noanionic donor atoms, indicating that axial ligation occurs in these complexes.

Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, Canada, N6A 5B7

Studies of Metal–Acetylene Complexes. 8. Syntheses and Molecular Structures of Two Platinum Complexes Containing Bulky Phosphine Ligands

DAVID H. FARRAR and NICHOLAS C. PAYNE*

Single-crystal, three-dimensional structure determinations have been completed on two new platinum acetylene complexes of formula PtL$_2$(CF$_3$C≡CCF$_3$), where L = P(C$_6$H$_{11}$)(C$_6$H$_5$)$_2$ (1) and P(C$_6$H$_{11}$)$_2$(C$_6$H$_5$) (2). Crystals of 2 are monoclinic, space group *Cc*, with *Z* = 4 in a cell of dimensions *a* = 22.829 (5) Å, *b* = 9.757 (2) Å, *c* = 19.509 (4) Å, and *β* = 111.21 (1)°; those of 1 are also monoclinic, space group *C*2, with *Z* = 2 and cell dimensions *a* = 16.321 (3) Å, *b* = 10.870 (2) Å, *c* = 11.282 (2) Å, and *β* = 110.54 (1)°. Intensity data collected on an automated four-circle diffractometer was used for full-matrix least-squares refinement on *F*, which converged for 1 at *R* = 0.036 and 3761 observations and for 2 at *R* = 0.049 and 3979 observations. In each complex the coordination at the Pt atom is essentially planar, and the same C≡C bond distance was observed (1, 1.294 (14); 2, 1.294 (16) Å). The deviation from linearity of the acetylene upon coordination was 43.5 (5)° in 1, while values of 40 (1) and 47 (1)° were found in 2. This variation in the dicyclohexylphenylphosphine complex has been attributed to predominantly steric interactions with the bulky phosphine ligands.

Introduction

Upon coordination to a transition metal an alkyne ligand adopts a cis-bent geometry. The magnitude of the deviation from linearity is referred to as the bend-back angle. A number of bis(triphenylphosphine)(alkyne)platinum(0) complexes have undergone crystallographic analysis, and the results indicate that a bend-back angle of about 40° is normal.[1] For example, a mean value of 39.9 (5)° was found in the complex bis(triphenylphosphine)(hexafluorobut-2-yne)platinum(0).[1] Bis-(tricyclohexylphosphine)(hexafluorobut-2-yne)platinum(0) was the subject of the first reported study of an alkyne complex of platinum(0) containing a phosphine ligand other than triphenylphosphine, PPh$_3$.[2] The mean bend-back angle in the tricyclohexylphosphine, PCy$_3$, complex is 45.5 (8)°. Whether the significant increase in bend-back angle is due to an electronic or a steric effect, or a combination of both, was uncertain.[2] In an attempt to answer this question, we decided to prepare and examine the complexes containing the phosphines cyclohexyldiphenylphosphine, PCyPh$_2$, and dicyclohexylphenylphosphine, PCy$_2$Ph, which presumably possess intermediate basicity and steric bulk. Published approaches were not successful for these syntheses, and we report herein a successful synthetic procedure and the results of our structural investigations.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere by employing standard inert-atmosphere techniques. Microanalyses were performed by Spang Inc., Ann Arbor, Mich.

PCyPh$_2$ and PCy$_2$Ph were prepared by Grignard reactions on PClPh$_2$ and PCl$_2$Ph, respectively.[3] Pt(1,5-C$_8$H$_{12}$)$_2$ was synthesized

as a solution in toluene by the method reported by Stone et al.[4]

Preparation of Complexes. PtL$_2$(F$_3$CC≡CCF$_3$). The complexes with L = PCyPh$_2$ and PCy$_2$Ph were prepared by the following method. The appropriate ligand (4 g) was added to a toluene solution of Pt(1,5-C$_8$H$_{12}$)$_2$ (1 g), and hexafluorobut-2-yne (3 g) was bubbled in slowly. After the solution was stirred under a hexafluorobut-2-yne atmosphere for 12 h, the solvent was removed on a rotary evaporator. Addition of dichloromethane (15 mL) and methanol (150 mL), followed by cooling, resulted in a white crystalline precipitate.

Pt(PCyPh$_2$)$_2$(F$_3$CC≡CCF$_3$): yield, 2.1 g; mp 200–201 °C dec. Anal. Calcd for C$_{40}$H$_{42}$F$_6$P$_2$Pt: C, 53.75; H, 4.74. Found: C, 52.23; H, 4.76.

Pt(PCy$_2$Ph)$_2$(F$_3$CC≡CCF$_3$)·CCl$_2$H$_2$: yield, 2.2 g, mp 206–207 °C dec. Anal. Calcd for C$_{41}$H$_{56}$Cl$_2$F$_6$P$_2$Pt: C, 49.70; H, 5.65. Found: C, 50.23; H, 5.65.

Structure Determination. Clear, colorless, prismatic crystals of bis(cyclohexyldiphenylphosphine)(hexafluorobut-2-yne)platinum(0) were obtained by recrystallization from dichloromethane/methanol mixtures. An extensive preliminary photographic investigation, employing Weissenberg and precession techniques, showed the crystals to be monoclinic with Laue symmetry 2/*m*. The systematic absence observed, *hkl* for *h* + *k* odd, is consistent with the space groups *Cm*, *C*2, or *C*2/*m*. The observed density indicates that the unit cell contains two molecules. Thus space group *C*2/*m* was eliminated since it would impose site symmetry 2/*m* upon the molecule, which it cannot possess. In view of the nature of the complex, symmetry 2 was thought to be more favorable than symmetry *m*, and the space group *C*2 (*C*$_2^3$, No. 5)[5] was chosen. This was later confirmed by the Bijvoet method.[6] The crystal data are summarized in Table I.

(1) Davies, B. W.; Payne, N. C. *Inorg. Chem.* **1974**, *13*, 1848.
(2) Richardson, J. F.; Payne, N. C. *Can. J. Chem.* **1977**, *55*, 3203.
(3) Issleib, K.; Völker, H. *Chem. Ber.* **1961**, *94*, 392.
(4) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271.
(5) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. 1.
(6) Srinivasan, R.; Vijayalakshme, B. K. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2615.

Table I. Crystal Data

	Pt(PCyPh$_2$)$_2$-(F$_3$CC≡CCF$_3$)	Pt(PCy$_2$Ph)$_2$-(F$_3$CC≡CCF$_3$)
molecular formula	C$_{40}$H$_{42}$F$_6$P$_2$Pt	C$_{40}$H$_{54}$F$_6$P$_2$Pt
mol wt	893.81	905.90
cryst system	monoclinic	monoclinic
systematic absences	hkl for h + k odd	hkl for h + k, h0l for l odd
space group	C2	Cc
cell const		
a, Å	16.321(3)	22.829(5)
b, Å	10.870(2)	9.757(2)
c, Å	11.282(2)	19.509(4)
β, deg	110.54(1)	111.21(1)
cell vol, Å^3	1874.4	4051.3
medium for density measmt (flotation)	CCl$_4$ and heptane	CCl$_4$ and cyclohexane
density (obsd), g cm^{-3}	1.60(1)	1.49(1)
density (calcd), g cm^{-3}	1.583	1.474
Z	2	4
symmetry constraints	site symmetry 2	none
μ, cm^{-1}	37.7 for Mo Kα	31.1 for Mo Kα

The crystal chosen for data collection was mounted on a Picker FACS-1 diffractometer with [001] offset approximately 30° from coincidence with the diffractometer ϕ axis. Five standard reflections were regularly monitored during data collection. These, together with an examination of crystal mosaicity at the beginning and the end of data collection, showed no significant decomposition had occurred. Details of the parameters associated with data collection are given in Table II.

After data collection was complete, the crystal was measured for an absorption correction. Seven faces were identified as (Ī11) and forms {001}, {110}, and {Ī10}. The recorded intensities were corrected for background, Lorentz, and polarization effects, and a standard deviation $\sigma(I)$ was assigned to each intensity (I) such that $(\sigma(I)^2) = C + \frac{1}{4}(t_c/t_b)(b_1 + b_h) + (pI)^2$, when C = total counts measured in time t_c, b_1 and b_h are background counts each measured in time t_b. p was chosen as 0.03. A total of 3862 reflections was measured. Bijvoet pairs $h1l$ and $h\bar{1}l$, for $0° < 2\theta < 25°$, were recorded to assist in the determination of the space group and to aid in assigning the "hand" of the crystal. There were 3614 unique data with $I > 3\sigma(I)$ which were used in the solution and preliminary refinement of the structure.

Clear, pyramidal crystals of bis(dicyclohexylphenylphosphine)-(hexafluorobut-2-yne)platinum(0) were obtained by recrystallization from an o-dichlorobenzene and methanol mixture. Crystal data are summarized in Table I. The systematic absences observed are consistent with the space groups Cc and C2/c. With four formula units per unit cell, no symmetry constraints would be imposed upon the molecule in space group Cc, while in space group C2/c, site symmetry 2 would be imposed, which the molecule could only possses in a highly

Table II. Experimental Conditions Associated with Data Collections

	Pt(PCyPh$_2$)$_2$(F$_3$CC≡CCF$_3$)	Pt(PCy$_2$Ph)$_2$(F$_3$CC≡CCF$_3$)
radiation	Mo Kα, graphite monochromatized	Mo Kα, graphite monochromatized
wavelength, Å	0.71073	0.70926
temp, °C	22	20
approximate cryst dimens, cm	0.015 × 0.010 × 0.011	0.009 × 0.019 × 0.016
mean ω scan width at half-height, deg	0.095	0.122
no. and 2θ range of centered reflctns	30, 20° < 2θ < 30°	30, 22° < 2θ < 28°
scan range and speed	initially 1.55° corrected for dispersion, at 1° per min; scan rate increased to 2° per min for 2θ > 45°	1.20° corrected for dispersion, at 1° per min
data collected	hkl and $\bar{h}kl$, for 0° < 2θ < 65°	hkl and $\bar{h}kl$ for 0° < 2θ < 60°
bgd count time	initially 10-s stationary crystal, stationary counter at limits of scan, increased to 20 s for 2θ > 45°	initially 10-s stationary crystal, stationary counter at limits of scan, increased to 20 s for 2θ > 45°
stds	110, 1̄10, 001, 200, 022 recorded every 200 reflctns	2̄00, 1̄10, 1̄1̄1, 002, 200 recorded every 250 reflctns
no. of measd intensities	3862, 3614 with $I > 3\sigma(I)$	4467, 3218 with $I > 3\sigma(I)$

Table III. Atomic Positional and Thermal Parameters ($\times 10^4$) for Pt(PCyPh$_2$)$_2$(F$_3$CC≡CCF$_3$)

atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	1/2	1/2	0	268 (1)	261 (1)	368 (1)	0	84 (1)	0
P	4289 (1)[b]	3653 (1)	−1599 (1)	329 (6)	322 (7)	364 (7)	−10 (5)	79 (6)	−13 (6)
C(1)	4272 (6)	7698 (8)	−1512 (11)	670 (51)	453 (41)	1053 (77)	207 (37)	358 (53)	295 (48)
C(2)	4732 (4)	6779 (6)	−580 (7)	478 (32)	385 (30)	562 (39)	61 (26)	234 (30)	37 (29)
F(1)	3457 (4)	7356 (7)	−2207 (8)	558 (30)	1087 (53)	1326 (60)	359 (33)	246 (36)	587 (49)
F(2)	4174 (7)	8772 (7)	−1024 (9)	2218 (99)	558 (38)	1525 (76)	715 (55)	629 (76)	237 (47)
F(3)	4661 (5)	7913 (7)	−2360 (7)	957 (51)	902 (52)	1118 (56)	106 (39)	473 (44)	564 (45)
C(11)	4976 (5)	2574 (8)	−2059 (8)	474 (36)	513 (40)	421 (35)	53 (31)	193 (30)	−12 (32)
C(12)	4639 (6)	1540 (8)	−2818 (10)	684 (48)	476 (42)	797 (59)	−31 (38)	355 (45)	−82 (44)
C(13)	5202 (7)	787 (10)	−3226 (10)	1079 (76)	724 (60)	815 (63)	134 (58)	559 (60)	−31 (54)
C(14)	6025 (8)	1230 (12)	−3107 (13)	933 (72)	862 (78)	1245 (97)	461 (66)	664 (74)	157 (75)
C(15)	6359 (6)	2262 (13)	−2407 (10)	551 (46)	1225 (98)	701 (59)	260 (56)	325 (44)	252 (64)
C(16)	5815 (6)	3008 (9)	−1961 (9)	473 (36)	665 (51)	694 (50)	19 (35)	235 (36)	30 (43)
C(21)	3435 (4)	2750 (6)	−1303 (6)	370 (26)	369 (28)	398 (30)	−50 (22)	139 (24)	−82 (25)
C(22)	3536 (5)	1542 (8)	−925 (8)	568 (39)	464 (38)	688 (49)	9 (33)	338 (38)	−30 (36)
C(23)	2881 (6)	915 (8)	−669 (9)	918 (59)	465 (39)	854 (60)	−193 (42)	570 (52)	−158 (42)
C(24)	2100 (6)	1489 (10)	−800 (10)	721 (53)	841 (68)	880 (65)	−387 (53)	502 (51)	−306 (59)
C(25)	1991 (5)	2710 (11)	−1147 (10)	387 (34)	983 (75)	925 (67)	−117 (41)	356 (41)	−234 (60)
C(26)	2652 (5)	3331 (8)	−1392 (8)	439 (32)	557 (41)	675 (47)	45 (31)	195 (33)	−66 (38)
C(31)	3695 (5)	4441 (7)	−3119 (6)	494 (33)	544 (39)	367 (30)	49 (31)	7 (26)	57 (30)
C(32)	4287 (5)	5128 (21)	−3630 (7)	673 (35)	618 (75)	575 (35)	91 (64)	209 (30)	271 (73)
C(33)	3812 (7)	5899 (13)	−4782 (10)	929 (69)	1062 (88)	687 (58)	199 (67)	341 (54)	354 (62)
C(34)	3110 (7)	5182 (27)	−5772 (8)	1216 (75)	1101 (148)	490 (39)	441 (124)	182 (46)	217 (88)
C(35)	2556 (7)	4474 (12)	−5273 (8)	973 (72)	1001 (81)	433 (42)	89 (63)	−53 (45)	−43 (49)
C(36)	3012 (6)	3703 (10)	−4123 (8)	740 (52)	708 (58)	517 (44)	−7 (47)	−32 (40)	−121 (43)

[a] The form of the thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ (Å^2).

[b] Estimated standard deviations are given in parentheses here and in other tables and refer to the least significant digits.

strained configuration. Thus space group Cc (C_s^4, No. 9),[5] was chosen, and this choice was later confirmed by the Bijvoet method.[6]

The crystal selected for data collection was mounted with [010] offset approximately 55° from coincidence with the diffractometer ϕ axis. The experimental conditions used for data collection are given in Table II. Bijvoet pairs $h1l$ and $h\bar{1}l$, for 0° < 2θ < 35°, were recorded to aid in the space group determination. No significant crystal decomposition was observed during data collection.

The crystal was measured to permit an absorption correction. Nine faces were identified as (00$\bar{1}$), ($1\bar{1}$0), (101), ($\bar{1}$01), (011), and the forms {100} and {11$\bar{1}$}. The data were processed, and p was chosen as 0.03. Of the 4467 data collected, 3218 unique data with $I > 3\sigma(I)$ were used in the solution and preliminary refinement of the structure.

The dicyclohexylphenylphosphine complex was also recrystallized from dichloromethane/methanol mixtures. A photographic study showed the crystals to be monoclinic, and the systematic absences observed are consistent only with the space group $P2_1/c$ (C_{2h}^5, No. 14).[5] Cell dimensions $a = 10.509$ (2) Å, $b = 23.681$ (4) Å, $c = 18.835$ (3) Å, and $\beta = 111.16$ (1)° with $Z = 4$ were obtained. However, significant decomposition was observed in the X-ray beam, and only a limited number of observations could be recorded. All attempts to refine the structure in $P2_1/c$ were unsatisfactory.

Structure Solution and Refinement

Pt(PCyPh₂)(F₃CC≡CCF₃). The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques on F. Scattering factors for neutral nonhydrogen atoms were taken from Vol. IV of ref 5, while those for H were from Stewart et al.[7] The real and imaginary corrections for anomalous dispersion of Cromer and Liberman[8] were included for the P and Pt atoms.

In the early stages of refinement the phenyl rings and the cyclohexyl rings were constrained as rigid groups (D_{6h}, C–C = 1.392 Å;[9] C–C–C angles of 109.47°, C–C = 1.54 Å[10]), and isotropic thermal parameters were assigned to nongroup atoms. Two cycles of refinement with all 25 nonhydrogen atoms included gave agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.08$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.09$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, and the weight w is given by $4F_o^2/\sigma^2(F_o^2)$. The data were then corrected for absorption effects, using the analytical method.[11] Transmission coefficients varied from 0.205 to 0.311.

Structure factor calculations, using only the Bijvoet pairs, for the solved hand and its enantiomer gave agreement factors $R_1 = 0.083$, $R_2 = 0.099$ and $R_1 = 0.066$, $R_2 = 0.076$, respectively. A comparison of observed vs. calculated structure factors indicated that the chosen hand was incorrect, so the model was inverted.

The refinement of the structure went smoothly. Rigid-group restraints were removed from the three rings, and all atoms were assigned anisotropic thermal parameters. The 21 hydrogen atoms were readily located in geometrically feasible regions with electron density ranging from 0.7 (1) to 0.4 (1) e Å^{-3}. These were included in idealized positions (sp² or sp³ hybridization at C, C–H 0.95 and 1.00 Å, respectively) but not refined. After several cycles of refinement, with H atom contributions recalculated after each cycle, the model converged (3761 unique data, 221 variables) with agreement factors $R_1 = 0.036$ and $R_2 = 0.038$. In the final cycle the largest shift, 0.14 esd, was associated with the z coordinate of C(34). Of the data for which $1 < I < 3\sigma(I)$ no structure factor was in error by greater than 4.7σ. A statistical analysis of R_2 over various ranges of $|F_o|$, $\lambda^{-1} \sin\theta$ and diffractometer setting angles χ and ϕ showed no abnormal trends. Secondary extinction effects could be ignored. The error in an observation of unit weight is 1.27 electrons. The highest peak in a difference Fourier synthesis is of electron density 0.99 (12) e Å^{-3} at fractional coordinates (−0.500, 0.474, 0.065) and is of no chemical significance.

For confirmation of the choice of hand for the dissymmetric space group, the model was inverted and converged. Final agreement factors of $R_1 = 0.0365$ and $R_2 = 0.0392$ indicated that the second model could be rejected at a confidence level greater than 99.5%.[12]

Table IV. Derived Hydrogen Atom Parameters for Pt(PCyPh₂)₂(F₃CC≡CCF₃)

atom[a]	x	y	z	B, Å²
H1C(12)	4034	1341	−3062	5.36
H1C(13)	5018	−5	−3574	6.84
H1C(14)	6367	805	−3503	7.52
H1C(15)	6951	2492	−2226	6.52
H1C(16)	6013	3789	−1596	5.18
H1C(22)	4068	1132	−834	4.66
H1C(23)	2969	75	−408	5.48
H1C(24)	1643	1051	−652	6.09
H1C(25)	1462	3133	−1222	5.95
H1C(26)	2575	4173	−1626	4.78
H1C(31)	3353	5099	−2880	4.33
H1C(32)	4665	5678	−2951	5.30
H2C(32)	4661	4514	−3866	5.30
H1C(33)	3550	6630	−4515	7.33
H2C(33)	4251	6190	−5165	7.33
H1C(34)	2727	5798	−6390	7.66
H2C(34)	3387	4629	−6208	7.66
H1C(35)	2155	5051	−5044	7.07
H2C(35)	2201	3905	−5953	7.07
H1C(36)	2571	3392	−3765	6.05
H2C(36)	3304	2995	−4374	6.05

[a] H1C(12) is bonded to C(12) etc.

Final positional and thermal parameters for nonhydrogen atoms are given in Table III, and hydrogen atom parameters are given in Table VI. Structure factor amplitudes are listed in Table V as $10|F_o|$ and $10|F_c|$, in electrons.

Pt(PCy₂Ph)₂(F₃CC≡CCF₃). The y coordinate of the Pt atom was readily obtained from a three-dimensional Patterson synthesis. The origin was defined by placing the Pt atom at $x = \frac{1}{4}$ and $z = \frac{1}{4}$. A series of difference Fourier syntheses and least-squares refinements revealed the positions of the remaining 48 nonhydrogen atoms. One cycle of full-matrix least-squares refinement on F, assigning all atoms isotropic thermal parameters and constraining the two phenyl rings and the four cyclohexyl rings as rigid groups, gave agreement factors $R_1 = 0.07$ and $R_2 = 0.08$. The data were corrected for absorption effects at this stage, using the analytical method. Transmission coefficients varied from 0.203 to 0.314.

The refinement converged, varying positional and anisotropic thermal parameters for the Pt atom, the two P atoms, and the alkyne ligand, a group origin, three orientation angles, and individual thermal parameters for six groups, at agreement factors $R_1 = 0.052$ and $R_2 = 0.060$. The model was then inverted, and one cycle of refinement, under identical conditions, resulted in $R_1 = 0.043$ and $R_2 = 0.045$. Inspection of the Pt–P bond distances for the two models revealed a large polar dispersion error.[13] The values for the original and inverted models, respectively, are as follows: Pt–P(1) = 2.289, 2.295 Å; Pt–P(2) = 2.234, 2.289 Å. Both the R factors and the Pt–P bond distances indicate that the inverted model is the correct choice.

The rigid-group constraints were removed from the phenyl and cyclohexyl rings, and the 36 C atoms were refined as individual atoms with isotropic thermal parameters. H atoms were located, with electron density ranging from 0.6 (1) to 0.3 (1) e Å^{-3}. Idealized positional coordinates were computed, by assuming either sp² or sp³ geometries and C–H bond distances of 0.95 or 1.0 Å, respectively. Thereafter the contribution from the H atoms was included in the calculations of F_c. The refinement of 261 variables, with 3979 observations ($I > \sigma(I)$), converged at residuals $R_1 = 0.0487$ and $R_2 = 0.0402$. In the final cycle the largest shift, 0.03 esd, was associated with the thermal parameter β_{33} of C(1). Of the data for which $0 < I < 3\sigma(I)$ no structure factor was in error by greater than 5.3σ. A statistical analysis of the data showed no abnormal trends. Secondary extinction effects were not observed. The error in an observation of unit weight is 1.17 electrons. The highest peak in a difference Fourier synthesis is of electron density 0.89 (15) e Å^{-3} at fractional coordinates (−0.248, 0.199, 0.243) and is of no chemical significance.

Final positional and thermal parameters for the nonhydrogen atoms are given in Table VI, and H atom parameters are given in Table VII. Observed and calculated structure factors (×10 in electrons) are listed in Table VIII.

(7) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(8) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(9) Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 773.

(10) Hassel, O.; Viervoll, H. *Acta Chem. Scand.* **1947**, *1*, 149.

(11) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, 19, 1014.

(12) Hamilton, W. C. *Acta Cystallogr.* **1965**, *18*, 502.

(13) Ueki, T.; Zalkin, A.; Templeton, D. H. *Acta Crystallogr.* **1966**, *20*, 836.

Table VI. Atomic Positional and Thermal Parameters (×10⁴) for Pt(PCy₂Ph)₂(F₃CC≡CCF₃)

atom	x	y	z	U_{11}ᵃ	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	1/4	4635.4 (4)	-1/4	371 (2)	462 (2)	412 (2)	-67 (5)	164 (1)	41 (6)
P(1)	3522 (1)ᵇ	3910 (4)	-1994 (2)	418 (16)	532 (21)	415 (16)	-83 (16)	219 (13)	-79 (16)
P(2)	1887 (1)	3218 (4)	-2107 (2)	332 (15)	566 (22)	465 (17)	-18 (15)	171 (13)	6 (16)
C(1)	2801 (9)	7340 (20)	-3416 (10)	998 (134)	771 (137)	785 (117)	-95 (110)	263 (104)	273 (103)
C(2)	2475 (6)	6316 (13)	-3138 (7)	785 (92)	452 (86)	530 (74)	-31 (73)	280 (69)	109 (67)
C(3)	1909 (6)	5991 (14)	-3197 (7)	529 (76)	586 (88)	585 (78)	-19 (69)	128 (64)	131 (70)
C(4)	1299 (9)	6559 (26)	-3611 (12)	569 (115)	985 (187)	1054 (163)	118 (116)	93 (110)	451 (143)
F(1)	2765 (6)	7040 (15)	-4081 (6)	2423 (143)	1944 (138)	1048 (83)	-795 (112)	1095 (95)	162 (85)
F(2)	3386 (5)	7566 (13)	-3040 (7)	867 (72)	1711 (121)	1756 (108)	-586 (77)	-66 (71)	998 (96)
F(3)	2514 (6)	8572 (13)	-3515 (8)	1577 (107)	768 (90)	2212 (141)	-51 (81)	918 (101)	626 (99)
F(4)	868 (5)	5638 (13)	-3898 (8)	622 (58)	1465 (125)	2133 (143)	-126 (72)	-257 (73)	901 (110)
F(5)	1286 (4)	7306 (12)	-4211 (5)	952 (71)	1407 (100)	1073 (74)	104 (66)	65 (57)	695 (74)
F(6)	1069 (6)	7429 (16)	-3246 (7)	1634 (114)	1865 (148)	1629 (118)	1190 (115)	694 (97)	519 (106)

atom	x	y	z	U	atom	x	y	z	U
C(41)	2179 (5)	1637 (13)	-1609 (6)	522 (32)	C(11)	3800 (5)	2761 (13)	-1196 (6)	476 (31)
C(42)	2498 (6)	741 (13)	-1902 (7)	602 (35)	C(12)	3556 (6)	2952 (14)	-637 (7)	597 (35)
C(43)	2706 (7)	-527 (18)	-1566 (8)	756 (43)	C(13)	3777 (7)	2163 (16)	10 (8)	766 (42)
C(44)	2544 (9)	-965 (21)	-994 (10)	972 (58)	C(14)	4253 (7)	1241 (18)	88 (8)	865 (46)
C(45)	2244 (7)	-83 (17)	-689 (8)	833 (46)	C(15)	4512 (7)	1018 (18)	-429 (9)	822 (44)
C(46)	2029 (6)	1216 (17)	-982 (8)	752 (41)	C(16)	4290 (6)	1826 (16)	-1062 (8)	655 (39)
C(51)	1513 (6)	4152 (15)	-1529 (7)	536 (37)	C(21)	4057 (5)	5358 (14)	-1643 (6)	466 (27)
C(52)	1997 (6)	4756 (16)	-845 (8)	771 (40)	C(22)	3861 (8)	6283 (22)	-1129 (9)	605 (49)
C(53)	1666 (8)	5493 (19)	-377 (9)	1001 (53)	C(23)	4247 (6)	7580 (15)	-909 (7)	645 (37)
C(54)	1215 (9)	6510 (20)	-829 (10)	1058 (57)	C(24)	4934 (7)	7239 (16)	-589 (8)	763 (42)
C(55)	736 (7)	5961 (19)	-1478 (9)	965 (51)	C(25)	5144 (6)	6364 (16)	-1075 (8)	751 (41)
C(56)	1054 (7)	5260 (18)	-1973 (8)	837 (43)	C(26)	4747 (6)	5067 (14)	-1334 (7)	618 (35)
C(61)	1213 (5)	2601 (13)	-2900 (6)	529 (31)	C(31)	3806 (5)	3115 (14)	-2675 (7)	548 (32)
C(62)	1400 (6)	1917 (16)	-3489 (7)	650 (37)	C(32)	3482 (6)	1716 (19)	-2962 (7)	700 (39)
C(63)	814 (7)	1532 (17)	-4167 (9)	768 (47)	C(33)	3739 (7)	1076 (19)	-3513 (9)	915 (48)
C(64)	332 (8)	753 (18)	-3975 (9)	955 (52)	C(34)	3616 (8)	2068 (19)	-4170 (9)	984 (53)
C(65)	172 (7)	1415 (18)	-3372 (9)	900 (49)	C(35)	3977 (7)	3434 (17)	-3884 (8)	856 (47)
C(66)	757 (6)	1725 (16)	-2702 (8)	742 (41)	C(36)	3727 (7)	4062 (18)	-3311 (8)	677 (45)

ᵃ The form of the thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ (Å²).
ᵇ Estimated standard deviations are given in parentheses here and in other tables and refer to the least significant digits.

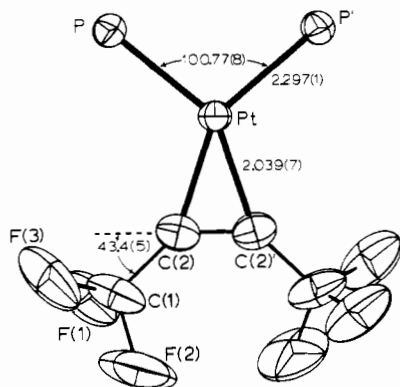**Figure 1.** Inner coordination sphere of Pt(PCyPh₂)₂(C₄F₆) (1) plotted as 50% probability thermal ellipsoids.

Description of the Structures

Selected intramolecular dimensions for the complexes are presented in Tables IX and X. The inner coordination spheres
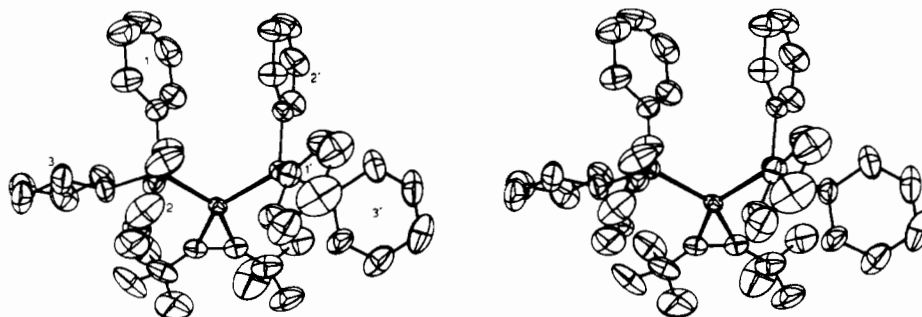
of the Pt atoms, together with the atom numbering schemes, are shown in Figures 1 and 3 while stereoviews of the molecules are given in Figures 2 and 4. Both crystal structures contain discrete molecular units; the closest intermolecular distance of approach is 2.45 Å between F(1) and H1C(15) (equivalent position $^1/_2 + x$, $^1/_2 + y$, z) for the PCyPh₂ species and 2.30 Å between atoms H1C(25) and H1C(66) (equivalent position $^1/_2 + x$, $^1/_2 + y$, z) for the PCy₂Ph complex.

In each complex the coordination about the Pt atom is essentially planar. The dihedral angle between the plane containing the Pt atom and the two acetylenic C atoms and that containing the Pt atom and the two P atoms is 1.4 (2)° for the PCyPh₂ complex and 3.7 (8)° for the PCy₂Ph complex. The results of a weighted least-squares plane calculation are given in Table XI. The Pt–P distance in the PCyPh₂ complex of 2.297 (1) Å is significantly longer than values observed in similar PPh₃ complexes, for example, 2.277 (1) and 2.285 (1) Å in Pt(PPh₃)₂(F₃CC≡CCF₃).[1] The two Pt–P distances found in the PCy₂Ph complex, 2.292 (3) and 2.287 (3) Å, are statistically equivalent and comparable to the value observed in

Figure 2. Stereoview of 1.

Table VII. Derived Hydrogen Atom Parameters for $Pt(PCy_2Ph)_2(F_3CC\equiv CCF_3)$

| atom[a]	x	y	z	B, Å²	atom	x	y	z	B, Å²
H1C(12)	3239	3620	−696	5.16	H1C(42)	2576	990	−2332	5.21
H1C(13)	3603	2265	382	6.63	H1C(43)	2963	−1090	−1739	6.57
H1C(14)	4409	724	531	7.53	H1C(44)	2639	−1871	−812	8.47
H1C(15)	4830	348	−363	7.17	H1C(45)	2176	−364	−257	7.23
H1C(16)	4479	1730	−1420	5.68	H1C(46)	1799	1790	−776	6.52
H1C(21)	3997	5940	−2085	4.05	H1C(51)	1264	3467	−1367	4.68
H1C(22)	3411	6542	−1380	5.31	H1C(52)	2269	4003	−547	6.68
H2C(22)	3909	5754	−671	5.31	H2C(52)	2262	5427	−988	6.68
H1C(23)	4164	8170	−1354	5.53	H1C(53)	1438	4803	−188	8.68
H2C(23)	4124	8087	−537	5.53	H2C(53)	1988	5967	47	8.68
H1C(24)	5180	8113	−493	6.59	H1C(54)	1002	6950	−520	9.20
H2C(24)	5021	6747	−111	6.59	H2C(54)	1453	7222	−990	9.20
H1C(25)	5121	6912	−1517	6.48	H1C(55)	480	5270	−1330	8.35
H2C(25)	5589	6085	−802	6.48	H2C(55)	456	6717	−1758	8.35
H1C(26)	4869	4615	−1723	5.36	H1C(56)	724	4828	−2408	7.28
H2C(26)	4836	4430	−906	5.36	H2C(56)	1288	5961	−2147	7.28
H1C(31)	4265	2936	−2425	4.71	H1C(61)	974	3442	−3134	4.56
H1C(32)	3561	1077	−2537	6.12	H1C(62)	1669	2562	−3645	5.66
H2C(32)	3019	1863	−3208	6.12	H2C(62)	1645	1068	−3281	5.66
H1C(33)	4201	916	−3270	7.99	H1C(63)	616	2394	−4427	6.69
H2C(33)	3524	182	−3693	7.99	H2C(63)	951	957	−4506	6.69
H1C(34)	3766	1646	−4545	8.50	H1C(64)	−59	685	−4423	8.31
H2C(34)	3155	2259	−4403	8.50	H2C(64)	498	−188	−3813	8.31
H1C(35)	4438	3243	−3647	7.40	H1C(65)	−57	2291	−3560	7.83
H2C(35)	3905	4086	−4301	7.40	H2C(65)	−106	784	−3223	7.83
H1C(36)	3961	4929	−3116	5.85	H1C(66)	629	2219	−2329	6.41
H2C(36)	3270	4273	−3560	5.85	H2C(66)	966	844	−2488	6.41

[a] H1C(12) is bonded to C(12) etc.
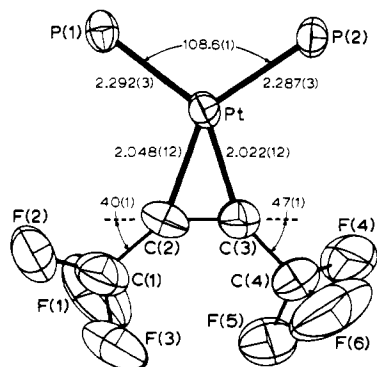
Figure 3. Inner coordination sphere of $Pt(PCy_2Ph)_2(C_4F_6)$ (2) plotted as 50% probability thermal ellipsoids.

the $PCyPh_2$ complex. The two P atoms of the $PCyPh_2$ ligands subtend an angle of 100.77 (8)° at the Pt atom. A comparable angle of 100.17 (4)° was reported for the analogous PPh_3 complex. The P atoms in the PCy_2Ph complex subtend an angle of 108.6 (1)° at the Pt atom. This value is less than the angle 110.23 (6)° found in the PCy_3 analogue. All Pt-acetylenic C bond distances are statistically equivalent and indistinguishable from the values reported for the PPh_3 and PCy_3 analogues. The C atoms, C(2) and C(2)', in the $PCyPh_2$ complex subtend an angle of 37.0 (4)° at the Pt atom, and the C(2)–Pt–C(3) angle in the PCy_2Ph complex is 37.1 (4)°. These angles are comparable to those observed in similar structures.

The $PCyPh_2$ ligand geometry is comparable to that found in the structure of $(\eta^5-C_5H_4Me)NiCo(CO)_4(PCyPh_2)$.[14] The mean P–C(phenyl ring) distance of 1.826 (5) Å is slightly shorter (3.6σ) than the P–C(31) bond distance. One of the most interesting aspects of the structure is the disposition of the phenyl rings with respect to the twofold axis. Phenyl ring 1 (i.e., atoms C(11)–C(16) inclusive) is situated roughly

parallel to, and about 3 Å from, phenyl ring 2′ in equivalent position $\bar{x}$, y, $\bar{z}$. The plane of phenyl ring 1 makes an angle of 15.0° to the plane of phenyl ring 2′. The same relationship exists between phenyl ring 2 and phenyl ring 1′ (see Figure 2). This disposition is reminiscent of that observed in graphite.[15] No dimension associated with the phenyl rings differs significantly from the mean dimensions reported in Table IX.

The mean P–C bond distance in the PCy_2Ph ligands is 1.841 (5) Å. There appears to be a weak interaction between the two phenyl rings, similar to that observed in the structure of the $PCyPh_2$ complex. The dihedral angle between the plane calculated for phenyl ring 1 and that calculated for phenyl ring 4 is 22.0° (see Figure 4). The C atoms of phenyl ring 4 range in distance from 3.0 to 4.0 Å from the plane calculated for phenyl ring 1. No dimension associated with the phenyl or cyclohexyl groups differs significantly from the weighted mean values given in Table X.

The acetylenic triple-bond length found in the $PCyPh_2$ complex, 1.294 (14) Å, is identical with the value observed for the PCy_2Ph complex, 1.294 (16) Å, and these distances are not significantly different from the values 1.255 (9) and 1.260 (10) Å observed for the PPh_3 and PCy_3 analogues. The alkyne bend-back angle in the $PCyPh_2$ complex, 43.5 (5)°, lies between the mean values 39.5 (5) and 45.5 (8)° reported for the two aforementioned complexes, respectively. The bend-back angles observed in the PCy_2Ph complex, 40 (1) and 47 (1)°, are statistically inequivalent (5.0σ). Interestingly, the value 40 (1)° is indistinguishable from the bend-back angles observed in the PPh_3 complex, while 47 (1)° is comparable with those found in the PCy_3 complex. The geometries of the CF_3 groups are normal.[1,2]

Discussion

A summary of the data for the hexafluorobut-2-yne complexes is presented in Table XII. At the commencement of this study the coordination geometry of the complexes was known, and the purpose was to obtain information as to the

(14) Campbell, I. L. C.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1975**, 337.

(15) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience Publishers: Toronto, Canada, 1972; p 288.
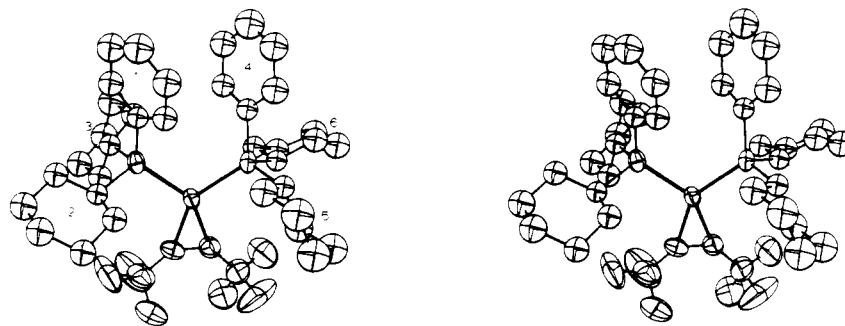
Figure 4. Stereoview of **2**.

Table IX

Selected Bond Distances and Angles for Pt(PCyPh$_2$)$_2$(F$_3$CC≡CCF$_3$)

bond	dist, A	bond	dist, A
Pt–P	2.297 (1)	C(31)–C(32)	1.49 (1)
Pt–C(2)	2.039 (7)	C(32)–C(33)	1.51 (1)
C(2)–C(2)′	1.294 (14)	C(33)–C(34)	1.51 (2)
C(1)–C(2)	1.453 (10)	C(34)–C(35)	1.44 (2)
C(1)–F(1)	1.34 (1)	C(35)–C(36)	1.50 (1)
C(1)–F(2)	1.32 (1)	C(36)–C(31)	1.51 (1)
C(1)–F(3)	1.34 (1)		
P–C(11)	1.820 (8)		
P–C(21)	1.829 (6)		
P–C(31)	1.857 (7)		

atoms	angle, deg	atoms	angle, deg
P–Pt–P′	100.77 (8)	Pt–P–C(11)	116.3 (3)
P–Pt–C(2)	111.1 (2)	Pt–P–C(21)	114.0 (2)
C(2)–Pt–C(2)′	37.0 (4)	Pt–P–C(31)	112.8 (3)
C(1)–C(2)–C(2)′	136.5 (5)	C(11)–P–C(21)	106.9 (3)
C(1)–C(2)–Pt	151.8 (7)	C(11)–P–C(31)	102.0 (3)
C(2)′–C(2)–Pt	71.5 (2)	C(21)–P–C(31)	103.4 (3)
F(1)–C(1)–F(2)	104.3 (8)	P–C(31)–C(32)	112.9 (5)
F(1)–C(1)–F(3)	104.6 (9)	P–C(31)–C(36)	117.1 (6)
F(2)–C(1)–F(3)	107.4 (9)	C(32)–C(31)–C(36)	112.6 (7)
C(2)–C(1)–F(1)	112.9 (7)	C(33)–C(32)–C(31)	113.9 (6)
C(2)–C(1)–F(2)	114.4 (10)	C(34)–C(33)–C(32)	112.2 (14)
C(2)–C(1)–F(3)	112.4 (7)	C(35)–C(34)–C(33)	113.8 (8)
P–C(11)–C(12)	122.7 (6)	C(36)–C(35)–C(34)	116.4 (9)
P–C(11)–C(16)	116.0 (6)	C(31)–C(36)–C(35)	111.3 (9)
P–C(21)–C(22)	123.6 (5)		
P–C(21)–C(26)	118.7 (5)		

Selected Bond Distances and Angles for Phenyl Rings
(Weighted Mean Dimensions)

bond	dist, A	atoms	angle, deg
C(1)–C(2),C(1)–C(6)	1.398 (5)	C(2)–C(1)–C(6)	118.0 (5)
C(2)–C(3),C(5)–C(6)	1.400 (5)	C(1)–C(2)–C(3),	120.6 (4)
		C(1)–C(6)–C(5)	
C(3)–C(4),C(4)–C(5)	1.380 (10)	C(2)–C(3)–C(4),	120.0 (4)
		C(4)–C(5)–C(6)	
		C(3)–C(4)–C(5)	119.9 (5)

Table X. Selected Bond Distances and Angles for
Pt(PCy$_2$Ph)$_2$(F$_3$CC≡CCF$_3$)

bond	dist, A	bond	dist, A
Pt–P(1)	2.292 (3)	P(1)–C(11)	1.835 (12)
Pt–P(2)	2.287 (3)	P(1)–C(21)	1.831 (13)
Pt–C(2)	2.048 (12)	P(1)–C(31)	1.846 (12)
Pt–C(3)	2.022 (12)	P(2)–C(41)	1.817 (13)
C(2)–C(3)	1.294 (16)	P(2)–C(51)	1.878 (14)
		P(2)–C(61)	1.845 (12)
C(1)–C(2)	1.46 (2)		
C(1)–F(1)	1.30 (2)	C(3)–C(4)	1.44 (2)
C(1)–F(2)	1.29 (2)	C(4)–F(4)	1.30 (2)
C(1)–F(3)	1.35 (2)	C(4)–F(5)	1.37 (2)
		C(4)–F(6)	1.33 (2)

atoms	angle, deg	atoms	angle, deg
P(1)–Pt–P(2)	108.6 (1)	C(1)–C(2)–C(3)	140 (1)
P(1)–Pt–C(2)	108.0 (4)	C(3)–C(2)–Pt	70.4 (8)
P(2)–Pt–C(3)	106.3 (4)	C(1)–C(2)–Pt	150 (1)
C(2)–Pt–C(3)	37.1 (4)	C(2)–C(3)–C(4)	133 (1)
		C(2)–C(3)–Pt	72.5 (8)
		C(4)–C(3)–Pt	154 (1)
F(1)–C(1)–F(2)	106 (2)	F(4)–C(4)–F(5)	103 (2)
F(1)–C(1)–F(3)	102 (1)	F(4)–C(4)–F(6)	107 (2)
F(2)–C(1)–F(3)	106 (2)	F(5)–C(4)–F(6)	103 (2)
C(2)–C(1)–F(1)	111 (1)	C(3)–C(4)–F(4)	114 (2)
C(2)–C(1)–F(2)	118 (1)	C(3)–C(4)–F(5)	114 (1)
C(2)–C(1)–F(3)	112 (1)	C(3)–C(4)–F(6)	116 (2)
Pt–P(1)–C(11)	122.7 (4)	Pt–P(2)–C(41)	122.9 (4)
Pt–P(1)–C(21)	111.1 (4)	Pt–P(2)–C(51)	112.0 (4)
Pt–P(1)–C(31)	112.8 (4)	Pt–P(2)–C(61)	110.0 (4)
C(11)–P(1)–C(21)	100.0 (5)	C(41)–P(2)–C(51)	104.4 (6)
C(11)–P(1)–C(31)	104.4 (6)	C(41)–P(2)–C(61)	101.8 (6)
C(21)–P(1)–C(31)	103.5 (5)	C(51)–P(2)–C(61)	103.8 (6)
P(1)–C(11)–C(12)	117.6 (10)	P(2)–C(41)–C(42)	117.4 (9)
P(1)–C(11)–C(16)	124.6 (10)	P(2)–C(41)–C(46)	122.8 (10)
P(1)–C(21)–C(22)	112.8 (9)	P(2)–C(51)–C(52)	112.0 (9)
P(1)–C(21)–C(26)	117.8 (10)	P(2)–C(51)–C(56)	111.6 (9)
P(1)–C(31)–C(32)	111.5 (10)	P(2)–C(61)–C(62)	114.6 (9)
P(1)–C(31)–C(36)	112.5 (9)	P(2)–C(61)–C(66)	113.6 (8)

Selected Bond Distances and Angles for Phenyl Rings
(Weighted Mean Dimensions)

bond	dist, A	atoms	angle, deg
C(1)–C(2),C(1)–C(6)	1.40 (1)	C(2)–C(1)–C(6)	118.4 (8)
C(2)–C(3),C(5)–C(6)	1.40 (1)	C(1)–C(2)–C(3),	120.1 (6)
		C(1)–C(6)–C(5)	
C(3)–C(4),C(4)–C(5)	1.36 (1)	C(2)–C(3)–C(4),	119.6 (7)
		C(4)–C(5)–C(6)	
		C(3)–C(4)–C(5)	122.0 (11)

Selected Bond Distances and Angles for Cyclohexyl Rings
(Weighted Mean Dimensions)

bond	dist, A	atoms	angle, deg
C(1)–C(2),C(1)–C(6)	1.52 (1)	C(2)–C(1)–C(6)	110.7 (6)
C(2)–C(3),C(5)–C(6)	1.54 (1)	C(1)–C(2)–C(3),	111.4 (4)
		C(1)–C(6)–C(5)	
C(3)–C(4),C(4)–C(5)	1.50 (1)	C(2)–C(3)–C(4),	110.7 (4)
		C(4)–C(5)–C(6)	
		C(3)–C(4)–C(5)	112.1 (7)

sensitivity of the alkyne ligand to changes in other parameters. In the series of compounds no significant variations in the C≡C and Pt–C bond distances can be detected by the X-ray method. This suggests that these parameters are not overly sensitive to the changes within the complexes. The alkyne ligand bend-back angle does vary significantly. Since the two extreme values are found in the PCy$_2$Ph complex (40 (1) and 47 (1)°), it seems likely that the principal cause of this variation is steric, rather than electronic.

Examining the structure of the complex Pt(PCyPh$_2$)$_2$-(F$_3$CC≡CCF$_3$), which has a bend-back angle of 43.5 (5)°, reveals that the cyclohexyl ring is directed toward the CF$_3$ group. The C(1)–Pt–P–C torsion angles, where C is the α-carbon C(11), C(21), or C(31), are 123.1 (3), –111.7 (3), and
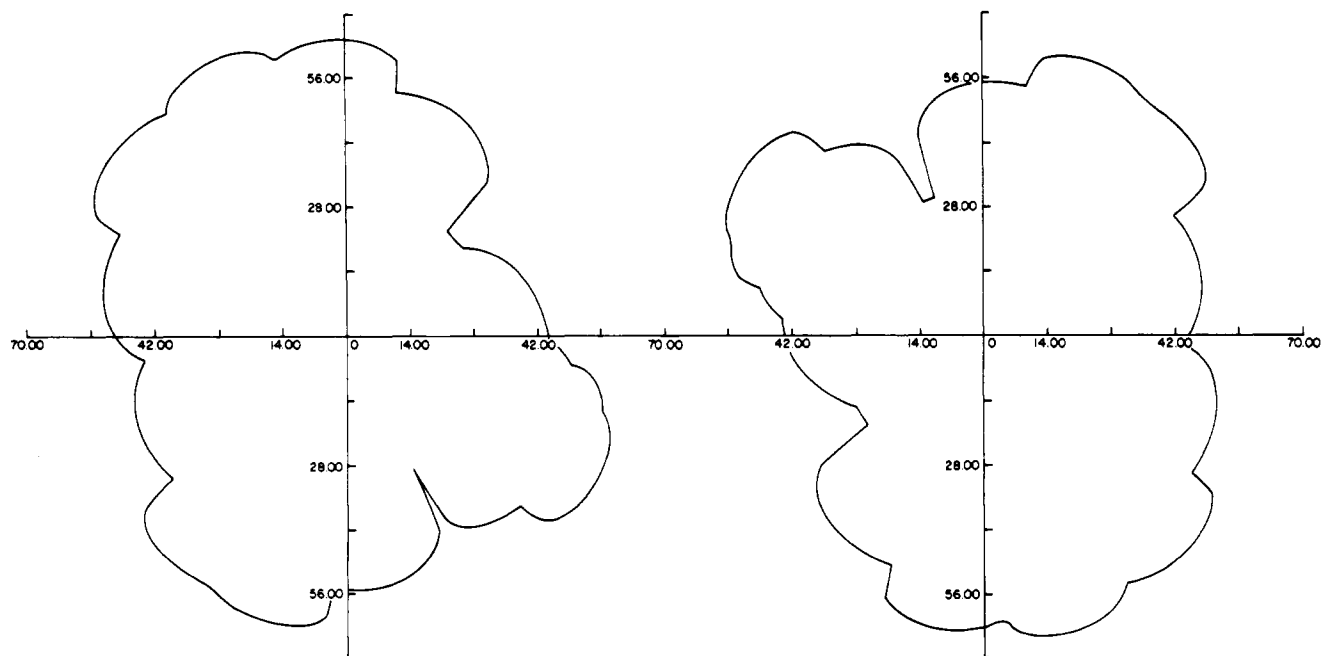
Figure 5. Ligand profile plot showing the steric natures of the dicyclohexylphenylphosphine ligands in **2**.

Table XI. Weighted Least-Squares Plane for
$Pt(PCy_2Ph)_2(F_3CC\equiv CCF_3)$ (Plane 1: $-3.539x + 5.820y + 15.417z = -2.041$)

atom	displacement, Å	atom	displacement, Å
Pt	0.0000 (3)	C(2)	0.003 (13)
P(1)	-0.004 (3)	C(3)	-0.076 (13)
P(2)	-0.002 (3)		

Table XII. Summary of the Results for the
$PtL_2(F_3CC\equiv CCF_3)$ Complexes

	L			
	PPh_3	$PCyPh_2$	PCy_2Ph	PCy_3
bend-back angles, deg	39.3 (6)	43.5 (5)	40 (1)	44.6 (8)
	40.4 (6)		47 (1)	46.3 (8)
P-Pt-P angle, deg	100.17 (4)	100.77 (8)	108.6 (1)	110.23 (6)
C≡C bond length, Å	1.255 (9)	1.294 (4)	1.294 (16)	1.260 (10)
Pt-C bond lengths, Å	2.024 (5)	2.039 (7)	2.022 (12)	2.045 (8)
	2.031 (5)		2.048 (12)	2.047 (7)
Pt-P bond lengths, Å	2.277 (1)	2.297 (1)	2.287 (3)	2.301 (2)
	2.285 (1)		2.292 (3)	2.309 (2)

6.8 (3)°, respectively. Thus the cyclohexyl ring C(31)–C(36) lies approximately in the same plane as the alkyne ligand. The significant increase in bend-back angle is therefore ascribed to a steric interaction between the cyclohexyl ring and the CF_3 group.

The complex $Pt(PCy_2Ph)_2(F_3CC\equiv CCF_3)$ supports the assertion that an increase in bend-back angle above 40° in these compounds is caused by steric effects. In this complex cyclohexyl ring 6 appears to be interacting with the $C(4)F_3$ group, while cyclohexyl rings 2 and 3 "bracket" the $C(1)F_3$ group. The bend-back angles are 47 (1) and 40 (1)°, respectively. This is illustrated in Figure 5 which shows the ligand profiles of the two PCy_2Ph ligands. The profiles are calculated by tracing around the outermost van der Waals radii of the atoms in the ligand at a specified distance from the metal. In the plot a distance of 2.9 Å from the metal was used, as this was found to be where the greatest ligand interaction occurs. The scale is in degrees and represents the angle that a point on the radial plot and the P atom subtend at the Pt atom. A van der Waals radius of 1.2 Å was used for the H atoms. The horizontal axis is defined by the PtP_2 fragment,

and the hexafluorobut-2-yne ligand is situated approximately parallel to it. The "graphitic relationship" is readily apparent. On the left side of the figure, H atom $H1C(66)$ crosses the axis at an angle of about 51°. On the right the traces around atoms $H1C(21)$ and $H1C(31)$ meet close to the horizontal axis at an angle of 45°. The 7° difference in these angles is reflected in the bend-back angles. An angle of 40 (1)° is observed for the $C(1)F_3$ group, while an angle of 47 (1)° is found for the group interacting with cyclohexyl ring 6. Therefore in these complexes a bend-back angle of about 40° appears to be normal, and larger values seem to arise from predominantly steric effects.

Another interesting facet of this structural determination is the conformation of the $PCyPh_2$ ligand. Conformational analysis of the PPh_3 molecule[16] and of the coordinated PPh_3 ligand[17] indicates that C_3 symmetry is not maintained in either case. The deviation from C_3 symmetry in the solid state is illustrated by the angles between the planes of the phenyl rings and the plane defined by the three α-C atoms of the rings, which are 68.0, 36.1, and 65.3°. If the plane of the cyclohexyl ring is calculated by using C(32), C(33), C(35), and C(36), then these angles for the $PCyPh_2$ ligand are 71.0, 25.9, and 53.3° (for phenyl rings 1 and 2 and cyclohexyl ring 3, respectively). Thus the presence of the bulkier cyclohexyl group and the preferred disposition of the phenyl rings does not appear to have introduced much strain into the $PCyPh_2$ ligand. The most noticeable deviation from the expected geometry is the P–C(11)–C(14) angle of 169.5 (5)°. This angle, which is ideally 180°, typically ranges between 175 and 180°.[17] The P–C(21)–C(24) angle is 176.8 (4)°.

This is the first report of a structural determination of a complex containing a PCy_2Ph ligand. Inspection of the bond distances and angles associated with these ligands did not reveal any abnormalities.

In both complexes the Pt–P–C angles, where C is an α-C atom of a phenyl or cyclohexyl ring, are worthy of mention. In the $PCyPh_2$ complex the Pt–P–C angles are 116.3 (3), 114.0 (2), and 112.8 (3)°. It was noted in the previous paragraph that the presence of a "graphitic interaction" did not introduce much strain into these phosphine ligands. In fact the inter-

(16) Brock, C. P.; Ibers, J. A. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2426.
(17) Horrocks, W. D.; Greenberg, E. S. *Inorg. Chem.* **1971**, *10*, 2190.

action may have alleviated some strain, for the corresponding angles in the PPh$_3$ complex are 116.3 (1), 114.7 (1), and 110.1 (1)° and 110.7 (1), 122.3 (1), and 111.3 (1)°. The two largest angles are associated with two phenyl rings in close proximity. The angles in the PCy$_2$Ph ligands are 122.7 (4), 111.1 (4), and 112.8 (4)°, and 122.9 (4), 112.0 (4), and 110.0 (4)°. These values are clearly normal and reflect the increasing steric interaction between the phosphine ligands.

Further studies will be reported on complexes of hexafluorobut-2-yne with ligands of varying basicity, in an attempt to determine the importance of this effect.

Preparation and Crystal Structure of Trisilver Undecaphosphide, Ag$_3$P$_{11}$, an Unusual Defect Tetrahedral Compound

MANFRED H. MÖLLER and WOLFGANG JEITSCHKO*

Single crystals of Ag$_3$P$_{11}$ were prepared by heating the elemental components in evacuated silica tubes in the presence of iodine. They are monoclinic with the space group *Cm* and the lattice constants a = 12.999 (3) Å, b = 7.555 (2) Å, c = 6.612 (2) Å, β = 118.84 (2)°, and Z = 2. The crystal structure was determined from single-crystal diffractometer data and refined to a conventional R value of 0.059 for 44 variable parameters and 865 structure factors. The Ag atoms are approximately tetrahedrally coordinated by P atoms at distances varying between 2.47 and 2.61 Å. The AgP$_4$ tetrahedra are linked by shared P atoms, thus forming infinite chains along the a axis. Most P atoms have tetrahedral coordination of one Ag and three P or two Ag and two P atoms. One kind of P atoms has three P neighbors with a lone pair of electrons as a fourth "ligand". Bonding in Ag$_3$P$_{11}$ is described with a simple covalent model where all near-neighbor interactions are rationalized as classical two-electron bonds in agreement with the diamagnetism and the semiconductivity of the compound. This also establishes the formal oxidation number +1 for the Ag atoms while the P atoms may be considered as forming a two-dimensionally infinite polyanion consisting of condensed 5-, 6-, and 14-membered rings. The structure of Ag$_3$P$_{11}$ can be derived from that of cubic diamond by ordering of Ag atoms, P atoms, and vacancies on the positions of the carbon atoms. It is unusual in that there are four vacant sites but also only four lone pairs per cell. It nevertheless obeys Parthé's definition of a defect tetrahedral structure.

Introduction

According to Haraldsen and Biltz[1] the system Ag–P is characterized by only two binary phases to which they ascribed the compositions AgP$_2$ and "AgP$_3$". Both compounds were prepared by direct reaction of the elemental components and according to their tensiometric studies are in equilibrium with P vapor. Olofsson[2] showed from X-ray powder data that AgP$_2$ is isotypic with CuP$_2$ but found little evidence for a compound with higher P content. Our present reinvestigation of the phosphorus-rich part of the Ag–P system confirms the existence of AgP$_2$. For the other compound with higher P content our structure determination yields the composition Ag$_3$P$_{11}$.

Experimental Section

Starting materials were Ag powder (Alfa Ventron, <100 mesh, >99.99%) and red P (Merck, "rein") which was purified with diluted NaOH solution.[3] The powders were mixed in various ratios and annealed in evacuated silica tubes. The Ag content was around 60 mg and about 1–3 mg of iodine was added to most samples. After the heat treatment the iodine was identified as AgI in the X-ray powder patterns. The presence of iodine resulted in a better crystallized product but was not necessary to produce Ag$_3$P$_{11}$. No long-range transport of silver phosphides was observed. Iodine probably aids catalytically in the evaporation of phosphorus.[4]

With the starting compositions Ag:P = 1:2 the products were always AgP$_2$ (7 days of annealing; temperatures varied for different samples between 550 and 700 °C). Compositions Ag:P = 1:3 gave two-phase products of AgP$_2$ and Ag$_3$P$_{11}$ (7 days; 400, 500, or 600 °C). Samples Ag:P = 1:4 and 1:5 resulted in Ag$_3$P$_{11}$ and white P (7 days at temperatures between 400 and 600 °C). Two samples with the composition Ag:P = 1:5 and 1:10 were kept at 370 °C for 35 days. Their powder patterns correspond to Ag$_3$P$_{11}$; in addition several broad lines indicated a poorly crystallized product which was possibly red P.

Even with the addition of iodine to the samples the crystals of Ag$_3$P$_{11}$ were small (typical size 6 × 10 × 60 μm). They had elongated lanceolate shape and a black shiny appearance. They are resistant to air and not soluble in nonoxidizing acids, but they dissolved in hot concentrated nitric acid. Magnetic measurements carried out with the Faraday technique showed Ag$_3$P$_{11}$ to be diamagnetic.

Structure Determination

X-ray powder patterns were recorded with a Guinier camera and Cu Kα$_1$ radiation. They were indexed with the monoclinic cell found from the single-crystal diffraction photographs. Least-squares refinement with α-quartz as standard (a = 4.9130, c = 5.4046 Å) resulted in the following lattice constants: a = 12.999 (3) Å, b = 7.555 (2) Å, c = 6.612 (2) Å, β = 118.84 (2)°, V = 568.8 (3) Å^3 (here and in subsequent tables the estimated standard deviations of the least significant figures are shown in parentheses). With Z = 2 formula weights per cell, the calculated density is 3.879 g cm^{-3}. This agrees perfectly with the density of 3.881 g cm^{-3} found for the phase "AgP$_3$" by Haraldsen and Biltz.[1] A typical powder pattern with intensities calculated[5] from the refined structure is shown in Table I.

Single crystals were examined in Buerger precession and Weissenberg cameras. They have monoclinic diffraction symmetry and no other systematic extinctions besides those for a *C*-centered cell. Thus, space groups *C2*, *Cm*, and *C2/m* were possible of which *Cm* was found to be correct during the structure determination.

(1) Haraldsen, H.; Biltz, W. *Z. Elektrochem.* **1931**, *37*, 502.
(2) Olofsson, O. *Acta Chem. Scand.* **1965**, *19*, 229.
(3) Brauer, G. "Handbuch der Präparativen Anorganischen Chemie", 3rd ed.; F. Enke: Stuttgart, 1975; Vol. 1, p 506.
(4) Schäfer, H.; Trenkel, M. *Z. Anorg. Allg. Chem.* **1972** *391*, 11.

(5) Yvon, K.; Jeitschko, W.; Parthé, E. *J. Appl. Crystallogr.* **1977**, *10*, 73.