*Inorganica Chimica Acta*, 22 (1977) L35–L36

# Reactions of *Trans*-{$PtH_2[P(C_6H_{11})_3]_2$} with Carbon Dioxide. X-Ray Structures of *Trans*-{$PtH(O_2CH)$-$[P(C_6H_{11})_3]_2$} and *Trans*-{$PtH(O_2COCH_3)$-$[P(C_6H_{11})_3]_2$}

A. IMMIRZI and A. MUSCO

*Istituto di Chimica Delle Macromolecole del CNR, Via A. Corti, 12, 20133 Milano, Italy*

Received March 1, 1977

The interaction of carbon dioxide with transition metal complexes is actively investigated with the aim to insert catalytically $CO_2$ in organic substrates. In this context the current interest on the investigation of metal complexes which may react with $CO_2$ is justified [1–3].

A few insertion reactions of $CO_2$ into a metal–hydrogen bond have recently been reported [1, 4, 5]. In the course of our studies [6] on the reactivity of *trans*-{$PtH_2[P(C_6H_{11})_3]_2$} (1) we have found that this complex is particularly reactive toward $CO_2$. Here we report the preparation and the structure of two reaction products, the formato *trans*-{$PtH(O_2CH)$-$[P(C_6H_{11})_3]_2$} (2) and the monomethyl carbonato *trans*-{$PtH(O_2COCH_3)[P(C_6H_{11})_3]_2$} (3).

The formato complex 2 is obtained in good yields at 8 °C as large white prismatic crystals containing solvated benzene from a concentrated benzene solution of 1 after saturation with $CO_2$. The $CO_2$ is reversibly bound to the metal. The hydrido complex 1 is restored by passing a stream of nitrogen in a toluene solution of 2. The PMR spectrum (270 MHz) in toluene-$d^8$ shows that the formato complex is extensively dissociated in solution to 1 and $CO_2$, the signals of 2 being very weak. However by using Fourier transform technique and $CO_2$ saturated solvent the signals of 2 were readily detected. The hydride signal is a sextet at 32.35 $\tau$ for the coupling with the phosphorus atoms and the hydrogen of the formato group ($J_{P-H} \sim 14$ Hz, $J^4_{H-H}$ 4.5 Hz) with $^{195}Pt$ satellites ($J_{Pt-H}$ 1148 Hz); the expected $-O_2CH$ doublet is at 0.81 $\tau$ with $^{195}Pt$ satellites ($J_{Pt-H}$ 50 Hz). A similar spectrum was observed for *trans*-$PtH(S_2CH)[P(C_6H_{11})_3]_2$ [6]. The IR spectrum (nujol) shows the $\nu$(Pt–H) at 2230 $cm^{-1}$ and OCO modes at 1620 and 1310 $cm^{-1}$ which compare with the frequencies previously reported for $HCO_2Co$-$[P(C_6H_5)_3]_3$ [7].

The monomethyl carbonato complex 3 was obtained by suspending 1 in methanol in an atmosphere of $CO_2$ for several hours. 1 slowly dissolves and 3 is obtained in good yields as white needle-shaped crystals containing solvated methanol from the filtered methanol solution on crystallization at 0 °C. The methanol insoluble material (very minute quantities) is mainly 2. The IR and PMR spectra are consistent with the structure of 3 as a monomethyl carbonato complex [IR, nujol (argon); $\nu$(Pt–H): 2240 (m) $cm^{-1}$; $-OCO_2$ modes: 1640 (s, vbr), 1295 (s, br), 1090(s) $cm^{-1}$; PMR, 270 MHz, toluene-$d^8$, $CO_2$ atmosphere; Pt–H 33.42 $\tau$ (triplet, $J_{P-H}$ 15 Hz, $^{195}Pt$ satellites observed with $J_{Pt-H}$ 1191 Hz), $OCH_3$ 6.25 $\tau$ (singlet)].

Whether complex 3 forms through attack of methanol on the formato group or, as proposed for $[Ru(O_2COR)(PMe_2Ph)_4]PF_6$ [4], through $CO_2$ insertion on a $Pt-OCH_3$ bond remains to be elucidated. The latter hypothesis is consistent with the recently reported reactions of Cu–OR complexes with $CO_2$ to yield monoalkylcarbonato complexes [8].

In order to elucidate the different behaviour in solution of 2 and 3 (the latter being more stable to decarboxylation), and to clarify the mode of bonding of the formato and methylcarbonato group, which may act either as a mono or bidentate ligand, an X-ray structure determination was undertaken.

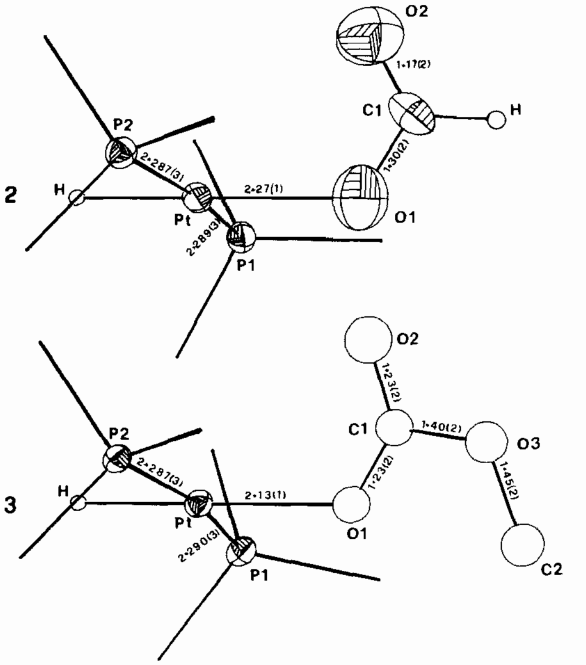
*Crystal data:* 2: $PtP_2C_{37}H_{68}O_2 + 2C_6H_6$, M = 958.2, $a$ = 28.011(2), $b$ = 17.801(2), $c$ = 9.698(1) Å, $\beta$ = 97.49(2)°, $D_c$ = 1.327 g $cm^{-3}$, $Z$ = 4, $F$(000) = 1992, space group $P2_1/n$, $\mu$ = 32.5 $cm^{-1}$; 3: $PtP_2C_{38}H_{70}O_3$ + 1 $CH_3OH$, M = 864.1, $a$ = 18.178(3), $b$ = 12.506(2), $c$ = 9.937(2) Å, $\alpha$ = 104.46(2), $\beta$ = 106.00(2), $\gamma$ = 73.63(2)°, $D_c$ = 1.401 g $cm^{-3}$, $Z$ = 2, $F$(000) = 896, spave group $P\bar{1}$, $\mu$ = 37.1 $cm^{-1}$, Mo-K$\alpha$ radiation ($\lambda$ = 0.71069 Å).

X-ray diffraction measurements were performed with a Philips single crystal diffractometer PW-1100 using the $\omega$-scan method. Structure determination and refinement is based on 4411 and 5451 non-zero intensities (those with $I > 3\sigma_I$) having $\theta < 23°$ ($d$ > 0.91 Å) for 2 and 3 respectively.

The structures were solved by the Patterson–Fourier method and refined by the least squares method using isotropic thermal vibration parameters except for Pt and P atoms and for the OCO group in 2. Disagreement index $\Sigma|\Delta|/\Sigma|F_{obs}|$ are 0.060 and 0.049 respectively. The molecular structures and the relevant bond lengths and angles are shown in Fig. 1.

In both cases the structure is planar with the two *trans* phosphines slightly bent toward the hydrido hydrogen. The O(1)–C(1)–O(2) groups of 2 and 3 form angles of 78° and 69° respectively with the metal coordination plane. The oxygen of the solvated methanol of 3 is at 2.75 Å from O(2) indicating hydrogen bonding.

The Pt–O(1) bond distances (2.27 for 2 and 2.13 Å for 3) are substantially longer than the sum of the covalent radii of Pt(1.35 Å, calcd on $Pt_3[P(C_6H_{11})_3]_4$-$(CO)_3$ [9]) and O (0.66 Å [10]) as well as longer



Bond and torsion angles (degrees)

| | 2 | 3 |
|---|---|---|
| P(1) – Pt – P(2) | 168.0(4) | 166.1(4) |
| P(1) – Pt – O(1) | 94.9(4) | 95.0(2) |
| P(2) – Pt – O(1) | 96.8(4) | 98.8(2) |
| Pt – O(1) – C(1) | 120.0(7) | 122.2(7) |
| O(1) – C(1) – O(2) | 119.9(9) | 130.6(7) |
| O(2) – C(1) – O(3) | | 113.6(7) |
| O(1) – C(1) – O(3) | | 115.7(7) |
| Pt – O(1) – C(1) – O(2) | 14.8 | -8.2 |

Fig. 1. Molecular structure, relevant bond lengths (Å) and angles of *trans*-$\{PtH(O_2CH)[P(C_6H_{11})_3]_2\}$ (2) and *trans*-$\{PtH(O_2COCH_3)[P(C_6H_{11})_3]_2\}$ (3).

than the Pt–O distances found in $Pt[PPh_3]_2O_2$ [11] (1.99 Å), $Pt[PPh_3]_2O_2CO(CH_3)_2$ [12] (2.00 Å) and $Pt_4(AcO)_6(NO)_2$ [13] (2.04 Å). The *trans* influence of the hydrido hydrogen, which is expected in both complexes, appears to be stronger in 2 than in 3. Accordingly the formato complex undergoes facile decarboxylation in solution. The C–O(2) bond is in both cases roughly eclipsed with the Pt–O(1) bond bringing the O(2) atom close to Pt but at a non-bonding distance (2: 3.18 Å; 3: 3.28 Å).

The C–O(2) distance of 3 (1.21 Å) compares with that usually found in carboxylic esters; on the other hand the C–O(1) bond appears to be rather short (1.23 Å) for a C–O single bond. Comments on this short distance are difficult since to the best of our knowledge this is the first structure of a monoalkylcarbonato complex.

The two C–O distances in 2 are rather short if compared to those reported for $RuH(O_2CH)(PPh_3)_3$ [14] (av. 1.28 Å) where the formato moiety acts as a bidentate group. However O(1) and O(2) atoms exhibit exceedingly large thermal vibrations (root mean displacements are in the range 0.35–0.45 Å) whereas Pt and P atoms show "normal" values (0.17–0.20 Å). This feature, while confirming the weakness of the Pt–O bond, causes a systematic but hardly evaluable underestimation of bond lengths [15]. As a consequence the "long" Pt–O bond distance we have discussed above might have an even larger value.

The thermal disorder of the O(1)–C(1)–O(2) group is consistent with the decarboxylation tendency of 2 in solution.

The implications that compounds 2 and 3 may have in the $CO_2$ assisted dimerization of butadiene and isoprene catalyzed by phosphine Pd complexes is currently being actively investigated [16].

## Acknowledgment

The authors thank Mr. S. Italia for his skillful technical help.

## References

1 M. E. Volpin and I. S. Kolomnikov, in *Organometallic Reactions*, Eds. E. I. Becker and M. Tsutsui, *5*, 313 (1975).
2 M. Aresta, C. F. Nobile, V. G. Albano, E. Forni and M. Manassero, *Chem. Comm.*, 636 (1975).
3 T. Herskovitz and Lloyd J. Guggenberger, *J. Am. Chem. Soc.*, *98*, 1615 (1976).
4 T. V. Ashworth and E. Singleton, *Chem. Comm.*, 204 (1976).
5 S. Komiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, *49*, 784 (1976).
6 A. Albinati, A. Musco, G. Carturan and G. Strukul, *Inorg. Chim. Acta*, *18*, 219 (1976).
7 A.Yamamoto, S. Kitazume, L. S. Pu and S. Ikeda, *J. Am. Chem. Soc.*, *93*, 371 (1971).
8 T. Tsuda, S. Sanada, K. Ueda and T. Saegusa, *Inorg. Chem.*, *15*, 2329 (1976).
9 A. Albinati, G. Carturan and A. Musco, *Inorg. Chim. Acta*, *16*, L3 (1976).
10 L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y. (1960).
11 C. D. Cook, P. Cheng and S. C. Nyburg, *J. Am. Chem. Soc.*, *91*, 2123 (1969).
12 R. Ugo, F. Conti, S. Ceninin, R. Mason and G B. Robertson, *Chem. Comm.*, 1498 (1968).
13 P. de Meester and A. C. Skapski, *J. Chem. Soc. Dalton*, 1194 (1973).
14 I. S. Kolomnikov, A. I. Gusev, G. C. Aleksandrov, T S. Lobeeva, Yu. T. Struchkov and M. E. Volpin, *J. Organometal. Chem.*, *59*, 349 (1973).
15 C. K. Johnson in "Crystallographic Computing", Ed. by F. R. Ahmed Muskgaard (1969) pp. 220–226.
16 A. Musco, *J. Mol. Cat.*, *1*, 443 (1975/1976).