Crystal Structures of Three *para*-substituted-styryl(pyridyl)platinum(II) Complexes; Effect of Substituent on Molecular Geometry

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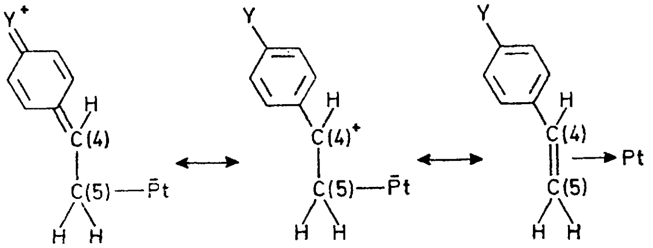
X-Ray crystal-structure analysis has been carried out on three square-planar *para*-substituted-styryl(pyridyl)-platinum(II) complexes $[(p\text{-YC}_6\text{H}_4\text{CH:CH}_2)\text{PtCl}_2(\text{NC}_2\text{H}_4\text{X})]$ where (I) Y = NMe_2, X = Me; (II) Y = H, X = Me; and (III) Y = NO_2, X = Cl. The distances of the platinum atom from the two ethylenic carbon atoms are well correlated with the n.m.r. ^{195}Pt–^{13}C coupling constants when both are plotted *vs.* σ_p^+, a measure of electron-donating power of the substituent Y. Both this, and the deviation of the co-ordination plane from the ethylenic bond, can be given a simple valence-bond explanation.



IN an examination of various *para*-substituted-styryl-(methylpyridine)platinum(II) complexes, Powell *et al.*[1] showed that the coupling constants $J(^{195}\text{Pt}-^{13}\text{C})$ are linearly correlated with σ_p^+ values [2] appropriate to the *para*-substituents, Y, of the styrene ligands. The Hammett *para*-substituent constant, σ_p^+, is a kinetic parameter measuring (increasing with) the electron-withdrawing properties of substituents. It was inferred by Powell *et al.* that Pt lies closer to C(5) than to C(4), and increasingly close as Y becomes less electron-withdrawing.

TABLE 1

Crystal data for $[(p\text{-YC}_6\text{H}_4\text{CH:CH}_2)\text{PtCl}_2(\text{NC}_5\text{H}_4\text{X})]$

	(I)	(II)	(III)
Y	NMe_2	H	NO_2
$\sigma_p^+(\text{Y})$	-1.70	0.0	$+0.79$
X	Me	Me	Cl
Colour	Orange	Yellow	Pale yellow
Formula	$\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pt}$	$\text{C}_{14}\text{H}_{15}\text{Cl}_2\text{NPt}$	$\text{C}_{13}\text{H}_{11}\text{Cl}_3\text{N}_2\text{O}_2\text{Pt}$
M	506.31	463.11	528.65
System	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	5.144(1)	13.928(6)	12.831(3)
b/Å	11.273(3)	8.963(5)	5.400(5)
c/Å	15.657(4)	12.084(6)	22.874(6)
α/°	94.24(1)		
β/°	95.44(2)	93.06(6)	97.42(5)
γ/°	103.28(2)		
U/Å^3	875.4	1 506.3	1 571.6
D_c/g cm^{-3}	1.92	2.04	2.24
Z	2	4	4
X-radiation	Cu-K_α	Cu-K_α	Mo-K_α
μ/cm^{-1}	180.8	209.2	99.0
Axis of mounting	a *	b *	b *
Scan rate/min^{-1}	1	1	2
Total no. reflns.	3 053	2 997	4 868
No. obs.	2 541	2 090	3 057($\theta > 8°$)
R	0.085	0.046	0.048
R' (weighted)	0.103	0.071	0.056

In this paper we describe the crystal and molecular structures of three complexes $[(p\text{-YC}_6\text{H}_4\text{CH:CH}_2)\text{PtCl}_2(\text{NC}_5\text{H}_4\text{X})]$ where (I) Y = NMe_2 X = Me; (II) Y = H, X = Me; and (III) Y = NO_2, X = Cl. (It was our original intention to keep X = Me throughout, but suitable crystals having Y = NO_2 and X = Me could not be prepared.)

EXPERIMENTAL

All compounds were crystallized from dichloromethane–n-hexane. Crystal data for each compound are set out in Table 1. Data were collected in the θ—2θ scan mode (minimum scan width, 2°) on a Canberra-automated Picker four-circle diffractometer by use of filtered radiation and pulse-height analyser. The standard deviation in raw intensity $\sigma(I)$ was taken as $(\text{scan} + \Sigma B)^{\frac{1}{2}}$ where ΣB = total background count. Reflections having $(\text{scan} - \Sigma B) < 2\sigma(I)$ were considered insignificant. $\sigma(F_o)$ Was taken as $[\{\sigma(I)/Lp\}^2 + 0.02F_o^4]^{\frac{1}{2}}/2F_o$, where Lp is the Lorentz-polarization factor. No absorption corrections were made.

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[1] D. G. Cooper, G. K. Hamer, J. Powell, and W. F. Reynolds, *J.C.S. Chem. Comm.*, 1973, 449.

[2] L. P. Hammett, 'Physical Organic Chemistry,' 2nd edn., 1970, p. 355; H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

TABLE 2

Positional and thermal parameters (× 10^4 for Pt and Cl, others × 10^3)

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
For (I)									
Pt(1)	6 256(11)	6 745(1)	−1 990(0)	511(4)	82(1)	43(0)	43(1)	21(1)	16(0)
Cl(2)	5 477(12)	4 723(4)	−1 716(4)	939(31)	86(4)	85(3)	11(8)	−18(7)	32(3)
Cl(3)	6 990(9)	8 793(4)	−2 200(3)	738(22)	89(3)	55(2)	58(7)	38(5)	26(2)
C(4)	450(4)	602(1)	−336(1)	73(9)	9(1)	5(0)	5(3)	1(2)	2(1)
C(5)	262(4)	639(2)	−285(1)	54(8)	19(3)	4(1)	4(4)	1(2)	1(1)
C(6)	577(3)	669(2)	−403(1)	51(7)	12(2)	5(1)	4(3)	1(2)	−1(1)
C(7)	509(4)	779(2)	−429(1)	81(11)	14(2)	5(1)	10(4)	−1(2)	3(1)
C(8)	622(4)	836(2)	−498(1)	77(11)	20(3)	4(1)	5(5)	0(2)	1(1)
C(9)	782(4)	786(2)	−546(1)	76(11)	17(3)	4(1)	−2(4)	−4(2)	0(1)
C(10)	849(4)	679(2)	−522(1)	62(9)	19(3)	6(1)	0(0)	2(2)	−3(1)
C(11)	744(4)	616(2)	−453(1)	58(9)	16(2)	5(1)	1(3)	0(0)	−2(1)
N(12)	912(2)	719(1)	−93(1)	42(5)	11(1)	3(0)	6(2)	1(1)	1(1)
C(13)	874(3)	670(2)	−18(1)	57(8)	12(2)	5(1)	5(3)	2(2)	1(1)
C(14)	1 052(4)	706(2)	55(1)	74(9)	11(2)	5(1)	8(3)	4(2)	3(1)
C(15)	1 290(4)	793(1)	52(1)	76(9)	7(1)	5(1)	9(3)	4(2)	1(1)
C(16)	1 342(4)	835(2)	−28(1)	64(9)	9(1)	5(1)	6(3)	1(2)	1(1)
C(17)	1 148(4)	800(2)	−97(1)	63(8)	10(1)	4(1)	4(3)	3(2)	1(1)
C(18)	1 490(5)	835(2)	131(1)	90(13)	13(2)	5(1)	9(4)	−2(3)	0(1)
N(19)	889(4)	850(3)	−616(1)	59(9)	31(4)	6(1)	−6(5)	4(2)	2(2)
C(20)	825(6)	957(3)	−637(2)	92(15)	18(3)	7(1)	−13(6)	−2(3)	4(2)
C(21)	1 029(7)	778(4)	−673(1)	122(20)	42(7)	5(1)	−22(9)	9(4)	−1(2)
For (II)									
Pt(1)	2 227(0)	2 597(0)	−201(0)	35(0)	108(1)	65(1)	2(0)	8(0)	0(0)
Cl(2)	2 916(2)	415(3)	−768(3)	48(2)	129(4)	118(3)	17(2)	12(2)	−10(3)
Cl(3)	1 510(2)	4 775(3)	337(3)	54(2)	132(3)	98(3)	13(2)	18(2)	−19(2)
C(4)	362(1)	381(1)	12(1)	5(1)	14(2)	7(0)	−2(1)	−1(1)	−2(1)
C(5)	339(1)	288(1)	106(1)	6(1)	22(2)	6(0)	−2(1)	−1(1)	−2(1)
C(6)	438(1)	349(1)	−67(1)	3(1)	10(1)	8(0)	−1(1)	0(0)	−1(1)
C(7)	510(1)	240(1)	−44(1)	5(1)	17(2)	9(1)	1(1)	0(1)	2(1)
C(8)	587(1)	227(1)	−115(1)	4(1)	15(2)	11(1)	1(1)	1(1)	−1(1)
C(9)	591(1)	317(1)	−205(1)	5(1)	15(2)	9(1)	−2(1)	2(1)	0(1)
C(10)	520(1)	424(1)	−227(1)	5(1)	15(2)	10(1)	−1(1)	1(1)	0(1)
C(11)	445(1)	441(1)	−160(1)	4(1)	17(2)	9(1)	−1(1)	0(1)	1(1)
N(12)	91(1)	186(1)	−90(1)	4(0)	12(1)	7(1)	0(1)	2(0)	0(1)
C(13)	11(1)	205(1)	−34(1)	5(1)	15(1)	7(1)	1(1)	1(0)	−1(1)
C(14)	−78(1)	151(1)	−75(1)	4(1)	15(2)	9(1)	0(1)	2(1)	0(1)
C(15)	−87(1)	82(1)	−175(1)	4(1)	17(2)	9(1)	−1(1)	1(1)	−2(1)
C(16)	−4(1)	64(1)	−237(1)	4(1)	16(2)	10(1)	−1(1)	0(1)	−1(1)
C(17)	83(1)	117(1)	−189(1)	5(1)	17(2)	7(1)	1(1)	0(1)	−3(1)
C(18)	−182(1)	29(2)	−226(1)	4(1)	30(3)	12(1)	−4(1)	0(1)	−5(2)
For (III)									
Pt(1)	3 115(0)	982(1)	−1 912(0)	30(0)	303(2)	13(0)	1(1)	2(0)	−3(0)
Cl(2)	1 348(2)	1 467(8)	−1 908(1)	35(1)	729(22)	20(1)	27(4)	2(1)	−38(3)
Cl(3)	4 904(2)	472(7)	−1 862(1)	33(1)	483(16)	20(1)	3(4)	4(1)	4(2)
C(4)	294(1)	−19(3)	−285(1)	4(1)	45(5)	1(0)	2(2)	0(0)	0(1)
C(5)	286(1)	−221(2)	−249(1)	6(1)	28(5)	2(0)	2(2)	0(0)	−2(1)
C(6)	205(1)	102(3)	−323(0)	4(1)	33(4)	1(0)	−1(2)	0(0)	0(1)
C(7)	102(1)	0(3)	−328(1)	4(1)	32(5)	2(0)	−1(2)	0(0)	2(1)
C(8)	22(1)	113(3)	−366(1)	4(1)	41(5)	2(0)	−2(2)	0(0)	−2(1)
C(9)	47(1)	318(3)	−396(1)	4(1)	36(5)	1(0)	2(1)	0(0)	0(1)
C(10)	145(1)	426(3)	−392(1)	4(1)	32(5)	2(0)	0(2)	0(0)	0(1)
C(11)	224(1)	309(3)	−355(1)	4(1)	40(5)	2(0)	−1(1)	0(0)	0(1)
N(12)	335(1)	320(2)	−117(0)	5(1)	29(3)	1(0)	0(1)	0(0)	0(1)
C(13)	401(1)	512(2)	−112(1)	4(1)	29(4)	2(0)	1(1)	0(0)	0(1)
C(14)	413(1)	662(2)	−63(1)	6(1)	30(5)	2(0)	−1(1)	−1(0)	1(1)
C(15)	359(1)	614(3)	−17(1)	5(1)	35(5)	2(0)	−3(2)	−1(0)	1(1)
C(16)	290(1)	415(3)	−19(1)	6(1)	42(5)	1(0)	−2(2)	0(0)	1(1)
C(17)	280(1)	267(2)	−70(1)	5(1)	36(5)	2(0)	−3(2)	1(0)	−2(1)
Cl(18)	3 742(3)	7 884(8)	457(2)	84(3)	556(18)	22(1)	−29(6)	−4(1)	47(3)
N(19)	−40(1)	439(2)	−436(0)	5(1)	45(5)	2(0)	3(2)	0(0)	−2(1)
O(20)	−29(1)	651(2)	−451(0)	7(1)	46(6)	2(0)	4(2)	0(0)	1(1)
O(21)	−121(1)	319(2)	−449(1)	5(1)	60(5)	3(0)	2(1)	−1(0)	−2(1)

In the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$.

Structure analysis was by the heavy atom method in each case. Refinement was by use of XFLS 3 [3] with scattering factors of ref. 4(*a*), and anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for platinum and chlorine from ref. 4(*b*). Anisotropic least-squares refinement was performed on non-hydrogen atoms. Observed and calculated structure amplitudes (which contain no contribution from hydrogen atoms) are listed in Supplementary Publication No. SUP 21702 (36 pp.,

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[3] XFLS 3, an extensively modified version of ORFLS: Report ORNL TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

[4] (*a*) D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321; (*b*) D. T. Cromer, *ibid.*, 1965, **18**, 17.

TABLE 3

Best least-squares planes (no atoms deviate by >0.035 Å from their planes)

(*a*) Coefficients of planes $AX + BY + CZ = D$ where X, Y, Z are real orthogonal co-ordinates (in Å) with X along x and Z along z*

Compound	Plane	Atoms	*A*	*B*	*C*	*D*
(I)	(1)	Pt(1), C(4), C(5), N(12)	0.08(2)	0.96(5)	0.27(2)	8.36(0)
	(2)	Pt(1), Cl(2), Cl(3), N(12)	0.80(1)	−0.06(0)	−0.59(1)	2.74(0)
	(3)	N(12), C(13)—(17)	0.64(2)	−0.72(2)	−0.25(2)	−3.49(1)
	(4)	Pt(1), C(4), C(5)	0.08(2)	0.96(4)	−0.28(2)	8.37(0)
	(5)	C(4)—(6)	−0.59(4)	−0.44(4)	−0.68(5)	−0.32(1)
	(6)	C(6)—(11)	−0.64(2)	−0.47(1)	−0.61(1)	−1.08(1)
	(7)	N(19), C(20), C(21)	−0.75(8)	−0.48(5)	−0.46(8)	−3.00(2)
(II)	(1)	Pt(1), C(4), C(5), N(12)	0.50(2)	−0.77(2)	−0.40(2)	−0.18(0)
	(2)	Pt(1), Cl(2), Cl(3), N(12)	0.25(3)	0.43(2)	−0.87(3)	1.99(0)
	(3)	N(12), C(13)—(17)	−0.15(3)	0.88(1)	−0.45(1)	1.76(0)
	(4)	Pt(1), C(4), C(5)	0.51(2)	−0.77(2)	−0.39(1)	−0.10(0)
	(5)	C(4)—(6)	−0.63(3)	−0.51(3)	−0.58(2)	−5.00(1)
	(6)	C(6)—(11)	−0.50(4)	−0.66(5)	−0.55(1)	−4.72(1)
(III)	(1)	Pt(1), C(4), C(5), N(12)	−0.99(1)	0.14(3)	−0.06(1)	−4.17(0)
	(2)	Pt(1), Cl(2), Cl(3), N(12)	0.11(0)	0.80(1)	−0.59(1)	3.44(0)
	(3)	N(12), C(13)—(17)	−0.70(1)	0.59(1)	−0.41(1)	−1.15(1)
	(4)	Pt(1), C(4), C(5)	−0.99(1)	0.14(3)	−0.06(1)	−4.15(0)
	(5)	C(4)—(6)	0.26(2)	−0.61(3)	−0.75(3)	6.11(1)
	(6)	C(6)—(11)	0.31(6)	−0.58(1)	−0.76(1)	6.35(1)
	(7)	N(19), O(20), O(21)	0.46(2)	−0.32(2)	−0.83(4)	7.76(1)

(*b*) Angles (°) between normals to planes

Compound	Plane	(2)	(3)	(4)	(5)	(6)	(7)
(I)	(1)	80.2(1.9)	55.4(2.1)	0.7(2.0)	106.5(3.0)	109.9(2.0)	
	(2)		44.6(1.2)	80.3(1.8)	92.9(2.2)	96.9(1.1)	
	(3)			124.7(2.1)	84.0(2.5)	85.0(1.5)	
	(4)				105.8(3.1)	109.2(2.1)	
	(5)					4.9(2.0)	
	(6)						10.9(3.9)
(II)	(1)	82.1(1.3)	125.3(1.4)	1.0(1.8)	71.6(2.1)	61.3(1.4)	
	(2)		43.3(0.6)	82.1(1.3)	82.5(1.6)	85.8(0.6)	
	(3)			125.3(1.4)	95.6(1.7)	105.1(0.8)	
	(4)				72.6(2.1)	62.3(1.4)	
	(5)					11.3(1.7)	
(III)	(1)	87.5(3.0)	37.0(3.1)	0.2(4.3)	107.0(4.0)	109.9(3.5)	
	(2)		50.5(7.0)	87.5(3.2)	91.0(1.7)	89.1(0.7)	
	(3)			37.0(3.5)	103.1(1.8)	104.1(0.8)	
	(4)				106.8(3.1)	109.7(3.2)	
	(5)					3.6(1.6)	
	(6)						17.3(1.7)

1 microfiche).* The final residuals *R* and *R′* are in Table 1. Final positional and thermal parameters are given in Table 2, derived bond lengths and angles in Figures 1—3, and best least-squares planes of interest in Table 3.

DISCUSSION

All three complexes crystallize as molecular crystals without specific interactions between molecules. The conformations of the molecules are shown in Figure 4. All three have square-planar co-ordination in which the styryl double bond is *trans* to the pyridyl nitrogen; the chlorine atoms are thus *trans*. The Pt–Cl distances are closely similar in all three complexes covering the short range 2.283(3)—2.306(4) Å. This matches distances found in comparable complexes: 2.30(4) in $[PtCl_2(NHMe_2)(C_2H_4)]$ [5] and 2.33(4) Å in $K[PtCl_3(C_2H_4)]\cdot H_2O$.[6]

In each case the four atoms C(4), C(5), Pt, N(12) are closely coplanar, making respectively angles 80.2(1.9), 82.1(1.3), and 87.5(3.0)° with the plane Pt,Cl(1),Cl(2),N(12) [see Table 3(*a*) and (*b*)].

In all three complexes the pyridine ring makes large angles with the central square plane: 44.6(1.2), 43.3(6), and 50.5(7)°. The Pt–N distances [2.065(11), 2.083(8), and 2.075(9) Å] are the same within experimental error and match those found in other Pt complexes whether the nitrogen is pyridyl or amino, *e.g.* 2.02(2) in $[PtCl_2(NHMe_2)(C_2H_4)]$,[5] and 2.10(1) Å in $[PtCl_2(Bu^tC{\vdots}CBu^t)(MeC_6H_4NH_2)]$.[7] These are presumably σ bonds and the ethylenic system has no discernible *trans*-effect on them.

In none of the three complexes is the styrene phenyl ring coplanar with the ethylenic system, the angles of twist being 4.9(2.0), 11.3(1.7), and 3.6(1.6)° (see Figure 4).

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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[6] J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Acta Cryst.*, 1971, **B27**, 366.

[7] G. R. Davies, W. Hewertson, R. H. B. Mais, P. G. Owston, and C. G. Patel, *J. Chem. Soc. (A)*, 1970, 1873.

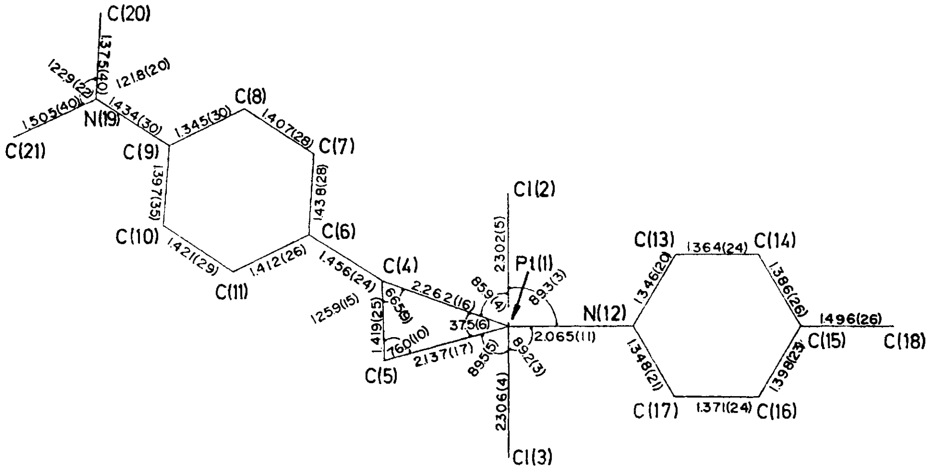

FIGURE 1 Bond lengths and angles for compound (I), [(p-$NMe_2C_6H_4CH{:}CH_2$)$PtCl_2(NC_5H_4Me)$]
Additional angles: Cl(2)–Pt(1)–Cl(C) 177.3(2), Cl(2)–Pt(1)–C(5) 91.35, Cl(3)–Pt(1)–C(4) 96.34, Pt(1)–C(4)–C(6) 115.9(10), C(9)–N(19)–C(21) 114.3(19)°

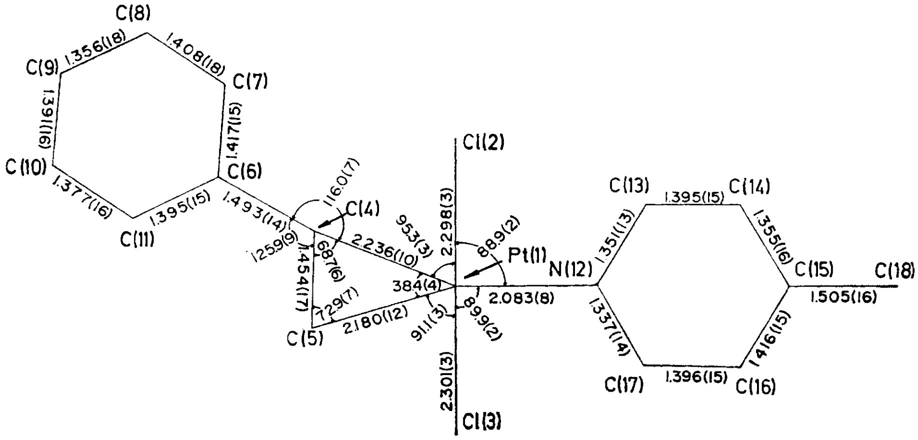

FIGURE 2 Bond lengths and angles for compound (II), [($C_6H_5CH{:}CH_2$)$PtCl_2(NC_5H_4Me)$]
Additional angles: Cl(2)–Pt(1)–Cl(3) 178.7(1), Cl(2)–Pt(1)–C(5) 90.1(3), Cl(3)–Pt(1)–C(4) 85.7(3)°

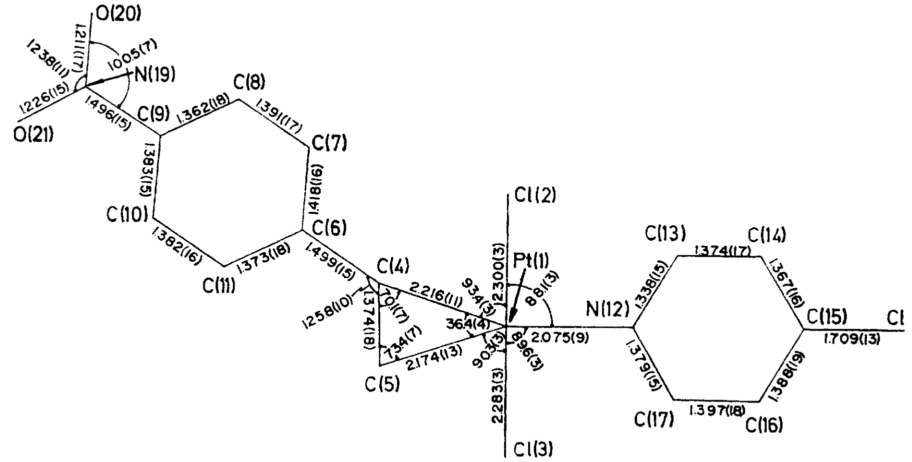

FIGURE 3 Bond lengths and angles for compound (III), [(p-$NO_2C_6H_4CH{:}CH_2$)$PtCl_2(NC_5H_4Cl)$]
Additional angles: Pt(1)–C(4)–C(6) 114.8(8), Cl(2)–Pt(1)–Cl(3) 177.0(1), Cl(2)–Pt(1)–C(5) 91.2(3), Cl(3)–Pt(1)–C(4) 89.4(3), C(9)–N(19)–O(21) 117.3(10)°

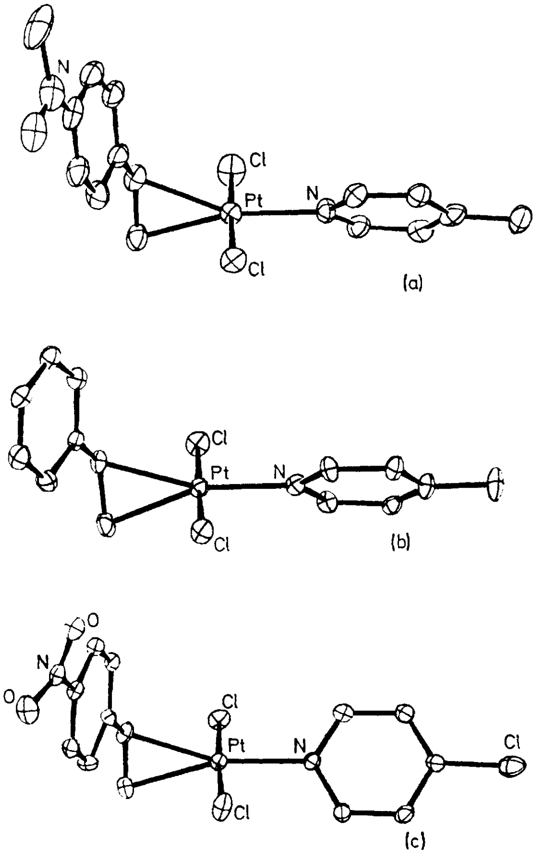

FIGURE 4 Conformation of (a) molecule (I), (b) molecule (II), and (c) molecule (III)

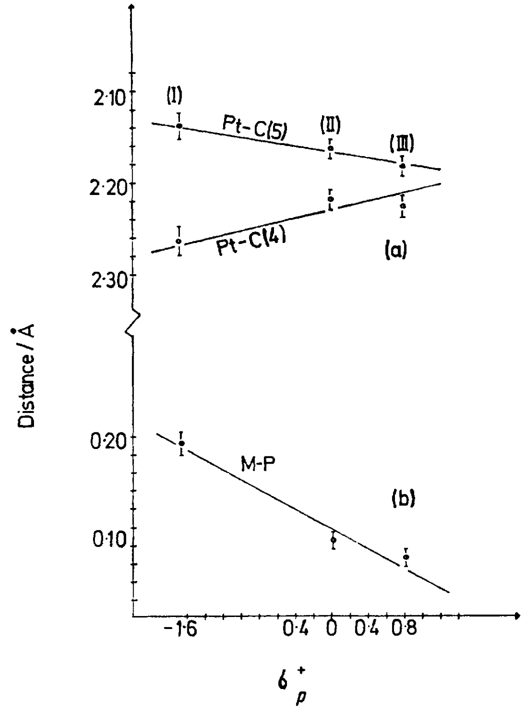

FIGURE 5 Lengths of (a) Pt–C and (b) M–P *vs.* σ_p^+, where M is the mid-point of bond C(4)–C(5) and P is where the perpendicular from Pt cuts this bond

The crystal structure of styrene itself is not known but in *trans*-stilbene[8] the angles of twist in the two centrosymmetric independent molecules are 3.4 and 5.9°. If styrene has a comparable angle of twist it would seem that complex formation has really little effect, any large angle of twist being due to packing forces. In a nickel(0) stilbene complex[9] the twist angles of the two phenyl groups are 16.7(1.2) and 28.1(1.1)°. In the 4,4′-dinitrostilbene complex of bis(triphenylphosphine)-platinum[10] the twist angles also differ considerably (8.4

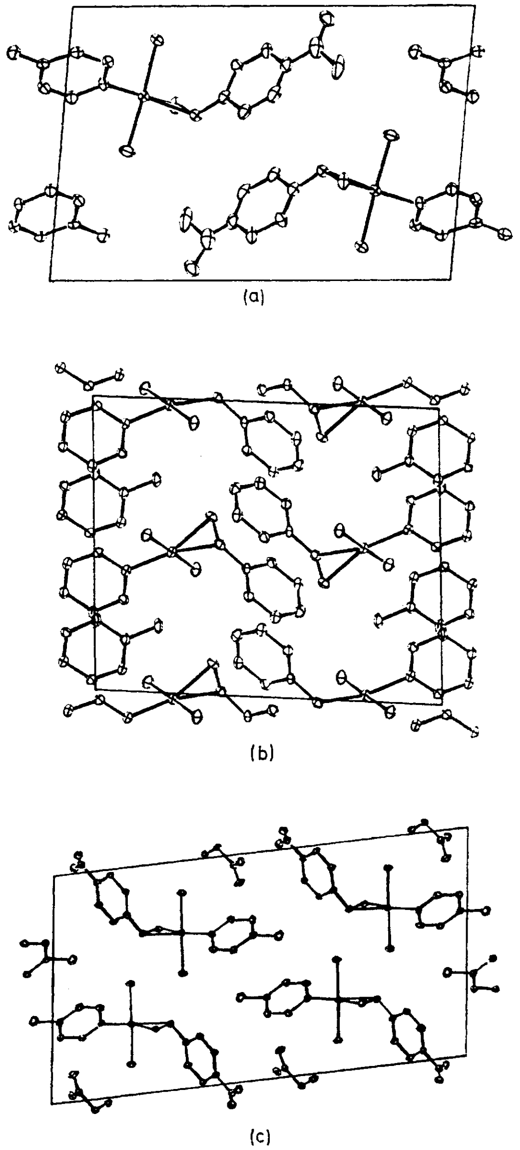

FIGURE 6 Structures in projection: (a) compound (I) (down *x*), (b) compound (II) (down *y*), and compound (III) (down *y*)

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[8] J. C. Finder, M. G. Newton, and N. L. Allinger, *Acta Cryst.*, 1974, **B30**, 411; J. Bernstein, *ibid.*, 1975, **B31**, 1268.

[9] S. D. Ittel and J. A. Ibers, *J. Organometallic Chem.*, 1974, **74**, 121.

[10] J. M. Baraben and J. A. McGinnety, *Inorg. Chem.*, 1974, **13**, 2864.

and 40.6°). These large differences suggest packing forces are responsible. The lowest possible angle of twist is probably *ca.* 5° due to conflict between *ortho* and ethylenic hydrogen atoms whose distances in the two independent stilbene molecules are 2.18 and 2.36 Å [molecule (1)] and 2.04 and 2.46 Å [molecule (2)].

The extent to which the transition element contributes electrons to ligands containing a double bond can be judged by the extent of ' bending back ' of the phenyl groups from the ethylenic plane. We have used the supplements of the angles between the planes C(4),C(5),-Pt,N(12) and C(4),C(5),C(6) as a measure of bending back. These angles are 16.5(3.0), 18.4(2.1), and 17.0(4.0)°. There are very wide variations in bending back reported for various related complexes. Thus in the [(styrene)-$PdCl_2$] complex[11] when the angle is calculated in the same way as for our platinum complexes there is no bending back. In the 4,4′-dinitrostilbene platinum complex, however, the bending back is 9.2 and 21.2° and in the nickel(0) stilbene complex, 5.5 and 11.7°.

The principal interest of the current studies concerns the nature of the C(4)–Pt–C(5) triangle. The first striking feature of the three structures concerns the variations in Pt–C distances, which are plotted in Figure 5(a). Pt–C(5) Is shorter than Pt–C(4) throughout and tends to lengthen with increasing σ_p^+ of the *p*-styrene substituent, namely 2.137(17), 2.180(12), and 2.174(13) Å when σ_p^+ is −1.7, 0.0, and 0.79 respectively. These results are in accord with the n.m.r. spectra, namely that the coupling constants $J(^{195}\text{Pt}-^{13}\text{C})$ are greater for C(5) than for C(4),[1] the difference decreasing with σ_p^+: (I) 178.9 *vs.* 104.6, (II) 165.8 *vs.* 136.7, and (III) 162.7 *vs.* 150.9 Hz. The second aspect of interest, correlated with the first, concerns how far from the centres (M) of C(4)–C(5) lie the perpendiculars from Pt to this bond (P). If the simple VB picture described is a good approximation, then it would be expected that as *p*-styryl substituents become more electron-withdrawing (larger σ_p^+) so this perpendicular will cut the double bond closer to its midpoint. This effect is in fact observed [Figure 5(b)] the distances being 0.193(13), 0.085(9), and 0.067(9) Å. In an analogous way the best least-squares central co-ordination plane cuts C(4)–C(5) increasingly closer to its midpoint: 0.211(13), 0.117(8), and 0.085(9) Å.

The simple VB scheme also implies that as σ_p^+ for Y decreases so the central double bond acquires more single-bond character. Thus there should be increasing lengthening of this bond relative to the free (*i.e.* unco-ordinated) ligand. However, since the crystal structures of the free ligands are unknown, no direct comparison can be made. Bond C(4)–C(5) has lengths 1.419(25), 1.454(17), and 1.374(18) Å respectively in (I), (II), and (III). Thus *prima facie* it would appear that this aspect of the simple VB scheme is unlikely to be confirmed, it being improbable that C(4)–C(5) in the free ligands would vary in such a way as to make the lengthening on co-ordination to platinum monotonic with σ_p^+.

Molecular packing in the three crystal structures is shown in Figure 6. There does not appear to be even approximate isostructurality.

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