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NOTE

CONCERNING THE PALLADIUM CARBONYL CHLORIDES $Pd_2(CO)_2Cl$ AND Pd(CO)Cl

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Recently, Fischer and Vogler[1] reported the preparation of the hitherto unknown dipalladium dicarbonyl chloride, $Pd_2(CO)_2Cl$, by reacting the palladium chloride benzonitrile complex, $Pd(C_6H_5CN)_2Cl_2$, with carbon monoxide in chloroform. Several attempted duplications of this procedure in our laboratory resulted inevitably in the formation of a product displaying the same typical IR features, insolubility in common organic solvents, and thermal stability as reported for $Pd_2(CO)_2Cl$, but having the emperical composition Pd(CO)Cl.

Earlier work by Dent *et al.*[2] on the carbonylation of allyl chloride in the presence of palladium chloride had resulted in the concomitant formation of an insoluble solid approaching the composition Pd(CO)Cl (Found: C, 8.1; H, 0.3; Cl, 19.0; Pd, 59.8. ClOPd calcd.: C, 7.07; Cl, 20.87; Pd, 62.63%.) and displaying an IR spectrum nearly identical with that reported by Fischer and Vogler for $Pd_2(CO)_2Cl$[1] and found by us for Pd(CO)Cl. Yet, in repeating Dent's procedure under slightly modified reaction conditions, Fischer and Vogler[1] claim again to have obtained $Pd_2(CO)_2Cl$. Therefore, we also repeated this experiment (1 g $PdCl_2$, 5 ml allyl chloride, 200 atm CO, 100° and 3 h reaction time). Again, we were not able to verify Fischer's and Vogler's result in as far as the insoluble solid had a composition (Found: C, 7.80; H, 0.3; Cl, 19.92; Pd, 60.24%.) which corresponded much more with that of Pd(CO)Cl than with that of $Pd_2(CO)_2Cl$ and, obviously, represents polymeric Pd(CO)Cl slightly contaminated with organic matter, *e.g.* a complex of allyl chloride with palladium chloride. In order to exclude the possibility of this contamination, we reacted palladium chloride in various non-complexing solvents with carbon monoxide at elevated pressures and temperatures. In each case, we obtained a product which had a composition in good agreement with that of Pd(CO)Cl and displayed the same typical IR features, physical and chemical properties as the product described by Fischer and Vogler[1]. Except for its instability in cold methanol, the properties of our product were also identical with the polymeric palladium carbonyl chloride, $[Pd(CO)Cl]_x$, which has been obtained by passing a wet stream of air or nitrogen through, or by adding 0.25 mole per cent of water to a suspension of $Pd(CO)Cl_2$ in methanol[3].

In related studies, we found that polymeric Pd(CO)Cl is also formed when

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palladium powder is reacted with carbon monoxide at approximately 200 atm and phosgene in *o*-dichlorobenzene at 190° for 90 min. The product thus obtained was contaminated with some unreacted metallic palladium, but otherwise had the same characteristics as the Pd(CO)Cl prepared according to our other procedures.

From the results reported here, we conclude that the formation of $Pd_2(CO)_2Cl$ as reported by Fischer and Vogler must be due to conditions which were accidental and are not readily recognizable from the experimental details. Obviously, under most conditions, the relevant reactions proceed with the formation of polymeric Pd(CO)Cl, which appears to be the most stable of the palladium carbonyl chloride species reported so far.

EXPERIMENTAL

Preparation of Pd(CO)Cl from $Pd(C_6H_5CN)_2Cl_2$

Anhydrous chloroform (400 ml) was charged into a 500 ml three-neck flask, equipped with a magnetic stirrer, gas inlet tube (subsurface) and gas outlet. The chloroform was then saturated with dry nitrogen. This was followed by addition of 1.9 g (0.005 mole) of bis(benzonitrile)palladium dichloride, $Pd(C_6H_5CN)_2Cl_2$. Passing of dry nitrogen through the stirred mixture, kept at room temperature, was continued until the $Pd(C_6H_5CN)_2Cl_2$ was completely dissolved. The nitrogen was then shut off and dry carbon monoxide was passed through the stirred solution for 3 h. During this time, the color of the formed precipitate changed from orange to red-brown and finally to yellowish-green. The product was isolated by filtration, washed with benzene and petroleum ether (b.p. 30–60°) and dried at room temperature *in vacuo*. Yield: 0.61 g (72% of theory). IR (KBr pellets): 1978 vs, 1940 (sh), 604 vs, 585 s, 432 m, 385 m cm^{-1}. (Found: C, 7.23; Cl, 20.98; Pd, 61.96. CClOPd calcd.: C, 7.07; Cl, 20.87; Pd, 62.63%.)

Preparation of Pd(CO)Cl from $PdCl_2$

(*a*). The procedure described above was repeated, except that 0.89 g (0.005) mole) of $PdCl_2$, instead of $Pd(C_6H_5CN)_2Cl_2$, was charged and that the reaction time was extended to 15 h. The yellowish-green product (yield: 0.80 g or 94% of theory) showed an IR spectrum identical with that obtained for the product prepared from $Pd(C_6H_5CN)_2Cl_2$. (Found: C, 7.04; Cl, 20.66; Pd, 62.30. CClOPd calcd.: C, 7.07; Cl, 20.87; Pd, 62.63%.)

(*b*). A rocking 100 ml autoclave, equipped with a glass insert liner, was charged with 0.36 g (0.002 mole) of palladium dichloride and 10 ml *ortho*-dichlorobenzene. The reactor was purged with dry carbon monoxide, pressurized with CO to 170 atm and then heated at 190° for 3 h. The yellowish-green reaction product (yield 0.31 g or 90% of theory) showed an IR spectrum which was identical with that of the product obtained from $Pd(C_6H_5CN)_2Cl_2$. (Found: C, 7.21; Cl, 20.64; Pd, 61.80%.) The Debye–Scherrer powder pattern revealed a high degree of crystallinity, Pd^0 or $PdCl_2$ were not detectable. Thermogravimetric analysis in an atmosphere of argon showed slow decomposition beginning at 180°.

Preparation of Pd(CO)Cl from metallic palladium

A glass lined rocking autoclave was charged with palladium powder (0.2 g) and 10 ml of *ortho*-dichlorobenzene containing 5% phosgene. The autoclave was pressur-

ized with carbon monoxide to 170 atm and heated at 190° for 3 h. The recovered yellowish-green reaction product (0.25 g) exhibited an IR spectrum which was essentially identical with that observed in the previous runs. The lower chlorine content (16.19%) indicated incomplete conversion.

Reaction of $PdCl_2$ with CO in allyl chloride

A glass lined rocking autoclave was charged with 1.0 g of palladium chloride and 5.0 ml allyl chloride. The reactor was pressurized with carbon monoxide and kept at 100° and 200 atm for 3 h. The grayish-green solid formed in the reaction was filtered and washed with benzene and petroleum ether (b.p. 30–60°). Yield: 0.6 g IR (KBr pellets): 1978 vs, 1942 (sh), 615 vs, 585 s, 435 m, 382 m. Results of the elementary analysis were in fair agreement with the values calculated for Pd(CO)Cl. (Found: C, 7.80; H, 0.3; Cl, 19.92; Pd, 60.24%.)

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