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Peroxocarbonato and Carbonato Derivatives of Pd(II)

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Palladium–phosphine complexes have been found to promote the fixation of CO_2 in some organic compounds [1] and to mediate the electrochemical reduction of CO_2 [2]; however there is no example reported of the isolation of a CO_2 palladium complex. The reaction between $[Pd(PCy_3)_2]$ [3] and CO_2 has already been studied and the conclusion was that there is no reaction at all [4].

We did not understand the reason for such a different behaviour compared to that of $[Ni(PCy_3)_3]$ [5], so we decided to reinvestigate the reaction of $[Pd(PCy_3)_2]$ with CO_2 and the first impression was that a reaction occurred*; however a careful check of the experimental conditions employed showed that the reaction takes place only in the presence of oxygen.

Results and Discussion

CO_2 and O_2 were bubbled into a toluene or n-hexane solution of $[Pd(PCy_3)_2]$ at room temperature and a white, microcrystalline product **1** formed in two hours. The IR spectrum of **1** shows strong absorptions at 1670 and 1250 cm^{-1}; these bands are shifted to 1620 and 1200 cm^{-1} respectively if the reaction is carried out with $^{13}CO_2$, so they can be assigned to $\nu(C{=}O)$ and $\nu_{as}(C{-}O)$. The ^{13}C NMR spectrum of **1** shows a broad signal at δ 169 ppm and the ^{31}P NMR spectrum shows two singlets at δ 47 and 41 ppm (1:1 ratio). CO_2 and O_2 were developed by treating a toluene solution of **1** with I_2, while **1** is stable in the solid state even under vacuum.

On the basis of these experimental data and taking into account the reaction of other palladium– and platinum–phosphino complexes with CO_2 in the presence of O_2 [7], we formulate **1** as the peroxycarbonate $[Pd(PCy_3)_2(OCO_3)]\cdot C_6H_5CH_3$ (the presence of toluene was inferred from the ^1H NMR spectrum and from analytical data). The non-equivalence of the two phosphorus atoms in the ^{31}P NMR spectrum agrees with the above formulation for **1**. Unfortunately, while some ^{13}C NMR spectra have been reported for the transition metal–CO_2 complexes [8] (δ 193–210 ppm) and carbonates [9] (δ 167–170 ppm), the lack of ^{13}C NMR data for peroxycarbonates prevents any comparison with our case.

1 is not stable in toluene solution under nitrogen and it slowly evolves spontaneously to a new product **2**. **2** is also obtained as a yellow crystalline solid by reacting $[Pd(PCy_3)_2]$ with CO_2 and O_2 in thf and keeping the resulting solution under nitrogen some days. The IR spectrum of **2** agrees with infrared data reported for some palladium–phosphine–carbonato compounds [7]: it shows two strong absorptions at 1655 and 1630 cm^{-1} of the same intensity ($\nu(C{=}O)$) and a band of medium intensity at 1190 cm^{-1} ($\nu_{as}(C{-}O)$). A direct comparison between the IR spectra of **1** and **2** shows the disappearance in **2** of a weak band at 780 cm^{-1}, which can be assigned to the $\nu(O{-}O)$ of the peroxycarbonate. Taking also into account that **2** is almost insoluble in all the common solvents, we formulate it as a carbonato derivative of unknown nuclearity $[Pd(PCy_3)_2(CO_3)]_n$.

Experimental

IR spectra were recorded on a Perkin-Elmer 283 instrument as nujol mulls. NMR spectra were recorded on a Varian 300 spectrometer; chemical shifts were referred to $SiMe_4$ for ^{13}C and ^1H nuclei, and to H_3PO_4 (85%, external) for ^{31}P. $Pd(PCy_3)_2$ was prepared as previously described [3].

$[Pd(PCy_3)_2(OCO_3)]\cdot C_6H_5CH_3$ (1)

CO_2 and O_2 were contemporaneously bubbled into a toluene (20 cm^3) solution of $[Pd(PCy_3)_2]$ (0.475 g, 0.71 mmol). A white, microcrystalline product formed slowly and after about 2 h it was filtered off and dried under vacuum (0.341 g, 58%). *Anal.* Found: C, 63.45; H, 8.88. Calc. for $C_{44}H_{74}O_4P_2Pd$: C, 63.28; H, 8.87%. NMR ^1H(thf-d_8) δ 7.14(s, 5H, C_6H_5), 2.30(s, 3H, CH_3), 1.99–1.19(br. m, 66H, C_6H_{11}); $^{31}P\{^1H\}(C_6D_6)$ δ 47(s, PCy_3), 41(s, PCy_3). IR 1670s ($\nu(C{=}O)$), 1250m ($\nu_{as}(C{-}O)$), 780w ($\nu(O{-}O)$) cm^{-1}.

$^{13}CO_2$-enriched compound was obtained by the same procedure using ^{13}C-enriched CO_2 obtained from $Ba^{13}CO_3$ and H_2SO_4. IR 1670m ($\nu(C{=}O)$),

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*We reported in previous communications the formation of an unidentified $[Pd(PCy_3)_2(CO_2)]$ species [6].

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1620s ($\nu(^{13}C{=}O)$), 1250w ($\nu_{as}(C{-}O)$), 1220m ($\nu_{as}(^{13}C{-}O)$) cm^{-1}. $^{13}C\{^1H\}$ NMR (C_6D_6) δ 169(br. s, C=O).

[Pd(PCy$_3$)$_2$(CO$_3$)]$_n$ (2)

CO_2 and O_2 were contemporaneously bubbled into a thf (15 cm^3) solution of [Pd(PCy$_3$)$_2$] (0.108 g, 0.16 mmol). The IR spectrum of the solution showed absorption at 1670 cm^{-1} of the peroxocarbonato complex. The solution was saturated with nitrogen and, after five days at room temperature, yellow crystals formed which were filtered and dried under vacuum. Yield 16 mg, 14%. *Anal.* Found: C, 60.55; H, 9.25. Calc. for $C_{37}H_{66}O_3P_2Pd$: C, 61.12; H, 9.08%. IR 1655s, 1630s ($\nu(C{=}O)$); 1190m ($\nu_{as}(C{-}O)$) cm^{-1}.

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