Cleavage and Reassembly of Trinuclear Palladium Clusters in Reactions with an Isocyanide Ligand†

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Reaction of the trinuclear cluster cation $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ [dppm = bis(diphenylphosphino)-methane] with excess xylyl isocyanide, $2,6\text{-}Me_2C_6H_3N{\equiv}C$, led to cleavage giving the binuclear palladium(I) complex cation $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}dppm)_2]^{2+}$, and unidentified palladium(0) species. The $2,6\text{-}Me_2C_6H_3NC$ ligands in $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}dppm)_2]^{2+}$ undergo rapid exchange with excess $2,6\text{-}Me_2C_6H_3N{\equiv}C$ and, at low temperature, an adduct is formed and identified spectroscopically as $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)(\mu\text{-}dppm)_2]^{2+}$. A dppm ligand of $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}dppm)_2]^{2+}$ is deprotonated and oxidized in the presence of an excess of dppm and oxygen to give $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2\{\mu\text{-}Ph_2PCHPPh_2({=}O)\text{-}C,P\}(\mu\text{-}dppm)]^+$, which has been characterized by a structure determination {crystal data for the $[PF_6]^-{\cdot}Me_2CO$ salt: triclinic, space group $P\bar{1}$, $a = 14.523(2)$, $b = 22.448(4)$, $c = 12.203(3)$ Å, $\alpha = 95.52(2)$, $\beta = 110.98(2)$, $\gamma = 108.21(1)°$, $Z = 2$, $R = 0.0563$, $R' = 0.0574$}. Complex $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}dppm)_2]^{2+}$ can react with the palladium(0) species, which is formed in the initial cluster cleavage reaction, by formal addition of $Pd(CNC_6H_3Me_2\text{-}2,6)_2$ to give the trinuclear A-frame cluster complex $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2\{\mu\text{-}Pd(CNC_6H_3Me_2\text{-}2,6)_2\}(\mu\text{-}dppm)_2]^{2+}$, thus completing the fragmentation and reassembly of trinuclear clusters. This complex has been characterized by a structure determination {crystal data for the $2[PF_6]^-{\cdot}0.5Me_2CO$ salt: orthorhombic, space group $P2_12_12_1$, $a = 21.810(3)$, $b = 21.879(4)$, $c = 18.274(5)$ Å, $Z = 4$, $R = 0.0566$, $R' = 0.0632$}; in solution, it slowly loses $Pd(CNC_6H_3Me_2\text{-}2,6)_2$ to reform $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}dppm)_2]^{2+}$.

Trinuclear nickel group clusters based on the *triangulo*-$M_3(\mu\text{-}dppm)_3$ unit [M = Ni, Pd or Pt, dppm = bis(diphenylphosphino)methane] now have an extensive chemistry.[1] One complete triad is known, namely the series $[M_3(\mu_3\text{-}Cl)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$,[2] but there are often differences in structure and reactivity between these and other nickel, palladium and platinum clusters.[3-6] For example, with alkyl and aryl isocyanide ligands, nickel forms the 48-electron cluster $[Ni_3(\mu_3\text{-}I)(\mu_3\text{-}CNR)(\mu\text{-}dppm)_3]^+$,[7,8] palladium forms the 42- and 44-electron clusters $[Pd_3(\mu_3\text{-}CNR)(\mu\text{-}dppm)_3]^{2+}$ and $[Pd_3(\mu_3\text{-}CNR)_2(\mu\text{-}dppm)_3]^{2+}$ (which easily loses one isocyanide ligand),[9] and platinum forms the 44-electron clusters $[Pt_3(\mu_3\text{-}CO)(CNR)(\mu\text{-}dppm)_3]^{2+}$ and $[Pt_3(CNR)_2(\mu\text{-}dppm)_3]^{2+}$.[10,11] The nickel and palladium clusters contain the unusual triply bridging isocyanide units, $M_3(\mu_3\text{-}CNR)$,[7,8] while the platinum complexes have terminal isocyanides only.[10,11] The easy interconversion of ligands between terminal and bridging bonding modes on the triangular face of the clusters is a feature of their chemistry and makes them useful mimics of the ligand bonding and mobility on metal surfaces.[1] One limitation to the scope of this surface mimetic chemistry arises when ligand addition to the trinuclear clusters causes fragmentation to bi- and/or mono-nuclear complexes, the reverse of the process by which the clusters are synthesised.[12] This article gives details of such a cluster fragmentation reaction arising from the reaction of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ with excess of the isocyanide $2,6\text{-}Me_2C_6H_3N{\equiv}C$.

Results and Discussion

The chemistry is summarized in Scheme 1. The rapid reactions of 1 or 2 equivalents of xylyl isocyanide with the cluster cation $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ **1** to give **2** or **3** respectively have been reported earlier.[9] Reaction of deep purple **1** as the trifluoroacetate salt with excess $2,6\text{-}Me_2C_6H_3NC$ occurred more slowly and gave the yellow dipalladium(I) complex $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}dppm)_2]^{2+}$ **4** as its $[CF_3CO_2]^-$ salt. The formation of **4** requires that 1 equivalent of a palladium(0) species should be formed; in this reaction a black, insoluble precipitate presumed to be palladium metal was formed. Anion exchange with NH_4PF_6 gave $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}dppm)_2][PF_6]_2$ which was more easily crystallized. Complex **4** reacted with excess $2,6\text{-}Me_2C_6H_3NC$ at −80 °C to give a complex cation which is proposed to be $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)(\mu\text{-}dppm)_2]^{2+}$ **5**. Similar cations with less bulky isocyanides have been prepared earlier,[13-15] but **5** was too unstable to isolate. At room temperature the equilibrium between **4** + $2,6\text{-}Me_2C_6H_3NC$ and **5** was almost entirely on the side of **4**, as was clearly shown by NMR spectroscopy. In addition, the exchange of free and co-ordinated $2,6\text{-}Me_2C_6H_3NC$ was rapid at room temperature such that only an average signal was observed for the methyl groups of free and co-ordinated $2,6\text{-}Me_2C_6H_3NC$. It is presumably the *ortho* methyl substituents which cause steric hindrance in **5** and hence favour the dissociation to **4**. The ^{31}P NMR spectrum of **5** is expected to appear as an $[AB]_2$ spin system due to the probable bent $\mu\text{-}CNC_6H_3Me_2\text{-}2,6$ ligand.[13-15] This spectrum was observed for the trifluoroacetate salt at − 80 °C but the hexafluorophosphate salt gave only a single resonance, although with very similar chemical shift.

When **1**, as the hexafluorophosphate salt in concentrated solution, was treated with excess $2,6\text{-}Me_2C_6H_3NC$ a yellow solution was obtained from which **7** could be crystallized. Under these conditions, no palladium metal was precipitated. Formation of complex **7** requires a dppm ligand to be deprotonated and oxidized; it is likely that these reactions take place in a stepwise manner and that **6** is an intermediate (Scheme 1). NMR analysis of the initial reaction mixture showed that **7** was the major constituent but **4** and other unidentified complexes were also present. Since no metallic palladium was formed, in this case a soluble palladium(0)

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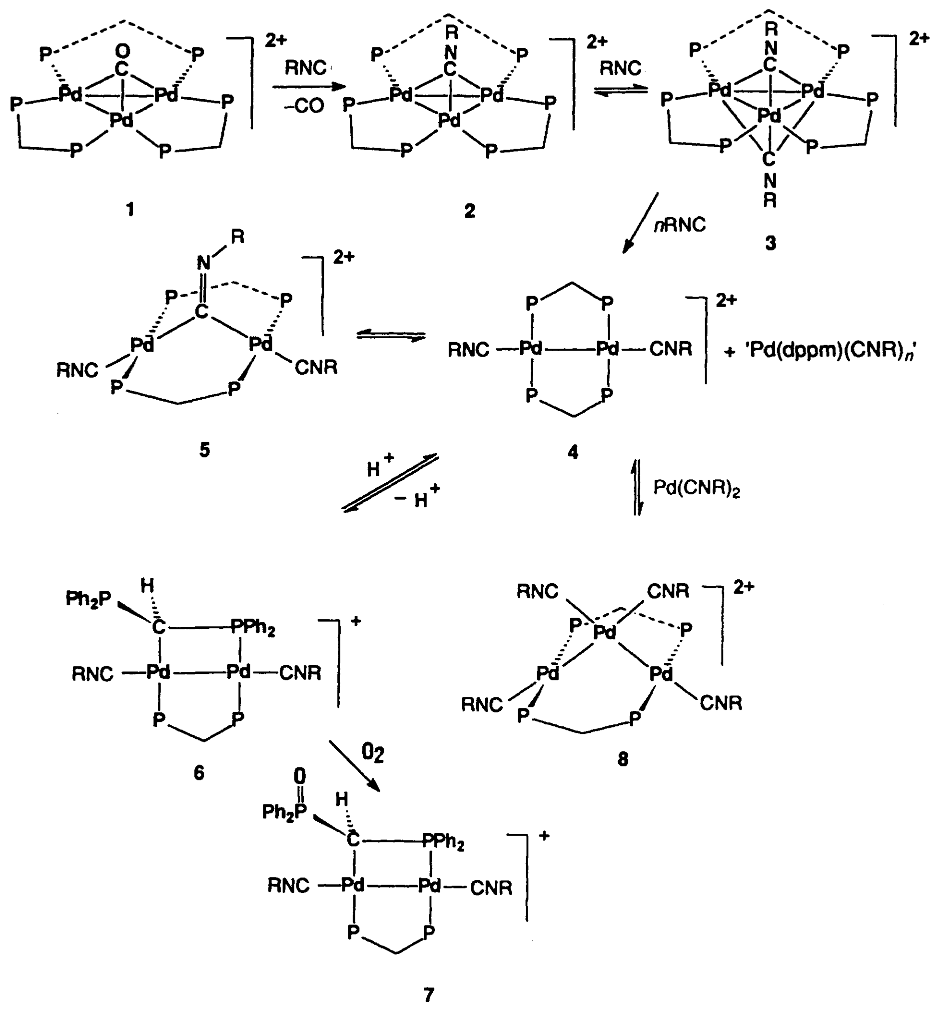
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 R = $2,6\text{-}Me_2C_6H_3$

species is presumably formed initially, but it could not be isolated or characterized. In Scheme 1, it is represented as $Pd(dppm)(CNC_6H_3Me_2\text{-}2,6)_n$, but a mixture of several palladium(0) complexes could be present. The observation that palladium metal is not precipitated when $[PF_6]^-$ is the counter ion but is when $[CF_3CO_2]^-$ is the counter ion is presumed to be related to the different products observed. Excess $2,6\text{-}Me_2C_6H_3NC$ does not appear to be sufficiently basic to drive the conversion of **4** to **6** to an appreciable extent but, if the soluble palladium(0) complexes can catalyse the air oxidation of **6** to **7**, the observed conversion to **7** can be effected. If this reaction mixture was slowly crystallized from a dilute solution, a mixture of yellow crystals of **7** and much deeper yellow crystals of **8**, each as the $[PF_6]^-$ salt, was obtained. The concentration of **8** in the original reaction mixture was low and it was barely detectable in the ^{31}P NMR spectrum of the reaction mixture. It seems that its formation must require reaction of **4** by formal addition of $Pd(CNC_6H_3Me_2\text{-}2,6)_2$ to the metal–metal bond to give the less soluble **8**. Dissolution of pure **8** was followed by its decomposition over a period of a few hours to regenerate **4** with precipitation of palladium metal.

Complexes **7** and **8** are types of palladium compounds which have not previously been structurally characterized, although the structures of related platinum complexes $[Pt_2(PPh_3)_2(\mu\text{-}Ph_2PCHPPh_2\text{-}P,C)(\mu\text{-dppm})]^+$ (ref. 16) and $[Pt_2(CNC_6H_3Me_2\text{-}2,6)_2\{\mu\text{-}Pt(CNC_6H_3Me_2\text{-}2,6)_2\}(\mu\text{-dppm})_2]^{2+}$ have been determined[10,17] and a heteronuclear analogue of **8**, $[Pd_2Cl_2\{\mu\text{-}Pt(PPh_3)_2\}(\mu\text{-dppm})_2]$ has also been prepared.[18] Hence the characterization is given in more detail. The ^{31}P NMR spectrum of **7** contained four multiplet resonances as expected. Two of these have a very large doublet splitting due to $^2J(PP)$ and are assigned to the mutually *trans* phosphorus atoms P^a and P^b. The dangling phosphine oxide, P^d, is assigned to the resonance at δ 27.4, since this is close to the chemical shift of free $CH_2(PPh_2O)_2$, and so the fourth resonance is assigned to P^c. In the ^1H NMR spectrum the resonance due to the CHP_2 proton occurred at δ 3.57 as a well defined multiplet with doublet splittings to P^b, P^c and P^d, while the CH_2P_2 resonances occurred at δ 4.65 and 4.66.

Complex **7** as its $[PF_6]^-$ salt was characterized by structure determination. The structure is shown in Fig. 1 and selected bond distances and angles are in Table 1.

The structure of **7** contains an approximately linear $Pd_2(CNC_6H_3Me_2\text{-}2,6)_2$ unit with the Pd–Pd bond bridged by one dppm ligand and by a $[Ph_2PCHPPh_2O]^-$ ligand. The dppm bridges in the usual way to give a five-membered Pd_2P_2C ring while the $[Ph_2PCHPPh_2O]^-$ ligand binds through the phosphine and carbon donors to give a four-membered ring. The angles within the four-membered ring are necessarily distorted from the natural values, with the angles P(1)–Pd(1)–Pd(2) and P(1)–C(4)–Pd(2) of 67.74(6) and 87.6(3) deviating most from the normal values of 90 and 109° respectively. Each palladium atom has distorted square-planar stereochemistry. The dihedral angles P(2)–Pd(1)–Pd(2)–P(3) and P(1)–Pd(1)–Pd(2)–C(4) of 35.5(1) and 25.1(2)° respectively give a measure of the twist of the co-ordination planes of the two palladium atoms with respect to one another. The Pd(1)–Pd(2) bond distance is in the usual range for dipalladium(I) complexes.

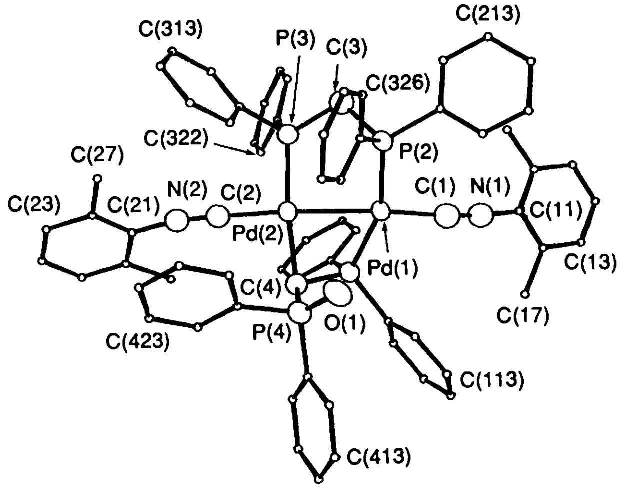


Fig. 1 A view of the structure of the cation **7**

Table 1 Selected bond distances (Å) and angles (°) for complex **7**

Pd(1)–Pd(2)	2.6127(9)	Pd(1)–P(1)	2.266(2)
Pd(1)–P(2)	2.336(2)	Pd(1)–C(1)	1.985(10)
Pd(2)–P(3)	2.294(2)	Pd(2)–C(2)	1.976(9)
Pd(2)–C(4)	2.153(8)	C(1)–N(1)	1.16(1)
N(1)–C(11)	1.36(1)	C(2)–N(2)	1.18(1)
N(2)–C(21)	1.363(9)	C(12)–C(17)	1.52(1)
C(16)–C(18)	1.50(1)	C(22)–C(27)	1.51(1)
C(26)–C(28)	1.60(1)	P(1)–C(4)	1.778(8)
P(2)–C(3)	1.843(9)	P(3)–C(3)	1.841(9)
P(4)–C(4)	1.786(8)	P(4)–O(1)	1.490(6)
P(1)–Pd(1)–Pd(2)	67.74(6)	P(2)–Pd(1)–Pd(2)	90.33(6)
P(2)–Pd(1)–P(1)	158.05(8)	C(1)–Pd(1)–Pd(2)	163.1(3)
C(1)–Pd(1)–P(1)	99.7(3)	C(1)–Pd(1)–P(2)	102.0(3)
P(1)–Pd(2)–Pd(1)	50.09(5)	P(3)–Pd(2)–Pd(1)	89.50(6)
P(3)–Pd(2)–P(1)	128.68(8)	C(2)–Pd(2)–Pd(1)	175.2(2)
C(2)–Pd(2)–P(1)	125.2(2)	C(2)–Pd(2)–P(3)	93.8(3)
C(4)–Pd(2)–Pd(1)	83.8(2)	C(4)–Pd(2)–P(1)	40.5(2)
C(4)–Pd(2)–P(3)	168.3(2)	C(4)–Pd(2)–C(2)	92.4(3)
C(4)–P(1)–Pd(1)	104.0(3)	N(1)–C(1)–Pd(1)	166.2(9)
N(2)–C(2)–Pd(2)	174.9(8)	P(3)–C(3)–P(2)	107.1(4)
P(1)–C(4)–Pd(2)	87.6(3)	P(4)–C(4)–Pd(2)	109.5(4)
P(4)–C(4)–P(1)	119.1(5)	C(11)–N(1)–C(1)	175.8(9)
C(21)–N(2)–C(2)	169.9(9)		

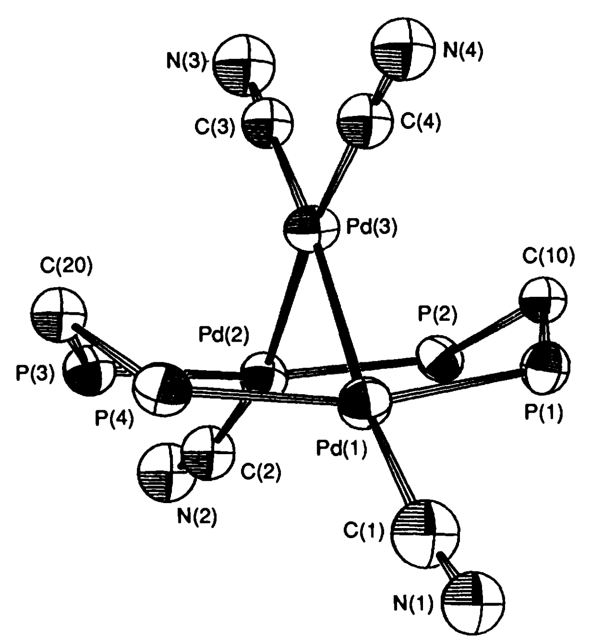


Fig. 2 A view of the structure of the cluster cation **8**; the 2,6-dimethylphenyl and phenyl rings are omitted for clarity

Table 2 Comparison of bond distances (Å) and angles (°) in $[M_2(CNC_6H_3Me_2\text{-}2,6)_2\{\mu\text{-}M(CNC_6H_3Me_2\text{-}2,6)_2\}(\mu\text{-dppm})_2][PF_6]_2$ (M = Pd or Pt^{II})

	M = Pd	Pt
M(1)–M(3)	2.548(1)	2.589(2)
M(2)–M(3)	2.563(1)	2.596(2)
M(1) ··· M(2)	3.379(1)	3.303(2)
M(1)–P(1)	2.315(4)	2.29(1)
M(1)–P(4)	2.308(4)	2.30(1)
M(2)–P(2)	2.300(4)	2.29(1)
M(2)–P(3)	2.305(4)	2.30(1)
M(1)–C(1)	2.02(2)	2.02(3)
M(2)–C(2)	2.04(2)	1.97(4)
M(3)–C(3)	1.98(1)	1.97(3)
M(3)–C(4)	2.00(1)	2.02(3)
M(1)–M(3)–M(2)	82.76(5)	79.14(6)
C(3)–M(3)–C(4)	99.5(6)	96(1)
C(1)–M(1)–M(3)	168.3(5)	169.2(8)
C(2)–M(2)–M(3)	164.8(4)	163(1)
P(1)–M(1)–P(4)	164.7(2)	168.4(4)
M(1)–M(3)–C(3)	172.1(4)	171.6(9)
M(2)–M(3)–C(4)	171.0(4)	171.3(9)
M(1)–C(1)–N(1)	171(2)	166(3)
M(2)–C(2)–N(2)	164(1)	168(3)
M(3)–C(3)–N(3)	179.7(7)	179(3)
M(3)–C(4)–N(4)	175(1)	178(3)
C(1)–N(1)–C(11)	179(1)	175(3)
C(2)–N(2)–C(21)	177(2)	171(4)
C(3)–N(3)–C(31)	174(2)	179(4)
C(4)–N(4)–C(41)	174(2)	170(4)

The ^{31}P NMR spectrum of **8** contained a sharp singlet due to the equivalent dppm protons while the CH_2P_2 resonance appeared as an AB multiplet. These are typical of symmetrical A-frame complexes.[19] There were two equal intensity resonances due to the methyl protons of the two types of xylyl isocyanide ligands. Complex **8** as its $[PF_6]^-$ salt was also characterized by a structure determination. The structure of the cation is shown in Fig. 2.

The complexes $[M_2(CNC_6H_3Me_2\text{-}2,6)_2\{\mu\text{-}M(CNC_6H_3Me_2\text{-}2,6)_2\}(\mu\text{-dppm})_2][PF_6]_2$ (M = Pd and Pt) are isomorphous and isostructural.[17] The geometry about each metal centre approximates to square planar, with M(1) and M(3) having MCP_2M co-ordination and M(3) having MC_2M_2 co-ordination. A comparison of selected bond parameters is given in Table 2. It can be seen that the metal–metal distances M(1)–M(3) and M(2)–M(3) are slightly shorter for M = Pd but, since the angle M(1)–M(3)–M(2) is somewhat larger for M = Pd, the non-bonded distance M(1) ··· M(2) is shorter for M = Pt. The M–P bonds are slightly longer for M = Pd than for M = Pt, consistent with there being weaker M–P d_π–d_π backbonding for M = Pd. Differences in M–C and C≡N distances are not significant. The angles M(1)–C(1)–N(1) and M(2)–C(2)–N(2) are somewhat distorted from 180° (mean 167° for both complexes) to minimize steric repulsion between the xylyl substituents, while the angles M(3)–C(3)–N(3) and M(3)–C(4)–N(4) are close to linear (Table 2). For **8** the angles C–N≡C fall in the range 174(2)–179(1)°, not significantly distorted from linearity.

Conclusion

This work has shown how surprisingly subtle chemistry can result from the cleavage of cluster cation **1** with excess xylyl isocyanide. Initially the cleavage gives a dipalladium(I) cation **4**, which is shown to react further in one or more of three ways. At low temperature, **4** adds a third $2,6\text{-}Me_2C_6H_3NC$ ligand to give

5. At room temperature **4** may undergo deprotonation and rearrangement with oxidation of a dppm ligand to give **7** or it may add the palladium(0) species formed by the initial cleavage reaction to regenerate a trinuclear cluster, namely the A-frame cluster cation **8**.

Experimental

The complexes $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$ and $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ were prepared by the literature method.[12] NMR spectra were recorded by using Varian XL200 (^1H, reference $SiMe_4$) or XL300 spectrometers (^{31}P, reference H_3PO_4).

Preparations.—$[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][CF_3CO_2]_2$. To a solution of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][CF_3CO_2]_2$ (50 mg) in acetone (5 cm^3) was added $2,6\text{-}Me_2C_6H_3NC$ (25 mg). The colour changed slowly from deep purple to yellow and a black precipitate settled. After 4 d, the solution was filtered and pentane (15 cm^3) was added to the filtrate to precipitate the product as a yellow solid, which was recrystallized from acetone–pentane. Yield 40 mg, m.p. 92–95 °C (Found: C, 55.9; H, 4.0; N, 1.6. Calc. for $C_{72}H_{62}F_6N_2O_4P_4Pd_2\cdot 4H_2O$: C, 56.0; H, 4.5; N, 1.8%). NMR $[(CD_3)_2CO]$: ^1H, δ 1.76 (s, 12 H, Me), 5.43 [qnt, 4 H, $J(PH)_{obs}$ 5 Hz, CH_2P_2], and 3.35 (s, 8 H, H_2O); ^{31}P, δ −3.0 (s, dppm). IR(Nujol): ν(N≡C) 2160s, ν(C=O) 1683s cm^{-1}.

$[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][PF_6]_2$. To a solution of $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][CF_3CO_2]_2$ (80 mg) in MeOH (1 cm^3) was added a saturated solution of NH_4PF_6 (1 cm^3). The yellow precipitate which settled was separated and recrystallized from CH_2Cl_2–pentane. Yield 75 mg, m.p. 138–142 °C (Found: C, 52.9; H, 4.1; N, 2.1. Calc. for $C_{68}H_{62}F_{12}N_2P_6Pd_2$: C, 53.2; H, 4.0; N, 1.8%). NMR $[(CD_3)_2CO]$: ^1H, δ 1.71 (s, 12 H, Me) and 5.30 [qnt, 4 H, $J(PH)_{obs}$ 5 Hz, CH_2P_2]; ^{31}P, δ −3.5 (s, dppm). IR(Nujol): ν(N≡C) 2161s cm^{-1}.

Reaction of $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][CF_3CO_2]_2$ *with* $2,6\text{-}Me_2C_6H_3NC$. To a solution of $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][CF_3CO_2]_2$ (10 mg) in $(CD_3)_2CO$ (0.4 cm^3) was added excess $2,6\text{-}Me_2C_6H_3NC$ (10 mg). NMR $[(CD_3)_2CO]$: 20 °C, ^1H, δ 2.27 (s, Me); ^{31}P, δ −4.5 (br s, dppm): −80 °C, ^1H, δ 1.50 (s, Me of co-ordinated $2,6\text{-}Me_2C_6H_3NC$), 2.31 (s, Me of free $2,6\text{-}Me_2C_6H_3NC$) and *ca.* 5.5 (br, 4 H, CH_2P_2); ^{31}P, δ 35.5 [d, $J(PP)$ 11.6, P^a of dppm] and 35.3 [d, $J(PP)$ 11.6 Hz, P^b of dppm]. Attempts to isolate this product by crystallization at −78 °C gave only $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][CF_3CO_2]_2$.

A similar reaction of $[Pd(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][PF_6]_2$ with $2,6\text{-}Me_2C_6H_3NC$ was carried out. NMR $[(CD_3)_2CO]$: 20 °C, ^1H, δ 2.24 (s, Me); ^{31}P, δ −4.5 (br s, dppm): −80 °C, ^1H, δ 1.51 (s, Me or co-ordinated $2,6\text{-}Me_2C_6H_3NC$), 2.21 (s, Me of free $2,6\text{-}Me_2C_6H_3NC$) and 5.4 (br, 4 H, CH_2P_2); ^{31}P, δ 35.5 (s, dppm). Again, attempts to isolate this product by crystallization at −78 °C gave only $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][PF_6]_2$.

$[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}Ph_2PCHPPh_2O\text{-}P,C)(\mu\text{-dppm})][PF_6]$. To a solution of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3][PF_6]_2$ (50 mg) in acetone (5 cm^3) was added $2,6\text{-}Me_2C_6H_3NC$ (17 mg). After 4 d pentane (15 cm^3) was added to the solution to precipitate a yellow solid. This was recrystallized from a concentrated solution in acetone by slow diffusion of *n*-pentane. Yield 30 mg, m.p. 157–160 °C (Found: C, 58.1; H, 4.4; N, 2.0. Calc. for $C_{68}H_{61}F_6N_2P_5Pd_2$: C, 58.8; H, 4.4; N, 2.0%). NMR $[(CD_3)_2CO]$: ^1H, δ 1.74 (s, 6 H, Me), 1.75 (s, 6 H, Me), 3.57 [ddd, 1 H, $^2J(PH)$ 9.8, 5.2 Hz, $^3J(P^cH)$ 1.1, CH^a], 4.65 [dd, 1 H, $^2J(PH)$ 11.2, 8.2 Hz, CH^b] and 4.66 [t, 1 H, $^2J(P^aH) = {}^2J(P^cH) = 9.9$ Hz, CH^c]; ^{31}P, δ 8.9 [dd, $^2J(P^aP^b)$ 376, $^2J(P^aP^c)$ 76, P^a], −4.9 [ddd, $^2J(P^bP^d)$ 14, $^2J(P^aP^b)$ 376, $^3J(P^bP^c)$ 26, P^b], 14.6 [ddd, $^3J(P^cP^d)$ 16, $^2J(P^cP^a)$ 76, $^3J(P^bP^c)$ 26, P^c] and 27.4 [t, $^3J(P^cP^d) = {}^2J(P^bP^d)$ 15 Hz, P^d]. IR(Nujol): ν(N≡C) 2139s cm^{-1}.

$[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2\{\mu\text{-}Pd(CNC_6H_3Me_2\text{-}2,6)_2\}(\mu\text{-dppm})_2][PF_6]_2$. This product was obtained from a similar reaction as above, with crystallization from a more dilute solution. The dark yellow crystals of the product were separated from paler yellow crystals of $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-}Ph_2PCHPPh_2O\text{-}P,C)(\mu\text{-dppm})][PF_6]$ by hand picking. Yield 5 mg. IR(Nujol): ν(N≡C) 2139s cm^{-1}. NMR $[(CD_3)_2CO]$: ^1H, δ 1.8, 2.0 (s, Me), 4.2 and 4.4 (m, CH_2); ^{31}P, δ 5.4 (s, dppm). After 2 h at room temperature the complex had decomposed to $[Pd_2(CNC_6H_3Me_2\text{-}2,6)_2(\mu\text{-dppm})_2][PF_6]_2$ and a black precipitate (Pd).

X-Ray Crystallography.—Compound **7** as its $[PF_6]^-\cdot Me_2CO$ salt and **8** as its $2[PF_6]^-\cdot 0.5Me_2CO$ salt were examined by similar experimental procedures. Single crystals were grown by solvent diffusion using acetone–*n*-pentane. Crystal densities were measured by the neutral buoyancy method in mixtures of carbon tetrachloride and *n*-pentane. The data collection was carried out by using an Enraf-Nonius CAD4F diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) at 18 °C.[20] Photo and automatic indexing routines, followed by least-squares fits of 21 accurately centred reflections (20.0 ⩽ 2θ ⩽ 25.8° for **7** and 24.0 ⩽ 2θ ⩽ 30.6° for **8**), gave cell constants and an orientation matrix. Intensity data were recorded in the ω mode, at variable scan speeds, with a maximum time per datum of 45 and 60 s respectively for **7** and **8**.

Background measurements were made by extending the scan by 25% on each side. Three standard reflections were monitored at regular intervals of time during data collection to check the crystal stability. The NRCVAX crystal structure programs[21] running on a SUN 3/80 workstation were used to process the data. The structures were solved by using the SHELXS 86 program[22] and subsequent Fourier difference routines. Refinements were by full-matrix least-squares techniques on *F* using the SHELX 76 software program.[23] Scattering factors for neutral non-hydrogen atoms were taken from ref. 24(*a*). The phenyl rings were treated as regular hexagons (with C–C 1.395 Å). All the other hydrogen atoms were placed in ideal positions (C–H 0.95 Å) and they were included for the purpose of structure-factor calculations only. A common thermal parameter was assigned for all the hydrogen atoms.

Complex **7**. A crystal (0.36 × 0.20 × 0.14 mm) was obtained by cleaving a large light yellow crystal. It was wedged inside a Lindemann capillary tube which was flame sealed. In total

Table 3 Crystal and experimental details

Compound	**7**	**8**
Formula	$C_{68}H_{61}F_6N_2OP_5Pd_2\cdot C_3H_6O$	$C_{86}H_{80}F_{12}N_4P_6Pd_3\cdot 0.5C_3H_6O$
M	1462.02	1931.73
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
Cell dimensions		
a/Å	14.523(2)	21.810(3)
b/Å	22.448(4)	21.879(4)
c/Å	12.203(3)	18.274(5)
α/°	95.52(2)	
β/°	110.98(2)	
γ/°	108.21(1)	
$U/Å^3$, *Z*	3430(1), 2	8720(3), 4
D_c,D_m/g cm^{-3}	1.415, 1.38(5)	1.471, 1.45(5)
μ/cm^{-1}	6.3	7.1
No. of observations [$I \geqslant 2.5\sigma(I)$], variables	5931, 323	5138, 410
Final model; *R*,*R′*	0.0563, 0.0574	0.0566, 0.0632

$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R' = [\Sigma w^{\frac{1}{2}}(||F_o| - |F_c||)/\Sigma w^{\frac{1}{2}}|F_o|]$.

Table 4 Atomic coordinates for complex **7**

Atom	*x*	*y*	*z*
Pd(1)	0.102 41(5)	0.285 51(3)	0.205 70(6)
Pd(2)	0.057 72(5)	0.240 91(3)	−0.020 56(2)
P(1)	0.250 52(17)	0.300 12(11)	0.171 51(21)
P(2)	−0.078 70(18)	0.251 77(11)	0.162 68(21)
P(3)	−0.086 59(18)	0.271 01(12)	−0.076 98(21)
P(4)	0.196 05(18)	0.155 44(11)	0.084 14(22)
C(1)	0.167 9(7)	0.340 9(5)	0.371 5(9)
C(2)	0.036 6(7)	0.211 0(4)	−0.188 6(8)
C(3)	−0.140 0(7)	0.284 6(4)	0.035 1(8)
C(4)	0.211 0(6)	0.233 0(4)	0.052 0(7)
O(1)	0.139 1(5)	0.138 2(3)	0.163 6(6)
N(1)	0.207 0(6)	0.383 3(4)	0.456 3(7)
N(2)	0.030 8(6)	0.197 2(3)	−0.287 2(7)
C(11)	0.246 3(5)	0.434 0(3)	0.552 6(7)
C(12)	0.348 7(5)	0.452 3(3)	0.642 3(7)
C(13)	0.386 7(5)	0.504 1(3)	0.740 4(7)
C(14)	0.322 2(5)	0.537 6(3)	0.748 6(7)
C(15)	0.219 8(5)	0.519 3(3)	0.658 9(7)
C(16)	0.181 9(5)	0.467 6(3)	0.560 8(7)
C(17)	0.419 2(9)	0.416 7(6)	0.629 1(12)
C(18)	0.073 1(10)	0.449 5(7)	0.462 2(14)
C(21)	0.043 0(4)	0.184 3(3)	−0.391 4(6)
C(22)	−0.039 8(4)	0.137 7(3)	−0.491 4(6)
C(23)	−0.025 0(4)	0.122 3(3)	−0.595 7(6)
C(24)	0.072 7(4)	0.153 5(3)	−0.600 1(6)
C(25)	0.155 5(4)	0.200 0(3)	−0.500 2(6)
C(26)	0.140 7(4)	0.215 5(3)	−0.395 8(6)
C(27)	−0.147 3(9)	0.105 6(6)	−0.490 0(10)
C(28)	0.231 1(8)	0.271 2(6)	−0.281 0(11)
C(111)	0.368 9(4)	0.308 8(3)	0.302 9(6)
C(112)	0.359 3(4)	0.265 8(3)	0.377 1(6)
C(113)	0.447 4(4)	0.272 0(3)	0.480 3(6)
C(114)	0.545 2(4)	0.321 2(3)	0.509 3(6)
C(115)	0.554 9(4)	0.364 2(3)	0.435 1(6)
C(116)	0.466 7(4)	0.358 0(3)	0.331 8(6)
C(121)	0.290 4(5)	0.371 0(3)	0.113 5(5)
C(122)	0.335 2(5)	0.371 8(3)	0.029 6(5)
C(123)	0.361 5(5)	0.426 5(3)	−0.015 6(5)
C(124)	0.343 0(5)	0.480 4(3)	0.023 2(5)
C(125)	0.298 2(5)	0.479 7(3)	0.107 2(5)
C(126)	0.271 9(5)	0.425 0(3)	0.152 3(5)
C(211)	−0.120 7(5)	0.277 8(3)	0.277 8(5)
C(212)	−0.202 7(5)	0.301 1(3)	0.252 7(5)
C(213)	−0.232 7(5)	0.318 1(3)	0.344 0(5)
C(214)	−0.180 8(5)	0.311 6(3)	0.460 3(5)
C(215)	−0.098 9(5)	0.288 2(3)	0.485 4(5)
C(216)	−0.068 8(5)	0.271 3(3)	0.394 1(5)
C(221)	−0.158 4(6)	0.165 8(3)	0.112 6(6)
C(222)	−0.111 3(4)	0.122 1(3)	0.096 4(6)
C(223)	−0.171 7(4)	0.056 0(3)	0.058 5(6)
C(224)	−0.279 1(4)	0.033 7(3)	0.036 9(6)
C(225)	−0.326 2(4)	0.077 3(6)	0.053 1(6)
C(226)	−0.256 9(4)	0.143 4(3)	0.091 0(6)
C(311)	−0.200 0(6)	0.212 5(3)	−0.206 1(7)
C(312)	−0.263 4(6)	0.230 0(3)	−0.303 3(7)
C(313)	−0.346 7(6)	0.182 6(3)	−0.401 5(7)
C(314)	−0.366 5(6)	0.117 5(3)	−0.402 6(7)
C(315)	−0.303 1(6)	0.099 9(3)	−0.305 4(7)
C(316)	−0.219 8(6)	0.147 4(3)	−0.207 2(7)
C(321)	−0.057 0(5)	0.346 8(3)	−0.123 9(7)
C(322)	0.032 9(5)	0.368 8(3)	−0.148 6(7)
C(323)	0.059 8(5)	0.427 6(3)	−0.181 5(7)
C(324)	−0.003 1(5)	0.464 3(3)	−0.189 7(7)
C(325)	−0.093 0(5)	0.442 3(3)	−0.165 0(7)
C(326)	−0.119 9(5)	0.383 5(3)	−0.132 1(7)
C(411)	0.324 6(5)	0.148 5(3)	0.146 2(6)
C(412)	0.335 7(5)	0.103 9(3)	0.217 3(6)
C(413)	0.432 1(5)	0.095 2(3)	0.264 6(6)
C(414)	0.517 4(5)	0.131 0(3)	0.240 7(6)
C(415)	0.506 3(5)	0.175 6(3)	0.169 7(6)
C(416)	0.409 9(5)	0.184 3(3)	0.122 4(6)
C(421)	0.127 6(4)	0.101 7(3)	−0.064 4(6)
C(422)	0.173 0(4)	0.104 1(3)	−0.147 8(6)
C(423)	0.114 1(4)	0.064 6(3)	−0.264 1(6)
C(424)	0.009 6(4)	0.022 7(3)	−0.296 9(6)
C(425)	−0.035 8(4)	0.020 4(3)	−0.213 4(6)
C(426)	0.023 1(4)	0.059 9(3)	−0.097 2(6)
P(5)	0.554 6(3)	0.303 6(2)	0.914 6(3)
F(1)	0.507 6(5)	0.356 9(3)	0.892 3(8)
F(2)	0.668 3(4)	0.355 2(3)	0.961 9(10)
F(3)	0.601 2(5)	0.250 5(3)	0.945 1(8)
F(4)	0.441 6(4)	0.252 6(3)	0.882 0(9)
F(5)	0.564 5(8)	0.317 2(5)	1.050 1(6)
F(6)	0.543 1(10)	0.289 0(5)	0.786 8(6)
C(1s)[a]	0.374 4(20)	0.070 4(13)	0.637 3(26)
O(s)[a]	0.406 1(20)	0.048 6(13)	0.724 0(26)
C(2s)[a]	0.377 1(20)	0.139 9(13)	0.656 4(26)
C(3s)[a]	0.354 3(20)	0.034 5(13)	0.512 7(26)
C(1a)[b]	0.386 8(13)	0.061 7(8)	0.649 1(15)
O(sa)[b]	0.401 8(13)	0.017 1(8)	0.605 1(15)
C(2a)[b]	0.341 4(13)	0.103 0(8)	0.566 2(15)
C(3a)[b]	0.450 6(13)	0.092 0(8)	0.786 4(15)

[a] Occupancy = 0.40. [b] Occupancy = 0.60.

10 405 reflections were collected in the 2θ range 2–46° ($-16 \leqslant h \leqslant 16$, $-24 \leqslant k \leqslant 24$, $-1 \leqslant l \leqslant 13$). An empirical absorption correction was applied to the data based upon the ψ scans of seven reflections with θ ranging from 5.2 to 10.3 ($\mu = 6.3\ \text{cm}^{-1}$). The minimum and maximum transmission factors were 0.799 and 0.838. The cell data indicated a triclinic system and the space group $P\bar{1}$ was assumed. The equivalent reflections were averaged ($R_{\text{int}} = 0.015$) to give 9407 unique reflections. The disorder present in the acetone solvate molecule was resolved into two models with multiplicities of 0.4 and 0.6. The C–O and C–C bond lengths were fixed at 1.2 and 1.54 Å respectively. Anisotropic thermal parameters were assigned and refined for the atoms Pd, P, O methyl C atoms and F. The full-matrix least-squares refinement converged using the weighting scheme $w = k/\sigma^2F + gF^2$ where $g = 0.000\,376$ and $k = 2.2343$. In the final Fourier difference synthesis the electron density ranged from 0.84 to −0.57 e Å^{-3}; of these the top peak was associated with the F(6) atom at distance of 0.90 Å. The maximum shift/e.s.d. in the final cycle was 0.0065. The secondary extinction coefficient was refined to 35(69) × 10^{-6}.

Complex **8**. An orange-yellow crystal (0.18 × 0.30 × 0.38 mm) was glued to a fibre and mounted on a goniometer head. The total intensity data recorded was 7521 in the 2θ range 0–46° ($-1 \leqslant h \leqslant 24$, $-1 \leqslant k \leqslant 24$, $-1 \leqslant l \leqslant 20$). An empirical absorption was applied using a 360° ψ scan for nine reflections in the θ range 4.45–11.70°. The maximum and minimum transmission factors were 0.855 and 0.802 ($\mu = 7.1\ \text{cm}^{-1}$). The space group $P2_12_12_1$ (no. 19) was uniquely determined from the systematic absences.[24b] The equivalent reflections were averaged ($R_{\text{int}} = 0.016$) leaving 7273 independent reflections. Anisotropic thermal parameters were assigned for Pd, P and methyl carbon atoms and were refined. The disorder in one of the $[PF_6]^-$ was resolved into two models with 0.5:0.5 occupancy factors. The geometry of all the $[PF_6]^-$ ions was treated as an ideal octahedron with P–F distances of 1.6 Å. The disorder in the half solvent molecule acetone was resolved. In the final cycles, the full-matrix least-squares refinement converged using the weighting scheme $w = k/\sigma^2F + gF^2$ where $g = 0.004\,427$ and $k = 0.8714$. In the final Fourier difference synthesis the electron density ranged from 1.20 to −0.88 e Å^{-3}. The top two peaks had electron density greater than 1.0 e Å^{-3} and were associated with the solvent acetone molecule.

Table 5 Atomic positional parameters for complex **8**

Atom	*x*	*y*	*z*
Pd(1)	0.197 61(5)	0.258 18(5)	0.220 82(6)
Pd(2)	0.349 77(5)	0.237 28(5)	0.248 31(7)
Pd(3)	0.260 61(5)	0.160 88(5)	0.238 87(7)
P(1)	0.218 31(17)	0.236 71(19)	0.098 93(21)
P(2)	0.355 25(18)	0.223 96(17)	0.123 32(22)
P(3)	0.323 59(17)	0.237 22(19)	0.370 81(22)
P(4)	0.187 93(17)	0.253 86(18)	0.346 81(22)
C(10)	0.289 2(6)	0.193 9(6)	0.073 7(8)
C(20)	0.249 0(7)	0.212 8(7)	0.401 1(8)
C(1)	0.133 6(8)	0.323 4(8)	0.202 0(10)
C(2)	0.431 9(8)	0.278 8(7)	0.268 7(10)
C(3)	0.319 4(7)	0.093 0(7)	0.254 8(9)
C(4)	0.183 4(7)	0.112 6(6)	0.226 2(8)
N(1)	0.093 2(6)	0.354 8(6)	0.186 8(7)
N(2)	0.482 7(7)	0.290 1(7)	0.288 6(9)
N(3)	0.352 7(7)	0.054 2(6)	0.263 7(8)
N(4)	0.142 2(6)	0.082 8(6)	0.215 3(8)
C(11)	0.046 5(5)	0.392 3(4)	0.169 9(6)
C(12)	−0.012 8(5)	0.369 5(4)	0.159 7(6)
C(13)	−0.060 8(5)	0.409 5(4)	0.142 8(6)
C(14)	−0.049 5(5)	0.472 2(4)	0.136 0(6)
C(15)	0.009 8(5)	0.494 9(4)	0.146 2(6)
C(16)	0.057 8(5)	0.455 0(4)	0.163 1(6)
C(17)	−0.023 3(8)	0.304 5(11)	0.166 9(12)
C(18)	0.120 5(11)	0.480 1(9)	0.177 6(14)
C(21)	0.539 7(6)	0.301 7(5)	0.314 6(6)
C(22)	0.586 5(6)	0.258 7(5)	0.305 2(6)
C(23)	0.644 2(6)	0.268 9(5)	0.336 1(6)
C(24)	0.655 2(6)	0.322 1(5)	0.376 4(6)
C(25)	0.608 5(6)	0.365 2(5)	0.385 8(6)
C(26)	0.550 7(6)	0.355 0(5)	0.354 9(6)
C(27)	0.573 5(11)	0.206 9(11)	0.259 3(19)
C(28)	0.503 7(13)	0.398 5(12)	0.369 2(15)
C(31)	0.390 8(5)	0.005 9(4)	0.281 7(6)
C(32)	0.453 8(5)	0.016 5(4)	0.288 4(6)
C(33)	0.493 0(5)	−0.031 0(4)	0.309 2(6)
C(34)	0.469 2(5)	−0.089 2(4)	0.323 4(6)
C(35)	0.406 2(5)	−0.099 8(4)	0.316 7(6)
C(36)	0.367 0(5)	−0.052 3(4)	0.295 9(6)
C(37)	0.478 0(9)	0.080 0(9)	0.271 4(14)
C(38)	0.298 1(10)	−0.063 8(10)	0.291 2(16)
C(41)	0.092 0(4)	0.050 0(5)	0.195 0(6)
C(42)	0.100 0(4)	−0.011 3(5)	0.175 4(6)
C(43)	0.049 3(4)	−0.046 7(5)	0.155 5(6)
C(44)	−0.009 4(4)	−0.020 9(5)	0.155 1(6)
C(45)	−0.017 4(4)	0.040 4(5)	0.174 7(6)
C(46)	0.033 3(4)	0.075 9(5)	0.194 7(6)
C(47)	0.160 9(9)	−0.043 5(10)	0.185 4(14)
C(48)	0.026 7(9)	0.142 8(9)	0.213 6(12)
C(111)	0.219 7(4)	0.303 5(4)	0.039 5(4)
C(112)	0.229 5(4)	0.361 7(4)	0.069 1(4)
C(113)	0.228 4(4)	0.413 2(4)	0.023 7(4)
C(114)	0.217 4(4)	0.406 5(4)	−0.051 3(4)
C(115)	0.207 6(4)	0.348 3(4)	−0.080 9(4)
C(116)	0.208 8(4)	0.296 8(4)	−0.035 5(4)
C(121)	0.157 2(4)	0.190 8(4)	0.060 2(5)
C(122)	0.163 5(4)	0.129 0(4)	0.042 1(5)
C(123)	0.113 2(4)	0.096 2(4)	0.015 5(5)
C(124)	0.056 5(4)	0.125 3(4)	0.007 0(5)
C(125)	0.050 1(4)	0.187 1(4)	0.025 1(5)
C(126)	0.100 5(4)	0.219 8(4)	0.051 8(5)
C(211)	0.417 0(4)	0.173 4(5)	0.095 3(6)
C(212)	0.407 5(4)	0.112 2(5)	0.076 1(6)
C(213)	0.457 3(4)	0.075 5(5)	0.056 0(6)
C(214)	0.516 5(4)	0.100 0(5)	0.055 3(6)
C(215)	0.526 0(4)	0.161 2(5)	0.074 5(6)
C(216)	0.476 3(4)	0.197 9(5)	0.094 5(6)
C(221)	0.371 0(4)	0.294 5(4)	0.073 3(4)
C(222)	0.375 5(4)	0.350 6(4)	0.109 7(4)
C(223)	0.386 7(4)	0.404 1(4)	0.070 1(4)
C(224)	0.393 4(4)	0.401 6(4)	−0.005 9(4)
C(225)	0.388 9(4)	0.345 6(4)	−0.042 4(4)
C(226)	0.377 7(4)	0.292 0(4)	−0.002 7(4)
C(311)	0.377 3(4)	0.187 5(4)	0.419 9(5)
C(312)	0.435 8(4)	0.210 4(4)	0.435 4(5)
C(313)	0.480 9(4)	0.171 7(4)	0.463 9(5)
C(314)	0.467 6(4)	0.110 1(4)	0.477 0(5)
C(315)	0.409 1(4)	0.087 2(4)	0.461 5(5)
C(316)	0.364 0(4)	0.125 9(4)	0.432 9(5)
C(321)	0.332 3(4)	0.312 2(5)	0.412 9(5)
C(322)	0.339 8(4)	0.364 5(5)	0.369 9(5)
C(323)	0.354 7(4)	0.421 8(5)	0.403 1(5)
C(324)	0.344 0(4)	0.426 8(5)	0.479 4(5)
C(325)	0.336 5(4)	0.374 5(5)	0.522 4(5)
C(326)	0.330 6(4)	0.317 2(5)	0.489 2(5)
C(411)	0.179 9(4)	0.326 4(4)	0.394 5(5)
C(412)	0.162 9(4)	0.325 3(4)	0.468 3(5)
C(413)	0.156 1(4)	0.380 1(4)	0.506 9(5)
C(414)	0.166 3(4)	0.436 0(4)	0.471 7(5)
C(415)	0.183 3(4)	0.437 1(4)	0.397 9(5)
C(416)	0.190 1(4)	0.382 3(4)	0.359 3(5)
C(421)	0.116 1(4)	0.219 3(4)	0.372 6(5)
C(422)	0.062 5(4)	0.253 3(4)	0.362 0(5)
C(423)	0.006 0(4)	0.230 0(4)	0.385 2(5)
C(424)	0.003 1(4)	0.172 7(4)	0.418 9(5)
C(425)	0.056 7(4)	0.138 7(4)	0.429 5(5)
C(426)	0.113 2(4)	0.162 0(4)	0.406 3(5)
P(5)	0.284 5(2)	0.989 2(2)	0.982 8(3)
F(1)	0.213 8(4)	1.001 8(9)	0.963 1(10)
F(2)	0.277 0(8)	1.025 6(7)	1.058 1(6)
F(3)	0.355 0(4)	0.976 1(9)	1.001 0(10)
F(4)	0.291 6(8)	0.952 8(7)	0.906 8(6)
F(5)	0.265 5(8)	0.926 8(5)	1.022 9(8)
F(6)	0.303 2(9)	1.051 5(5)	0.942 4(8)
F(1a)	0.292 7(10)	1.060 2(4)	0.965 6(10)
F(2a)	0.284 8(10)	1.003 9(9)	1.069 1(5)
F(3a)	0.276 7(10)	0.917 6(4)	1.000 7(10)
F(4a)	0.284 3(9)	0.973 9(9)	0.897 2(5)
F(5a)	0.211 4(3)	0.996 5(10)	0.981 9(11)
F(6a)	0.357 5(3)	0.981 0(10)	0.984 8(11)
P(6)	0.304 4(3)	0.538 0(3)	0.216 1(3)
F(11)	0.259 8(5)	0.531 2(6)	0.147 2(6)
F(12)	0.362 9(5)	0.541 6(6)	0.162 8(7)
F(13)	0.348 9(6)	0.546 7(6)	0.285 5(6)
F(14)	0.246 5(5)	0.536 2(6)	0.270 4(6)
F(15)	0.311 6(6)	0.465 9(3)	0.221 6(7)
F(16)	0.297 8(6)	0.611 4(3)	0.210 9(7)
O(1)	0.348 7(20)	0.228 0(22)	0.682 4(27)
C(1)	0.327 1(20)	0.257 5(22)	0.731 8(27)
C(2)	0.286 7(20)	0.225 5(22)	0.789 9(27)
C(3)	0.347 7(20)	0.324 4(22)	0.743 5(27)
O(1a)	0.256 4(22)	0.256 9(18)	0.726 2(24)
C(1a)	0.310 6(22)	0.250 7(18)	0.736 6(24)
C(2a)	0.356 7(22)	0.264 0(18)	0.674 4(24)
C(3a)	0.333 8(22)	0.227 2(18)	0.811 5(24)

The largest shift/e.s.d. = −0.59. A secondary extinction coefficient was refined to $4(28) \times 10^{-6}$. For the inverted model with the same ratio of observations to variables, the refinement converged at $R = 0.0582$ and $R' = 0.0652$.

Crystallographic data are summarized in Table 3, while atomic positional parameters for **7** and **8** are given in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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