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Preliminary communication

^{31}P NMR SPECTRA AND THE METAL—METAL BOND STRENGTH IN SOME BIS-μ-[BIS(DIPHENYLPHOSPHINO)METHANE] DIPLATINUM COMPLEXES

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Summary

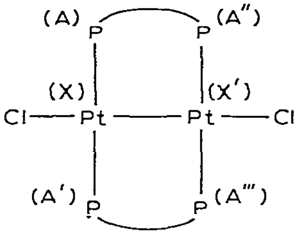
It is proposed that the magnitudes of the ^{31}P—^{31}P and ^{195}Pt—^{31}P long-range coupling constants in the title complexes may provide a measure of the strength of the Pt—Pt bonding.

A substantial number of complexes (I—V) containing the $Pt_2(\mu\text{-dppm})_2$ unit (dppm = bis(diphenylphosphino)methane) have been prepared recently [1—6]. Complexes I [1, 3], II [3, 5] and III [6] are believed to contain a strong Pt—Pt bond, whereas complexes IV [6] and V [2, 4] have either weaker Pt—Pt interactions, or no Pt—Pt bonding at all. The ^{31}P NMR spectra of the complexes can usually be interpreted readily, and the various coupling constants J(PtP) and J(PP) can be determined [1, 4].

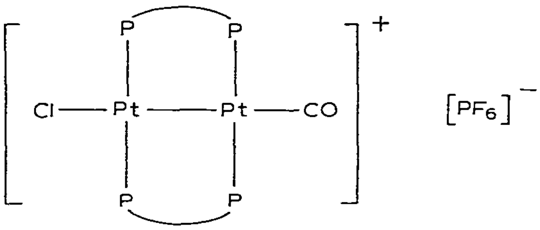
Using the nomenclature shown for structure I, the ^{31}P—^{31}P coupling constant $J(AA'')$ will have through-bond contributions $^2J(PCH_2P)$ and ^3J(PPtPtP), and $J(AA''')$ will have a similar contribution ^3J(PPtPtP) and a longer range coupling $^4J(PPtPCH_2P)$. Similarly, the ^{195}Pt—^{31}P coupling constant $J(AX')$ will have through-bond contributions ^2J(PPtPt) and $^3J(PCH_2PPt)$. It might be expected that the coupling constants $J(AA''')$ and $J(AX')$ will be very sensitive to the strength and length of the Pt—Pt bond, since a major contribution is expected from coupling through the Pt—Pt bond. Some typical coupling constants are given in Table 1.

Of the ^{31}P—^{31}P coupling constants, $J(AA'')$ does not vary greatly, and is presumably dominated by the contribution $^2J(PCH_2P)$. In contrast, however, the magnitude of $J(AA''')$ varies between 0 and 43 Hz in different complexes: it is largest for complexes I– III, less for V, and very small or zero for complexes IV. Thus, the magnitude of the coupling constant appears to increase with increasing Pt—Pt bond strength, as expected if the contribution ^3J(PPtPtP) is dominant. Indeed. ^4J(PPtPCH$_2$P) would be expected to be vanishingly small.

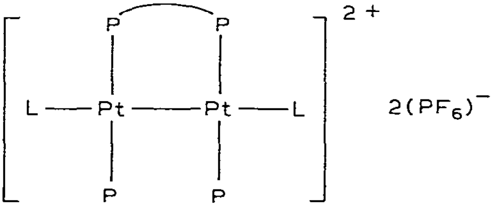
An even greater range is observed for the ^{195}Pt–^{31}P coupling constant, J(AX′). This has large negative values for complexes I—III, small negative or positive values for V, and large positive values for IV. These results can be explained if the contribution ^3J(PCH$_2$PPt) is positive, and ^2J(PPtPt) is negative. Thus, when the Pt—Pt bonding is strong, the negative contribution of ^2J(PPtPt) dominates, in



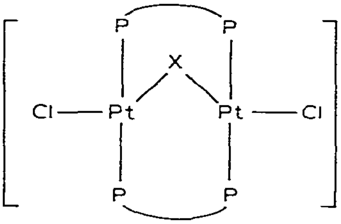
(I)



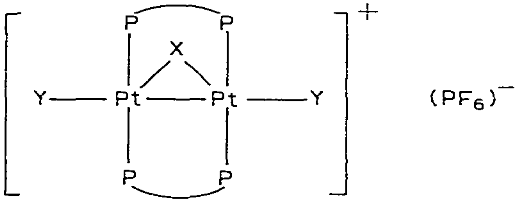
(II)



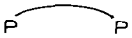
(IIIa) L = NH$_3$
(IIIb) L = C$_5$H$_5$N
(IIIc) L = CO



(IVa) X = CO
(IVb) X = S
(IVc) X = SO$_2$
(IVd) X = CH$_2$



(Va) X = Y = H
(Vb) X = Cl, Y = H
(Vc) X = H, Y = Cl



= Ph$_2$PCH$_2$PPh$_2$ = dppm

TABLE 1

SELECTED COUPLING CONSTANTS FROM THE ^{31}P NMR SPECTRA OF COMPLEXES I—V

Complex	$J(AA''')^a$ (Hz)	$J(AA''')^a$ (Hz)	$J(AX')^a$ (Hz)
II	46	43	62.92 [b]
IIIc	46	33	−96
IIIb	58	30	−113
IIIa	61	29	−124
I	63	26	−136
Vc	52	21	−40
Va	56	18	+16
Vb	55	17	0
IVd	23	6	+73
IVc	43	0	+283
IVa	65	0	+367

[a] For nomenclature, see structure I. [b] Sign unknown, but presumably negative.

intermediate situations the contributions cancel out, and when Pt—Pt bonding is very weak or absent, the positive contribution of $^3J(PCH_2PPt)$ predominates.

It is thus proposed that the coupling constants $J(AA''')$ and $J(AX')$ are dependent on the strength of the Pt—Pt bonding, and will provide a measure of that bond strength within each type of compound (I—V), as well as from one type to another, since this is a group of structurally related complexes. Confirmation of this prediction should be obtained by correlation of coupling constants with bond lengths obtained from X-ray studies (N.B. crystals of II, IVc and IVd are currently under active investigation), and it should then be possible to estimate the strength of the Pt—Pt interaction by measurement of these coupling constants. In the interim, it is apposite to note that the molecular structures of the related systems $[Pd_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2]$ [7], $[Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-dppm})_2]$ [8], $[Pd_2Br_2(\mu\text{-dppm})_2]$ [9] and $[Pd_2Cl_2(\mu\text{-}CO)(\mu\text{-dam})_2]$ [10] (where dam = bis(diphenylarsino)methane) show metal—metal bond lengths totally in accord with our predictions for their platinum analogues, and that $[Pt_2Cl_2(\mu\text{-dppm})_2]$ has a Pt—Pt bond length of 0.2652 nm [3].

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