

Preliminary communication

The Structure of $[\text{Pd}_3(\eta^3\text{-2-Methylallyl})_2\text{Cl}_4]$

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SUMMARY. An X-ray crystal structure determination of $[\text{Pd}_3(2\text{-methylallyl})_2\text{Cl}_4]$ shows it to be centrosymmetric with a rippled near-planar arrangement of $\text{PdCl}_2\text{PdCl}_2\text{Pd}$, the terminal Pd atoms being η^3 -bonded to the 2-methylallyl ligand.

A common feature of preparations involving the reactions of PdCl_2 with unsaturated hydrocarbons is the formation of rather insoluble brown compounds of the types $[\text{LPdCl}(\text{PdCl}_2)_n]$ (A) [1-3] or $[\text{L}'\text{PdCl}_2(\text{PdCl}_2)_n]$ (B) [4-5]. Until recently the constitution of neither was known and it was not apparent what, if any, mechanistic implications these compounds had in organo-palladium chemistry. We recently reported the structure of a compound of type (B), a cyclobutadiene complex of empirical formula $[\text{Pd}_3(\text{CB})_2\text{Cl}_6]$ (I), which we found to be ionic with the structure $2[(\text{CB})\text{PdCl}_3\text{Pd}(\text{CB})][\text{Pd}_2\text{Cl}_6]$. (CB = η^4 -1,2-di-*t*-butyl(3,4-dimethyl)cyclobutadiene) [6]. We now report the structure determination of a complex of type (A), derived from di- μ -chlorobis(η^3 -2-methylallylpalladium), (II).

Reaction of (II) with $[\text{PdCl}_2(\text{PhCN})_2]$ in a variety of solvents produced an insoluble red-brown precipitate which analysed for $[\text{Pd}_3(2\text{-MeC}_3\text{H}_4)_2\text{Cl}_4]_n$ (III). Small crystals were eventually obtained by allowing the complex to crystallise slowly from hot nitromethane/nitroethane solution.

Crystal data for (III). $\text{C}_8\text{H}_{14}\text{Cl}_4\text{Pd}_3$, $M = 571.2$, triclinic, $a = 8.281(5)$, $b = 8.969(6)$, $c = 6.025(4)\text{\AA}$, $\alpha = 102.28(2)$, $\beta = 87.11(1)$, $\gamma = 125.25(1)^\circ$, $Z = 1$ space group $\text{P}\bar{1}$. Single crystals of the sample could not be found, the crystals in general being twinned such that their c axes were apparently coincident but in opposite directions. A zero level Weissenberg photograph of the sample

showed that the twinning corresponded to rotational separation of the chosen \underline{b}^* axes in the two components of approximately 15° ; this was however sufficient to enable a determination of the unit cell. Three dimensional X-ray data were collected with the crystal mounted along the \underline{c} axis, using Mo-K α radiation and a Stoe STADI-2 diffractometer in the stationary-counter-moving-crystal mode. The data were carefully scrutinised for possible overlap of reflections from the two crystals; any which showed such interference were scanned manually and excluded where the ambiguity could not be satisfactorily resolved. A total of 1024 independent reflections were obtained with $I_{\text{obs}} \geq 3\sigma(I_{\text{obs}})$.

The structure was solved by Patterson and Fourier methods, and refined using block diagonal least-squares to $R = 0.067$, at which stage the thermal parameters were anisotropic for the palladium and chlorine atoms, and isotropic for the carbon atoms.

The structure is shown in the Figure. The molecule (III) has a centre of symmetry at Pd(1) and each half includes a 2-methylallyl symmetrically η^3 -bonded, in the conventional manner [7], to Pd(2).* The two Pd(2) atoms are bonded to Pd(1) via Cl-bridges and the complex may be thought of as derived from (II) by the insertion of PdCl₂ into the Pd₂Cl₂ bridge. The η^3 -allyl group lies at an angle of 113° to the Pd(2)Cl(1)Cl(2) coordination plane and the plane defined by Pd(1)Cl(1)Cl(2) is at an angle of 158° to Pd(2)Cl(1)Cl(2), giving a rather flat rippled appearance to the Pd₃Cl₄ unit. The Pd(1)-Cl bonds [average 2.305(9)Å] are significantly shorter [0.11Å, 1 σ] than the Pd(2)-Cl bonds [2.417(9)Å] and it should be noted that the former distance is very close to Pd-Cl (terminal) in (NH₄)₂PdCl₄ [2.299(4)Å] [8] while the latter is close to Pd-Cl (bridging) in di- μ -chlorobis(η^3 -allylpalladium) [2.413(2)Å] [9].

The structure found for (III) is very similar to that which was originally suggested by Moiseev [1]. The point has however been made [2] that the far-i.r. spectra of complexes of this type show a very strong $\nu(\text{Pd-Cl})$ in the region

* The atomic coordinates 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 communication.

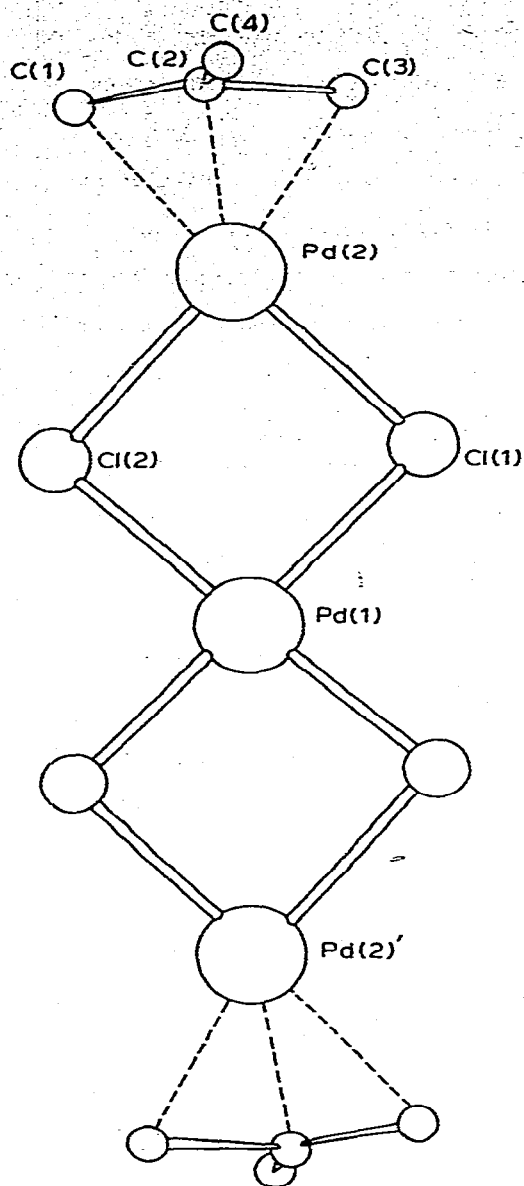
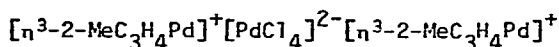


Figure. The structure of $[\text{Pd}_3(\eta^3\text{-2-MeC}_3\text{H}_4)_2\text{Cl}_4]$ (III).

Bond lengths: Pd(1)-Cl(1) 2.313(9), Pd(1)-Cl(2) 2.297(9), Pd(2)-Cl(1) 2.416(9), Pd(2)-Cl(2) 2.418(9), Pd(2)-C(1) 2.14(4), Pd(2)-C(2) 2.08(4), Pd(2)-C(3) 2.05(4), C(1)-C(2) 1.29(6), C(2)-C(3) 1.43(6), C(2)-C(4) 1.58(5) Å, and bond angles: Cl(1)Pd(1)Cl(2) 88.7(3), Pd(1)Cl(1)Pd(2) 91.4(3), Pd(1)Cl(2)Pd(2) 91.8(3), Cl(1)Pd(2)Cl(2) 83.6(2)°.

(> 300 cm^{-1}) normally associated with a terminal Pd-Cl bond and only much weaker bands in the lower frequency region (< 300 cm^{-1}) associated with bridging Pd-Cl bonds; for example, $\nu(\text{Pd-Cl})$ for (III) are observed at 326(vs), 268(m), 246(w) and 200(w) cm^{-1} . By comparison $\nu(\text{Pd-Cl})$ for (II) occur at 259(vs) and 248(vs) cm^{-1} and for $\text{M}_2[\text{PdCl}_4] \nu_6$ is observed as a very strong band between 332 and 317 cm^{-1} the exact position depending on the nature of M^+ [10,11]. Furthermore, the Raman spectrum of (III) shows major bands at 214(w), 267(m-w), 306(vs) and 387(m) cm^{-1} which correlate well with bands in K_2PdCl_4 at 196(m-s), 274(m-w) and 306(vs) cm^{-1} .

We suggest that a significant contribution to the bonding in (III) is given by the ionic form,



and it is interesting that in nitromethane solution complex (III) shows some conductivity ($\Lambda_M = 25 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$). While this value is very low for a 2:1 electrolyte it may be noted that even complex (I), which is known to be a 2:1 salt in the solid, shows a low conductivity in nitromethane ($\Lambda_M = 106 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$).

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