A Lightly Stabilized Model for Acid and Base Reactions, Carbonylation, and β-Hydride Elimination in Organopalladium Chemistry. Reactions of $[\overline{C_5Me_5CHPhCH_2Pd}Cl]_2$[1]

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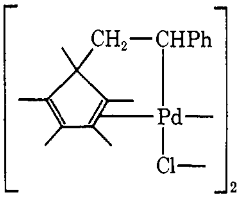
Abstract: The complexes **1** and **2** are very suitable lightly stabilized models for investigating the reactivity of palladium alkyls such as are postulated in catalytic reactions. Acid (HCl) does not cleave the Pd–C σ bond in **1** *directly*, and the products are styrene and dichloro(pentamethylcyclopentadiene)palladium. Alkoxide, hydrazine, and hydrogen all give 1-(pentamethylcyclopentadienyl)-1-phenylethane, and these reactions are postulated to go *via* a common palladium hydride intermediate. Carbonylation in neutral or acidic medium gives a mixture of two *trihapto*bicyclo[3.3.0]octen-8-one complexes (**7** and **8**); in the presence of alkoxide, methyl 3-(pentamethylcyclopentadienyl)-3-phenylpropionate (**10**) is formed. β-Elimination to give $C_5Me_5CHPh{=}CH_2$ (**11**) and $(Ph_3P)_2PdHCl$ occurs when **1** is allowed to react with triphenylphosphine, and observations on the reactivity of the hydride are recorded. Mechanisms are proposed for these reactions.

In the preceding paper, we have reported on the preparation, characterization, and structure of a novel organopalladium complex, **1**, and its analogs derived from the cyclotrimerization of 2-butyne and "phenylpalladium chloride."[3] This complex is not appreciably air sensitive and is moderately thermally stable so that it can be easily handled. It also possesses a Pd–C σ and Pd–C π bond, the former in particular giving it a degree of kinetic lability which makes it a very attractive substrate for investigating the reactions and reactivities of organopalladium compounds.

The importance of this lies in the vast number of palladium-catalyzed organic reactions which are now known, the greater number of which probably involve σ-bonded organopalladium intermediates.[4] From the point of view of determining the mechanisms of these reactions, however, the worker in this area is faced with the problem that these catalytic reactions are almost invariably very fast (owing to the very high lability of the coordinatively unsaturated intermediates), and even careful kinetic analysis, where this is feasible, cannot by itself elucidate all the details of the processes involved.

It is therefore necessary to go to model compounds containing Pd–C σ bonds and to investigate their behavior under various conditions. To some extent this has been attempted by a number of workers who have examined the reaction of palladium alkyls in stabilized complexes. Two main types of complexes have been so investigated: L_2PdRX (where L is usually a tertiary phosphine, R is the alkyl group, and X can be either another alkyl or an anionic ligand, usually a halide), and the alkoxy–enyl complexes, for example, **2**.[5]



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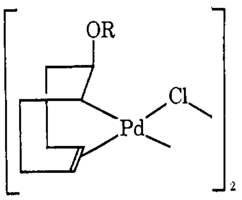

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It is found that where the complexes L_2PdRX are sufficiently stable to be conveniently handled they are also insufficiently reactive to act as a convenient model for the normally very fast reactions of organopalladium compounds.[6] In addition, there is some evidence that such "strongly stabilized" complexes often react somewhat differently to "unstabilized" organopalladium compounds, and lastly there is always the possibility of the complications which can result from the labilization and liberation of an L (phosphine) ligand during the reaction in question.

The alkoxy–enyl complexes such as **2** appear at first sight to be better potential models; they are easily obtained from diene–$PdCl_2$ complexes and are relatively stable, and useful studies have been carried out on such systems.[5,8,9] However, these complexes suffer from the serious disadvantage that cleavage of the alkoxy group occurs very easily in the presence of acid with re-formation of the diene–$PdCl_2$ complex and consequent complication of the overall reaction.[8]

The complex **1** is a "lightly stabilized" complex which suffers from none of these problems and appears well suited as a model. The reactions we have so far investigated include those with acids and bases, hydrogen, hydrazine, and carbon monoxide. We have also observed the elimination of HPdCl from **1**.[1]

1. Reaction with Hydrogen Chloride. The reaction of **1** with acid was very unusual. On treatment with HCl in chloroform the solution slowly turned orange-yellow, and when this solution was monitored by nmr

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[1] Part of this work has already been communicated [T. Hosokawa and P. M. Maitlis, *J. Amer. Chem. Soc.*, **94**, 3238 (1972)], and was also presented in a Plenaryl ecture to the XIVth International Conference on Coordination Chemistry, Toronto, June 1972; *Pure Appl. Chem.*, **33**, 489 (1973).

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[3] (a) T. Hosokawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **95**, 4914 (1973); (b) C. Calvo, T. Hosokawa, H. Reinheimer, and P. M. Maitlis, *ibid.*, **94**, 3237 (1972).

[4] For a comprehensive review, see P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. II, Academic Press, New York, N. Y., 1971.

[5] Reactions of σ- and π-bonded organopalladium compounds have been reviewed: P. M. Maitlis "The Organic Chemistry of Palladium," Vol. I, Academic Press, New York, N. Y. 1971, pp 89–103.

[6] An illustration of this is provided by the reaction of *trans*-$(Ph_3P)_2Pd(CH_2Ph)Cl$ with acetate which is not fast even at 100°.[7]

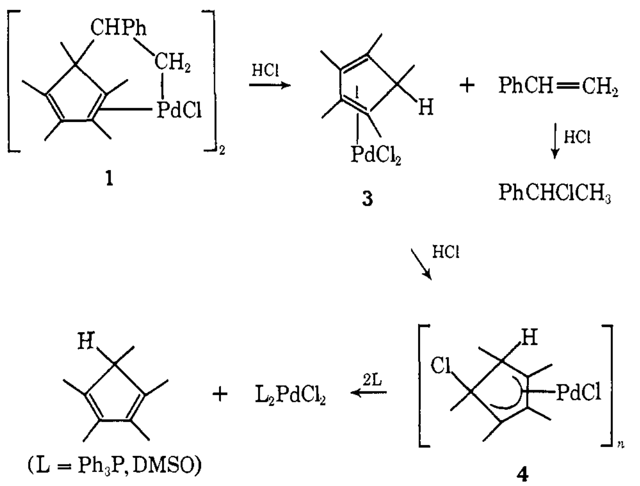
[7] R. Fitton, J. E. McKeon, and B. C. Ream, *Chem. Commun.*, 1530 (1968).

[8] L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, **94**, 485 (1972).

[9] G. Carturan, M. Graziani, R. Ros, and U. Belluco, *J. Chem. Soc., Dalton Trans.*, 263 (1972).

it was observed that the original peaks of **1** were slowly replaced by new ones. After 3.5 hr these peaks, corresponding to styrene and dichloro(pentamethylcyclopentadiene)palladium (**3**), had reached their maxima. The reaction was then quenched by pouring the solution into light petroleum whereupon **3** was obtained in 77% yield and was characterized by comparison with an authentic sample.[10]

If the reaction was allowed to proceed further by leaving the HCl-saturated solution standing for 18 hr at 20°, orange crystals of a new complex, **4**, were obtained, together with an organic liquid. This was purified by vpc and was shown to be 1-chloro-1-phenylethane, and is the normal product from the addition of HCl to styrene.

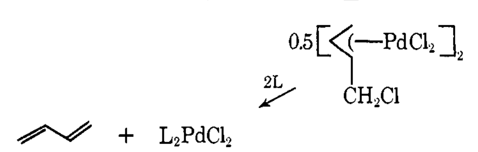


(L = Ph$_3$P, DMSO)

The solid **4**, once obtained, was extremely insoluble in all but strongly complexing solvents; in dimethyl-d_6 sulfoxide (DMSO-d_6) it was soluble and stable for a short time and gave resonances at δ 0.94 (d, 3 H, J(Me–H) = 8 Hz), 1.58 (s, 6 H), 1.71 (s, 3 H), and 1.77 (s, 3 H). On standing, these changed rapidly and the spectrum then became identical with one of pentamethylcyclopentadiene. An identical reaction occurred with triphenylphosphine in benzene; the orange **4** gave a yellow solid which was shown to be dichlorobis(triphenylphosphine)palladium. Only pentamethylcyclopentadiene remained in solution.

The complex **4** was also obtained in high yield by the action of hydrogen chloride on the cyclopentadiene complex **3**, and analysis showed **4** to be isomeric with **3**. The ir spectrum of **4** showed a broad band centered at 287 cm^{-1} (ν_{Pd-Cl}) and bands at 749 and 764 cm^{-1} (ν_{C-Cl}), but did not show any peak due to a free double bond. On the basis of this evidence, we propose the π-cyclopentenyl structure shown for **4**.

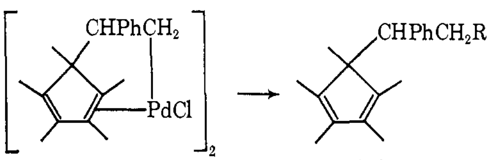
The reaction of allylic palladium chloride complexes which are chlorine substituted on the organic ligand on, or α to, the allylic group with phosphines or DMSO to give the diene and L$_2$PdCl$_2$ is a well-established one.[11,12] The reverse reaction, of 1,3-dienes with PdCl$_2$ to give chloro allylic complexes, is also well known and has been shown to proceed *via* a *dihapto* diene complex which then undergoes a cis-ligand transfer (eq 1).[13,14]



(1)

However, the acid catalysis of the rearrangement **3** → **4** is quite unusual; on standing **3** in chloroform for 1 month an insoluble brown solid, but with *different* properties to **4**, was obtained. The complex was not further investigated but it may well be an isomer of **4** with a different arrangement of the C–Cl and/or the C–H group relative to the metal.

2. Reaction with Sodium Methoxide, Hydrogen, and Hydrazine. The complex **1** reacted readily with all these reagents under very mild conditions (20° in methanol, tetrahydrofuran, or benzene) to give 1-(pentamethylcyclopentadienyl)-1-phenylethane (**5a**).



1

5a, R = H
b, R = D

The most significant experiment was that using hydrazine-d_4 in D$_2$O–THF. In this case nmr and mass spectroscopic examination of the product showed it to contain 90% of the monodeuterio hydrocarbon, **5b**, the remainder being undeuterated **5a**.

The nmr spectrum of the undeuterated product, **5a**, showed a quartet at δ 2.82 (J(H–Me) = 7 Hz) due to the benzylic hydrogen and a doublet at δ 1.07 with relative intensity 1:3. By contrast, **5b** showed only a broadish triplet at δ 2.82 and a doublet of triplets at δ 1.07 (J(H–D) ~1 Hz) in the approximate ratio of 1:2. This showed that the deuterium label was exclusively on the methyl group and was of considerable help in elucidating the structure of **1** since it indicated that the metal was bonded directly to this carbon.

The acetylacetonate **6** derived from **1** reacted very similarly with sodium methoxide; the only products were **5a**, acetylacetone, and palladium.

$$\underset{\mathbf{6}}{\overline{C_5Me_5CHPhCH_2Pd}(acac)} \longrightarrow C_5Me_5CHPhCH_3 + CH_3COCH_2COCH_3 + Pd$$

3. Reaction with Carbon Monoxide. Two different types of product were obtained depending on the conditions used. In benzene or methanol alone or in the presence of hydrochloric acid or DMSO, carbonylation (20°, 1 atm) gave a mixture of two cyclic ketone complexes. They were separated by fractional crystallization and were identified as the *exo*- and *endo*-phenyl (with respect to the metal) complexes **7** and **8**. Integration of the nmr spectrum of the crude mixture showed the two complexes to be present in the ratio of 55:45; there was no significant change in these pro-

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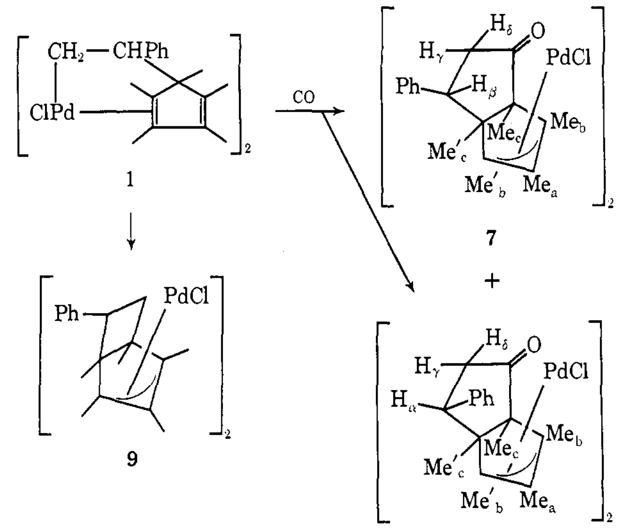
[10] P. V. Balakrishnan and P. M. Maitlis, *J. Chem. Soc. A*, 1721 (1971).

[11] A. D. Ketley and J. A. Braatz, *J. Organometal. Chem.*, 9, P5 (1967).

[12] M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc. A*, 1687 (1966).

[13] B. L. Shaw, *Chem. Ind. (London)*, 1190 (1962).

[14] M. Donati and F. Conti, *Tetrahedron Lett.*, 1219 (1966).



portions with change in conditions and a virtually quantitative yield was obtained, there being only a very small amount of decomposition to metal.

The structures of **7** and **8** were assigned on the basis of the analyses, molecular weights, and nmr and ir spectra. Many features of the nmr spectra were similar to that of the bicyclo[3.2.0]heptenyl complex **9**,[3] and the main resonances are assigned by analogy. The nmr of **7** (*exo*-phenyl) showed peaks ($CDCl_3$, 100 MHz) at δ 0.44 (s, 3 H, Me_c'), 0.99 (s, 3 H, Me_c), 1.36 (s, 3 H, Me_b'), 1.43 (s, 3 H, Me_b), 2.06 (s, 3 H, Me_a), 2.79 (dd, 1 H, H_γ, $J_{\gamma\beta} = 2.7$ Hz, $J_{\gamma\delta} = 20$ Hz), 3.88 (dd, 1 H, H_β, $J_{\beta\gamma} = 2.7$ Hz, $J_{\beta\delta} = 10$ Hz), 5.09 (dd, 1 H, H_δ, $J_{\delta\beta} = 10$ Hz, $J_{\delta\gamma} = 20$ Hz), and 7.20 (m, 5 H, phenyl).

That of **8** (*endo*-phenyl) ($CDCl_3$, 100 MHz) showed resonances at δ 0.64 (s, 3 H, Me_c'), 1.02 (s, 3 H, Me_c), 1.05 (s, 3 H, Me_b'), 1.40 (s, 3 H, Me_b), 2.01 (s, 3 H, Me_a), 2.65 (dd, 1 H, H_γ, $J_{\gamma\alpha} = 8$ Hz, $J_{\gamma\delta} = 18$ Hz), 3.09 (dd, 1 H, H_α, $J_{\alpha\gamma} = 8$ Hz, $J_{\alpha\delta} = 14$ Hz), 5.14 (dd, 1 H, H_δ, $J_{\delta\alpha} = 14$ Hz, $J_{\delta\gamma} = 18$ Hz) and 7.33 (m, 5 H, phenyl).

The noteworthy points are as follows.

(i) The similarity of the chemical shifts of Me_a, Me_b, Me_c, H_γ and H_δ in **7** and **8**.

(ii) Me_c' is more shielded (by the *exo*-phenyl) in **7**, while Me_b' is more shielded (by the *endo*-phenyl) in **8**. In both isomers Me_b is slightly deshielded by the carbonyl group.

(iii) The very low field shifts of H_δ in both complexes; part of this is due to deshielding by the adjacent carbonyl while the remaining deshielding is probably caused by the metal.[15]

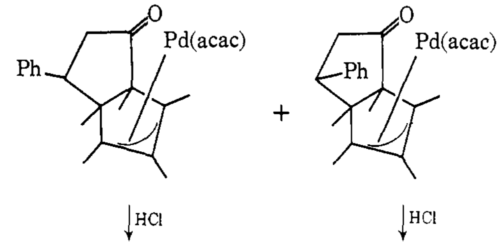
(iv) The coupling constants of H_β, H_γ, and H_δ in **7** are reasonable if the five-membered ring has a planar geometry and the dihedral angle between C–H_β and C–H_γ is about 120° while that between C–H_β and C–H_δ is almost 0°.[16] For **8**, however, the large trans coupling, $J_{\alpha\delta}$, of 14 Hz must correspond to a dihedral angle between C–H_α and C–H_δ of at least 160°, and similarly the cis coupling, $J_{\alpha\gamma}$, of 8 Hz is consistent with a dihedral angle between C–H_α and C–H_γ of about 40°. These results indicate a considerable deviation of the five-membered ring from planarity in **8**, which can be ascribed to nonbonded repulsions between the *endo*-phenyl and (presumably) the metal.

All these effects are consistent with the structures and geometries indicated and with the metal on the same side of the cyclopentenyl ring as the fused cyclopentanone ring. Both complexes showed ν_{CO} at 1730 cm^{-1}, in agreement with the presence of a cyclopentanone ring.[17]

Completely analogous reactions occurred on carbonylating the acetylacetonate **6**; in this case the acetylacetonates of the *exo*- and *endo*-phenyl isomers were obtained in a ratio of 60:40 (by nmr). The isomers were not separated but were converted into the chlorides **7** and **8** and acetylacetone by brief treatment with hydrogen chloride.

$[C_5Me_5CHPhCH_2Pd(acac)] \xrightarrow{CO}$

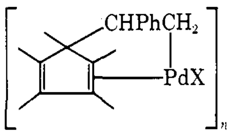
6



7 **8**

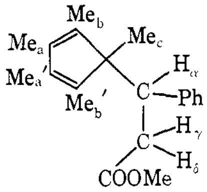
It is interesting that in this case the cyclization occurred more readily, if anything, for the acetylacetonate **6** than for the chloride **1** whereas the internal cyclization of **1** to **9** did not occur as easily with the acetylacetonate **6**.[3]

In complete contrast to the reactions under neutral or acidic conditions, both complexes **1** and **6** reacted extremely rapidly with carbon monoxide (20°, 1 atm) in the presence of sodium methoxide in methanol–benzene to give virtually quantitative yields of an ester (ν_{CO} 1747 cm^{-1}). This was identified as methyl 3-(pentamethylcyclopentadienyl)-3-phenylpropionate (**10**): nmr ($CDCl_3$, 100 MHz) δ 0.89 (s, 3 H, Me_c), 1.54, 1.60, 1.69, 1.85 (very narrow multiplets, probably quartets owing to homoallylic coupling, 3 H each, Me_a, Me_a', Me_b, Me_b'), 2.40 (d, 1 H, H_α, $J_{\gamma\alpha} = 4.6$ Hz), 2.51 (d, 1 H, H_δ, $J_{\delta\gamma} = 10.5$ Hz), 3.27 (dd, 1 H, H_γ, $J_{\gamma\alpha} = 4.6$ Hz, $J_{\gamma\delta} = 10.5$ Hz), 3.43 (s, 3 H, OMe), and 7.15 (s, 5 H, phenyl).



$+ \; CO \; + \; NaOMe \xrightarrow{MeOH}$

1, X = Cl; n = 2
6, X = acac; n = 1



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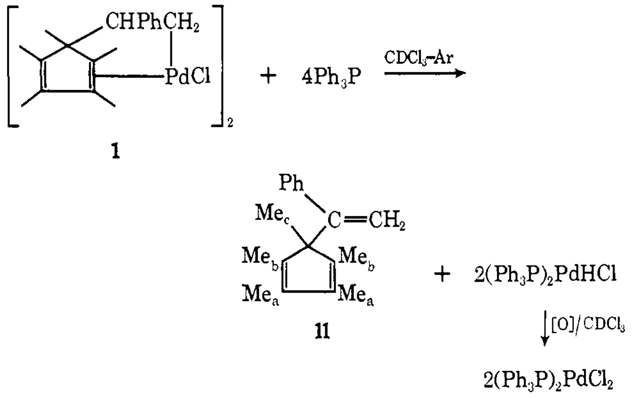
(15) Reference 23 in ref 3a.

(16) S. Sternhell, *Quart. Rev., Chem. Soc.*, 23, 236 (1969).

(17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 1st ed, Methuen, London, 1954, p 117.

There is an asymmetric center at the benzylic carbon which gives rise to the differences between Me_a and Me_a', and Me_b and Me_b'. Since there is also free rotation about the C_5Me_5–CPhH and the C_5Me_5-CPhH-CH_2COOMe bonds the chemical shifts observed for H_α, H_γ, and H_δ and the coupling constants $J_{\alpha\gamma}$ and $J_{\alpha\delta}$ are presumably the average values for a number of possible conformers.

4. Reactions with Triphenylphosphine and *o*-Phenanthroline. The chloro complex **1** reacted very rapidly with triphenylphosphine to give α-(pentamethylcyclopentadienyl)styrene (**11**) as the sole organic product.



This was identified by ir ($\nu_{C=C}$ 1570 (m), 1585 (m) cm^{-1}) and nmr ($CDCl_3$, 100 MHz): δ 1.12 (s, 3 H, Me_c), 1.64 (s, 12 H, Me_a, Me_b), 5.17 (d, 1 H, J_{gem} = 1.5 Hz), 5.26 (d, 1 H, J_{gem} = 1.5 Hz) and 7.05 (m, 5 H, phenyl).

When this reaction was carried out very carefully in an nmr tube under argon using deacidified $CDCl_3$, in addition to the resonances of **11** and peaks due to the phenyl group, we also observed a broadish ($W_{1/2}$ = 6 Hz) high-field resonance at τ 24.8 which must be due to a metal hydride and which we ascribe to *trans*-$(Ph_3P)_2PdHCl$.[18,20] No coupling to ^{31}P could be observed at 36°, probably owing to rapid exchange. At ambient temperature under argon the signal remained surprisingly stable ($t_{1/2}$ *ca.* 18 hr) but even on brief exposure to air it rapidly disappeared with the concurrent precipitation of $(Ph_3P)_2PdCl_2$, which was isolated and identified.

All attempts to detect $CHDCl_2$ from this reaction failed and we conclude that this is not a major product in the presence of air.[21] However, when **1** was allowed to react with triphenylphosphine under argon in deacidified carbon tetrachloride, no hydride signal could be detected. Instead, $(Ph_3P)_2PdCl_2$ slowly precipitated and $CHCl_3$, together with **11**, was readily observed in the nmr spectrum of the remaining solution.

$$[\overline{C_5Me_5CHPhCH_2Pd}Cl]_2 + 4Ph_3P + 2CCl_4 \longrightarrow \underset{\textbf{11}}{2C_5Me_5CHPh{=}CH_2} + 2(Ph_3P)_2PdCl_2 + 2CHCl_3$$

The acetylacetonate **6** also reacted with triphenylphosphine in chloroform under argon. In this case, however, no high field hydride signal was detected, and the nmr spectrum showed the presence of only **11** and acetylacetone, apart from phenyl resonances. Presumably the hydride here is very unstable and decomposes to acetylacetone and a zerovalent triphenylphosphinepalladium complex; no attempt was made to isolate this.

$$\overline{C_5Me_5CHPhCH_2Pd}(acac) + PPh_3 \longrightarrow \underset{\textbf{11}}{C_5Me_5CHPh{=}CH_2} + MeCOCH_2COMe + (Ph_3P)_xPd(?)$$

$$\underset{\textbf{12}}{[\overline{C_5Me_5CHPhCH_2Pd}(o\text{-phen})]Cl} \xrightarrow{CHCl_3} \underset{\textbf{11}}{C_5Me_5CHPh{=}CH_2} + (o\text{-phen})PdCl_2$$

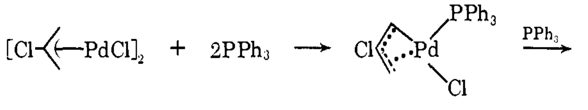
Although the *o*-phenanthroline adduct **12** was moderately stable as a solid, in solution it very rapidly decomposed to **11**. The other product was dichloro(*o*-phenanthroline)palladium, and was probably formed by reaction of a hydride with the HCl which normally contaminates chloroform. The reaction was not studied in deacidified chloroform.

When the reaction of **1** and triphenylphosphine in chloroform was rapidly quenched by adding hexane, a yellow solid, which analyzed reasonably satisfactorily for **13**, was obtained. This complex was very unstable, both in the solid and particularly in solution, and it could not be purified. The nmr spectrum was complex and showed considerable variation with temperature, indicating that some exchange process was occurring.

Owing to its instability the complex **13** was not further investigated but a parallel can be drawn between the behavior of **1** and that of certain π-allylic complexes. In both cases an intermediate monotriphenylphosphine complex (**13** and **14**, respectively)

$$[\overline{C_5Me_5CHPhCH_2Pd}Cl]_2 + 2Ph_3P \longrightarrow \underset{\textbf{13}}{2\overline{C_5Me_5CHPhCH_2Pd}Cl(PPh_3)}$$

$$\xrightarrow{PPh_3} \underset{\textbf{11}}{C_5Me_5CHPh{=}CH_2} + (Ph_3P)_2PdHCl$$



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$$CH_2{=}C{=}CH_2 + (Ph_3P)_2PdCl_2$$

may be isolated which then reacts further with triphenylphosphine to eliminate $(Ph_3P)_2PdClX$.

Discussion

The reactions of **1** with acids, bases, hydrogen, carbon monoxide, and triphenylphosphine all serve to illustrate fundamental aspects of organopalladium chemistry.

The reaction with acid (HCl) proceeds in a most unusual way, and the expected product, the cyclopentadienyl(phenyl)ethane, **5a**, which is formed in the reaction with base or hydrogen, is not obtained here. The products are styrene and dichloro(pentamethyl-

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(18) This complex has been reported[19] but no nmr data were given.

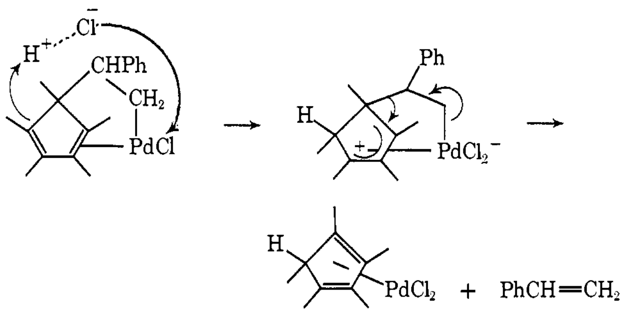
(19) K. Kudo, M. Hidai, J. Murayama, and Y. Uchida, *Chem. Commun.*, 1701 (1969).

(20) Reference 5, pp 103–105.

(21) See, for example, K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc. A*, 2875 (1970), where the reaction

$$C_5Me_5IrH(Cl)(PPh_3) + CDCl_3 \longrightarrow C_5Me_5IrCl_2(PPh_3) + CHDCl_2$$

was observed to occur.



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cyclopentadiene)palladium (**3**), and it is evident that direct cleavage of the Pd–C σ bond in **1** does not occur.

Instead, we propose that initial protonation occurs at a cyclopentadiene carbon in **1** to give a cyclopentenyl intermediate which then falls apart to give the observed products.

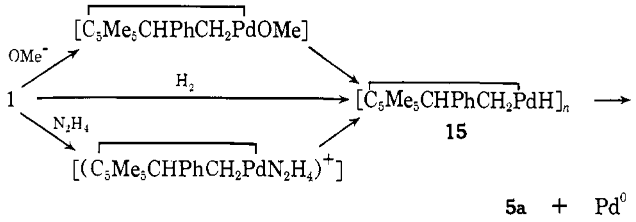
Both styrene and **3** can react further with more HCl in the manner indicated previously.

The low reactivity of the Pd–C σ bond is, however, not really surprising. Since this bond is very unpolar, ionic-type displacement reactions are inherently unlikely. In fact, although no studies on the mechanism of Pd–C bond cleavage by acid have been carried out, a number of workers have looked at Pt(II)–C cleavage under similar conditions. They concluded that this occurs by a fast oxidative addition of H–X to Pt(II), giving an octahedral Pt(IV) intermediate which then undergoes a slow reductive elimination, with loss of RH.[22]

$$L_2Pt(R)X + HX \longrightarrow [L_2PtR(H)Y(X)] \longrightarrow L_2PtXY + RH$$

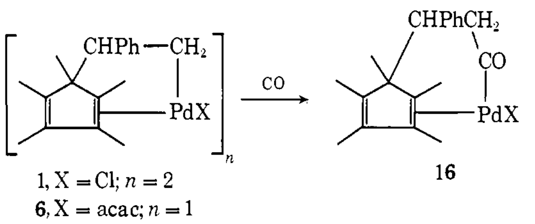
In view of the much greater reluctance of Pd(II) to be oxidized to Pd(IV),[23] it is to be expected that Pd–C σ bonds will not be readily cleaved by acids and other reagents for which the most probable mechanism involves an oxidative addition. One would, therefore, in general predict a lower reactivity for Pd(II) toward these reagents than for Pt–C bonds, other factors remaining constant.

In contrast, bases (alkoxide, hydrazine) and hydrogen all do cleave the Pd–C σ bond. Since it is well known that all these reagents can commonly be used to form hydrides of the group VIII metals from the chlorides,[24,25] it is reasonable to suppose that this occurs here too and that we are in each case observing the decomposition of an alkylpalladium hydride intermediate such as **15**.



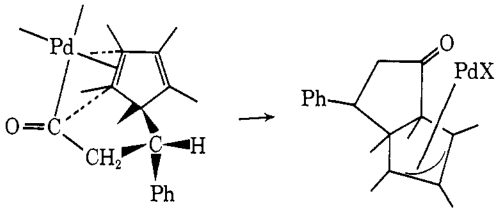
Ligands which cannot give rise to hydrides (CO, PPh_3, *o*-phenanthroline) also react with **1** but in completely different ways.

The reaction with carbon monoxide is particularly interesting since we observe two types of product; the one, which is formed only under basic conditions, is the ester **10**. Under all other conditions we have tried the product was a 55:45 mixture of the two cyclic ketone complexes **7** and **8**; the acetylacetonate **6** underwent exactly the same reactions as the chloride **1**. These results can very easily be understood, the first step in both processes being the formation of an acyl–palladium intermediate, **16**. Models show that the geometry of this intermediate is such that a coordinated C=C bond can now very easily become coplanar with the coordination plane of the metal in one of two ways, **16a** or **16b**. This is generally accepted to be the most suitable transition state for a cis-ligand migration to occur,[26] in this case, a cyclization to give **7** (*exo*-phenyl) from **16a** and **8** (*endo*-phenyl) from **16b**.



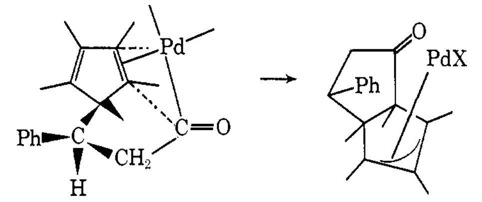
1, X = Cl; *n* = 2
6, X = acac; *n* = 1

16



16a

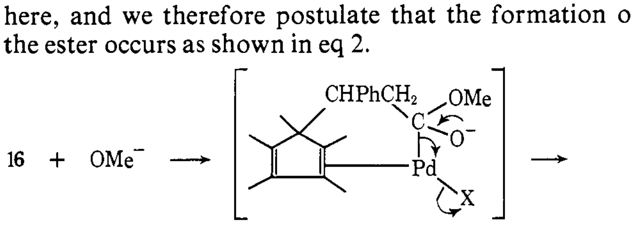
7, X = Cl



16b

8, X = Cl

The alternative is that **16** undergoes nucleophilic attack; Johnson and Pearson[27] have recently shown that base cleavage of the acetyl-manganese bond in $MeCOMn(CO)_5$ is similar to that of amide cleavage and that it occurs by attack of OR^- at the carbonyl carbon. We see no reason to expect different behavior here, and we therefore postulate that the formation of the ester occurs as shown in eq 2.



$$C_5Me_5CHPhCH_2COOMe + Pd + X^-$$

10

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[22] U. Belluco, U. Croatto, P. Uguagliati, and R. Pietropaolo, *Inorg. Chem.*, **6**, 718 (1967); U. Belluco, M. Giustiniani, and M. Graziani, *J. Amer. Chem. Soc.*, **89**, 6494 (1967).

[23] Reference 5, pp 32–33, 89–91.

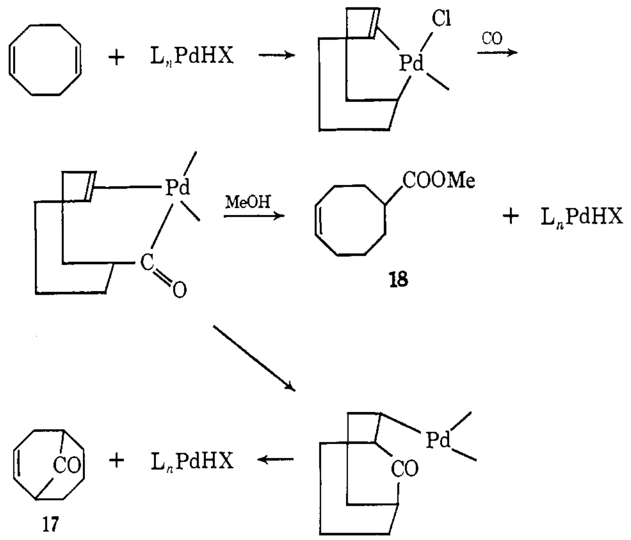
[24] M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965); A. P. Ginsberg, *Progr. Transition Metal Chem.*, **1**, 111 (1965).

[25] R. A. Schunn in "Transition Metal Hydrides," E. Muetterties Ed., Marcel Dekker, New York, N. Y., 1971, p 208 ff.

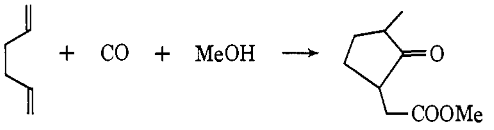
[26] B. L. Shaw, *Chem. Commun.*, 464 (1968).

[27] R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, **10**, 2091 (1971).

This duality of reaction (in which either the cyclic ketones *or* the esters are obtained as sole products) is particularly interesting since there has been some confusion in the literature. For example, using $(n\text{-}Bu_3P)_2PdI_2$ as catalyst, 1,5-cyclooctadiene was carbonylated in THF to give the bicyclic ketone **17** and in methanol to give the ester **18**.[28,29] The suggestion made by Brewis and Hughes[28] was that the reactive species in both solvents was a hydride, L_nPdHX, and that reaction occurred *via* an acyl–Pd intermediate which was either solvolyzed (to **18**) or underwent a cis-ligand migration, followed by elimination of L_nPdHX, to give **17**.



However, under similar conditions in methanol, 1,5-hexadiene was carbonylated to the γ-keto ester **19**.



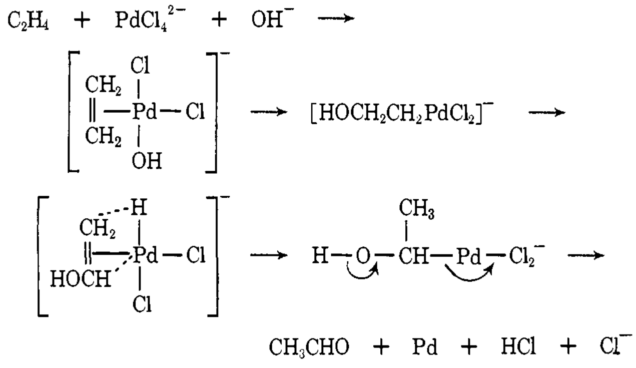
19

This result suggested that the relative rates of cyclization and methanolysis of an acyl–palladium intermediate were comparable and therefore it was surprising that none of the bicyclic ketone **17** was found in the carbonylation of 1,5-cyclooctadiene in methanol.

These results can now be understood since we have shown that the formation of the ester is only a function of the basicity of the medium.[30]

It is also noteworthy that we found carbonylation of **1** to give only **7** and **8**, even in the presence of HCl. Evidently, therefore, the acyl–Pd σ bond in **16** is much less readily cleaved by acid than by base. This result confirms our overall conclusion about the low reactivity of Pd–C σ bonds toward acids.

The β-elimination of Pd–H from organopalladium complexes has, implicitly or explicitly, been postulated to occur in a very large number of stoichiometric and catalytic reactions. The best known example is in the Wacker oxidation of ethylene to acetaldehyde, where the observation that no deuterium incorporation into the acetaldehyde occurs when the reaction is run in D_2O implies a fast 1,2-hydride shift in which the β hydroxyethylpalladium intermediate is isomerized to the α-hydroxyethyl isomer. This is generally believed to occur *via* β-elimination to give a π-vinyl alcohol–palladium hydride intermediate which then re-adds Pd–H in the opposite sense.[31]



Owing to the high reactivity of palladium hydrides, the β elimination had not, until now, been unambiguously demonstrated in a stoichiometric reaction. The complex **1** readily reacted with triphenylphosphine to give, first, a monomeric phosphine **13** adduct in which the chloride bridges of the dimer were cleaved; this then reacted further with more triphenylphosphine to give the styrene **11** and $(Ph_3P)_2PdHCl$. Perhaps the most surprising feature of this reaction is the stability of the hydridopalladium complex, even in chloroform solution, in the absence of oxygen or acid. In view of this and similar observations on other palladium hydrides[19,20] there is now ample evidence to support the intermediacy of palladium hydrides in catalytic reactions.

This type of β-elimination from **1** (and **6**) to give **11** also occurs with other Lewis bases, for example, *o*-phenanthroline. We also attempted to prepare both the bromide and the iodide corresponding to **1** by standard methods. While we appear to have been successful in making the bromide, albeit in an impure state, it decomposed on attempts to purify it. The attempts to form the iodide

$$[\overline{C_5Me_5CHPhCH_2Pd}I]_2$$

by reaction of **1** with iodide ion, were all quite unsuccessful and the only product which we could detect was the styrene **11**. Iodide is evidently a good enough Lewis base to facilitate the elimination as well.

Experimental Section

Reagents were of AR quality, and all reactions were carried out under nitrogen unless otherwise stated. The complexes **1**, **6**, and **12** were all prepared as described in ref 3. Light petroleum is that fraction with bp 30–60°.

Reaction of $[\overline{C_5Me_5CHPhCH_2Pd}Cl]_2$ (1) with HCl. (i) A solution of **1** (0.05 g, 0.07 mmol) in $CDCl_3$ (0.5 ml) was treated with a slow stream of dry hydrogen chloride for 15 min. The solution slowly changed color from yellow to orange-red and its nmr spectrum was then taken at intervals over 3.5 hr. This showed the growth of two new sets of resonances; one, with peaks at δ 5.24 (dd, 1 H), 6.75 (dd, 1 H), and 7.4 (m, 5 H) was identified as styrene

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[28] S. Brewis and P. R. Hughes, *Chem. Commun.*, 489 (1965); 6 (1966).

[29] It is instructive to note that the carbonylation of 1,5-cyclooctadiene needs 1000 atm and 150° while that of 1 (or 6), in an admittedly stoichiometric reaction, proceeds under ambient conditions.

[30] A somewhat similar conclusion regarding the effect of base in carbonylation reactions of organopalladium compounds has, quite independently, been arrived at by Hines and Stille, based on their work on cyclic enyl complexes.[8]

[31] Reference 4, pp 82–89, 141–142.

(see also below); the other, with resonances at 1.04 (d, 3 H), 1.72 (s, 6 H), 2.24 (s, 6 H), and 3.54 (q, 1 H), was shown to be dichloro(pentamethylcyclopentadiene)palladium (**3**). This latter material was precipitated (0.017 g, 77%) on pouring the chloroform solution into light petroleum (30 ml) and was identified by comparison with an authentic sample (nmr, ir, decomposition point).[10] In addition, some of the rearranged complex **1**[3] was also obtained on chromatography of the mother liquors.

(ii) Dry hydrogen chloride was passed slowly through a solution of **1** (0.17 g, 0.21 mmol) in chloroform (10 ml) for 15 min at 20°. The color change (above) was again noted, but in this case the solution was now left standing for 18 hr; it was then concentrated to 5 ml whereupon some orange crystals formed. These were filtered off and light petroleum was added to the filtrate to give more of the same solid (total yield, 0.13 g, 93%) and a mother liquor (A). This orange-red solid was shown to be di-μ-chlorobis(1,2,3-*trihapto*-4-chloro-1,2,3,4,5-pentamethylcyclopentenyl)dipalladium (**4**), mp 165° dec. *Anal.* Calcd for $[C_{10}H_{16}Cl_2Pd]_n$: C, 38.30; H, 5.14; Cl, 22.61. Found: C, 38.54; H, 5.49; Cl, 22.42.

This complex was almost totally insoluble in all solvents except dimethyl sulfoxide, with which it slowly reacted to give pentamethylcyclopentadiene as the only organic product. An analogous reaction occurred when the complex was added to a solution of 2.5 equiv of triphenylphosphine in benzene. In this case pentamethylcyclopentadiene was identified by nmr spectrum, and $(Ph_3P)_2PdCl_2$ (65%) was isolated and identified by comparison with an authentic sample.

The cyclopentenyl complex (**4**) was also formed when dichloro(pentamethylcyclopentadiene)palladium (**3**) was reacted with hydrogen chloride in chloroform, yield 73%. The ir spectra, decomposition points, and chemical behavior of the two samples were identical.

The solvent was removed from the mother liquor (A) to leave an oil (0.072 g) which was purified by chromatography on alumina in light petroleum and identified as 1-chloro-1-phenylethane by comparison with an authentic sample: nmr δ 1.79 (d, 3 H, $J = 7$ Hz), 5.08 (q, 1 H, $J = 7$ Hz), and 7.38 (m, 5 H, phenyl). The vpc retention times of the two samples were identical.

Reaction of 1 with Hydrazine, Hydrogen, or Sodium Methoxide to Give 1-(Pentamethylcyclopentadienyl)-1-phenylethane (5). (i) Anhydrous hydrazine (0.2 ml) was added to a solution of **1** (0.11 g, 0.14 mmol) in benzene (10 ml) at 20°. The initial yellow color of the solution faded; metal was rapidly deposited and removed by filtration. Evaporation of the filtrate gave a colorless oil (0.03 g, 43%) which, after purification by vpc (20% SE-30 at 190°), was shown to be 1-(pentamethylcyclopentadienyl)-1-phenylethane (**5a**). Vpc analysis showed the absence of any other significant products. *Anal.* Calcd for $C_{18}H_{24}$: C, 89.93; H, 10.06; mol wt, 240. Found: C, 89.82; H, 9.90; mol wt (mass spectrum), 240. Nmr ($CDCl_3$ at 100 MHz): δ 0.95 (s, 3 H, Me), 1.07 (d, 3 H, J(Me-H) = 7 Hz), 1.52, 1.56, 1.66, 1.85 (all s, diene methyls), 2.82 (q, 1 H, J(H-Me) = 7 Hz), 7.11 (m, 5 H, phenyl).

(ii) A similar reaction was carried out using hydrazine-d_4, prepared *in situ* by reaction of $N_2D_4 \cdot 2DCl$ with NaOD in D_2O (0.4 g of sodium in 3 ml of D_2O). To this solution was added **1** (0.23 g) in tetrahydrofuran (5 ml), and the resultant solution was stirred at 20° for 1.5 hr. The (pentamethycyclopentadienyl)phenylethane-*d* (**5b**) was purified as described and was shown to contain 90% d_1, by mass spectrum. The nmr spectra showed, by the decrease in intensity of the methyl peak at δ 1.07, that deuterium incorporation had occurred there. This peak was now also resolvable into a doublet of closely spaced triplets [J(H-D) *ca.* 1 Hz] and in addition the resonance at δ 2.82 was now a triplet ($J = 7$ Hz), arising from coupling to CH_2D, superimposed on a very weak quartet.

(iii) A solution of **1** (0.21 g, 0.27 mmol) in anhydrous tetrahydrofuran (10 ml) was hydrogenated (1 atm, 20°) for 24 hr. The metal was removed by filtration and the solvent was evaporated under reduced pressure to leave a colorless oil which was chromatographed on alumina in light petroleum. The resultant oil (0.14 g) was analyzed by nmr and vpc and was found to contain four components, the major one of which was the (pentamethylcyclopentadienyl)phenylethane **5a** (62% overall yield).

(iv) A solution of sodium methoxide (1.4 mmol, prepared from 0.033 g of sodium and 5 ml of methanol) was added to a solution of **1** (0.10 g, 0.13 mmol) in methanol (10 ml) and benzene (2 ml). The solution was stirred at 20° for 45 min until the decomposition was complete. The metal was removed and the filtrate worked up as before to give the (pentamethylcyclopentadienyl)phenylethane **5a** (0.06 g, 90%) as the only product.

Di-μ-chloro-bis(1,2,3,4,5-pentamethyl-6-phenyl-2,3,4-trihaptobicyclo[3.3.0]octen-8-one)dipalladium (7 and 8). (i) Carbon monoxide (1 atm, 20°) was passed into a solution of **1** (0.06 g, 0.08 mmol) in benzene (5 ml) for 2 hr. Nmr analysis of the product (after removal of solvent) showed the presence of two complexes in a 55:45 ratio. These were separated by crystallization from light petroleum–benzene; the first crop of colorless crystals (0.31 g) was shown to be the pure *exo*-phenyl isomer **7**, mp 200–202° dec, ν_{CO} 1731 cm^{-1}. *Anal.* Calcd for $[C_{19}H_{23}ClOPd]_2$: C, 55.76; H, 5.66; Cl, 8.66; mol wt, 818. Found: C, 55.15; H, 5.45; Cl, 8.83; mol wt, 841.

The mother liquors were evaporated to dryness to leave 0.03 g of crystals (mixture of exo and endo isomers) which, after crystallization from methanol–light petroleum gave pale yellow crystals of the pure *endo*-phenyl isomer (**8**), mp 189–190° dec, ν_{CO} 1730 cm^{-1}. *Anal.* Calcd for $[C_{19}H_{23}ClOPd]_2$: C, 55.76; H, 5.66; Cl, 8.66; mol wt, 818. Found: C, 55.79; H, 5.82; Cl, 8.55; mol wt, 760.

(ii) Carbon monoxide (1 atm, 20°) was passed into a solution of **6**[6] (0.085 g, 0.19 mmol) in benzene (10 ml) for 20 min. A small amount of palladium which was formed was filtered off and the filtrate was evaporated to dryness. Examination by nmr showed the presence of a 40:60 mixture of the *endo*- and *exo*-phenyl complexes **7** and **8**; these were not separated but were converted into the chlorides **7** and **8** and acetylacetone, identified by their nmr spectra, on brief exposure to dry hydrogen chloride. Nmr of *exo*-phenyl **7**: δ 0.48 (s, Me_c'), 1.00 (s, Me_c), 1.36 (s, Me_b'), 1.44 (s, Me_b), 2.08 (s, Me_a), 1.90 (s, acac Me's), 2.62 (dd, H_γ, $J_{\gamma\beta} = 3$ Hz, $J_{\gamma\delta} = 20$ Hz), 3.90 (dd, H_β, $J_{\beta\gamma} = 3.0$ Hz, $J_{\beta\delta} = 11$ Hz), 4.96 (dd, H_δ), 5.24 (s, acac H), 7.4 (m, phenyl). Nmr of *endo*-phenyl **8**: δ 0.64 (s, Me_c'), 1.03 (s, Me_c), 1.06 (s, Me_b'), 1.36 (s, Me_b), 2.04 (s, Me_a), 1.96 (s, acac Me's), 2.24 (dd?, H_γ, $J_{\gamma\delta} = 18$ Hz), 3.16 (dd?, H_α, $J_{\alpha\delta} = 11$ Hz), 5.18 (dd?, H_δ), 5.32 (s, acac H), 7.4 (m, phenyl).

Methyl 3-(Pentamethylcyclopentadienyl)-3-phenylpropionate (10). (i) Sodium methoxide (1.5 mmol, prepared from 0.034 g of sodium in 5 ml of methanol) was added to a solution of **1** (0.10 g, 0.13 mmol) in methanol (10 ml) and benzene (4 ml) at 20° and carbon monoxide (1 atm) was immediately passed through the solution. A very fast reaction occurred, with deposition of metal. After 20 min the stream of CO was stopped, the metal was filtered off, the filtrate was washed with water and dried, and the solvent was removed on a rotary evaporator. The product was a colorless oil (0.08 g, 96%) which was shown by nmr and vpc to contain only one component. This was purified by preparative vpc (15% Carbowax at 140°) and characterized as methyl 3-(pentamethylcyclopentadienyl)-3-phenylpropionate (**10**), ν_{CO} 1747 cm^{-1}. *Anal.* Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78; mol wt, 298. Found: C, 81.02; H, 9.14; mol wt (mass spectrum), 298.

(ii) Sodium methoxide (1.5 mmol, prepared from 0.033 g of sodium in 5 ml of methanol) was added to a solution of **6** (0.07 g, 0.17 mmol) in methanol (10 ml) and benzene (2 ml) at 20° and carbon monoxide (1 atm) was immediately passed through the solution. A very fast reaction occurred with deposition of metal. The product was worked up as described above to yield methyl 3-(pentamethylcyclopentadienyl)-3-phenylpropionate (**10**) (0.14 g, 82%) as the sole product, identified by nmr.

α-(Pentamethylcyclopentadienyl)styrene (11). (i) A solution of **12**[3] (0.38 g, 0.67 mmol) was stirred in chloroform (20 ml) for 24 hr at 20°. The insoluble precipitate (dichloro(*o*-phenanthroline)palladium) was filtered off, and the solvent was removed from the filtrate to give an oil (0.04 g) which was shown by vpc, analysis, nmr, and mass spectrum to consist almost entirely of α-(pentamethylcyclopentadienyl)styrene **11** (yield, 50%). The analytical sample was obtained by preparative vpc on a column of 20% SE-30 at 175°. *Anal.* Calcd for $C_{18}H_{22}$: C, 90.69; H, 9.30; mol wt, 238. Found: C, 90.72; H, 9.30; mol wt (mass spectrum), 238.

(ii) A solution of **1** (0.06 g, 0.08 mmol) and triphenylphosphine (0.08 g, 0.30 mmol) was made up in purified $CDCl_3$ (1 ml) under an argon atmosphere. After 30 min at 20° the nmr spectrum was run; this showed only resonances due to phenyl groups at δ 7.0–7.8; those due to α-(pentamethylcyclopentadienyl)styrene at δ 1.12 (s, 3 H), 1.64 (s, 12 H), 5.17 (d, 1 H), and 5.26 (d, 1 H); and a high field resonance at τ 24.80 (δ −14.80) (s) which is ascribed to *trans*-$(Ph_3P)_2PdHCl$. This latter signal slowly decreased on standing ($t_{1/2}$ *ca.* 18 hr at 25°) and the insoluble $(Ph_3P)_2PdCl_2$ slowly precipitated. The dichloride was isolated in 92% and the styrene **11** in 78% yield after completion of the reaction.

The decomposition of the hydridochloride and the formation of the dichloride were both greatly accelerated on brief exposure to air. In no case could any $CHDCl_2$ be detected.

When the reaction was carried out in CCl_4 instead of $CDCl_3$, the yellow precipitate of $(Ph_3P)_2PdCl_2$ began to appear immediately after the reactants were mixed and reaction was complete after 30 min. In this case examination by nmr showed only the resonances for α-(pentamethylcyclopentadienyl)styrene and no high-field hydride signal. When the solvent was distilled (to remove the styrene and triphenylphosphine) $CHCl_3$ was clearly observed in the nmr spectrum.

The reaction of **6** with 2 equiv of triphenylphosphine in $CDCl_3$ under argon gave an orange yellow solution, the nmr of which (taken immediately after mixing) showed the presence of only the styrene and an acetylacetonate which was not further characterized. Yield of the styrene was quantitative.

$\overline{C_5Me_5CHPhCH_2Pd}(PPh_3)Cl$ (**13**).[32] This complex could be obtained, albeit somewhat impure owing to the rapidity with which it decomposed, by reaction of triphenylphosphine (220 mg) and the complex **1** (160 mg) in 25 ml of chloroform. When the reaction was rapidly quenched by adding hexane (50 ml), it gave a yellow solid, mp 104° dec, which could not be purified owing to decomposition. *Anal.* Calcd for $C_{36}H_{38}ClPPd$: C, 67.19; H, 5.95; Cl, 5.51; P, 4.81. Found: C, 67.21; H, 5.70; Cl, 6.28; P, 5.36.

The decomposition was also evident from the nmr spectrum; however, broad peaks in the methyl region at δ 0.86, 1.76, 1.86, 1.98, 2.06, and 2.29 as well as small broad multiplets at 2.7 and 3.7, and complex resonances at 7.33 and 7.68 (phenyl) owing to **13** were observed. The spectrum at −60° showed further splitting and indicated that some exchange process was occurring.

Acknowledgment. We thank the National Research Council of Canada for supporting this work and Johnson Matthey and Mallory for the loan of palladium salts.

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[32] We are indebted to Dr. K. L. Kaiser for preparing and characterizing this complex.

Anion-Catalyzed Ester Aminolyses in a Hydrocarbon Solvent

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Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322. *Received January 15, 1973*

Abstract: Tetra-*n*-hexylammonium benzoate hemihydrate (THAB) catalyzes the reaction between piperidine and *p*-nitrophenyl acetate in toluene. For example, 0.054 *M* THAB increases the rate more than 1200-fold. The acceleration arises from removal of a proton residing on the nitrogen of a tetrahedral intermediate; the intermediate can then collapse to products without first forming an N-protonated amide. In toluene, benzoate is a 10^3 better proton acceptor than piperidine (corresponding to a 10^{10} reversal in basicity relative to that in water). THAB displays an even greater catalysis in the aminolysis of *p*-nitrophenyl acetate by imidazole. Thus, the half-life of the ester in toluene at 25.0° with 0.0104 *M* imidazole and no THAB is about 25 hr. Addition of 0.059 *M* THAB decreases the half-life to 7.5 sec! A plot of k_{obsd} *vs.* [THAB] curves downward with the rate becoming independent of the [THAB] above 0.1 *M*. We conclude that THAB induces a change in rate-determining step. The behavior at high [THAB], where formation of intermediate is rate limiting, permits the first determination of the rate constant for addition of imidazole to an ester carbonyl in an aprotic solvent. This rate is 29 times *faster* than the corresponding rate in water. Therefore, the slowness of ester aminolyses in aprotic solvents can be ascribed solely to an unfavorable partitioning of a tetrahedral intermediate to products.

Enzymes might activate their ionic catalytic groups by holding them in hydrophobic portions of the active sites.[2-4] This idea has appeal because impaired ion solvation often leads to huge rate and equilibrium enhancements. Thus, the equilibrium constant for heterolysis of trityl chloride in ether increases 7×10^9-fold upon addition of 5.05 *M* $LiClO_4$.[5] Chloride ion reacts with methyl iodide 2×10^6 times faster in acetonitrile than in methanol.[6] We now report a study of the effect of carboxylate anion on ester aminolyses in toluene. The work was stimulated in particular by the observation that chymotrypsin has its Asp-102 carboxylate buried in a nonpolar region[7] where it can accept a proton from the adjacent catalytically important imidazole.[8] Only one previous publication relates directly to our model investigations. Haake and coworkers[9] reacted *p*-nitrophenyl acetate with imidazole in acetonitrile in the presence of tetramethylammonium benzoate. Benzoate causes a catalysis, although of much smaller magnitude than the ones described below. Moreover, in the present paper we interpret our results in terms of recent mechanistic thought, namely, that collapse of a tetrahedral intermediate is rate limiting with aprotic aminolyses.[10] This is not a technicality; we will show that carboxylate anion in an aprotic solvent can change the nature of the rate-determining step.

Experimental Section

Materials. Spectrograde toluene was distilled over calcium hydride through a 30-cm Vigreux column. No water could be detected by glc. Piperidine (Aldrich) was also distilled over calcium hydride and then stored under N_2. Imidazole, *p*-nitrophenyl acetate, and 2,4-dinitrophenyl acetate (all Eastman) were crystal-

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[1] Recipient of a Camille and Henry Dreyfus Foundation Teacher-Scholar grant and a National Institutes of Health Career Development Award.

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