Platinum(I) Dimer Chemistry: Distortion of Co-ordination Geometry in $[Pt_2Br_2(\mu\text{-}CO)(PPh_3)_3]$

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X-Ray crystal structure determination and spectroscopic measurements on the title compound show it to have an asymmetrically bridging CO ligand which is believed to lead to some valence disproportion in contrast to its precursor $[Pt_2Br_4(CO)_2]^{2-}$.

There are several examples of dimers of type M_2L_6 in which there are 9 d-electrons per metal. Most of the previously reported geometries can be classified as structures (I) or (II) where the metal is in a square planar environment or structure (III) which has tetrahedral co-ordination about the metal.[1,2]

These types are exemplified by $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$,[2] $[Pt_2Cl_4(CO)_2]^{2-}$,[3] and $[Fe_2(\mu\text{-}I)_2(NO)_4]$,[4] respectively. Another, highly distorted, geometry structure (IV) has been found for $[Rh_2(\mu\text{-}CO)_2(PPh_3)_4]$.[5] In the course of exploring Pt^I dimer chemistry, we have observed a new structural form (V) which represents a novel distortion of (II) and provides useful insight into form (IV).

Depending on stoicheiometry, treatment of $[Pt_2X_4(CO)_2]^{2-}$, (**1a**) and (**1b**), with PPh_3 in CH_2Cl_2 affords a variety of phosphine substituted derivatives, as shown in Scheme 1. Three spectroscopic features are relevant to the present discussion as they differentiate the structural form of species (**5**) and (**6**) from that of (**1**)—(**4**).† Firstly, i.r. spectra of (**2**), (**3**), and (**4**) in solution show two CO stretching frequencies in the range 2 075—2 025 cm^{-1} comparable with the spectrum of (**1**).[6] In contrast, (**5b**) and (**6b**) show single CO stretches at 1 825 and 1 820 cm^{-1}, respectively, consistent with a bridging CO ligand. Secondly, analyses of the n.m.r. spectra of samples of (**2**), (**3**), and (**4**) containing ^{13}C enriched carbonyl show that $^2J(PtC)$ is small and negative (> -60 Hz) similar to that observed for (**1**).[7] However, species (**5**) and (**6**) have large

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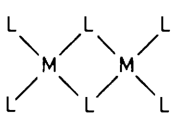
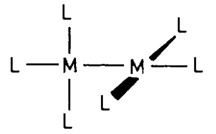
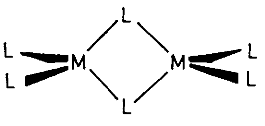
† Full details of the spectroscopic characterisation and chemistry of these species will be reported elsewhere.



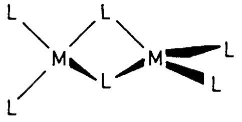
(I)



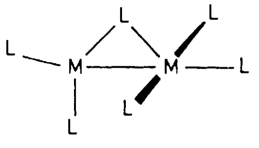
(II)



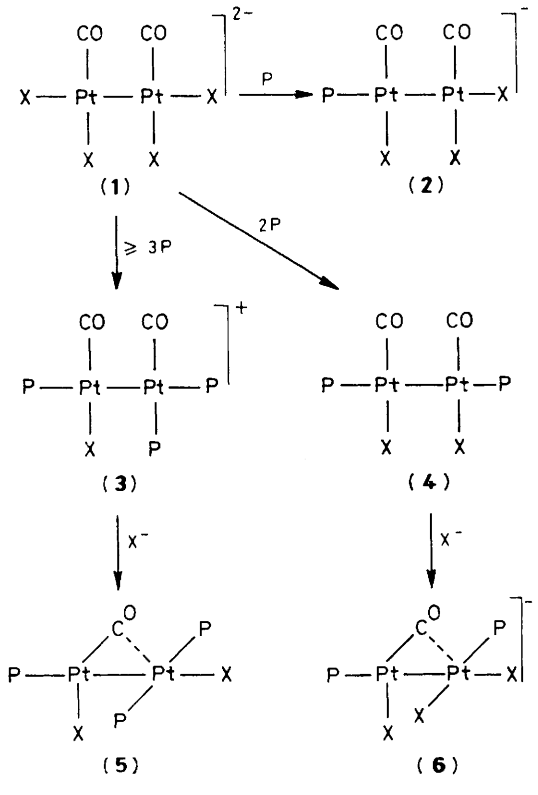
(III)



(IV)



(V)



P = PPh_3
a; X = Cl
b; X = Br

Scheme 1. Reactions of $[NBu^n_4]_2[Pt_2X_4(CO)_2]$ with PPh_3.

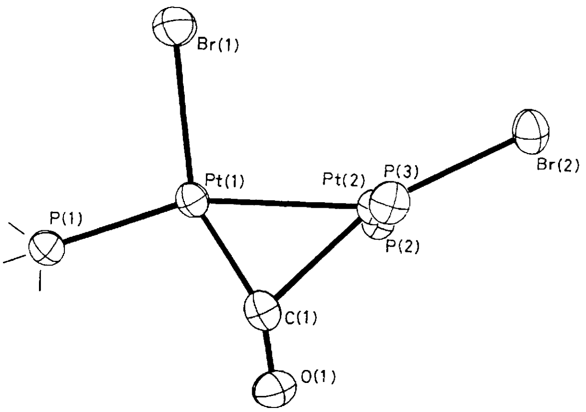


Figure 1. The molecular structure of (**5b**); phenyl groups are omitted for clarity. Important geometric parameters are: bond lengths Pt(1)–Pt(2) 2.654(1), Pt(1)–Br(1), 2.507(2), Pt(1)–P(1) 2.243(3), Pt(1)–C(1) 1.901(13), Pt(2)–Br(2) 2.533(1), Pt(2)–P(2) 2.321(3), Pt(2)–P(3) 2.319(3), Pt(2)–C(1) 2.218(13) Å; bond angles Pt(2)–Pt(1)–C(1) 55.3(4), Pt(1)–C(1)–O(1) 156.1(11), Pt(2)–C(1)–O(1) 124.1(10), Br(1)–Pt(1)–P(1) 102.4(1), P(1)–Pt(1)–C(1) 104.4(4), P(1)–Pt(1)–Pt(2) 159.6(1), P(2)–Pt(2)–P(3) 171.5(1), Br(1)–Pt(1)–C(1) 153.1(4)°.

positive ^2J(PtC) (*ca.* 450—650 Hz) indicating a substantial interaction between CO and the second platinum atom. Finally, ^1J(PtP) for the phosphine *trans* to the Pt–Pt bond lies in the range 2 150—2 550 Hz for (**2**), (**3**), and (**4**), whereas for (**5**) and (**6**) it is over twice as large (in the range 5 350—5 760 Hz). We conclude that the geometries of (**2**), (**3**), and (**4**) resemble that of (**1**) and belong to type (II) whereas (**5**) and (**6**) belong to a different structural class. The details of the solid state structure of (**5b**) were revealed by an *X*-ray diffraction study on its hemi dichloromethane solvate.

Crystal data for (**5b**)·$0.5CH_2Cl_2$: $C_{55}H_{45}Br_2OP_3Pt_2 \cdot C_{0.5}HCl$, M = 1 401.4, monoclinic, space group $P2_1/c$, a = 12.615(4), b = 18.369(6), c = 22.515(7) Å, β = 99.66(3)°, U = 5 143(3) Å^3, Z = 4, D_c = 1.81 g cm^{-3}, $F(000)$ = 2 784, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 72.2 cm^{-1}. Data were collected at room temperature on a Nicolet *P*3*m* diffractometer by a $\theta/2\theta$ scan technique in the range $4° < 2\theta < 50°$. The structure was solved by direct and Fourier methods and refined by least squares to give a current residual index R = 0.036 for 4 142 unique, absorption corrected, observed intensity data with $I > 2\sigma(I)$.‡

The molecular geometry is illustrated in Figure 1. The Pt–Pt separation of 2.654(1) Å, although slightly longer than for (**1a**) [2.584(2) Å], is still consistent with a formal bond order of unity. Similar short metal–metal distances are characteristic of all types (I)—(IV). The carbonyl ligand asymmetrically bridges the Pt–Pt bond, being more tightly bound to Pt(1). The two, approximately planar, PtL_3 fragments are mutually orthogonal. Whilst the inter-bond angles within the $Pt(2)P_2Br$ fragment correspond approximately to square planar co-ordination as found for the $PtCl_2CO$ unit of (**1a**)[3] and most d^8 platinum(II) complexes, the angles about Pt(1) are significantly greater. Thus the ligand arrangement at Pt(1) is intermediate between mono-vacant square-planar and trigonal planar: the latter is, of course, a common structure for d^{10} platinum(0). A partial zero-valent character would offer an explanation of the large value of ^1J(PtP) to Pt(1), *e.g.* compare values for $[Pt_3(PR_3)_3(CO)_3]$.[8] Thus the geometric features of the solid state structure are entirely in accord with the solution state spectroscopic evidence and suggest some degree of mixed valence character in structure (V).

To investigate this further we have carried out EHMO calculations[9] on model complexes $[Pt_2Cl_2(CO)(PH_3)_3]$ and

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‡ The atomic co-ordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communcation.

$[Pt_2Cl_5(CO)]^{3-}$ with geometries respectively derived from the structure of (**5b**) and idealised from type (II) [with PtL_3 planes mutually orthogonal unlike (**1a**)]. These calculations show that, in the latter case, as is known,[10] each PtL_3 fragment has a high-lying orbital of σ symmetry, which is half occupied for the formal oxidation state $+1$; it is the overlap of these orbitals which gives rise to the Pt–Pt bond. Changing the geometry from type (II) to type (V) markedly lowers the energy of this orbital on Pt(1) by mixing it with a CO π^* orbital. As a consequence the HOMO of $[Pt_2Cl_2(CO)(PH_3)_3]$ with structure (V) is concentrated on the $PtCl(CO)(PH_3)$ fragment rather than evenly shared as in structure (II). Thus the CO ligand allows charge to be transferred from Pt(2) to Pt(1) by adopting the observed asymmetric bridging geometry. The ability of semi-bridging carbonyls to transfer charge between metal atoms has been noted previously;[11] usually such transfer *reduces* any charge imbalance associated with differences in formal oxidation state.

It is notable here that a movement of the CO from a terminal site as in (**1**) to a semi-bridging position brings about partial valence disproportionation, *i.e.* charge *separation* in a formal sense, the converse of the usual role of this bonding mode. It is significant that the bridged geometry occurs only for the mono-carbonyl species (**5**) and (**6**) where the Pt atom not carrying a CO ligand would be most loaded with electron density.

In structure (IV) each Rh is almost coplanar with its three nearest ligands and the bond angles at the metal are >90°. The two planes are approximately orthogonal with both carbonyls asymmetrically bridging. It can be viewed, therefore, as a double distortion of the sort shown by (**5b**) although allowing charge delocalisation rather than charge transfer.

We thank the S.E.R.C. for funds for the purchase of equipment and the University of Bristol for a studentship (to I. R. H.).

Received, 31st August 1983; Com. 1173

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