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Reaction of Pt–OH Complexes with CO_2: Synthesis and X-Ray Structure of $(PBz_3)_4Pt_2(Ph)_2(\eta^1,\eta^1,\mu\text{-}CO_3)\cdot$(toluene)

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The reaction of (diphoe)Pt(CH_2CN)(OH) and trans-*(PBz_3)$_2$Pt(Ph)(OH) with CO_2 is reported as producing dimeric, bridged carbonato complexes of the type: $P_4Pt_2(R)_2(CO_3)$. The crystal and molecular structure of $(PBz_3)_4Pt_2(Ph)_2(\mu\text{-}CO_3)\cdot$(toluene) is also reported, showing η^1, η^1 bonding. The reaction is recognized to proceed in a stepwise fashion through bicarbonato intermediates.*

Introduction

In recent years the preparation of stable hydroxo complexes of platinum(II) has been investigated systematically [1–4], since they have proved rather versatile reagents toward a variety of reactions involving the Pt–O bond. Within this framework, we have previously reported insertion reactions with CO, COS, CS_2, SO_2 [3], RNC [5] and condensation reactions with weak sulfur, nitrogen, and carbon acids [3] and with hydrogen peroxide [6] and t-butylhydroperoxide [7] to give the corresponding peroxo complexes.

A characteristic feature encountered in the synthesis of these hydroxo complexes is the appearance in some cases of carbonato IR bands around 1600 and 1350 cm^{-1}, indicative of interaction of the OH moiety with carbon dioxide. Similar reactions with other d^8 systems have been clearly identified for some Rh complexes [8] while in the case of Pt they have only been inferred in the reaction of $Pt(PCy_3)_2$ with wet CO_2 [9].

In order to get a better understanding of the nature of the species involved in the insertion of CO_2 into the Pt–O bond, we chose two representative hydroxo complexes with different geometries: (diphoe)Pt(CH_2CN)(OH) (*1*) [3] (diphoe = 1,2-bis-diphenylphosphinoethylene) and *trans*(PBz_3)$_2$Pt(Ph)(OH) (*2*) [10]. In this paper we report the crystal and molecular structure of the dimeric complex $(PBz_3)_4Pt_2(Ph)_2(\eta^1, \eta^1, \mu\text{-}CO_3)\cdot$(toluene) (*3*) prepared by reaction of (*2*) with CO_2, which represents the first X-ray analysis of an η^1, η^1 bridging carbonate moiety bound to a d^8 metal species.

Experimental

When a benzene solution of either (*1*) or (*2*) is put in contact with CO_2, white solids can be isolated showing IR bands (nujol) at 1535(s), 1305(vs), 840(m) cm^{-1} and at 1525(m), 1300(s) cm^{-1} which are attributed to carbonato moieties on the basis of X-ray analysis (*vide infra*).

Suitable crystals of the dimeric complex (*3*) have been obtained by slow evaporation in the air of a toluene solution of complex (*2*).

The crystals are monoclinic with unit cell parameters $a = 26.38(1)$, $b = 13.576(7)$, $c = 28.05(1)$ Å, $\beta = 116.6(1)°$, $D_{exp} = 1.41$ g cm^{-3}, $D_{calc} = 1.42$ g cm^{-3}, with $Z = 4$ $[Pt(PBz_3)_2Ph]_2CO_3\cdot$toluene units, space group $C2/c$. X-ray intensity data were collected on a Siemens AED automated single crystal diffractometer. A total of 3511 independent reflec-

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TABLE I. Positional Parameters (10^4) of non Hydrogen Atoms. The Star indicates the Atoms Refined Anisotropically.

	X	Y	Z	B (Å^2)
Pt	609(0)	141(0)	3717(0)	*
P(1)	1452(1)	378(2)	3667(1)	*
P(2)	−219(1)	−122(3)	3783(1)	*
O(1)	253(3)	−384(6)	2936(3)	*
O(2)	0	1042(9)	2500	*
C(1)	1456(5)	1477(9)	3295(5)	*
C(2)	1406(5)	2432(9)	3556(6)	*
C(3)	874(6)	2806(10)	3417(6)	*
C(4)	810(7)	3657(12)	3683(9)	*
C(5)	1285(7)	4158(12)	4049(8)	*
C(6)	1806(6)	3790(11)	4174(8)	*
C(7)	1874(6)	2938(11)	3919(7)	*
C(8)	2086(5)	433(10)	4314(5)	*
C(9)	2654(5)	156(11)	4336(5)	*
C(10)	2919(6)	−681(12)	4592(7)	*
C(11)	3455(7)	−940(15)	4654(8)	*
C(12)	3705(7)	−341(14)	4411(8)	*
C(13)	3444(7)	502(15)	4156(9)	*
C(14)	2913(6)	778(12)	4108(7)	*
C(15)	1592(5)	−590(9)	3285(5)	*
C(16)	1790(5)	−1572(9)	3552(5)	*
C(17)	1568(6)	−2001(10)	3871(7)	*
C(18)	1756(7)	−2908(13)	4116(9)	*
C(19)	2178(9)	−3377(13)	4036(11)	*
C(20)	2387(9)	−2978(15)	3702(11)	*
C(21)	2200(7)	−2087(12)	3478(8)	*
C(22)	−803(5)	−448(11)	3132(5)	*
C(23)	−1352(5)	−816(12)	3110(5)	*
C(24)	−1769(6)	−138(15)	3029(6)	*
C(25)	−2308(7)	−540(19)	2953(7)	*
C(26)	−2391(8)	−1503(19)	2970(8)	*
C(27)	−1970(9)	−2188(18)	3055(8)	*
C(28)	−1455(7)	−1814(14)	3129(7)	*
C(29)	−463(6)	953(10)	4035(6)	*
C(30)	−687(5)	1833(11)	3656(6)	*
C(31)	−495(6)	2115(11)	3292(6)	*
C(32)	−696(7)	2935(12)	2973(7)	*
C(33)	−1111(8)	3512(15)	3011(8)	*
C(34)	−1303(10)	3239(18)	3369(11)	*
C(35)	−1104(7)	2442(13)	3700(8)	*
C(36)	−186(5)	−990(10)	4288(5)	*
C(37)	−64(5)	−2080(10)	4228(5)	*
C(38)	−152(6)	−2740(12)	4554(7)	*
C(39)	−60(7)	−3724(13)	4525(9)	*
C(40)	127(7)	−4097(12)	4172(8)	*
C(41)	214(7)	−3446(12)	3846(7)	*
C(42)	139(7)	−2428(11)	3884(7)	*
C(43)	972(4)	495(11)	4474(5)	*
C(44)	1037(6)	1546(12)	4640(6)	*
C(45)	1346(7)	1819(15)	5185(7)	*
C(46)	1554(6)	1152(17)	5542(6)	*
C(47)	1509(5)	161(15)	5438(5)	*
C(48)	1213(5)	−131(13)	4896(5)	*
C(49)	0	126(11)	2500	*
C(50)	0	5345(29)	2500	10.4(9)
C(51)	569(21)	5533(41)	2663(20)	8.2(12)
C(52)	694(28)	6459(49)	2725(25)	9.3(15)
C(53)	192(21)	7217(35)	2540(28)	6.8(15)
C(541)	394(27)	7112(49)	2611(28)	7.9(16)
C(551)	466(27)	6142(53)	2566(25)	9.2(15)
C(561)	1103(26)	5924(43)	2783(23)	11.2(15)

TABLE I. *(continued)*

tions having $I > 3\sigma(I)$ and $\theta < 28°$ (MoKα) were corrected for Lorentz-polarization and absorption effects (μ = 34 cm^{-1}, $0.015 < r_{\text{cryst}} < 0.025$ cm). The structure was solved by Patterson and Fourier methods and refined by least-squares methods to an R value of 0.045, including the contribution (held constant (B = 5 Å^2)), of hydrogen atoms at calculated positions and anisotropic temperature factors for all atoms of the dimeric unit. The toluene molecules were found to occupy two different orientations around the twofold axes and refined isotropically. A list of the observed and calculated structure factors, tables of hydrogen atom coordinates and thermal parameters are available from the authors. The final atomic parameters of non-hydrogen atoms are given in Table I.

Results and Discussion

The numbering scheme of the crystallographically-independent atoms is shown in Fig. 1. A sketch of the dimer is shown in Fig. 2, together with some bond lengths and angles on interest. The crystals consist of the discrete dimers lying on crystallographic twofold axes, passing through the C(49) and O(2) atoms of the bridging carbonate ligands. The coordination planes of the two Pt atoms make an interplanar angle of 39.0°. The coordination about the platinum atoms is best described as square planar: the P(1), P(2), O(1), C(43) atoms are coplanar within ±0.04 Å, and the Pt atom is displaced 0.06 Å from their mean plane. The Pt–P bond lengths of 2.313(4) and 2.300(4) Å are quite normal for two phosphines *trans* to each other [11], as well as the Pt–C (phenyl) distance of 1.958(12) Å [10]. The Pt–O distance of 2.087(7) Å is significantly shorter than those reported for $(PCy_3)_2Pt(H)(O_2CH)$ (2.27(1) Å) [11] and $(PCy_3)_2Pt(H)(O_2COCH_3)$ (2.13(1) Å) [11] where the O atom is *trans* to a hydride ligand, but is longer than the Pt–O bond length of 1.99(1) Å found in the peroxo derivative *trans*-$(PPh_3)_2Pt(Ph)(OO\text{-}t\text{-}Bu)$ [10]. The crystallographic symmetry imposes to the carbonate group to be planar. Its plane makes an angle of 97.3° with the Pt(1) coordination plane. The C(49)–O(1) bond length of 1.29(1) Å is virtually identical with that reported for calcite (1.294(4)

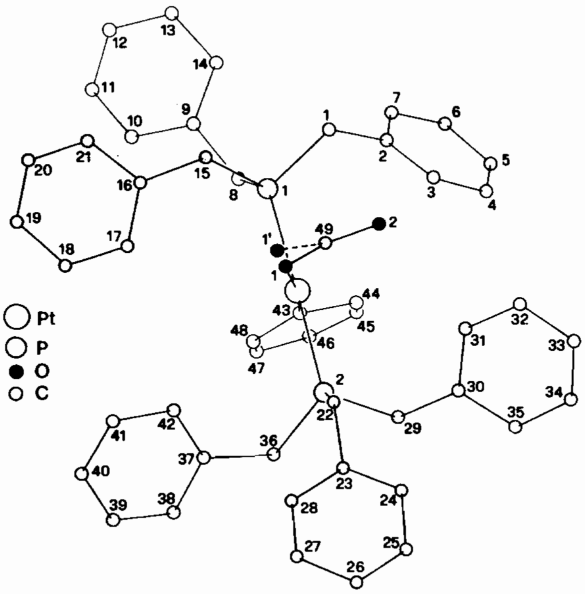


Fig. 1. Numbering scheme for the non-hydrogen atoms of the crystallographically independent moiety of the dimer.

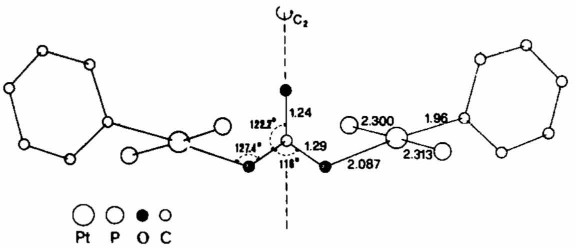
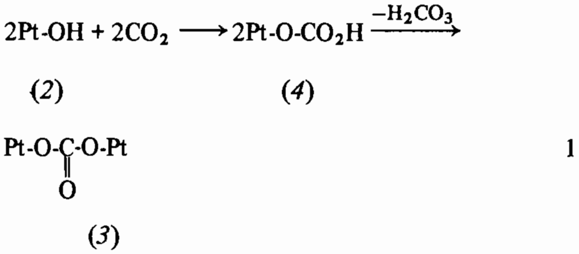


Fig. 2. A sketch of the dimer, together with some bond lengths and angles of interest. E.s.d's are 0.004 for Pt–P, 0.007 for Pt–O and 0.01–0.02 for the others. Only the donor atoms of phosphines are shown.

Å) [12]. On the contrary the C(49)–O(2) distance of 1.24(2) Å appears shorter, although its large e.s.d. does not allow any comparison. Finally the phenyl group, planar within ±0.01 Å, is nearly perpendicular to the coordination plane, making an interplanar angle of 95.9°. It is of interest to compare the structure of the present compound with that of $(PPh_3)_5Rh_2(CO_3)\cdot$benzene [13] where the two Rh atoms, having square planar coordination, are linked by a nearly planar carbonate ligand. Two carbonato oxygens are linked to one Rh atom, while the third oxygen atom is coordinated to the second metal atom giving η^1,η^2,μ-carbonato species. In the Pt dimer the two Pt atoms have the same coordination, the carbonato ligand acting as an η^1,η^1 bridging group.

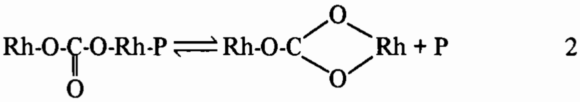
The CO_2 insertion in complex (*2*) appears to proceed in a stepwise fashion, since the crude reaction product that is precipitated upon treatment with Et_2O shows additional IR absorptions at 1625(m), 1310(s) cm^{-1}, which could well be attributed to an intermediate bicarbonato complex. These additional bands disappear when the crude product is recrystallized (reaction sequence 1, ancillary ligands omitted). Formulation of bicarbonato binding geometry as in (*4*) from IR data is favoured by comparison with



$$2Pt\text{-}OH + 2CO_2 \longrightarrow 2Pt\text{-}O\text{-}CO_2H \xrightarrow{-H_2CO_3} Pt\text{-}O\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}O\text{-}Pt \qquad 1$$

(*2*) (*4*) (*3*)

similar *trans* complexes $(PCy_3)_2Pt(H)(OCO_2CH_3)$ (1640, 1295 cm^{-1}) [11] and $(PEt_3)_2Pd(Me)(OCO_2H)$ (1634, 1353 cm^{-1}) [14]. This behavior resembles that reported for analogous Rh(I) systems [9] for which the additional equilibrium 2



$$Rh\text{-}O\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}O\text{-}Rh\text{-}P \rightleftharpoons Rh\text{-}O\text{-}C\langle{}^{O}_{O}\rangle Rh + P \qquad 2$$

$P = P(i\text{-}Pr)_3, PCy_3$

has been detected, the η^1,η^1 derivative only being stable at low temperature. The fact that we failed to observe an equilibrium analogous to 2 in our system probably reflects the more limited capacity of Pt(II) with respect to Rh(I) to undergo neutral ligand displacement.

The structural results reported here complement those reported by Ibers *et al.* on rhodium, for which X-ray analysis was possible only for η^1,η^2,μ-carbonato species [13].

References

1 T. Yoshida, T. Okano and S. Otsuka, *J. Chem. Soc. Dalton,* 993 (1976).
2 M. A. Bennett and T. Yoshida, *J. Am. Chem. Soc., 100,* 1750 (1978).
3 R. A. Michelin, M. Napoli and R. Ros, *J. Organometal. Chem., 175,* 239 (1979).
4 D. P. Arnold and M. A. Bennett, *J. Organometal. Chem., 199,* 119 (1980).
5 R. A. Michelin and R. Ros, *J. Organometal. Chem., 169,* C42 (1979).
6 R. A. Michelin, R. Ros and G. Strukul, *Inorg. Chim. Acta, 37,* L491 (1979).
7 G. Strukul, R. Ros and R. A. Michelin, *Inorg. Chem., 21,* 495 (1982).

8 B. R. Flynn and L. Vaska, *J. Am. Chem. Soc., 95,* 5082 (1973);
T. Yoshida, D. J. Thorn, T. Okano, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc., 101,* 4212 (1979).
9 M. G. Mason and J. A. Ibers, *J. Am. Chem. Soc., 104,* 5153 (1982).
10 G. Strukul, R. A. Michelin, J. D. Orbell and L. Randaccio, *Inorg. Chem.,* in press.
11 A. Immirzi and A. Musco, *Inorg. Chim. Acta, 22,* L35 (1977).
12 R. L. Sass, R. Vidale and J. Donohue, *Acta Cryst., 10,* 567 (1957).
13 S. Krogsrud, S. Komiya, T. Ito, J. A. Ibers and A. Yamamoto, *Inorg. Chem., 15,* 2798 (1976).
14 R. J. Crutchley, J. Powell, R. Faggiani and C. J. L. Lock, *Inorg. Chim. Acta, 22,* L35 (1977).