8. On the Synthesis and Characterization of Pd(CO)(PPh$_3$)$_3$

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Summary

Pd(CO)(PPh$_3$)$_3$ could be isolated from the reaction mixture arising from cyclohexene hydrocarboxylation by PdCl$_2$(PPh$_3$)$_2$ as the catalyst precursor; furthermore, it has also been prepared through direct reaction of Pd(PPh$_3$)$_4$ with CO in benzene. For this complex, ^{31}P- and ^{13}C-NMR. spectra suggest a rapid dissociation of PPh$_3$ at room temperature and a tetrahedral structure at $-70°$ in solution.

Pd(0) carbonyl phosphine complexes are believed to be intermediates in the Pd-catalyzed hydrocarboxylation reaction of olefinic substrates [1]. In line with our interest in asymmetric hydrocarboxylation [2], we are studying some aspects of the reaction mechanism which are still unclear [3].

From the reaction mixture obtained in the hydrocarboxylation of cyclohexene using ethanol as the hydrogen donor in the presence of PdCl$_2$(PPh$_3$)$_2$ and of a two molar excess of triphenylphosphine, a complex was isolated in 80% yield, the elemental analysis of which corresponded to the formula Pd(CO)(PPh$_3$)$_3$.

The IR. spectrum of this product in nujol mull showed a strong band at 1957 cm^{-1}, assigned to a terminal carbonyl stretching vibration and was superimposable with that obtained with a sample of Pd(CO)(PPh$_3$)$_3$ by the method of *Misono et al.* [4].

The fact that we could isolate the complex in high yield in the presence of an excess of triphenylphosphine prompted us to investigate the direct reaction of carbon monoxide with the Pd(PPh$_3$)$_4$ complex.

Contrary to preceding reports [4] [5], it was possible to obtain Pd(CO)(PPh$_3$)$_3$ by treating Pd(PPh$_3$)$_4$ in benzene at room temperature with carbon monoxide (1 atm). Pd(CO)(PPh$_3$)$_3$ when heated in a sealed capillary tube under vacuum shows a colour change at about 100-120° and eventually melts with decomposition between 190 and 200°. This temperature corresponds to that reported for the decomposition of the complex Pd(PPh$_3$)$_3$ [6].

Release of CO at 100-120° is also suggested both by DTA. measurements and by the disappearance of the carbonyl band from the IR. spectrum of the complex which was measured after the KBr disc was left for a few minutes under vacuum at 100°.

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The ^{31}P-NMR. spectrum of the complex in toluene-d_8/CH_2Cl_2 2:1 ($c = 1.6 \times 10^{-2}$ M) at room temperature showed a sharp singlet at +13.9 ppm (H_3PO_4 as external standard; positive values are downfield). Upon cooling to −70°, the signal shifted downfield, *i.e.*, occurring at +21.6 ppm; a second signal having low intensity simultaneously appeared at −8.2 ppm and was assigned to the free PPh_3 ligand. Addition of 2 equivalents of triphenylphosphine did not cause further movement of the resonance at +21.6 ppm but only an increase in the intensity of the signal corresponding to the free phosphine. The same solution, at room temperature, gave rise to only one signal at +8.7 ppm. This behaviour can be understood on the basis of ligand dissociation and a rapid (at room temperature) ligand exchange according to an equilibrium of the type

$$Pd(CO)(PPh_3)_3 \rightleftarrows Pd(CO)(PPh_3)_2 + PPh_3$$

To obtain a better idea about the nature of the predominating species arising from $Pd(CO)(PPh_3)_3$ in solution, we have studied the ^{13}C-NMR. spectrum of $Pd(^{13}CO)(PPh_3)_3$ (90% isotopic enrichment). This complex was prepared in the same way as the unlabelled one, by reacting $Pd(PPh_3)_4$ with ^{13}CO.

The ^{13}C-NMR. spectrum at −70° in toluene-d_8/CH_2Cl_2 2:1 ($c = 1.6 \times 10^{-2}$ M) showed a quartet centered at +196.7 ppm with relative intensities 1:3:3:1 ($J_{^{13}C,^{31}P} = 5.8$ Hz). Correspondingly the ^{31}P-NMR. spectrum of the same solution at −70° showed a doublet centered at +21.6 ppm ($J_{^{31}P,^{13}C} = 5.8$ Hz) and, in addition, a small singlet at −8.2 ppm.

Upon raising the temperature to −50° the quartet observed in the ^{13}C-NMR. and the doublet in the ^{31}P-NMR. collapsed to broad singlets. The predominant species in solution should therefore be the tetracoordinated $Pd(CO)(PPh_3)_3$. According to the signal pattern, the complex should possess in solution a pseudo-tetrahedral structure, analogous to that found for crystalline $Pt(CO)(PPh_3)_3$ [7]. However, it cannot be completely excluded that a fluxional behaviour of the tetracoordinated Pd-complex is still operative at −70°.

The IR. spectrum of the labelled compound in nujol mull shows two bands assigned to the terminal carbonyl stretching vibration: the first one with low intensity at 1957 cm^{-1} ($\nu\,^{12}CO$), the second one with strong intensity at 1914 cm^{-1} ($\nu\,^{13}CO$). The ratio between the two frequencies corresponds to that expected on the basis of the different isotopic masses. Furthermore, the difference of 43 cm^{-1} between the two bands confirms that only one carbon monoxide is bound to the Pd-atom and gives further evidence of the stoichiometry of the complex studied [8].

$Pd(CO)(PPh_3)_3$ does not show any catalytic activity in the hydrocarboxylation of olefins, analogously to $Pd(PPh_3)_4$ [9]. Addition of traces of hydrochloric acid, however, promotes the formation, under carbon monoxide pressure, of a catalytic active system [10]. The nature of the catalytically active complexes formed in the above conditions is under investigation.

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Experimental Part

The solvents used were *'puriss'* grade quality and were dried and degassed before use. ^{13}CO (90% isotopic enrichment) was a *Merck, Sharp* and *Dohme* product. Melting points were determined on a *Tottoli*-apparatus and are uncorrected. IR. spectra were recorded on a 177 *Perkin Elmer* spectrometer. NMR. spectra were recorded at 90 MHz with a WH 90 *Bruker* Spectrometer. $(Ph_3P)_2PdCl_2$ [11] and $Pd(PPh_3)_4$ [12] were prepared according to literature methods.

Preparation of $Pd(CO)(PPh_3)_3$ *under hydrocarboxylation conditions.* Cyclohexene (0.06 mol) in 27.6 g of ethanol (containing 2.43 g of *m*-xylene) [10] were introduced into a glass vial containing 0.42 g of $PdCl_2(PPh_3)_2$ and 0.32 g of PPh_3. The vial was placed in a 250 ml stainless autoclave. After flushing 3 times with carbon monoxide, carbon monoxide was pressurized in order to reach 200 atm at the reaction temperature (100°). The reaction time was 20 h (conversion of cyclohexene to ethyl cyclohexanecarboxylate ~ 95%). Upon cooling down the reaction mixture and venting the gas from the resulting yellow solution, in the course of a few minutes yellow-cream colored crystals were formed. The compound was filtered off and washed with pentane under CO and dried i.V. The yield was about 80% with respect to the initial $PdCl_2(PPh_3)_2$.

$C_{55}H_{45}OP_3Pd$ (921.55) Calc. C 71.68 H 4.92 P 10.08% Found C 71.58 H 5.06 P 9.79%

Preparation of $Pd(CO)(PPh_3)_3$ *from* $Pd(PPh_3)_4$ *and CO.* A suspension of $Pd(PPh_3)_4$ (1 g) in 20 ml of benzene previously saturated with CO, at room temperature and 1 atm rapidly (3 min) adsorbed CO (about 0.9 mol per mol of $Pd(PPh_3)_4$) giving a yellow solution. Addition of 20 ml of heptane under CO atmosphere brought about separation of a yellow-cream colored precipitate, which was filtered off and washed with heptane. The crude product was further purified by crystallization from benzene/heptane under a CO atmosphere. The yield of the yellow-cream colored product was about 90% based on the starting $Pd(PPh_3)_4$.

$C_{55}H_{45}OP_3Pd$ (921.55) Calc. C 71.68 H 4.92 P 10.08% Found C 70.70 H 5.05 P 9.89%

Preparation of $Pd(^{13}CO)(PPh_3)_3$ *from* $Pd(PPh_4)$. The compound was synthesized and purified analogously to the unlabelled one using ^{13}CO.

$C_{55}H_{45}OP_3Pd$ (922.55) Calc. C 71.71 H 4.91 P 10.07% Found C 72.05 H 5.26 P 9.84%

REFERENCES

[1] *J. Tsuji*, Accounts chem. Res. *2*, 144 (1969).
[2] *C. Botteghi, G. Consiglio & P. Pino*, Chimia *27*, 477 (1973).
[3] *P. Pino, F. Piacenti & M. Bianchi*, in 'Organic Syntheses via Metal Carbonyls', Ed. I. Wender and P. Pino, Vol. II, J. Wiley Inc., New York 1977, p. 233ff.
[4] *A. Misono, Y. Uchida, M. Hidai & K. Kudo*, J. organometal. Chemistry *20*, P7 (1969).
[5] *K. Kudo, M. Hidai & Y. Uchida*, J. organometal. Chemistry *33*, 393 (1971).
[6] *W. Kuran & A. Musco*, Inorg. chim. Acta *12*, 187 (1975).
[7] *V.C. Albano, G.M. Basso Ricci & P.L. Bellon*, Inorg. Chemistry *8*, 2109 (1969).
[8] *G. Bor*, Inorg. chim. Acta *3*, 191 (1969).
[9] *K. Bittler, N.v. Kutepow, D. Neubauer & H. Reis*, Angew. Chem. *80*, 352 (1968).
[10] *F. Wenzinger*, Dissertation ETH Zürich 1978.
[11] *J. Chatt & F.G. Mann*, J. chem. Soc. *1939*, 1623.
[12] *D.R. Coulson*, Inorganic Synth. *13*, 121 (1972).