Methyl Isocyanide Complexes of a Trinuclear Platinum Cluster: A Model for Chemisorption of Isocyanides on Platinum Surfaces. Crystal Structure of $[Pt_3(CNMe)_2(\mu\text{-}Ph_2PCH_2PPh_2)_3][PF_6]_2\cdot 3Me_2CO$†

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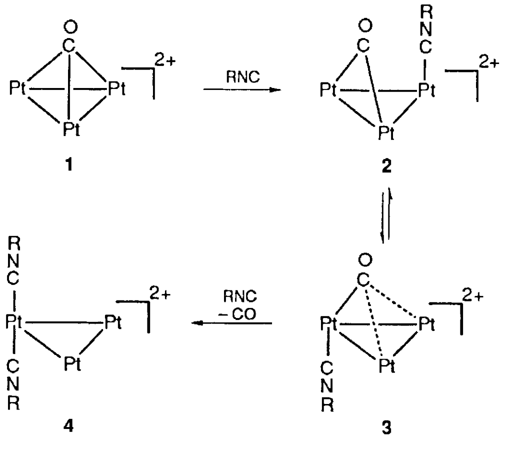
The complex cation $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ **1**, dppm = $Ph_2PCH_2PPh_2$, reacts with 1 equivalent of MeNC to give an intermediate $[Pt_3(CNMe)(\mu\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ **2**, which then rearranges to $[Pt_3(CNMe)(\eta_3\text{-}CO)(\eta\text{-dppm})_3]^{2+}$ **3**. Reaction with a second equivalent of MeNC leads to displacement of CO and formation of $[Pt_3(CNMe)_2(\mu\text{-dppm})_3]^{2+}$ **4**. Excess of MeNC reacts with **1** or **4** to displace a platinum(0) fragment and form $[Pt_2(CNMe)_2(\mu\text{-dppm})_2]^{2+}$ **7**, $[Pt_2(CNMe)_2(\mu\text{-}CNMe)(\mu\text{-dppm})_2]^{2+}$ **8**, and $[Pt_2(CNMe)_3(\mu\text{-dppm})_2]^{2+}$ **9**. Complexes **8** and **9** easily lose MeNC to give **7**. The complexes have been characterized by IR and by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopies and **4** has also been characterized crystallographically. Complex **4** is an unusual 44-electron cluster which contains two approximately square-planar fragments and one octahedral platinum fragment forming the Pt_3 triangle, and with no single-atom bridging group. Complexes **3** and **4** are fluxional such that they appear to attain three-fold symmetry by a process in which the isocyanide ligands migrate easily around the Pt_3 triangle. It is suggested that the binding of isocyanides in the Pt_3 clusters resembles the binding to a Pt(111) surface, and that the fluxionality models the mobility of isocyanide ligands on a platinum surface.

Isocyanides can bind to both metal surfaces and metal cluster complexes as terminal, doubly bridging or triply bridging ligands.[1–11] Methyl isocyanide adsorbs on Pt(111) initially as a terminal ligand with ν(NC) 2265–2240 cm^{-1}, depending on coverage, but at high coverage doubly bridging isocyanide with ν(NC) 1600–1770 cm^{-1} is also present.[1] For comparison, free MeNC has ν(NC) at 2175 cm^{-1}. The strong surface binding of isocyanides has been used in the self-assembly of monolayers of redox-active molecules containing isocyanide units on a platinum surface.[5] The complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$, dppm = $Ph_2PCH_2PPh_2$, can model some of the chemical properties of a Pt(111) surface[12] and, in an earlier paper, its reactions with bulky isocyanide ligands were reported.[13] Amongst other compounds, the complex $[Pt_3(CNR)_2(\mu\text{-dppm})_3]^{2+}$, R = *o*-xylyl, was of particular interest since it contained the first example of a Pt_3 triangle with no single-atom bridging group. Since this unusual bonding situation[14–18] might be due to steric effects of the bulky *o*-xylyl isocyanide ligands, the related chemistry with the smaller ligand MeNC has now been studied and the results are reported.

Results and Discussion

(*a*) *Reactions in which the* Pt_3 *Core is retained*.—The reaction of MeNC with $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ **1** at room temperature leads to partial fragmentation of the cluster (see below) and so many reactions were carried out at low temperature in order to overcome this problem. The fragmentation occurs much more easily than in the related chemistry of *o*-xylyl isocyanide and other bulky isocyanide ligands.[13] The cluster chemistry is shown in Scheme 1.



Scheme 1 R = Me

When 1 equivalent of MeNC was added to a solution of complex **1** at −78 °C an intermediate, believed to have structure **2**, was formed and this rearranged to **3** on warming to room temperature. Complex **3** was isolated in pure form; it is fluxional in solution but the structure **3** was identified by low-temperature NMR studies and no detectable reversion to **2** occurred on extended storage at low temperature. Surprisingly, however, when free MeNC was added to a solution of **3** at −78 °C the initial product was **2** as detected by NMR spectroscopy. As the solution was allowed to warm, carbon monoxide was lost and complex **4** was formed in high yield. Complex **4** is stable and was isolated in pure form. It was also formed by the slow decomposition of **3** in solution at room temperature, which occurs according to equation (1); slow crystallization of **3** gave large single crystals but these were

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† Tris[μ-bis(diphenylphosphino)methane]-1:2κ^2*P*:*P*′; 1:3κ^2*P*:*P*′; 2:3κ^2-*P*:*P*′-bis(methyl isocyanide)-1κ^2*C*-*triangulo*-triplatinum bis(hexafluorophosphate)–acetone (1/3).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

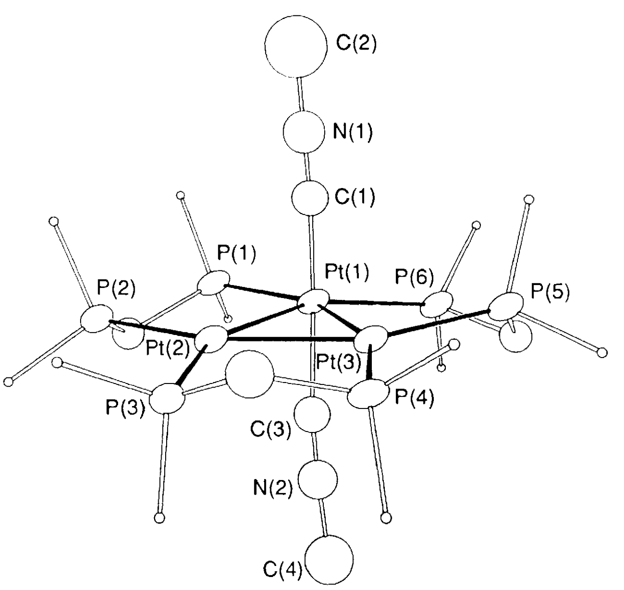
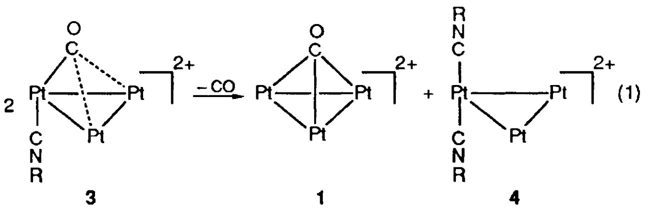


Fig. 1 A view of the cluster cation **4** with only *ipso*-carbon atoms of the phenyl rings shown as small spheres of abitrary radius, emphasizing the co-ordination of the MeNC ligands and the conformation of μ-dppm ligands



shown by NMR spectroscopy to contain a mixture of **3** and **4**, which cocrystallize.

The structure of complex **4** was determined crystallographically and a view of the cation is shown in Fig. 1. Crystallographic data are given in Table 1, positional parameters in Table 2 and selected bond distances and angles in Table 3. The three platinum atoms define an approximately isosceles triangle with the distance Pt(2)–Pt(3) 2.565(1) Å significantly shorter than the Pt(1)–Pt(2) and Pt(1)–Pt(3) 2.635(1) and 2.651(1) Å respectively. Nevertheless, all Pt–Pt distances fall in the range expected for single bonds and the mean 2.617 Å is somewhat shorter than in **1** (2.634 Å)[19] Both isocyanide ligands are bonded only to Pt(1), with Pt(1)–C(1) 1.94(2) and Pt(1)–C(3) 1.98(2) Å; the remaining Pt–C distances [Pt(2)···C(1) 3.097(1), Pt(2)···C(3) 2.939(1), Pt(3)···C(1) 3.037(1) and Pt(3)···C(3) 2.995(1) Å] are clearly too long for there to be any significant bonding interaction. The isocyanide ligands remain approximately linear [C(1)–N(1)–C(2) and C(3)–N(2)–C(4) 174(2) and 176(2)° respectively], but they are displaced from the idealized positions normal to the Pt_3 plane towards the centre of the Pt_3 triangle [C(1)–Pt(1)–C(3) 158.0(7)°]. The structure is very similar to that of $[Pt_3(CNR)_2(\mu\text{-dppm})_3]^{2+}$ (R = *o*-xylyl), which is somewhat less regular, presumably due to increased steric effects.[13] A comparison of some bond parameters is given in Table 4. In both cases, the mean Pt–Pt and Pt–P distances are longest about the Pt(1) centre, presumably due the higher co-ordination number of Pt(1). A view of **4** including the phenyl groups is shown in Fig. 2; there are no short non-bonded contacts and it is clear that the structure with terminal isocyanide ligands is adopted for electronic rather than steric reasons.

Complex **4** was characterized by the following spectroscopic data. The IR spectrum gave ν(CN) 2187 cm^{-1}, that is at slightly higher frequency than for the free ligand, showing that the isocyanide ligands were terminally bound. The room-temperature ^1H NMR spectrum gave single resonances for the CH_3NC protons and the CH_2P_2 protons and the ^{31}P NMR spectrum gave a single broad resonance for the dppm phosphorus atoms. These data indicate fluxionality of **4**, since, for example, the ground-state structure should have three different ^{31}P environments, and this was confirmed by the low-temperature NMR spectra. Thus, at −80 °C, the ^{31}P NMR spectrum contained three resonances due to P^a, P^b and P^c (Fig. 3), and the ^{195}Pt NMR spectrum contained two resonances, as expected for structure **4**. The relative magnitudes of the $^1J(PtP)$ coupling constants showed a correlation with the corresponding average bond distances [$^1J(Pt^1P^a)$ = 1790 Hz, *d*(PtP) = 2.416 Å; $^1J(Pt^2P^b)$ = 2500 Hz, *d*(PtP) = 2.283 Å; $^1J(Pt^2P^c)$ = 4060 Hz, *d*(PtP) = 2.211 Å]. It was difficult to prove that the fluxionality of **4** is intramolecular because free MeNC causes degradation of the cluster. However, by adding 0.5 equivalent of free MeNC to an NMR solution of **4** at low temperature and then allowing the solution to warm to room temperature in the NMR probe, a spectrum in the fast-fluxionality region but still showing separate ^1H NMR peaks due to free and co-ordinated MeNC protons was obtained. Hence the fluxionality is intramolecular and the mechanism in Scheme 2 involving an intermediate or transition state **5** with $Pt_3(\mu_3\text{-CNR})$ groups is most probable, although an intermediate with lower symmetry cannot be disproved.

The characterization of complex **3** was similar but was aided by the additional data obtained from the ^{13}CO-labelled

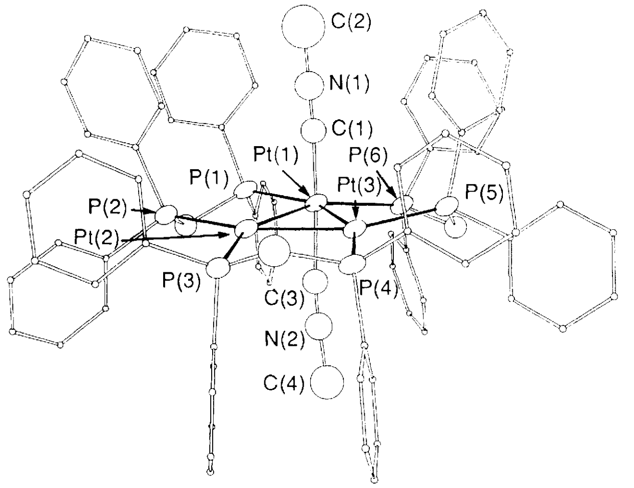
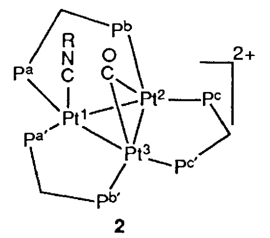


Fig. 2 A view of the cluster cation **4** with phenyl groups included as small spheres of arbitrary radius, illustrating the steric environment of the MeNC ligands



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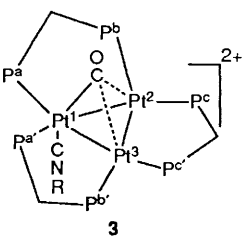

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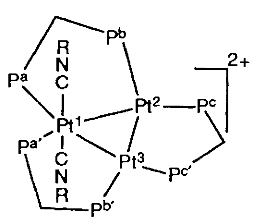

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Table 1 Summary of X-ray structure determination

Compound, *M*	$C_{79}H_{72}F_{12}N_2P_8Pt_3\cdot3C_3H_6O$, 2284.75
Crystal system, space group	Monoclinic, $P2_1/n$
Cell dimensions	a = 14.6168(6), b = 28.671(2), c = 21.501(2) Å, β = 98.778(6)°
T/°C	23
U/Å^3, Z	8905(2), 4
D_m, D_c/g cm^{-3}	1.73(5), 1.70
F(000)	4484
Diffractometer, filter	Enraf Nonius CAD4F, nickel
Radiation, Å	Cu-Kα, 1.541 84
Approximate crystal dimensions/mm	0.14 × 0.16 × 0.30
No. of faces, face indices	11, {001}, {110}, {110}, $\{11\bar{1}\}$
ω-Scan widths; before, after	0.11, 0.11
Scan mode, width/°	ω–2θ, 0.9 + 0.14 tanθ
Index, ranges	$-15 \leqslant h \leqslant 15$, $-2 \leqslant k \leqslant 30$, $-2 \leqslant l \leqslant 22$
θ range/°	3.0–110
Scan speed/° min^{-1}	1.37–4.12
No of data, standards collected	12 592, 240
μ/cm^{-1}	106.9
No of unique data	11 178
No. of observations, variables	6039 [$I \geqslant 2.5\sigma(I)$], 384
k, g in weighting scheme $w = k/[\sigma^2(F_o) + gF_o{}^2]$	0.0455, 0.0475
Final R and R'	1.4708, 0.000 599
Residual electron density range (e Å^{-3})	1.37 to −1.05
Largest shift/e.s.d.	−0.8228 on z of O(3)

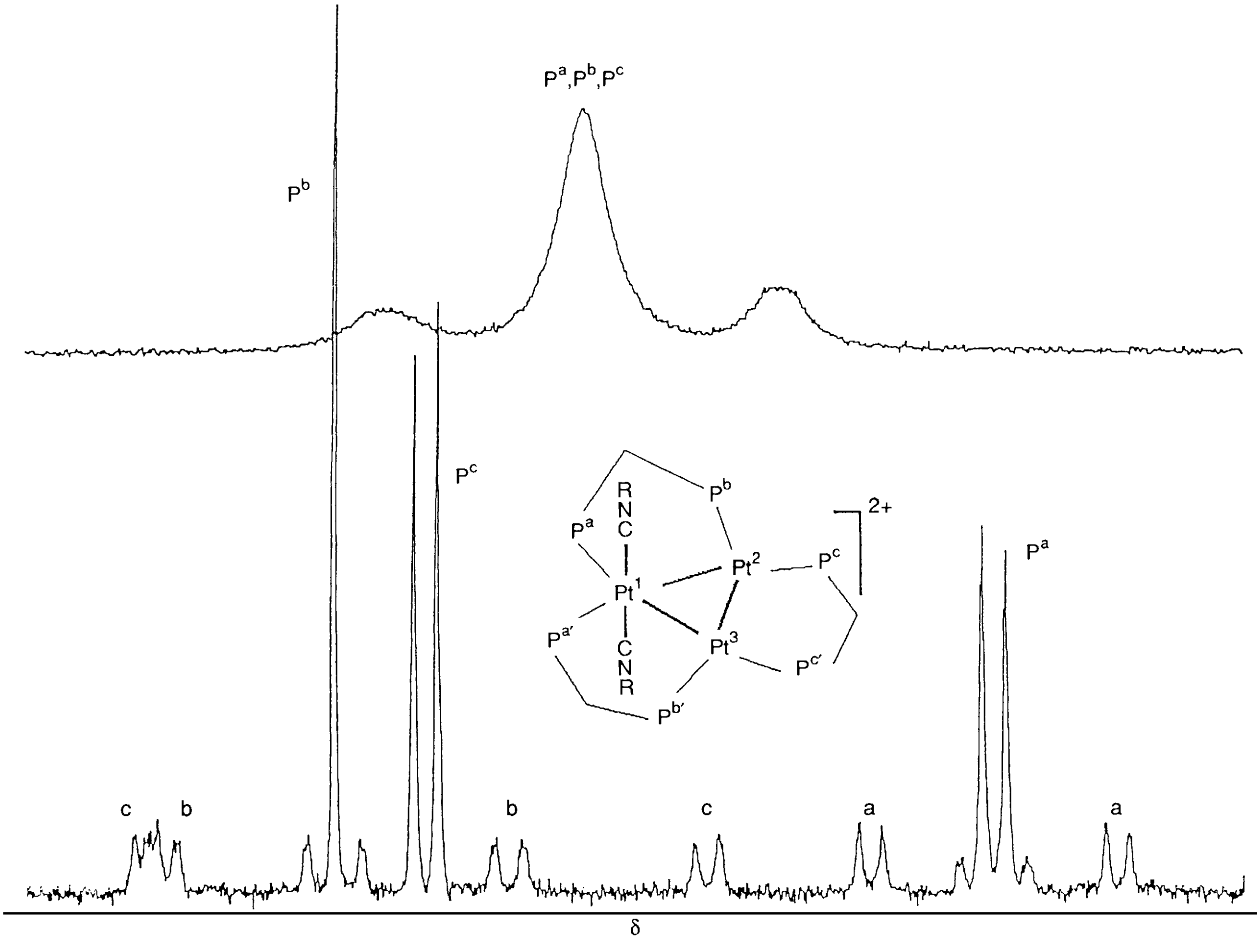


Fig. 3 The ^{31}P NMR spectra (121.5 MHz) of complex **4**; above, at room temperature showing the averaged phosphorus signal with ^{195}Pt satellites; below, at −80 °C at which temperature the fluxionality is frozen out

isotopomer, **3***. The IR spectrum of **3** gave ν(CN) 2207 cm^{-1} and ν(CO) 1816 cm^{-1}, consistent with a terminal isocyanide and semibridging carbonyl ligand being present. The ν(CN) stretching frequency is higher than for **4**, presumably because the back bonding is stronger to CO than to MeNC in **3**. For comparison, the ν(CN) frequency for MeNC on Pt(111) is 2265–2240 cm^{-1}, indicating weaker back bonding than in **3** or **4**. The room-temperature ^{31}P and ^{195}Pt NMR spectra of **3** each contained one resonance, while the corresponding spectra at −80 °C contained three and two resonances respectively. These data indicate that **3** is fluxional in a similar way to **4**. At room temperature the ^{13}CO resonance of the carbonyl ligand of **3***

Table 2 Positional (× 10^4) parameters for complex **4**

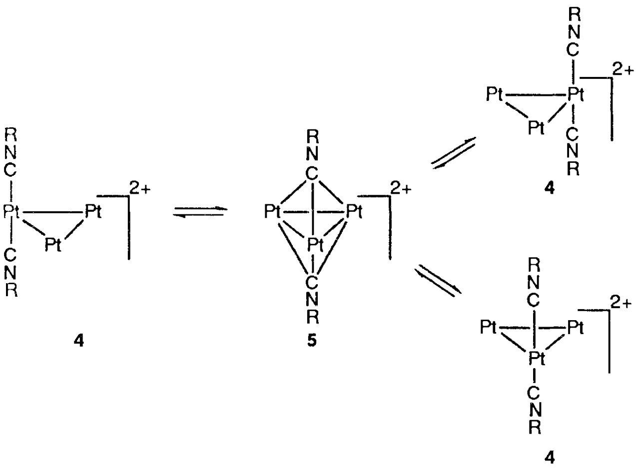
Atom	x	y	z	Atom	x	y	z
Pt(1)	446.1(5)	1596.3(3)	2056.0(3)	C(423)	385(7)	1424(4)	5545(5)
Pt(2)	94.8(5)	2380.6(2)	2613.1(3)	C(424)	−280(7)	1131(4)	5766(5)
Pt(3)	−312.5(5)	1605.7(3)	3100.2(3)	C(425)	−1181(7)	1088(4)	5415(5)
P(1)	1083.5(30)	1993.3(16)	1227.5(19)	C(426)	−1418(7)	1338(4)	4843(5)
P(2)	703.9(31)	2883.4(16)	1960.3(20)	C(511)	−1013(7)	511(3)	3673(4)
P(3)	−568.5(31)	2816.0(15)	3263.8(21)	C(512)	−1970(7)	618(3)	3525(4)
P(4)	−985.1(30)	1912.8(16)	3861.3(19)	C(513)	−2617(7)	398(3)	3859(4)
P(5)	−242.9(30)	816.9(15)	3241.4(20)	C(514)	−2307(7)	71(3)	4341(4)
P(6)	175.2(32)	774.0(15)	1866.1(20)	C(515)	−1350(7)	−37(3)	4489(4)
C(1)	1570(11)	1600(6)	2666(7)	C(516)	−703(7)	183(3)	4155(4)
N(1)	2289(10)	1606(5)	2969(7)	C(521)	876(8)	604(3)	3574(5)
C(2)	3208(17)	1599(9)	3283(11)	C(522)	1461(8)	901(3)	3988(5)
C(3)	−870(12)	1710(6)	1708(7)	C(523)	2362(8)	750(3)	4251(5)
N(2)	−1636(10)	1735(5)	1492(6)	C(524)	2679(8)	302(3)	4102(5)
C(4)	−2593(14)	1737(7)	1241(9)	C(525)	2094(8)	4(3)	3688(5)
C(10)	627(11)	2596(5)	1176(7)	C(526)	1193(8)	155(3)	3424(5)
C(20)	−584(12)	2519(6)	4017(8)	C(611)	−537(6)	635(4)	1126(5)
C(30)	−493(10)	538(5)	2464(6)	C(612)	−103(6)	572(4)	584(5)
C(111)	2311(9)	2068(4)	1275(6)	C(613)	−647(6)	479(4)	−8(5)
C(112)	2913(9)	1735(4)	1612(6)	C(614)	−1626(6)	450(4)	−59(5)
C(113)	3887(9)	1784(4)	1652(6)	C(615)	−2060(6)	514(4)	482(5)
C(114)	4259(9)	2168(4)	1355(6)	C(616)	−1516(6)	606(4)	1075(5)
C(115)	3658(9)	2501(4)	1019(6)	C(621)	1111(9)	362(3)	1898(6)
C(116)	2684(9)	2451(4)	979(6)	C(622)	2040(9)	519(3)	2042(6)
C(121)	748(6)	1792(4)	428(5)	C(623)	2780(9)	193(3)	2093(6)
C(122)	1414(6)	1562(4)	120(5)	C(624)	2590(9)	−290(3)	2001(6)
C(123)	1147(6)	1364(4)	−486(5)	C(625)	1661(9)	−447(3)	1857(6)
C(124)	213(6)	1396(4)	−784(5)	C(626)	921(9)	−121(3)	1805(6)
C(125)	−454(6)	1626(4)	−477(5)	P(7)	2625(4)	2303(2)	4898(3)
C(126)	−186(6)	1823(4)	129(5)	F(1)^a	3222(12)	2413(6)	5601(8)
C(211)	1905(8)	3035(4)	2194(5)	F(2)^a	1698(12)	2424(6)	5227(8)
C(212)	2377(8)	2837(4)	2758(5)	F(3)^a	3534(15)	2258(8)	4591(10)
C(213)	3315(8)	2955(4)	2972(5)	F(4)^a	1987(14)	2227(7)	4228(9)
C(214)	3782(8)	3273(4)	2622(5)	F(5)^a	2681(11)	2852(6)	4723(7)
C(215)	3309(8)	3472(4)	2058(5)	F(6)^a	2542(14)	1789(7)	5075(9)
C(216)	2371(8)	3353(4)	1844(5)	F(1′)^a	2962(43)	2641(23)	4383(28)
C(221)	180(8)	3442(4)	1763(5)	F(2′)^a	3504(28)	1998(16)	4783(19)
C(222)	−599(8)	3482(4)	1282(5)	F(3′)^a	2191(40)	1859(20)	5339(26)
C(223)	−1046(8)	3919(4)	1160(5)	F(4′)^a	1671(41)	2600(22)	4976(29)
C(224)	−715(8)	4317(4)	1518(5)	F(5′)^a	3361(35)	2470(18)	5397(24)
C(225)	63(8)	4278(4)	1998(5)	F(6′)^a	1999(36)	1979(20)	4321(24)
C(226)	510(8)	3841(4)	2121(5)	P(8)	4084(5)	−603(2)	7989(3)
C(311)	−1736(7)	2947(4)	2920(5)	F(7)	4377(12)	−1099(6)	8262(8)
C(312)	−1984(7)	2868(4)	2263(5)	F(8)	3029(12)	−764(6)	7852(7)
C(313)	−2908(7)	2948(4)	1968(5)	F(9)	5093(15)	−428(7)	8157(9)
C(314)	−3584(7)	3106(4)	2328(5)	F(10)	4198(13)	−767(7)	7305(9)
C(315)	−3336(7)	3185(4)	2984(5)	F(11)	3860(13)	−422(6)	8667(9)
C(316)	−2412(7)	3105(4)	3280(5)	F(12)	3772(15)	−127(7)	7688(10)
C(321)	−31(8)	3363(3)	3519(5)	O(1)	5666(15)	4289(7)	2515(9)
C(322)	911(8)	3345(3)	3804(5)	C(11)	6517(19)	4344(9)	2625(12)
C(323)	1388(8)	3762(3)	4006(5)	C(12)	6956(17)	4475(9)	3271(12)
C(324)	923(8)	4198(3)	3922(5)	C(13)	7016(18)	4292(9)	2084(12)
C(325)	−18(8)	4216(3)	3636(5)	O(2)	1499(15)	6422(7)	5257(10)
C(326)	−495(8)	3799(3)	3435(5)	C(21)	913(15)	6159(7)	4961(10)
C(411)	−2222(9)	1970(4)	3728(5)	C(22)	1190(15)	5688(7)	4778(10)
C(412)	−2729(9)	1827(4)	3142(5)	C(23)	−16(15)	6343(7)	4709(10)
C(413)	−3700(9)	1899(4)	3014(5)	O(3)	899(25)	4261(13)	370(16)
C(414)	−4166(9)	2114(4)	3472(5)	C(31)^b	790(25)	3872(13)	118(16)
C(415)	−3659(9)	2258(4)	4057(5)	C(31′)^b	606(25)	4175(13)	−190(16)
C(416)	−2688(9)	2185(4)	4185(5)	C(32)^b	1552(25)	3528(13)	216(16)
C(421)	−753(7)	1631(4)	4622(5)	C(32′)^b	789(25)	4507(13)	−684(16)
C(422)	148(7)	1674(4)	4973(5)	C(33)	−40(25)	3781(13)	−353(16)

[a] Occupancy 0.80/0.20. [b] Occupancy 0.50/0.50.

was at δ 195.5 with an 'average' J(PtC) = 709 Hz, but at −80 °C the resonance was at δ 222 (significantly shifted to higher δ) with separate couplings ^1J(Pt^{1}C) = 1193 Hz and ^1J(Pt^{2}C) = 384 Hz. The expected 'average' J(PtC), in the rapid-fluxionality region, would then be expected to be $\frac{1}{3}$ × 1193 + $\frac{2}{3}$ × 384 = 654 Hz, that is significantly lower than the observed value of 709 Hz. These changes in chemical shift and coupling constant with temperature suggest a change in equilibrium geometry, and are consistent with the carbonyl ligand shifting more towards terminal binding at high temperature and bridging binding [though still unsymmetrical, as indicated by the very different values of J(Pt^{1}C) and J(Pt^{2}C) at low temperature. Bridging carbonyls have higher δ(^{13}C) values than those of terminal carbonyls.[20] The complex [Pt$_3$(CO)(μ-CO)(μ-

Table 3 Selected bond distances (Å) and angles (°)

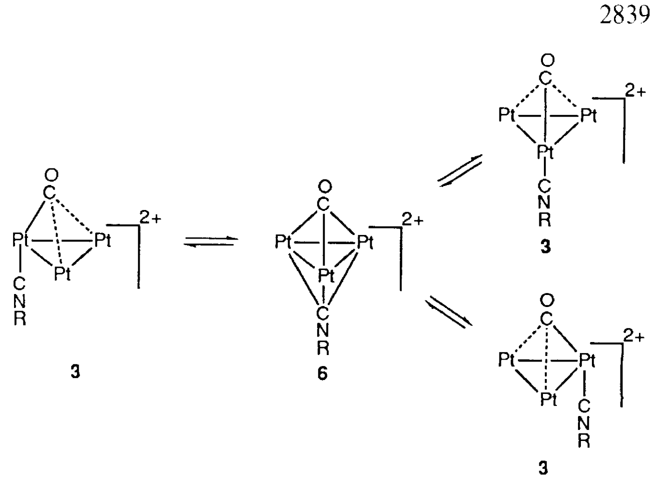
Pt(2)–Pt(1)	2.6350(10)	Pt(3)–Pt(1)	2.6515(9)
Pt(3)–Pt(2)	2.5646(10)	C(1)–Pt(1)	1.940(16)
C(3)–Pt(1)	1.982(17)	P(1)–Pt(1)	2.417(4)
P(6)–Pt(1)	2.415(4)	P(2)–Pt(2)	2.285(5)
P(3)–Pt(2)	2.207(5)	P(4)–Pt(3)	2.216(4)
P(5)–Pt(3)	2.282(4)	N(1)–C(1)	1.148(18)
C(2)–N(1)	1.410(25)	N(2)–C(3)	1.147(19)
C(4)–N(2)	1.420(22)	C(10)–P(1)	1.849(16)
C(10)–P(2)	1.864(15)	C(20)–P(3)	1.834(17)
C(20)–P(4)	1.848(17)	C(30)–P(5)	1.839(14)
C(30)–P(6)	1.857(15)		
Pt(3)–Pt(1)–Pt(2)	58.04(3)	Pt(3)–Pt(2)–Pt(1)	61.30(2)
Pt(2)–Pt(3)–Pt(1)	60.66(3)	P(1)–Pt(1)–Pt(2)	93.26(11)
P(1)–Pt(1)–Pt(3)	151.30(11)	P(6)–Pt(1)–Pt(2)	150.65(12)
P(6)–Pt(1)–Pt(3)	94.26(11)	P(2)–Pt(2)–Pt(1)	97.93(12)
P(2)–Pt(2)–Pt(3)	159.03(12)	P(3)–Pt(2)–Pt(1)	154.95(13)
P(3)–Pt(2)–Pt(3)	94.55(12)	P(4)–Pt(3)–Pt(1)	156.83(12)
P(4)–Pt(3)–Pt(2)	96.56(12)	P(5)–Pt(3)–Pt(1)	94.96(12)
P(5)–Pt(3)–Pt(2)	154.74(12)	C(1)–Pt(1)–Pt(2)	83.7(5)
C(1)–Pt(1)–Pt(3)	81.2(5)	C(3)–Pt(1)–Pt(2)	77.7(5)
C(3)–Pt(1)–Pt(3)	79.1(5)	C(1)–Pt(1)–P(1)	96.5(5)
C(1)–Pt(1)–P(6)	102.7(5)	C(3)–Pt(1)–P(1)	96.1(5)
C(3)–Pt(1)–P(6)	88.4(5)	C(3)–Pt(1)–C(1)	158.0(7)
P(6)–Pt(1)–P(1)	114.00(15)	P(3)–Pt(2)–P(2)	106.41(15)
P(5)–Pt(3)–P(4)	108.14(17)	N(1)–C(1)–Pt(1)	172.1(15)
N(2)–C(3)–Pt(1)	174.0(15)	C(2)–N(1)–C(1)	174.0(20)
C(4)–N(2)–C(3)	176.2(18)	C(10)–P(1)–Pt(1)	107.9(5)
C(10)–P(2)–Pt(2)	107.5(5)	C(20)–P(3)–Pt(2)	111.3(6)
C(20)–P(4)–Pt(3)	110.1(6)	C(30)–P(5)–Pt(3)	108.2(5)
C(30)–P(6)–Pt(1)	109.2(5)	P(2)–C(10)–P(1)	112.8(8)
P(4)–C(20)–P(3)	108.9(9)	P(6)–C(30)–P(5)	114.7(8)



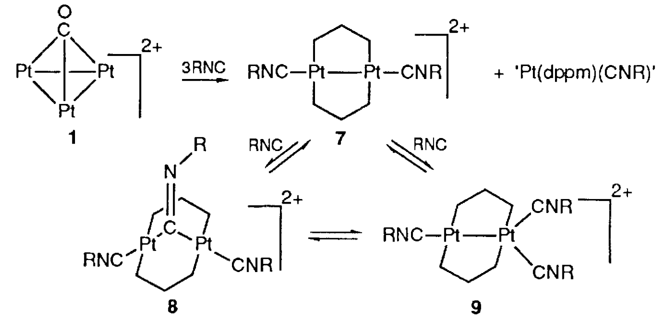
Scheme 2

dppm)$_3$]$^{2+}$ has a similar structure to that of **3** but the activation energy to fluxionality is much lower.[20] Thus, for **3** the major contribution to the activation energy is probably conversion of the terminal isocyanide into a μ_3-bonded isocyanide (complex **6**, Scheme 3) and this is clearly more difficult than with the corresponding carbonyl analogue, as expected from the rarity of $M_3(\mu_3\text{-CNR})$ compared to $M_3(\mu_3\text{-CO})$ linkages.[6]

The intermediate **2**, which is only stable at low temperature, was characterized by its NMR spectra at −80 °C. The ^{31}P and ^{195}Pt NMR spectra contained three and two resonances respectively, as expected for a cluster with two-fold symmetry. The ^{13}C NMR spectrum of the ^{13}C labelled complex **2*** contained a 1:8:18:8:1 quintet, indicating a carbonyl group bridging between two platinum atoms; a much smaller coupling to the third platinum atom was also resolved (Fig. 4). The position of the isocyanide cannot be determined directly but, in order to have two-fold symmetry, it must be bonded to Pt^1. If the isocyanide were on the opposite side of the Pt$_3$ triangle from the carbonyl ligand, the complex should be able to collapse very easily to **3** but this is not the case. That is why we tentatively propose that the isocyanide and carbonyl ligands are on the same side of the Pt$_3$ triangle. Isomerization of **2** to **3** then requires dissociation of MeNC followed by reco-ordination on the opposite side or, in the presence of free MeNC, by direct displacement of co-ordinated MeNC by free MeNC. Complex **2** appears to be thermodynamically more stable at low temperature while **3** is more stable at high temperature and, in the absence of free MeNC, there is a significant barrier to their interconversion.



Scheme 3



Scheme 4

(*b*) *Reactions which give Cluster Fragmentation*.—The reaction of complex **1** with ⩾3 equivalents of MeNC led to cluster fragmentation according to Scheme 4.

With 3 equivalents of MeNC the major product was **7** and, with excess of MeNC, **8** and **9** were formed, all of which are diplatinum(I) complexes. The stoichiometry requires the formation of a platinum(0) complex (Scheme 4), and some evidence for this was obtained by NMR studies. Thus, in the ^{195}Pt NMR spectrum of reaction mixtures a doublet signal at $\delta = -3736$ with ^1J(PtP) = 5400 Hz was present, and was essentially unchanged at −80 °C. This is most readily attributed to a complex $Pt_2(CNMe)_n(\mu\text{-dppm})$, since the large coupling constant indicates platinum(0) and the multiplicity shows that there is only one phosphorus co-ordinated to each platinum atom. Some free dppm was also detected by ^{31}P NMR spectroscopy. Attempts to isolate this complex were unsuccessful and, in the presence of air, it appeared to be oxidized to **7**, which was therefore formed in high yield. Complexes **8** and **9** easily lost MeNC to form **7**. Analogues of **7** and **8** with other isocyanides have been reported previously,[21] but **9** appears to be novel. However, Ni$_2$, NiPd and NiPt analogues of **9** are known and so its formation is reasonable.[11,22] Complexes **7** and **9** were isolated in pure form but **8** was characterized in solution only.

Table 4 Comparison of selected bond distances (Å) and angles (°) in the cluster cations $[Pt_3(CNR)_2(\mu\text{-dppm})_3]^{2+}$, where R = Me or *o*-xylyl

	R = Me	R = *o*-xylyl		R = Me	R = *o*-xylyl
Pt(1)-Pt(2)	2.635(1)	2.647(1)	C(1)-N(1)-C(2)	174(2)	167(3)
Pt(1)-Pt(3)	2.651(1)	2.653(1)	C(3)-N(2)-C(4)	176(2)	174(2)
P(2)-Pt(3)	2.565(1)	2.582(1)	Pt(1)-C(1)-N(1)	172(2)	171(2)
Pt(1)-P(1)	2.417(4)	2.514(7)	Pt(1)-C(3)-N(2)	174(2)	173(2)
Pt(1)-P(6)	2.415(4)	2.390(7)	C(1)-Pt(1)-C(3)	158.0(7)	151.9(9)
Pt(2)-P(2)	2.285(5)	2.416(8)	Pt(2)-Pt(1)-C(1)	83.7(5)	78.7(6)
Pt(2)-P(3)	2.207(5)	2.203(7)	Pt(3)-Pt(1)-C(1)	81.2(5)	77.6(7)
Pt(3)-P(4)	2.216(4)	2.164(7)	Pt(2)-Pt(1)-C(3)	77.7(5)	73.3(7)
Pt(3)-P(5)	2.282(4)	2.249(7)	Pt(3)-Pt(1)-C(3)	79.1(5)	87.9(8)
Pt(1)-C(1)	1.94(2)	1.97(2)			
Pt(1)-C(3)	1.98(2)	1.93(2)			
C(1)-N(1)	1.15(2)	1.16(3)			
C(3)-N(2)	1.15(2)	1.22(3)			

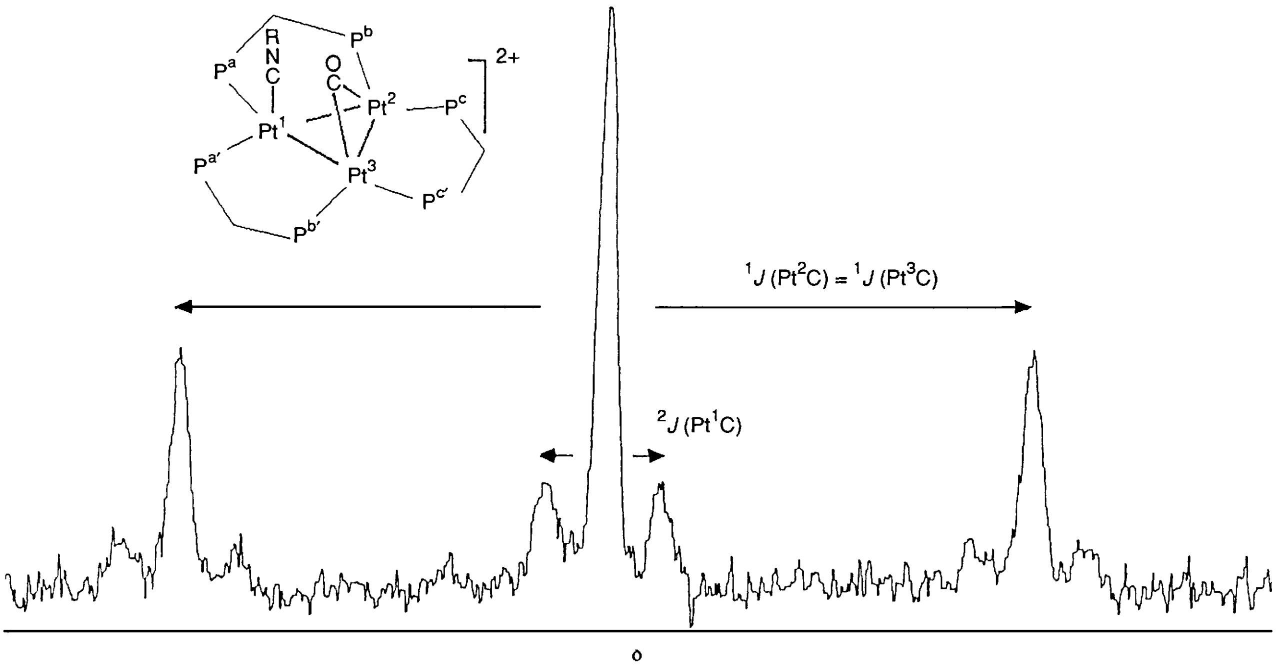


Fig. 4 The ^{13}C NMR spectrum (75.6 MHz) of complex **2***, ^{13}CO labelled, showing only the carbonyl resonance. Only the inner three lines of the 1:8:18:8:1 quintet due to the coupling $^1J(Pt^2C) = {}^1J(Pt^3C)$ are shown; the outer peaks were observed but barely above the noise level

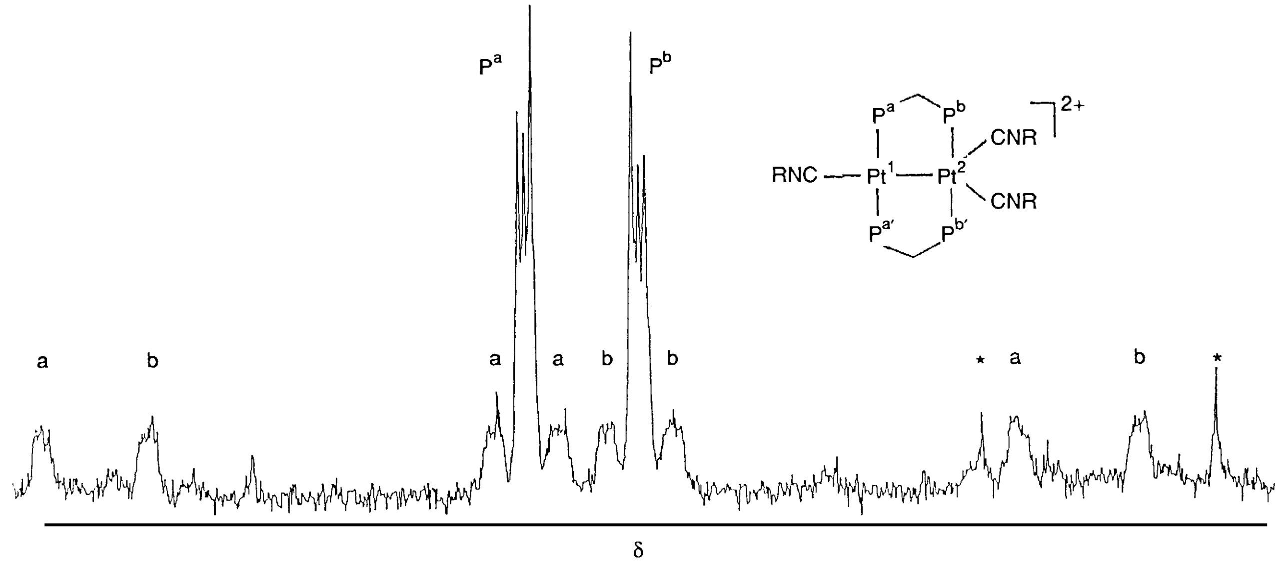
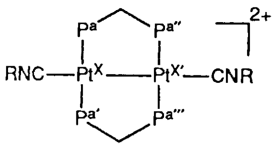
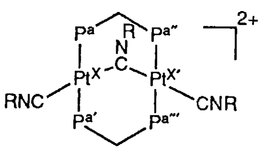


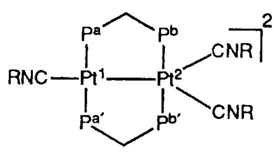
Fig. 5 The ^{31}P NMR spectrum (121.5 MHz) of complex **9** at −80 °C, showing the non-equivalent ^{31}P environments. The peaks labelled * are due to minor amounts of complexes **7** and **8**. At room temperature the two resonances due to **9** coalesce to give a broad singlet and partial dissociation of MeNC to give **7** occurs



7



8



9

Details of the NMR spectra are given in the Experimental section, and the NMR labelling system is given above. Complex **9** was fluxional and was characterized by its low-temperature NMR spectra (Fig. 5).

The cluster fragmentation occurred very easily whereas bulky isocyanides do not easily fragment the cluster **1**.[13] For example, excess of *o*-xylyl isocyanide reacted very slowly (several days) with **1** in the presence of iodide catalyst by partial displacement of dppm to give $[Pt_3(CNR)_4(\mu\text{-dppm})_2]^{2+}$ (R = *o*-xylyl) but does not cause fragmentation of the Pt_3 cluster.[13] The reaction of **1** with excess of MeNC initially gives **4** and this then reacts easily with more MeNC to give fragmentation. Presumably, the analogue of **4** with *o*-xylyl isocyanide ligands is protected by the bulky xylyl substituents and so further direct attack by free ligand leading to fragmentation cannot occur.

Conclusion

There are now well characterized examples of 44-electron clusters $[Pt_3L(L')(\mu\text{-dppm})_3]^{2+}$, based on the roughly planar $Pt_3(\mu\text{-dppm})_3$ core, in which the ligands L and L′ are both triply bridging (L = L′ = SnF_3^-), in which one is triply bridging and one terminal (L = μ_3-CO, L′ = SCN^- or PR_3), and in which both are terminal (L = L′ = MeNC or *o*-xylyl isocyanide).[12] The energy difference between these structural forms is probably small in all cases and is proved for the complexes with less than three-fold symmetry by the observation of easy fluxionality.[12] Earlier theoretical studies had suggested that a one-atom bridging group was important in stabilizing Pt_3 clusters,[15-17] but the present work and the complementary work with bulkier isocyanide ligands[13] show that such bridging groups are not always necessary. Complex **4** contains one 18-electron and two 16-electron platinum centres and it is not obvious why structure **4** rather than **5** (Scheme 2) is preferred. However, there are a number of heteronuclear clusters which may be considered to be isolobal with **4**; for example, the complexes $[Pt_2Fe(CO)_6(\mu\text{-dppm})]$ and $[Pt_2Fe(CO)_4(\mu\text{-dppm})_2]$ have similar structures and contain an 18-electron iron centre in place of the 18-electron platinum centre in **4**.[23] We note also that MeNC is adsorbed on Pt(111) mainly as a terminal ligand, whereas it binds on Ni(111) as a μ_3-η^2-MeNC and in $[Ni_3(\mu_3\text{-I})(\mu_3\text{-CNMe})(\mu\text{-dppm})_3]^+$ as a μ_3-σ-MeNC ligand, and so there is a clear metal dependence. To some extent, the complexes **3** and **4** can be thought to mimic the MeNC on a Pt(111) surface and the easy fluxionality of the complexes mimics the mobility of chemisorbed ligands on a platinum surface.

Experimental

Proton NMR spectra were recorded by using a Varian XL-200 spectrometer, ^{31}P, ^{195}Pt and ^{13}C NMR spectra by using a Varian XL-300 spectrometer. References were $SiMe_4$ (^1H), H_3PO_4(^{31}P), aqueous $K_2[PtCl_4]$(^{195}Pt) and $SiMe_4$ (^{13}C). Where coupling constants were obtained from spectra of more than one nucleus the separate values are given; those from ^{195}Pt NMR spectra are least accurate because linewidths are greatest. The compounds MeNC,[24] $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$,[19] and the corresponding ^{13}C-enriched $[Pt_3(\mu_3\text{-}^{13}CO)(\mu\text{-dppm})_3][PF_6]_2$[20] were prepared by the published methods.

$[Pt_3(\mu\text{-CO})(CNMe)(\mu\text{-dppm})_3][PF_6]_2$.—Methyl isocyanide (2.64 µl, 1 equivalent) in CD_2Cl_2 (0.2 cm^3) was added to a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CD_2Cl_2 (0.3 cm^3) at −80 °C in an NMR tube. The solution at −80 °C was shown to contain $[Pt_3(\mu\text{-CO})(CNMe)(\mu\text{-dppm})_3][PF_6]_2$ by spectroscopic methods. The corresponding ^{13}C-labelled cluster, $[Pt_3(\mu\text{-}^{13}CO)(CNMe)(\mu\text{-dppm})_3][PF_6]_2$, was prepared similarly using $[Pt_3(\mu\text{-}^{13}CO)(\mu\text{-dppm})_3][PF_6]_2$. NMR data in CD_2Cl_2 at −80 °C: ^{31}P, δ −20.6 [m, $^1J(P^aPt^1)$ = 3512, $^3J(P^aP^c)$ = 197, $2P^a$], −51.2 [s, $^1J(P^bPt^2)$ = 3232, $^2J(P^{b'}Pt^2)$ = 337, $^3J(P^bP^{b'})$ = 174, $2P^b$] and −43.0 [d, $^1J(P^cPt^2)$ = 2080, $^2J(P^cPt^1)$ = 254, $^3J(P^cP^a)$ = 195.3, $2P^c$]; ^{195}Pt, δ −2483 [m, $^1J(Pt^1P^a)$ = 3537, 1 Pt^1] and −3185 [m, $^1J(Pt^2P^c)$ = 2146, $^1J(Pt^2P^b)$ = 3341, $^2J(Pt^2P^{b'})$ = 334, $^1J(Pt^2\text{–}^{13}CO)$ = 900, $2Pt^2$]; ^{13}C, δ 208 [m, $^1J(CPt^2)$ = 909, $^2J(CPt^1)$ = 95 Hz, 1C of CO]; ^1H, δ 3.36 (s, 3 H of MeNC) and 5.2 (br, 6 H of dppm ligands).

$[Pt_3(CO)(CNMe)(\mu\text{-dppm})_3][PF_6]_2$.—Methyl isocyanide (2.64 µl, 1 equivalent) in CH_2Cl_2 (0.2 cm^3) was added to a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CH_2Cl_2 (0.3 cm^3) at −80 °C in an NMR tube and was shaken for 5 min at this temperature. The solution was gradually warmed to room temperature while shaking, then filtered, the solvent removed and the residue was dried in air. The product as a red powder was identified as $[Pt_3(CO)(CNMe)(\mu\text{-dppm})_3][PF_6]_2$ by spectroscopic methods. Yield 95%, m.p. 210–215 °C (decomp.) {Found: C, 44.5; H, 3.4; N, 0.6. Calc. for $[Pt_3(CO)(CNMe)(\mu\text{-dppm})_3][PF_6]_2$: C, 44.6; H, 3.3; N, 0.7%}. NMR data in CD_2Cl_2 at −80 °C: ^{31}P, δ −9.9 (br, $2P^b$), −25.8 (br, $2P^c$) and −37.8 (br, $2P^a$); ^{195}Pt, δ −3331 [t, $^1J(Pt^1P^a)$ = 2643, $^1J(Pt^1\text{–}^{13}CO)$ = 1250, 1 Pt^1] and −2488 [m, $^1J(Pt^2P^b)$ = 3257, $^1J(Pt^2P^c)$ = 3988, $^2J(Pt^2\text{–}^{13}CO)$ observed as shoulder, but not measurable, $2Pt^2$]; ^{13}C, δ 222 [m, $^1J(CPt^1)$ = 1193, $^2J(CPt^2)$ = 384 Hz, C of ^{13}CO]; ^1H, δ 3.32 [s, 3 H of $CNCH_3$] and 5.26 (br, 6 H of CH_2 groups of dppm ligands). NMR data at room temperature in CD_2Cl_2: ^{31}P, δ −19.0 [s, $^1J(PPt)$ = 3288, 6P]; ^{195}Pt, δ −2713 [br s, $^1J(PtP)$ = 3286, 3Pt]; ^{13}C, δ 195.5 [m, $^1J(CPt)$ = 709, $^2J(CP)$ = 11 Hz, 1C of ^{13}CO]; ^1H, δ 3.37 (s, 3 H of $CNCH_3$) and 5.20 [br, 6 H of CH_2 groups of dppm ligands). IR data (Nujol): ν(CO) 1816 (br), ν(CN) 2207 (sharp) cm^{-1}.

Attempts to grow crystals of this cluster by dissolving it in acetone and layering with pentane resulted in large single crystals shown spectroscopically to contain a mixture of $[Pt_3(CO)(CNMe)(\mu\text{-dppm})_3][PF_6]_2$ and $[Pt_3(CNMe)_2(\mu\text{-dppm})_3][PF_6]_2$.

$[Pt_3(CNMe)_2(\mu\text{-dppm})_3][PF_6]_2$.—Methyl isocyanide (5.3 µl, 2 equivalents) in CH_2Cl_2 (6 cm^3) was added to a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (0.1 g) in CH_2Cl_2 (10 cm^3) and stirred for 15 min. The solvent was removed, the residue was dissolved in acetone (5 cm^3) and the solution was layered with pentane. Red crystals formed which were separated and dried in air. Yield 75%, m.p. = 250–252 °C {Found: C, 46.0; H, 3.7; N, 0.9. Calc. for $[Pt_3(CNMe)_2(\mu\text{-dppm})_3][PF_6]_2\cdot 2Me_2CO$: C, 45.8; H, 3.8; N, 1.3%}. NMR data in CD_2Cl_2 at −80 °C: ^{31}P, δ −9.1 [s, $^1J(P^bPt^2)$ = 2500, $^3J(P^bP^{b'})$ = 210, $^2J(P^bPt^{2'})$ = 210, $2P^b$], −14.6 [d, $^1J(P^cPt^2)$ = 4060, $^3J(P^cP^a)$ = 168, $2P^c$], and −48.4 [d, $^1J(P^aPt^1)$ = 1790, $^2J(P^aPt^2)$ = 300, $^3J(P^aP^c)$ = 161.4, $2P^a$]; ^{195}Pt, δ −3630 [m, $^1J(Pt^1P^a)$ = 1763, $^1J(Pt^1Pt^2)$ = 767, 1Pt^1] and −4018 [m, $^1J(Pt^2P^b)$ = 2700, $^1J(Pt^2P^c)$ = 4000 Hz, $2Pt^2$]; ^1H, δ 3.6 (s, 6 H of 2 MeNC) and 5.2 (br, 6 H, CH_2). NMR data at room temperature (in CD_2Cl_2): ^{31}P, δ −23.8 [br s, $^1J(PPt)$ = 2850 Hz, 6P]; ^1H, δ

3.67 (s, 6 H, MeNC) and 5.16 (br, 6 H, CH_2). IR data (Nujol): ν(CN) 2187 cm^{-1}.

When CO was bubbled through a solution of $[Pt_3(CNMe)_2(\mu\text{-dppm})_3][PF_6]_2$ (30 mg) in CD_2Cl_2 (0.5 cm^3) for 1 min at room temperature the ^{31}P NMR spectrum showed that no reaction occurred.

Reaction of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ *with* MeNC.—(*a*) *3 equivalents:* Methyl isocyanide (4 μl, 3 equivalents) in CD_2Cl_2 (0.2 cm^3) was added at room temperature to a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (50 mg) in CD_2Cl_2 (0.3 cm^3). The solution was shown by spectroscopic techniques to contain a mixture of $[Pt_2(CNMe)_2(\mu\text{-dppm})_2][PF_6]_2$ (see below) and $[Pt_2(\mu\text{-CNMe})(CNMe)_2(\mu\text{-dppm})_2][PF_6]_2$. Attempts to obtain the latter complex in pure form failed. However, it was characterized by spectroscopic techniques. NMR data in CD_2Cl_2: ^{31}P, δ −1.5 [m, $^1J(PPt) = 2954$, $^2J(PPt) = 41$, $^3J(P^AP^{A''}) = 61$, $^3J(P^AP^{A'''}) = 22$; ^{195}Pt, δ −2851 [m, $^1J(PtP) = 2950$]; ^1H, δ 1.94 [s, $^4J(HPt) = 15.5$ Hz, 6 H, terminal CH_3NC] and 2.9 (s, 3 H, bridging CH_3NC). IR data (Nujol): ν(CN) 2190 cm^{-1}.

(*b*) ⩾4 *equivalents: preparation of* $[Pt_2(CNMe)_3(\mu\text{-dppm})_2][PF_6]_2$. Methyl isocyanide (5.3, 6.6 or 8 μl) in CH_2Cl_2 (0.3 cm^3) was added at room temperature to a solution of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (50 mg) in CH_2Cl_2 (0.3 cm^3) in a sealed tube and shaken for 2 min. A dark yellow precipitate formed after some time. This was left aside for 1 week. Crystals were separated and washed with CH_2Cl_2 (0.5 cm^3) and dried in air. Yield 50–60%, m.p. = 176–178 °C (decomp.) {Found: C, 41.10; H, 2.95; N, 2.75. Calc. for $[Pt_2(CNMe)_3(\mu\text{-dppm})_3][PF_6]_2$: C, 42.80; H, 3.35; N, 2.65%}. NMR data in $[^2H_6]$acetone (the crystals were dissolved in the solvent in an NMR tube which was then tightly stoppered) at −80 °C: ^{31}P, δ 7.8 [m, $^1J(P^bPt^2) = 3300$, $^2J(P^bPt^1) = 220$, $2P^b$] and 10.9 [m, $^1J(P^aPt^1) = 3180$, $^2J(P^aPt^2) = 220$, $2P^a$]; ^{195}Pt, δ = −3022 [m, $^1J(Pt^1P^a) = 3198$, $^2J(Pt^1P^b) = 196$, $^1J(Pt^1Pt^2) = 1792$, $1Pt^1$] and −2874 [m, $^1J(Pt^2P^b) = 3215$, $^2J(Pt^2P^a) = 200$, $^1J(Pt^2Pt^1) = 1792$ Hz, $1Pt^2$]; ^1H, δ 3.00 (s, 3 H, MeNC) and 3.36 (s, 6 H, MeNC). NMR data in $[^2H_6]$acetone at room temperature {as a mixture of $[Pt_2(CNMe)_2(\mu\text{-dppm})_2][PF_6]_2$ (see below) and $[Pt_2(CNMe)_3(\mu\text{-dppm})_2][PF_6]_2$}: ^{31}P, δ 10.6 [s, $^1J(PPt) = 3300$ Hz, 6P]; ^1H, δ 3.00 (br s, MeNC). IR data (Nujol): ν(CN) 2208 cm^{-1}.

$[Pt_2(CNMe)_2(\mu\text{-dppm})_2][PF_6]_2$.—The complex $[Pt_2(CNMe)_3(\mu\text{-dppm})_2][PF_6]_2$ (50 mg) was dissolved in acetone (5 cm^3) and the solvent was evaporated slowly in air. This was repeated two more times when a golden powder was obtained. Yield 100%, m.p. = 172–176 °C {Found: C, 42.40; H, 3.35; N, 1.95. Calc. for $[Pt_2(CNMe)_2(\mu\text{-dppm})_2][PF_6]_2$: C, 42.35; H, 3.25; N, 1.85. NMR data in CH_2Cl_2: ^{31}P, δ −9.2 [s, $^1J(PPt) = 2580$, $^2J(PPt) = -92$, $^3J(P^aP^{a''}) = 52.6$, $^3J(P^aP^{a'''}) = 30.4$ ($N^1 = {}^1J(PtP) + {}^2J(PtP)$, calc. 2488, found 2495)]; ^{195}Pt, δ −2989 [m, $^1J(PtP) = 2582$, $^2J(PtP) = 85$]; ^1H, δ 2.28 [s, $^4J(HPt) = 10$, 6 H, MeNC] and 4.92 [m, $^3J(HPt) = 58$, $^2J(HP) = 6$ Hz, 4 H, CH_2]. IR data (Nujol): ν(CN) 2200 cm^{-1}.

X-Ray Structure Determination.—Data are given in Table 1. A red crystal of $[Pt_3(CNMe)_2(\mu\text{-dppm})_3][PF_6]_2 \cdot 3Me_2CO$ was mounted inside a capillary tube under argon. The crystal density was determined by the neutral-buoyancy method using a mixture of CCl_4 and $C_2H_4Br_2$.

Cell constants and an orientation matrix were determined and refined by using the angular settings for 20 high-angle reflections with $50 < 2\theta < 59.9°$. Intensity data were recorded at variable scan speeds chosen so as to optimize counting statistics within a maximum time per datum of 60 s. Background estimates were made by extending the scan by 25% on each side. Standard reflections were monitored every 3 h and showed no average decline over the total period of 215.4 h. Corrections were made for Lorentz, monochromator and crystal polarization, and background radiation effects, using the SDP-PLUS package [25] running on a PDP11/23+ computer. An absorption correction was applied using the program AGNOST.[26] The transmission factors ranged from 0.369 to 0.213. The space group was assigned as $P2_1/n$ on the basis of systematic absences and was confirmed by successful solution and refinement of the structure. The structure was solved by a combination of MULTAN [27] and Fourier difference techniques. Refinement was made by full-matrix least-squares refinement on *F*, using the SHELX 76 software [28] running on a SUN 3/50 workstation. Scattering factors were from ref. 29. A rigid group symmetry (C–C 1.392 Å) was imposed on the phenyl rings and the individual thermal parameters for the carbon atoms were refined isotropically. The hydrogen atoms were placed in idealized positions (C–H 0.95 Å) and were included for structure-factor calculations only. A common thermal parameter was assigned to all H atoms and was refined. One of the PF_6^- anions (with occupancy 0.80/0.20) and one acetone solvate (C–O and C–C fixed at 1.23 and 1.48 Å respectively) showed disorder.

There were 10 peaks in the final Fourier difference synthesis with electron density in the range 1.366–0.720 e $Å^{-3}$, of which the top three were associated with the disordered acetone molecule and the others were of no chemical significance.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council (Canada) for financial support, Dr. N. C. Payne for access to X-ray equipment and software and Shiraz University for granting a summer leave to M. R.

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Received 8*th March* 1991; *Paper* 1/01097B