

314. Some Observations on the Preparation of π -Allylic Palladium Chloride Complexes.

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π -Allylic palladium chloride complexes are formed in high yield when carbon monoxide is passed through a mixture of an allylic chloride and a palladium salt dissolved in methanol. The nature of the insoluble substances obtained when carbon monoxide is passed through a suspension of a π -allylic palladium chloride complex in a methanolic solution of an allylic halide is discussed.

π -ALLYLIC palladium chloride complexes have been prepared previously by the action of palladium chloride on either an allylic alcohol^{1,2} or an allylic chloride,^{3,4} but the yields (based on palladium chloride) have seldom exceeded 50%. We have now found (Table 1) that

TABLE 1.
Preparation of π -allylic palladium chloride complexes.

Expt. no.	Allylic chloride	Wt. (g.)	Na ₂ PdCl ₄ ¹ (g.)	PdCl ₂ (g.)	NaCl (g.)	CaCl ₂ (g.)	H ₂ O (g.)
1	Allyl chloride	18.6	20.0	—	—	—	—
2	Allyl chloride	27.9	—	17.7	—	11.1	—
3	Methallyl chloride	20.2	20.0	—	—	—	—
4	Methallyl chloride	20.2	—	6.3	—	5.0	—
5	3-Chlorobut-1-ene	19.0	20.0	—	—	—	—
6	1-Chlorobut-2-ene	19.0	20.0	—	—	—	—
7	1-Chlorobut-2-ene	10.0	—	4.44	3.4	—	—
8	1-Chlorobut-2-ene	10.0	—	4.44	2.95	—	2.25
9	1-Chlorobut-2-ene	10.0	—	4.44	2.95	—	13.5
10	1-Chlorobut-2-ene	10.0	—	4.44	—	2.8	—

Expt. no.	Palladium chloride complex			Insoluble by-product					
	π -Allylic group	Wt. (g.)	Yield ⁵ (%)	Ref.	Wt. (g.)	Found (%)			
						C	H	Cl	Pd
1	Allyl ²	8.5	84	—	—	—	—	—	—
2	Allyl	12.25	67.5	A	1.5	13.8	1.5	18.9	58.1
3	Methallyl ³	10.1	92.5	—	—	—	—	—	—
4	Methallyl	5.3	76	B	1.6	16.2	2.7	18.1	51.3
5	But-2-enyl ⁴	10.7	98	—	—	—	—	—	—
6	But-2-enyl	9.1	83.5	—	—	—	—	—	—
7	But-2-enyl	1.05	21.2	—	—	—	—	—	—
8	But-2-enyl	4.95	100	—	—	—	—	—	—
9	But-2-enyl	4.95	100	—	—	—	—	—	—
10	But-2-enyl	4.8	97.5	C	0.15	16.0	2.1	18.9	55.4

¹ Na₂PdCl₄, palladium content 29.6%, water content *ca.* 2 mols. ² M. p. 158° (decomp.) (Found: C, 19.7; H, 2.9; Cl, 19.4. Calc. for C₆H₁₀Cl₂Pd₂: C, 19.6; H, 2.75; Cl, 19.4%). ³ M. p. 166—168° (decomp.) (Found: C, 24.4; H, 3.6; Cl, 18.1. Calc. for C₈H₁₄Cl₂Pd₂: C, 24.4; H, 3.6; Cl, 17.95%). ⁴ M. p. 136—137° (Found: C, 24.3; H, 3.8; Cl, 17.3. Calc. for C₈H₁₄Cl₂Pd₂: C, 24.4; H, 3.6; Cl, 17.95%). ⁵ Yield based on palladium content of starting materials.

these complexes are formed almost quantitatively by the action of carbon monoxide at atmospheric pressure and room temperature on solutions of allylic chlorides in methanol containing sodium chloropalladite. Initially a commercial sample of sodium chloropalladite was used (experiments 1, 3, 5, and 6) and the yields of complexes were greater than 80%. Subsequently, a mixture of dried sodium chloride and palladium chloride was used (experiment 7), and the yield then fell to 21%. This variation in yield is apparently associated with the quantity of water available, because when experiment 7 was repeated

¹ Smidt and Hafner, *Angew. Chem.*, 1959, **71**, 284.

² Moiseev, Fedorovskaya, and Syrkin, *J. Inorg. Chem. U.S.S.R.*, 1959, **4**, 2461.

³ Hüttel and Kratzer, *Angew. Chem.*, 1959, **71**, 456.

⁴ Hüttel, Kratzer, and Bechter, *Ber.*, 1961, **94**, 766.

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in the presence of quantities of water (experiments 8 and 9) quantitative yields of the complex were obtained. Analysis of the commercial sodium chloropalladite showed slightly more than two molecules of water.

When mixtures of palladium and calcium chlorides were used (experiments 2, 4, and 10), in addition to the formation of the π -allylic palladium chloride complexes, some chloroform-insoluble material was isolated. These insoluble materials (A, B, and C; Table 1) decomposed without melting, were insoluble in the usual organic solvents, and gave elemental analyses which did not correspond with any simple formulation although in each case the palladium:chlorine ratio was approximately 1:1. When solid B was repeatedly extracted with undried chloroform some material dissolved; evaporation of the filtered solution then gave a small yield of di- μ -chloro-di- π -methallyldipalladium which suggests that the π -methallyl ligand was originally present in B. The preparation of similar insoluble materials was achieved by passing carbon monoxide through suspensions of π -allylic palladium chloride complexes in methanol containing equivalents of palladium chloride and hydrogen chloride under anhydrous conditions. Table 2 records some typical results.

TABLE 2.

Palladium complex	PdCl ₂ (g.)	HCl ¹ (g.)	Ref.	Product					
				Ref.	(g.)	Found (%)			
						C	H	Cl	Pd
π -Allylic group									
Allyl.....	2.3	2.2	1.0	D ²	2.7	15.6	2.0	18.8	55.3
Methallyl.....	3.5	4.4	1.8	E	5.8	17.4	2.1	19.3	57.6
But-2-enyl.....	5.0	4.4	1.8	F	7.0	16.8	2.3	19.0	56.4

¹ Formed by the addition of an equivalent amount of acetyl chloride. ² For a structure C₅H₅Cl₂O₂Pd₂ (I) the required figures are C, 15.75; H, 1.3; Cl, 18.6; Pd, 56.0%.

Infrared Spectra.—The insolubility of the solid products A—F in all common solvents prevented n.m.r. examination. The substances were amorphous and therefore not amenable to X-ray study. The infrared-spectra, however, proved informative. The frequencies observed for A and B (Table 1) and for D, E, and F (Table 2) are listed in Table 3. For

TABLE 3.

Infrared spectra.

Solids A and D, 1937vs 1908sh 1458m 1387s 1196w 1020m 999w 991w 961m 948m 761m 630vs 600m 504w 441m 394w 368w
 $[\pi$ -Allyl PdCl₂], 3077w 3045w 3003w 1910w 1460s 1385s 1230w 1193w 1024m 1005sh 999m 968m 961sh 943s 911w 767w 510s 401m 377sh 366m
 Solids B and E, 3069m 2988w 2967w 2926w 2853vw 1977vw 1943vs 1908w 1479w 1467m 1449w 1431m 1382m 1337w 1051m 1031m 961m 945m 833s 782m 633vs 597s 441s 393w 376m
 $[\pi$ -Methallyl-PdCl₂], 3067w 3057w 2978w 2955w 2913w 2855w 1466w 1449w 1425w 1379m 1350w 1335w 1046m 1030m 952m 933s 833s 787m 567m 447s 404w 383s 368m
 Solid F, 3074w 2963m 2935w 2876w 1941vs 1908w 1504w 1460m 1432s 1377s 1187w 1031m 994m 969w 956m 880w 855w 627vs 525w 441w 391w 358w
 $[\pi$ -Crotyl-PdCl₂], 3057w 2991w 2958w 2946w 2843w 1508m 1460m 1437s 1377s 1241w 1194w 1117w 1035s 1003s 982m 955s 887m 855s 762m 530s 446s 416w 365s
 π -C₅H₅·Fe(CO) π -but-2-enyl, 3090w 3050w 2995m 2960m 2940m 2895m 2850m 1948vs 1503w 1490m 1459m 1447m(sh) 1435m [1417m] 1391m [1363m] 1300w 1224w 1195w 1167w 1114m 1059m 1030s [1015s] [995m] 946w 910w 886vw 856s [820s] 772w

comparison the Table also includes frequencies for the three associated π -allylic palladium chloride complexes, recorded on the same instruments under the same conditions, and for the compound π -C₅H₅Fe(CO)- π -C₄H₇ given by Green and Nagy.⁵ Fritz⁶ has previously reported the spectra of the π -allylic palladium complexes and our results are largely in agreement, with the exception of two bands in the spectrum of the π -methallyl compound listed by Fritz at 353 and 343 cm.⁻¹ which we find at 383 and 368 cm.⁻¹. It is evident that

⁵ Green and Nagy, *J.*, 1963, 189.

⁶ Fritz, *Ber.*, 1961, 94, 1217.

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the pairs A and D, and B and E are essentially the same. These products together with compound F all exhibit very strong absorption at *ca.* 1940 cm^{-1} assignable to the stretching frequencies of terminal carbonyl groups. Absorptions, also very strong, in the region 600—645 cm^{-1} are probably associated with carbonyl bending vibrations. Weak absorptions usually observed at *ca.* 1910 cm^{-1} can be attributed to a vibration involving carbon-13 (cf. Jones,⁷ and Shuffler, Sternberg, and Friedel⁸) while similar weak absorptions on the high-frequency side of the carbonyl band are plausibly combination bands.

Apart from the absorptions associated with carbonyl groups, there are very marked resemblances between the spectra of A and D and that of the π -allylpalladium chloride complex, between the spectra of B and E and that of the π -methallylpalladium chloride complex, and between the spectrum of F and that of the π -but-2-enylpalladium chloride complex. The similarity is particularly striking in the last case and affords strong evidence for the presence of a π -but-2-enyl ligand in F, a view supported by consideration of the data for $\pi\text{-C}_5\text{H}_5\text{Fe(CO)}\text{-}\pi\text{-C}_4\text{H}_7$. If the absorptions assigned to $\pi\text{-C}_5\text{H}_5$ and C—O are disregarded, the spectra of all these substances are very similar and can be taken as essentially characteristic of the π -but-2-enyl ligand. For the other groups of compounds the similarities in the spectra are almost as great and it seems certain that all the substances A—F contain π -allylic structures. Other related compounds whose spectra display similar features include the π -allylic iron tricarbonyl halides described by Murdoch and Weiss.⁹

None of the substances A—F displays strong absorption in the spectral region 360—286 cm^{-1} . Bands associated with Pd—Cl stretching vibrations have been observed in the region 359—283 cm^{-1} in chloropalladates by Adams¹⁰ and in a large number of complexes of general formula L_2PdCl_2 by Coates and Parkin.¹¹ We have also observed very strong and characteristic absorptions in this region¹² for complexes of this general type (*e.g.*, where L = nitrile and π -diolefin). In contrast, the π -allylic complexes examined by Fritz⁶ and by ourselves, and which contain only bridging chlorine atoms, display only weak absorptions below 360 cm^{-1} . In the spectrum of π -ethylenepalladous chloride, a compound containing both bridging and terminal chlorine atoms, Fritz and Kreiter¹³ have assigned very strong absorptions at *ca.* 350 and 300 cm^{-1} to terminal Pd—Cl vibrations

and very strong, broad absorption at 270 cm^{-1} to bridging Pd—Cl—Pd. It seems clear that the intense absorptions in the region 360—286 cm^{-1} (usually >300 cm^{-1}) characterise terminal, *i.e.*, non-bridging, Pd—Cl groups and that bridging lowers the frequency below 286 cm^{-1} (the low-frequency limit

of our spectrometer). The infrared evidence therefore suggests strongly that the chlorine atoms in materials A—F are bridging, and that they contain terminal carbonyl groups and π -allylic ligands. A structure such as (I) would combine these features, and the analytical data for D (Table 2) is in reasonable agreement with (I) despite the lack of any means of purification. However, the analytical data for the other products do not correspond to any simple formulation and it is possible that chain structures are involved in which the number of carbon monoxide ligands can vary.

EXPERIMENTAL

Melting points were determined on the Kofler block.

Infrared spectra in the range 2—15 μ were measured as mulls in Nujol and hexachlorobutadiene on a Grubb-Parsons GS2 instrument and those in the range 15—35 μ were measured as Nujol mulls on a Grubb-Parsons DM2.

⁷ Jones, *J. Chem. Phys.*, 1955, **23**, 2448.

⁸ Shuffler, Sternberg, and Friedel, *J. Amer. Chem. Soc.*, 1956, **78**, 2687.

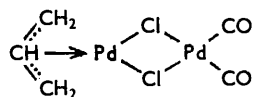
⁹ Murdoch and Weiss, *Helv. Chim. Acta*, 1962, **45**, 1927.

¹⁰ Adams, *Proc. Chem. Soc.*, 1961, 335.

¹¹ Coates and Parkin, *J.*, 1963, 421.

¹² A. J. Wilkinson, unpublished observations.

¹³ Fritz and Kreiter, *Ber.*, 1963, **96**, 1672.



(I)

Palladium chloride and sodium chloropalladite were purchased from Johnson, Matthey and Co.

Preparation of π -Allylic Palladium Chloride Complexes.—(i) With either sodium chloropalladite (experiments 1, 3, 5, and 6; Table 1) or a mixture of palladium chloride and sodium chloride (experiments 7, 8, and 9; Table 1). Known weights of the salts were dissolved in methanol (150 ml.) to which was added the allylic chloride. Carbon monoxide was passed at 2–2.5 l./hr. for 30 min. The mixture was poured into water (1 l.) and repeatedly extracted with chloroform. Evaporation of the dried extract gave the corresponding π -allylic palladium complex; recrystallisation failed to raise the m. p. In experiment 7 care was taken to exclude moisture, and when the mixture was poured into water copious quantities of a black precipitate, presumably palladium, were deposited in contrast to all the other experiments.

(ii) With a mixture of palladium chloride and calcium chloride (experiments 2, 4, and 10; Table 1). The reaction was carried out as described above. When the mixture was added to water (1 l.) and extracted with chloroform a buff coloured solid settled out at the solvent interface. This solid was isolated by centrifuging and filtration. Evaporation of the chloroform extract gave the π -allylic complex as before.

Reaction of Carbon Monoxide with a Mixture of π -Allylic Palladium Chloride Complex and Palladium Chloride (Table 2).—A known weight of finely divided π -allylic palladium chloride complex was suspended in a solution of palladium chloride in methanol (150 ml.) containing hydrogen chloride (ca. 2 mols. per mol. of PdCl_2). A stream of carbon monoxide (2.5 l./hr.) was passed through the stirred suspension and during the first 5 min. all the reactants went into solution. Subsequently a bright yellow solid was filtered off, washed with light petroleum (b. p. 40–60°), and dried.

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