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Reactivity of palladium(II) methyl complexes towards CO₂: formation of carbonate complexes

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Abstract

Treatment of a benzene solution of (tmeda)PdMe₂ or (dppe)PdMe₂ with carbon dioxide gives the corresponding methyl bicarbonate complex, (L–L)PdMe(O₂COH). These were characterised by NMR spectroscopy and elemental analysis. Under strictly dry conditions no reaction was observed. Recrystallisation of the tmeda bicarbonate complex from acetone yields the corresponding η^2 -carbonate complex, which was characterised by X-ray crystallography. The reaction probably proceeds through attack by free carbonic acid on the dimethyl complex.

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1. Introduction

The use of carbon dioxide as a C_1 building block has received a lot of attention recently. The attractiveness of this approach is due to the fact that CO_2 is abundant, inexpensive, non-toxic and renewable [1]. However, carbon dioxide is inherently unreactive and thermodynamically stable and hence only a few processes have reached industrial scale [1a]. Especially interesting are reactions that form a new C-C bond such as the classical carboxylation of phenoxide to give salicylic acid [2,3]. Although π -allyl palladium complexes are known to insert CO₂ there are few reports of such insertions into late transition metal-carbon σ -bonds [4,5]. We are interested in the reactivity of Pd-C bonds towards carbon dioxide and here we report the reaction of palladium dimethyl complexes with CO₂ to give bicarbonate complexes. The molecular structure of a palladium η^2 carbonate complex is also reported together with a possible reaction mechanism.

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2. Experimental

2.1. General considerations

Benzene solvent and CD₃OD were vacuum-distilled from sodium/benzophenone ketyl and CaH₂, respectively. Dry carbon dioxide was obtained by passing it through a -78 °C trap on the vacuum-line. PdMe₂(tmeda) (1) and PdMe₂(dppe) (2) (tmeda = N, N, N', N'-tetramethylethylenediamine; dppe = bis(diphenylphosphino) ethane) were prepared according to literature procedures [6]. PdCl₂(dppe) (3) was prepared in benzene from the corresponding tmeda complex by ligand substitution. All other reagents are commercially available and were purchased and used as received.

NMR spectra were recorded either on a Varian Unity 300 MHz instrument (¹H, ³¹P) or a Bruker DRX 400 MHz spectrometer (¹³C). Chemical shifts are given in ppm downfield from Me₄Si using residual solvent peaks (¹H and ¹³C NMR) or H₃PO₄ (³¹P NMR δ 0) as internal and external references, respectively. IR spectra were recorded as KBr discs on a Bio-Rad FTS 6000 FT-IR spectrometer. The elemental analyses were performed by MikroKemi AB, Uppsala, Sweden or by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

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2.2. Preparations

cis-Pd(*Me*)(O_2COH)(*tmeda*) (4). Under an atmosphere of nitrogen a small autoclave was charged with 1 (0.100 g, 0.791 mmol) and dry benzene was added. The reaction vessel was pressurised with approximately 10 atm of CO₂ straight from the gas cylinder and stirred over-night at room temperature. This gave 0.062 g (52%) of a white, air-stable solid which was collected on a frit and washed twice with benzene. NMR (CD₃OD, RT): ¹H δ 0.38 (br, 3H) 2.49 (br, 6H) 2.56 (m, 2H) 2.64 (s, 6H) 2.77 (m, 2H). IR *v*(C–O) 1621 cm⁻¹. *Anal.* Calc. for C₈H₂₀N₂O₃Pd: C, 32.2; H, 6.7; N 9.4; O 16.1. Found: C, 32.2; H, 7.1; N 9.2; O 16.0%.

cis-Pd(Me)(O_2COH)(*dppe*) $\cdot \frac{1}{2}C_6H_6$ (**5**). Starting from 0.129 g of **2** and using a similar procedure as for **4** gave 0.039 g (26%) of **5** as an off-white, air-stable solid. NMR (CD₃OD): ¹H δ 0.54 (dd, ³*J*_{PH} = 7.2 and 2.7 Hz, 3H) 2.21 (m, 2H) 2.51 (m, 2H) 7.35–7.85 (m, 20H) ³¹P {¹H} δ 36.9 (d, ²*J*_{PP} = 62 Hz) 62.1 (d) ¹³C {¹H} δ 161.4 (s). IR *v*(C–O) 1613 cm⁻¹. *Anal.* Calc. for C₂₈H₂₈O₃P₂ Pd $\cdot \frac{1}{2}C_6H_6$: C, 60.06; H, 5.04. Found: C, 60.16; H, 5.02%.

cis-Pd(O_2CO)(*dppe*) (6). In a round-bottom flask 0.049 g of **3** was dissolved in 20 ml of CH₂Cl₂. Silver carbonate (0.029 g) was added and the reaction mixture was stirred overnight with exclusion of light. The silver chloride formed was filtered off and the filtrate was stripped from solvent and recrystallised from CH₂Cl₂/ pentane giving 0.020 mg of **6**. NMR (C₆D₆): ¹H δ 2.67 (s, 4H) 6.89–7.01 (m, 12H) 7.64–7.76 (m, 8H) ³¹P {¹H} δ 30.2 (s).

2.3. NMR experiments

Typically, a J. Young NMR-tube was charged with a few mg of the complex and evacuated on the high-vacuum line. The dry NMR-solvent was then vacuumtransferred onto the solid at -78 °C. If applicable, CO₂ was condensed in at -196 °C to give a pressure of 4–5 atm. The tube was thawed and any reaction was allowed to evolve.

2.4. Structure determinations

Recrystallisation of 4 from acetone under ambient conditions gave needle-like crystals that were mounted in a capillary. The X-ray analysis showed that the recrystallisation had given *cis*-Pd(O₂CO)(tmeda) (7), which co-crystallised with one mole of water. Intensity data were collected at 293 K with a Bruker Smart CCD system using ω scans and a rotating anode with Mo K α radiation ($\lambda = 0.71073$ Å) [7]. The intensity was corrected for Lorentz, polarisation and absorption effects using SADABS [8]. The first 50 frames were collected again at the end to check for decay. No decay was observed. All reflections were merged and integrated using SAINT [9]. The structure was solved by direct methods and refined by full matrix least-square calculations on F^2 using SHELXTL 5.1 [10]. Non-H atoms were refined with anisotropic displacement parameters. All hydrogen atoms except those on the water molecule were constrained to parent sites, using a riding model. Friedel pairs were not merged. Based on the systematic extinctions either of the two space groups Pc and P2/c could be chosen and we initially solved the structure in Pcbased on the value of |E * E - 1| (0.605), which indicates a non-centrosymmetric space group. This was shown to be the correct choice, since there is no twofold axis present in the refined structure.

2.4.1. Crystal data and collection and refinement details

 $C_7H_{18}N_2O_4Pd$, M = 300.63, monoclinic, a = 5.8716(12) Å, b = 6.9687(14) Å, c = 13.600(3) Å, $\beta = 95.72(3)^{\circ}$ V = 553.69(19) Å³, space group Pc (no. 7), Z = 2, $\mu = 1.669$ mm⁻¹, 5567 reflections measured, 3301 unique ($R_{int} = 0.0496$) which were used in all calculations. The final $wR(F^2)$ was 0.0910 and the *S* value 0.999 (all data). The R(F) was 0.0461 ($I > 2\sigma(I)$).

3. Results and discussion

3.1. Reactivity towards CO₂

All reactions are depicted in Scheme 1. Pressurising a solution of 1 or 2 in dry C_6D_6 in a J. Young NMR-tube with approximately 4 atm of CO_2 gave a precipitate after one day. In solution it was observed that the signals for the starting materials decreased in intensity but apart from small signals from unidentified decomposition products no new product was observed. A peak always appearing at 0.29 ppm was assigned to methane. Running the reaction on a preparative scale gave



products 4 and 5 in 25–90% yield. Typical yields are given in the experimental section; the variation in yield is probably due to different amounts of water present. Both products are air-stable white to off-white solids. In a parallel experiment the carbon dioxide was dried by passing it through a -78 °C trap on the vacuum-line before admitting it to the NMR tube. In this case no precipitate was observed and there was no sign of any reaction in solution. Compounds 4 and 5 turned out to be difficult to analyse in solution; they are insoluble in hydrocarbon and ether solvents and quickly decompose to the corresponding dichlorides, L₂PdCl₂, in chlorinated solvents.

In dry CD₃OD **4** is stable enough to obtain a ¹H NMR spectrum. The complex is asymmetric as seen by the fact that the two sides of the tmeda ligand are inequivalent. There is also a peak at 0.38 ppm assigned to a Pd–Me group. No other ligands (apart from tmeda and Me) could be identified in solution, but the elemental analysis speaks in favour of a bicarbonate complex and this is also supported by the IR-spectrum which displays a ν (C–O) at 1621 cm⁻¹. Furthermore, it is clear that there is a dynamic process in solution (broad peaks for the methyl group and the N–Me peaks on one side) and this is probably an exchange between coordinated bicarbonate and methanol solvent. Recrystallisation of **4** gave the corresponding η^2 -carbonate, **7** (vide infra).

Dissolving **5** in dry CD₃OD gives rise to static ¹H and ³¹P NMR spectra. Just as **4**, the complex has C₁-symmetry with inequivalent sides of the dppe ligand as seen by for example the appearance of two doublets in the ³¹P NMR spectrum. In the ¹H spectrum there is one peak at 0.54 ppm (dd) corresponding to *one* methyl group. The bicarbonate ligand was not observed in the ¹H spectrum, presumably due to H/D exchange, but in the carbon spectrum there is a peak at 161.4 ppm assigned to the bicarbonate. Attempts at obtaining X-ray quality crystals invariably gave a microcrystalline material which diffracted poorly. The static behaviour of **5** as compared to **4** is probably due to steric reasons; the sterically demanding dppe ligand slows down the attack by the solvent.

The type of reactions reported here are not unprecedented. Crutchley et al. [11] report a similar reaction, in which a *trans*-bis(phosphine)-bicarbonatomethyl complex is formed from the reaction of CO₂ with the corresponding dimethyl complex in the presence of water. Also, it was recently reported that the reaction of a (tmeda)Pd(OAr)₂ complex with CO₂ and water gave a Pd η^2 -carbonate complex [12].

It has been suggested that the formation of bicarbonate from a methyl ligand takes place via water hydrolysis to give a hydroxide and methane; the hydroxide subsequently undergoes insertion of CO_2 [11]. We decided to probe the mechanism and for a closer investigation 5 was chosen. To study the possible formation of an OH-complex, a C_6D_6 solution of 5 was saturated with water by addition of 10 µl of water and the reaction was followed by ¹H and ³¹P NMR spectroscopy. After 10 days there was still more than 90% starting material in addition to 3 peaks from unidentified decomposition products, none of which contained the spectral signature (e.g., ²*J*_{PP}) of a *cis*-L₂PdMe(OH) complex. Addition of KHCO₃ slowly (several days) yielded methane and one symmetric metal species that was identified as **6** by comparison with an authentic sample.

It therefore seems that the presence of water in a benzene solution of the dimethyl complexes does not lead to formation of a hydroxide to any measurable extent. This is in agreement with a recent investigation of the hydrolysis of similar platinum complexes, which only undergo reaction under acidic conditions [13]. The only way the bicarbonate could form via the hydroxide is thus if there is a fast pre-equilibrium between the hydroxide and dimethyl complex followed by a slower CO_2 insertion. This seems highly unlikely since that would involve a fast and reversible C-H activation of methane. We therefore favour a mechanism in which molecular carbonic acid is formed from carbon dioxide and water and this species (or possibly a proton followed by free bicarbonate) attacks the dimethyl complex to give the bicarbonate or carbonate complex along with methane. It seems that the amount of water present is crucial in determining whether a bicarbonate or a carbonate complex is formed. Although in principle the methyl bicarbonate complex could rearrange into an



Fig. 1. Diamond drawing with atomic numbering of $7 \cdot H_2O$. The thermal ellipsoids denote 30% probability. Bond distances (Å) and angles (deg) with estimated standard deviations: Pd–N1 = 2.060(7); Pd–N2 = 2.041(5); Pd–O2 = 2.015(5); Pd–O3 = 2.008(6); C7–O1 = 1.221(8);C7–O2 = 1.335(7); C7–O3 = 1.317(9); N1–Pd–N2 = 84.9(2); N1–Pd–O2 = 103.4(2); N2–Pd–O3 = 106.2(2); O2–Pd–O3 = 65.4(2); O1–C7–O3 = 126.3(7); O1–C7–O2 = 123.5(6); O3–C7–O2 = 110.2(6).

 η^2 -carbonate complex (and split off methane) this does not seem to happen unless there is additional water present as for example in the recrystallisation of **4**.

Finally, we can conclude that the present dimethyl complexes are not suitable for CO_2 activation in order to make new C–C bonds. We are currently investigating more electron rich Pd complexes in this laboratory.

3.2. Crystal structure

The crystals formed on recrystallisation of 4 from acetone consist of discrete molecules of 7 packed by dispersive forces together with one water molecule per complex. The molecular structure is shown in Fig. 1. The coordination geometry around Pd is distorted square-planar with a mean deviation from a leastsquares plane through PdN_2O_2 of 0.0023 Å. The angles deviate substantially from 90°, the smallest being the O-Pd–O angle which is $65.4(2)^{\circ}$ due to the η^2 -coordination of the carbonate. The carbonate moiety is planar and has O-C-O angles ranging between 110 and 126°. The C-O double bond is clearly localised with a C7-O1 distance of 1.221(8) A which is some 0.1 A shorter than the other two C-O distances. The molecular structure of 7 was recently reported but in crystals of a different space group with no water molecules in the unit cell [12]. Angles and distances in [12] are similar to those presently reported.

4. Supplementary material

Complete crystallographic data in the CIF format have been deposited with the CCDC (no. 220158). In addition, tables of structure factors have been deposited and are available from the authors upon request.

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