

Reactions of *Trans*-[PtH₂[P(C₆H₁₁)₃]₂] with Carbon Dioxide. X-Ray Structures of *Trans*-[PtH(O₂CH)-[P(C₆H₁₁)₃]₂] and *Trans*-[PtH(O₂COCH₃)-[P(C₆H₁₁)₃]₂]

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The interaction of carbon dioxide with transition metal complexes is actively investigated with the aim to insert catalytically CO₂ in organic substrates. In this context the current interest on the investigation of metal complexes which may react with CO₂ is justified [1–3].

A few insertion reactions of CO₂ into a metal–hydrogen bond have recently been reported [1, 4, 5]. In the course of our studies [6] on the reactivity of *trans*-[PtH₂[P(C₆H₁₁)₃]₂] (**1**) we have found that this complex is particularly reactive toward CO₂. Here we report the preparation and the structure of two reaction products, the formate *trans*-[PtH(O₂CH)-[P(C₆H₁₁)₃]₂] (**2**) and the monomethyl carbonato *trans*-[PtH(O₂COCH₃)[P(C₆H₁₁)₃]₂] (**3**).

The formate 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 CO₂. The CO₂ 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-d₈ shows that the formate complex is extensively dissociated in solution to **1** and CO₂, the signals of **2** being very weak. However by using Fourier transform technique and CO₂ saturated solvent the signals of **2** were readily detected. The hydride signal is a sextet at 32.35 τ for the coupling with the phosphorus atoms and the hydrogen of the formate group ($J_{\text{P-H}} \sim 14$ Hz, $J_{\text{H-H}}^4$ 4.5 Hz) with ¹⁹⁵Pt satellites ($J_{\text{Pt-H}}$ 1148 Hz); the expected –O₂CH doublet is at 0.81 τ with ¹⁹⁵Pt satellites ($J_{\text{Pt-H}}$ 50 Hz). A similar spectrum was observed for *trans*-PtH(S₂CH)[P(C₆H₁₁)₃]₂ [6]. The IR spectrum (nujol) shows the $\nu(\text{Pt-H})$ at 2230 cm⁻¹ and OCO modes at 1620 and 1310 cm⁻¹ which compare with the frequencies previously reported for HCO₂Co-[P(C₆H₅)₃]₃ [7].

The monomethyl carbonato complex **3** was obtained by suspending **1** in methanol in an atmosphere of CO₂ 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); $\nu(\text{Pt-H})$: 2240 (m) cm⁻¹; –OCO₂ modes: 1640 (s, vbr), 1295 (s, br), 1090(s) cm⁻¹; PMR, 270 MHz, toluene-d₈, CO₂ atmosphere; Pt–H 33.42 τ (triplet, $J_{\text{P-H}}$ 15 Hz, ¹⁹⁵Pt satellites observed with $J_{\text{Pt-H}}$ 1191 Hz), OCH₃ 6.25 τ (singlet)].

Whether complex **3** forms through attack of methanol on the formato group or, as proposed for [Ru(O₂COR)(PMe₂Ph)₄]PF₆ [4], through CO₂ insertion on a Pt–OCH₃ bond remains to be elucidated. The latter hypothesis is consistent with the recently reported reactions of Cu–OR complexes with CO₂ 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.

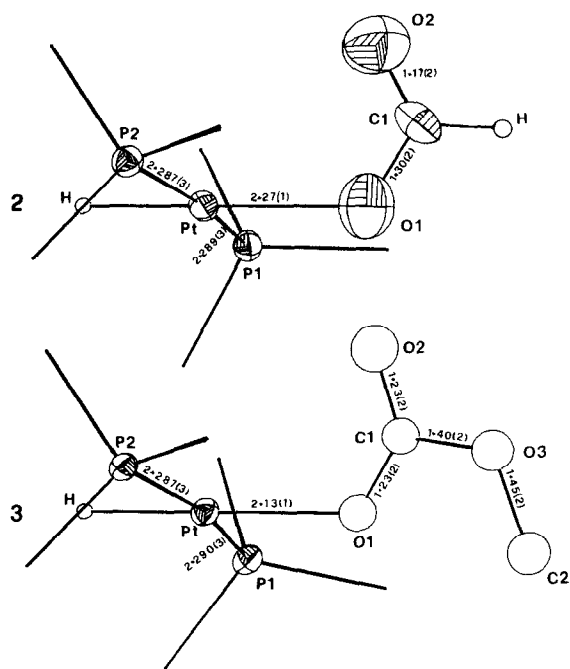
Crystal data: **2**: PtP₂C₃₇H₆₈O₂ + 2C₆H₆, *M* = 958.2, *a* = 28.011(2), *b* = 17.801(2), *c* = 9.698(1) Å, β = 97.49(2)°, *D*_c = 1.327 g cm⁻³, *Z* = 4, *F*(000) = 1992, space group P2₁/n, μ = 32.5 cm⁻¹; **3**: PtP₂C₃₈H₇₀O₃ + 1 CH₃OH, *M* = 864.1, *a* = 18.178(3), *b* = 12.506(2), *c* = 9.937(2) Å, α = 104.46(2), β = 106.00(2), γ = 73.63(2)°, *D*_c = 1.401 g cm⁻³, *Z* = 2, *F*(000) = 896, space group P1, μ = 37.1 cm⁻¹, Mo-K α radiation (λ = 0.71069 Å).

X-ray diffraction measurements were performed with a Philips single crystal diffractometer PW-1100 using the ω -scan method. Structure determination and refinement is based on 4411 and 5451 non-zero intensities (those with *I* > 3 σ _{*I*}) having θ < 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 $\Sigma|\Delta|/\Sigma|F_{\text{obs}}|$ 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 Pt₃[P(C₆H₁₁)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(O₂CH)[P(C₆H₁₁)₃]₂] (2) and *trans*-[PtH(O₂COCH₃)[P(C₆H₁₁)₃]₂] (3).

than the Pt-O distances found in Pt[PPh₃]₂O₂ [11] (1.99 Å), Pt[PPh₃]₂O₂CO(CH₃)₂ [12] (2.00 Å) and Pt₄(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 formate 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 monoalkyl-carbonato complex.

The two C-O distances in 2 are rather short if compared to those reported for RuH(O₂CH)(PPh₃)₃ [14] (av. 1.28 Å) where the formate 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 CO₂ assisted dimerization of butadiene and isoprene catalyzed by phosphine Pd complexes is currently being actively investigated [16].

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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).