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ALKOXY CARBONYL COMPLEXES OF PALLADIUM AND THEIR ROLE IN ALCOHOL CARBONYLATION

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Summary

The behaviour of phosphinepalladium(II) complexes in methanol/carbon monoxide systems has been investigated. $Pd(COOCH_3)(OAc)(PPh_3)_2$ and $Pd(COOCH_3)_2(PPh_3)_2$ have been isolated and characterized. A scheme is presented for the formation of oxalate esters in alcohol carbonylation in the presence of palladium complexes.

Introduction

Our interest in alcohol carbonylation led us to investigate the behaviour of phosphinepalladium complexes in alcohols under carbon monoxide. Alcohol carbonylation in the presence of palladium salts is reported to give both dialkyl carbonates [1] and oxalates [2]. During our investigation we have identified two new alkoxycarbonylpalladium complexes, i.e. $Pd(COOCH_3)(OAc)(PPh_3)_2$ (I) and $Pd(COOCH_3)_2(PPh_3)_2$ (II), which appear to be involved in methanol carbonylation to oxalate esters and whose formation sheds some light on the reaction route.

Although alkoxycarbonylpalladium complexes are well known [3,14] little attention has been devoted to alkoxycarbonyl carboxylate complexes of this metal [4], only $Pd(COOCH_3)(OCOCF_3)(PPh_3)_2$ having been described [5], in spite of their interest as reaction intermediates. For example, for olefin carboxylation Heck [6] used a combination of $Pd(OAc)_2$ and $Hg(COOCH_3)(OAc)$, and assumed that methoxycarbonylpalladium acetate was produced as the active species in the reaction medium.

As for II, the analogous platinum compound has previously been made by several routes [5,7—10]. It is said to be the only example of a species having two metal-bonded COOR groups [9].

Results

When $Pd(OAc)_2(PPh_3)_2$ was suspended in CH_3OH under CO (20—50 atm) at 50°C (or higher temperatures) for 2—4 h, reduction occurred to give phosphinepalladium(0) carbonyls: $Pd_3(CO)_3(PPh_3)_3$ and $Pd(CO)(PPh_3)_3$ were identified by their infrared spectra [11]. In the presence of an additional mol of PPh_3 per mol of Pd, only the latter complex was formed. GLC analysis of the methanolic filtrate indicated the formation of dimethyl oxalate and acetic acid in almost quantitative yields [12], indicating the stoichiometry depicted in eq. 1.

$$Pd(OAc)_2(PPh_3)_2 + 3\ CO + 2\ CH_3OH \xrightarrow{PPh_3} Pd(CO)(PPh_3)_3 + (COOCH_3)_2 + 2\ AcOH \qquad (1)$$

However, when the reaction was carried out at room temperature, no reduction of palladium(II) to palladium(0) was observed, and complex I was isolated, m.p. 129—136°C (dec.); IR: 1655, 1070 cm^{-1} (methoxycarbonyl) and 1605, 1325 (acetate); ^1H NMR: δ (ppm) 7.6 and 7.3 (m, 30H, phenyl) 2.42 (s, 3H, methoxy), 0.85 (s, 3H, acetate). Its identity was confirmed synthetizing it by an independent route, viz. metathetical reaction of $Pd(COOCH_3)(Cl)(PPh_3)_2$ (III) with the stoichiometric amount of silver acetate in CH_2Cl_2 at room temperature. Eqs. 2 and 3 depict the routes to I.

$$Pd(OAc)_2(PPh_3)_2 + CO + CH_3OH \rightarrow Pd(COOCH_3)(OAc)(PPh_3)_2 + AcOH \qquad (2)$$

$$Pd(COOCH_3)(Cl)(PPh_3)_2 + AgOAc \rightarrow Pd(COOCH_3)(OAc)(PPh_3)_2 + AgCl \qquad (3)$$

II was obtained by the reaction of III with an excess of sodium methoxide under CO (2—3 atm) at 0°C for 4—5 h (eq. 4). It had m.p. 118—134°C (dec.); IR: 1630 and 1010 cm^{-1} (methoxy carbonyl); NMR: δ (ppm) 7.6 and 7.3 (m, phenyls, 30H), 2.44 (s, methoxy, 6H).

$$Pd(COOCH_3)(Cl)(PPh_3)_2 + NaOCH_3 + CO \rightarrow Pd(COOCH_3)_2(PPh_3)_2 + NaCl \qquad (4)$$

A similar synthesis was also attempted from $PdCl_2(PPh_3)_2$, but the product was a mixture of II and unreacted material. At lower temperatures no reaction occurred, while raising the temperature to 20°C resulted in reduction of the palladium to phosphinepalladium(0) carbonyls.

II appeared to be indefinitely stable as the solid, even in the air, but its solutions in chlorinated solvents decomposed within a few hours. It was stable for several hours in methanol under CO atmosphere at room temperature, but quickly decomposed at 50°C to give carbonyls. Dimethyl oxalate could be detected by GLC of the liquid solution. We believe that for the formation of oxalate esters, our results indicate, but do not conclusively confirm the route depicted in eq. 5.

$$(Ph_3P)_2Pd(OAc)_2 \xrightarrow[-AcOH]{CO,\ CH_3OH} (Ph_3P)_2Pd(COOCH_3)(OAc) \xrightarrow[-AcOH]{CO,\ CH_3OH}$$

$$(Ph_3P)_2Pd(COOCH_3)_2 \rightarrow [Pd^0] + (COOCH_3)_2 \qquad (5)$$

This route involves substitution of anionic ligands on palladium by alkoxycarbonyl groups, probably through intermediate cationic carbonyl species, to give mono- and bis-alkoxycarbonyl complexes such as I and II, followed by reductive coupling of the latter.

The alternative route requires CO insertion into a Pd—COOR bond to give an alkoxalyl complex Pd—COCOOR followed by RO^- attack to give the oxalate. Although such complexes have been obtained by oxidative addition of oxalyl chloride to palladium(0) [13] insertion of CO into Pd—COOR bonds was never firmly established [13,14].

Experimental

All reactions, including isolations and recrystallizations, were performed under carbon monoxide or nitrogen, as appropriate. Melting points were taken in the air. $Pd(COOCH_3)(Cl)(PPh_3)_2$ [15] and $Pd(OAc)_2(PPh_3)_2$ [16] were prepared by published methods. IR spectra were recorded on a Perkin—Elmer 577 as Nujol mulls and ^1H NMR spectra on a Varian HA-100 spectrometer with $CDCl_3$ as solvent and HMDS as internal standard. GLC analyses were carried out on 8 ft × 1/4″ Carbowax 20M on Chromosorb WS 60/80 mesh with benzofuran as internal standard.

Preparation of $Pd(COOCH_3)(OAc)(PPh_3)_2$

Method A. A suspension of $Pd(OAc)_2(PPh_3)_2$ (0.58 g) in CH_3OH (20 cm^3) was autoclaved for 6 h under CO (50 atm) at room temperature with stirring. The resulting solution was filtered and the volume reduced under vacuum. Addition of diethyl ether to the complex precipitated white air stable crystals. Recrystallization was from CH_2Cl_2/pentane (0.28 g, 48%). (Found: C, 63.7; H, 4.8; $C_{40}H_{36}O_4P_2Pd$ calcd.: C, 64.1; H, 4.84%).

Method B. $Pd(COOCH_3)(Cl)(PPh_3)_2$ (0.84 g) was dissolved in CH_2Cl_2 (20 cm^3) with stirring, and silver acetate (0.19 g) was added at room temperature. After 15 min the Ag salt was filtered off and the solution reduced to a small volume by evaporation under reduced pressure. Addition of pentane gave the complex (0.72 g, 83%).

Preparation of $Pd(COOCH_3)_2(PPh_3)_2$

$Pd(COOCH_3)(Cl)(PPh_3)_2$ (0.65 g) was suspended in CH_3OH (20 cm^3) under CO (3 atm) and sodium methoxide (0.20 g) in methanol (5 cm^3) was added the mixture being kept at —78°C with an acetone/dry ice bath. The temperature was then raised up to 0°C. After 5 h the autoclave was open and the solid quickly filtered off and washed with cold methanol. The product (0.65 g) was dissolved in CH_2Cl_2, and after filtration of the solution was precipitated with pentane as white crystals. (Found: C, 63.5; H, 5.1; $C_{40}H_{36}O_4P_2Pd$ calcd.: C, 64.1; H, 4.84%). Recrystallization is best carried out at 0°C or below to avoid decomposition.

References

1 M. Graziani, P. Uguagliati and G. Carturan, J. Organometal. Chem., 27 (1971) 275.
2 D.M. Fenton and P.J. Steinwand, J. Org. Chem., 39 (1974) 701.

3 R.J. Angelici, Accounts Chem. Res., 5 (1972) 335.
4 D.M. Barlex and R.D.W. Kemmitt, J. Chem. Soc. Dalton, (1972) 1436.
5 W. Beck and K.W. Werner, Chem. Ber., 105 (1972) 3947.
6 R.F. Heck, J. Amer. Chem. Soc., 91 (1969) 6707; 93 (1971) 6896.
7 W. Beck, W. Rieber, S. Cenini, F. Porta and G. La Monica, J. Chem. Soc. Dalton, (1974) 298.
8 I.S. Kolomnikov, P. Svoboda and M.E. Vol'pin, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 2752.
9 G. Minghetti, F. Bonati and G. Banditelli, Syn. Inorg. Metal. Org. Chem., 3 (1973) 415.
10 W.J. Cherwinsky and H.C. Clark, Inorg. Chem., 10 (1971) 2263.
11 K. Kudo, M. Hidai and Y. Uchida, J. Organometal. Chem., 33 (1971) 393.
12 G. Cipriani and C. Neri, unpublished results.
13 E.D. Dobrzynsky and R.J. Angelici, Inorg. Chem., 14 (1975) 59.
14 S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, J. Amer. Chem. Soc., 95 (1973) 3180.
15 M. Hidai, M. Kokura and Y. Uchida, J. Organometal. Chem., 52 (1973) 431.
16 T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer and G. Wilkinson, J. Chem. Soc., (1965) 3362.