STUDIES ON METAL-ACETYLENE COMPLEXES

X *. SPECTROSCOPIC STUDIES OF HEXAFLUOROBUT-2-YNE COMPLEXES, AND THE X-RAY STRUCTURE OF AN ACETYLENE COMPOUND CONTAINING A CHIRAL, CHELATING DIPHOSPHINE

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(Received March 13th, 1981)

Summary

The acetylene complex (—)-(*N,N*-bis(diphenylphosphino)-1-phenethylamine) (hexafluorobut-2-yne)platinum(0) has been prepared, and its structure determined by X-ray analysis. Crystals are monoclinic, space group $P2_1$, with a cell of dimensions $a = 11.177(2)$, $b = 15.690(3)$, $c = 19.655(4)$ Å and $\beta = 94.46(1)°$. Intensity data collected on an automated four-circle diffractometer was used for full-matrix least-squares refinement on F, which converged at $R = 0.059$, 5851 observations. There are two molecules in the asymmetric unit. The coordination at the Pt atoms is essentially planar, and the C≡C bond distances are 1.26(2) and 1.25(2) Å. The deviations from linearity of the alkyne ligand upon coordination are $38(2)°$ and $46(2)°$ in one molecule, while values of $40(2)°$ and $39(2)°$ are found in the other. IR, ^{19}F NMR and ^{31}P NMR spectra are reported and discussed for this species and for the series of hexafluorobut-2-yne complexes of general formula ML_2-(acetylene) which we have studied by X-ray techniques.

Introduction

We have recently reported the results of our investigations into how steric [1] and electronic [2] factors affect the activation of an alkyne ligand. In these studies the magnitude of the deviation from linearity of the alkyne ligand (bend-back angle) was determined for several complexes of the type ML_2-($F_3CC≡CCF_3$), where M is Pt or Pd, and L is a phosphine or arsine ligand. It was found that values significantly larger than the 'normal' value of $40°$ [3]

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* For part IX see ref. 2.

result when triphenylphosphine is replaced by ligands of greater steric bulk, such as tricyclohexylphosphine [4]. In order to determine whether a smaller bend-back angle results when the steric bulk of the phosphine ligand is reduced, we undertook the synthesis and structural determination of the complex (—)-(N,N-bis(diphenylphosphino)-1-phenethylamine)(hexafluorobut-2-yne)-platinum(0), 1. We thought that the chiral aminophosphine ligand 2 [5], which forms a four-membered chelate ring upon coordination, would have very little steric effect upon the alkyne ligand. We now report the results of the X-ray

(2)
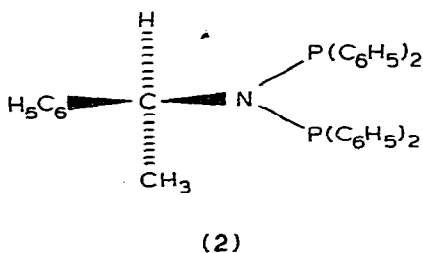
study, together with some spectroscopic data obtained for the complex 1.

Our earlier studies had led us to conclude that diffraction techniques were a relatively insensitive method for detecting small differences in C≡C and M—C bond lengths in a series of these compounds. We therefore routinely recorded the infrared spectra, and the ^{13}C, ^{19}F and ^{31}P nuclear magnetic resonance spectra of the $ML_2(RC≡CR^1)$ complexes. In the final paper of this series the spectral data are presented, correlated with the structural parameters, and discussed for the complexes where M = Pt, R, R' = CF_3, and L = PPh_3, $PCyPh_2$, PCy_2Ph, PCy_3, and $AsPh_3$; M = Pt, L = PPh_3, and R = Ph, R' = Ph, Me and CCO_2Et; and M = Pd, R, R' = CF_3, and L = PCy_3.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer, as Nujol mulls on NaCl plates. ^{19}F and ^{31}P nuclear magnetic resonance spectra were obtained using a Varian XL-100 spectrometer operating at 94.1 MHz and 40.5 MHz, respectively, with 'spectro' grade dichloromethane as the solvent. ^{19}F chemical shifts are given in parts per million downfield from the internal reference $CFCl_3$. ^{31}P chemical shifts are reported in parts per million downfield from the external reference $PO(OCH_3)_3$. Microanalyses were performed by Spang Inc., Ann Arbor, Michigan. All reactions were carried out under a dry nitrogen atmosphere employing standard inert atmosphere techniques.

Preparation of Pt{(—)-(MePhHC)N(PPh$_2$)$_2$}(F$_3$CC≡CCF$_3$)

(—)-(MePhHC)N(PPh$_2$)$_2$, 2 [5], (1.3 g) was added to a toluene solution of Pt(C$_8$H$_{12}$)$_2$ [6] (1 g), and hexafluorobut-2-yne (3 g) was bubbled in slowly. After stirring for 12 h the solvent was removed on a rotary evaporator. Addition of dichloromethane (15 ml) and methanol (150 ml), followed by cooling, gave a white crystalline precipitate. Yield 1.5 g, m.p. 174—176°C (decomp.) Anal. Found: C, 51.07, H, 3.43. Calcd. for C$_{36}$H$_{29}$F$_6$NP$_2$Pt: C, 51.07; H, 3.45%. Mol. wt. by osmometry in benzene 813 g mol^{-1}; Required, 846.67 g mol^{-1}.

Preparation of Pt(PCy₃)₂(F₃CC≡CCF₃)

Preparation of Pt(PCy$_3$)$_2$(F$_3$CC≡CCF$_3$)

PCy$_3$ (4.0 g), obtained by decomposing PCy$_3$ · CS$_2$ in toluene, 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 stirring for 12 h the solvent was removed on a rotary evaporator. Addition of CCl$_2$H$_2$ (15 ml) and CH$_3$OH (150 ml), followed by cooling, resulted in a white crystalline precipitate. Yield 2.0 g (22%). The infrared spectrum was identical to that of an authentic sample [4].

Preparation of (PPh$_3$)$_2$Pt(PhC≡CCO$_2$Et)

Pt(PPh$_3$)$_4$ (0.5 g) and ethylphenylpropiolate (0.3 ml) were stirred in dichloromethane (30 ml) for 35 min. The solvent was removed by a rotary evaporator, and the resulting yellow oil was washed with 2 × 20 ml portions of 60—80 petroleum ether. The residue was dissolved in dichloromethane (10 ml) and passed through a Florisil column. Addition of methanol (40 ml), followed by cooling, resulted in a pale yellow solid. Yield 0.25 g (70%). M.p. 162—164°C (decomp.). Anal. Found: C, 63.15; H, 4.56. Calcd. for C$_{47}$H$_{40}$O$_2$P$_2$Pt: C, 63.15; H, 4.51%.

The following compounds were prepared by published methods: Pt(PPh$_3$)$_2$-(F$_3$CC≡CCF$_3$) [7]; Pt(PCyPh$_2$)$_2$(F$_3$CC≡CCF$_3$) [1]; Pt(PCy$_2$Ph)$_2$(F$_3$CC≡CCF$_3$) [1]; Pd(PCy$_3$)$_2$(F$_3$CC≡CCF$_3$) [8]; Pt(AsPh$_3$)$_2$(F$_3$CC≡CCF$_3$) [7]; Pt(PPh$_3$)$_2$-(PhC≡CPh) [9]; Pt(PPh$_3$)$_2$(PhC≡CMe) [9].

Structure determination

Colourless, transparent crystals of the chiral diphosphine complex **1** were obtained by recrystallization from dichloromethane/methanol mixtures. The systematic absences observed, 0k0 for k odd, and the requirement of an acentric space group for an optically active molecule, determined the space group to be $P2_1$, C_2^2, No. 4 [10]. The density, 1.66(1) g cm^{-3}, was measured by the flotation method; the calculated density is 1.639 g cm^{-3}, assuming $Z = 4$. Thus there are two formula units in the asymmetric unit. Crystal data are given in Table 1.

The crystal chosen for data collection was mounted on a Picker FACS-1 diffractometer with [010] approximately 10° from coincidence with the diffractometer ϕ axis. The measurement of five standard reflections over the course of data collection and an examination of ω-scans for several intense, low-angle reflections before and after data collection, showed no significant degradation of crystal quality had occurred. Details of the parameters associated with data collection are presented in Table 2.

After data collection was complete, the crystal was measured for an absorption correction. Eight faces were identified as the forms {100}, {001}, and {011}, and two broken faces were assigned Miller Indices (1$\bar{4}$0) and (1$\bar{2}$3). The recorded intensities were corrected for monochromator polarization, background, Lorentz and polarization effects, and a standard deviation $\sigma(I)$ assigned to each intensity (I), such that $(\sigma(I)^2) = C + 1/4 (tc/tb)^2 — (bl + bh) + (pI)^2$, when C = total counts measured in time tc, bl and bh are background counts each measured in time tb. p was chosen as 0.03. A total of 6790 reflections was measured. Bijvoet pairs $h1l$ and $h\bar{1}l$ for $0 < 2\theta < 30°$ were recorded to confirm [11] the absolute configuration of **2** [12]. There were 4727 unique

TABLE 1

CRYSTAL DATA

$C_{36}H_{29}F_6NP_2Pt$	F.w. 846.67
Crystal system	Monoclinic
Systematic absences	$0k0$ for k odd
Space group	$P2_1$
Cell constants	$a = 11.177(2)$ Å
	$b = 15.690(3)$ Å
	$c = 19.655(4)$ Å
	$\beta = 94.46(1)°$
Cell volume	3436.5 Å^3
Density measured by flotation in CCl_4 and CH_2BrCH_2Br	
Density (observed)	1.66(1) g cm^{-3}
Density (calculated)	1.639 g cm^{-3}
z	4
μ	40.5 cm^{-1} for Mo-K_α

data with $I > 3\sigma(I)$ which were used in the solution and preliminary refinement of the structure.

Structure solution and refinement

The positional parameters for the two Pt atoms were determined from a three-dimensional Patterson synthesis. The origin was defined by Pt(1) at $y = 1/4$. A series of Fourier syntheses and least-squares refinements revealed the positions of the remaining 90 non-hydrogen atoms. The absolute configuration of the α-C atom of the phenethylamine fragment of the phosphine ligands is known to be S [12], and this enabled the choice of the correct hand for the

TABLE 2

EXPERIMENTAL CONDITIONS ASSOCIATED WITH DATA COLLECTION

Radiation	Mo-K_α, graphite monochromatized
Wavelength (Å)	0.70926
Temperature (°C)	18
Approximate crystal dimensions (cm)	0.013 × 0.026 × 0.006
Mean ω-scan width at 1/2 height	0.072°
No. and 2θ range of centered reflections	30, $20 < 2\theta < 27°$
Scan range and speed	1.10° corrected for dispersion, at 1° per min. Scan range was increased to 1.20° for $2\theta > 30°$
Data collected	$h\bar{k}l$ and $\bar{h}\bar{k}l$, for $0 < 2\theta < 55°$
Background count time	10 s stationary crystal, stationary counter at limits of scan, increased to 20 s for $2\theta > 40°$
Standards	$\bar{2}00, 0\bar{2}0, 200, 1\bar{1}1, 002$ recorded every 250 reflections

TABLE 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}
Pt(1)	3716.9(5) [b]	1/4	5000.7(3)	436(3)	474(4)	378(3)	-28(3)	33(2)	-13(4)
Pt(2)	-1718.6(5)	-1096.1(6)	-35.2(3)	445(4)	428(4)	471(4)	11(3)	110(3)	-14(4)
P(1)	5667(3)	2665(3)	5374(2)	459(21)	524(33)	401(22)	65(20)	64(17)	-23(22)
P(2)	3814(3)	3072(3)	6050(2)	407(23)	484(30)	437(26)	40(21)	78(19)	20(23)
P(3)	-1886(3)	-1606(3)	-1100(2)	371(22)	428(28)	520(27)	1(20)	27(19)	27(23)
P(4)	107(3)	-1076(4)	-464(2)	439(20)	472(25)	433(22)	-23(25)	43(16)	-30(26)
N(1)	5363(9)	3098(9)	6140(6)	397(66)	585(93)	379(71)	53(63)	24(54)	-70(69)
N(2)	-418(9)	-1415(7)	-1251(6)	403(61)	314(77)	424(70)	-27(51)	67(51)	-56(59)
C(1)	3132(21)	1514(14)	3459(10)	1242(185)	543(148)	451(120)	-57(131)	-61(122)	203(109)
C(2)	3041(14)	1997(12)	4107(9)	538(102)	650(128)	507(105)	83(93)	146(82)	87(98)
C(3)	2180(15)	2254(10)	4431(7)	811(118)	310(112)	386(89)	-113(87)	-170(81)	-78(79)
C(4)	866(20)	2483(40)	4844(19)	418(136)	3029(533)	1313(251)	-250(275)	-319(149)	-950(365)
C(5)	6190(12)	3471(9)	6709(7)	481(83)	322(90)	429(89)	-20(70)	-162(68)	-44(76)
C(6)	5563(15)	3672(16)	7343(8)	866(119)	1259(219)	344(92)	140(134)	-39(81)	-153(124)
C(7)	-4387(18)	-1105(26)	600(16)	530(132)	1352(258)	1611(254)	248(195)	442(149)	-285(261)
C(8)	-3078(15)	-947(11)	540(9)	599(105)	438(132)	638(113)	180(91)	139(88)	-119(98)
C(9)	-218(14)	-056(10)	882(9)	608(104)	143(84)	642(116)	-13(76)	76(88)	-116(84)
C(10)	-1840(23)	-211(16)	1536(12)	1223(201)	701(183)	749(167)	-49(154)	401(150)	-114(144)
C(11)	3(12)	-1363(10)	-1952(7)	552(90)	536(129)	391(88)	114(80)	99(69)	102(83)
C(12)	-97(15)	-475(14)	-2248(10)	690(128)	811(161)	784(142)	175(111)	184(101)	348(125)
F(1)	4097(11)	1783(10)	3142(6)	1250(105)	1566(144)	747(87)	2(102)	199(75)	-119(94)
F(2)	3299(16)	709(9)	3585(7)	2678(190)	534(93)	970(107)	353(104)	85(109)	-53(82)
F(3)	2226(11)	1622(9)	2999(6)	1305(100)	1377(126)	592(72)	20(93)	-282(69)	-12(82)
F(4)	426(14)	2765(22)	4826(14)	583(94)	4399(498)	2724(258)	481(162)	101(114)	-1692(284)
F(5)	410(20)	2630(37)	3823(12)	993(130)	7063(839)	1761(188)	1320(286)	-410(122)	393(348)
F(6)	379(21)	1676(19)	4391(29)	791(142)	2352(310)	7349(886)	-573(180)	10(275)	-935(419)
F(7)	-5017(13)	-723(22)	147(11)	585(89)	5066(514)	2137(202)	781(170)	115(100)	1633(262)
F(8)	-4840(12)	-832(15)	1117(8)	941(98)	3088(301)	1585(145)	-112(135)	721(98)	-770(177)
F(9)	-4680(16)	-1876(14)	573(19)	944(129)	1304(171)	6585(605)	-486(127)	1452(227)	-958(275)
F(10)	-2756(13)	-131(10)	1931(6)	1760(128)	1339(131)	983(97)	-376(106)	825(94)	-452(95)
F(11)	-996(14)	-648(10)	1909(6)	1814(142)	1248(131)	748(93)	25(108)	-230(91)	8(90)
F(12)	-1406(12)	539(9)	1435(6)	1534(117)	731(97)	970(97)	-429(87)	411(82)	-180(80)

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

model from the beginning. Rigid group constraints were imposed upon the ten phenyl rings, D_{6h}, C—C 1.392 Å [13].

The data were corrected for absorption effects using the Gaussian method with $6 \times 8 \times 4$ grid [14]. Transmission coefficients varied from 0.222 to 0.405. The structure was refined by full-matrix least-squares techniques on F. Scattering factors for neutral non-hydrogen atoms were taken from Volume IV [10], while those for H were from Stewart et al. [15]. The real and imaginary corrections for anomalous dispersion of Cromer and Liberman [16] were included for the Pt and P atoms.

A correlation between the thermal parameters of the Pt atoms was noted in the least-squares refinements during the solution of the structure. Therefore, in the initial stages of full matrix least-squares refinement of the complete structure the thermal parameters for all atoms were restricted to partial shifts. One cycle of refinement varying positional and anisotropic thermal parameters for the Pt and P atoms, positional parameters for the remaining non-group atoms, and a group origin, three orientation angles and individual isotropic thermal parameters for each group gave agreement factors $R_1 = \Sigma \|Fo| - Fc\| / \Sigma |Fo| = 0.062$ and $R_2 = (\Sigma w(|Fo| - |Fc|)^2 / \Sigma wFo^2)^{1/2} = 0.069$. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$, and the weight w is given by $4Fo^2/\sigma^2(Fo^2)$. In subsequent refinement anisotropic thermal parameters were assigned to firstly the F atoms, then to the N atoms and lastly to the non-group C atoms. Refinement proceeded slowly, and some oscillation of parameters was observed. The restriction on the shifts of the thermal parameters was removed, and the 58 H atoms were located in regions of positive electron density in a difference Fourier synthesis. Electron densities for these atoms ranged from 0.7(1) to 0.2(1) e Å^{-3}. The contribution from the H atoms was included in the calculations of Fc. Two cycles of refinement resulted in agreement factors $R_1 = 0.0398$ and $R_2 = 0.0397$. An examination of the Bijvoet pairs ($k = \pm 1$) confirmed the choice of hand. The refinement of 408 variables, with 5851 observations ($I > \sigma(I)$), converged at residuals $R_1 = 0.0587$ and $R_2 = 0.0480$.

In the final cycle the largest shift was 0.165 esd. A statistical analysis of R_2 over various ranges of $|Fo|$, $\lambda^{-1} \sin \theta$ and diffractometer setting angles χ and ϕ

TABLE 4

RIGID GROUP PARAMETERS

Group	x_g [a]	y_g	z_g	δ	ϵ	η
Ph-2	0.8234(6)	0.2394(6)	0.7116(4)	0.939(8)	2.877(7)	—0.223(8)
Ph-3	0.7208(7)	0.0954(6)	0.5559(3)	0.522(7)	3.066(8)	—0.017(7)
Ph-4	0.7220(6)	0.3966(6)	0.4553(4)	2.440(9)	—2.551(8)	—2.201(9)
Ph-5	0.2893(5)	0.1919(5)	0.7256(4)	—0.469(9)	2.280(6)	2.141(9)
Ph-6	0.2598(6)	0.4905(5)	0.6176(3)	—2.671(7)	3.060(8)	0.000(7)
Ph-7	0.2381(6)	—0.2087(5)	—0.2090(3)	1.170(6)	—2.971(6)	—2.834(7)
Ph-8	—0.2493(6)	—0.3589(5)	—0.1340(3)	—0.236(6)	—3.053(7)	3.066(6)
Ph-9	—0.3609(6)	—0.0636(5)	—0.2223(4)	—2.266(9)	—2.453(6)	2.026(9)
Ph-10	0.1984(6)	—0.2375(5)	0.0306(4)	0.789(8)	2.653(7)	1.294(8)
Ph-11	0.1480(6)	0.0720(5)	—0.0485(3)	2.665(6)	—3.136(7)	3.042(7)

[a] x_g, y_g and z_g are the fractional coordinates of the group origin; δ, ϵ and η (radians) are the group orientation angles [13].

TABLE 5. DERIVED GROUP ATOM PARAMETERS

Atom	x	y	z	$B\ (\text{Å}^2)$	Atom	x	y	z	$B\ (\text{Å}^2)$
Ph2					**Ph5**				
C(21)	7261(8)[a]	2899(7)	6888(6)	4.0(3)	C(51)	3261(8)	2435(7)	6735(4)	3.7(3)
C(22)	8421(11)	3225(6)	6901(6)	5.9(4)	C(52)	2870(9)	2802(5)	7323(6)	4.8(4)
C(23)	9394(7)	2720(9)	7129(7)	7.1(5)	C(53)	2502(9)	2287(8)	7844(4)	5.6(4)
C(24)	9209(9)	1888(9)	7344(7)	7.6(5)	C(54)	2525(9)	1404(7)	7777(5)	5.6(4)
C(25)	8048(11)	1562(6)	7332(6)	6.3(5)	C(55)	2917(10)	1036(5)	7190(6)	5.5(4)
C(26)	7075(7)	2068(8)	7104(6)	4.6(4)	C(56)	3285(9)	1552(8)	6668(5)	4.4(4)
Ph3					**Ph6**				
C(31)	6586(9)	1721(6)	5478(6)	3.5(3)	C(61)	3163(9)	4117(6)	6144(6)	3.5(3)
C(32)	7835(9)	1720(7)	5550(6)	5.4(4)	C(62)	1916(8)	4163(7)	6118(6)	5.3(4)
C(33)	8457(7)	953(9)	5630(6)	7.0(5)	C(63)	1352(7)	4951(8)	6150(6)	6.8(5)
C(34)	7829(12)	187(7)	5640(7)	7.4(6)	C(64)	2034(11)	5693(6)	6209(7)	7.3(5)
C(35)	6580(12)	189(6)	5568(7)	7.4(5)	C(65)	3281(11)	5647(6)	6235(7)	5.8(4)
C(36)	5959(7)	955(8)	5487(5)	4.7(4)	C(66)	3845(6)	4859(8)	6202(6)	4.6(4)
Ph4					**Ph7**				
C(41)	6551(9)	3403(8)	4918(5)	3.1(3)	C(71)	1248(7)	−1745(7)	−2020(5)	3.7(3)
C(42)	7059(11)	3128(7)	4332(6)	7.5(6)	C(72)	1361(8)	−2575(7)	−2258(5)	4.5(3)
C(43)	7728(10)	3691(10)	3967(5)	7.5(5)	C(73)	2494(10)	−2916(6)	−2328(6)	5.7(4)
C(44)	7890(10)	4529(9)	4188(7)	7.0(5)	C(74)	3515(7)	−2428(8)	−2160(6)	5.8(4)
C(45)	7382(12)	4804(7)	4775(7)	8.3(6)	C(75)	3402(7)	−1599(8)	−1922(6)	6.0(4)
C(46)	6712(10)	4241(9)	5139(5)	6.0(5)	C(76)	2269(10)	−1257(6)	−1852(6)	5.8(4)
Ph8					**Ph10**				
C(81)	−2202(9)	−2730(5)	−1264(5)	3.2(3)	C(101)	1201(8)	−1823(7)	−61(5)	3.3(3)
C(82)	−3398(7)	−2986(7)	−1302(5)	5.3(4)	C(102)	1455(10)	−1705(7)	638(5)	5.0(4)
C(83)	−3689(7)	−3845(8)	−1378(5)	5.8(4)	C(103)	2238(11)	−2257(8)	1004(4)	6.4(5)
C(84)	−2784(11)	−4448(5)	−1415(6)	6.1(5)	C(104)	2767(9)	−2927(7)	673(6)	5.7(4)
C(85)	−1588(9)	−4193(6)	−1377(6)	5.9(4)	C(105)	2513(10)	−3044(7)	−25(6)	6.7(5)
C(80)	−1297(6)	−3334(7)	−1302(5)	4.2(3)	C(106)	1731(9)	−2492(8)	−392(4)	4.7(3)
Ph9					**Ph11**				
C(91)	−2869(8)	−1075(7)	−1740(5)	3.9(3)	C(111)	907(9)	−68(6)	−506(6)	3.7(3)
C(92)	−3409(9)	−315(8)	−1563(4)	4.9(4)	C(112)	2150(8)	−24(6)	−392(6)	4.4(4)
C(93)	−4150(10)	124(6)	−2046(6)	6.0(4)	C(113)	2723(6)	764(8)	−370(5)	4.8(4)
C(94)	−4350(9)	−198(8)	−2706(5)	5.3(4)	C(114)	2053(10)	1508(6)	−463(6)	6.0(4)
C(95)	−3809(10)	−957(8)	−2882(4)	5.9(4)	C(115)	810(10)	1465(6)	−577(6)	5.7(4)
C(90)	−3069(9)	−1396(6)	−2399(5)	4.6(4)	C(116)	237(6)	677(8)	−599(5)	5.0(4)

[a] Positional parameters ×10⁴.

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 1.34(15) e Å^{-3} at fractional coordinates (0.332, 0.153, 0.477) and is of no chemical significance.

Final positional and thermal parameters for non-H atoms are given in Table 3, rigid group parameters in Table 4, and derived group atom parameters in Table 5. H atom parameters and structure amplitudes as $10|Fo|$ and $10|Fc|$, in electrons, have been deposited* .

Description of the structure

Principal bond distances and bond angles are presented in Table 6, and some weighted least-squares planes are given in Table 7. The inner coordination spheres of the Pt atoms, together with the atom labeling scheme and some bond distances and angles, are shown in Figs. 1 and 2. Stereoviews of molecules A and B are presented in Figs. 3 and 4, respectively, and a stereoview of the unit cell is given in Fig. 5. The atoms N(1), C(5), C(6), and C(21) through C(26) are the phenethylamine fragment of the phosphine ligand in molecule A. Atom N(1) is bonded to atoms P(1), P(2), and C(5). Atom C(5) is bonded to the methyl group C atom C(6), and to phenyl group C(21) to C(26). Likewise the phenethylamine fragment of the phosphine ligand in molecule B is numbered N(2), C(11), C(12), and C(71) through C(76). The structure consists of discrete molecular units, for the closest intermolecular distance of approach is 2.43 Å between hydrogen atoms H1C(6) and H1C(84) in the equivalent position $(1 - x, 1 - y, 1 - z)$.

The coordination about the Pt atoms is essentially planar. The dihedral angles between the planes containing the PtP$_2$ moieties, and those containing the Pt atoms and the acetylenic C atoms are 4.0(11) and 3.1(6)°, for molecules A and B respectively. While the Pt—P bond distances in molecule A, 2.245(4) and 2.260(4) Å, are statistically equivalent, the bond distances in molecule B, 2.236(4) and 2.267(3) Å, are significantly different (6.2σ). No chemical significance is assigned to this difference. The mean Pt—P bond distance is 2.254(2) Å. The P atoms subtend angles of 71.3(1) and 70.7(1)° at the Pt atoms. The mean Pt—C bond length, where C is an acetylenic C atom, is 2.009(8) Å. This bond distance is comparable to those observed in analogous structures [2]. The C(2)—Pt(1)—C(3) angle is 36.4(6)° and the C(8)—Pt(2)—C(9) angle is 36.2(6)°.

The molecular dimensions of the N,N-bis(diphenylphosphino)-1-phenethyl-amine ligands 2 are similar to those observed for the N,N-bis(diphenylphos-phino)ethylamine ligand [17]. The bond angles around the P atoms indicate that they adopt a greatly distorted tetrahedral geometry. A mean P—C distance of 1.815(4) Å is comparable to values observed in previous structures [2]. The two P, the N, and the α-C atom of each phosphine ligand are essentially copla-nar (see Table 7). The plane calculated using these atoms makes an angle of

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TABLE 6

SELECTED BOND DISTANCES AND ANGLES

Molecule A		Molecule B	
Bond	Distance (Å)	Bond	Distance (Å)
Pt(1)—P(1)	2.260(4)	Pt(2)—P(3)	2.236(4)
Pt(1)—P(2)	2.245(4)	Pt(2)—P(4)	2.267(3)
Pt(1)—C(2)	2.019(18)	Pt(2)—C(8)	1.977(15)
Pt(1)—C(3)	2.014(15)	Pt(2)—C(9)	2.034(16)
C(2)—C(3)	1.26(2)	C(8)—C(9)	1.25(2)
C(1)—C(2)	1.49(2)	C(7)—C(8)	1.50(2)
C(3)—C(4)	1.51(2)	C(9)—C(10)	1.49(3)
C(5)—N(1)	1.51(2)	C(11)—N(2)	1.49(2)
C(5)—C(6)	1.51(2)	C(11)—C(12)	1.51(2)
C(5)—C(21)	1.52(2)	C(11)—C(71)	1.53(2)
P(1)—N(1)	1.710(12)	P(3)—N(2)	1.716(10)
P(2)—N(1)	1.727(11)	P(4)—N(2)	1.697(11)

Atoms	Angle (deg)	Atoms	Angle (deg)
P(1)—Pt(1)—P(2)	71.3(1)	P(3)—Pt(2)—P(4)	70.7(1)
P(1)—Pt(1)—C(2)	127.8(4)	P(3)—Pt(2)—C(8)	124.5(5)
P(2)—Pt(1)—C(3)	124.5(5)	P(4)—Pt(2)—C(9)	128.5(5)
C(2)—Pt(1)—C(3)	36.4(6)	C(8)—Pt(2)—C(9)	36.2(6)
C(1)—C(2)—C(3)	134(2)	C(7)—C(8)—C(9)	140(2)
C(3)—C(2)—Pt(1)	71(1)	C(9)—C(8)—Pt(2)	74(1)
C(1)—C(2)—Pt(1)	153(1)	C(7)—C(8)—Pt(2)	145(2)
C(2)—C(3)—C(4)	142(2)	C(8)—C(9)—C(10)	141(2)
C(2)—C(3)—Pt(1)	72(1)	C(8)—C(9)—Pt(2)	69(1)
C(4)—C(3)—Pt(1)	143(2)	C(10)—C(9)—Pt(2)	149(1)
P(1)—N(1)—P(2)	99.6(6)	P(3)—N(2)—P(4)	99.5(6)
P(1)—N(1)—C(5)	130.8(9)	P(3)—N(2)—C(11)	122.9(9)
P(2)—N(1)—C(5)	129.4(9)	P(4)—N(2)—C(11)	135.5(9)
N(1)—C(5)—C(6)	113(1)	N(2)—C(11)—C(12)	113(1)
N(1)—C(5)—C(21)	112(1)	N(2)—C(11)—C(71)	114(1)
C(6)—C(5)—C(21)	110(1)	C(12)—C(11)—C(71)	112(1)
Pt(1)—P(1)—N(1)	94.5(4)	Pt(2)—P(3)—N(2)	94.0(4)
Pt(1)—P(2)—N(1)	94.6(4)	Pt(2)—P(4)—N(2)	94.4(4)
C(5)—C(21)—C(26)	119.4(10)	C(11)—C(71)—C(72)	120.2(9)
C(5)—C(21)—C(22)	120.3(10)	C(11)—C(71)—C(76)	119.8(9)

TABLE 7

WEIGHTED LEAST-SQUARES PLANES

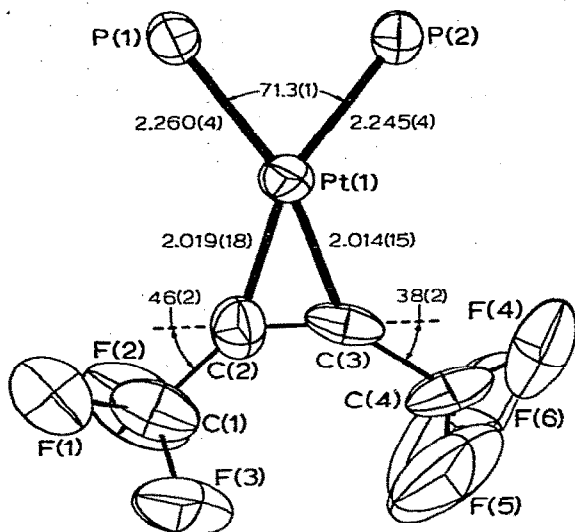| Atom	Displacement (Å)	Atom	Displacement (Å)
Plane 1. $-0.307x - 14.380y + 7.862z = 0.222$			
Pt(1)	0.0000(2)	C(2)	0.041(18)
P(1)	−0.003(5)	C(3)	−0.047(16)
P(2)	−0.000(5)		
Plane 2. $1.690x - 14.467y + 6.750z = 1.271$			
Pt(2)	0.0005(9)	C(8)	−0.057(17)
P(3)	−0.009(5)	C(9)	−0.096(16)
P(4)	−0.009(5)		
Plane 3. $-0.034x - 14.163y + 8.437z = 0.741$			
P(1)	−0.001(4)	N(1)	0.033(13)
P(2)	−0.001(5)	C(5)	−0.019(15)
Plane 4. $2.923x - 14.874y + 3.154z = 1.493$			
P(3)	−0.002(5)	N(2)	0.095(5)
P(4)	−0.007(5)	C(11)	−0.080(16)

Fig. 1. An ORTEP illustration of the inner coordination sphere of molecule A, with thermal ellipsoids drawn at 50% probability.

2.4° to the coordination plane in molecule A, and one of 12.0° in molecule B. The major difference between the two molecules, in the crystal structure, is the position of the methyl group in the aminophosphine ligand. In molecule A the methyl atom C(6) is 0.234 Å from the plane of the aminophosphine ligand, while in molecule B C(12) is 1.524 Å from the analogous plane. Thus two different conformers of the complex have crystallized in the asymmetric unit.
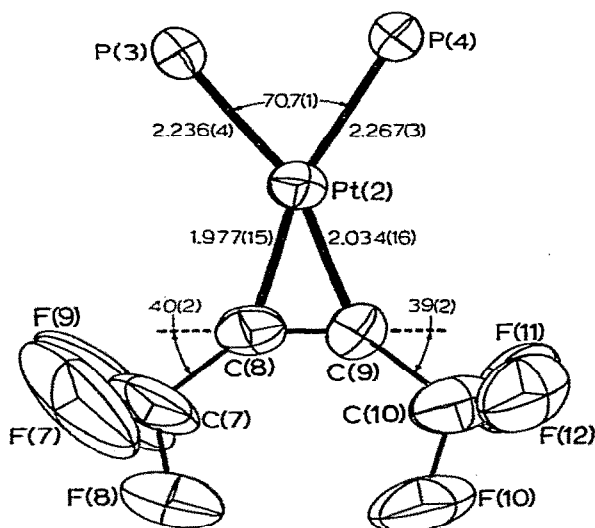
Fig. 2. An ORTEP illustration of the inner coordination sphere of molecule B, with thermal ellipsoids drawn at 50% probability.
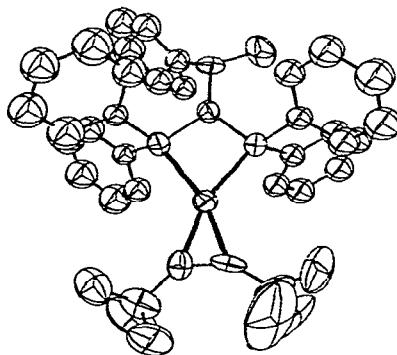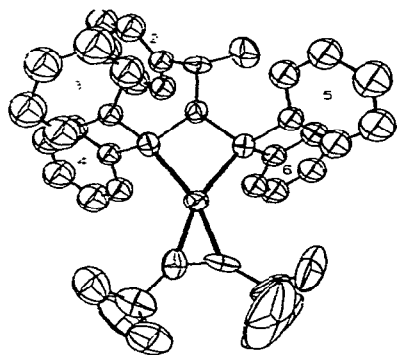
Fig. 3. A stereoview of molecule A.
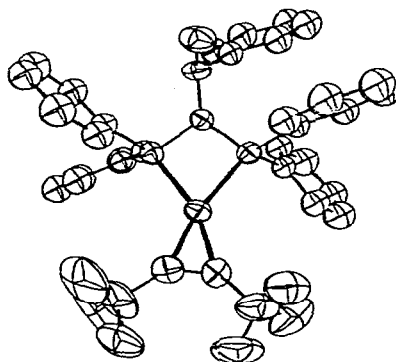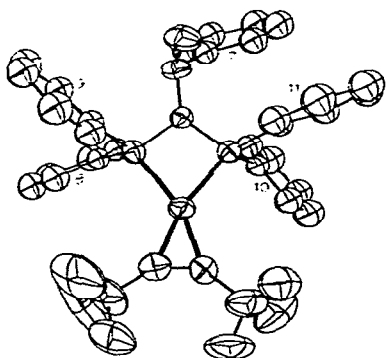
Fig. 4. A stereoview of molecule B.
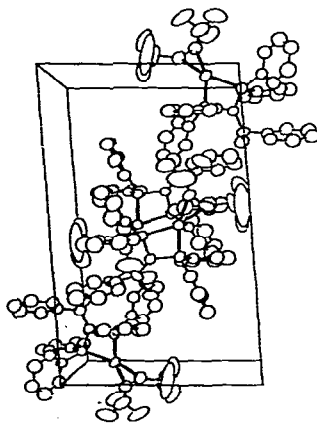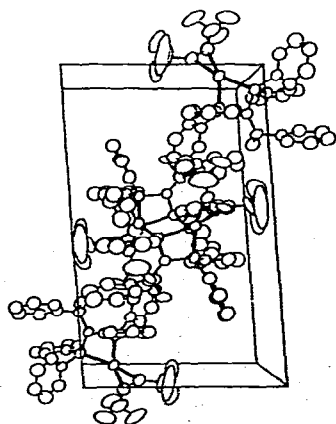
Fig. 5. A stereoview of the unit cell. The *a* axis runs from left to right, with *c* vertical.

TABLE 8

SUMMARY OF STRUCTURAL RESULTS

Complex	Bond distances (Å)		C≡C	Bond angles (deg)				Reference
	M–L	M–C		L–M–L	C–M–C	dihedral angle	bend-back angle	
(PPh₃)₂Pt(F₃CC≡CCF₃)	2.277(1) 2.285(1)	2.024(5) 2.031(5)	1.255(9)	100.17(4)	36.1(2)	3.7(4)	39.3(6) 40.4(6)	3
(PCyPh₂)₂Pt(F₃CC≡CCF₃)	2.297(1)	2.039(7)	1.294(14)	100.77(8)	37.0(4)	1.4(2)	43.5(5)	1
(PCy₂Ph)₂Pt(F₃CC≡CCF₃)	2.292(3) 2.287(3)	2.048(12) 2.022(12)	1.294(16)	108.6(1)	37.1(4)	3.7(8)	40(1) 47(1)	1
(PCy₃)₂Pt(F₃CC≡CCF₃)	2.309(2) 2.301(2)	2.047(7) 2.045(8)	1.260(10)	110.23(6)	35.9(3)	6.5(5)	46.3(8) 44.6(8)	5
(PCy₃)₂Pd(F₃CC≡CCF₃)	2.358(2) 2.363(2)	2.040(8) 2.053(8)	1.271(10)	111.01(7)	36.2(3)	2.8(4)	42.9(9) 45.0(8)	2
(AsPh₃)₂Pt(F₃CC≡CCF₃)	2.3900(7) 2.3884(8)	2.036(6) 2.003(6)	1.282(9)	99.01(2)	37.0(3)	3.0(4)	40.1(7) 41.6(4)	2
((–)-(MePhHC)N(PPh₂)₂)-Pt(F₃CC≡CCF₃)	2.245(4) 2.260(4) 2.236(4) 2.267(3)	2.014(15) 2.019(18) 1.977(15) 2.034(16)	1.26(2) 1.25(2)	71.3(1) 70.7(1)	36.4(6) 36.2(6)	4.0(11) 3.1(6)	38(2) 46(2) 40(2) 39(2)	
(PPh₃)₂Pt(PhC≡CPh)	2.28 2.27	2.01 2.06	1.32(9)	102	39	14	40 41	26

Compound								Ref.
(PPh₃)₂Pt(PhC≡CMe)	2.277(3) 2.298(4)	2.014(16) 2.044(17)(Ph)	1.277(25)	103.3(2)	36.7(7)	6.4(7)	38.2(18) 41.0(16)(Ph)	27
(PPh₃)₂Pt(PhC≡CCO₂Et)	2.269(1) 2.289(1)	2.046(5) 2.014(5)(CO₂Et)	1.286(8)	109.84(5)	36.9(2)	5.2(3)	39.0(6) 39.7(6)(CO₂Et)	28
(PPh₃)₂Pt(cyclo-C₆H₈)	2.271(1) 2.264(1)	2.044(5) 2.034(6)	1.297(8)	109.54(5)	37.1(2)	4.4(3)	58.6(5) 51.9(6)	29, 31
(PPh₃)₂Pt(cyclo-C₇H₁₀)	2.270(1) 2.264(1)	2.064(4) 2.035(4)	1.283(5)	102.58(3)	36.5(1)	7.9(3)	43.6(4) 38.6(4)	30, 31
(PPh₃)₂Pt(p-NO₂C₆H₄C≡CCO₂Et)	2.278(1) 2.286(1)	2.033(5) 2.015(5)(CO₂Et)	1.313(7)	103.42(4)	37.8(2)	9.1(3)	40.4(5) 37.9(5)(CO₂Et)	28
(PPh₃)₂Pt(HC≡CC₆H₁₀OH)	2.298(4) 2.306(4)	2.069(13)(H) 2.097(13)	1.302(16)	109.3(1)	36.4(4)	6.7(8)	40.6(12	
	2.287(4) 2.301(4)	2.061(15)(H) 2.067(14)	1.322(18)	108.0(1)	37.4(5)	7.2(7)	33.2(14)	32
(PPh₃)₂Pd(MeO₂CC≡CCO₂Me)	2.321(2) 2.330(—)	2.074(6) 2.051(6)	1.279(11)	107.43(6)	36.1(3)	9.7(4)	33.6(7) 35.1(7)	33

TABLE 9

SUMMARY OF NMR ^{a} AND IR SPECTROSCOPIC DATA

Complex	δ(^{31}P) ^{b,c}	|^1J(Pt–P)|	δ(^{19}F) ^{d}	|^4J(P–F)| ^{e}	|^3J(Pt–F)|	ν(C≡C) (cm^{-1})
(PPh$_3$)$_2$Pt(F$_3$CC≡CCF$_3$)	19.4	3587	–54.1	10.5	66.1	1775
(PCyPh$_2$)$_2$Pt(F$_3$CC≡CCF$_3$)	24.5	3529	–53.7	10.6	65.2	1750
(PCy$_2$Ph)$_2$Pt(F$_3$CC≡CCF$_3$)	27.3	3535	–53.0	10.4	61.0	1740
(PCy$_3$)$_2$Pt(F$_3$CC≡CCF$_3$)	28.0	3486	–51.9	10.3 ^{f}	58.9	1730
(PCy$_3$)$_2$Pd(F$_3$CC≡CCF$_3$)	38.9		–50.9	10.8		1762
(AsPh$_3$)$_2$Pt(F$_3$CC≡CCF$_3$)			–55.7			1775
((–)-(MePhHC)N(PPh$_2$)$_2$)Pt(F$_3$CC≡CCF$_3$)	57.7	2929	–56.3	14.9	82.7	1755
(PPh$_3$)$_2$Pt(PhC≡CPh)	25.4	3456			78.6	1740
(PPh$_3$)$_2$Pt(PhC≡CMe)	27.1, 26.0	3393, 3450				1757
(PPh$_3$)$_2$Pt(PhC≡CCO$_2$Et)	24.8, 23.5	3623, 3520				1735
(PPh$_3$)$_2$Pt(cyclo-C$_6$H$_8$) ^{f}	27.6	3409				1721
(PPh$_3$)$_2$Pt(cyclo-C$_7$H$_{10}$) ^{g}	27.7	3420				1770

^{a} Chemical shifts are in ppm and coupling constants in Hz. Spectra were recorded as CH$_2$Cl$_2$ solutions. ^{b} Downfield from external PO(OCH$_3$)$_3$ in (CD$_3$)$_2$CO. Chemical shifts for the free phosphines, measured in (C$_2$H$_5$)$_2$O: PPh$_3$, –8.3; PCyPh$_2$, –6.1; PCy$_2$Ph, 0.8; PCy$_3$, 5.3; (MePhHC)N(PPh$_2$)$_2$, 51.5 ppm. Data from Payne and Stephan [34]. ^{c} |^2J(P–P')| is 9.1 Hz for (PCy$_3$)$_2$Pt(F$_3$CC≡CCF$_3$), 33.6 Hz for (PPh$_3$)$_2$Pt(PhC≡CMe) and 23.5 Hz for (PPh$_3$)$_2$Pt(PhC≡CCO$_2$Et). ^{d} Downfield from internal CFCl$_3$. Chemical shift for neat.F$_3$CC≡CCF$_3$ is –57.0 ppm [22]. ^{e} |^4J(P–F)$_{cis}$ + ^4J(P–F)$_{trans}$. ^{f} ^4J(P–F)$_{cis}$(calcd.) = 0. ^{g} Data from ref. 24.

Related to this is the fact that in molecule A the plane of phenyl ring 2 is almost parallel (an angle of 15.3°) to the plane of ring 3, with the atoms C(31) through C(36) being 3.1 to 3.8 Å from the plane of ring 2. No such interaction exists in molecule B. The bond angles subtended at the N atoms indicate that the atoms may be considered as sp^2 hybridized. The mean P—N bond length, 1.713(5) Å, is less than the sum of the covalent radii of the atoms (1.81 Å), which may reflect the presence of some multiple bonding. There are no other deviations from the expected geometries of the ligands [17]. The absolute configuration of the α-C atom of the phenethylamine fragment was confirmed as S.

The C≡C bond lengths, 1.26(2) and 1.25(2) Å, are equivalent. The alkyne bend-back angles range from 38(2) to 46(2)°. Those values associated with the hexafluorobut-2-yne ligands, and the geometries of the CF₃ groups, are normal [1—4]. The mean C—F bond distance is 1.294(7) Å and the mean F—C—F angle is 105.7(7)°.

Discussion of the structure

A summary of the structural data for the hexafluorobut-2-yne complexes is given in Table 8. In the present study of complex 1, the use of a chelating ligand has considerably reduced the spatial requirements for the phosphine ligands, as shown by the P—Pt—P angles of 71.3(1) and 70.7(1)°. These values are about 30° less than those found in the PPh₃ complex [3]. In spite of the small angle, three of the four bend-back angles observed are indistinguishable from the values found in the PPh₃ complex. Even the smallest is only 38(2)°. It is not clear why one value, 46(2)°, should be much larger than the others. All the phenyl C atoms in that molecule are further than 3.5 Å from the atoms of the CF₃ group, and the closest contact in the crystal is 2.56 Å between atoms F(3) and H1C(96) in equivalent position ($-x$, 1/2 + y, $-z$), so packing forces cannot be adduced. In spite of this variation, the mean bend-back angle in the two molecules of 1 is 40.7(10)°. Thus it appears that reducing the steric size of the phosphines to less than that of PPh₃ does not result in a corresponding decrease in bend-back angle. Moreover, in the case of Pt(PPh₃)₂(HC≡CH), a value of 41° was calculated from the $^1J(^{13}C—^1H)$ coupling constant [18]. From these and our previous results we therefore conclude that a value close to 40° is the 'normal' bend-back angle due to electronic effects in these PtP₂(hexafluorobut-2-yne) complexes, and that larger values arise from predominantly steric effects. This conclusion is in accord with the value of 27° reported for the diacetylene complex Pt(PhC₂Ph)₂ [19]. In this study the authors attributed the smaller bend-back angle to the reduced back-donation resulting from the absence of the phosphine ligands.

There is no particular trend apparent in the C≡C bond distances. The values in 1, 1.26(2) and 1.25(2) Å, are not significantly different from the values found for the other hexafluorobut-2-yne complexes. Metal atom—alkyne C atom bond distances in the series range from 1.977(15) to 2.053(8) Å, a variation of 4.5σ. There are no obvious trends within the values. Examination of the structural parameters associated with the metal—alkyne interaction reveals that in the X-ray experiment only the bend-back angle is sensitive to changes within the complexes.

A summary of the spectroscopic data is given in Table 9. Some trends are more evident here.

1. IR spectra

The diphosphine complex 1 has a strong absorption at 1755 cm^{-1}, which, as in all the complexes, is in the range 1700—1800 cm^{-1} and assigned to the ν_1 stretching vibration of the acetylene moiety [20]. Variations within the series are consistent with the Dewar-Chatt-Duncanson bonding theory [9,21]. As the Lewis basicity of the phosphine ligands is increased, from that of PPh$_3$ to that of PCy$_3$, there is a corresponding decrease in $\nu(C\equiv C)$ from 1775 cm^{-1} to 1730 cm^{-1}. This is interpreted as a lowering of the triple bond order, as a result of an increase in transfer of electron density to the π^*-orbitals. The same effect can be caused by changing the substituents of the alkyne ligand. For example, replacing the methyl group in Pt(PPh$_3$)$_2$(PhC$\equiv$CMe) with a more electronegative group, such as CO$_2$Et, would increase the back-bonding and lower the triple bond order. This is indeed observed, as the change in $\nu(C\equiv C)$ upon coordination, $\Delta\nu(C\equiv C)$, is 478 cm^{-1} for PhC$\equiv$CMe and 502 cm^{-1} for PhC$\equiv$CCO$_2$Et. The degree of synergic bonding can also be altered by changing the metal. The C$\equiv$C stretching vibration for the Pd complex is 1762 cm^{-1}. The Pt analogue has a much lower value, 1730 cm^{-1}. Replacement of the phosphine ligands by a second acetylene molecule also results in less back donation, with $\Delta\nu(C\equiv C)$ values ranging from 285 to 350 cm^{-1} being observed for a series of compounds [19]. As was previously noted, IR spectra provide a much more sensitive probe of the C$\equiv$C bond strength. Using these data, the basicity of ligand 2 would appear to be comparable to that of PCyPh$_2$ in its effects on the metal to alkyne back donation.

2. NMR spectra

^{19}F and ^{31}P NMR spectra of the aminophosphine complex have been recorded, and the results are given in Table 9, together with values for the other compounds. Complex 1 exhibits an A$_3$A$_3'$XX$'$ pattern (A = F and X = P) with Pt satellites. The P resonance, 57.7 ppm, is at the lowest field of all the compounds reported. This is attributed to the presence of some multiple bonding between the P atoms and the N atom. It was noted earlier that the mean P—N bond distance, 1.713(5) Å, is less than the sum of the covalent radii of the atoms. The smaller $|^1J(Pt-P)|$ value is consistent with this, or may be due to the strained four-membered ring.

The ^{19}F chemical shift for neat hexafluorobut-2-yne is —57.0 ppm [22]. Thus the ^{19}F resonance of —56.3 ppm ($|^3J(Pt-F)|$ = 78.6 Hz) means that the aminophosphine complex has the lowest complexation shift, 0.7 ppm. This suggests that the phosphine ligand is the poorest σ-donor within the series of complexes.

The observed A$_3$A$_3'$XX$'$ spectra for all the complexes indicates that in each case the alkyne ligand is not fluxional at room temperature on the NMR time scale, and that the P—M—P plane is not perpendicular to the C—M—C plane. The centreband regions of the spectra are generally unresolved multiplets. Only the complex Pt(PCy$_3$)$_2$(F$_3$CC$\equiv$CCF$_3$) gives a sufficiently resolved spectrum to permit complete spectral analysis. Theoretical ^{19}F and ^{31}P NMR spectra were

calculated for the PCy_3 complex, using the equations published by Anet [23]. The analysis was facilitated by the extremely large difference between the resonance frequencies of the ^{19}F and ^{31}P nuclei, and by the reasonable assumption that $^5J(F-F')$ is zero. $|^2J(P-P')|$ was calculated to be 9.1 Hz. Singlets were observed in the proton-decoupled ^{19}F NMR spectrum of the arsine complex, and in the ^{31}P NMR spectrum of $Pt(PPh_3)_2(PhC\equiv CPh)$. The complexes where the alkyne is $PhC\equiv CMe$ and $PhC\equiv CCO_2Et$ have AB type ^{31}P NMR spectra with $|^2J(P-P)|$ being 33.6 and 23.5 Hz, respectively.

Trends within the NMR data can be rationalized. In both the ^{19}F and ^{31}P NMR spectra of the hexafluorobut-2-yne complexes, shielding is in the order $PPh_3 > PCyPh_2 > PCy_2Ph > PCy_3$. The $\delta(^{31}P)$ values, for the complexes where L is one of the aforementioned phosphines, range from 19.4 to 28.0 ppm downfield from $PO(OCH_3)_3$, and the ^{19}F chemical shifts are from 54.1 to 51.9 ppm upfield from $CFCl_3$. The lowfield shift of the ^{31}P nuclei in the PCy_3 complex is consistent with PCy_3 being the strongest σ-donor within the series. The Pt atom in $Pt(PCy_3)_2(F_3CC\equiv CCF_3)$ should therefore be the most electron-rich in the series, and would form the strongest synergic bond with the alkyne ligand. This argument is supported by the ^{19}F NMR data. The PCy_3 complex exhibits the largest ^{19}F complexation shift, 5.1 ppm downfield from free $F_3CC\equiv CCF_3$ (see Table 9). The magnitude of the coupling constants $^1J(Pt-P)$
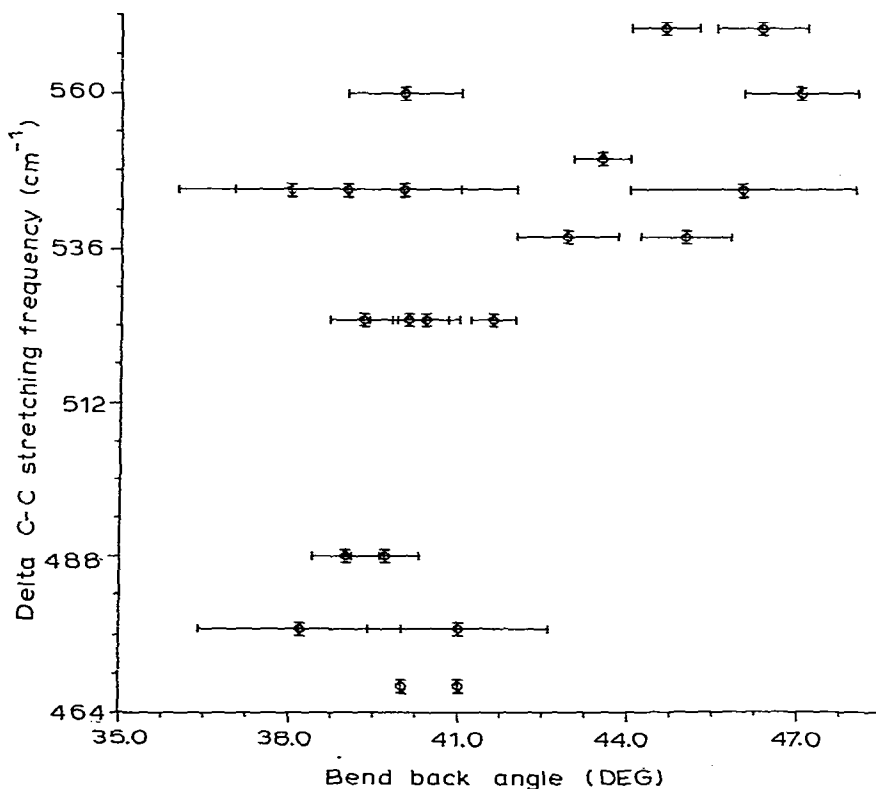

Fig. 6. A plot of bend-back angle against $\Delta\nu(C\equiv C)$ for the alkyne complexes.

and $^3J(\text{Pt—F})$ also decreases from the PPh_3 to PCy_3 complexes. There is no significant variation in $|^4J(\text{P—F})|$.

The ^{31}P and ^{19}F chemical shifts for the Pd complex are 38.9 and -50.9 ppm, respectively. Both the P and F nuclei are less shielded in this complex than in the Pt analogue, which is consistent with the nature of the metals. The same effect was noted in the discussion of the IR stretching frequencies of the two complexes.

In the PPh_3 complexes, the shielding at the P nuclei increases with the electron-withdrawing strength of the alkyne substituents. For example, $\delta(^{31}\text{P})$ is 19.4 ppm when the ligand is $\text{F}_3\text{CC} \equiv \text{CCF}_3$ and 25.4 ppm for $\text{PhC} \equiv \text{CPh}$. The Pt coupling constants increase in magnitude in the same direction. For the unsymmetrical alkyne $\text{PhC} \equiv \text{CMe}$ the chemical shift of 27.1 ppm is assigned tentatively to the P nucleus *trans* to the methyl group, and that of 26.0 ppm to that *trans* to the phenyl substituent, on the basis of the proximity of the latter shift to that of the $\text{PhC} \equiv \text{CPh}$ compound. Likewise for the alkyne $\text{PhC} \equiv \text{CCO}_2\text{Et}$, the $\delta(^{31}\text{P})$ values of 24.3 and 23.5 ppm are assigned to the P nuclei *trans* to the phenyl and ethylester substituents, respectively. The ^{31}P NMR data suggest that the electron density at the P nuclei increases with the electronegativity of the alkyne substituent. The synergic bonding theory predicts that the π-component
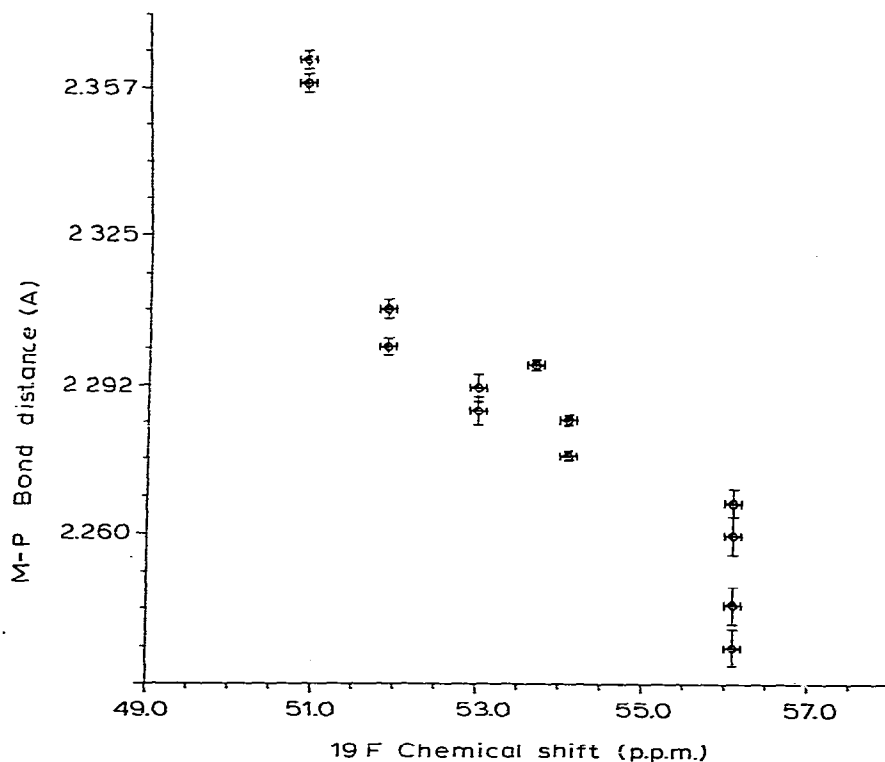

Fig. 7. A plot of $\delta(^{19}\text{F})$ against M—P distance for the hexafluorobut-2-yne complexes.

of the Pt—alkyne interaction should increase in the same direction. Therefore increasing the Pt—alkyne π-bonding may cause a strengthening of the Pt—P σ-bond. This is supported by the larger $|^1J(Pt—P)|$ values. It should be noted, however, that the $^1J(Pt—P)$ results are also consistent with the more electronegative alkyne ligands being poorer σ-donors.

All attempts to locate the acetylenic C atom resonances in the ^{13}C NMR spectra were unsuccessful, as has been observed for other alkyne complexes [24]. However, in the absence of phosphine ligands, downfield shifts have been observed of the order of 30—40 ppm upon coordination [19].

Correlation of structural and spectroscopic results

Very few simple linear relationships exist between the spectroscopic parameters and the structural results. Earlier, on the basis of a limited number of structural determinations, we had reported a relationship between bend-back angle and acetylenic stretching frequency for a number of η^2-alkyne complexes of transition metals in different oxidation states and geometries [3]. An updated plot of bend-back angle versus $\Delta\nu(C{\equiv}C)$ for the trigonal alkyne complexes, presented in Fig. 6, reveals that no good correlation exists for these complexes. There is, however, a trend towards lower stretching frequency with larger bend-back angles. Variations in the bend-back angles are not reflected in any of the other spectroscopic data. The remaining structural parameters associated with the alkyne ligands, M—C and C≡C bond distances, and C—M—C and dihedral angles, either do not vary significantly, or vary randomly. No direct relationships between these and the spectroscopic values were observed.

The M—P bond distances do correlate with the ^{19}F chemical shifts. A plot is given in Fig. 7. A non-weighted least-squares line calculated from the data has a correlation coefficient of 0.92. Therefore, the electron density at the F nuclei appears to be related to the strength of the metal—phosphorus bond. The magnitude of $^1J(Pt—P)$ also reflects the Pt—P bond length for the hexafluorobut-2-yne complexes. The same effect has been observed in trialkylphosphine complexes of Pt^{II} [25].

Thus, the spectroscopic results do not generally correlate with the structural parameters. Variations within the spectroscopic data can be explained by electronic arguments, while many of the structural differences originate from steric interactions [1].

Acknowledgment

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