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ACETATO-BRIDGED ACETOXY- AND METHOXY-PALLADIUM ADDUCTS OF 1,5-CYCLOOCTADIENE

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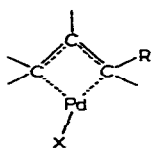
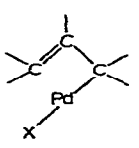
The development of processes for making acetaldehyde and vinyl acetate, as well as other carbonyl compounds and allylic esters, from alkenes using salts of palladium[1] has stimulated special interest in the chemistry of olefin and π-allylic complexes of palladium and related metals. The formation of allylic products, for example 2-cyclohexenyl acetate from the reaction of cyclohexene and palladous acetate in acetic acid[2], has been ascribed to a mechanism involving π-allylic, (I), or σ-allylic, (II), palladium intermediates[3] which in some cases exist in equilibrium with each other[4].



(I)



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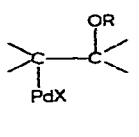
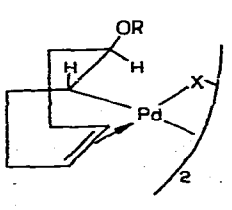
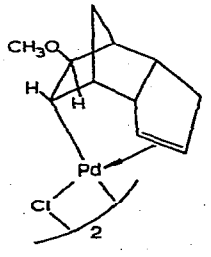


(III)

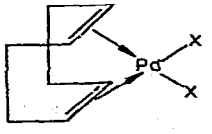
Solvolysis of allylic metal compounds leads to allylic products[5]. Other possible reaction paths involving oxypalladium adducts, (III) (R = alkyl, acyl, hydrogen) as intermediates have been suggested[6]. The vinyl and also possibly the allylic products might be derived by elimination of the elements HPdX, from an oxypalladium adduct. Such a mechanism seems to be ruled out as the source of allylic products for mercuric acetate and lead tetraacetate oxidations. In the oxidation of cyclohexene-1-^{13}C by these reagents, the degree of ^{13}C enrichment at C-1 in the product, 2-cyclohexenyl acetate, was found to be inconsistent with the elimination from an oxymetal adduct but in agreement with an allylic metal mechanism[7]. Carbonyl products, like cyclo-



(IVa) R = CH_3, X = Cl
(IVb) R = Ac , X = OAc
(IVc) R = CH_3, X = OAc
(IVd) R = Ac, X = Cl



(V)



(VIa) X = Cl
(VIb) X = OAc

hexanone from cyclohexene[6], could be formed from an adduct by heterolysis of the carbon–palladium bond coupled with hydride migration. Formation of acetaldehyde has been shown to involve hydride migration[1].

A few examples of such oxypalladium olefin adducts, the methoxypalladium adducts of 1,5-cyclooctadiene, (IVa), and dicyclopentadiene (V), were prepared by Chatt and coworkers[8]. In the case of these dienes, the olefin ligand stabilizes the otherwise labile palladium–carbon σ-bond. The dienepalladium chloride complex, (VIa), was treated with sodium carbonate in hot methanol, forming the adduct, (IVa), as a chloro-bridged dimer. The exo stereochemistry of the methoxy group in the methoxypalladium adduct of dicyclopentadiene, (V), has only very recently been determined. Stille and coworkers[9] reduced bis(dicyclopentadiene methoxide) μ,μ'-dichlorodipalladium, (V), with sodium borohydride to octahydro-*exo*-5-methoxy-4,7-*endo*-methanoindene. The exo configuration was also supported by the spin–spin coupling of the proton on the carbon bearing the methoxy group in the oxyadduct. Consequently the addition of the methoxy group and palladium to the double bond in dicyclopentadiene is trans.

Various methyl butadienes have also been treated with sodium chloropalladite in methanol, but are found to yield methoxymethyl π-allylic palladium compounds, (I) (*e.g.* $R=CH_3OCH_2$)[10].

We have prepared both chloro- and acetato-bridged acetoxy- and methoxypalladium adducts of 1,5-cyclooctadiene, (IVa-d). The acetato-bridged compounds, hitherto unknown, are more soluble than Chatt's chloro analog. A description of the preparation, physical and spectral properties and some interesting chemical aspects of these new compounds follow.

Attempts in this laboratory to prepare the diene complex, 1,5-cyclooctadienediacetatopalladium(II), (VIb), by reaction of cyclooctadiene with mixtures of palladous and sodium acetate were unsuccessful, yielding palladium black. Attempted preparation of the complex by reaction of silver acetate with 1,5-cyclooctadienedichloropalladium, (VIa), also failed, but did instead yield the isomeric compound, di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium(II), (IVb). It is interesting to note that although here the dienepalladium acetate complex could not be isolated, the binuclear di-μ-acetatodi-1,5-cyclooctadienedirhodium(I) was prepared by Chatt utilizing similar procedures[11]. The two other new oxypalladium compounds were prepared similarly. Di-μ-acetatobis(2-methoxycycloocta-5-enyl)dipalladium(II), (IVc), was prepared by the reaction of the cyclooctadienepalladium chloride complex with silver acetate in methanol. The di-μ-chlorobis-(2-acetoxycycloocta-5-enyl)-dipalladium(II), (IVd), was prepared by treating the cyclooctadiene complex with one equivalent of silver acetate in ether. The oxyadduct structure is supported by infrared and nuclear magnetic resonance spectral measurements and cryoscopic measurements. Elemental analyses were satisfactory although difficult because the compounds are not stable for long periods of time at room temperature.

The infrared spectrum (Table 1) of the di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium, (IVb), showed absorption bands at 1725, 1575, and 1425 cm^{-1} which are ester and ionic acetate carbon–oxygen stretching frequencies. The chloro-bridged acetoxyadduct, (IVd), has the 1725 cm^{-1} band but not those associated with the acetate ion. The acetato-bridged methoxyadduct, (IVc), has bands at 1575 and 1425 cm^{-1} as well as ether C–O absorptions at 1170 and 1070 cm^{-1}.

TABLE 1

INFRARED ABSORPTION SPECTRA

Di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium, (IVb)	3000 s	1725 s	1575 s	1425 s	1250 s	
Di-μ-acetatobis(2-methoxycyclooct-5-enyl)dipalladium, (IVc)	3000 s		1575 s	1425 s	1170 m	1070 m
Di-μ-chlorobis(2-acetoxycyclooct-5-enyl)dipalladium, (IVd)	3000 s	1725 s	1250 s			

The NMR spectra (Table 2) also appropriately support the oxyadduct structures. In the NMR spectrum of the acetato-bridged acetoxypalladium adduct, (IVb), the ester and ionic acetate protons appear as singlet signals at τ 7.85 and 7.97 ppm respectively. Presumably the exchange of the acetate ligands is fast enough so that signals are not seen for the several isomers which are conceivable by virtue of different possible orientations of the cyclooctenyl moieties. The vinyl protons ($H_{5,6}$) and the proton on the carbon bearing the acetoxy group (H_2) give broad signals at τ 4 and 4.3 ppm respectively. The proton at C-1 (H_1) which is bonded to palladium may be the broad signal at 8.3 ppm which appears in this and the other compounds and integrates for one proton. The remainder of the ring protons appear as broad bands from 6.6 to 8.1 ppm. The spectrum integrates correctly.

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA

Chemical shift from internal tetramethylsilane given in τ values and measured at 60Mc/sec.

Compound	*Solvent*	*Chemical shift*[a]					
		H_1	H_2	$H_{5,6}$	H_{OAc-}	H_{ROAC}	H_{OME}
Di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium(II), (IVb)	$DCCl_3$	8.3 B	4.3 B	4 B	7.97 S	7.85 S	
Di-μ-acetatobis(2-methoxycyclooct-5-enyl)dipalladium(II), (IVc)	D_3CCO_2D	8.4 B	4.5 B	4 B			
	$DCCl_3$	8.3 B	5.9 B	4 B	7.96 S		6.45 S
Di-μ-chlorobis(2-acetoxycyclooct-5-enyl)dipalladium(II), (IVd)	$DCCl_3$	8.4 B	4.4 B	3.8 B		7.87 S	
Di-μ-chlorobis(2-methoxycyclooct-5-enyl)dipalladium(II), (IVa)	$DCCl_3$	8.4 B	6.2 B	4 B			6.5 S
Palladous acetate	$DCCl_3$				7.96 S		
Cyclooctyl acetate	$DCCl_3$		4.7 B[b]			7.87 S	
Cyclooctyl methyl ether	$DCCl_3$		6.4 B[b]				6.5 S

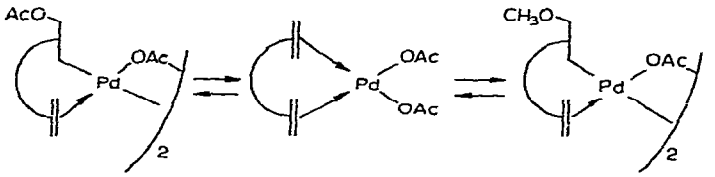
[a] S, singlet; B, broad signal. [b] Signal for proton at C-1.

From the Table 2 it will be noticed that the proton on C-2 bearing the oxy-substituent in each adduct is shifted down field substantially compared to the chemical shift of such a proton at the C-1 carbon bearing the same substituent on cyclooctane. The signal for proton H_2 in the di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium(II), (IVb), is at τ 4.3 ppm whereas the C-1 proton in cyclooctyl acetate is at 4.7 ppm. The ester acetate signal is at the same chemical shift in the two compounds. The di-μ-acetatobis(2-methoxycyclooct-5-enyl)dipalladium, (IVc), shows the H_2 signal at τ 5.9 ppm while cyclooctyl methyl ether has the analogous C-1 proton at

6.4 ppm. Similar comparisons can be made for the chloro-bridged compounds. If the H_2 proton in the adducts were on the opposite side of the cyclooctane ring from the palladium, one would expect that the chemical shift would be essentially that of the C-1 proton in the oxy-substituted cyclooctane. However, if the H_2 proton in the adduct is cis to the palladium and its acetate ligands, it would be expected that the chemical shift would be affected and probably the proton would be deshielded by the proximity of the $Pd(OAc)_2$ groups. Consequently, this down-field shift of the H_2 proton of the adduct relative to the C-1 proton of the oxycyclooctane is evidence for trans oxypalladium addition to cyclooctadiene. Stille and coworkers[9] give the chemical shifts of the proton on the carbon bearing the methoxy group in the bis(dicyclopentadiene methoxide)-μ,μ'-dichlorodipalladium and the proton at C-5 of the octahydro-*exo*-5-methoxy-4,7-*endo*-methanoindene as τ 6.25 and 6.55 ppm respectively. Thus in this case where the trans addition could be shown by other criteria, the protion cis-1,2 to the palladium chloride groups is shifted down-field also.

Cryoscopically the molecular weight of the di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium, (IVb), in bromoform was found to be 671 indicating a binuclear structure. However, in acetic acid the molecular weight was found to be 321, indicating the monomeric $C_8H_{12} \cdot Pd(OAc)_2$ (mol.wt. 332.66) which could be the complex, cyclooctadienediacetatopalladium(II), (VIb), or the monomeric oxypalladium adduct. The NMR spectrum of the compound in deuterioacetic acid is substantially the same as that in chloroform with respect to the chemical shift and signal integration of the vinyl protons, $H_{5,6}$, and the proton at C-2, H_2. Consequently, the monomeric species is a monomeric acetoxypalladium adduct presumably with a molecule of acetic acid as the fourth ligand to palladium.

When di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium, (IVb), in methanol was reduced with sodium borohydride, the products found by gas chromatography were cyclooctyl methyl ether and cyclooctene. The products were identified by retention times and their IR and NMR spectra. The cyclooctyl methyl ether could result from reduction of methoxycyclooctenyl palladium adduct which might be formed by exchange of the acetoxy group. Exchange of the acetoxy group could occur by deoxypalladation to the cyclooctadienepalladium acetate complex followed by methoxypalladation.



Sodium borohydride reduction of di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium in tetrahydrofuran resulted in good yields of cyclooctyl acetate, cyclooctane, and cyclooctene. The products, cyclooctane and cyclooctene, are understandable as the hydrogenation products of the cyclooctadienediacetatopalladium or cyclooctadiene itself. Reduction of the methoxypalladium adduct yielded cyclooctyl methyl ether, cyclooctane, and cyclooctene.

The speed of this exchange of the oxy group is evident upon dissolving the compound in deuterioacetic acid. As soon as the NMR spectrum could be obtained,

the signals for the ester and ionic acetate protons had disappeared and a singlet for the protons of protio-acetic acid remained. Even in chloroform to which a drop of deuterioacetic acid was added, the exchange was complete in the minute or less necessary to take the spectrum. The di-μ-acetatobis(2-methoxycyclooct-5-enyl)-dipalladium behaves analogously.

How these *trans*-oxypalladium adducts figure in the oxidation of olefins is somewhat puzzling. If the acetoxy group is trans to the palladium, heterolysis of the carbon–palladium bond upon heating the adduct in acetic acid should be accompanied by acetoxy participation resulting in diacetate products[2] which have not been found (at least upon preliminary investigation) whereas a cyclooctenone and an allylic ester are among the products. Furthermore the mechanism described above for the formation of carbonyl compounds is stereochemically reasonable from a *cis*-oxyadduct but does not seem favorable from a *trans*-oxyadduct because the migrating hydride should be best trans to the palladium. Consequently the *trans*-oxypalladium compound seems unlikely to be an intermediate in the oxidation of cyclooctadiene or other cycloalkenes. A similar situation obtains in the case of mercuric acetate where a *trans*-oxymercurial can be isolated easily but has now been shown not to be an intermediate in mercuric acetate oxidations to allylic esters[7].

EXPERIMENTAL

Di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium(II), (IVb)

Silver acetate (1.5 g, 0.009 mole) and 1,5-cyclooctadienedichloropalladium(II) (0.6 g, 0.002 mole) which was prepared by the method of Chatt[8] were stirred in 100 ml of ethyl ether for one hour during which time the yellow color disappeared. The ether solution was filtered, concentrated under reduced pressure at room temperature, and cooled in an ice bath. A white solid (0.46 g) precipitated in 67% yield. It decomposed at 120° without melting. Found: C, 43.58; H, 5.54; Pd, 32.36; Mol. wt. cryoscopically in 1.2% solution in bromoform, 671; in 3.0% solution in dry acetic acid, 321. $C_{12}H_{18}O_4Pd$ calcd.: C, 43.34; H, 5.45; Pd, 32.0%; mol.wt., 665.3.)

Di-μ-acetatobis(2-methoxycyclooct-5-enyl)dipalladium(II), (IVc)

Silver acetate (1.0 g, 0.006 moles) and 1,5-cyclooctadienedichloropalladium (0.4 g, 0.0014 moles) were stirred in 60 ml of methanol for one hour during which time the yellow color disappeared. The solution was filtered, concentrated and cooled. The very light yellow crystals which precipitated (0.25 g, 60% yield) decomposed without melting at 115–130°. Found: C, 41.20; H, 6.04; Pd, 36.11. $C_{11}H_{18}O_3Pd$ calcd.: C, 41.24; H, 6.18; Pd, 36.23%.)

Di-μ-chlorobis(2-acetoxycyclooct-5-enyl)dipalladium(II), (IVd)

Silver acetate (0.25 g, 0.0015 moles) and 1,5-cyclooctadienedichloropalladium (0.4 g, 0.0014 moles) were stirred in 100 ml of chloroform for one hour during which time the bright yellow color disappeared. The solution was filtered and evaporated under reduced pressure leaving a light yellow solid (0.3 g, 75% yield). The solid was washed with chloroform, and the solvent was removed under vacuum. It decomposed without melting at 95–130°. (Found: C, 38.58; H, 5.09. $C_{10}H_{15}ClO_2Pd$ calcd.: C, 38.86; H, 4.89%.)

Spectra

Infrared spectral measurements listed in Table 1 were obtained with a Perkin–Elmer Infrared Spectrophotometer Model 339. The NMR spectra listed in Table 2 were obtained from a Varian A-60 NMR spectrometer. The following ultraviolet spectra were obtained with a Cary 14 recording spectrophotometer.

TABLE 3

ULTRAVIOLET SPECTRA

Compound	*Solvent*	λ_{max}	ε
(IVb)	ethyl ether	2875Å	6530
(IVc)	ethyl ether	2875Å	6530
(IVd)	chloroform	3250Å	3420
(IVa)	chloroform	3250Å	3430
(VIa)	chloroform	3475Å	4280

Borohydride reductions

A 0.5-g sample of di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium(II), (IVb), was dissolved in 50 ml of methanol, and 0.1 g of sodium borohydride was added. Palladium black precipitated immediately. The palladium was filtered off, and the clear solution was concentrated on the steam bath. The solution was analyzed by gas chromatography at 104° on a 2 meter column of 20% carbowax 4000 on 60/80 mesh Chromosorb W. Peaks corresponding to cyclooctene and cyclooctyl methyl ether were found. Peaks were identified by retention time and, in the case of ether, by comparison of the infrared and NMR spectra of a collected peak with those of an authentic sample.

A 1.0 gram sample of di-μ-acetatobis(2-acetoxycyclooct-5-enyl)dipalladium was dissolved in 50 ml of dried tetrahydrofuran, and 0.2 g of sodium borohydride was added. The solution was filtered and concentrated on the steam bath as above. Analysis of the solution was by gas chromatography under the same conditions. Peaks having retention times appropriate for cyclooctane, cyclooctene and cyclooctyl acetate were found. The infrared spectrum of the collected peak for cyclooctyl acetate corresponded to the spectrum of an authentic sample.

A 1.0-g sample of di-μ-acetatobis(2-methoxycyclooct-5-enyl)dipalladium, (IVc), was dissolved in 50 ml of tetrahydrofuran and treated with 0.2 g of sodium borohydride. The solution was treated as above. Gas-chromatographic analysis as above showed peaks for cyclooctane, cyclooctene and cyclooctyl methyl ether.

SUMMARY

The preparation and properties of two acetato-bridged binuclear acetoxy- and methoxypalladium(II) olefin adducts are described. The addition to the olefin double bond is found to be trans by an NMR spectral analysis. The oxypalladium adduct is found to exchange the oxy group rapidly indicating a facile equilibrium with what is presumed to be the dienepalladium(II) π-complex.

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