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CHEMISTRY OF METAL HYDRIDES

XXI *. INSERTION OF ACETYLENES INTO PALLADIUM HYDRIDES

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Summary

trans-$Pd(NO_3)H(PCy_3)_2$ (I) when treated with Et_4NCl forms the hydride *trans*-$PdClH(PCy_3)_2$ which in turn reacts with $AgPF_6$ in acetonitrile to give *trans*-$[PdH(CH_3CN)(PCy_3)_2]PF_6$ (III). Both I and III react smoothly with acetylenes containing one electron-withdrawing group to give alkenyl products. The geometry of the resulting alkenyl ligand implies that *cis* addition has occurred and that the hydridic hydrogen adds to the acetylenic carbon containing the electron-withdrawing group.

Acetylenes containing two electron-withdrawing groups give mixtures from which both alkenyl and zerovalent acetylene compounds can sometimes be isolated. In the presence of proton sponge, monosubstituted acetylenes still give alkenyl products while those substituted with two electron-withdrawing groups give the zerovalent products in good yield. The relevance of these results to an understanding of the nature of the migratory insertion reaction is discussed.

Introduction

The migratory insertion of unsaturated organic molecules into metal—hydrogen bonds is thought to be one of the key steps in many homogeneous catalytic reactions [1].

In order to understand the various factors which may influence the course of this insertion process, we have been conducting an extensive investigation of the reactions of platinum(II) hydrides with substituted acetylenes [2,3,4]. To this end we have examined the effect on the course of the insertion reaction of changing the solvent, the ligands (both anionic and neutral) about the Pt atom, and the substituents on the acetylene. We felt it would be of interest to probe

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* For part XX see ref. 2.

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the changes (if any) in the course of the reaction, produced by replacing platinum by another transition metal. We have briefly investigated [5] the reactions of a nickel hydride with acetylenes, to find that they follow a quite different course.

We now describe some insertion reactions of a palladium hydride with substituted acetylenes. There have been only three previous reports of reactions of acetylenes with palladium hydrides.

trans-$PdClH(PEt_3)_2$ is reported [6] to react with acetylenes to give uncharacterizable oils. Maitlis has reported [7] that cationic palladium hydrides, prepared in situ, react with acetylenes but the resulting products were not characterized. Hagihara has reported [8] the insertion of $CH_3OOCC{\equiv}CCOOCH_3$ into a rather ill-defined hydrido species to give an alkenyl product.

This meagre amount of information, when compared to the extensive literature on reactions of platinum hydrides with unsaturated species, can no doubt be attributed to the lack of suitable synthetic routes to hydridopalladium compounds and also to their instability. Recently, however, Saito has reported [9, 10] the facile preparation of a comparatively stable palladium hydride, namely *trans*-$Pd(NO_3)H(PCy_3)_2$. Not only might the stability of this hydride allow the easy investigation of its reactions with acetylenes but the results may also be directly comparable to those obtained with the analogous platinum [2] and nickel [5] hydrides.

Results

The palladium hydride *trans*-$Pd(NO_3)H(PCy_3)_2$ (I) reacted smoothly in dichloromethane solution with acetylenes containing one electron-withdrawing group to give alkenyl complexes (eq. 1), where R' = electron-withdrawing group.

$$trans\text{-}Pd(NO_3)H(PCy_3) + RC{\equiv}CR' \rightarrow trans\text{-}Pd(NO_3)[CR{=}CR'(H)](PCy_3)_2 \qquad (1)$$

The reaction was complete in 3—4 h and the resulting alkenyl product could be isolated as white air stable crystals.

Treatment of I with a ten-fold excess of Et_4NCl in dichloromethane gave the hydride *trans*-$Pd(Cl)H(PCy_3)_2$ (II), which has been prepared previously by Green [11]. Although II did not react with acetylenes at room temperature, addition of one equivalent of $AgPF_6$ to a suspension of II in acetonitrile caused an immediate precipitate of AgCl and white air stable crystals of the solvated cation *trans*-$[PdH(CH_3CN)(PCy_3)_2]PF_6$ (III) could be isolated in good yield.

Compound III reacted rapidly in a variety of solvents, with one equivalent of an acetylene substituted with one electron-withdrawing group to give an alkenyl product isolated as the neutral chloride by quenching the reaction solution with a methanolic solution of LiCl. The rate of reaction was somewhat solvent dependent, decreasing in the order CH_2Cl_2 > acetone > CH_3CN. Reaction of I or III with the acetylenes $MeOOCC{\equiv}CCOOMe$ (DMA) or $CF_3C{\equiv}CCF_3$ was much more complicated. With I or III, addition of DMA in dichloromethane solution produced complicated mixtures from which no single compound could be isolated. After the addition of one equivalent of DMA, some of the starting

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR *trans*-BISTRICYCLOHEXYLPHOSPHINE PALLADIUM COMPOUNDS[a]

Compound	Colour	M.p. (°C)	Analysis (found (calcd.) (%))	
			H	C
$PdNO_3[CH_3C{=}C(COOCH_3)H]L_2$	white	140—142(dec)	59.21 (59.42)	8.50 (8.81)
$PdNO_3[PhC{=}C(COOCH_3H]L_2$ [b]	white	134—135(dec)	64.23 (64.48)	8.88 (8.43)
$PdNO_3[PhC{=}C(CF_3)H]L_2$	cream	155—157(dec)	59.46 (60.03)	8.24 (8.06)
$PdNO_3[HC{=}C(COOCH_3)H]L_2$	cream	110—112(dec)	58.81 (58.97)	8.54 (8.60)
$PdCl[CH_3C{=}C(COOCH_3)H]L_2$	white	145—146(dec)	61.68 (61.43)	9.02 (9.12)
$PdCl[PhC{=}C(COOCH_3H]L_2$	white	139—141(dec)	63.72 (63.42)	8.61 (8.80)
$PdCl[PhC{=}C(CF_3)H]L_2$	cream	165—167(dec)	62.24 (61.86)	8.22 (8.25)
$[Pd(H)(CH_3CN)L_2]PF_6$	white	145—146(dec)	53.64 (53.40)	8.33 (8.20)
$PdNO_3[CF_3C{=}C(CF_3)H]L_2$	white	174—174(dec)	53.88 (53.81)	7.61 (7.51)
$Pd[CF_3C{\equiv}CCF_3]L_2$	white	148—149(dec)	57.86 (57.90)	7.84 (7.96)
$Pd[CH_3OOCC{\equiv}CCOOCH_3]L_2$	cream	135—137(dec)	62.58 (62.30)	9.18 (8.90)
$PdCl[HC{=}C(COOCH_3)H]L_2$	white	117—119(dec)	61.23 (60.95)	8.95 (9.02)

[a] L = PCy_3. [b] Analyzed as $PdNO_3[PhC{=}C(COOCH_3)H]L_2 \cdot C_6H_6$.

material was still present. Similar behaviour occurred on addition of $CF_3C{\equiv}CCF_3$ to III.

However, if $CF_3C{\equiv}CCF_3$ was allowed to react with I at one atmosphere pressure the zerovalent complex $Pd[CF_3C{\equiv}CCF_3](PCy_3)_2$ (IV) was obtained. At 2—3 atmospheres of $CF_3C{\equiv}CCF_3$ the expected alkenyl product was isolated along with some of compound IV.

Both compound IV and the corresponding zerovalent complex Pd[DMA]-$(PCy_3)_2$ could be obtained in virtually quantitative yield by introducing the acetylene to a solution containing the hydride I or III and proton sponge [12]. After a few minutes a heavy precipitate of proton sponge acid was evident and from the mother liquor could be isolated the zerovalent compound.

A similar experiment using acetylenes containing only one electron-withdrawing group gave no zerovalent complexes but only the alkenyl complex.

Analytical and physical data for the new compounds are contained in Table 1.

^1H, ^{19}F and infrared spectroscopic data

The ^1H NMR spectra (Table 2) of the alkenyl products *trans*-PdX(alkenyl)-$(PCy_3)_2$ (X = Cl or NO_3) show the expected broad signal (1.0—2.5 ppm), due to the cyclohexyl protons. The resonances for the alkenyl protons appear

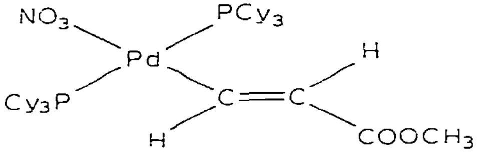
TABLE 2

^1H AND ^{19}F NMR DATA FOR COMPOUNDS OF THE TYPE *trans*-$PdX[R^1C{=}C(R^2)H](PCy_3)_2$ [a]

X	R^1	R^2	δH	Other resonances
NO_3	CH_3	$COOCH_3$	6.07	$\delta(CH_3)$ 2.67, $\delta(COOCH_3)$ 3.60
NO_3	Ph	$COOCH_3$	5.78	$\delta(COOCH_3)$ 3.53
NO_3	Ph	CF_3	5.94, J(F—H) = 10	$\delta(CF_3)$ 54.16, J(P—F) 5.1
NO_3	H	$COOCH_3$	5.90, J(H—H) = 16	δ(H) 8.69, J(P—H) 6.0, $\delta(COOCH_3)$ 3.66
NO_3	CF_3	CF_3	5.72, $J(F^2$—H) = 9.5	$\delta(CF_3{}^1)$ 42.51, $(CF_3{}^2)$ 51.00, $J(F^1$—$F^2)$ 12.2
Cl	CH_3	$COOCH_3$	6.11	$\delta(CH_3)$ 2.68, $\delta(COOCH_3)$ 3.60
Cl	Ph	$COOCH_3$	5.81	$\delta(COOCH_3)$ 3.68
Cl	Ph	CF_3	5.83, J(F—H) = 10	$\delta(CF_3)$ 54.35, J(P—F) 4.2
Cl	H	$COOCH_3$	5.91, J(H—H) = 15.8	δ(H) 8.60, J(P—H) 6.1, $\delta(COOCH_3)$ 3.66

[a] Spectra obtained in $CDCl_3$; ^1H chemical shifts are in positive ppm downfield from TMS; coupling constants are in Hz.

between 5.5 and 9.0 ppm. For R = H, two vinylic hydrogen resonances are observed, one a doublet of triplets centred at 8.69 ppm (J(P—H) 6.0 Hz, J(H—H) 16 Hz) and the other a doublet centred at 5.90 ppm (J(H—H) 16 Hz). Irradiation of the signal at 8.69 ppm causes the signal at 5.90 ppm to collapse to a singlet and irradiation of the signal at 5.90 ppm causes the signal at 8.69 to collapse to a triplet of relative intensities 1/2/1. The large value of J(H—H) necessitates the two vinylic hydrogens having a *trans* disposition about the double bond [13]. The triplet appearance of the low field resonance is due to coupling to the mutually *trans* phosphorus atoms and implies that it is due to the hydrogen atom on the carbon α to palladium. Such a low chemical shift for a vinylic proton on the carbon in the α position of a metal-bonded alkenyl derivative has been observed previously [14]. Thus the structure of this alkenyl derivative is unambiguously determined as VIII in which *cis* addition has occurred and the hydride atom has added to the carbon containing the electron-withdrawing group.



(VIII)

The alkenyl hydrogen resonance of the product with $CF_3C{\equiv}CPh$, appears as a 1/3/3/1 quartet with J(F—H) 10 Hz, consistent with hydrogen on the same carbon as the trifluoromethyl group [15].

The insertion product derived from the acetylene $CF_3C{\equiv}CCF_3$ shows, in its ^1H NMR spectrum, one vinylic hydrogen resonance at 5.72 ppm which is a

TABLE 3

INFRARED DATA FOR *trans*-BIS(TRICYCLOHEXYLPHOSPHINE)PALLADIUM COMPOUNDS [a, b]

Compound	ν(C=C)	ν(C=O)	$\nu(NO_3)$	$\nu(CF_3)$
$PdNO_3[CH_3C{=}C(COOCH_3)H]L_2$	1572	1702	1285	
$PdNO_3[PhC{=}C(COOCH_3)H]L_2$	1554	1717, 1684	1284	
$PdNO_3[PhC{=}C(CF_3)H]L_2$	1576		1286	1243, 1117
$PdNO_3[HC{=}C(COOCH_3)H]L_2$	1558	1712	1292	
$PdCl[CH_3C{=}C(COOCH_3)H]L_2$	1570	1699		
$PdCl[PhC{=}C(COOCH_3)H]L_2$	1565	1720		
$PdCl[PhC{=}C(CF_3)H]L_2$	1580			1242, 1117
$PdCl[HC{=}C(COOCH_3)H]L_2$	1556	1710		
$PdNO_3[CF_3C{=}C(CF_3)H']L_2$	1616		1285	1253, 1111

[a] All values in cm^{-1}; spectra recorded as nujol mulls. [b] L = PCy_3.

1/3/3/1 quartet with J(F—H) 10.0 Hz. The ^{19}F NMR spectrum displays two equally intense sets of signals. The low field resonance centred at 42.51 ppm is a 1/3/3/1 quartet due to coupling to the other CF_3 group with J(F—F) 12.2 Hz. The high field resonance centred at 51.00 ppm is a doublet of quartets due to coupling not only to the low field fluorine atoms but to the vinylic hydrogen atom. Noise decoupling of the proton region causes this signal to collapse to a quartet. The large value of J(F—F) implies that the two CF_3 groups are *cis* to one another about the alkenyl carbon—carbon bond [15].

The infrared spectra of all the alkenyl products (Table 3) show a band between 1550 and 1620 cm^{-1}, of weak to medium intensity, which may be assigned to ν(C=C). For those products containing an ester group a band at around 1720 cm^{-1} due to ν(C=O) is observed, and for those products containing CF_3 groups strong bands between 1100—1400 cm^{-1} due to ν(C—F) are observed. The nitrato derivatives all contain a strong band at around 1285 cm^{-1} indicative of a coordinated nitrate anion. The two zerovalent acetylene compounds $Pd(RC{\equiv}CR)(PCy_3)_2$ both show a sharp intense band, at 1813 cm^{-1} for R = $COOCH_3$ and at 1762 cm^{-1} for R = CF_3. This band is due to $\nu(C{\equiv}C)$ which is lowered in frequency upon coordination to the metal [16].

Infrared and ^{19}F and ^1H NMR data for the two zerovalent compounds are contained in Table 4. The ^1H NMR spectra of the zerovalent compounds $Pd(RC{\equiv}CR)(PCy_3)_2$ (R = CF_3 or $COOCH_3$) shows the broad resonance (1.00—2.5 ppm) of the cyclohexyl protons and in the case of R = $COOCH_3$ a singlet at 3.69 ppm due to the methyl ester protons. The ^{19}F NMR spectrum of

TABLE 4

SPECTROSCOPIC DATA FOR $Pd(ACETYLENE)(PCy_3)_2$ COMPOUNDS [a]

Acetylene	NMR (ppm)	IR (cm^{-1})
$CF_3C{\equiv}CCF_3$	$\delta(CF_3)$ 51.29	$\nu(C{\equiv}C)$ 1762, ν(C—F) 1285, 1245, 1160, 1115
$CH_3OOCC{\equiv}CCOOCH_3$	$\delta(COOCH_3)$ 3.69	$\nu(C{\equiv}C)$ 1813, ν(C=O) 1683

[a] NMR spectra recorded in CD_2Cl_2; infrared spectra as Nujol mulls. [b] Both compounds also showed a broad intense signal in the ^1H NMR spectrum between 1 and 3 ppm due to the cyclohexyl protons.

$Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$ exhibits a broad resonance at 51.2 ppm, similar in shape to that observed for the analogous platinum compound. The appearance of this signal is consistent with that expected for an $A_3A_3'XX'$ spectrum $X = P$, $A = F$.

Discussion

The hydrides *trans*-$Pd(NO_3)H(PCy_3)_2$ and *trans*-$[PdH(CH_3CN)(PCy_3)_2]PF_6$ react with one equivalent of an acetylene substituted with one electron-withdrawing group to give alkenyl complexes in which the palladium atom and the hydridic hydrogen have a *cis* disposition about the double bond. In addition the β position of the alkene is occupied by the more electronegative substituent of the original acetylene.

In contrast, the alkenyl products derived from reaction of platinum(II) hydrides with substituted acetylenes, although having a stereochemistry about the double bond which implies *cis* addition, often incorporate the more electronegative substituent of the acetylene on the α carbon.

Thus, for the alkenyl compounds derived from insertion into the Pt—H bond at *trans*-$PtXH(PEt_3)_2(X = Cl, NO_3)$ the most electron-withdrawing substituent of the acetylene occupies the β position, but if the cationic complex *trans*-$[PtH(solvent)(PEt_3)_2]PF_6$ was used the alkenyl product often contained the electron-withdrawing group on the α-carbon [2]. Moreover, the alkenyl products obtained by reaction of the directly analogous platinum hydride *trans*-$[PtH(solvent)(PCY_3)_2]PF_6$ tended to have the α position occupied by the more electron-withdrawing substituent [2].

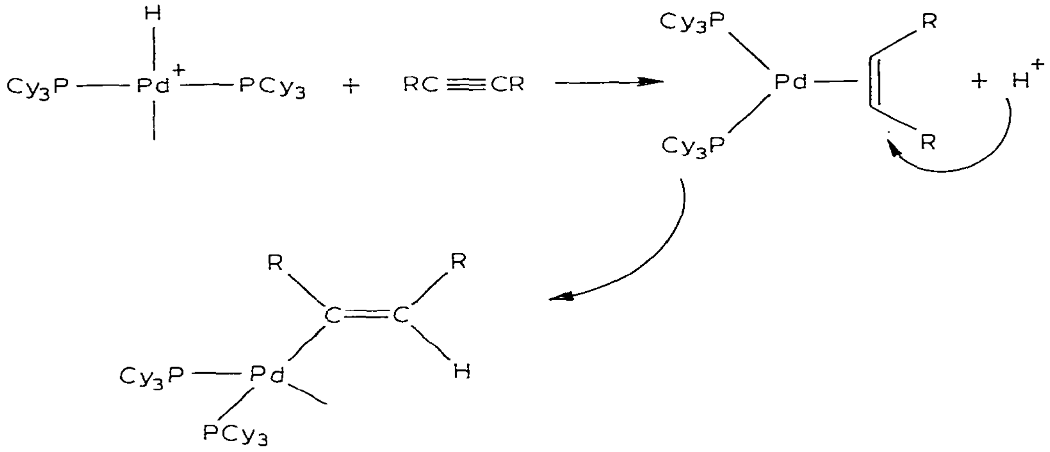
Obviously the substitution of Pd for Pt in a well-defined hydrido complex can have a significant effect on the stereochemical course of the insertion reaction. Assuming that insertion takes place via a four centred intermediate, the replacement of Pt by Pd must alter the relative charge densities on the metal and hydride causing a reversal of the mode of addition to an unsymmetrical acetylene.

The assumption that a four centred intermediate may be involved is not necessarily correct. Reaction of the hydrides I or III with the acetylene $CF_3C{\equiv}CCF_3$ afforded solutions which contained starting material, alkenyl product and the zerovalent acetylene compound. Indeed, addition of the acetylene to a solution containing the hydride and proton sponge gave the zerovalent complex in good yield, for both $CF_3C{\equiv}CCF_3$ and DMA.

Detection and isolation of zerovalent species during an insertion reaction was also observed [2] in the analogous reaction of the platinum hydride *trans*-$[Pt(H)(solvent)(PCy_3)_2]PF_6$ with the acetylenes $CF_3C{\equiv}CCF_3$ and DMA.

One interpretation of this behaviour is that the hydrido complex and the acetylene are in equilibrium with the zerovalent compound and acid. Insertion could then occur by external attack of the proton on the coordinated acetylene (eq. 2).

On the other hand, insertion could occur by reformation of the metal—hydrogen bond and migration to the acetylene, a process which implies that the equilibrium between the hydride and zerovalent complex is only a side reaction. To distinguish between these two routes, the insertion reaction was car-



(2)

ried out in the presence of proton sponge. If formation of a zerovalent species is necessary for insertion, then the insertion reaction would be prevented by the removal of acid by the proton sponge. For acetylenes substituted with one electron-withdrawing group the insertion proceeded smoothly to give the alkenyl product with no detectable formation of a zerovalent species or of proton sponge acid. Thus, in these cases, insertion apparently occurs via an intermediate in which the hydride hydrogen remains on the metal throughout.

As mentioned earlier, for the acetylenes $CF_3C{\equiv}CCF_3$ and DMA zerovalent products are obtained.

Experimental

Palladium powder was obtained from Johnson Matthey Mallory Ltd. and $NaBH_4$ from Fischer Scientific. Tricyclohexylphosphine was purchased as the carbon disulphide adduct from Strem Chemicals Inc. and was decomposed to the free phosphine by refluxing in ethanol. $CH_3C{\equiv}CCOOCH_3$ was obtained by the methylation of tetrolic acid with methanol using sulphuric acid as a catalyst and was purified by distillation under vacuum. $CF_3C{\equiv}CPh$ was kindly provided by Dr. C.S. Wong.

All reactions involving palladium hydride complexes were carried out under an inert atmosphere using standard techniques. Solvents were dried over molecular sieves and degassed by the freeze—thaw method prior to use.

Preparation of trans-$PdClH(PCy_3)_2$.

trans-$PdNO_3H(PCy_3)_2$ [9] (3.00 g) and Et_4NCl (3.4 g) were dissolved in dichloromethane and stirred for 1 h. The solvent was removed and the residue extracted with three 50 ml portions of benzene. The benzene extracts were reduced to a small volume and pentane added to induce crystallization, yield 2.19 g (76%).

Preparation of trans-$[PdHCH_3CN(PCy_3)_2]PF_6$

To a suspension of *trans*-$PdClH(PCy_3)_2$ (1.00 g) in acetonitrile (10 ml) was added $AgPF_6$(0.359 g) in 3 ml of acetonitrile. The thick white precipitate of silver chloride was removed by centrifugation to give a clear solution. This solution was concentrated and dichloromethane (4 ml) added. After filtration through celite diethyl ether was added to the filtrate to produce white crystals, yield 0.96 g (79%).

Preparation of trans-$PdNO_3[RC{=}C(R^1)H]PCy_3)_2$

trans-$PdNO_3H(PCy_3)_2$ (0.250 g) was dissolved in dichloromethane (10 ml) and one equivalent of the appropriate acetylene was added. After 4 h the solvent was removed and the residue taken up in benzene, and passed through a column containing florisil. Methanol was added to the filtrate to give white crystals of the vinylic product. In this way were prepared *trans*-$PdNO_3[CH_3C{=}C(COOCH_3)H](PCy_3)_2$ (73% yield), *trans*-$PdNO_3[PhC{=}C(COOCH_3)H](PCy_3)_2$ (71% yield), *trans*-$PdNO_3[PhC{=}C(CF_3)H](PCy_3)_2$ (65% yield), and *trans*-$PdNO_3[HC{=}C(COOCH_3)H](PCy_3)_2$ (68% yield).

Preparation of trans-$PdNO_3[CF_3C{=}C(CF_3)H](PCy_3)_2$

trans-$PdNO_3H(PCy_3)_2$ (0.250 g) was dissolved in 0.5 ml of CD_2Cl_2 and the solution transferred to a thick-walled NMR tube. A large excess of the acetylene $CF_3C{\equiv}CCF_3$ was condensed into the tube and the tube sealed. The ^1H NMR spectrum was monitored. The appearance of a 1/3/3/1 quartet in the region of 5—6 ppm indicated that a vinylic product was being formed. After 4 h this signal ceased to gain in intensity. At this point the tube was opened and the contents chromatographed on a silica gel column. Elution with diethyl ether gave two bands. The second band contained the title compound in 45% yield. The first band contained too little material for identification.

Preparation of $Pd(CF_3C{\equiv}CCF_3)(PCy_3)_2$

(a) *trans*-$PdNO_3H(PCy_3)_2$ (0.250 g) in dichloromethane (10 ml) was stirred under an atmosphere of $CF_3C{\equiv}CCF_3$. After 8h the solvent was removed and the residue recrystallized from benzene/methanol to give white crystals of acetylene complex in 45% yield.

(b) A benzene solution (10 ml) of *trans*-$PdNO_3H(PCy_3)_2$ (0.300 g) and proton sponge (0.088 g) was stirred under one atmosphere pressure of hexafluoro-2-butyne. After several minutes a white precipitate, identified as the acid salt of the proton sponge, was apparent. This precipitate was filtered off and the filtrate passed through a column containing florisil. The eluent was taken to dryness and recrystallized from benzene/methanol to give white crystals of the title compound, yield 0.211 g (62%).

Preparation of $Pd[CH_3OOCC{\equiv}CCOOCH_3](PCy_3)_2$

To a benzene solution (10 ml) of *trans*-$PdNO_3H(PCy_3)_2$ (0.300 g) and proton sponge (0.088 g) was added 50 μl of $CH_3OOCC{\equiv}CCOOCH_3$. After several minutes a white precipitate, identified as the acid salt of the proton sponge, was apparent. This precipitate was filtered off and the filtrate passed through a column containing florisil. The eluent was taken to dryness and recrystallized from dichloromethane/methanol to give cream crystals of the title compound, yield 0.261 g (78%).

Preparation of trans-$PdCl[RC{=}C(R^1)H](PCy_3)_2$

To a solution of *trans*-$[PdH(CH_3CN)(PCy_3)_2]PF_6$ (0.250 g) in 10 ml of dichloromethane, acetonitrile or acetone was added one equivalent of acetylene. After 3 h an excess of LiCl dissolved in methanol was added and the solvents then removed. The product was extracted from the residue with benzene and precipitated as white crystals upon the addition of methanol. In this way were prepared *trans*-$PdCl[CH_3C{=}C(COOCH_3)H](PCy_3)_2$ (68% yield), *trans*-$PdCl[PhC{=}C(COOCH_3)H](PCy_3)_2$ (65% yield), *trans*-$PdCl[PhC{=}C(CF_3)H](PCy_3)_2$ (61% yield), and *trans*-$PdCl[HC{=}C(COOCH_3)H](PCy_3)_2$ (72% yield).

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