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The Formation and Molecular Structure of a Monodentate Bicarbonate Complex of Palladium(II)

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A recent communication [1] concerning the reaction of CO_2 with *trans*-$[PtH_2(Pc\text{-hexyl}_3)_2]$ to give formato and methylcarbonato derivatives, prompts us to report our findings concerning the reaction of CO_2 with $[PdMe_2(PEt_3)_2]$.

Previously the reaction of CO_2 with the complexes $[PdMe_2L_2]$ (L = PEt_3, $PMePh_2$) in hexane was reported to yield unusual complexes of stoichiometry $[PdMe(CO_2)L_2]$ [2]. These complexes were formulated as being *either* palladium(I) dimers with a Pd–Pd bond, *or* five coordinate, phosphine metallated palladium(II) species containing coordinated CO_2 [2]. We wish to reformulate these complexes as *trans*-$[PdMe(HOCO_2)L_2]$ (1), a rare example of organometallic bicarbonato complexes, on the basis of the following evidence. When dry CO_2 is passed through a dry hexane solution of $[PdMe_2(PEt_3)_2]$, room temperature for 15 h, the yield of 1 was less than 1%. When the reaction was repeated in the presence of an equimolar quantity of water 1 was obtained in >75% yield in 1½ h. Thus formation of 1 requires the presence of water. In the PMR spectrum the palladium bound methyl group of 1 exhibits a 1:2:1 triplet resonance indicating a *trans* arrangement of the two PEt_3 ligands. The IR spectrum of 1 (L = PEt_3) exhibited νO–H at 2603 cm^{-1} (v.w.) and $-OCO_2$ modes at 1634 (s), 1353 (s) and 830 (m) cm^{-1} {assigned by analogy to the IR data reported for $KHCO_3$ [3] and $[M(HOCO_2)(CO)(PPh_3)_2]$ (M = Rh or Ir) [4]}. When the reaction of dry CO_2 with $[PdMe_2(PEt_3)_2]$ in hexane is carried out in the presence of ROH (R = Me, Et, ^{n}Bu) colourless oils are obtained which, on the basis of PMR, IR and microanalytical data, are formulated as monoalkyl carbonato complexes *trans*-$[PdMe(ROCO_2)(PEt_3)_2]$ (2) (*e.g.* for R = Me: PMR; δCH_3, 0.15 ppm; 1:2:1 triplet; $J_{^3P-H}$ = 6Hz; δOCH_3, 3.75 ppm, singlet. IR; $-OCO_2$ absorptions (cm^{-1}): 1667 (s); 1298 (s); 1084 (s); Calc: C, 41.63; H, 8.38; Found; C, 41.74; H, 8.17%). The complexes 2 are structurally analogous to the monomethylcarbonato complex *trans*-$[PtH(MeOCO_2)(Pc\text{-hexyl}_3)_2]$ whose structure has been recently determined [1]. The reformulation of 1 as bicarbonato complexes has been confirmed by an X-ray crystallographic study of 1 (L = PEt_3)$_2$.

Crystal Data

Bicarbonatomethyl-*trans*-bis(triethylphosphine)-palladium(II), $PdC_{14}H_{34}O_3P_2$, M = 418.8, *a* = 7.713 (5), *b* = 9.014 (5), *c* = 15.339 (8) Å, α = 111.35 (4), β = 94.80 (5), γ = 90.77 (5)°, D_c = 1.407 g cm^{-3}, Z = 2, D_o = 1.40 (1) g cm^{-3}, F(000) = 366. Space group P1 (No. 2, C_i), μ = 10.66 cm^{-1}, Mo-Kα radiation (λ = 0.71069 Å).

X-ray diffraction measurements were made with a Syntex $P2_1$ diffractometer using the θ(crystal)–2θ-(counter) scan method. All reflections for $0 < 2\theta > 35°$ were collected and data with limits h = 0 to 10, k = 5 to +6, l = 12 to +7 were collected in the range $35 < 2\theta < 50°$. On averaging, this gave 1598 independent reflections of which 1308 ($I > 3\sigma(I)$) and 227 ($3\sigma(I) > I > \sigma(I)$) were used in structure solution and refinement. The remaining 63 reflections ($I < \sigma(I)$) were rejected.

The structure was solved by the Patterson–Fourier method and refined by full matrix least squares using anisotropic temperature factors for the Pd, P atoms and atoms of the CO_3 unit. Other carbon atoms had anisotropic temperature factors. The function minimized was $\epsilon w(|F_o| - |F_c|)^2$ and disagreeement indeces were R = 0.0746, R_w = 0.0638. The relevant bond lengths and angles are shown in the Figure and Table. There is a rough square plane of ligand atoms about the palladium atom and the bicarbonate group is monodentate. There is a large dihedral angle (73°) between the plane of the CO_3 unit and the best plane through the four ligand atoms. The Pd–C, Pd–P, Pd–O bond lengths are in the normal range [5] although the Pd–O distance (2.13(2)Å) is at the upper limit of this range (1.97–2.16 Å) and is about 0.2 Å longer than expected if the Pd–X distances are compared with Pauling covalent radii [6]. The C–O distances in the bicarbonate group are insignificantly different, which might appear unexpected. Nevertheless, as the Figure shows, one molecule is related by

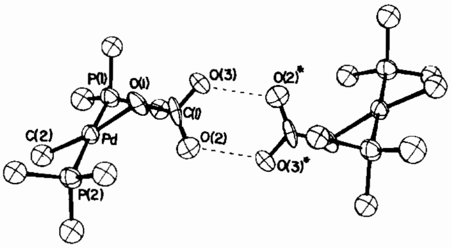

Figure. Starred atoms are related to corresponding unstarred atoms by inversion through ½, 0, ½. Dotted lines indicate hydrogen bonds.

inversion to another such molecule so that hydrogen bonding can occur and the O(2)–O(3)*, O(3)–O(2)* distances of 2.60 (2) Å are consistent with strong hydrogen bonds. Thus each oxygen atom in the bicarbonate group is involved in bonding and this is consistent with the C–O distances not differing. Both the general and specific features of the molecular structure are similar to those observed for *trans*-{PtH(O_2COCH_3)[$P(C_6H_{11})_3$]$_2$} [1].

Since alcohols are known to react with [$PdMe_2(PR_3)_2$] liberating one mol of methane [7], it seems likely that the formation of **1** and **2** occurs *via* initial formation of [$PdMe(OR)(PEt_3)_2$] (R = H, alkyl) followed by CO_2 insertion. A similar mechanism has been suggested previously for the formation of [$M(HOCO_2)(CO)(PPh_3)_2$] [4] and [$Ru(ROCO_2)(PMe_2Ph)_4$]PF_6 [8].

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TABLE. Selected Interatomic Distances (Å) and Angles (deg.).

Atoms	Distance	Atoms	Distance	Atoms	Distance
Pd–P(1)	2.314(6)	Pd–P(2)	2.292(6)	Pd–O(1)	2.13(2)
Pd–C(2)	2.05(2)	P(1)–C(3)	1.87(2)	P(1)–C(5)	1.88(2)
P(1)–C(7)	1.82(2)	P(2)–C(9)	1.83(2)	P(2)–C(11)	1.83(2)
P(2)–C(13)	1.85(2)	O(1)–C(1)	1.27(4)	O(2)–C(1)	1.31(3)
O(3)–C(1)	1.28(3)	O(2)–O(3)	2.60(2)		
Atoms	**Angle**	**Atoms**	**Angle**	**Atoms**	**Angle**
P(1)–Pd–P(2)	176.5(2)	P(1)–Pd–O(1)	84.6(4)	P(1)–Pd–C(2)	92.3(6)
P(2)–Pd–O(1)	97.1(4)	P(2)–Pd–C(4)	86.5(6)	P(2)–Pd–C(2)	86.5(6)
O(1)–Pd–C(2)	171.5(6)	Pd–O(1)–C(1)	131(1)	O(1)–C(1)–O(2)	121(3)
O(1)–C(1)–O(3)	119(2)	O(2)–C(1)–O(3)	120(3)		

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