 (9)
C(82)*	0.006 (8)	C(85)*	0.003 (8)
C(83)*	−0.007 (10)	C(86)*	−0.004 (7)
P(3)	0.021 (2)	Rh	−0.0264 (5)
Ag(1)	2.4121 (6)	Ag(2)	−2.6415 (6)
Plane Ph9*: $-0.65396X + 0.72399Y + 0.21948Z = 7.7795$			
C(91)*	0.036 (7)	C(94)*	0.074 (10)
C(92*)*	−0.001 (14)	C(95*)*	−0.039 (17)
C(93*)*	−0.051 (17)	C(96*)*	−0.020 (14)
P(3)	−0.052 (2)	Rh	−2.1971 (5)
Plane Ph9: $0.07878X + 0.91090Y + 0.40503Z = 7.7199$			
C(91)*	0.023 (7)	C(94)*	0.010 (10)
C(92)*	−0.026 (17)	C(95)*	−0.011 (20)
C(93)*	0.009 (20)	C(96)*	−0.003 (17)
P(3)	0.022 (2)	Rh	−1.7491 (5)

Dihedral Angles, Deg

Ph7*-Ph7	58.95	Ph9*-Ph9	45.82

[a] Equations of planes are expressed in the orthonormal (Å) coordinate system given by $X = xa + zc \cos\beta$, $Y = yb$, and $Z = zc \sin\beta$. Atoms marked by an asterisk were assigned unit weight; all others were given zero weight. Estimated standard deviations for atom-to-plane distances are approximated by $[(a^2\sigma^2(x) + b^2\sigma^2(y) + c^2\sigma^2(z))/3]^{1/2}$ for the atom involved.

Table VII

A. Torsion about C(1x)–C(2x) Bonds

System	Angle,[a] deg	System	Angle,[a] deg
Rh–C(1A)–C(2A)–C(3A)	+32.13	Rh–C(1D)–C(2D)–C(3D)	−94.87
Rh–C(1B)–C(2B)–C(3B)	−112.66	Rh–C(1E)–C(2E)–C(3E)	+149.56
Rh–C(1C)–C(2C)–C(3C)	−158.79		

B. Resolved Deviations of Atoms from C(1x)–C(2x) Line

	∥ dev[b]		⊥ dev[b]	
Defining plane	C(3x)	Rh	C(3x)	Rh
Ag(1)–C(1A)–C(2A)	+0.107 Å (4.33°)	−0.042 Å (1.18°)	+0.234 Å (9.43°)	+0.309 Å (8.70°)
Ag(1)–C(1B)–C(2B)	+0.140 Å (5.50°)	−0.067 Å (1.92°)	+0.062 Å (2.43°)	+0.063 Å (1.81°)
Ag(1)–C(1C)–C(2C)	+0.128 Å (5.07°)	−0.297 Å (8.41°)	+0.013 Å (0.52°)	+0.082 Å (2.31°)
Ag(2)–C(1A)–C(2A)	−0.054 Å (2.21°)	+0.106 Å (3.02°)	+0.252 Å (10.13°)	+0.293 Å (8.25°)
Ag(2)–C(1D)–C(2D)	+0.054 Å (2.14°)	−0.121 Å (3.46°)	+0.040 Å (1.57°)	+0.139 Å (3.95°)
Ag(2)–C(1E)–C(2E)	+0.259 Å (10.21°)	−0.047 Å (1.34°)	−0.034 Å (1.34°)	+0.037 Å (1.05°)

[a] Angles are defined looking down C≡C from Rh toward C(3x) and defining a counterclockwise (right-handed) rotation from Rh to C(3x) as positive. [b] Values below are the deviations of atoms from the C(1x)–C(2x) line resolved into components parallel with and perpendicular to the appropriate Ag(1 or 2)–C(1x)–C(2x) plane. The sign conventions are as follows: for "parallel deviations" a positive sign indicates displacement away from the appropriate silver atom; for "perpendicular deviations" the deviation of the rhodium atom is arbitrarily assigned a positive sign.

It should be noted that the acetylenic grouping labeled "A" is the only one which is coordinated to each of the two silver atoms; the angle at this acetylene, ∠Ag(1)–M(A)–Ag(2), is 137.2°.

Simultaneous metal–alkynyl σ bonding and alkynyl→metal' π bonding are not a common phenomenon, but they have also been shown to occur in such species as $[(PhC{\equiv}C)Ag(PMe_3)]_\infty$,[11] $[(PhC{\equiv}C)Cu(PMe_3)]_4$,[21] $[PhC{\equiv}CCu]_\infty$,[22] $[(\pi\text{-}C_5H_5)Fe(CO)_2(C{\equiv}CPh)CuCl]_2$,[23,24] and $Ir_2Cu_4(PPh_3)_2(C{\equiv}CPh)_8$.[1,2]

The acetylenic linkages, C(1x)≡C(2x), range from 1.196 (8) to 1.225 (8) Å, the average value being 1.210 Å [σ(ext) = 0.012 Å, σ(aver) = 0.005 Å]. This value is not significantly different from the accepted distance of 1.202 ± 0.005 Å[25] for a free (i.e., noncoordinated) acetylenic linkage. Each of the acetylenic skeletons (defined by Rh–C(1x)–C(2x)–C(3x)) is distorted slightly from linearity; Rh–C(1x)–C(2x) angles range from 171.2 (6) to 178.3 (8)°, whereas C(1x)–C(2x)–C(3x) angles vary from 169.6 (7) to 177.3 (9)°. The bending is, in each case, fairly small and torsional angles in the Rh–C(1x)–C(2x)–C(3x) systems vary widely (see Table VII). To a first approximation, however, the system Rh–C(1A)–C(2A)–C(3A) is a cis-bent system (observed torsional angle +32.13°, idealized cis-bent angle 0°) while the other four systems have a slightly "trans-bent" geometry (idealized torsional angle 180°, observed values being −94.87, −112.66, +149.56, and −158.79°). Table VIIB shows the bending of substituents on the acetylenic fragments broken down into components in the plane of the silver–acetylene interaction ("∥ dev") and perpendicular to this plane ("⊥ dev"). It is interesting to note that in no case does the silver–acetylene interaction force a cis bending of the acetylene within the Ag–C(1x)–C(2x) plane. This result is contrary to all previous studies on species with isolated metal–acetylene interactions[26] and suggests that the observed torsional conformations of the Rh–C(1x)–C(2x)–C(3x) moieties are probably sterically, rather than electronically, enforced.

The C(2x)–C(3x) linkages range from 1.430 (9) to 1.460 (9) Å, averaging 1.449 Å (σ(ext) = 0.013 Å, σ(aver) = 0.006 Å). This value is in good agreement with, but is more accurate than, the documented C(sp)–C(sp^2) single-bond distance of 1.45 ± 0.02 Å.[25]

As may be seen in Table VI, each of the C_6F_5 systems is approximately planar, *maximum* deviations of atoms from their appropriate least-squares plane being 0.050 Å for an atom in plane A, 0.023 Å for plane B, 0.029 Å for plane C, 0.028 Å for plane D, and 0.026 Å for plane E. Both carbon–carbon and carbon–fluorine distances appear to show systematic fluctuations as a function of their position within the C_6F_5 system. Thus, average carbon–carbon distances are C(3x)–C(ortho) = 1.372 Å (σ(ext) = 0.015 Å, σ(aver) = 0.005 Å), C(ortho)–C(meta) = 1.410 Å (σ(ext) = 0.025 Å, σ(aver) = 0.008 Å), and C(meta)–C(para) = 1.327 Å (σ(ext) = 0.028 Å, σ(aver) = 0.009 Å). We thus have C(ortho)–C(meta) > C(3x)–C(ortho) > C(meta)–C(para) by successive increments of 0.038 (9) and 0.045 (10) Å—differences that are, in each case, statistically significant. Similarly, average carbon–fluorine distances are C–F(ortho) = 1.332 Å (σ(ext) = 0.009 Å, σ(aver) = 0.003 Å), C–F(meta) = 1.338 Å (σ(ext) = 0.019 Å, σ(aver) = 0.006 Å), and C–F(para) = 1.374 Å (σ(ext) = 0.013 Å, σ(aver) = 0.006 Å).

Since the longest C–C and C–F bonds are coparallel and are along the major axes of the (almost linear) Rh—C≡C—C_6F_5 systems, it is probable that these variations appear as a result of rigid-body motion of the C_6F_5 groups. [See, also, the shapes of the thermal ellipsoids of the fluorine atoms in Figures 2 and 3.]

External angles for the C_6F_5 rings are collected in section E of Table V, while interior angles are in section F. Average interior angles are 116.3° at C(3x), 122.0° at C(ortho), 117.9° at C(meta), and 123.7° at C(para).

The triphenylphosphine groups have the expected geometry although there is disorder of two phenyl groups attached to P(3) [see Figure 2]. P–C distances range from 1.793 (8) to 1.832 (7) Å, averaging 1.814 Å (σ(ext) = 0.012 Å, σ(aver) = 0.004 Å), and the angles about phosphorus show the characteristic distortion from T_d toward C_{3v} symmetry,[27] with (Ag or Rh)–P–C = 111.1 (2)–117.1 (2)° and C–P–C = 101.2 (3)–105.7°.

Average distances within the phenyl rings (excluding any contributions from the disordered phenyl groups) are as follows: C(P bonded)–C(ortho) = 1.380 Å (σ(ext) = 0.015 Å, σ(aver) = 0.004 Å), C(ortho)–C(meta) = 1.398 Å (σ(ext) = 0.017 Å, σ(aver) = 0.005 Å), and C(meta)–C(para) = 1.358

Å (σ(ext) = 0.023 Å, σ(aver) = 0.006 Å). The order C(ortho)–C(meta) > C(P bonded)–C(ortho) > C(meta)–C(para) is precisely that found in the C_6F_5 groups (vide supra) and, again, can be explained as a systematic error induced by thermal motion of the phenyl groups. [This result, incidentally, provides excellent evidence that the treatment of phenyl groups as systems having precise D_{6h} symmetry is *not* the ideal description for the X-ray diffraction experiment.]

Intermolecular Contacts

There are no extraordinarily short intermolecular contacts, the molecules being separated by normal van der Waals distances. Shortest intermolecular contacts of each type, excluding those involving hydrogen atoms, are F(4A)···F(6E, *n*) = 2.789 (8) Å, F(7A)···C(8E, $\bar{1}$) = 3.017 (10) Å, and C(6D)···C(95, $\bar{1}$) = 3.208 (22) Å.

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Registry No. $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$, 54873-31-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reducton negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy of \$2.50 for microfiche, referring to code number AIC503935-11-75.

References and Notes

(1) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, *J. Chem. Soc., Chem. Commun.*, 858 (1972).
(2) M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, **13**, 1418 (1974).
(3) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 688 (1974).
(4) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).
(5) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(7) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(8) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(9) "International Tables for X-Ray Crystallography", Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 4.3, pp 278–285.
(10) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, Table 7–13, p 246.
(11) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **20**, 502 (1966).
(12) F. J. Hollander and D. Coucouvanis, *Inorg. Chem.*, **13**, 2381 (1974).
(13) B. K. Teo and J. C. Calabrese, *J. Am. Chem. Soc.*, **97**, 1256 (1975).
(14) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **14**, 2502 (1975).
(15) J. H. Meiners, J. C. Clardy, and J. G. Verkade, *Inorg. Chem.*, **14**, 632 (1975).
(16) See Ref 10, Table 7-15, p 249.
(17) P. G. H. Troughton and A. C. Skapski, *Chem. Commun.*, 575 (1968).
(18) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440 (1970).
(19) *Chem. Soc., Spec. Publ.*, **No. 18**, S14s–S15s (1965). This value is obtained by subtracting half of the C(sp^3)–C(sp^3) bond distance of 1.537 ± 0.005 Å from the recognized C(sp^3)–C(sp) distance of 1.459 ± 0.005 Å.
(20) M(A) is the midpoint of the acetylenic bond C(1A)–C(2A): M(B) etc. are the midpoints of the other alkynyl linkages, while M(x) represents the general case.
(21) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **21**, 957 (1966).
(22) P. W. R. Corfield and H. M. M Shearer, quoted by M. L. H. Green, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, p 275.
(23) M. I. Bruce, R. Clark, J. Howard, and P. Woodward, *J. Organomet. Chem.*, **42**, C107 (1972).
(24) R. Clark, J. Howard, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2027 (1974).
(25) See ref 22, p S15s–S16s.
(26) Structural data for acetylene complexes of transition metals have been summarized in Table VIII of B. W. Davies and N. C. Payne, *Inorg. Chem.*, **13**, 1848 (1974).
(27) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968); see Table 7.

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Crystal and Molecular Structure of Dibenzotellurophene, $C_{12}H_8Te$

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The structure of dibenzotellurophene, $C_{12}H_8Te$, has been determined by use of data collected on an automated diffractometer with monochromatized Mo Kα radiation. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions a = 12.621 (7) Å, b = 16.192 (7) Å, c = 4.637 (2) Å, and V = 947.6 (8) Å^3. The density of 1.962 (2) g cm^{-3} calculated on the basis of four molecules per unit cell agrees well with the flotation value of 1.95 (2) g cm^{-3}. The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to a conventional R index of 2.9% based on 1210 observed reflections. The dibenzotellurophene molecule is slightly folded, with dihedral angles of 1.4 (2) and 0.6 (2)° between the five-membered and the six-membered rings. The observed Te–C bond distances are 2.084 (5) and 2.089 (5) Å (average 2.087 Å) and the C–Te–C bond angle is 81.7 (2)°. The intra-ring bond distances and angles in the six-membered rings are close to those observed in dibenzoselenophene, dibenzothiophene, and dibenzofuran. Trends in the geometry of the five-membered rings in the four dibenzochalcophenes are noted.

Introduction

The crystal and molecular structures of dibenzoselenophene,[1] dibenzothiophene,[2] and dibenzofuran[3] have been reported. The present study of the structure of dibenzotellurophene was undertaken primarily as an interesting extension of that series. A second objective was a comparison of the structure of the uncombined dibenzotellurophene molecule with that of the dibenzotellurophene moiety in the diiodide.[4]

Experimental Section

Crystals of dibenzotellurophene were prepared as described earlier.[5] These were pale yellow needles elongated on the crystallographic c axis with principal faces belonging to the forms {120} and {100}. A preliminary study of two crystals by Weissenberg and precession methods showed orthorhombic symmetry with systematic absences of h00 with h odd, 0k0 with k odd, and 00l with l odd. The space group was thus indicated to be $P2_12_12_1$. A crystal fragment bounded prismatically by six faces of the forms indicated above and terminated by fractures approximating faces of the form {001} was selected for data collection. The dimensions were 0.25 mm between (120) and ($\bar{1}\bar{2}$0), 0.25 mm between ($\bar{1}$20) and (1$\bar{2}$0), 0.30 mm between (100) and ($\bar{1}$00), and 0.35 mm between the approximate (001) and (00$\bar{1}$) surfaces. The crystal was mounted with the normal to (120) approximately along the φ axis of a four-circle computer-controlled diffractometer (Syntex $P\bar{1}$ autodiffractometer) equipped with a scintillation counter and a graphite monochromator. The automatic