X-Ray Crystal Structure of a Unique Cyano-bridged Cyclic Palladium(II) Trimer †

Julian A. Davies
Department of Chemistry, University of Toledo, Toledo, Ohio 43606, U.S.A.
Frank R. Hartley * and Stephen G. Murray *
Department of Chemistry and Metallurgy, Royal Military College of Science, Shrivenham, Swindon, Wilts. SN6 8LA
Melanie A. Pierce-Butler
Propellant, Explosives and Rocket Motors Establishment, Waltham Abbey, Essex EN9 1BP

The crystal structure of $[Pd_3(dppe)_3(\mu\text{-}CN)_3][ClO_4]_3$ (dppe = $Ph_2PCH_2CH_2PPh_2$) is reported. The complex crystallizes in the trigonal space group $R\bar{3}$ with unit-cell parameters a = 22.737(3) Å, α = 40.288(4)°, and Z = 6. The final R index was 0.052 using 1 495 independent reflections in the least-squares refinement. The structure is based on a $Pd_3(\mu\text{-}CN)_3$ cyclic trimer unit and ^{31}P n.m.r. indicates an unsymmetrical arrangement of the cyano-bridges. The angles Pd–C–N = 165(2) and Pd–N–C = 164(1)° make the cyano-bridge significantly non-linear at both ends. There are seven perchlorate sites within the unit cell, two of which are only partially occupied.

During our investigations into the preparation and properties of palladium(II) complexes containing weakly bonded ligands (solvento-complexes) we have prepared species of the type $[Pd(dppe)Cl(S)][ClO_4]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) only where S is a reasonably good donor such as pyridine or dimethyl sulphoxide.[1,2] If weak donors are used such as acetone or methanol then the initial complex formed (as shown above) instantly dimerises [2] to form $[Pd_2(dppe)_2(\mu\text{-}Cl)_2][ClO_4]_2$. Since cyano-bridged complexes are uncommon [3,4] it was of interest to attempt the formation of the above dimer in which the chloride ligand has been replaced by cyanide. Preliminary work [5] showed that when $[Pd(dppe)(CN)_2]$ was treated with one equivalent of silver perchlorate in acetonitrile solution, a bridged cyano-complex was formed. However, analytical and spectroscopic techniques could not determine the structure unambiguously. We thus report the *X*-ray crystal structure determination of the complex $[Pd_3(dppe)_3(\mu\text{-}CN)_3][ClO_4]_3$.

Experimental

Preparation of the Complex.—The complex $[Pd(dppe)(CN)_2]$ (1.0 mmol) was dissolved in acetonitrile (30 cm³). Silver perchlorate (1.0 mmol) dissolved in acetonitrile (20 cm³) was added with stirring. The solution was refluxed for 15 min and then stirred for a further 3 h whilst cooling during which time a precipitate formed. The solution was evaporated to dryness, extracted with dichloromethane and after filtration and reduction to a small volume a white solid was precipitated by dropwise addition of diethyl ether. The product was recrystallised twice from nitromethane–diethyl ether.

X-*Ray Crystal Structure Determination.*—*Crystal data.* $C_{81}H_{72}Cl_3N_3O_{12}P_6Pd_3$, M = 1 891, space group $R\bar{3}$,‡ a = 22.737(3) Å, α = 40.288(4)°, U = 4 431 Å³, Z = 6, $F(000)$ = 1 908, μ = 0.848 mm⁻¹; crystal dimensions 0.38 × 0.35 × 0.36 mm.

The crystals grown from nitromethane solution were clear brittle hexagonal plates or pyramids. Both crystal types gave identical *X*-ray powder diffraction patterns. A pyramidal crystal was chosen for diffractometry. Data were collected on a Hilger and Watts Y290 four-circle automatic diffractometer using niobium-filtered Mo-K_α radiation (λ = 0.710 73 Å) and the ω—2θ scan technique. Preliminary Weissenbergs had shown that reflections of the type *hhh* were strongest and broadest, therefore a wider scan was used for these (scans varied from 0.56 to 0.72° for *hhh* and from 0.4 to 0.56° for the remainder). The scan rate was 0.03° s⁻¹ throughout. Backgrounds were measured on each side of the peak for half the peak scan time. A 3.5-mm direct beam collimator was used to minimise interference from neighbouring reflections because of the large size of the unit cell. Three standards were monitored at intervals of 50. A unique set of 2 031 reflections was collected from 3 to 18° in θ; beyond this the crystal deteriorated rapidly. Of the 2 031 reflections, 1 453 with $I/\sigma(I) > 3$ were considered ' observed ' and used in the refinement. Parameters were refined by least-squares fit to the reflecting positions of fourteen planes. Intensities were corrected for Lorentz and polarisation effects and also for absorption. Scattering factors were taken from ref. 6. All calculations were performed on an IBM 360/195 at the Rutherford Appleton Computer Laboratory using the *X*-RAY 74 suite of programs.[7]

The palladium atom and one of the chlorine atoms were located by the heavy-atom method. The remaining atoms were found by repeated difference syntheses. Least-squares refinement was applied to all atoms, with anisotropic thermal parameters allowed in the final cycles for the palladium and phosphorus atoms and those oxygen atoms not on the triad axis. A final difference synthesis showed no features with density greater than ±1 electron although ripples were visible around the perchlorate positions. The weighting scheme used was $w = 1/(A + DF_o + EF_o{}^2)$ which was adjusted to minimise $w\Delta^2$. Only those unobserved reflections (42) calculating greater than measured were included in the refinement. Final R = 0.052 (1 495 reflections); R' = 0.061. Atomic co-ordinates are given in Table 1 and selected bond lengths and angles in Table 2.

Results and Discussion

The main feature of the structure is the central ring composed of three palladium atoms bridged in a linear fashion by three

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† *Supplementary data available* (No. SUP 23583, 21 pp.): structure factors, isotropic and anisotropic thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ Referred to rhombohedral axes. Alternative hexagonal cell has a = 15.600, c = 62.586 Å, $\alpha = \beta$ = 90°, γ = 120°, U = 13 293 Å³, and Z = 18.

Table 1. Positional parameters with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pd	0.465 9(1)	0.148 3(1)	0.133 3(1)
P(1)	0.599 9(3)	0.002 3(3)	0.166 2(3)
P(2)	0.581 8(3)	0.195 3(3)	−0.026 8(3)
N(1)	0.279(1)	0.359(1)	0.103(1)
C(1)	0.352(1)	0.285(1)	0.101(1)
C(2)	0.712(1)	−0.007(1)	0.046(1)
C(3)	0.711(1)	0.097(1)	−0.032(1)
C(11)	0.515(1)	0.168(1)	0.422(1)
C(12)	0.556(1)	0.229(1)	0.365(1)
C(13)	0.646(1)	0.187(1)	0.364(1)
C(14)	0.688(1)	0.081(1)	0.424(1)
C(15)	0.646(1)	0.022(1)	0.480(1)
C(16)	0.557(1)	0.066(1)	0.481(1)
C(21)	0.537(2)	0.218(2)	0.790(2)
C(22)	0.476(1)	0.298(1)	0.812(1)
C(23)	0.491(1)	0.290(1)	0.869(1)
C(24)	0.568(1)	0.205(1)	0.897(1)
C(25)	0.635(1)	0.126(1)	0.872(1)
C(26)	0.617(2)	0.131(2)	0.820(2)
C(31)	0.085(1)	0.238(1)	0.569(1)
C(32)	0.004(1)	0.217(1)	0.631(1)
C(33)	−0.076(1)	0.231(1)	0.721(1)
C(34)	−0.067(2)	0.266(2)	0.746(2)
C(35)	0.011(2)	0.287(1)	0.686(2)
C(36)	0.085(1)	0.276(1)	0.598(1)
C(41)	0.449(1)	0.251(1)	0.581(1)
C(42)	0.430(1)	0.290(1)	0.619(2)
C(43)	0.399(2)	0.252(2)	0.717(2)
C(44)	0.385(1)	0.159(1)	0.793(1)
C(45)	0.411(1)	0.115(1)	0.750(1)
C(46)	0.438(1)	0.158(1)	0.649(1)
Cl(1)	0.129 0(1)	0.129 0	0.129 0
Cl(2)	0.314 3(2)	0.314 3	0.314 3
Cl(3)	0.028 4(3)	0.028 4	0.028 4
Cl(4)	0.500 0	0.500 0	0.500 0
O(11)	0.106 4(4)	0.106 4	0.106 4
O(12)	0.051(1)	0.225(1)	0.130(1)
O(21)	0.336 5(7)	0.336 5	0.336 5
O(22)	0.217(2)	0.391(2)	0.335(2)
O(23)	0.353(5)	0.308(4)	0.235(4)
O(31)	0.048 1(7)	0.048 1	0.048 1
O(32)	0.012(2)	0.124(2)	−0.063(2)
O(41)	0.478 4(9)	0.478 4	0.478 4
O(42)	0.594(3)	0.487(9)	0.432(8)

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Pd–P(1)	2.263(4)	P(1)–Pd–N(1)	95.0(3)
Pd–P(2)	2.251(3)	P(2)–Pd–C(1)	92.6(4)
Pd–C(1)	2.02(1)	P(1)–Pd–P(2)	85.0(2)
Pd–N(1)	2.07(1)	C(1)–Pd–N(1)	87.6(5)
C(1)–N(1)	1.15(2)	Pd–C(1)–N(1)	165(2)
P(1)–C(2)	1.86(2)	Pd–N(1)–C(1)	164(1)
P(2)–C(3)	1.86(2)	Pd–P(1)–C(2)	108.9(6)
C(2)–C(3)	1.53(3)	Pd–P(2)–C(3)	109.7(5)
		P(1)–C(2)–C(3)	107(1)
		P(2)–C(3)–C(2)	110(2)

Phenyl rings

Ring 1:	C(11)—C(16)	C–C (av.)	1.40	Int. angles 720°
Ring 2:	C(21)—C(26)	C–C (av.)	1.41	
Ring 3:	C(31)—C(36)	C–C (av.)	1.40	
Ring 4:	C(41)—C(46)	C–C (av.)	1.41	

(e.s.d.s range from 0.02 to 0.08 Å and from 2 to 5°)

Perchlorates

Cl–O(av.) 1.38 O–Cl–O(av.) 108

(e.s.d.s range from 0.01 to 0.11 Å and from 1 to 10°)

cyano-ligands (Figure 1). The C–N distance of 1.15(2) Å is consistent with a triple bond although some rehybridisation is indicated as the Pd–N–C and N–C–Pd angles at 164(1) and 165(2)° respectively are significantly removed from the 180° required by a linear Pd–C–N–Pd arrangement. It should, however, be noted that in the cyano-bridged complex $[(NC)_5Co(\mu\text{-}CN)Co(NH_3)_5]\cdot H_2O$ where there are no obvious strain effects the Co–C–N angle is 172.4° but the C–N–Co angle is 159.8°.[8] We believe the present complex to be the first example of a complex in which a cyano-bridge linking two metal atoms is significantly non-linear at both ends. The cyano-bridges all lie to one side of the Pd_3 plane, the N atoms 0.21 Å and the C atoms 0.16 Å out of that plane.

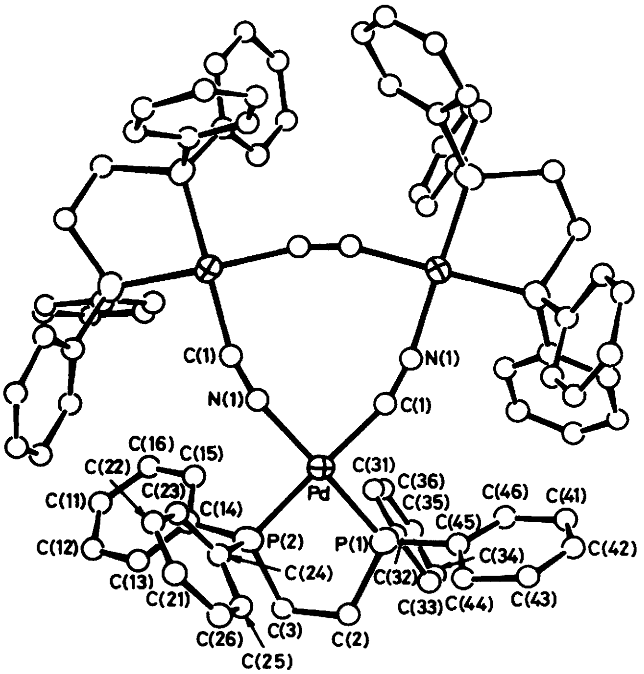

Figure 1. Structure of the $[Pd_3(dppe)_3(\mu\text{-}CN)_3]^{3+}$ trimer unit viewed vertically down the three-fold axis of symmetry

The question remains as to the relative orientation of the three cyano-groups in the ring. Because of the high proportion of heavy atoms and the restricted data set it is doubtful whether the carbon and nitrogen atoms of C–N are distinguishable. To investigate this the positions of these atoms were interchanged and then allowed to refine. The results were identical with the Pd–C and Pd–N bond lengths agreeing to within a standard deviation between each set. It thus appears that although the true symmetry around the three-fold axis would be lost if the cyano-bridge orientations were unsymmetrical, in practice the effect would be negligible from a crystallographic standpoint. A study of the ${}^{31}P\text{-}\{{}^{1}H\}$ n.m.r. (Figure 2) indicates that the relative orientations are as shown in Figure 3(*a*). There are only two possible arrangements for the cyano-bridges, one symmetrical and one unsymmetrical (Figure 3). As there are four signals of relative intensities 2 : 1 : 1 : 2 with coupling (*ca.* 7 Hz) evident on the centre

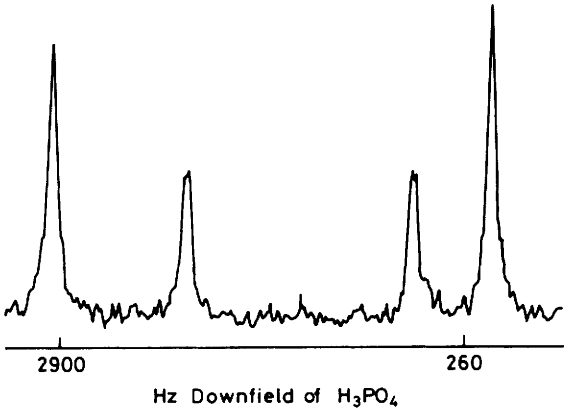

Figure 2. $^{31}P-\{^1H\}$ N.m.r. spectrum of $[Pd_3(dppe)_3(\mu-CN)_3][ClO_4]_3$

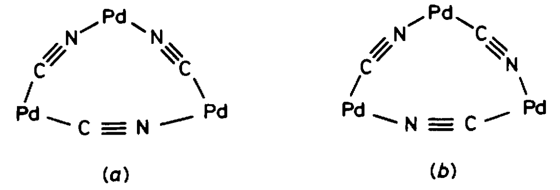

Figure 3. Possible relative orientations of the cyano-bridges

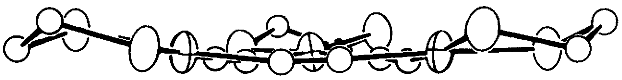

Figure 4. View through the Pd_3 plane

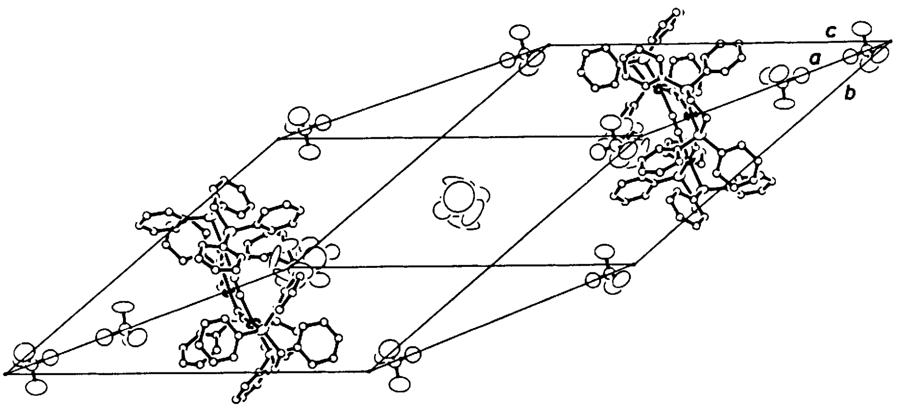

Figure 5. Unit cell of $[Pd_3(dppe)_3(\mu-CN)_3][ClO_4]_3$ illustrating the ionic arrangement

signals, we interpret this as the centre signals being from a *cis*-PdP_2CN co-ordination sphere and the outer signals being one from *cis*-PdP_2C_2 and the other from *cis*-PdP_2N_2. In support of this the ^{13}C n.m.r. shows two signals at -126.6 and -127.7 p.p.m. ($SiMe_4$ standard), approximate ratio 1 : 2, very close to those of the phenyl carbons.

The geometry about the palladium is essentially planar and this plane [PdP(1)P(2)N(1)C(1)] intersects the Pd_3 ring plane at an angle of 12° (Figure 4). This minimises the steric interaction between the phenyl rings and probably relieves any strain caused by the central nine-membered ring. There is nothing remarkable about the geometry of the palladium monomer units or the diphosphine ligand. The arrangement of the ions within the unit is illustrated in Figure 5 and shows some interesting features. The chlorine atom and one oxygen atom from each ClO_4^- ion are situated on the long body diagonal of the cell (1 1 1). (This is equivalent to the unique three-fold axis of the corresponding hexagonal cell). The large thermal parameters for the oxygen atoms and the residual electron density around the oxygen positions indicate that the ClO_4^- units are somewhat disordered. This is particularly evident for the oxygen atoms around Cl(2) not on the three-fold axis which resolved into two independent groups with relative population densities of 0.7 and 0.3. The position of Cl(4) at the body centre $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ indicates that there are seven perchlorate sites within the cell although only six are required for stoicheiometry. The ClO_4^- based on Cl(3) is only partially occupied. There are no significant non-bonded interactions and disorder is commonly found for such perchlorate groups.

Although dimeric complexes with single linear cyano-bridges are well documented[9] as are polymeric complexes,[4] cyclic cyano-bridged complexes are extremely rare.[3,10,11] It is remarkable that in this case the cyclic trimer is the preferred oligomer since the preparative method would seem to allow any value of *n* for $[\{Pd(dppe)(CN)\}_n][ClO_4]_n$. A value of four would be suggested by analogy to other cyano-bridged species such as $[\{AuPr_2(CN)\}_4]$[10] and $[\{Pd(\eta^3-C_3H_2Me_3-1,2,3)(CN)\}_4]$.[11]

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