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THE SYNTHESIS, CHARACTERISATION AND CRYSTAL STRUCTURE OF $[Pt_3(PPh_3)_2(CNC_6H_3Me_2)_6](PF_6)_2$; A LINEAR TRINUCLEAR CLUSTER OF PLATINUM

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Summary

$[Pt_2(PPh_3)_2(CN\text{-xylyl})_4]^{2+}$ (CN-xylyl = 2,6-dimethylphenyl isocyanide) and $[Pt_3(PPh_3)_2(CN\text{-xylyl})_6]^{2+}$ have been synthesized by reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with either $[Pt(PPh_3)_2Cl_2]$ and CN-xylyl or $[Pt(CN\text{-xylyl})_4]^{2+}$. The products have been characterised by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy, and a single crystal X-ray diffraction study of the trinuclear compound has demonstrated that the skeletal atoms are linear.

Although many heterometallic clusters exhibiting a linear skeletal geometry have been characterised [1], few homonuclear cluster compounds displaying a linear skeletal framework have been reported e.g. $[H_3Rh_4Cl(CN(CH_2)_3NC)_8](CoCl_4)_4 \cdot nH_2O]$ [2], $[Pd_3(CNMe)_6(PPh_3)_2]^{2+}$ [3] and $[Pd_3(SO_2)_2(CNBu^t)_5]$ [4]. No examples of homonuclear linear triatomic clusters are known in platinum cluster chemistry although $[Pt_3(\mu\text{-}PPh_2)_3(Ph)(PPh_3)_2]$ [5] has a marked C_{2v} distortion away from the D_{3h} geometry commonly found for the skeletal atoms in trinuclear cluster compounds of platinum. This paper reports the synthesis and characterisation of $[Pt_3(PPh_3)_2(CNC_6H_3Me_2)_6]^{2+}$, the first example of a trinuclear linear platinum cluster.

Results and discussion

$[Pt_2(PPh_3)_2(CN\text{-xylyl})_4](PF_6)_2$ (I) and $[Pt_3(PPh_3)_2(CN\text{-xylyl})_6](PF_6)_2$ (II) (CN-xylyl = 1,6-xylyl isocyanide) were obtained as mixtures from the reaction of $[Pt(PPh_3)_2(C_2H_4)]$ and either $[Pt(CN\text{-xylyl})_4]^{2+}$ or $[PtCl_2(PPh_3)_2]$ in the presence of excess isocyanide. I and II show very similar solubility properties and could only be satisfactorily separated by repeated fractional recrystallisation from acetone/diethyl ether. I is a white crystalline solid and analysed satisfactorily for

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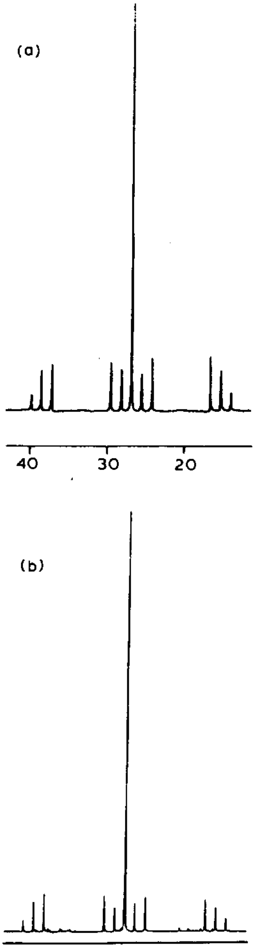
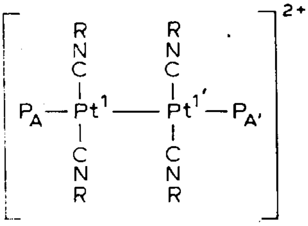


Fig. 1. (a) Observed and (b) calculated $^{31}P\{^1H\}$ NMR spectrum for $[Pt_2(PPh_3)_2(CN\text{-}xylyl)_4]^{2+}$.

$\{[Pt(PPh_3)(CN\text{-}xylyl)_2](PF_6)\}_x$ and showed IR bands consistent with the presence of terminal isocyanide (ν(CN) 2140 cm^{-1}) and PF_6 ($\nu(PF_6)$ 840 cm^{-1}). The dimeric formulation of the compound was confirmed by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR studies. The $^{31}P\{^1H\}$ spectrum recorded in CD_2Cl_2 and shown in Fig. 1(a) shows a multiplet at 26.8 ppm with respect to trimethylphosphate. This spectrum has been satisfactorily simulated using a computer analysis based on the isotopomers with the following spin systems: A_2 (44.4% abundance, no ^{195}Pt nuclei), AA'X (44.4% abundance, 1 ^{195}Pt nucleus, X) and AA'XX' (11.1% abundance, 2 ^{195}Pt nuclei, X and X') (See Fig. 1(b)). The coupling constants derived from the computer simulation are summarised in Table 1. The dimeric nature of the complex is confirmed by the appearance of the ^{195}Pt satellites as an 'AB' quartet arising from the AA'X isotopomer with an additional outer line due to the AA'XX' isotopomer. This type of spectrum has been discussed by Brown et al. for the complexes $[Pt_2(dppm)_2L_2]^{2+}$ (L = PPh_3, or PPh_2Me) [6] and is particularly characteristic of a linear $[Pt_2(PR_3)_2]$ system. The coupling constants derived from the computer simulation are compara-

TABLE 1

CHEMICAL SHIFTS (δ (ppm)) AND COUPLING CONSTANTS (J (Hz)) FOR $[Pt_2(PPh_3)_2(CN\text{-}xylyl)_4](PF_6)_2$



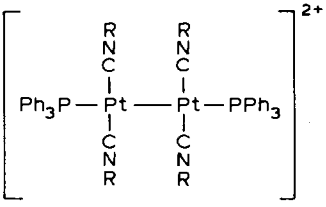
	$\delta(P_A/P_{A'})$		$\delta(Pt^1/Pt^{1'})$	
	26.8		−4370	

J	P_A	$P_{A'}$	$Pt^{1'}$	Pt^1
Pt^1	2214.0	408.0	[a]	–
P_A	–	137.0	408.0	2214.0
$P_{A'}$	137.0		2214.0	408.0

[a] $^1J(Pt^1\text{-}Pt^{1'})$ could not be estimated from either the $^{31}P\{^1H\}$ or $^{195}Pt\{^1H\}$ spectra.

ble with those found for related linear $[Pt_2(PR_3)_2]$ [6] systems. Table 2 summarises the coupling constants found for linear Pt_2L_2 (L = phosphine) complexes.

The $^{195}Pt\{^1H\}$ NMR spectrum of I shows a doublet of doublets centred at −4370 ppm relative to Na_2PtCl_6. The appearance of the large doublet splitting arises from the $^1J(Pt\text{-}P)$ couplings and the small doublet splitting arises from to $^2J(Pt\text{-}P)$ coupling. Low intensity signals due to the AA'XX' (11.1% abundance, 2 ^{195}Pt nuclei, X and X') were not observed and therefore a $^1J(Pt\text{-}Pt)$ coupling constant could not be estimated. The above NMR data are consistent with the metal–metal bonded structure illustrated in III.



(III)

Similar structures based on two square planar palladium and platinum units sharing a metal–metal bond have been reported for $[Pd_2(CNR)_6]^{2+}$ [7],

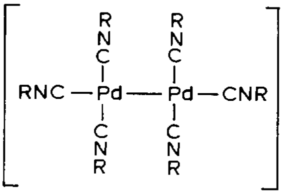
TABLE 2

COUPLING CONSTANTS FOR LINEAR $[Pt_2(PR_3)_2]$ COMPLEXES (Hz)

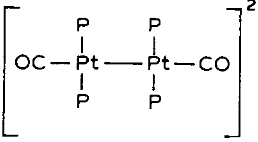
Complex	$^1J(Pt\text{-}P)$	$^2J(Pt\text{-}P)$	$^3J(P\text{-}P)$
$[Pt_2(PPh_3)_2(CN\text{-}xylyl)_4]^{2+}$	2214	408	137
$[Pt_2(dppm)_2(PMe_2Ph)_2]^{2+}$ [6]	1938	650	195
$[Pt_2(dppm)_2(PPh_2Me)_2]^{2+}$ [6]	1914	750	[a]
$[Pt_2(dppm)_2(PPh_3)_2]^{2+}$ [6]	1680	[a]	[a]

[a] Not given in literature.

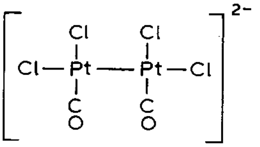
$[Pt_2(CO)_2(dppm)_2]^{2+}$ [8], and $[Pt_2Cl_2(CO)_2]^{2-}$ [9] and are illustrated below in IV to VI.



(IV)



(V)



(VI)

The analytical and infra-red data for II were very similar to that described for I above (ν(CN) 2180, $\nu(PF_6)$ 850 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum of III however, is very different from II (see Fig. 2(a)). The $^{31}P\{^1H\}$ NMR spectrum shows a multiplet centred at 39.4 ppm with respect to trimethylphosphate. The $^{31}P\{^1H\}$ NMR spectrum has been satisfactorily simulated using a computer analysis

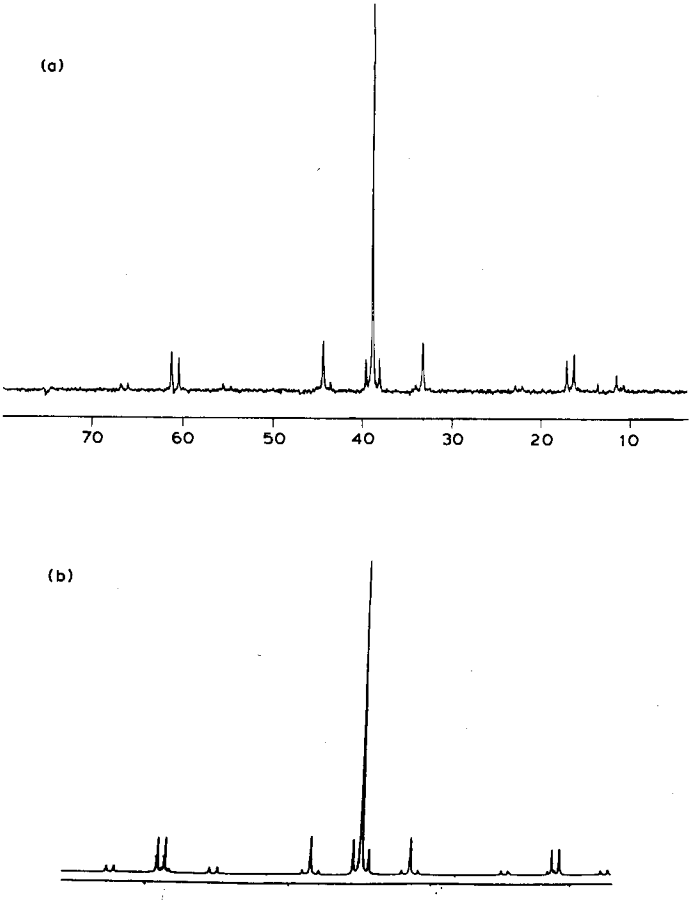


Fig. 2. (a) Observed and (b) calculated $^{31}P\{^1H\}$ NMR spectrum for $[Pt_3(PPh_3)_2(CN\text{-}xylyl)_6]^{2+}$.

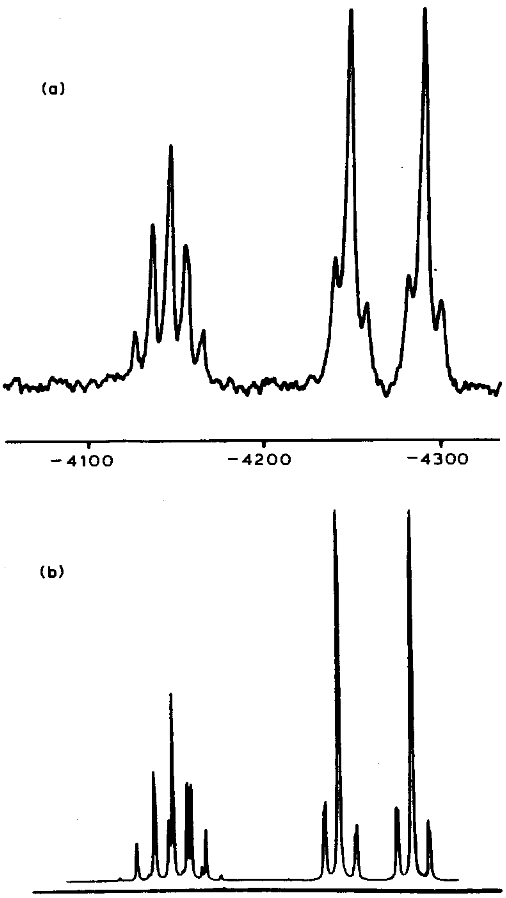
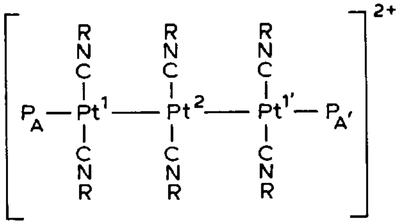


Fig. 3. (a) Observed and (b) calculated $^{195}P\{^1H\}$ NMR spectrum for $[Pt_3(PPh_3)_2(CN\text{-xylyl})_6]^{2+}$.

TABLE 3

CHEMICAL SHIFTS (δ (ppm)) AND COUPLING CONSTANTS (J (Hz)) FOR $[Pt_3(PPh_3)_2(CN\text{-xylyl})_6](PF_6)_2$

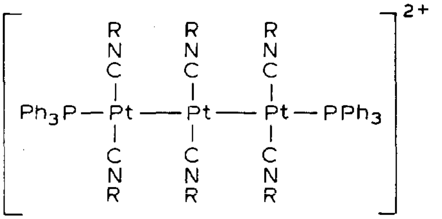


$$\left[P_A\text{—}Pt^1(CNR)_2\text{—}Pt^2(CNR)_2\text{—}Pt^{1'}(CNR)_2\text{—}P_{A'}\right]^{2+}$$

	$\delta(P_A/P_{A'})$ 39.3945		$\delta(Pt^1/Pt^{1'})$ −4248	$\delta(Pt^2)$ −4126.6
J	Pt^1	Pt^2	$Pt^{1'}$	$P_{A'}$
P_A	2232.0	565.0	48.7	41.2
$P_{A'}$	48.7	565.0	2232.0	–
Pt^1	[a]	970.0	–	2232.0
Pt^2	970.0	–	970.0	565.0

[a] ^2J(Pt–Pt) could not be estimated from either the $^{31}P\{^1H\}$ or $^{195}Pt\{^1H\}$ spectra.

based on a spin system comprising of the isotopomers: A_2 (29.6% abundance, no ^{195}Pt nuclei), AA′X (29.6% abundance, 1 ^{195}Pt nucleus X), A_2Y (14.8% abundance, 1 ^{195}Pt nucleus Y), AA′XY (14.8% abundance, 2 ^{195}Pt nuclei abundance, X and Y), AA′XX′ (7.4% abundance, 2 ^{195}Pt nuclei, X and X′) and AA′XX′Y (3.7% abundance, 3 ^{195}Pt nuclei, X, X′ and Y) (see Fig. 2(b)). The ^{195}Pt{^{1}H} NMR spectrum shows two multiplets centred at −4248 and −4126.6 ppm with respect to Na_2PtCl_6 in the ratio of 2/1 (see Fig. 3(a)). The above spectrum has been simulated using the isotopomer system described above (see Fig. 3(b)). The coupling constants derived from the computer simulation are given in Table 3. The data are consistent with the formulation of III as $[Pt_3(PPh_3)_2(CN\text{-}xylyl)_6](PF_6)_2$ with the phosphines lying *trans* to each other.



$$\left[\begin{array}{ccccccc} & \mathrm{R} & & \mathrm{R} & & \mathrm{R} & \\ & \mathrm{N} & & \mathrm{N} & & \mathrm{N} & \\ & \mathrm{C} & & \mathrm{C} & & \mathrm{C} & \\ & | & & | & & | & \\ \mathrm{Ph_3P}- & \mathrm{Pt} & - & \mathrm{Pt} & - & \mathrm{Pt} & -\mathrm{PPh_3} \\ & | & & | & & | & \\ & \mathrm{C} & & \mathrm{C} & & \mathrm{C} & \\ & \mathrm{N} & & \mathrm{N} & & \mathrm{N} & \\ & \mathrm{R} & & \mathrm{R} & & \mathrm{R} & \end{array}\right]^{2+}$$

(II)

In order to confirm the structure of II a single crystal X-ray structural analysis was undertaken. A single crystal was grown by slow diffusion of diethyl ether into acetone over a period of approximately two weeks and the resulting pale yellow crystals were shaken with hexane to dislodge small quantities of I. Details of the data collection and crystal data are given in the Experimental section. Selected intramolecular bond lengths and angles derived from the X-ray crystallographic analysis are given in Table 4. The fractional coordinates and temperature factors of the non-hydrogen atoms are given in Table 5. The structure of the cation is illustrated in Fig. 4.

The three platinum atoms are colinear with the two phosphorus atoms of the triphenylphosphine groups, forming a five atom chain (since a centre of symmetry is imposed crystallography in the space group $P\bar{1}$, the Pt–Pt–Pt angle is constrained to be 180° and the Pt(1)–Pt(2)–P(1) angle is 171.24(8)°). Each platinum atom is coordinated to two 2,6-xylyl isocyanide ligands and exhibits approximately square-planar geometry. The square planes defined by Pt(1)–C(101)–C–(101′)–Pt(2) and Pt(2)–C(201)–C(203)–P(1) are twisted away from each other such that the angle between the planes is 95.35°. The C(203)–Pt(2)–Pt(1) and C(203)–Pt(2)–C(201) bond angles of 79.7(3) and 108.5(4)° respectively indicate that the $(Pt(PPh_3)(CN\text{-}xylyl)_2)$ moiety is significantly distorted away from the idealised T-shape geometry about platinum. One isocyanide of the $(Pt(PPh_3)(CN\text{-}xylyl)_2)$ is bent towards the central platinum (C(203)–Pt(2)–Pt(1) 79.7(3)°) accompanied by a lengthening of the C–N triple bond of this isocyanide ligand by 0.05 Å. This effect has been previously observed in $[Pd_3(CNCH_3)_6(PPh_3)_2]^{2+}$ and has been attributed to an interaction of the filled *d* orbitals of the central atom to empty π^* orbitals of the isocyanide ligands. The platinum–platinum bond length of 2.6437(4) Å is comparable with those reported for other homonuclear trinuclear platinum cluster compounds III is the first example of a trinuclear platinum cluster having a linear skeletal geometry and is isostructural with $[Pd_3(CNCH_3)_6(PPh_3)_2](PF_6)_2$ [3].

TABLE 4

SELECTED MOLECULAR DIMENSIONS (Å) AND BOND ANGLES (°) FOR [$Pt_3(PPh_3)_2$(CN-xylyl)$_6$](PF_6)$_2$ WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Pt(1)–Pt(2)	2.6437(4)
Pt(1)–C(101)	1.95(1)
Pt(2)–P(1)	2.334(3)
Pt(2)–C(201)	1.91(1)
Pt(2)–C(203)	1.93(1)
C(101)–N(102)	1.14(2)
C(201)–N(202)	1.19(1)
C(203)–N(204)	1.18(1)
Pt(2)–Pt(1)–Pt(2′)	180
Pt(2)–Pt(1)–C(201)	82.2(4)
Pt(2)–Pt(1)–C(101)	97.8(4)
Pt(1)–Pt(2)–P(1)	171.24(8)
Pt(1)–Pt(2)–C(201)	79.7(3)
Pt(1)–Pt(2)–C(203)	89.0(3)
Pt(1)–C(101)–N(102)	176(1)
Pt(2)–C(201)–N(202)	177(1)
Pt(2)–C(203)–N(204)	177(1)
C(101)–Pt(1)–Pt(2)	82.2(4)
C(201)–Pt(2)–P(1)	94.9(4)
C(203)–Pt(2)–P(1)	96.0(3)
C(203)–Pt(2)–C(201)	168.5(4)
C(203)–Pt(2)–Pt(1)	89.0(3)
C(201)–Pt(2)–Pt(1)	79.7(3)

Angle between least-squares planes defined by Pt(1)–C(101)–Pt(2) and Pt(2)–C(201)–C(203), 95.35°

Balch et al. synthesised $[Pd_3(CH_3NC)_6(PPh_3)_2]^{2+}$ by the following series of reactions [10]:

$$[Pd(CH_3NC)_4]^{2+} + [Pd(CH_3NC)_x] \rightarrow [Pd_2(CH_3NC)_6]^{2+}$$

$$[Pd_2(CH_3NC)_6]^{2+} + [Pd(CH_3NC)_x] \rightarrow [Pd_3(CH_3NC)_8]^{2+}$$

$$[Pd_3(CH_3NC)_8]^{2+} + 2PPh_3 \rightarrow [Pd_3(PPh_3)_2(CH_3NC)_6]^{2+}$$

The reaction of a Pd^{II} isocyanide species with the Pd^0 isocyanide complexes by oxidative addition gives the metal–metal bonded dimeric and trimeric complexes. The Pd^0 isocyanide species is conveniently prepared by the reaction of excess isocyanide with $[Pd_2(dba)_3 \cdot CHCl_3]$ (dba = dibenzylideneacetone) [11]. $[Pd_2(dba)_3 \cdot CHCl_3]$ has been shown to be an extremely useful precursor for the synthesis of mononuclear Pd^0 compounds [12].

$[Pt(COD)_2]$ and $[Pt(C_2H_4)_3]$ have been succesfully employed by Stone et al. in a wide variety of metal–metal bond forming reactions [13]. However in the presence of free isocyanide $[Pt(COD)_2]$ and $[Pt(C_2H_4)_3]$ both form the trinuclear platinum cluster $[Pt_3(\mu\text{-}CNR)_3(CNR)_3]$ [14] and therefore these reagents were not employed as a source of Pt^0 in the synthesis of the dimer and trimer.

Mason et al. [15] showed that the reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with isocyanides gave the complexes $[Pt(PPh_3)_2(CNR)_2]$, but only for ^{t}BuNC was a stable product

TABLE 5

FINAL FRACTIONAL COORDINATES FOR NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	*U*(iso)
Pt(1)	0	0	0	305
Pt(2)	−1022.3(4)	693.2(3)	−1641.9(3)	301
P(1)	−1632(3)	1446(2)	−3025(2)	357
N(102)	2416(10)	374(8)	−411(8)	521(27)
C(101)	1541(12)	207(9)	−250(9)	422(30)
N(202)	−93(10)	2636(8)	−297(7)	479(26)
C(201)	−475(10)	1889(9)	−806(8)	336(26)
N(204)	−1612(9)	−1438(8)	−2691(7)	468(25)
C(203)	−1374(10)	−638(8)	−2269(8)	311(25)
C(11)	3366(11)	489(9)	−782(9)	416(29)
C(12)	4319(13)	1256(11)	−313(10)	551(36)
C(13)	5253(16)	1314(13)	−725(12)	716(45)
C(14)	5251(15)	685(12)	−1431(11)	658(41)
C(15)	4307(16)	−54(13)	−1874(12)	730(45)
C(16)	3353(14)	−183(11)	−1524(11)	583(37)
C(17)	2337(18)	−949(14)	−1954(14)	843(52)
C(18)	4310(18)	1925(14)	491(14)	837(52)
C(21)	374(11)	3469(9)	361(8)	386(28)
C(22)	1274(13)	4097(11)	230(10)	541(35)
C(23)	1715(14)	4889(12)	908(11)	593(38)
C(24)	1344(15)	5076(13)	1653(12)	676(43)
C(25)	472(15)	4446(12)	1762(12)	663(41)
C(26)	−67(13)	3613(11)	1106(10)	552(36)
C(28)	−986(16)	2909(13)	1196(13)	760(47)
C(27)	1705(16)	3916(13)	−565(12)	743(46)
C(31)	−1935(11)	−2367(9)	−3195(9)	410(29)
C(32)	−1453(12)	−2654(10)	−3875(10)	479(32)
C(33)	−1835(15)	−3588(12)	−4350(11)	631(40)
C(34)	−2634(15)	−4191(13)	−4184(12)	689(43)
C(35)	−3120(14)	−3877(11)	−3516(11)	587(38)
C(36)	−2774(13)	−2973(11)	−2989(10)	536(35)
C(37)	−3274(17)	−2614(14)	−2255(13)	766(47)
C(38)	−572(16)	−1978(13)	−4072(12)	713(44)
C(111)	−2913(9)	2258(7)	−3203(8)	380(26)
C(112)	−3321(10)	2523(7)	−2465(8)	488(30)
C(113)	−4285(11)	3141(8)	−2598(9)	604(34)
C(114)	−4842(11)	3480(8)	−3449(10)	627(35)
C(115)	−4463(11)	3223(8)	−4191(9)	585(34)
C(116)	−3488(10)	2603(7)	−4064(8)	481(29)
C(121)	−2177(9)	609(7)	−4134(7)	393(27)
C(122)	−1594(11)	627(8)	−4787(9)	591(33)
C(123)	−2047(12)	−32(10)	−5609(10)	718(38)
C(124)	−3032(13)	−674(10)	−5761(10)	783(41)
C(125)	−3601(11)	−703(9)	−5142(9)	599(34)
C(126)	−3170(10)	−50(8)	−4311(8)	458(29)
C(131)	−293(10)	2175(8)	−3028(6)	399(27)
C(132)	907(11)	1838(8)	−2605(6)	482(29)
C(133)	1975(13)	2358(10)	−2583(7)	609(34)
C(134)	1858(13)	3230(10)	−2974(7)	620(35)
C(135)	701(12)	3574(9)	−3378(7)	553(32)
C(136)	−379(11)	3052(9)	−3412(6)	496(30)

TABLE 5 (continued)

Atom	x	y	z	U(iso)
P(2)	2757(4)	6346(3)	6465(3)	625
F(1)	3717(15)	6813(11)	7445(9)	1447
F(2)	1760(13)	5907(12)	5467(9)	1490
F(3)	2477(20)	7421(10)	6187(11)	1653
F(4)	2906(19)	5251(9)	6617(13)	1447
F(5)	3787(13)	6288(13)	6009(10)	1303
F(6)	1696(14)	6408(14)	6873(11)	1405

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	399(40	300(4)	268(3)	79(3)	143(3)	36(3)
Pt(2)	420(3)	251(2)	259(2)	45(2)	117(2)	9(2)
P(1)	428(18)	367(18)	282(16)	43(13)	117(14)	5(14)
P(2)	834(29)	559(25)	595(25)	23(19)	335(22)	123(21)
F(1)	1682(141)	1910(164)	970(99)	−264(101)	−139(95)	−601(123)
F(2)	1359(120)	2294(191)	1045(103)	−563(112)	−43(89)	146(118)
F(3)	3497(279)	908(107)	2046(183)	328(111)	1516(191)	643(137)
F(4)	2549(199)	656(84)	2187(183)	366(99)	1091(160)	316(101)
F(5)	1127(98)	2184(171)	1392(119)	196(112)	830(93)	7(102)
F(6)	1510(127)	2181(178)	1656(142)	−216(125)	1176(117)	29(120)

obtained. Reaction of CN-xylyl with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] gave an orange solution. The resulting pale yellow air sensitive compound which is soluble in most organic solvents, analysed satisfactorily for [Pt(PPh$_3$)$_2$(CN-xylyl)$_2$] and showed bands in the infrared consistent with terminal bonded isocyanide (ν(CN) 2043 and 1991

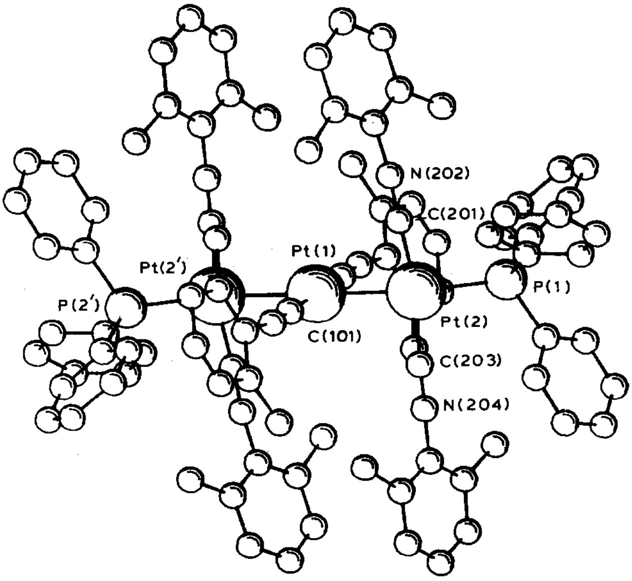


Fig. 4. Illustration of the molecular geometry of [Pt$_3$(PPh$_3$)$_2$(CN-xylyl)$_6$]$^{2+}$ (Hydrogens omitted for clarity).

cm^{-1}). The solution infrared showed bands for bridging and terminal isocyanide (ν(CN) 2044, 2007, 1626, and 1586 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum shows a broad peak in the region associated with free triphenylphosphine, however the other peaks could not be assigned.

The data suggest that $[Pt(PPh_3)_2(CN\text{-xylyl})_2]$ is formed initially but is labile in solution giving higher nuclearity species with bridging isocyanide ligands, and it was therefore decided to utilise the lability of the $[Pt(PPh_3)_2(CNR)_2]$ as a source of a coordinatively unsaturated $[Pt(CNR)_x(PPh_3)_y]$ species.

In order to devise a rational synthesis of II and III by a related series of reactions to those described above, the reactions between Pt^0 and Pt^{II} complexes were investigated, e.g.

$$Pt^0 + Pt^{II} \rightarrow [Pt\text{–}Pt]^{2+} \tag{1}$$

$$2Pt^0 + Pt^{II} \rightarrow [Pt\text{–}Pt\text{–}Pt]^{2+} \tag{2}$$

In order to confirm the generality of reaction I the following reactions were performed:

$$[Pt(PPh_3)_2(C_2H_4)] + [PtCl_2(PPh_3)_2] + \text{excess CN-xylyl} \rightarrow$$

$$[Pt(PPh_3)_2(C_2H_4)] + [Pt(CN\text{-xylyl})_4]^{2+} \rightarrow$$

The main product from both reactions was $[Pt_2(PPh_3)_2(CN\text{-xylyl})_4]^{2+}$ identified on the basis of its characteristic $^{31}P\{^1H\}$ NMR spectrum. The above reactions were repeated on a 2/1 molar ratio of Pt^0/Pt^{II} and the main product was found to be $[Pt_2(PPh_3)_2(CN\text{-xylyl})_4]^{2+}$, identified by $^{31}P\{^1H\}$ NMR and small quantities (< 10%) of $[Pt_3(PPh_3)_2(CN\text{-xylyl})_6]^{2+}$ The reactions indicate that oxidative-addition reactions occur between the Pt^0 isocyanide species and Pt^{II} compounds with the formation of the metal–metal bonded dimer but we have not been able to determine the course of those reactions which lead to the trimetallic compound.

Experimental

Reactions were routinely carried out using standard Schlenk-line procedures, under pure dry N_2 and using dry dioxygen-free solvents. Microanalysis (C, H, N) were carried out by Mr. M. Gascoyne and his staff at this laboratory. Infrared spectra were recorded as Nujol mulls, using a Pye-Unicam SP2000 spectrometer. $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR were recorded using a Bruker Am250 spectrometer. The samples were referenced as follows: ^{31}P to $[P(OMe)_3O]$ in D_2O and ^{195}Pt to Na_2PtCl_6 in D_2O. The machine operating frequencies were ^{31}P, 102.26 and ^{195}Pt, 53.55 MHz. All samples were run in deuterated solvents. Proton-decoupled ^{31}P NMR computer simulations were carried out using the Oxford University VAX/VMS computer system utilising a program developed by Prof. R.K. Harris, then of the University of East Anglia and adapted for use at Oxford by Dr. A.E. Derome. $[Pt(PPh_3)_2(C_2H_4)]$ [16], $[M(PPh_3)_2Cl_2]$ (M = Pt, Pd) [17] and were made by standard literature preparations. The ethylene complex was recrystallised from CH_2Cl_2/hexane under ethylene before use.

Reaction of $[Pt(PPh_3)_2(C_2H_4)]$ and $[Pt(PPh_3)_2Cl_2]$ and CN-xylyl

$[Pt(PPh_3)_2Cl_2]$ (0.10 g, 0.126 mmol) was added to $[Pt(PPh_3)_2(C_2H_4)]$ (0.105 g, 0.140 mmol) in CH_2Cl_2 (50 cm^3). On addition of $CNC_6H_3Me_2$ the colour of the solution deepened to an orange colour which lightened on stirring for 1 h. The solution was evaporated to dryness and the resulting solid extracted with ethanol. NH_4PF_6 was added with stirring and the solution then filtered and the resulting pale yellow solid was washed with ethanol and diethyl ether and dried in vacuo. (Found: C, 49.4; H, 3.8; N, 3.2%; $C_{72}H_{66}N_4P_4F_{12}Pt_2$ calcd.: C, 50.0; H, 3.8; N, 3.2%; ν(CN) at 2140s, $\nu(PF_6)$ at 840s cm^{-1}. $^{31}P\{^1H\}$ (to high frequency of TMP) 22.8 ppm [m, 2P, $[Pt(PPh_3)(CN\text{-xylyl})_2]$, ^1J(Pt–P) −2214.0, ^2J(Pt–P) 408.0 and ^3J(P–P) 137.0 Hz. $^{195}Pt\{^1H\}$ (to low frequency of Na_2PtCl_6) −4370 ppm, doublet of doublets.

The reaction was repeated as above in a 2/1 molar ratio of $[Pt(PPh_3)_2(C_2H_4)]$ to $[Pt(PPh_3)_2Cl_2]$, as small quantities of orange-yellow crystals were obtained by slow diffusion of diethyl ether into an acetone solution, in addition to $[Pt_2(PPh_3)_2(CN\text{-xylyl})_4](PF_6)_2$. [Found: C, 49.0; H, 3.99; N, 3.6%; $C_{90}H_{84}N_6F_{12}Pt_3$ calcd.: C, 49.4; H, 3.84; N, 3.84%] ν(CN) at 2180s and 1710w cm^{-1}. $^{31}P\{^1H\}$ (to high frequency of TMP) 39.39 ppm [m, 2P, $[Pt(PPh_3)(CN\text{-xylyl})_2]$, ^1J(Pt–P) 2232.0, ^2J(Pt–P) 565.0, ^3J(Pt–P) 48.7, ^4J(Pt–P) 41.2, ^1J(Pt–Pt) 970.0 Hz, $^{195}Pt\{^1H\}$ (to low frequency of Na_2PtCl_6) −4248 and −4126.6 ppm.

Synthesis of $[Pt(CN\text{-xylyl})_4](PF_6)_2$

CN-xylyl (0.12 g, 0.99 mmol) was added to $[Pt(CN\text{-xylyl})Cl_2]$ (0.5 g, 0.49 mmol) in CH_2Cl_2 (50 cm^3) with stirring. The solid dissolved to give a clear solution and stirring was continued for 1 h. The solution was evporated to dryness in vacuo and the solid was washed with benzene and dried in vacuo. The solid was dissolved in ethanol (50 cm^3) and NH_4PF_6 added with stirring. The resulting solid was extracted with CH_2Cl_2 (20 cm^3) and precipitated as a white solid by addition of hexane. The supernatant liqour was removed and the resulting solid was washed with diethyl ether and dried in vacuo. ν(CN) at 2209s and $\nu(PF_6)$ at 844s cm^{-1}. Found: C, 42.8; N, 5.03; $C_{36}H_{36}N_4P_2F_{12}Pt$ calcd.: C, 42.8; N, 5.5%.

Reaction between $[Pt(CN\text{-xylyl})_4]^{2+}$ and $[Pt(PPh_3)_2(C_2H_4)]$

$[Pt(CN\text{-xylyl})_4(PF_6)]$ (0.067 g, 0.067 mmol) was added to $[Pt(PPh_3)_2(C_2H_4)]$ (0.1 g, 0.133 mmol) with stirring. The solution developed a pale yellow colour and stirring was continued for 1 h. The solution was evaporated to dryness and the solid washed with benzene and diethyl ether. The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra showed the solid to be a mixture of $[Pt_2(PPh_3)_2(CN\text{-xylyl})_4](PF_6)_2$ and $[Pt_3(PPh_3)_2(CN\text{-xylyl})_6](PF_6)_2$.

Reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with CNC_8H_9

CN-xylyl (0.0755 g, 0.58 mmol) was added to $[Pt(PPh_3)_2(C_2H_4)]$ (0.2 g, 0.27 mmol) in benzene (30 cm^3) with stirring. The colour of the solution turned orange and stirring was continued for 1 h. The solution was evaporated to dryness in vacuo and dissolved in petroleum ether (b.p. 80–100°C) and left to stand at −30°C to give a pale yellow air-sensitive solid. ν(CN) at 2043s and 1991s cm^{-1}. [Found: C, 65.14; H, 5.40, N, 2.77. $C_{54}H_{48}N_2P_2Pt$ calcd.: C, 66.0; H, 4.89; N, 2.85%].

Crystal data for $[Pt_3(PPh_3)_2(CN\text{-xylyl})_6](PF_6)_2$. $C_{90}H_{84}N_6F_{12}P_4Pt_3$, M = 2186.6, triclinic, a 11.428(8), b 13.739(7), c 15.278(8) Å, α 96.14(4), β 111.49(5), γ 91.58(5)° U 2210.6 Å^3 (by least-squares refinement of the diffractometer angles for 25 automatically centred reflections λ 0.7106 Å) space group, $P\bar{1}$, $Z = 1$, D_c 1.642 g cm^{-3}; Orange-yellow crystals grown by slow diffusion of diethyl ether into acetone solution. Crystal size 0.15 × 0.09 × 0.025 mm μ(Mo-K_α) 51.23 cm^{-1}.

Data collection and processing. A CAD4 diffractometer in $\omega/2\theta$ mode with θ-scan width 0.9° was used with graphite-monochromated Mo-K_α radiation; 7145 reflections were measured ($1 < \theta < 22.5°$) with 4113 unique absorption-corrected reflections with $I > 3\sigma(I)$.

Structure analysis and refinement. Patterson followed by normal heavy-atom techniques. Blocked matrix least-squares refinement was carried out with the Pt, P and F anisotropic and remainder isotropic. Ring hydrogens were placed in calculated positions (C–H 0.99 Å) and with U_{iso} 0.05 Å^3. A Chebyshev weighting scheme was applied with coefficients 114.6, 157.1 and 58.5 gave satisfactory agreement analyses. Final R and R' values were 0.0470 and 0.573. Programs and computers used and sources of scattering factor data are given in [18]. Lists of thermal parameters and structure factors are available from the authors.

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