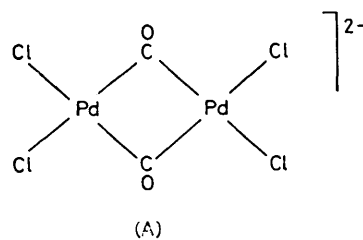


Bridging by Carbonyl *vs.* Halide Ligands: X-Ray Crystal Structure of of $[\text{NBu}_4^+]_2[\text{Pd}_2\text{Cl}_4(\mu\text{-CO})_2]^{2-}$

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Summary The dimeric d^8 Pd^{II} dianion $[\text{Pd}_2\text{Cl}_4(\text{CO})_2]^{2-}$ is shown to have two bridging carbonyl ligands, both in the solid state and in solution, by X-ray structure analysis and i.r. spectroscopy; this is in contrast with a large number of d^8 di- and polymeric metal carbonyl halide complexes where the halide ligands are bridging.

FROM an analysis of its vibrational spectra, Goggin and Mink¹ proposed structure (A) for the dianion $[\text{Pd}_2\text{Cl}_4(\text{CO})_2]^{2-}$.



The observed carbonyl stretching frequencies (1 966m, 1 906s, $[\text{NBu}_4]^+$ salt, CH_2Cl_2 solution) are well above the usual wavenumber range for bridging CO groups and such a structure contravenes the rule that in metal carbonyl halide complexes, any bridging is by halide rather than CO.² {The compound $[\text{Pd}_2\text{Cl}_4(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2)_2(\text{CO})]$ is also an exception to this rule but in this case the CO stretching frequency is very low ($1\,720\text{ cm}^{-1}$)³ and the complex can be envisaged as a di-palladium ketone derivative.} The original routes¹ to salts of $[\text{Pd}_2\text{Cl}_4(\text{CO})_2]^{2-}$ did not give crystals suitable for X-ray crystallographic study. However, following our investigations into the preparation of platinum(II) carbonyl halide anions,⁴ we find that suitable crystals of $[\text{NBu}_4]^2_2[\text{Pd}_2\text{Cl}_4(\text{CO})_2]$ (1) are produced when $[\text{NBu}_4]^+[\text{PdCl}_3(\text{CO})]$ is treated with trimethylamine in acetone followed by addition of diethyl ether to enhance crystallisation. The structure of (1) was determined by X-ray diffraction.

Crystal data: $\text{C}_{34}\text{H}_{72}\text{Cl}_4\text{O}_2\text{Pd}_2$, $M = 866.8$, monoclinic, space group $P2_1/c$, $a = 18.007(12)$, $b = 15.136(5)$, $c = 18.709(6)$ Å, $\beta = 122.48(5)^\circ$, $U = 4\,302(4)$ Å³, $Z = 4$, $D_c = 1.33\text{ g cm}^{-3}$, $F(000) = 1\,864$ electrons, $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 11.04\text{ cm}^{-1}$. The structure was solved by conventional heavy atom methods (Patterson and Fourier) and refined by full-matrix blocked-cascade least squares.† For 4 177 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at 195 K on a Nicolet R3m diffractometer in the range $3 < 2\theta < 50^\circ$ the current R is 0.0353.‡ The structure consists of two independent $[\text{Pd}_2\text{Cl}_4(\mu\text{-CO})_2]^{2-}$ units, each centred on a crystallographic centre of inversion, and two $[\text{NBu}_4]^+$ cations in general positions within the unit cell. The $\text{Pd}_2(\mu\text{-C})_2$ moieties are therefore strictly planar and show Pd-Pd separations [mean Pd-Pd $2.697(5)$ Å] consistent with a formal metal-metal bond order of one. The geometry of the dianion is illustrated in Figure 1. Both dianions show a significant tetrahedral distortion of the Pd coordination geometry, the PdCl_2 planes being twisted from

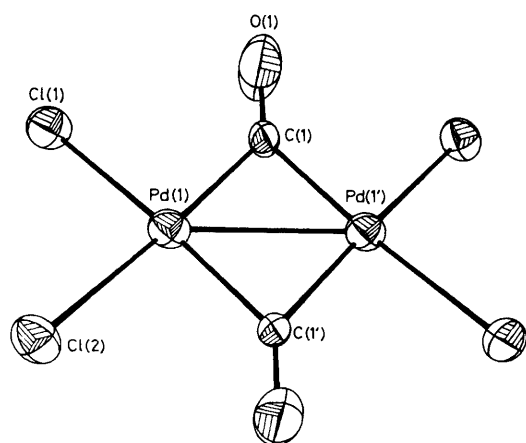


FIGURE 1. Molecular structure of one of $[\text{Pd}_2\text{Cl}_4(\mu\text{-CO})_2]^{2-}$ ions viewed perpendicular to the $(\mu\text{-CO})_2\text{Pd}_2$ unit. Mean dimensions: Pd-Pd $2.697(3)$, Pd-C $1.994(9)$, Pd-Cl $2.372(4)$, C-O $1.140(10)$ Å, Pd-C-Pd $85.2(3)^\circ$.

† All calculations were carried out with the SHELXTL program package on the Nicolet R3m structure determination system.

‡ Atomic co-ordinates 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 communication.

the $\text{Pd}_2(\mu\text{-C})_2$ by 8.1 and 10.5° in the two independent anions. The planarity of the dibridged unit is in accord with the solid state i.r. spectrum of this crystal modification which shows only the asymmetric stretches ($1\,896$ and $1\,903\text{ cm}^{-1}$ corresponding to the two independent molecules). The presence of the band at $1\,966\text{ cm}^{-1}$, due to the symmetric stretch, in i.r. spectra of solutions¹ indicates that the $\text{Pd}_2(\mu\text{-C})_2$ moiety becomes puckered.

The statement that 'when they (metal carbonyl halide complexes) are dimeric or polymeric they are invariably bridged by the halogen atom and not by carbonyl bridges'² implies that μ -halide and μ -carbonyl ligands are interchangeable structural units. Although both ligands have orbitals of σ and π symmetry available for co-ordination, these π orbitals are filled for μ -halide anions (*e.g.* 3p orbitals in Cl^-) and empty in the case of $\mu\text{-CO}$ (*i.e.* the π^* orbitals). This implies differing structural behaviour, resulting from

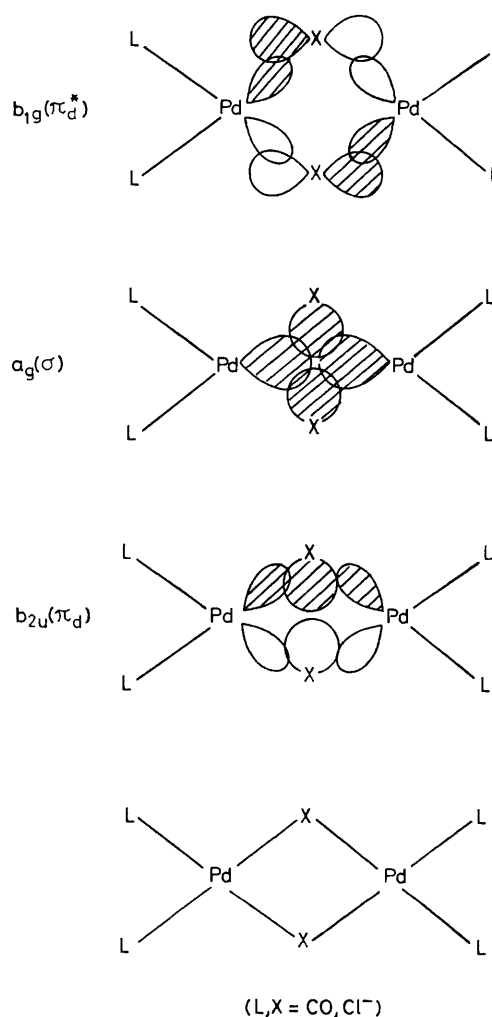


FIGURE 2. Frontier molecular orbitals involved in bridging ligand bonding in $[\text{Pd}_2\text{L}_4(\mu\text{-X})_2]$; labels assume local D_{2h} symmetry of the $\text{Pd}_2(\mu\text{-X})_2$ unit, labels in parentheses refer to fragment orbitals of planar Pt_2L_4 fragment (ref. 5).

the ability of (μ -CO) to stabilise filled metal orbitals of suitable symmetry, which orbitals will be destabilised by interaction with filled π orbitals when (μ -CO) is replaced by μ -halide.

We expect the frontier orbitals of a planar $L_2Pd-PdL_2$ fragment to be qualitatively similar to those of $L_2Pt-PtL_2$ whose bonding capabilities have been analysed by Dedieu and Hoffmann.⁵ In this analysis there are three in-plane fragment orbitals (f.o.'s) which may interact with the in-plane orbitals of two bridging ligands (X) as depicted in Figure 2. In the case where X is CO and $PdL_2 = [PdCl_2]^-$ (*i.e.* the metals are in oxidation state +1) only the b_{2u} , a_g , and b_{1g} m.o.'s will be filled (those arising from the π_d , σ , and π_d^* f.o.'s in the notation of ref. 5). The a_g and b_{1g} orbitals are greatly lowered in energy by interaction of the σ and π^* CO ligand orbitals with the σ and π_d^* f.o.'s, giving a net Pd-Pd bond order of one; similar behaviour has been

noted for μ -Fe(CO)₄ bridging of the Pt_2L_4 fragment.⁵ Bridging by chloride [$X = Cl^-$, $PdL_2 = Pd(CO)Cl$] will likewise result in occupancy of these three m.o.'s. However the b_{1g} orbital will be much higher in energy because of the unfavourable interaction between the filled π_d^* and Cl π orbitals. Consequently this chloride-bridged geometry is not favoured for Pd^I; for Pd^{II} the b_{1g} m.o. is not occupied, so bridging by halide is preferred.⁶

Finally, the absence of any bridging ligands in the Pt^I analogue⁷ of the title complex follows the established tendency of the third row transition elements towards solely terminal CO co-ordination.

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