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METAL-METAL BONDING IN DINUCLEAR COMPLEXES OF PLATINUM(I). THE CRYSTAL AND MOLECULAR STRUCTURE OF CARBONYL(CHLORO)-BIS-μ-[BIS(DIPHENYLPHOSPHINO)METHANE]DIPLATINUM HEXAFLUOROPHOSPHATE

Lj. MANOJLOVIĆ-MUIR*, K.W. MUIR and T. SOLOMUN
Department of Chemistry, University of Glasgow,
Glasgow G12 8QQ (Great Britain)

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Summary

The structure of $[Pt_2Cl(CO)(\mu\text{-}Ph_2PCH_2PPh_2)_2][PF_6]$ was determined by *X*-ray methods and refined to *R* = 0.082, using diffractometric intensities of 5646 independent reflections. The crystals are monoclinic, space group $P2_1/n$, *a* = 12.919(3), *b* = 15.576(6), *c* = 25.151(5)Å, β = 94.82(3)°, *Z* = 4. They are built of octahedral hexafluorophosphate anions and dinuclear platinum(I) cations. The latter contain Pt-Cl and Pt-CO fragments linked to one another by a Pt-Pt σ-bond and by two bridging bis(diphenylphosphino)methane ligands. The platinum atoms are in square planar environments and the dihedral angle between the two coordination planes is 40.1°. Selected bond lengths are: Pt-Pt 2.620(1), Pt-Cl 2.384(5), Pt-C 1.89(3) and Pt-P 2.291(5) - 2.308(5)Å.

Introduction

Brown and coworkers have made and characterised a large number of dinuclear complexes of platinum, in which the metal centres are bridged by two bis(diphenylphosphino)methane, dppm, ligands [1-4]. Vibrational and n.m.r. spectra indicate that in some of these complexes the metal atoms are also linked directly by Pt-Pt bonds. The existence of such bonds has been established by X-ray diffraction studies, first in $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [5,6] and now in the title compound, $[Pt_2Cl(CO)(\mu\text{-dppm})_2][PF_6]$. Detailed structural features of these two complexes are also of interest in view of the recent suggestion of Brown et al. that the magnitudes of ^{31}P-^{31}P and ^{195}Pt-^{31}P coupling constants may provide a measure of the strength of metal-metal bonding in the complexes containing $Pt_2(\mu\text{-dppm})_2$ units [7].

Experimental

Crystal Data

$C_{51}H_{44}ClF_6OP_5Pt_2$, M = 1367.4. Monoclinic, a = 12.919(3), b = 15.576(6), c = 25.151(5)Å, β = 94.82(3)°, U = 5043Å^3, Z = 4, D_c = 1.800g cm^{-3}, $F(000)$ = 2640. Space group $P2_1/n$ (C^5_{2h}, No. 14). Mo-K_α radiation, λ = 0.71069Å, μ(Mo-K_α) = 59 cm^{-1}.

Measurements

The space group and preliminary unit cell dimensions were determined from rotation and Weissenberg photographs. Final values of cell dimensions and the intensities of all independent reflections with $\theta(\text{Mo-}K_\alpha) \leq 25°$ were measured on a Hilger and Watts Y290 diffractometer equipped with a graphite monochromator. A symmetrical θ-2θ scan technique was employed. Each reflection was scanned over a range of 0.50° in θ, taking 2s counts at 0.02° steps; the background was measured for 15s at each end of the scan range.

The integrated intensities, I, and their standard deviations, $\sigma(I)$, were derived in the way described elsewhere (q = 0.04) [8]. They were corrected for Lorentz-polarization effects and also for the variations in intensity of two periodically remeasured standard reflections. A satisfactory allowance for absorption was precluded by the poorly developed shape of the crystal specimen. The subsequent analysis was based on 5646 independent reflections for which $I>3\sigma(I)$.

Structure Analysis

The positions of the platinum atoms were determined from a Patterson function and those of the other non-hydrogen atoms from successive difference syntheses.

The structure was refined by blocked-matrix least-squares minimisation of the function $\Sigma(|F_o|-|F_c|)^2/\sigma^2(|F_o|)$. Anisotropic temperature factors were used for Pt, Cl, P, O, F and C(51) atoms only. The atomic scattering factors were taken from ref. 9, and the anomalous scattering of platinum, chlorine and phosphorus atoms was accounted for [9]. No allowance was made for the scattering of hydrogen atoms. The refinement converged at R = 0.082 and R_w = 0.098. In the last cycle of refinement no parameter shifted by more than 0.1σ. An analysis of $<(|F_o|-|F_c|)^2/\sigma^2(|F_o|)>$ as a function of $|F_o|$ and sinθ revealed no unexpected trends.

Final atomic parameters, and a selection of the molecular geometry functions derived from them, are presented in Tables 1 and 2.*

The computer programs used are those listed in ref. 10.

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* A table of the observed and calculated structure amplitudes can be obtained from the authors on request.

Results and Discussion

The crystal structure is built of discrete dinuclear $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$ cations and octahedral $[PF_6]^-$ anions, the shortest distances between atoms in different ions being close to the sums of the appropriate van der Waals radii.

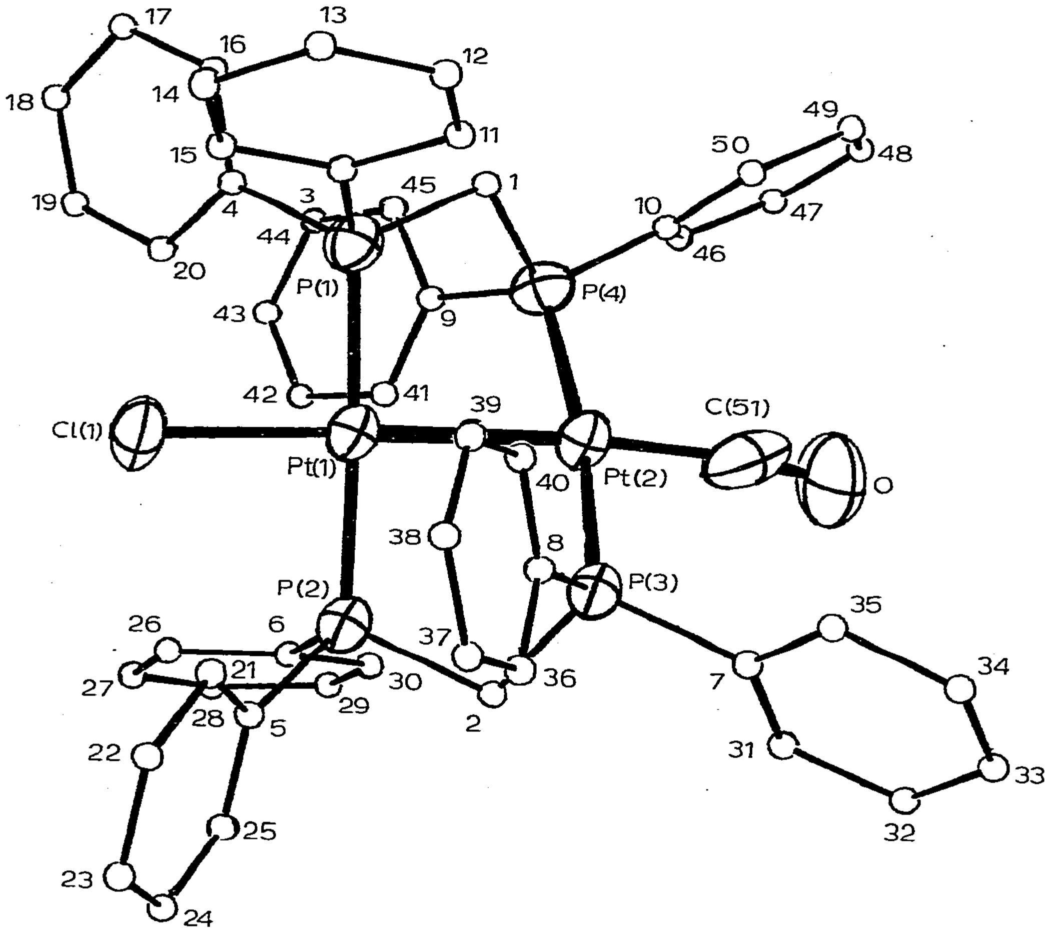

Figure - A view of the structure of $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$. The vibrational ellipsoids of Pt, P, Cl, O and C(51) atoms display 50% probability. For clarity, the remaining carbon atoms are represented by circles of arbitrary size; they are labelled by numbers only, corresponding to those listed in Table 1.

(Continued on p. 485)

Table 1

Fractional coordinates (x10^5 for Pt, x 10^4 for the other atoms) and vibrational parameters of atoms

Atom	x	y	z	U_{iso}x10^3
Pt(1)	31035(6)	37598(5)	18583(3)	*
Pt(2)	31310(6)	22834(5)	13607(3)	*
Cl(1)	3057(4)	5082(3)	2333(2)	*
P(1)	4270(4)	4350(3)	1326(2)	*
P(2)	2056(4)	3154(3)	2451(2)	*
P(3)	1375(4)	2308(3)	1460(2)	*
P(4)	4866(4)	2544(3)	1270(2)	*
P(5)	7341(6)	2592(5)	4540(3)	*
F(1)	8235(25)	2550(26)	4240(14)	*
F(2)	6969(19)	1779(18)	4281(12)	*
F(3)	7715(21)	3463(13)	4802(11)	*
F(4)	6365(21)	2622(27)	4800(13)	*
F(5)	6722(31)	3074(24)	4108(14)	*
F(6)	7971(22)	2156(15)	5016(11)	*
O	3038(18)	0437(12)	0967(9)	*
C(1)	4854(16)	3581(13)	0918(8)	55(5)
C(2)	1299(15)	2248(12)	2170(8)	50(5)
C(3)	3715(16)	5163(14)	0870(8)	60(5)
C(4)	5375(14)	4897(12)	1677(7)	49(5)
C(5)	1037(15)	3781(13)	2712(8)	54(5)
C(6)	2841(15)	2787(13)	3037(8)	51(5)
C(7)	0573(14)	1443(12)	1174(7)	47(5)
C(8)	0678(14)	3252(12)	1229(7)	44(4)
C(9)	5767(16)	2668(13)	1872(8)	57(5)
C(10)	5508(16)	1777(13)	0858(8)	56(5)
C(11)	3331(19)	4885(16)	0313(10)	74(6)
C(12)	2923(18)	5577(16)	-0004(10)	71(6)
C(13)	2923(19)	6379(16)	0136(10)	73(7)
C(14)	3296(22)	6655(19)	0646(11)	91(8)
C(15)	3682(18)	6006(15)	1011(9)	65(6)
C(16)	6068(18)	5359(15)	1400(9)	68(6)
C(17)	6883(20)	5796(17)	1683(11)	83(7)
C(18)	7033(21)	5707(18)	2226(11)	88(8)
C(19)	6381(18)	5233(16)	2505(9)	70(6)

Table 1 (continued)

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{U}_{iso}$ $\times 10^3$
C(20)	5532(16)	4818(14)	2241(9)	62(5)
C(21)	0637(17)	4511(15)	2432(9)	65(6)
C(22)	−0269(22)	4915(18)	2585(11)	92(8)
C(23)	−0716(25)	4591(21)	3062(13)	106(10)
C(24)	−0324(23)	3873(19)	3308(12)	93(8)
C(25)	0536(19)	3487(16)	3153(10)	74(7)
C(26)	3110(19)	3409(16)	3428(10)	77(7)
C(27)	3776(21)	3079(18)	3892(11)	84(7)
C(28)	4129(21)	2289(18)	3919(11)	82(7)
C(29)	3853(22)	1671(18)	3520(11)	89(8)
C(30)	3218(17)	1954(14)	3059(9)	64(6)
C(31)	0437(17)	0688(14)	1446(9)	63(6)
C(32)	−0174(18)	0011(15)	1214(9)	67(6)
C(33)	−0618(20)	0087(17)	0704(11)	82(7)
C(34)	−0542(24)	0846(21)	0434(12)	104(9)
C(35)	0123(22)	1534(18)	0659(11)	90(8)
C(36)	−0334(17)	3373(15)	1364(9)	62(6)
C(37)	−0873(18)	4141(16)	1214(9)	72(6)
C(38)	−0416(19)	4742(16)	0879(10)	76(7)
C(39)	0514(19)	4604(16)	0725(10)	74(7)
C(40)	1096(16)	3843(13)	0897(8)	56(5)
C(41)	5362(16)	2485(14)	2372(8)	58(5)
C(42)	6070(18)	2638(15)	2832(10)	70(6)
C(43)	7049(19)	2943(15)	2799(10)	72(6)
C(44)	7415(21)	3093(18)	2289(11)	85(7)
C(45)	6764(17)	2970(14)	1830(9)	62(6)
C(46)	6190(24)	1223(19)	1076(12)	99(9)
C(47)	6712(30)	0573(25)	0780(16)	133(12)
C(48)	6404(25)	0548(20)	0232(13)	103(9)
C(49)	5695(28)	1151(22)	0008(15)	117(11)
C(50)	5203(23)	1766(19)	0316(12)	94(8)
C(51)	3098(19)	1144(18)	1101(10)	*

Table 1 (continued)

*These atoms were assigned anisotropic temperature factors of the form $\exp(-2\pi^2 \times 10^{-n} \sum_{i=1}^{3} \sum_{j=1}^{3} \underline{U}_{ij} \underline{h}_i \underline{h}_j \underline{a}_i^* \underline{a}_j^*)$, where n is 4 for Pt and 3 for other atoms. The $\underline{U}_{ij}$ parameters are:

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{12}$	$\underline{U}_{13}$	$\underline{U}_{23}$
Pt(1)	453(4)	406(4)	330(4)	-23(3)	-33(3)	-8(3)
Pt(2)	466(4)	447(4)	377(4)	-14(4)	-16(3)	-44(3)
Cl(1)	65(3)	47(3)	72(4)	-3(3)	-2(3)	-19(3)
P(1)	51(3)	47(3)	36(3)	-3(2)	-3(2)	2(2)
P(2)	46(3)	45(3)	33(2)	-5(2)	-4(2)	-2(2)
P(3)	47(3)	45(3)	32(2)	-6(2)	-1(2)	-4(2)
P(4)	46(3)	50(3)	42(3)	2(2)	4(2)	6(2)
P(5)	78(5)	94(5)	46(3)	3(4)	-11(3)	-1(3)
F(1)	204(30)	384(46)	224(31)	-133(31)	121(26)	-166(33)
F(2)	149(19)	178(23)	277(31)	-52(17)	10(20)	-144(24)
F(3)	213(25)	96(14)	222(27)	5(16)	-66(21)	-4(16)
F(4)	142(22)	411(50)	207(30)	-28(26)	64(21)	-159(33)
F(5)	278(40)	264(38)	209(32)	-38(30)	-145(30)	76(29)
F(6)	217(26)	160(21)	212(26)	-5(18)	-88(21)	113(19)
O	149(19)	58(12)	122(17)	3(12)	22(14)	-36(11)
C(51)	66(15)	90(19)	72(16)	-30(14)	-6(12)	33(15)

The small $[PF_6]^-$ ion is subject to relatively high thermal motion and its geometry displays no unexpected features. The P-F bond lengths are 1.43(3) - 1.57(2)Å and the F-P-F bond angles are 83(2) - 96(2)° and 175(2) - 178(2)°.

The structure of the $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$ cation, shown in the Figure, is compatible with spectroscopic evidence [3] and is closely similar to that of the parent compound $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [5,6]. It comprises Pt-Cl and Pt-CO fragments bridged by two dppm ligands and linked directly through a Pt-Pt bond. Each platinum atom is in a somewhat distorted square planar environment, the distortions being larger around the platinum atom coordinated by the carbonyl group. They are

Table 2

Selected interatomic distances and angles in $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$

(a) Bond lengths (Å)

Pt(1)-Pt(2)	2.620(1)	Pt(2)-C(51)	1.89(3)
Pt(1)-Cl(1)	2.384(5)	C(51)-O	1.15(3)
Pt(1)-P(1)	2.291(5)	Pt(2)-P(4)	2.308(5)
Pt(1)-P(2)	2.298(5)	Pt(2)-P(3)	2.303(5)
P(1)-C(1)	1.79(2)	P(4)-C(1)	1.84(2)
P(1)-C(3)	1.82(2)	P(4)-C(9)	1.84(2)
P(1)-C(4)	1.83(2)	P(4)-C(10)	1.83(2)
P(2)-C(2)	1.82(2)	P(3)-C(2)	1.80(2)
P(2)-C(5)	1.81(2)	P(3)-C(7)	1.81(2)
P(2)-C(6)	1.81(2)	P(3)-C(8)	1.80(2)

(b) Bond angles (°)

P(1)-Pt(1)-P(2)	174.8(2)	P(4)-Pt(2)-P(3)	168.9(2)
Cl(1)-Pt(1)-Pt(2)	178.3(1)	C(51)-Pt(2)-Pt(1)	171.3(8)
Cl(1)-Pt(1)-P(1)	89.5(2)	C(51)-Pt(2)-P(4)	97.2(8)
Cl(1)-Pt(1)-P(2)	89.4(2)	C(51)-Pt(2)-P(3)	93.4(7)
P(1)-Pt(1)-Pt(2)	92.1(1)	P(4)-Pt(2)-Pt(1)	86.8(1)
P(2)-Pt(1)-Pt(2)	89.0(1)	P(3)-Pt(2)-Pt(1)	83.1(1)
P(1)-C(1)-P(4)	107(1)	P(2)-C(2)-P(3)	106(1)
Pt(1)-P(1)-C(1)	113.4(7)	Pt(2)-P(4)-C(1)	103.4(7)
Pt(1)-P(1)-C(3)	113.9(7)	Pt(2)-P(4)-C(9)	119.4(7)
Pt(1)-P(1)-C(4)	115.5(6)	Pt(2)-P(4)-C(10)	115.6(7)
Pt(1)-P(2)-C(2)	113.1(6)	Pt(2)-P(3)-C(2)	104.1(6)
Pt(1)-P(2)-C(5)	120.1(7)	Pt(2)-P(3)-C(7)	118.7(6)
Pt(1)-P(2)-C(6)	109.7(7)	Pt(2)-P(3)-C(8)	116.8(6)
C(1)-P(1)-C(3)	105.6(10)	C(1)-P(4)-C(9)	106.4(9)
C(1)-P(1)-C(4)	103.9(9)	C(1)-P(4)-C(10)	106.6(9)
C(3)-P(1)-C(4)	103.4(9)	C(9)-P(4)-C(10)	104.5(9)
C(2)-P(2)-C(5)	100.1(9)	C(2)-P(3)-C(7)	106.2(9)
C(2)-P(2)-C(6)	108.4(9)	C(2)-P(3)-C(8)	107.2(9)
C(5)-P(2)-C(6)	104.4(9)	C(7)-P(3)-C(8)	103.0(8)
		Pt(2)-C(51)-O	176(2)

Table 2 (continued)

(c) Torsion angles (°)

Pt(2)-P(4)-C(1)-P(1)	59.6(10)	Pt(2)-Pt(1)-P(1)-C(1)	-10.5(8)
Pt(2)-P(3)-C(2)-P(2)	56.8(9)	Pt(2)-Pt(1)-P(2)-C(2)	-25.7(7)
Pt(1)-P(1)-C(1)-P(4)	-28.1(12)	Pt(1)-Pt(2)-P(4)-C(1)	-57.1(7)
Pt(1)-P(2)-C(2)-P(3)	-14.9(11)	Pt(1)-Pt(2)-P(3)-C(2)	-65.2(7)
P(1)-Pt(1)-Pt(2)-P(4)	34.9(2)	P(2)-Pt(1)-Pt(2)-P(3)	44.8(2)

evident from the bond angles subtended at the metal centres (Table 2) and also from the displacements of atoms from the two coordination planes. These displacements do not exceed 0.10Å, except for the carbonyl carbon [C(51)] which lies -0.27Å away from the mean Pt_2P_2C plane. The out-of-plane bending of the carbonyl group introduces a significant non-linearity of the Cl-Pt-Pt-CO fragment, the Pt(1)-Pt(2)-C(51) angle being 171.3(8)°.

The flexibility of the dppm ligands enables the molecule to adopt a stable twisted configuration: the Pt_2P_2Cl and Pt_2P_2C coordination planes are mutually rotated around the Pt-Pt bond to afford a dihedral angle of 40.1°. This allows the molecule to weaken considerably any antibonding interactions between filled interaxial metal d orbitals, which are almost as far from one another as possible (dihedral angle 45°).

The two dppm ligands display similar orientations with respect to the Cl-Pt-Pt-CO fragment, and the molecule therefore approximates to C_2 symmetry. As is evident from the torsion angles listed in Table 2, the conformations about the C(1)-P(4) and C(2)-P(3) bonds are practically staggered, while those about the C(1)-P(1) and C(2)-P(2) bonds are closer to eclipsed. The Pt-Pt bond is nearly eclipsed by the P(1)-C(1) and P(2)-C(2) bonds. The P(1)...P(4) and P(2)...P(3) non-bonding distances

[2.924(7) and 2.889(7)Å] are *ca.* 0.3Å longer than the Pt-Pt bond [2.620(1)Å]. This contraction of the $Pt_2C_2P_4$ fragment along the Pt-Pt bond leads to the unusually small Pt(2)-P(4)-C(1) and Pt(2)-P(3)-C(2) angles [103.4(7) and 104.1(6)°, respectively]. The other bond angles and the bond lengths within the dppm ligands are unexceptional. Thus the Pt(1)-P-CH_2 and Pt-P-C(phenyl) angles are larger, the C-P-C angles are smaller, and P-CH_2-P angles are close to the tetrahedral value (Table 2). The P-C bond lengths are 1.79(2) - 1.84(2)Å.

The Pt-P distances [2.291(5) - 2.308(5)Å] can be compared with the corresponding ones [2.250(7) - 2.294(7)Å] in [Pt_2Cl_2(μ-dppm)$_2$] [6] and with Pd-P distances [2.26(1) - 2.32(1)Å] in [Pd_2Br_2(μ-dppm)$_2$] [11]. The Pt-C and C-O bond lengths are 1.89(3) and 1.15(3)Å, respectively. The Pt-Cl distance [2.384(5)Å] lies within the range of Pt-Cl (*trans* to Pt) distances [2.382(10) - 2.426(9)Å] observed in [Pt_2Cl_2(μ-dppm)$_2$] and [$Pt_2Cl_4(CO)_2$]$^{2-}$, and may be considered indicative of high *trans*-influence of the Pt-Pt bond [6,12]. Indeed, the ability of carbon monoxide to compete with chloride for a metal centre in [Pt_2Cl_2(μ-dppm)$_2$], and thus form [$Pt_2Cl(CO)$(μ-dppm)$_2$]$^+$, has been attributed partly to the weakness of Pt-Cl bonds in the parent compound [3]. Displacement of chloride by carbon monoxide is not observed in the chemistry of square planar platinum(II) complexes.

The Pt-Pt distance [2.620(1)Å] is compared in Table 3 with Pt(I)-Pt(I) bond lengths found in other dinuclear complexes with, and without, bridging ligands. These bond lengths [2.58 - 2.65Å] are somewhat shorter than Pt(O)-Pt(O) distances in dinuclear complexes and clusters [2.65 - 2.79Å] (17,18]. The range of values they display (*ca.* 0.1Å) is likely to reflect different electronic properties and

Table 3

Metal-metal bond lengths in dinuclear complexes of platinum(I)

Compound	Pt-Pt(Å)	Ref.
$[NPr_4]_2[Pt_2Cl_4(CO)_2]$	2.584(2)	12
$[Pt_2(C_8H_{12})_2\{\mu-(CF_3)_2CO\}]$	2.585(1)	13
$[Pt_2(PPh_3)_2(\mu-PPh_2)_2]$	2.604(1)	14
$[Pt_2Cl(CO)(\mu-dppm)_2][PF_6]$	2.620(1)	This work
$[Pt_2\{P(OPh)_3\}_2(\mu-SPEt_2)_2]$	2.628(1)	15
$[Pt_2(PPh_3)_3(CO)(\mu-S)]$	2.647(2)	16
$[Pt_2Cl_2(\mu-dppm)_2]$	2.651(1)	6

perhaps even steric requirements of the ligands involved.

The only complexes in Table 3 which are closely related to each other are $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (I) and $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$ (II). They display a trend in the Pt-Pt distances which is compatible with their Raman and n.m.r. spectra. The Pt-Pt bond lengths are 2.651(1) and 2.620(1)Å, the ν(Pt-Pt) frequencies are 150 and 157 cm^{-1} and the $^{195}Pt-^{31}P$ coupling constants are -136 and -62, -92 Hz in I and II, respectively [1,3,7]. Thus the bond lengths in I and II lend some support to the suggestion of Brown *et al.* [7] that in complexes containing the $Pt_2(\mu\text{-dppm})_2$ unit the $^{195}Pt-^{31}P$ coupling constants depend on the strength of metal-metal bonding.

The square planar coordination geometry of the metal atoms in I and II indicates that in these d^9 complexes dsp^2 hybrid orbitals are used to form platinum-ligand bonds. Overlap of singly-occupied metal hybrid orbitals leads to formation of a metal-metal two-electron σ-bond. Replacement of one chloride ligand in I by a strongly electron withdrawing carbonyl group results in a contraction of the Pt–Pt bond by ca. 0.03Å. This can be attributed to some transfer of electron density from the filled anti-bonding *d* orbitals of platinum to the vacant π^* orbitals of the carbonyl group. Such an effect can be expected to weaken repulsive interactions between the antibonding orbitals of the metal atoms and thus contribute to further stabilisation of the metal-metal bonding.

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