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Structures of Pd[(PPh₂)₂(NMe)]Cl₂, Pt[(PPh₂)₂(NMe)]Cl₂ and Pt[(PPh₂)₂(NMe)](CN)₂

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(Received 10 April 1991; accepted 9 October 1991)

Abstract. [Bis(diphenylphosphino)methylamine]dichloropalladium (1), C₂₅H₂₃Cl₂P₂PdN, *M_r* = 576.7, monoclinic, *P*2₁/*n*, *a* = 9.202 (1), *b* = 13.814 (1), *c* = 19.420 (1) Å, β = 92.45 (3)°, *V* = 2466 (1) Å³, *Z* = 4, *D_x* = 1.54 g cm⁻³, graphite-monochromatized Mo *Kα* radiation, λ = 0.71073 Å, μ = 10.9 cm⁻¹, *F*(000) = 1160, room temperature, *R* = 0.039 for 3345 observed reflections [*I* > 3σ(*I*)]. [Bis(diphenylphosphino)methylamine]dichloroplatinum (2), C₂₅H₂₃Cl₂P₂PtN, *M_r* = 665.41, monoclinic, *P*2₁/*n*, *a* = 9.246 (2), *b* = 13.916 (4), *c* = 19.333 (5) Å, β = 92.65 (2)°, *V* = 2485 (2) Å³, *Z* = 4, *D_x* = 1.78 g cm⁻³, graphite-monochromatized Mo *Kα* radiation, λ = 0.71073 Å, μ = 60.62 cm⁻¹, *F*(000) = 1288, room temperature, *R* = 0.048 for 2329 observed reflections.

[Bis(diphenylphosphino)methylamine]dicyanoplatinum (3), C₂₇H₂₃P₂PtN₃, *M_r* = 646.56, monoclinic, *P*2₁/*n*, *a* = 9.506 (3), *b* = 13.635 (5), *c* = 19.669 (7) Å, β = 93.32 (3)°, *V* = 2545 (3) Å³, *Z* = 4, *D_x* = 1.69 g cm⁻³, graphite-monochromatized Mo *Kα* radiation, λ = 0.71073 Å, μ = 57.1 cm⁻¹, *F*(000) = 1256, room temperature, *R* = 0.041 for 3798 observed reflections. Three crystal structures of the bis(diphenylphosphino)methylamine (dppma) ligand chelating to a Pt-group metal atom are reported. The complexes (1) and (2) have chloride ligands *trans* to the dppma ligand while the third complex, (3), has cyanide ligands *trans* to the dppma ligand. The complexes have a highly distorted, square-planar coordination geometry. The ring strain associated with the four-membered chelate rings is evident in the distorted tetrahedral angles at P, which range from 93.3 (2) to 122.2 (5)°, and the

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Table 1. *Data collection and refinement parameters*

	(1)	(2)	(3)
Dimensions (mm)	0.10 × 0.12 × 0.30	0.06 × 0.25 × 0.25	0.08 × 0.40 × 0.41
Reflections for cell			
Number	25	20	25
θ range (°)	9–15	9–13	8–12
Crystal faces	{001}, {101}, {101}	{001}, {101}, {101}	{001}, {101}, {111}
	{011}	{011}	{011}
Intensity measurements			
θ_{\max} (°)	25	22	25
<i>h</i>	0→10	0→10	0→11
<i>k</i>	0→16	0→16	0→16
<i>l</i>	–23→23	–22→22	–23→23
Total reflections	4611	4633	4603
Intensity decrease (%)	0.1	0	0.5
<i>R</i> for averaged reflections	0.014	0.011	0.017
Structure refinement			
Number of parameters	160	160	178
<i>wR</i>	0.054	0.049	0.052
Weighting scheme	$4F_o^2/\sigma^2(F_o^2)$	$1/[\sigma^2(F_o) + 0.00132(F_o)^2]$	$1/[\sigma^2(F_o) + 0.0234(F_o)^2]$
Goodness of fit	1.37	1.08	0.87
Δ/σ_{\max}	0.01	0.01	0.01
Highest peak in difference Fourier map			
Electron density (e Å ⁻³)	1.54	1.65	1.92
Position	(0.443, 0.375, 0.416)	(0.050, 0.209, 0.201)	(0.050, 0.290, 0.182)
Associated with atom	C14	Pt	Pt

trigonal-planar angles at N which are in the range 100.0 (6) to 128.7 (3)°.

Introduction. We have found that the bidentate ligand bis(diphenylphosphino)amine (dppa) and its derivatives form stable chelate complexes with Pt-group metals despite the strain caused by the formation of a four-membered chelate ring. The small bite angle of the coordinated ligand compresses the P—N—P angle to approximately 100° which is a severe distortion from the ideal trigonal-planar angle expected at the *sp*²-hybridized nitrogen. Competition studies between dppa and bis(diphenylphosphino)methane (dppm) reveal that Pt^{II} centres bind preferentially to dppa (Browning & Farrar, 1991). This observation lies in contrast to *ab initio* studies which suggest that the energy increase of bending the N atom in dppa from the free ligand geometry to the chelate geometry is greater than that required to bend the C atom in dppm (Browning, Farrar & Peterson, 1991). The structures of the title complexes were examined as part of our study into the structure and stability of dppa complexes of Pt-group metals.

Experimental. Colourless crystals of (1), (2) and (3) were grown from dichloromethane solutions of the complexes by slow evaporation. Compounds (1) and (2) formed brick-shaped crystals; (3) formed plate-shaped crystals. Crystal dimensions and other experimental data are given in Table 1. The crystals were mounted on glass fibres and accurate cell dimensions and crystal orientation matrices were determined on a CAD-4 diffractometer by a least-squares treatment

of the setting angles. Intensities of reflections were measured using ω - 2θ scans, ω -scan width (0.75 + 0.35tan θ)°; intensities of two control reflections measured every 4 h during data collection. Space group *P2*₁/*n*, for (1), (2) and (3), was determined by the systematic absences (*0k0* absent if *k* = 2*n* + 1, *h0l* absent if *h* + *l* = 2*n* + 1). The reflections measured were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data for (1) based upon φ scans of six reflections with θ values in the range 7 to 13°. The transmission factors range from 89.37 to 99.70%. An empirical absorption correction to the data for (3) was applied based upon ψ scans of four reflections with θ values in the range 5 to 11°. The transmission factors range from 87.25 to 99.56%. The structures were solved by the heavy-atom method. Crystals of (2) are isomorphous with those of (1). Refinement was by full-matrix least-squares calculations with isotropic thermal parameters for the atoms of the phenyl rings and with anisotropic thermal parameters for the remaining atoms. The difference maps showed maxima in positions consistent with the expected locations of H atoms. In the final rounds of calculations the H atoms were positioned on geometric grounds and included (as riding atoms) in the structure factor calculations. An absorption correction for (2) was applied using the program *DIFABS* (Walker & Stuart, 1983). No corrections for secondary extinction. The atomic coordinates are given in Table 2. Scattering factors as neutral atoms. For all the structures, calculations were carried out on a PDP 11/23 computer using *SDP* (Frenz, 1982) and an Apollo

Table 2. *Positional and thermal parameters*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, B_{eq} , defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. The form of the isotropic equivalent thermal parameter U_{eq} is defined as: $(U_{11} + U_{22} + U_{33})/3$. Numbers in parentheses are estimated standard deviations in the least significant digits.

Compound (1)				
	x	y	z	$B_{\text{eq}}/B_{\text{iso}}(\text{\AA}^2)$
Pd	0.14452 (4)	0.20946 (2)	0.17361 (2)	2.156 (6)
C11	-0.0669 (1)	0.2068 (1)	0.10085 (7)	3.82 (3)
C12	0.0296 (2)	0.1575 (1)	0.27392 (7)	3.83 (3)
P1	0.3697 (1)	0.21763 (8)	0.21928 (6)	2.31 (2)
P2	0.2902 (1)	0.26087 (9)	0.09326 (6)	2.45 (2)
N	0.4383 (4)	0.2654 (3)	0.1477 (2)	2.65 (8)
C	0.5910 (6)	0.2736 (5)	0.1294 (3)	4.4 (1)
C11	0.4150 (5)	0.2948 (3)	0.2915 (3)	2.76 (8)
C12	0.3862 (7)	0.2602 (5)	0.3561 (3)	4.3 (1)
C13	0.4146 (7)	0.3187 (5)	0.4132 (4)	5.0 (1)
C14	0.4746 (7)	0.4086 (5)	0.4053 (3)	4.8 (1)
C15	0.5041 (7)	0.4423 (5)	0.3422 (3)	4.4 (1)
C16	0.4741 (6)	0.3865 (4)	0.2843 (3)	3.5 (1)
C21	0.4579 (5)	0.1045 (3)	0.2405 (2)	2.60 (8)
C22	0.6028 (6)	0.1021 (4)	0.2630 (3)	3.7 (1)
C23	0.6680 (7)	0.0129 (4)	0.2776 (3)	4.3 (1)
C24	0.5890 (6)	-0.0703 (4)	0.2705 (3)	4.2 (1)
C25	0.4476 (6)	-0.0685 (4)	0.2485 (3)	4.0 (1)
C26	0.3795 (6)	0.0192 (4)	0.2325 (3)	3.19 (9)
C31	0.2662 (6)	0.3783 (4)	0.0555 (3)	3.28 (9)
C32	0.3294 (6)	0.4591 (4)	0.0867 (3)	4.3 (1)
C33	0.3067 (8)	0.5504 (5)	0.0565 (4)	5.3 (1)
C34	0.2228 (8)	0.5582 (5)	-0.0020 (4)	5.5 (1)
C35	0.1579 (8)	0.4821 (5)	-0.0333 (4)	5.7 (1)
C36	0.1795 (7)	0.3890 (5)	-0.0045 (3)	4.5 (1)
C41	0.3251 (5)	0.1791 (4)	0.0235 (3)	2.94 (9)
C42	0.3940 (7)	0.2091 (4)	-0.0346 (3)	4.5 (1)
C43	0.4233 (8)	0.1441 (5)	-0.0863 (4)	5.4 (1)
C44	0.3819 (7)	0.0510 (5)	-0.0808 (3)	4.7 (1)
C45	0.3131 (7)	0.0184 (4)	-0.0234 (3)	4.3 (1)
C46	0.2854 (6)	0.0834 (4)	0.0287 (3)	3.4 (1)

Compound (2)				
	x	y	z	$U_{\text{eq}}/U_{\text{iso}}(\text{\AA}^2)$
Pt	0.14709 (6)	0.20908 (5)	0.17301 (3)	0.0294 (3)
C11	0.0276 (5)	0.1587 (3)	0.2718 (2)	0.053 (3)
C12	-0.0683 (4)	0.2059 (4)	0.1035 (2)	0.053 (2)
P1	0.2903 (5)	0.2588 (3)	0.0923 (2)	0.036 (2)
P2	0.3699 (4)	0.2179 (3)	0.2189 (2)	0.033 (2)
N	0.4387 (13)	0.2637 (8)	0.1465 (6)	0.033 (7)
C	0.5892 (18)	0.2726 (13)	0.1293 (9)	0.058 (12)
C11	0.2652 (16)	0.3756 (12)	0.0541 (8)	0.041 (4)
C12	0.3285 (21)	0.4555 (14)	0.0859 (10)	0.068 (6)
C13	0.3074 (23)	0.5504 (17)	0.0558 (11)	0.081 (7)
C14	0.2227 (22)	0.5548 (17)	-0.0040 (11)	0.078 (6)
C15	0.1596 (26)	0.4766 (16)	-0.0355 (12)	0.087 (7)
C16	0.1796 (21)	0.3879 (16)	-0.0069 (10)	0.069 (6)
C21	0.3238 (16)	0.1802 (10)	0.0227 (8)	0.037 (4)
C22	0.2858 (16)	0.0843 (11)	0.0264 (8)	0.037 (4)
C23	0.3118 (19)	0.0187 (13)	-0.0243 (9)	0.055 (5)
C24	0.3818 (23)	0.0502 (15)	-0.0815 (11)	0.077 (6)
C25	0.4217 (23)	0.1466 (15)	-0.0874 (11)	0.075 (6)
C26	0.3957 (20)	0.2124 (15)	-0.0350 (9)	0.063 (5)
C31	0.4580 (15)	0.1077 (10)	0.2418 (7)	0.033 (3)
C32	0.6048 (19)	0.1036 (13)	0.2621 (9)	0.053 (4)
C33	0.6753 (21)	0.0165 (13)	0.2777 (9)	0.060 (5)
C34	0.5903 (20)	-0.0682 (14)	0.2722 (9)	0.062 (5)
C35	0.4455 (19)	-0.0658 (13)	0.2510 (8)	0.052 (5)
C36	0.3822 (18)	0.0209 (11)	0.2336 (8)	0.044 (4)
C41	0.4157 (14)	0.2922 (11)	0.2916 (7)	0.033 (3)
C42	0.4741 (18)	0.3859 (12)	0.2844 (9)	0.053 (4)
C43	0.5026 (20)	0.4396 (14)	0.3433 (9)	0.061 (5)
C44	0.4686 (19)	0.4065 (14)	0.4078 (10)	0.060 (5)
C45	0.4119 (21)	0.3149 (14)	0.4160 (11)	0.069 (6)
C46	0.3842 (20)	0.2614 (14)	0.3548 (10)	0.064 (5)

Table 2 (cont.)

Compound (3)				
	x	y	z	$U_{\text{eq}}/U_{\text{iso}}(\text{\AA}^2)$
Pt	0.14712 (2)	0.29192 (2)	0.17197 (1)	0.0307 (2)
P1	0.3705 (2)	0.2820 (1)	0.21813 (9)	0.034 (1)
P2	0.2913 (2)	0.2383 (1)	0.09165 (9)	0.0361 (9)
C1	0.0468 (8)	0.3381 (6)	0.2548 (4)	0.047 (4)
N1	-0.0042 (10)	0.3625 (6)	0.3017 (4)	0.073 (5)
C2	-0.0330 (10)	0.2961 (4)	0.1134 (4)	0.043 (5)
N2	-0.1317 (8)	0.2987 (4)	0.0762 (4)	0.052 (5)
N	0.4333 (6)	0.2346 (4)	0.14663 (3)	0.036 (3)
C	0.5859 (9)	0.2269 (7)	0.1313 (5)	0.069 (6)
C11	0.4139 (9)	0.2020 (4)	0.2888 (4)	0.039 (2)
C12	0.3760 (10)	0.2348 (7)	0.3513 (4)	0.059 (2)
C13	0.4078 (11)	0.1708 (8)	0.4093 (5)	0.076 (2)
C14	0.4753 (10)	0.0877 (8)	0.4008 (5)	0.075 (2)
C15	0.5149 (10)	0.0568 (7)	0.3381 (4)	0.063 (2)
C16	0.4839 (8)	0.1138 (5)	0.2834 (4)	0.047 (2)
C21	0.4608 (8)	0.3941 (4)	0.2400 (3)	0.036 (1)
C22	0.6015 (8)	0.3966 (5)	0.2668 (4)	0.048 (2)
C23	0.6615 (9)	0.4854 (6)	0.2817 (4)	0.058 (2)
C24	0.5886 (9)	0.5692 (6)	0.2734 (4)	0.057 (2)
C25	0.4545 (9)	0.5688 (6)	0.2470 (4)	0.055 (2)
C26	0.3873 (7)	0.4836 (5)	0.2295 (3)	0.043 (2)
C31	0.3227 (8)	0.3194 (5)	0.0230 (4)	0.042 (1)
C32	0.3880 (11)	0.2869 (6)	-0.0391 (5)	0.063 (2)
C33	0.4134 (10)	0.3519 (7)	-0.0858 (5)	0.068 (2)
C34	0.3780 (10)	0.4482 (6)	-0.0811 (4)	0.064 (2)
C35	0.3177 (8)	0.4832 (6)	-0.0235 (4)	0.053 (2)
C36	0.2885 (8)	0.4186 (6)	0.0289 (4)	0.048 (2)
C41	0.2684 (8)	0.1192 (5)	0.0540 (3)	0.043 (2)
C42	0.3349 (9)	0.0363 (6)	0.0831 (4)	0.057 (2)
C43	0.3199 (11)	-0.0551 (7)	0.0583 (5)	0.073 (2)
C44	0.2285 (11)	-0.0651 (8)	-0.0012 (5)	0.075 (3)
C45	0.1575 (12)	0.0121 (8)	-0.0303 (5)	0.086 (3)
C46	0.1790 (10)	0.1068 (6)	-0.0019 (4)	0.062 (2)

computer using *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986).*

Discussion. Selected bond lengths and angles for molecules (1), (2) and (3) are listed in Table 3. Table 4 provides a comparison of the three structural studies together with some related data from the literature. Figs. 1, 2 and 3 present views of the molecules prepared using *ORTEP* (Johnson, 1976) with H atoms omitted for clarity. Phenyl ring labelled 1 is composed of C atoms C11 through C16, etc. The angles subtended by the metal atoms suggest that the coordination geometries about those atoms is best described as highly distorted, square-planar arrangements of the two phosphine P atoms and two chloride or cyanide ligands. The largest deviations from the least-squares planes defined by the metal atoms and the four atoms directly bound to them are 0.038 (1) Å (P1) for (1), 0.027 (4) Å (P2) for (2) and 0.027 (1) Å (P1) for (3). The N atoms of the dppe ligands sit out of the planes by 0.114 (4) Å, (1), 0.101 (5) Å, (2) and 0.109 (11) Å, (3).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and mean-plane data for all three compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54736 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond distances (Å) and angles (°)

Compound (1)							
Pd	C11	2.355 (1)	P1	C21	1.801 (4)		
Pd	C12	2.367 (1)	P2	N	1.690 (3)		
Pd	P1	2.222 (1)	P2	C31	1.789 (4)		
Pd	P2	2.217 (1)	P2	C41	1.804 (4)		
P1	N	1.686 (3)	N	C	1.468 (5)		
P1	C11	1.797 (4)					
C11	Pd	C12	95.89 (4)	C11	Pd	P1	166.56 (4)
C11	Pd	P2	95.24 (4)	C12	Pd	P1	97.38 (4)
C12	Pd	P2	168.83 (4)	P1	Pd	P2	71.52 (4)
Pd	P1	N	93.8 (1)	Pd	P1	C11	121.5 (1)
Pd	P1	C21	116.8 (1)	N	P1	C11	109.2 (2)
N	P1	C21	110.3 (2)	C11	P1	C21	104.4 (2)
Pd	P2	N	93.9 (1)	Pd	P2	C31	120.7 (2)
Pd	P2	C41	117.4 (1)	N	P2	C31	107.7 (2)
N	P2	C41	109.2 (2)	C31	P2	C41	106.5 (2)
P1	N	P2	100.4 (2)	P1	N	C	128.7 (3)
P2	N	C	127.3 (3)				
Compound (2)							
Pt	C11	2.357 (4)	P1	C21	1.77 (1)		
Pt	C12	2.350 (4)	P2	N	1.69 (1)		
Pt	P1	2.204 (4)	P2	C31	1.78 (1)		
Pt	P2	2.209 (4)	P2	C41	1.78 (1)		
P1	N	1.69 (1)	N	C	1.45 (2)		
P1	C11	1.80 (2)					
C12	Pt	C11	92.4 (1)	C21	P1	C11	105.7 (7)
P1	Pt	C12	97.0 (1)	N	P2	Pt	93.9 (4)
P2	Pt	C12	168.7 (1)	C31	P2	Pt	117.3 (5)
P1	Pt	C11	170.6 (1)	C41	P2	Pt	122.2 (5)
P2	Pt	C11	98.8 (1)	C31	P2	N	110.2 (6)
P2	Pt	P1	71.8 (1)	C41	P2	N	110.5 (6)
N	P1	Pt	94.0 (4)	C41	P2	C31	102.4 (7)
C11	P1	Pt	120.3 (5)	P2	N	P1	100.0 (6)
C21	P1	Pt	118.4 (5)	C	N	P1	128.4 (10)
C11	P1	N	107.8 (6)	C	N	P2	128.7 (11)
C21	P1	N	109.3 (7)				
Compound (3)							
Pt	P1	2.265 (2)	P2	N	1.681 (6)		
Pt	P2	2.272 (2)	P2	C31	1.784 (7)		
Pt	C1	2.035 (7)	P2	C41	1.793 (7)		
Pt	C2	2.008 (9)	C1	N1	1.12 (1)		
P1	N	1.688 (6)	C2	N2	1.16 (1)		
P1	C11	1.795 (7)	N	C	1.50 (1)		
P1	C21	1.793 (7)					
P2	Pt	P1	70.73 (7)	N	P2	Pt	93.2 (2)
C1	Pt	P1	99.8 (2)	C31	P2	Pt	117.4 (2)
C2	Pt	P1	168.5 (3)	C41	P2	Pt	121.0 (2)
C1	Pt	P2	170.4 (2)	C31	P2	N	110.0 (3)
C2	Pt	P2	98.0 (2)	C41	P2	N	108.2 (3)
C2	Pt	C1	91.6 (3)	C41	P2	C31	105.7 (3)
N	P1	Pt	93.3 (2)	N1	C1	Pt	177.5 (7)
C11	P1	Pt	121.0 (3)	N2	C2	Pt	175.8 (8)
C21	P1	Pt	118.0 (2)	P2	N	P1	102.4 (3)
C11	P1	N	109.6 (3)	C	N	P1	125.9 (5)
C21	P1	N	109.8 (3)	C	N	P2	128.5 (5)
C21	P1	C11	104.3 (3)				

The Pd—Cl bond lengths differ by 8.5σ in (1) while the Pt—Cl bond lengths in (2) are statistically equivalent. The Pt—C distances in (3) differ by 3.5σ . No chemical significance is assigned to the different $M—X$ values in (1) and (3). The symmetric diphosphine ligand has the same *trans* influence on both $M—X$ distances and the P nuclei are equivalent in

the solution ^{31}P NMR spectra. The differences in the $M—X$ bond lengths in (1) and (3) are ascribed to packing effects. The average value of 2.361 (1) Å for the Pd—Cl bond length in (1) is comparable to the values observed for the complexes $\text{Pd}[(\text{PPh}_2)_2\text{NEt}]\text{Cl}_2$ (Mokuolu, Payne & Speakman, 1973) and $\text{Pd}[\text{dppm}]\text{Cl}_2$ (Steffen & Palenik, 1976). The Cl—Pd—Cl angle in (1), $95.89(4)^\circ$, is equivalent to the value reported for the complex $\text{Pd}[(\text{PPh}_2)_2\text{NEt}]\text{Cl}_2$ and just significantly higher than the angle reported for $\text{Pd}[\text{dppm}]\text{Cl}_2$. The $X—Pt—X$ angles, where $X = \text{Cl}$ or $\text{C}(\text{N})$, in (2) and (3), $92.4(1)$ and $91.6(3)^\circ$, are indistinguishable.

The Pd—P bond distances in (1) are just significantly different (3.5σ) but comparable to the distances reported for $\text{Pd}[(\text{PPh}_2)_2\text{NEt}]\text{Cl}_2$. The two Pt—P bond lengths in (2) and (3) are identical, the averages being 2.206 (4) and 2.268 (2) Å, respectively. The longer Pt—P bond lengths in (3) are consistent with the higher *trans* influence of the cyanide ligand. The P—M—P bond angles in the complexes (1), (2), (3) and $\text{Pd}[(\text{PPh}_2)_2\text{NEt}]\text{Cl}_2$ are equivalent and average to a value of $71.36(11)^\circ$. This average value is significantly smaller than the P—Pd—P angle of $72.68(3)^\circ$ reported for $\text{Pd}[\text{dppm}]\text{Cl}_2$.

The P—N bond lengths in the complexes (1), (2) and (3) are equivalent [average 1.687 (4) Å] and indistinguishable from the value 1.692 (2) Å reported for the free dppa ligand (Noth & Fluch, 1984). The P—N bond lengths in the complexes are slightly shorter (3.5σ) than the values 1.73 (1) and 1.72 (1) Å reported for the complex $\text{Pd}[(\text{PPh}_2)_2\text{NEt}]\text{Cl}_2$. The accepted P—N single (1.77 Å) and double (1.6 Å) bond lengths (Greenwood & Earnshaw, 1984) bracket the average value observed for (1), (2) and (3). *Ab initio* calculations (Browning, Farrar & Peterson, 1991) suggest that the P—N bond order in the ligands is one and thus the value 1.77 Å, normally associated with a single-bond length, may be long. The strained geometry of the chelate ring is evident in the P—N—P angles of $100.4(2)$, $100.0(6)$ and $102.4(3)^\circ$ for (1), (2) and (3), respectively, which are significantly compressed from the value of $118.9(2)^\circ$ observed in the free dppa ligand (Noth & Fluch, 1984). The P—N—C angles are consistent with a distorted trigonal-planar arrangement of atoms about the N atoms. Five of the six P—N—C angles are equivalent, with an average of $128.3(4)^\circ$, while the remaining C—N—P1 angle, of $125.9(5)^\circ$ in (3), is just significantly smaller. The chelate bite angles are $71.52(4)$, $71.80(15)$ and $70.73(7)^\circ$ for (1), (2) and (3), respectively. The P atoms also are severely distorted from the expected tetrahedral configuration with the $M—\text{P1—N}$ and $M—\text{P2—N}$ angles being $93.8(1)$ and $93.9(1)^\circ$ respectively for (1), $94.0(4)$ and $93.9(4)^\circ$ for (2) and $93.3(2)$ and $93.2(2)^\circ$ for (3).

Table 4. Comparison of X-ray structures

	Pd[dppma]Cl ₂ (1)	Pt[dppma]Cl ₂ (2)	Pt[dppma](CN) ₂ (3)	Pd[(PPh ₂) ₂ NEt]Cl ₂ (e)	Pd[dppm]Cl ₂ (f)
Bonds (Å)					
M—X ^a	2.355 (1)	2.357 (4)	2.035 (7)	2.370 (5)	2.362 (1)
M—P	2.367 (1)	2.350 (4)	2.008 (9)	2.370 (5)	2.352 (1)
M—N	2.222 (1)	2.204 (4)	2.265 (2)	2.220 (4)	2.234 (1)
P—N	2.217 (1)	2.209 (4)	2.272 (2)	2.230 (4)	2.250 (1)
P—C	1.686 (3)	1.689 (13)	1.688 (6)	1.73 (1)	1.834 (3) ^b
N—C	1.690 (3)	1.689 (12)	1.681 (6)	1.72 (1)	1.830 (3) ^b
	1.468 (5)	1.45 (2)	1.50 (1)	1.45 (2)	—
Angles (°)					
X—M—X ^a	95.89 (4)	92.4 (1)	91.6 (3)	94.8 (3)	93.63 (3)
P—M—P	71.52 (4)	71.8 (1)	70.73 (7)	71.4 (3)	72.68 (3)
P—N—P	100.4 (2)	100.0 (6)	102.4 (3)	97.7 (10)	93.0 (1) ^f
M—P—N	93.8 (1)	94.0 (4)	93.3 (2)	95.2 (10)	94.7 (1) ^d
	93.9 (1)	93.9 (4)	93.2 (2)	95.0 (10)	94.3 (1) ^d

Notes: (a) X is *trans* atom. (b) P—C. (c) P—C—P. (d) Pt—P—C. (e) Mokuolu, Payne & Speakman (1973). (f) Steffen & Palenik (1976).

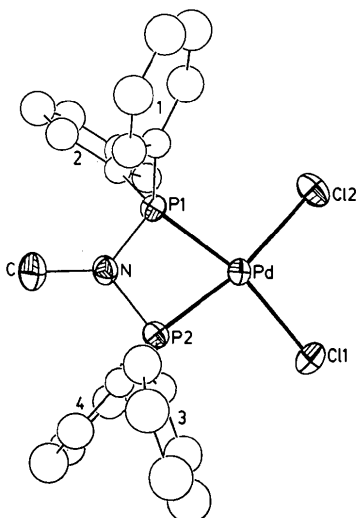


Fig. 1. ORTEP diagram of Pd[dppma]Cl₂, (1), showing atom and ring numbering schemes.

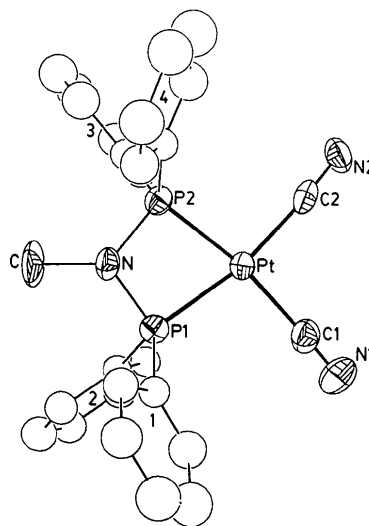


Fig. 3. ORTEP diagram of Pt[dppma](CN)₂, (3), showing atom and ring numbering schemes.

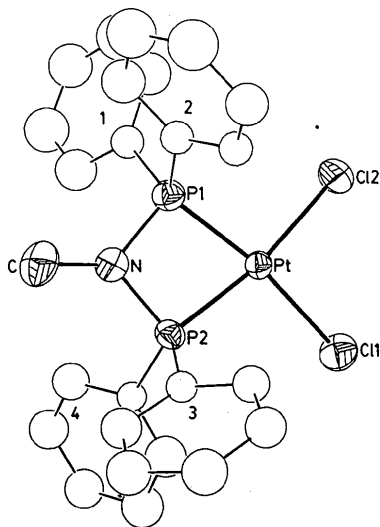


Fig. 2. ORTEP diagram of Pt[dppma]Cl₂, (2), showing atom and ring numbering schemes.

The structural parameters associated with the phenyl rings and the cyanide ligand are normal (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

We thank the Natural Sciences and Engineering Research Council of Canada for operating, infrastructure and equipment grants.

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An Organometallic Cyanine: μ -1,3,5-Heptatriene-1,7-diylidene-bis[μ^2 -carbonyl-dicarbonylbis(η^5 -cyclopentadienyl)diiron] Tetrafluoroborate

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(Received 13 May 1991; accepted 11 October 1991)

Abstract. $C_{33}H_{25}Fe_4O_6^+ \cdot BF_4^-$, $M_r = 827.75$, monoclinic, $C2/c$, $a = 32.289$ (10), $b = 8.984$ (3), $c = 28.024$ (10) Å, $\beta = 126.84$ (2)°, $V = 6506$ (4) Å³, $Z = 8$, $D_x = 1.69$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 18.2$ cm⁻¹, $F(000) = 3328$, $T = 297$ K, $R = 0.047$ for 2619 reflections with $F_o^2 > 0$. This compound has an intense low-energy visible absorption band ($\epsilon = 165\,500$ at 630 nm); the material is likely to be useful in non-linear optical devices. The $Fe_2-C_7-Fe_2$ group is planar within ± 0.14 Å and all the C—C bonds in the bridge are essentially the same length, 1.379 (11) Å.

Introduction. Organometallic compounds are potentially useful as second-order and third-order non-linear optical materials (Jones, 1989; Marder, Sohn & Stucky, 1991). The most useful materials will have large extinction coefficients, obtained by optimizing the electronic coupling between the metal center(s) and the organic ligand. Because organic cyanines have among the largest extinction coefficients known, we have synthesized organometallic cyanines and examined them for useful properties, reasoning that these organometallic analogs would have low-energy transitions with large transition dipole moments. The title compound was synthesized by the reaction of $\{(\eta-C_5H_5)_2Fe_2(CO)_2(\mu-CO)(\mu-C-CH_3)\}^+ \cdot BF_4^-$ with 1,1',3,3'-tetramethoxypropane,

with added water in THF at 333 K. The compound precipitates as essentially pure blue microcrystals from the reaction mixture in 60% yield. The ultraviolet-visible spectrum of the compound, in methylene chloride, shows an intense band centered at 630 nm with an extinction coefficient of 160 000 LM⁻¹cm⁻¹ and an oscillator strength of 1.12. The compound thus fulfills our expectations for a highly absorbing material with a low-energy transition. This low-energy absorption is most likely a consequence of high-energy orbitals of the electro-positive iron centers mixing efficiently with the frontier orbitals of the carbon skeleton. This highly delocalized organometallic cyanine is a prototype for a class of materials which may be of interest for electron transfer and non-linear optical studies that are currently under way.

Experimental. Material synthesized as described by Spotts, Schaefer & Marder (1991); crystal a rectangular plate, 0.077 × 0.250 × 0.378 mm; CAD-4 diffractometer; cell dimensions from 25 reflections with $30 < 2\theta < 33^\circ$; a cell with a smaller β angle, but with symmetry $C2/n$, can be obtained by transformation with the matrix $(\bar{1}00; 0\bar{1}0; 101)$ ($c = 27.255$ Å, $\beta = 124.62^\circ$), or one with $I2/a$ symmetry with the matrix $(\bar{1}0\bar{1}; 0\bar{1}0; 001)$ ($a = 27.255$, $b = 8.984$, $c = 28.024$ Å, $\beta = 108.54^\circ$); we chose to use the standard $C2/c$ setting; analytical absorption correction by Gaussian integration over an 8 × 8 × 8 grid, maximum trans-

* Contribution No. 8234.