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CLEAVAGE OF THE C_5H_5-PALLADIUM BOND IN CYCLOPENTADIENYLALLYLPALLADIUM

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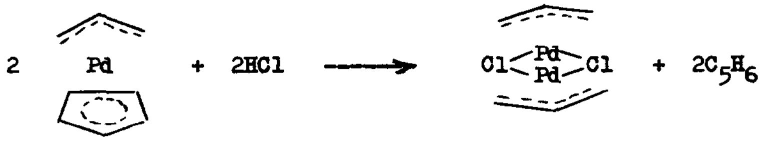
Of the cyclopentadienyl compounds from the 8th group of metals, the least well known and the least investigated are those containing palladium and platinum. In 1960 Shaw(1) and in 1961 McClellan(2) described the synthesis of cyclopentadienylallylpalladium—a red crystalline compound, easily soluble in nonpolar solvents. NMR(1) and IR(3) spectra showed that the compound could be considered as having a sandwich structure. We have investigated several reactions of cyclopentadienylallylpalladium and wish to report on the extreme lability of the bond between the five-membered ring and the palladium atom.

When cyclopentadienylallylpalladium is treated with hydrochloric acid, there is an instantaneous reaction, producing cyclopentadiene (identified via gas-liquid chromatography) and pi-allylpalladium chloride:



Analogous reactions take place with various other mineral and organic acids. In these instances, allylpalladium halides could

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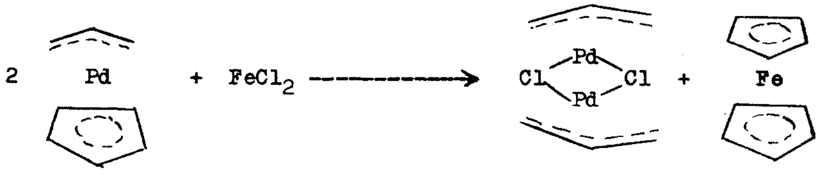
be obtained only after the addition of an excess of an alkali metal halogenide. All reactions were carried out in alcohol at temperatures ranging from 20 to -70°C. That Lewis Acids also cause cleavage of the parent compound was shown by the isolation of allylpalladium chloride from the reaction of C_5H_5-Pd-C_3H_5 with aluminum chloride in carbon tetrachloride at room temperature

Halogenation with bromine or iodine under mild reaction conditions (chloroform at room temperature) as well as bromination with N-bromosuccinimide (in benzene at 0° or in chloroform at -30°) likewise cause cleavage of the compound at the C_5-ring. Here again, allylpalladium halides were isolated.

The behavior of cyclopentadienylallylpalladium under metallation reaction conditions was also studied. When an ether-tetrahydrofuran solution of the compound was treated with n-butyllithium at - 70°, there was an immediate reaction. Upon the addition of solid carbon dioxide and excess potassium chloride to the reaction solution, it was possible to isolate allylpalladium chloride and the dimer of cyclopentadienylcarboxylic acid. Without the addition of potassium chloride, only metallic palladium and tarry products were obtained.

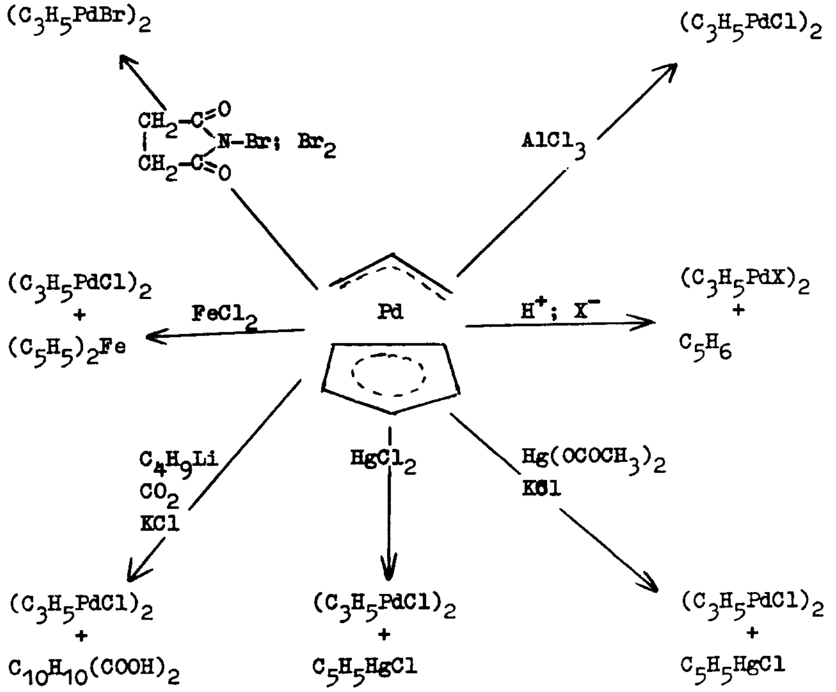
Similar results were obtained when C_5H_5-Pd-C_3H_5 was reacted with mercuric acetate in methanol at -70°. Upon the addition of excess potassium chloride, allylpalladium chloride and cyclopentadienylmercuric chloride were isolated. The same rapid reaction also took place upon the addition of a methanolic solution of mercuric chloride (not a mercurating agent) at -70°C. Thus, the first step in the attempted metallations with n-butyllithium and mercuric acetate is not metallation at all, but rather cleavage of the C_5H_5-Pd bond.

The reaction of cyclopentadienylallylpalladium with ferric chloride in either tetrahydrofuran or ethanol gave rise to allylpalladium chloride and ferrocene:



When the parent compound was treated with maleic anhydride in benzene at room temperature, a palladium-containing adduct was obtained that was insoluble in organic solvents.

We may summarize our report thus far by saying that when cyclopentadienylallylpalladium is treated with either electrophylic or nucleophylic reagents, in acid, neutral or basic media, the result is always the same—rapid cleavage of the cyclopentadienyl ligand. If a halogen containing alkali metal salt is present it is possible to isolate allylpalladium chloride in almost quantitative yield.[+] The following scheme applies:



[+] Allylpalladium chloride was characterized by elemental analysis for C, H, Pd and Hal., and by IR and NMR spectra.

The easy cleavage of the cyclopentadienyl ligand which we found is not characteristic of pi-bonded sandwich compounds of the transition metals. In this respect, cyclopentadienylallylpalladium is similar to such cyclopentadienyl compounds as those of Mn, Tl, Ti^+ and Hg. However, as earlier mentioned, the IR and NMR data show that the compound is actually a sandwich compound with a pi-bond between the C_5H_5-moiety and palladium. In further support of this position, we found a great similarity between the UV spectra of cyclopentadienylallylpalladium and ferrocene in nonpolar solvents, especially when ferrocene was substituted with strong electron-withdrawing groups.

TABLE I

Comparative Absorption between $C_5H_5PdC_3H_5$ and $C_5H_5FeC_5H_5$ in the UV and Visible Region[++]

No.	Compound	Solvent	$\lambda_{max.}(\epsilon)$[+++]		
1	$C_5H_5PdC_3H_5$	Heptane	470(215)	320(7200)	260(29300)
2	"	Methanol	400sh(840)	305(3500)	247sh(7500)
3	$C_5H_5FeC_5H_5$	Heptane	440(91)	325(60)	260sh(2000)
4	"	Ethanol	440(96)	325(55)	260sh(2200)
5	$C_5H_5FeC_5H_4NO_2$	Heptane	473(781)	365(1300)	273(7600)

[++] Spectra taken with an SF-4A Spectrophotometer with interval concentrations of 10^{-3} - 10^{-5}.

[+++] $\lambda_{max.}$ in mμ and ϵ in liters $mole^{-1}$ cm^{-1}.

As can be seen from Table I, the spectra of $C_5H_5PdC_3H_5$ varies greatly in both maxima and intensity when changing from nonpolar to highly polar solvents.

[+] According to Nesmeyanov, Nogina and Dubovitsky[4], $C_5H_5Ti(OC_2H_5)$ also reacts rapidly with ferric chloride to yield ferrocene.[5]

In this, it differs from typical sandwich compounds having a pi-bond between the ring and the metal atom. Such differences as are exhibited in the spectra of $C_5H_5PdC_3H_5$ cannot be explained on the basis of solvation alone. Rather, the alcohol probably coordinates with the palladium atom to cause some disruption in the sandwich structure of the compound.

Cyclopentadienylallylpalladium is easily reduced by general reducing agents. This fact, along with the UV data, speaks for the degree with which the palladium atom withdraws electrons within the compound. The polarographic potentials obtained for the palladium complexes which we studied are shown in Table II.

TABLE II

Results of Polarographic Reduction of Some Allyl Complexes of Palladium^{+}

Compound		$PdCl_2$	C_3H_5PdCl	C_3H_5PdI	$C_3H_5PdC_5H_5$	C_3H_5Cl
E1/2^{++}	1	0.330	0.235	0.230	0.225	—
	2^{+++}	-	1.15	1.15	1.13	1.25

\+ Measurements were made with a dropping mercury electrode in 50% aqueous methanol; electrolyte, 0.5N KCl.

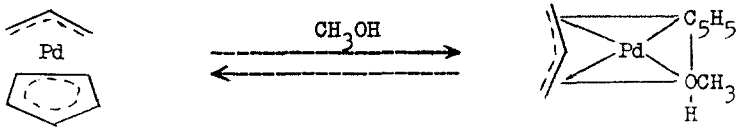
++ In volts vs aqueous saturated calomel electrode (SCE).

+++ The second wave had a small maximum.

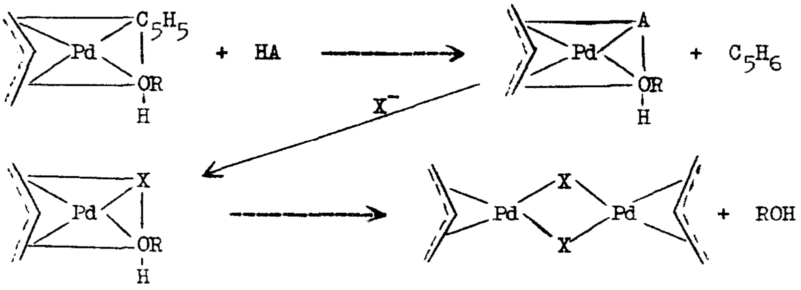
The first wave represents a two electron process. The similarity between the half-wave potentials of palladium chloride, allylpalladium halides and cyclopentadienylallylpalladium, as well as the E_{f_0} value (0.235 v. vs SCE), obtained by potentiometric reduction of cyclopentadienylallylpalladium with chromous acetate, indicates that the electron change is localized on an orbital of the metal atom(5). The second wave probably represents the reduction of the bond between the allyl ligand and palladium.

Thus, the major factors at work in all of the reactions discussed above appear to be the strong electron-withdrawing effect of and the easy polarizability of the palladium atom.

In nonpolar solvents cyclopentadienylallylpalladium probably actually exists in sandwich form with a pi-bond between the C_5H_5-ring and the palladium atom. In polar solvents that can coordinate with the palladium atom, there is undoubtedly a disruption of the sandwich structure to form a nearly square-planar structure around the central atom. This is very characteristic of palladium complexes:



In further reactions of the labile 20 electron complex shown above, a normal exchange of the ligand moiety in the square-planar complex can proceed. For example:



X = Cl^-, Br^- or I^-

In nonpolar solvents an analogous transformation from the sandwich structure to a square-planar configuration can take place by the interaction of the reagent involved.

Our results show that of the two organic moieties bonded to palladium under the conditions discussed above, the cyclopentadienyl-moiety is less strongly held.

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