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STUDIES ON METAL-ACETYLENE COMPLEXES

IX *. THE STRUCTURES OF $Pt(As(C_6H_5)_3)_2F_3CC{\equiv}CCF_3$ AND $Pd(P(C_6H_{11})_3)_2F_3CC{\equiv}CCF_3$

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Summary

The molecular structures of the complexes $Pt(As(C_6H_5)_3)_2(F_3CC{\equiv}CCF_3)$, 1, and $Pd(P(C_6H_{11})_3)_2(F_3CC{\equiv}CCF_3)$, 2, have been determined from three-dimensional X-ray data collected by counter methods. Crystals of 1 are monoclinic, space group $P2_1/c$, with $Z = 4$ in a cell of dimensions $a = 11.373(2)$, $b = 15.154(2)$, $c = 21.171(3)$ Å and $\beta = 96.74(1)°$; those of 2 are also monoclinic, space group Cc, with $Z = 4$, and cell dimensions $a = 21.168(4)$, $b = 10.603(2)$, $c = 18.756(3)$ Å and $\beta = 92.58(1)°$. Intensity data collected on an automated four-circle diffractometer was used for full-matrix least-squares refinement on F, which converged for 1 at $R = 0.038$, 5687 observations, and for 2 at $R = 0.049$, 4386 observations. The coordination at the metal atom in the complexes is essentially planar, and the C≡C bond distances are not significantly different (1, 1.282(9); 2, 1.271(10) Å). The mean deviation from linearity of the alkyne molecule upon coordination is 40.8(5)° in 1 and 44.1(6)° in 2. These values are in agreement with the proposal that predominantly steric interactions, not electronic effects, cause variations in this angle.

Introduction

When an alkyne molecule interacts with a transition metal it adopts a *cis*-bent geometry, and crystallographic studies on a number of bis(triphenylphosphine)(alkyne)platinum(0) complexes have indicated that a bend-back angle of about 40° is normal. For example, a mean value of 39.9(5)° was found in the complex bis(triphenylphosphine)(hexafluorobut-2-yne)platinum(0) [1], which increased

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* For part VIII, see ref. 3.

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TABLE 1

CRYSTAL DATA

	$Pt(AsPh_3)_2(F_3CC{\equiv}CCF_3)$, 1	$Pd(PCy_3)_2(F_3CC{\equiv}CCF_3)$, 2
Molecular formula	$C_{40}H_{30}As_2F_6Pt$	$C_{40}H_{66}F_6P_2Pd$
Molecular weight	969.61	829.31
Crystal system	Monoclinic	Monoclinic
Systematic absences	$h0l$ for l odd and $0k0$ for k odd	hkl for $h+k$ odd and $h0l$ for l odd
Space group	$P2_1/c$	Cc
Cell constants	$a = 11.373(2)$ Å	$a = 21.168(4)$ Å
	$b = 15.154(2)$ Å	$b = 10.603(2)$ Å
	$c = 21.171(3)$ Å	$c = 18.756(3)$ Å
	$\beta = 96.74(1)^\circ$	$\beta = 92.58(1)^\circ$
Cell volume	3623.6 Å^3	4205.6 Å^3
Density measured by flotation in	CCl_4 and n-pentane	CCl_4 and n-pentane
Density (observed)	1.79(1) g cm^{-3}	1.33(1) g cm^{-3}
(calculated)	1.783 g cm^{-3}	1.316 g cm^{-3}
Z	4	4
μ	55.4 cm^{-1} for Mo-K_α	5.1 cm^{-1} for Mo-K_α

to 45.5(8)° upon replacement of the triphenylphosphine ligands with the sterically bulkier tricyclohexylphosphine species [2]. In a recent study of complexes of the type $PtL_2(F_3CC{\equiv}CCF_3)$, where L is either cyclohexyldiphenylphosphine or dicyclohexylphenylphosphine, we attributed the variation in the bend-back angle to predominantly steric interactions [3]. We now consider the effect on the alkyne ligand of changes in the Group V donor atom from P to As, and changes in the metal atom from Pt to Pd.

Experimental

The complex $Pt(As(C_6H_5)_3)_2(F_3CC{\equiv}CCF_3)$, 1, was prepared by published methods [4], and $Pd(P(C_6H_{11})_3)_2(F_3CC{\equiv}CCF_3)$, 2, was kindly supplied by C.R.C. Milne. (a) Clear, prismatic crystals of 1 were obtained by recrystallisation from dichloromethane/methanol mixtures. A photographic examination suggested the monoclinic space group $P2_1/c$ [5], and preliminary cell constants were measured. Crystal data are presented in Table 1.

The crystal chosen for data collection was mounted on a Picker FACS-1 diffractometer with [001] offset approximately 40° from coincidence with the diffractometer ϕ axis. Five standard reflections, regularly monitored during data collection, showed no significant decomposition had occurred. Details of the experimental conditions are summarized in Table 2. Eight crystal faces were identified as the forms {100}, {001} and {011}. The intensity data were processed as described previously [3], using a p value of 0.03. *

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* Computing was performed on the DEC PDP-10 and the CDC Cyber 73/14 at the University of Western Ontario. Among the programs used were: cell refinement and orientation matrix, PICKTT, based on the logic of Hamilton's MODE 1; Fourier syntheses, Zalkin's FORDAP; least-squares refinement, WOCLS, a version of Ibers' NUCLS: absorption correction AGNOST, by Cahen and Ibers; Johnson's ORTEP for illustrations and ORFFE, Busing, Martin and Levy's function and error program

A total of 8547 reflections was measured; 5687 unique data with $I > 3\sigma(I)$ were used in the refinement of the structure. The data were corrected for absorption effects using the analytical method [6]. Transmission coefficients varied from 0.266 to 0.367. As a check on the quality of the data, the 8547 reflections collected included 601 pairs of reflections for the equivalent forms hll and $h\bar{l}l$ [7]. These reflections gave a weighted agreement factor of 0.021 based on F^2. (b) The Pd complex was first recrystallized from dichloromethane and methanol mixtures. A photographic examination revealed space group $P2_1/n$ (alternate setting of $P2_1/c$, No 14 [5]) with cell dimensions $a = 10.829(2)$, $b = 21.899(4)$, $c = 17.959(3)$ Å, and $\beta = 96.86(1)°$. Several attempts were made to record intensity data from these crystals; however, significant decomposition occurred in the X-ray beam, and all attempts to refine the structure were unsatisfactory.

Suitable, clear, distorted pyramidal crystals of 2 were obtained by recrystallization from benzene/methanol mixtures. Preliminary photography showed the crystals belonged to the monoclinic system, with systematic extinctions consistent with the space groups Cc and $C2/c$. Crystal data are given in Table 1.

The crystal selected for data collection was mounted with [010] offset approximately 60° from coincidence with the spindle axis. A total of 4748 reflections was measured. These included Bijvoet pairs hll and $h\bar{l}l$, which were recorded to provide a check on crystal quality [7]. No crystal decomposition was observed. The experimental conditions associated with data collection are given in Table 2.

The crystal was measured following data collection. Nine faces were identified as $(00\bar{1})$, $(1\bar{1}0)$, (101), $(\bar{1}01)$, (011), $(11\bar{1})$, $(1\bar{1}\bar{1})$ and the form $\{100\}$. The recorded intensities were processed and p was chosen as 0.03. The structure was solved using 3732 unique reflections with $I > 3\sigma(I)$. All reflections were corrected

TABLE 2

EXPERIMENTAL CONDITIONS ASSOCIATED WITH DATA COLLECTIONS

	$Pt(AsPh_3)_2(F_3CC{\equiv}CCF_3)$, 1	$Pd(PCy_3)_2(F_3CC{\equiv}CCF_3)$, 2
Radiation	Mo-K_α, graphite monochromatized	Mo-K_α, graphite monochromatized
Wavelength (Å)	0.70926	0.70926
Temperature (°C)	21	24
Approximate crystal dimensions (cm)	0.025 × 0.030 × 0.023	0.012 × 0.031 × 0.016
Mean ω-scan width at 1/2 height	0.075	0.084
No. and 2θ range of centered reflections	30, $21 < 2\theta < 38°$	28, $19 < 2\theta < 34°$
Scan range and speed	1.30° corrected for dispersion, at 1° min^{-1}	1.20° corrected for dispersion, at 2° min^{-1}
Data collected	hkl and $\bar{h}kl$, for $0 < 2\theta < 60°$	$h\bar{k}l$ and $\bar{h}kl$, for $0 < 2\theta < 65°$
Background count time	10 s stationary crystal, stationary counter at limits of scan, 20 s for $2\theta > 50°$	10 s stationary crystal, stationary counter at limits of scan, 20 s for $2\theta > 50°$
Standards	$\bar{1}00$, 020, 111, 100, 002 recorded every 250 reflections	$\bar{2}00$, 002, 200, $1\bar{1}0$, $1\bar{1}1$ recorded every 250 reflections

TABLE 3

$Pt(AsPh_3)_2(F_3CC{\equiv}CCF_3)$: ATOMIC POSITIONAL AND THERMAL PARAMETERS (× 10^4)

Atom	x	y	z	U_{11} [a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	1533.0(2) [b]	3861.8(2)	2624.5(1)	367(1)	377(1)	420(1)	−12(1)	41(1)	65(1)
As(1)	−571(0)	3981(0)	2576(0)	376(3)	371(3)	436(3)	−3(2)	15(3)	22(3)
As(2)	1988(1)	3569(0)	3734(0)	408(3)	411(3)	427(3)	1(3)	16(3)	36(3)
C(1)	1976(9)	4102(6)	1087(4)	1198(77)	794(63)	502(49)	15(54)	184(51)	55(45)
C(2)	2178(6)	3984(4)	1771(3)	625(42)	494(40)	511(40)	−34(32)	177(33)	52(32)
C(3)	3034(6)	3873(4)	2215(3)	446(33)	512(37)	643(43)	−8(31)	144(31)	112(36)
C(4)	4318(7)	3783(7)	2280(5)	543(48)	944(69)	1141(80)	−16(48)	297(53)	119(62)
F(1)	2935(7)	4032(7)	818(3)	1661(65)	4232(146)	724(41)	904(82)	667(45)	417(63)
F(2)	1243(8)	3525(4)	811(3)	3220(106)	983(46)	686(38)	−435(55)	−525(51)	−50(33)
F(3)	1519(6)	4857(4)	894(2)	1940(61)	868(38)	644(33)	188(37)	115(35)	303(28)
F(4)	4691(5)	3013(5)	2137(4)	765(39)	1305(57)	3263(113)	353(37)	422(55)	−246(64)
F(5)	4819(5)	3907(6)	2873(4)	533(32)	3040(110)	1505(65)	−51(46)	−108(38)	−200(69)
F(6)	4845(5)	4328(5)	1947(4)	625(34)	1905(67)	2872(99)	−94(38)	542(47)	1312(67)

Atom	x	y	z	U	Atom	x	y	z	U
C(11)	−1387(5)	2979(4)	2884(3)	432(14)	C(41)	3067(5)	2586(4)	3904(3)	450(14)
C(12)	−1036(6)	2150(4)	2683(3)	557(17)	C(42)	3567(6)	2375(5)	4516(4)	644(19)
C(13)	−1665(7)	1418(5)	2831(4)	706(21)	C(43)	4310(6)	1646(5)	4620(4)	685(20)
C(14)	−2601(7)	1478(5)	3163(4)	734(21)	C(44)	4536(6)	1127(5)	4122(4)	641(18)
C(15)	−2933(6)	2281(5)	3390(4)	709(21)	C(45)	4035(7)	1313(5)	3522(4)	756(22)
C(16)	−2308(6)	3043(4)	3244(3)	559(17)	C(46)	3298(6)	2047(5)	3418(3)	629(19)
C(21)	−1427(5)	4102(4)	1729(3)	439(14)	C(51)	2770(5)	4538(4)	4222(3)	504(16)
C(22)	−2357(6)	3551(5)	1506(4)	621(18)	C(52)	2902(6)	4558(5)	4878(4)	668(20)
C(23)	−2931(6)	3681(5)	896(4)	683(20)	C(53)	3505(7)	5285(6)	5204(4)	832(24)
C(24)	−2608(7)	4337(5)	523(4)	694(20)	C(54)	3884(8)	5931(6)	4854(5)	874(26)
C(25)	−1684(7)	4883(5)	733(4)	738(22)	C(55)	3744(8)	5959(6)	4222(5)	889(26)
C(26)	−1110(6)	4757(5)	1345(4)	652(19)	C(56)	3164(7)	5245(5)	3876(4)	725(22)
C(31)	−1202(5)	5001(4)	2974(3)	466(15)	C(61)	752(5)	3229(4)	4241(3)	455(14)
C(32)	−2399(6)	5182(5)	2882(3)	595(18)	C(62)	117(6)	3862(4)	4534(3)	557(16)
C(33)	−2859(7)	5922(5)	3165(4)	757(22)	C(63)	−810(7)	3593(5)	4866(4)	706(21)
C(34)	−2104(7)	6464(5)	3520(4)	767(22)	C(64)	−1094(7)	2728(5)	4897(4)	699(21)
C(35)	−932(7)	6314(5)	3614(4)	759(22)	C(65)	−483(6)	2110(5)	4613(4)	658(19)
C(36)	−446(6)	5569(5)	3340(3)	604(18)	C(66)	452(5)	2355(4)	4284(3)	537(16)

[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.

for absorption using the analytical method. The minimum and maximum transmission coefficients were 0.051 and 0.066, respectively.

Normalized structure factors were calculated, and the statistical distribution which was observed strongly suggested the acentric space group *Cc*, No. 9 [5]. With four formula units per cell, no symmetry constraints are imposed upon the molecule. The centric space group *C2/c* is also possible, in which case the molecule must lie on either a centre, which is impossible, or upon a 2 fold axis. The acentric space group was assumed, and confirmed by a successful analysis.

Solution and refinement of the structures

(a) $Pt(As(C_6H_5)_3)_2(F_3CC{\equiv}CCF_3)$, *1*

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 Volume IV [5], while those for H were from Stewart, et al. [8]. The real correction for anomalous dispersion of Cromer and Liberman [9] was included for the Pt and As atoms. The 30 H atoms were located in a difference Fourier synthesis with electron density varying from 0.7(1) to 0.2(1) e Å^{-3}, and their contributions included in the calculations of Fc (idealized positions, sp^2 hybridization, C—H 0.95 Å). In the final cycles positional and anisotropic thermal parameters were refined for the Pt, the two As and the ten atoms of the hexafluorobut-2-yne ligand, and positional and isotropic thermal parameters were varied for the phenyl C atoms. The refinement of 262 variables with 5687 observations ($I > 3\sigma(I)$), converged at agreement factors $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.0376$ and $R_2 = (\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2)^{1/2} = 0.0384$. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$ where the weight w is given by $4Fo^2/\sigma^2(Fo^2)$. The largest shift in the final cycle was 0.05 esd. A statistical analysis of R_2 over various ranges of $|Fo|$, $\lambda^{-1} \sin\theta$ 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 1.26 electrons. The highest peak in a difference Fourier synthesis is of electron density 0.87(12) e Å^{-3} at fractional coordinates (—0.393, 0.112, 0.044) and is of no chemical significance. Final positional and thermal parameters for the non-H atoms are given in Table 3. H atom parameters and a list of observed and calculated structure amplitudes (× 10 in electrons) have been deposited. *

(b) $Pd(P(C_6H_{11})_3)_2(F_3CC{\equiv}CCF_3)$, *2*

Positional parameters for the Pd and P atoms were determined from a three-dimensional Patterson synthesis. The origin was defined by the Pd atom at $x = 0$ and $z = 0$. The remaining 46 non-hydrogen atoms were located from a series of difference Fourier syntheses and least-squares refinements. The model was refined by varying positional and anisotropic thermal parameters for the Pd, the P atoms and the atoms of the alkyne ligand, and positional and isotropic thermal parameters for the cyclohexyl C atoms. To choose the correct enantiomer of

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the crystal, one cycle of refinement was performed in each hand, giving residuals $R_1 = 0.058$ and $R_2 = 0.064$, and $R_1 = 0.059$ and $R_2 = 0.065$. An examination of the molecular geometries also favoured the first model, which was adopted. All 56 H atoms were located, with electron densities ranging from 0.7(1) to 0.3(1) e Å^{-3}. Idealized parameters were computed (tetrahedral, C—H 1.00 Å) and the contribution to Fc was included in subsequent calculations. Three cycles of refinement using the data with $I > 3\sigma(I)$ converged at agreement factors $R_1 = 0.054$ and $R_2 = 0.049$. In the final cycles of refinement all data with $I > \sigma(I)$ were used. The refinement of 260 variables with 4386 observations converged at $R_1 = 0.054$ and $R_2 = 0.049$. In the final cycle the largest shift was 0.092 esd. A statistical examination of the structure factors showed no abnormal trends. Secondary extinction effects could be ignored. The error in an observation of unit weight is 1.38 electrons. The highest peak in a difference Fourier synthesis is of electron density 0.69(9) e Å^{-3}, at fractional coordinates (—0.321, 0.116, 0.420), and is of no chemical significance. Final positional and thermal parameters for the non-H atoms are given in Table 4. H atom parameters and a list of observed and calculated structure amplitudes (× 10 in electrons) have been deposited. *

Description of the structures

The principal bond lengths and bond angles for the Pt compound are given in Table 5. The inner coordination sphere of the Pt atom and the atom labeling scheme are shown in Fig. 1. A stereoview of **1** is presented in Fig. 2. The structure consists of discrete molecular units, for the closest intermolecular distance of approach is 2.38 Å between atom HlC(43) and HlC(23) in equivalent position (x, $1/2 - y$, $1/2 + z$). Intramolecular dimensions for the Pd species are given in Table 6, while the analogous illustrations form Figs. 3 and 4. This crystal is also built up from discrete molecules, since the closest distance of approach is 2.19 Å between H2C(15) and atom H2C(33) in equivalent position (x, $1 - y$, $1/2 + z$).

In each complex the coordination about the metal atom is essentially planar. The dihedral angle between the plane containing the Pt and the two acetylenic C atoms, and that containing the Pt and the two As atoms, is 3.0(4)°. The analogous value for **2** is 2.8(4)°. Pt—As bond distances of 2.3900(7) and 2.3884(8) Å are statistically equivalent, and longer than the Pt—P bond lengths, 2.277(1) and 2.285(1) Å observed in the complex $Pt(PPh_3)_2(F_3CC{\equiv}CCF_3)$ [1]. The two As atoms subtend an angle of 99.01(2)° at the Pt atom. The Pt—C(2) and Pt—C(3) bond distances, 2.036(6) and 2.003(6) Å, are significantly different (3.9 σ). This probably reflects an underestimation of the errors on the distances. Both values are comparable to 2.031(5) and 2.024(5) Å, observed in the PPh_3 complex. The C(2)—Pt—C(3) angle is 37.03(3)°.

In the Pd species, the two Pd—P distances, 2.358(2) and 2.363(2) Å, are statistically equivalent, and significantly longer than the values 2.321(2) and 2.330(2) Å observed in the structure of $(PPh_3)_2Pd(MeO_2CC{\equiv}CCO_2Me)$ [10].

(Continued on p. 247)

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* See footnote on p. 243.

TABLE 4

$Pd(PCy_3)_2(F_3CC{\equiv}CCF_3)$: ATOMIC POSITIONAL AND THERMAL PARAMETERS ($\times 10^4$)

Atom	x	y	z	U_{11} [a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0	1364.0(5) [b]	0	306(2)	440(3)	355(2)	8(4)	10(2)	46(4)
P(1)	915(1)	2624(2)	145(1)	332(9)	481(13)	360(10)	−2(9)	−2(8)	31(10)
P(2)	−802(1)	2079(2)	738(1)	338(9)	423(13)	398(10)	48(9)	21(8)	29(10)
C(1)	635(5)	−581(13)	−1231(6)	693(69)	973(100)	793(80)	114(41)	−62(57)	−602(76)
C(2)	200(4)	−9(9)	−718(4)	632(50)	575(58)	433(44)	−71(47)	12(38)	−205(43)
C(3)	−354(4)	−216(9)	−509(4)	489(44)	604(61)	480(45)	−54(44)	−22(37)	−176(45)
C(4)	−854(5)	−1128(10)	−697(5)	670(58)	689(82)	709(62)	−101(55)	−21(51)	−226(59)
F(1)	519(4)	−226(13)	−1853(4)	1491(66)	3610(177)	526(40)	1209(92)	226(42)	−156(68)
F(2)	1211(3)	−503(8)	−1073(4)	640(38)	1822(83)	1585(64)	117(47)	1343(57)	−1018(62)
F(3)	548(4)	−1842(9)	−1273(6)	1807(85)	1251(73)	2682(127)	−412(66)	1355(87)	−1206(86)
F(4)	−1255(3)	−715(7)	−1202(4)	1343(52)	1190(63)	1719(69)	−528(52)	−949(55)	247(58)
F(5)	−664(3)	−2206(7)	−950(5)	1217(57)	943(58)	1905(78)	−357(48)	348(53)	−839(59)
F(6)	−1204(4)	−1425(7)	−178(4)	1575(63)	1414(67)	1112(50)	−1088(55)	536(48)	−549(50)

Atom	x	y	z	U	Atom	x	y	z	U
C(11)	870(4)	4256(8)	493(4)	468(19)	C(41)	−1491(3)	2689(8)	196(4)	456(19)
C(12)	399(4)	5082(10)	51(5)	663(24)	C(42)	−1787(4)	1742(9)	−318(5)	663(25)
C(13)	267(5)	6295(12)	463(6)	892(32)	C(43)	−2347(5)	2364(11)	−762(6)	830(31)
C(14)	881(6)	7029(13)	640(6)	1004(38)	C(44)	−2150(5)	3519(11)	−1142(6)	835(30)
C(15)	1365(5)	6223(12)	1026(6)	903(33)	C(45)	−1856(4)	4476(10)	−626(5)	694(26)
C(16)	1484(4)	4998(11)	623(5)	721(27)	C(46)	−1301(4)	3904(9)	−194(4)	583(23)
C(21)	1516(3)	1880(8)	763(4)	422(18)	C(51)	−1098(4)	668(9)	1192(4)	516(21)
C(22)	1623(4)	502(9)	570(4)	560(22)	C(52)	−1659(4)	810(11)	1674(5)	728(27)
C(23)	2128(4)	−99(10)	1083(5)	717(26)	C(53)	−1885(5)	−525(12)	1915(6)	947(35)
C(24)	1964(4)	8(10)	1849(5)	722(26)	C(54)	−1364(5)	−1291(12)	2259(6)	978(36)
C(25)	1851(4)	1323(10)	2050(5)	716(26)	C(55)	−809(5)	−1409(11)	1782(5)	761(28)
C(26)	1345(4)	1963(9)	1547(4)	561(22)	C(56)	−559(5)	−130(11)	1539(6)	661(30)
C(31)	1319(3)	2651(8)	−711(4)	465(19)	C(61)	−665(4)	3353(8)	1414(4)	443(20)
C(32)	890(5)	3200(12)	−1223(6)	828(34)	C(62)	−234(4)	2943(8)	2054(4)	514(20)
C(33)	1186(5)	2938(12)	−2053(6)	912(34)	C(63)	−36(5)	4089(9)	2513(5)	676(24)
C(34)	1856(6)	3430(13)	−2061(7)	1109(42)	C(64)	−612(4)	4777(10)	2783(5)	789(29)
C(35)	2271(5)	2845(12)	−1464(6)	908(34)	C(65)	−1079(4)	5110(11)	2171(5)	733(27)
C(36)	1986(5)	3165(11)	−741(6)	826(31)	C(66)	−1262(4)	3994(9)	1706(4)	569(23)

[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.

TABLE 5

$Pt(AsPh_3)_2(F_3CC{\equiv}CCF_3)$: SELECTED BOND DISTANCES AND ANGLES

Bond	Distance (Å)	Bond	Distance (Å)
Pt—As(1)	2.3900(7)	As(1)—C(11)	1.932(6)
Pt—As(2)	2.3884(8)	As(1)—C(21)	1.947(6)
Pt—C(2)	2.036(6)	As(1)—C(31)	1.937(6)
Pt—C(3)	2.003(6)	As(2)—C(41)	1.937(6)
C(1)—C(2)	1.451(10)	As(2)—C(51)	1.947(6)
C(2)—C(3)	1.282(9)	As(2)—C(61)	1.935(6)
C(3)—C(4)	1.457(10)		
mean C—F	1.298(4)		

Atoms	Angle (deg)	Atoms	Angle (deg)
As(1)—Pt—As(2)	99.01(2)	C(1)—C(2)—C(3)	139.9(7)
As(1)—Pt—C(2)	114.7(2)	C(3)—C(2)—Pt	70.1(4)
As(2)—Pt—C(3)	109.3(2)	C(1)—C(2)—Pt	150.0(6)
C(2)—Pt—C(3)	37.0(3)	C(2)—C(3)—C(4)	138.4(4)
		C(2)—C(3)—Pt	72.9(4)
		C(4)—C(3)—Pt	148.6(6)
Pt—As(1)—C(11)	116.4(2)	Pt—As(2)—C(41)	112.6(2)
Pt—As(1)—C(21)	115.9(2)	Pt—As(2)—C(51)	114.5(2)
Pt—As(1)—C(31)	117.5(2)	Pt—As(2)—C(61)	120.4(2)
C(11)—As(1)—C(21)	100.1(2)	C(41)—As(2)—C(51)	104.0(2)
C(11)—As(1)—C(31)	105.2(2)	C(41)—As(2)—C(61)	100.3(2)
C(21)—As(1)—C(31)	99.9(2)	C(51)—As(2)—C(61)	102.9(3)
mean C—C—F	113.8(3)	mean F—C—F	104.8(3)
Phenyl rings (weighted mean dimensions)			
C(1)—C(2), C(1)—C(6)	1.382(2)	C(2)—C(1)—C(6)	119.3(2)
C(2)—C(3), C(5)—C(6)	1.397(3)	C(1)—C(2)—C(3), C(1)—C(6)—C(5)	119.7(2)
C(3)—C(4), C(4)—C(5)	1.353(3)	C(2)—C(3)—C(4), C(4)—C(5)—C(6) C(3)—C(4)—C(5)	119.8(2)

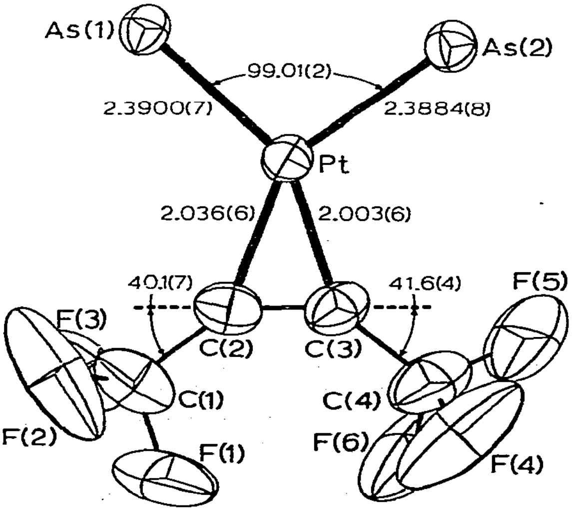

Fig. 1. Inner coordination sphere of the Pt complex, 1, showing distances (Å) and angles (deg). Atoms are shown as 50% probability thermal ellipsoids.

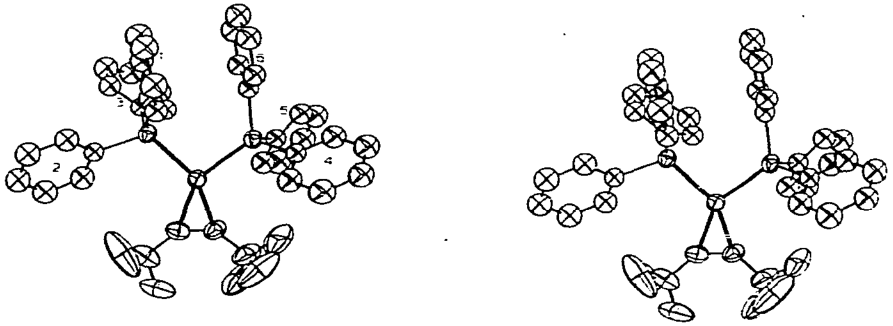

Fig. 2. Stereoview of $Pt(As(C_6H_5)_3)_2F_3CC{\equiv}CCF_3$.

The P(1)—Pd—P(2) bond angle is 111.07(7)°. This is larger (9.1 σ) than the value 110.23(6)° found in the Pt analogue $Pt(PCy_3)_2(F_3CC{\equiv}CCF_3)$ [2]. No significant difference was observed in the Pd—C or Pt—C distances. The Pd—C(2) and Pd—

TABLE 6

$Pd(PCy_3)_2(F_3CC{\equiv}CCF_3)$: SELECTED BOND DISTANCES AND ANGLES

Bond	Distance (Å)	Bond	Distance (Å)
Pd—P(1)	2.358(2)	P(1)—C(11)	1.854(9)
Pd—P(2)	2.363(2)	P(1)—C(21)	1.859(7)
Pd—C(2)	2.040(8)	P(1)—C(31)	1.852(7)
Pd—C(3)	2.053(8)	P(2)—C(41)	1.855(8)
C(1)—C(2)	1.49(1)	P(2)—C(51)	1.846(9)
C(2)—C(3)	1.271(10)	P(2)—C(61)	1.867(8)
mean C—F	1.290(5)		

Atoms	Angle (deg)	Atoms	Angle (deg)
P(1)—Pd—P(2)	111.01(7)	C(1)—C(2)—C(3)	137.1(9)
P(1)—Pd—C(2)	106.6(2)	C(3)—C(2)—Pd	72.5(5)
P(2)—Pd—C(3)	106.1(2)	C(1)—C(2)—Pd	150.3(7)
C(2)—Pd—C(3)	36.2(3)	C(2)—C(3)—C(4)	135.0(8)
		C(2)—C(3)—Pd	71.3(5)
		C(4)—C(3)—Pd	153.4(6)
Pd—P(1)—C(11)	121.0(2)	Pd—P(2)—C(41)	111.0(2)
Pd—P(1)—C(21)	111.5(2)	Pd—P(2)—C(51)	106.1(3)
Pd—P(1)—C(31)	108.5(2)	Pd—P(2)—C(61)	122.4(2)
C(11)—P(1)—C(21)	102.7(3)	C(41)—P(2)—C(51)	105.1(3)
C(11)—P(1)—C(31)	108.9(4)	C(41)—P(2)—C(61)	102.4(4)
C(21)—P(1)—C(31)	102.6(3)	C(51)—P(2)—C(61)	108.5(4)
mean C—C—F	113.7(4)	mean F—C—F	104.7(4)

Cyclohexyl rings (weighted mean dimensions)

Bond	Distance (Å)	Atoms	Angle (deg)
C(1)—C(2), C(1)—C(6)	1.533(3)	C(2)—C(1)—C(6)	109.9(3)
C(2)—C(3), C(5)—C(6)	1.533(3)	C(1)—C(2)—C(3), C(1)—C(6)—C(5)	110.7(2)
C(3)—C(4), C(4)—C(5)	1.508(3)	C(2)—C(3)—C(4), C(4)—C(5)—C(6)	111.8(2)
		C(3)—C(4)—C(5)	111.4(4)

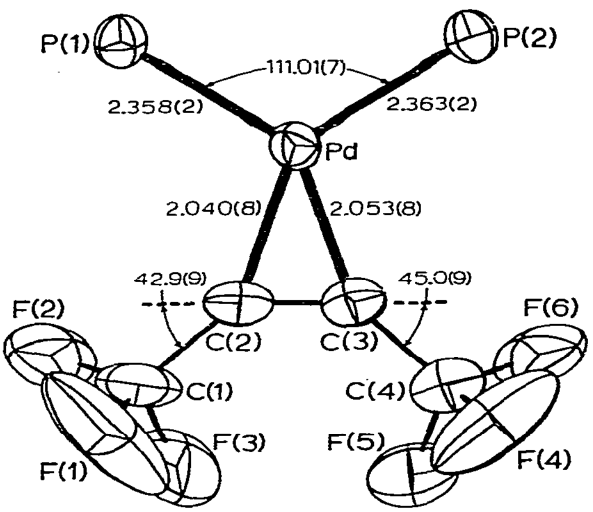

Fig. 3. Inner coordination sphere of the Pd complex, 2. Atoms are shown as 50% probability thermal ellipsoids.

C(3) bond lengths are 2.040(8) and 2.053(8) Å, respectively. Acetylenic C atoms C(2) and C(3) subtend an angle of 36.2(3)° at the Pd atom. The As—C distances in the $AsPh_3$ ligands range from 1.932(6) to 1.947(6) Å, with a mean value of 1.939(2) Å. The mean angle subtended by the α-C atoms at the As atoms is 102.0(1)°. These values are comparable to means of 1.922(7) Å and 105(4)° observed for the $AsPh_3$ ligands in $Pt(C_2(CN)_4O)(AsPh_3)_2$ [11]. The geometries of the arsine ligands are normal [11,12]. The mean P—C bond distance in the PCy_3 ligands, 1.856(3) Å, is identical to that observed in the Pt analogue [2]. The geometries of the PCy_3 ligands are normal [2].

The acetylenic triple bond length, 1.282(9) Å, found in the complex **1** is not significantly different from the value 1.255(9) Å observed in the PPh_3 analogue. The alkyne ligand bend-back angles, 40.1(7) and 41.6(4)°, are statistically equivalent, and indistinguishable from the values 39.3(6) and 40.4(6)° found in the phosphine complex. The C(2)—C(3) bond length in **2**, 1.271(10) Å, is statistically equivalent to the value 1.260(10) Å found in the Pt species [2]. The bend-back angles, 42.9(9) and 45.0(8)°, are significantly larger than those in **1**, and are comparable to the mean value 45.5(8)° observed in the PCy_3 complex of Pt.

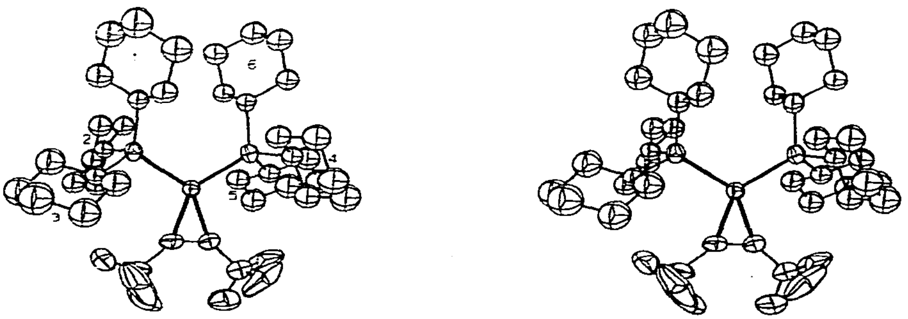

Fig. 4. Stereoview of $Pd(P(C_6H_{11})_3)_2F_3CC{\equiv}CCF_3$.

Discussion

Within the series of complexes, no significant trends in C≡C and M—C bond lengths can be detected by the X-ray method. However, the alkyne ligand bend-back angle does vary significantly. We previously assigned this effect to steric requirements of the bulky phosphine ligands [3]. A value of about 40° appears to be normal for PPh_3 complexes, while larger back-bend angles are found in complexes with bulkier phosphine ligands. Angles 40.1(7) and 41.6(4)° observed in **1** suggest that the electronic properties of the other donor atoms have little effect on the alkyne ligand geometry. The nature of the metal may be more important, because noticeably smaller angles, 33.6(7) and 35.1(7)°, are observed in the complex $Pd(PPh_3)_2(MeO_2CC{\equiv}CCO_2Me)$ [10]. This effect is not reflected in the mean bend-back angles of the complexes $M(PCy_3)_2(F_3CC{\equiv}CCF_3)$, which are 45.6(6) and 44.1(6)°, where M is Pt and Pd, respectively. The increased steric bulk of the PCy_3 ligands may be counteracting the effects of the metal in these complexes.

The opposite effect to that observed in the hexafluoro-but-2-yne complexes is present in the cycloalkyne complexes [13—15]. In the complex $Pt(PPh_3)_2$-(*cyclo*-C_7H_{10}), the mean bend-back angle, 41.1(3)°, and the P—Pt—P angle, 102.58(3)°, are normal. Changing the alkyne to *cyclo*-C_6H_8 is reflected by a greater mean bend-back angle of 52.9(4)° and a corresponding increase in the P—Pt—P angle to 109.54(5)°.

The geometries of the $AsPh_3$ ligands are essentially as expected [13,14]. The deviation of the $AsPh_3$ ligands from C_3 symmetry can be illustrated by the angles between the planes of the phenyl rings and the plane defined by the α-C atoms, as was described for triphenylphosphine [16]. In the solid state, these angles are 68.0, 36.1 and 65.3°. In this structure the angles 82.0, 44.8 and 54.7°, and 85.7, 22.7 and 75.7°, were calculated for the As(1) and As(2) ligands, respectively.

All geometrical features of complex **2** are similar to those found in the Pt analogue [2]. Inspection of the PCy_3 ligands shows that even the cyclohexyl rings have adopted similar orientations. The Pd—P—Cl angles are 121.0(2), 111.5(2) and 108.5(2)°, and 111.0(2), 106.1(3) and 122.4(2)° for P(1) and P(2), respectively. The two largest values, 121.0(2) and 122.4(2)°, are associated with the juxtaposed rings, and presumably are increased by steric repulsion. The corresponding angles in the Pt complex are 120.2(2), 109.5(2) and 109.6(2)°, and 110.5(2) and 105.2(2) and 124.6(2)°. The similarities between the complexes are also reflected by the angles that the planes of the cyclohexyl rings, calculated from ring atoms C(2), C(3), C(5) and C(6), make to the plane defined by the Pd and P atoms. These angles are 40.6, 66.8 and 47.3°, and 68.7, 51.8 and 46.4° for the Pd complex (calculated from rings 1 through 6, in order). The values for the Pt complex are 45.8, 66.6 and 53.7°, and 69.9, 45.7 and 49.8°. Thus changing the metal has not significantly perturbed the geometry of the complexes in the solid state.

In the following paper we report the results of spectroscopic studies on the alkyne complexes, and the first structure determination of an acetylene complex containing a chelating diphosphine of small steric bulk.

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