TRANSITION METAL-CARBON BONDS

IV*. CARBOXYLATO-BRIDGED π-ALLYLIC PALLADIUM(II) COMPLEXES

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Recently there has been great interest in olefin and π-allylic complexes of palladium(II) and important industrial processes for making acetaldehyde[1] and vinyl acetate from ethylene using a palladium(II) catalyst have been developed which probably involve intermediate ethylene–palladium hydroxide or ethylene–palladium acetate complexes. Since some olefin–palladium(II) complexes are readily converted into π-allylic palladium(II) complexes[2] we thought it of interest to make carboxylato-bridged π-allylic palladium complexes and study their properties. In this paper we describe the preparation and properties of this new series of complexes.

Very few carboxylato-bridged organometallic complexes of transition metals have been prepared. Chatt and Venanzi[3] prepared di-μ-acetatodi(1,5-cyclooctadiene)-dirhodium by treating the corresponding bridged-chloro complex with potassium acetate in boiling acetone. This compound was remarkably stable, melting at 197–198° without decomposition. When we tried to replace the bridging chloro group of di-μ-chlorodiallyldipalladium(II) (π-allylpalladium chloride) by a similar method we obtained a mixture from which only the unchanged bridged-chloro complex was isolated. However, when this bridged-chloro complex was shaken with a suspension of silver acetate in acetone for several hours, silver chloride gradually formed and a good yield of the corresponding bridged-acetato complex was isolated as a pale yellow crystalline solid. Cryoscopic measurements in benzene showed the complex to be dimeric. It decomposed slightly in boiling benzene but again ebullioscopic measurements suggested it was dimeric. It was less stable than the bridged-chloro complex, decomposing after several days at room temperature and rapidly at 100–130°, without melting. Similarly di-μ-acetatobis(2-methylallyl)dipalladium(II) was prepared and also complexes containing bridging propionate, trimethylacetate and benzoate groups, using the corresponding silver carboxylates. A bridged-trifluoroacetate complex $[Pd(OOCCF_3)_2(C_3H_5)_2]$ was prepared by the action of trifluoroacetic acid on the corresponding acetato-bridged complex. Our complexes show very strong absorption bands at *ca.* 1575 and 1425 cm^{-1} due to the bridging carboxylate groups and no bands at *ca.* 1700 cm^{-1} which would be expected for an uncomplexed carbonyl group. Attempts to convert the chloro-bridged alkoxyl π-allylic palladium(II) complexes recently described by us[4] gave complexes which were low melting and could not be purified; possibly they were mixtures of geometrical isomers due to the asymmetrical structures of the π-allylic ligands in these complexes.

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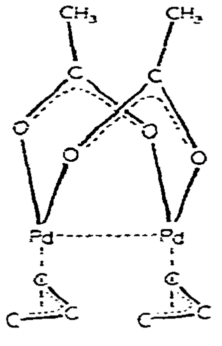
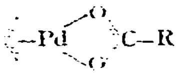
* Part III, in press.

An X-ray structural determination by Churchill and Mason[5] shows di-μ-acetatodiallyldipalladium(II) to have the unexpected structure (I). The palladium–palladium distance of only 2.94 Å suggests some weak metal–metal bonding and the planes of the bridging acetate groups are at an angle of 94°. The dimeric copper(II) acetate monohydrate forms a very similar arrangement of metal atoms and acetate groups. Copper(II) is a d^9 system and the weak copper–copper bond provides a mechanism for electron pairing and accounts for the low magnetic moment of copper(II) acetate monohydrate. It is difficult to see which orbitals are involved in forming the palladium–palladium bond in di-μ-acetatodiallyldipalladium(II), however. The *cis*-arrangement of the two allyl groups means that in the solid state at least the two palladium atoms are not equivalent.



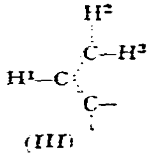
(I)



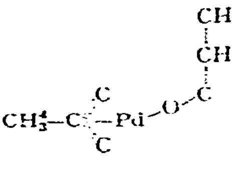
(II)

Presumably a monomeric structure such as (II) with the carboxylate group in a four-membered ring is not formed because the high electronegativity of oxygen makes the formation of bonds at angles as small as 90° unlikely. The 2-methylallyl and acetate groups are isoelectronic but presumably the high electronegativity of oxygen makes the π-electrons of the acetate group not available for bonding; *i.e.*, a π-acetate is not formed. Morehouse *et al.*[6] have suggested that four-membered rings such as in (II) are present in palladium(II) acetate, which is trimeric in freezing benzene.

The nuclear magnetic resonance spectra of these carboxylato-bridged complexes were particularly valuable in confirming the structures. The data are given in Table 1 with the different types of protons numbered as in (III) and (IV). Data for the corresponding chloro-bridged complexes[4] are given for comparison. The absorptions had the expected intensities and multiplicities in all cases.



(III)



(IV)

The carboxylato bridge could be replaced readily by more strongly co-ordinating ligands, thus treatment of di-μ-acetatodiallyldipalladium(II) with dry hydrogen

TABLE 1

NUCLEAR MAGNETIC RESONANCE DATA FOR CARBOXYLATO-BRIDGED π-ALLYLIC PALLADIUM(II) COMPLEXES

Measured in deuterochloroform at 60 Mc/sec. J in cps.

Complex	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	J_{12}	J_{13}	J_{14}
Allyl-Pd-acetate	4.53	6.12	7.15		7.97		6.5	12	
Allyl-Pd-propionate	4.53	6.12	7.13		7.68	8.92	6.7	12	7.0
Allyl-Pd-pivalate	4.56	6.17	7.15			8.91	6.8	12	
Allyl-Pd-chloride	4.57	5.93	6.91				6.9	12	
2-Methylallyl-Pd-acetate		6.30	7.29	7.75	7.97				
2-Methylallyl-Pd-propionate		6.32	7.27	7.74	7.69	8.92			7.3
2-Methylallyl-Pd-benzoate*		6.24	7.17	7.70					
2-Methylallyl-Pd-chloride		6.15	7.12	7.86					

* The phenyl group showed two complex bands at 2.05 and 2.71 τ.

chloride gave di-μ-chlorodiallyldipalladium(II) and with trifluoroacetic acid the corresponding bridged-trifluoroacetate complex, $[Pd_2(OOCCF_3)_2(C_3H_5)_2]$. With acetylacetone and sodium carbonate in acetone the monomeric (acetylacetonato)allylpalladium(II)[4] was formed. The carboxylato-bridged complexes reacted with typical bridge splitting ligands such as pyridine or quinoline but stable products could not be isolated. Preliminary observations have shown that on thermal decomposition carboxylato-bridged π-allylic palladium complexes give metallic palladium, and a mixed organic product containing the allyl ester of the bridging acid, the olefin corresponding to the allylic group: *e.g.*, propylene from π-allyl, and other products.

EXPERIMENTAL

Melting or decomposition points were determined on a Kofler hot-stage apparatus and are corrected.

Preparation of carboxylato-bridged π-allylic palladium(II) complexes: general method

A solution of the corresponding chloro complex in acetone was treated with the silver salt (2.2 mole) of the appropriate carboxylic acid and the suspension shaken for 12 h. The resultant precipitate of silver chloride was filtered off and the filtrate evaporated to dryness at reduced pressure. Recrystallisation of the residue from methylene chloride/light petroleum (b.p. 60–80°) or, in the case of acetates, from ethyl acetate gave the required product. Prepared in this manner were:

Di-μ-acetatodiallyldipalladium(II) (yield 65 %) as yellow prisms from ethyl acetate decomposing without melting 100–130°. (Found: C, 29.05; H, 4.0; mol. wt. cryoscopically in 1.4 % benzene solution, 396. $C_{10}H_{16}O_4Pd_2$ calcd.: C, 29.05; H, 3.9 %; mol. wt., 413.)

Di-μ-acetatobis(2-methylallyl)dipalladium(II) (yield 60 %) as yellow prisms from ethyl acetate decomposing without melting 100–130°. (Found: C, 32.35; H, 4.45; mol. wt. cryoscopically in 1.0 % benzene solution, 430; in 1.4 % benzene solution, 424. $C_{12}H_{20}O_4Pd_2$ calcd.: C, 32.65; H, 4.55 %; mol. wt., 441.)

Di-μ-propionatodiallyldipalladium(II) (yield 60 %) as yellow prisms subliming

110–120°, m.p. 120–130° decomp. (Found: C, 32.8; H, 4.65. $C_{12}H_{20}O_4Pd_2$ calcd.: C, 32.65; H, 4.55 %.)

Di-μ-benzoatobis(2-methylallyl)dipalladium(II) (yield 52 %) as yellow prisms decomposing without melting 148–152°. (Found: C, 47.05; H, 4.0. $C_{22}H_{24}O_4Pd_2$ calcd.: C, 46.75; H, 4.3 %.)

Bis(μ-trimethylacetato)diallyldipalladium(II) (yield 25 %) as yellow prisms decomposing without melting above 150°. (Found: C, 38.1; H, 5.45. $C_{16}H_{28}O_4Pd_2$ calcd.: C, 38.65; H, 5.7 %.)

Preparation of bis(μ-trifluoroacetato)diallyldipalladium(II) from di-μ-acetatodiallyldipalladium(II) and trifluoroacetic acid

Di-μ-acetatodiallyldipalladium (0.16 g) was dissolved in acetone (10 cc), trifluoroacetic acid (0.2 cc) was added and the mixture warmed on a steambath for 2 min. The solution was evaporated to dryness at reduced pressure and the residue re-treated with trifluoroacetic acid (0.2 cc) in acetone (10 cc). The residue left after evaporation was recrystallised from methylene chloride/light petroleum (b.p. 60–80°) to give the required product as cream microcrystals (0.10 g) decomposing without melting 155–165°. (Found: C, 23.15; H, 2.05. $C_{10}H_{10}F_6O_4Pd_2$ calcd.: C, 23.05; H, 1.95 %.)

Conversion of di-μ-acetatodiallyldipalladium(II) to (acetylacetonato)allylpalladium(II)

Di-μ-acetatodiallyldipalladium(II) (0.26 g) in acetone (10 cc) was shaken with sodium carbonate (1.0 g) and acetylacetone (0.5 cc) for 1 h. The resultant suspension was evaporated to dryness at reduced pressure. Recrystallisation of the residue from light petroleum (b.p. 60–80°) gave (acetylacetonato)allylpalladium (0.15 g), m.p. 72–75°. The infrared spectrum of this product was identical with that of an authentic sample.

Conversion of di-μ-acetatodiallyldipalladium(II) to di-μ-chlorodiallyldipalladium(II)

Di-μ-acetatodiallyldipalladium (0.10 g) dissolved in methylene chloride (10 cc) was treated with dry hydrogen chloride for 3 min. The solution was evaporated at reduced pressure and the residue washed with methanol to yield the required bridged-chloro complex (0.065 g), identified by its infrared spectrum.

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SUMMARY

The preparation and properties of a new series of carboxylato-bridged binuclear π-allyl and π-2-methylallyl complexes of palladium(II) are described. Nuclear magnetic resonance data are given.

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