Novel Metallacycle Formation in the Reaction of Carbon Dioxide with the Rhodium complex *mer*-[$HRh(CH_2COMe)(PMe_3)_3Cl$]

Michael Farmer, Masood A. Khan,† and Kenneth M. Nicholas*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, U.S.A.

The title compound (1) reacts with CO_2, apparently reversibly, to form [$Rh(CH_2CHMeOCO_2)(PMe_3)_3Cl$] (2), the structure of which has been established by *X*-ray diffraction.

There has been intense interest in the activation of carbon dioxide by transition metal complexes,[1] both with respect to simple reduction and towards incorporation into organic compounds. In an effort to determine the relative ease of insertion of CO_2 into an M–H as opposed to an M–C bond, we have examined the interaction of *mer*-[$HRh(CH_2COMe)(PMe_3)_3Cl$] (1) (which contains both bond types) with CO_2. Herein we report the novel and unexpected results.

When a solution of (1), preformed in propylene oxide from [$Rh(PMe_3)_3Cl$], [2]‡ was placed under *ca.* 1.1 atm of CO_2 at −20 °C for 3—4 days, a yellow crystalline precipitate (2) was formed (80—85%). That the product (2) had incorporated CO_2 was suggested by its i.r. spectrum (KBr), which exhibited prominent absorptions at 1650 and 1275 cm^{-1}, which shifted to 1610 and 1255 cm^{-1} when $^{13}CO_2$ was employed.§ An *X*-ray diffraction study of (2) at 160 K¶ revealed (Figure 1) that CO_2 had not been inserted into either the Rh–H or the Rh–C bond. The most interesting and novel feature of the structure is the presence of a six-membered metallacycle incorporating both propylene oxide and CO_2 fragments. This appears to be the first example of such a metallacarbonate ring system. The bond lengths and angles within the metallacycle are unexceptional except for the pronounced inequality of the two endocyclic C–O bonds, which suggests some multiple bond character in the C(3)–O(1) bond.** The ligand array about the Rh^{III} centre is essentially octahedral, with typical shortening of the M–P bond *trans* to the O-donor.[4]

The formation of (2) apparently is reversible; its dissolution in a variety of solvents at 20 °C immediately and quantitatively regenerated the starting complex (1), as revealed by ^1H and ^{31}P n.m.r. monitoring. This process even appears to occur in the solid state, albeit at a much lower rate, judged by the

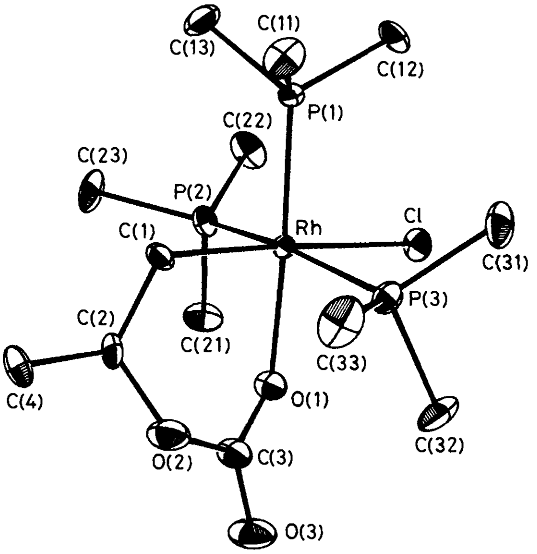
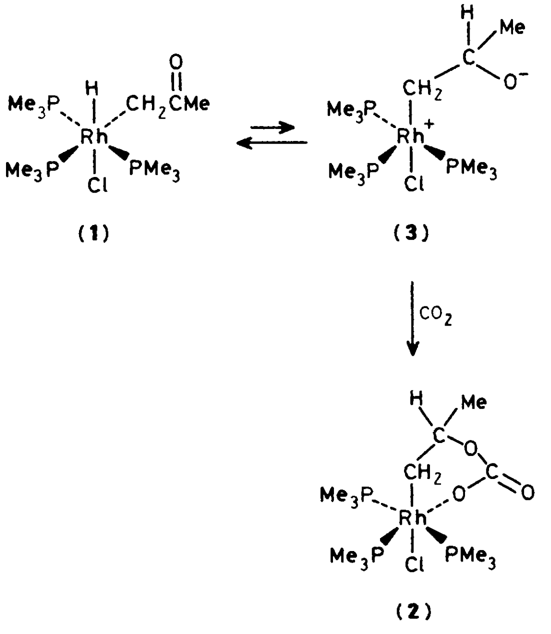


Figure 1. ORTEP plot for the complex (2). Thermal ellipsoids are shown at the 50% level. Selected bond lengths (Å) and angles (°) (estimated standard deviations in the least significant digit given in parentheses): Rh–Cl 2.512(3), Rh–P(1) 2.247(3), Rh–P(2) 2.345(3), Rh–P(3) 2.338(3), Rh–O(1) 2.126(7), Rh–C(1) 2.09(1), O(1)–C(3) 1.27(1), O(2)–C(2) 1.43(1), O(2)–C(3) 1.39(1), O(3)–C(3) 1.20(1), C(1)–C(2) 1.52(1), C(2)–C(4) 1.55(2); Cl–Rh–P(1) 95.95(5), Cl–Rh–P(2) 87.41(9), Cl–Rh–P(3) 86.55(9), Cl–Rh–O(1) 87.5(2), Cl–Rh–C(1) 176.9(3), P(1)–Rh–P(2) 95.0(1), P(1)–Rh–P(3) 93.2(1), P(1)–Rh–O(1) 176.6(2), P(1)–Rh–C(1) 87.2(3), P(2)–Rh–P(3) 170.3(1), P(2)–Rh–O(1) 85.2(2), P(2)–Rh–C(1) 92.0(3), P(3)–Rh–O(1) 87.0(2), P(3)–Rh–C(1) 93.6(3), O(1)–Rh–C(1) 89.4(3).



Scheme 1

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† Enquiries regarding the crystallographic analysis should be made directly to this author.

‡ The formation of (1) was verified by comparison of its i.r., ^1H n.m.r., and ^{31}P n.m.r. spectra with those reported.

§ Calculated $\nu(^{13}CO_2)$ 1615 and 1245 cm^{-1}.

¶ *Crystal data* for (2): $C_{13}H_{33}ClO_3P_3Rh$, $M = 268.68$, orthorhombic, space group *Pbca*, $a = 13.486(3)$, $b = 16.685(6)$, $c = 17.394(5)$ Å, $U = 3914$ Å^3, $\mu(Mo\text{-}K_\alpha) = 11.1$ cm^{-1}. Data were collected at 160 ± 2 K with an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α(λ 0.71069 Å) radiation. The data were corrected for Lorentz and polarization effects; no absorption correction was applied since it was judged to be negligible. Full-matrix least-squares refinement of 190 parameters gave $R = 0.048$, $R_w = 0.064$ for 2471 unique reflections. Refinement with the hydrogen atoms was unstable and they were not included in the calculations. Atomic co-ordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

** A similar effect has been noted in the structure of [$IrCl(C_2O_4)(PMe_3)_3$].[3]

gradual reappearance of the Rh–H stretching absorption of (**1**) (1940 cm^{-1}) in the i.r. spectrum of (**2**) (in air) over several hours.

Although we can only speculate on the mechanism of formation of (**2**) from (**1**) at present, the connectivity within the metallacyle suggests its formation *via* nucleophilic attack of the epoxide oxygen on the electrophilic CO_2 carbon, *i.e.* as in (**3**). The intermediate (**3**), in turn, could be derived *via* reversible β-hydride addition from (**1**) (Scheme 1). The complex (**3**) has been postulated as an intermediate in the formation of (**1**) from $[(Me_3P)_3RhCl]$.[2]

The formation of the metallacarbonate (**2**) described here may have particular relevance to the mechanisms of a number of catalytic processes involving carbon dioxide and epoxides, *e.g.* the Ni[5]- and Rh[6]-catalysed production of propylene carbonate†† and the copolymerization of CO_2 and epoxides to form polycarbonates.[7] Indeed, an analogous nickelacycle has been proposed as an intermediate in the former process.[5]

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†† Experiments to determine whether (**2**) decomposes thermally to produce propylene carbonate are planned.

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