216. Reactions of Cyclopalladated Benzylidene-aniline *Schiff*'s Base Complexes. Selective Synthesis of 2'-Substituted *Schiff*'s Base Derivatives and the X-Ray Crystal Structure of the Dimer $[Pd(\mu\text{-}OAc)(5'\text{-}OCH_3\text{–}C_6H_3CH{=}NC_6H_4\text{-}4\text{-}CH_3)]_2$

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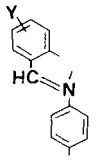
The 2'-cyclopalladated imine complex $[Pd(\mu\text{-}OAc)(5'\text{-}OCH_3\text{–}C_6H_3CH{=}NC_6H_4\text{-}4\text{-}CH_3)]_2$, $[Pd(\mu\text{-}OAc)(\mathbf{1a})]_2$, reacts with CO in MeOH to afford the 2'-substituted aryl imine 2'-CO_2CH_3-5'-OCH_3–$C_6H_3CH{=}$NTol (Tol = C_6H_4-4-CH_3). The product of this reaction can be altered by changing the bridging ligand from AcO to Cl, in which case *only* the 5-membered ring heterocyclic compound 5'-$OCH_3C_6H_3CH(OCH_3)$–N(Tol)–CO is obtained. $[Pd(\mu\text{-}OAc)(\mathbf{1a})]_2$ with 2 equiv. of Ph_3P and CO (1 atm) gives the heterocyclic 5'-OCH_3–$C_6H_3CH(CO_2CH_3)$–N(Tol)–CO which arises from two CO insertion reactions, whereas $[PdX(\mathbf{1a})]_2$ (X = AcO, Cl) with 4 equiv. of C≡NBu^t and 4 equiv. of $Ph_2PCH_2CH_2PPh_2$ affords the heterocyclic ketenimine 5'-$OCH_3C_6H_3$–C(=C=NBu^t)–N(Tol)–C=NBu^t. $[PdCl(\mathbf{1a})]_2$ reacts with $CH_2{=}CHCO_2CH_2CH_3$ to afford 2'(–CH=$CHCO_2CH_2CH_3$)-5'-$OCH_3C_6H_3CHO$, and $[Pd(\mu\text{-}OAc)(\mathbf{1a})]_2$ with I_2 to give 2'-I-5'-$OCH_3C_6H_3CHO$. Excess $CH_3O_2CC{\equiv}CCO_2CH_3$ reacts with various substituted cyclopalladated *Schiff*'s bases in MeOH to afford $[Pd(YC_6H_3CH{=}NTol)\ O{=}C(OCH_3)\text{–}C{=}C(OCH_3)CO_2CH_3]$ (Y = 4'-NO_2, 5'-NO_2, 4'-Cl, 5'-Cl, 5'-OCH_3) which we formulate as possessing two Pd–C bonds, and one coordinated ester O atom. The X-ray crystal structure of $[Pd(\mu\text{-}OAc)(\mathbf{1a})]_2$ has been determined; relevant bond lengths [Å] and bond angles [°] are: Pd–O(1), 2.139(6), Pd–O(2), 2.026(6), Pd–N, 2.039(6), Pd–C(2'), 1.951(8), Pd–Pd, 3.113(1), N–Pd–C(2'), 80.9(3), N–Pd–O(1), 97.5(2), C(2')–Pd–O(2), 91.7(3), O(1)–Pd–O(2), 89.2(2).

Introduction. – Organopalladium complexes [1] and specifically cyclic Pd compounds [2] are recognized as valuable intermediates in synthetic organic chemistry. Cyclopalladated complexes containing five-membered rings are readily available starting from a variety of organic N compounds [3] and react further in the presence of ligands which are capable of coordination to Pd, *e.g.*, CO, to give *ortho*-substituted aromatic compounds [4] [5].

$$[Pd(OAc)(\mathbf{1})]_2 \xrightarrow[MeOH]{CO\ (1\ atm)} \mathbf{2} + Pd(O) + HX \qquad (1)$$



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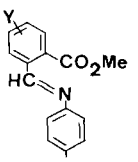
a Y = 5'-OCH_3
b Y = 4'-CH_3
c Y = 5'-NO_2
d Y = 4'-NO_3
e Y = 5'-Cl
f Y = 4'-Cl



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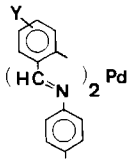
We have recently [6] studied the carbonylation of the *Schiff*'s complexes $[Pd(OAc)(\mathbf{1})]_2$, to give the *ortho*-substituted esters **2**. The Pd complexes $[Pd(OAc)(\mathbf{1})]_2$ are masked metallated aldehydes; indeed the *ortho*-substituted aldehydes corresponding to **2** are available *via* hydrolysis. The yields and reaction rates for the chemistry in *Eqn. 1* are a function of the group Y with faster reactions associated with electron donor groups. With Y-substituents such as 4′- or 5′-NO_2, a side reaction occurs leading to $[Pd(\mathbf{1})_2]$, **3**.



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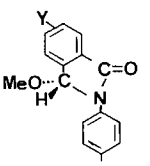

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We report here an extension of this chemistry in which we *a*) change *Reaction 1* so as to suppress the formation of **2** and obtain **4** selectively, *b*) prepare a novel heterocyclic ketenimine from $[PdCl(\mathbf{1})]_2$ and Bu^{t}N≡C, *c*) react cyclopalladated complexes with ethyl acrylate and I_2 thereby selectively synthesizing *ortho*-substituted aldehydes, *d*) explore the organopalladium chemistry of our complexes with the acetylene $CH_3O_2CC{\equiv}CCO_2CH_3$ in MeOH, and *e*) report the molecular structure of $[Pd(OAc)(\mathbf{1a})]_2$.

Results and Discussion. – *The Solid State Structure of* $[Pd(OAc)(\mathbf{1a})]_2$. As $[Pd(OAc)(\mathbf{1a})]_2$ reacts with CO in MeOH > 20 times faster than the analogous 5′-NO_2 complex [6], we considered it worthwhile to determine its structure.

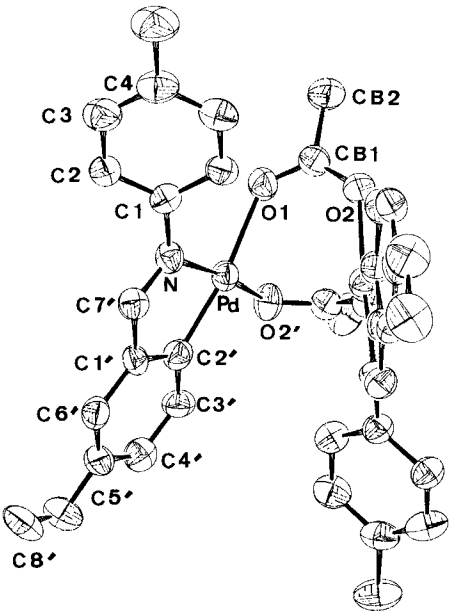


Fig. *ORTEP plot of* $[Pd(\mu\text{-}OAc)(\mathbf{1a})]_2$

Table 1. *A Selection of Interatomic Distances and Angles for [Pd(OAc)(* **1a***)]$_2$*

Bond Distances	[Å]	Bond Angles	[°]
Pd–O(1)	2.139(6)	Pd–O(1)–C(B1)	132.0(3)
Pd–O(2')[a]	2.026(6)	Pd–O(2')–C(B1')	125.3(4)
Pd–N	2.039(6)	Pd–N–Cl	127.6(1)
Pd–C(2')	1.951(8)	Pd–N–C(7')	114.7(5)
N–C(1)	1.439(9)	Pd–C(2')–C(1')	113.9(5)
N–C(7')	1.281(11)	Pd–C(2')–C(3')	128.4(4)
O(1)–C(B1)	1.243(11)	O(1)–C(B1)–O(2)	126.1(5)
O(2)–C(B2)	1.274(11)	O(1)–C(B1)–C(B2)	117.9(6)
C(B1)–C(B2)	1.508(13)	O(2)–C(B1)–C(B2)	116.0(6)
O(3)–C(5')	1.374(11)	N–Cl–C(2)	119.0(5)
O(3)–C(8')	1.430(13)	N–Cl–C(7)	120.2(5)
C(1)–C(2)	1.38(1)	N–C(7')–C(1')	116.4(6)
C(2)–C(3)	1.40(1)	Cl–N–C(7')	117.7(5)
C(3)–C(4)	1.40(1)	C(7')–C(1')–C(2')	113.9(6)
C(4)–C(5)	1.55(1)	C(7')–C(1')–C(6')	122.4(5)
C(4)–C(6)	1.36(1)	C(4')–C(5')–C(6')	120.9(6)
C(6)–C(7)	1.39(1)	O(3)–C(5')–C(4')	115.7(6)
C(1)–C(7)	1.40(1)	O(3)–C(5')–C(6')	123.4(6)
C(1')–C(7')	1.44(1)	C(5')–O(3)–C(8')	116.3(6)
C(1')–C(2')	1.41(1)	C(3)–C(4)–C(5)	118.8(7)
C(1')–C(6')	1.41(1)	C(6)–C(4)–C(5)	121.7(6)
C(2')–C(3')	1.42(1)	N–Pd–C(2')	80.9(3)
C(3')–C(4')	1.39(1)	N–Pd–O(1)	97.5(2)
C(4')–C(5')	1.41(1)	C(2')–Pd–O(2')	91.7(3)
C(5')–C(6')	1.40(1)	O(1)–Pd–O(2')	89.2(2)
Pd–Pd'	3.113(1)		

Internal Rotation Angles	[°]
Pd–N–Cl–C(2)	51.1
Pd–N–C(7')–C(1')	2.9
Pd–O(1)–C(B1)–O(2)	0.7
Pd–C(2')–C(1')–C(7')	−2.8
N–Pd–O(1)–C(B1)	−98.5
C(2')–Pd–O(1)–C(B1)	−178.0
N–C(7')–C(1')–C(2')	−0.1
C(6')–C(5')–O(3)–C(8')	4.1
C(2)–C(3)–C(4)–C(5)	−178.5

[a]) Double primed atoms are related to the unprimed atoms by the symmetry operation: -x, y, (1/2-z).

A perspective view of the complex is given in the *Fig.* and a list of relevant bond distances and bond angles may be found in *Table 1*. The molecule is dimeric and has the *sym-trans*-geometry with respect to the N donors. Due to the presence of a crystallographic symmetry element, only half of the molecule is independent. The local geometry at the Pd-atom is distorted square planar with the four donors arising from the imine N-nitrogen, the 2'-aryl-C-, and two O-atoms, one from each bridging acetate. The molecule is bent with a hinge angle of 136.2°.

Focussing on the coordination sphere, the two Pd–O distances are significantly different as one O-atom is *trans* to a C ligand (Pd–O) = 2.139(6) Å, and the other *trans* to a N donor (Pd–O) = 2.026(6) Å, consistent with relatively large and small *trans*-influences, for the C and N ligands, respectively. The 2.139(6) Å Pd–O distance *trans* to C is

one of the longest of its type and is consistent with the 5′-OCH_3 aryl moiety functioning as a strong σ-donor. The Pd–N bond distance, 2.039(6) Å, is normal [7–12], and the Pd–C bond relatively short at 1.951(8) Å, although not unprecedented as the cyclometallated complex $[Pd(OAc)(C_6H_4CH_2SCH_2Ph)]_2$ [13] has a Pd–C bond separation of 1.945(2) Å. Our *Schiff*'s base C–N bond separation, 1.281(11) Å, has been observed previously for this type of complex [8] [10] [12].

The angles about Pd are typical for a chelating five-membered ring involving a metallated aryl moiety. Specifically, we note that our N–Pd–C angle of 80.9(3)° is in very good agreement with the analogous angles for the cation $[\overbrace{Pd(o\text{-}C_6H_4CH{=}N}CH_2CH_2NH_2(NH_2CH_2CH_2NH_2)]^+$ $(81.3(9)°)_{ave}$ [10] and the cyclopalladated thioether mentioned above, 81.9(8)° [13].

There is no compelling feature of this structure to which we could attribute the observed relatively fast kinetics; although we note that the long Pd–O bond *trans* to the C donor would certainly facilitate bridge cleavage if this were of any importance.

Carbonylation. As we noted above, the acetate bridged compounds carbonylate smoothly in MeOH under CO (1 atm) at room temperature to give the methyl esters **2** [6]. Interestingly, ester formation is markedly dependent on the bridging ligand and can be suppressed completely. Using similar conditions but starting from $[PdCl(\mathbf{1a})]_2$, we obtain the heterocyclic compound **4** in good yield; however, the reaction once again becomes quantitative in ester, **2**, when an aliphatic amine is introduced, see *Eqns. 2* and *3*. A summary of these and other results is shown in *Table 2*.

$$[PdCl(\mathbf{1a})]_2 + CO + CH_3OH \rightarrow \mathbf{4a} \quad (2)$$

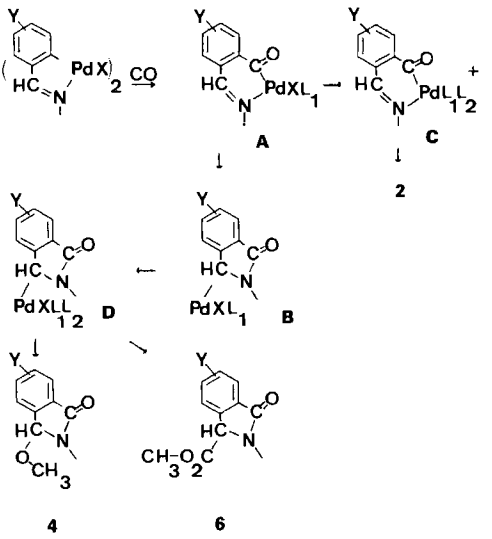
$$[PdCl(\mathbf{1a})]_2 + CO + CH_3OH \xrightarrow{NEt_3} \mathbf{2a} \quad (3)$$

Table 2. *Results for the Carbonylation of Various Cyclopalladated* Schiff's *Base Complexes* (MeOH, r.t.)

Complex	Ester **2** [%]	Yield[a]) [%] Heterocycle **4**	Ligand Added[b])
1. $[Pd(OAc)(\mathbf{1a})]_2$	100	0	
2. $[PdCl(\mathbf{1a})]_2$	a) 0	80	
	b) 100	0	Et_3N
	c) 100	0	Et_2NH
	d) 0	55	2 equiv. py per Pd
	e) 100	0	py and Et_3N
	f)	95	2,6-Bu^t py
	g)	10	4 equiv. py per Pd (3 h)
	h)	80	$Me_2NCH_2CH_2NMe_2$
3. $[Pd(OAc)(\mathbf{1a})]_2$	complex **6**	90	Ph_3P
4. $[PdCl(\mathbf{1a})]_2$	a) 0	5	Ph_3P (1 h)
	b) 0	40	Ph_3P (20 h)
	c) 10	5	Ph_3P and Et_3N
	d) 0	5	Diphos
	e) 0	40	Diphos and Et_3N
5. $[Pd(OAc)(\mathbf{1b})]_2$	a) 100	0	
	b) 100	0	$EtPr^i_2N$
6. $[PdCl(\mathbf{1b})]_2$	a) 0	100	
	b) 100	0	Bu_3N
	c) 85	10	$EtPr^i_2N$
	d) 0	100	py

Note that addition of pyridine affords reduced yields of heterocyclic **4** and no ester, whereas mono- or bidentate phosphine ligands tend to favor **4**, albeit in poorer yield. The nature of the aliphatic amine is not important. A similar palladated *Schiff*'s base has been carbonylated previously in toluene at 100° or in alcohols at 50°, and similar products obtained [5] although in lower yield. In toluene, a heterocycle is formed in which the CH_3O group of **4** is replaced by AcO, whereas in MeOH a mixture of derivatives of **2** and **4** was reported [5]. We attribute our observed selectivity to *a*) milder reaction conditions, and *b*) control of the Pd coordination sphere, and this brings us to *Scheme 1*.

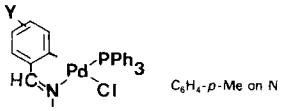
Scheme 1



We can visualize the carbonylation reaction as proceeding *via* the complexes shown in *Scheme 1* (the Tol group on N is omitted for clarity). *Thompson* and *Heck* [5] have suggested the intermediates **A** and **B**, which arise after CO coordination to Pd(II) and subsequent insertion into the Pd–C bond. Using **A** and **B**, we can rationalize our results assuming the importance of coordinated MeOH and, eventually, methoxide. Starting from [Pd(OAc)(**1**)]$_2$, which contains the good-leaving group AcO, **A** is readily converted to cation **C**, with L_1 = CO and L_2 = CH_3OH. Cation **C** deprotonates to form a CH_3O complex which reductively eliminates the product ester **2**. This is a facile process which is 50% complete in *ca.* 2–3 min starting from [Pd(OAc)(**1a**)]$_2$. Starting from [PdCl(**1a**)]$_2$, we reach the Cl analog of **A** in which Cl is not readily displaced by MeOH. Although the solvent can coordinate loosely in an axial position, this is presumably insufficient to induce deprotonation; however, in the presence of a base, the weakly coordinated MeOH is deprotonated and the reaction proceeds to give **2**. In the absence of base, **A** is transformed into the three-coordinate Cl complex **B**, L_1 = CO, which now accepts the loosely bound fifth ligand MeOH to give **D**, L_2 = CH_3OH. Proton loss followed by reductive elimination gives the product, in this case, the heterocycle. We have noted earlier [6] that the quantitative conversion of [Pd(OAc)(**1a**)]$_2$ to **2a** is complete in less than

0.5 h. The synthesis of heterocycle **4a** from $[PdCl(\mathbf{1a})]_2$ is *ca.* 80% complete after 1.5 h and quantitative conversion requires more than 3 h of reaction time. Presumably the conversion of **A** to **B** is relatively slow. We note that the conversion of $[PdCl(\mathbf{1a})]_2$ to **2a** in the presence of Et_3N is also complete within 0.5 h. Changing the base from a monodentate aliphatic amine to a pyridine suppresses ester formation, and slows the reaction. This is related to the coordination of the pyridine to Pd to give isolable [PdCl(py)(**1**)]. Addition of excess pyridine (2 equiv. per Pd) slows the reaction further, as does the presence of the chelate $Me_2NCH_2CH_2NMe_2$. Consequently, blocking one or more coordination sites allows the reaction to eventually reach **B** or some modified form of **B** where methanol coordination becomes easier.

Interestingly, in the presence of the bulky base 2,6-di(*tert*-butyl)-4-methylpyridine, conversion of $[PdCl(\mathbf{1})]_2$ to the analog of **4** is essentially quantitative, and proceeds at about the same rate as the reaction in its absence. Since this pyridine does not react[1]) with either $[PdCl(\mathbf{1a})]_2$ (in the absence of CO) or with the model complex *sym-trans*-$[Pd(\mu\text{-}Cl)Cl(PEt_3)]_2$, which does react with simple pyridines and picolines [14], this base is most probably not involved at all in the reaction and may even be too bulky to efficiently deprotonate coordinated MeOH.



5

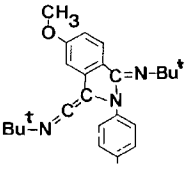
The carbonylation of $[PdCl(\mathbf{1a})]_2$ or $[PdCl(\mathbf{1b})]_2$ in the presence of 2 equiv. of Ph_3P begins from the crystalline phosphine complex **5** (see *Table 2* and *Experimental*) and proceeds slowly to give reduced yields of the heterocyclic product **4**. Here again, the blocking action of a coordinated ligand is important.

Interestingly, carbonylation using $[Pd(OAc)(\mathbf{1a})]_2$ and Ph_3P gives the double insertion product **6** shown in *Scheme 1*. We assume that **6** stems from CO insertion into the Pd–C bond of **D**, L_1 and/or L_2 = CO (if the acetate has dissociated, one of the coordinated ligands might be CH_3OH) followed by the usual reductive elimination after methoxide is generated. Small quantities of **6** (< 1%) were observed in the chemistry starting from either $[PdCl(\mathbf{1a})]_2$ or $[PdCl(\mathbf{1b})]_2$ (the methine proton of **6** appears at δ 5.68 and, consequently, is easily monitored). We presume the higher conversion to **6** starting from the acetate bridged complex is related to the ability of AcO to dissociate from **D** thereby promoting CO coordination and subsequent second insertion. Although we have no data which would allow us to select the slow step(s) in this chemistry, accepting complexes **A**–**D** helps us to understand the products, and **D** is especially attractive in rationalizing the double insertion of CO and this brings us to C≡NBu^t as reagent.

Insertion of C≡NBu^t. Four equiv. of C≡NBu^t react with either $[Pd(OAc)(\mathbf{1a})]_2$ or $[PdCl(\mathbf{1a})]_2$[2]) in CH_2Cl_2 solution in the presence of 4 equiv. of $Ph_2PCH_2CH_2PPh_2$ (diphos) to give the ketenimine **7**, which is the result of incorporation of two isonitrile molecules into the *Schiff*'s base skeleton. The compound **7** has been characterized using IR (ν(C=C=N) = 2010 cm^{-1}, ν(–C=N) = 1630 cm^{-1}), ^{1}H- and ^{13}C-NMR

[1]) ^{1}H- and ^{31}P-NMR studies.

[2]) We obtain better yields with the Cl complex.



7

(δ^{13}C(N=*C*=C) = 190.38, δ^{13}C(N=C=*C*) = 62.63 [15]), MS techniques, and elemental analysis. There are 2 *t*-Bu CH_3 groups in the ratio 1:1 in both NMR forms.

In view of the number of possible ligands available for the Pd, we begin by elucidating the role of the chelating phosphine. In the absence of Bu^{t}N≡C the diphos ligand reacts as shown in *Eqn. 4* to give the isolable cationic complex **8** (see *Experimental*). Since the halogen in **8** is not coordinated, it is clear why starting from [Pd(OAc)(**1a**)]$_2$ leads to the same product.

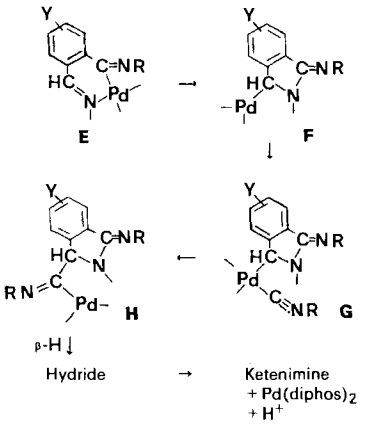
$$[PdCl(\mathbf{1a}]_2 + 2\ \text{diphos} \rightarrow \quad \text{(8)} + Cl^- \qquad (4)$$

8

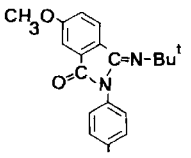
Addition of a second equivalent of diphos to **8** gives a material whose ^{1}H-NMR spectrum shows broad lines, suggesting an exchange process, perhaps *via* a five-coordinate intermediate. Alternatively, the N ligand might be displaced [8]. In any case, the exchange suggests that, in the presence of Bu^{t}N≡C, competition for a coordination position is possible. Consequently, we feel that one function of the diphos is to create a labile coordination sphere. In its second capacity the diphos serve to stabilize the Pd(O) eventually formed, as [Pd(diphos)$_2$]. This latter complex has been identified during the reaction *via* ^{31}P-NMR and synthesized independently [16]. The complex [Pd(diphos)$_2$] is presumed to be the product of the decomposition of the hydride stemming from the *β*-H-abstraction reaction shown in *Scheme 2*.

Scheme 2 provides a possible sequence of reactions to account for the formation of **7**. In view of the chemistry of *Eqn. 4*, we feel that the diphos ligand occupies two coordi-

Scheme 2



nation positions throughout the reaction. Complex **E** arises from isonitrile coordination and insertion into the Pd–C bond. The conversion to **F** is suggested in analogy to **B** in *Scheme 1*. Coordination of a second Bu^{t}N≡C to give **G**, followed by a second insertion affords **H** which can then undergo a β-H-abstraction reaction, quite common in Pd(II) chemistry, [17] to form a hydride. Decomposition of the hydride gives the products. We note that **7** can be obtained in the absence of diphos using [Pd(OAc)(**1a**)]$_2$ and 12 equiv. of C≡NBu^t. We assume that the mechanism in this case is similar to that described above except that the coordinated diphos is replaced by isonitrile ligands. The excess isonitrile is necessary to stabilize the Pd(O) complex which is generated when the hydride complex decomposes. [Pd(OAc)(**1a**)]$_2$ with only 2 equiv. of C≡NBu^t affords simple bridge cleavage as shown by ^{1}H-NMR spectroscopy (δ (*H*C=N) = 8.03, δ (*B*u^{t}N≡C) = 1.59).



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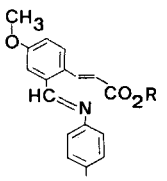
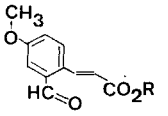
In view of the uncommon nature of **7**, we reacted it with H_2O in acetone in the expectation of obtaining an amide of simpler form. The product **9** was obtained in *ca.* 30% yield and showed bands in the IR at 1739 (ν(C=O)) and 1650 cm^{-1} (ν(C=N)). The ^{1}H- and ^{13}C-NMR spectra were consistent with the proposed structure as is the parent ion in the MS at *m/e* 322. The same product is obtained using HCl/acetone to hydrolyse **7**. The modest yield is suggestive of additional hydrolysis products and indeed, in the chromatographic workup, several other compounds were eluted; however, these were not identified.



10 R = Et



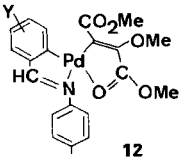
11 R = Et

Vinylation with CH_2=$CHCO_2Et$. Ethylacrylate reacts with [PdCl(**1a**)] in refluxing benzene or toluene to give the α,β-unsaturated ester **10** plus metallic Pd. Since the purification of **10** was accompanied by partial hydrolysis the workup was modified to include deliberate HCl hydrolysis and gave **11** ((*E*)-olefin). Compound **11** is a consequence of insertion of the olefin into the Pd–C bond followed by β-H elimination to give the product. This reaction is an extension of well-known chemistry [17] and requires no further comment. We have also prepared the 4′-Cl analog of **11**.

Reaction with I_2. Treatment of a suspension of [Pd(OAc)(**1a**)]$_2$ with I_2 in MeOH at 40° and subsequent hydrolysis with HCl affords 2′-iodo-5′-methoxybenzaldehyde in 52% yield. The use of $CHCl_3$ as solvent resulted in mixtures of products. The product shows the expected C=O stretch at 1680 cm^{-1} and has M^+ at *m/e* = 262. In addition to the aldehyde-C resonance at δ = 195.91, C(2′) shows the characteristic high-field shift (δ = 89.98) associated with a C–I bond.

Transformations Involving $MeO_2C-C\equiv C-CO_2Me$. In contrast to other reagents, dimethylacetylene dicarboxylate does not insert into the Pd–C bond. An excess of $MeO_2C-C\equiv C-CO_2Me$ reacts with the bridged acetate dimers having electron-withdrawing Y substituents, in MeOH, to give **12** in good yield (see *Eqn. 5*). Electron-donor substituents give much poorer yields and are accompanied by a side reaction.

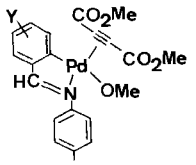
$$[Pd(OAc)(\mathbf{1})]_2 + \text{XS } MeO_2C-C\equiv C-CO_2Me \xrightarrow[MeOH]{} \mathbf{12a\text{–}d} \qquad (5)$$



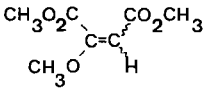
12

a) 5′-NO_2, 89%
b) 4′-NO_2, 8%
c) 5′-Cl, 77%
d) 4′-Cl, 89%
e) 5′-OCH_3, 31%

The structure of **12** is supported by molecular weight (525 ± 30, for **12a**), microanalytical, IR, and NMR data. The ^{1}H-NMR data reveal the *Schiff*'s base resonances and the appropriate number of CH_3O groups[3]) plus the toluidine CH_3. The ^{13}C-NMR spectra show the corresponding signals as well as two carbonyl carboxylate resonances. The ^{13}C methyl-ether signal is markedly shifted to low field, by *ca.* 7–9 ppm, relative to the methyl ester signals in keeping with [18]. Based on the NOE enhanced coupled ^{13}C-NMR spectrum of **12e** (the analogs **12a–d** are not as soluble), we assign the resonance at $\delta = 155.41$, to the acetylene-C-atom coordinated to Pd, since this appears as a singlet (no $^2J(^{13}C, ^1H)$ or $^3J(^{13}C, ^1H)$ interactions). The remaining acetylene-C-atom appears at $\delta = 144.55$. We initially considered the product **12** to have a structure similar to **13**; however, this is not compatible with the observed lower symmetry of the acetylene



13



14

moiety. (Note that d^8-metal complexes coordinate olefins and acetylene perpendicular to the coordination plane [19] so that **13** should exhibit equivalent CO_2R groups.) Chemical support for structure **12** comes from its reaction with glacial AcOH in that complex **12a** is converted quantitatively to $[Pd(OAc)(\mathbf{1a})]_2$ and **14**. Compound **14** has an MS with a parent ion at *m/e* 174 and shows three ^{1}H CH_3O resonances ($\delta = 3.96, 3.86, 3.77$) and the vinyl proton ($\delta = 6.20$). The ^{13}C-NMR spectrum reveals the expected 7 resonances with the 2 carboxylate resonances at $\delta = 165.02$ and 163.59 and the olefin signals at $\delta = 155.13$ and 108.19. The CH_3O signals appear at $\delta = 61.30$, 53.03 and 51.91 with the ether methyl assigned to the lowest field resonance. The geometry about the double bond is uncertain, as indicated by the wavy lines; however, we do not observe the relatively large

[3]) Three for **12a–d**, four for the 5′-OCH_3 analog.

$^3J(OC-C=C-H)$ coupling typical for a *trans* three-bond interaction [20] so that we favor the (*E*)-geometry for this olefin.

There are several interesting points associated with *Reaction* 5:

a) The product **12** has a structural unit which appears to develop from MeOH (or MeO) attack on the coordinated acetylene. In Pt chemistry attack of Cl on this coordinated acetylene gives the $\overline{Pt-C(CO_2CH_3)=C(Cl)COOCH_3}$ moiety [21].

b) The reaction does not proceed starting from the Cl-bridged starting material.

c) One equivalent of acetylene reacts very slowly, if at all (no reaction observed after 3 days).

d) The rate of disappearance of starting complex[4]) monitored by UV/VIS spectroscopy, depends on Y such that electron donors accelerate the reaction. The difference in rate is small, a factor of *ca.* 6, with the faster reaction finished in 5–10 minutes.

e) **14** can be identified in the reaction solutions which lead to **12.**

We assume that the acetylene does not readily coordinate to Pd in our complex and, therefore, that an excess is required to shift the equilibrium. An analogous reaction with diphenylacetylene gave no observable product. The (*E*)-geometry of the two carbonyl groups in **12** and **14** is suggestive of external MeOH attack, in analogy to [22]; however, this remains an open question.

Conclusion. – The work described here shows the potential for using cyclopalladated *Schiff*'s base compounds in the specific synthesis of *ortho*-substituted aromatic compounds. The substituents CO_2CH_3, $CH=CHCO_2Et$ and I have been introduced in good yield, but more importantly, we have shown that control of the metal coordination sphere, as in the carbonylation, can lead to product selectivity. Specifically, we can 'tailor' this chemistry so as to obtain either **2** or the heterocyclic **4**, both in excellent yield. Additionally, in our isonitrile chemistry, we have prepared a novel ketenimine *via* two separate insertion steps. Not all of the reactions lead to rapid production of organic compounds as revealed by our $MeO_2CC{\equiv}CCO_2Me$ chemistry, in which we isolate organometallic complexes of type **12**. These are useful models and provide hints as to how other products may develop. The proper modification of other simple organic compounds should also make these amenable to cyclopalladation and subsequent transformation.

We thank Prof. *L.M. Venanzi* for helpful discussion. *R.R.* thanks the *Swiss National Science Foundation* and *Ciba-Geigy*, Basel, for support. *A.A.* acknowledges support from the *M.P.I.* Italy and we thank the *Johnson Matthey Research Centre*, England, for the loan of $PdCl_2$.

Experimental. – $Pd(OAc)_2$ was prepared by reaction of $PdCl_2$, initially with NaOH, and eventually AcOH as described in [23], and was purified before use by dissolving in hot benzene, filtration and removal of the solvent. This procedure removes traces of Pd metal which arise from slow decomposition. Diphos, dimethylacetylene dicarboxylate, (*tert*-butyl)isonitrile and 2,6-di(*tert*-butyl)pyridine were obtained from *Fluka AG* (*purum*) and were used without further purification. Ethyl acrylate was also obtained from *Fluka AG* and was distilled before use. The cyclopalladated complexes were prepared as described in [6]. Microanalytical data for representative complexes are shown in *Table 3*.

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[4]) $[CH_3CO_2C{\equiv}C-CO_2CH_3]/[complex] \approx 10{,}000$.

Table 3. *Analytical Data*

Compound	C [%]		H [%]		N [%]	
	Found	Calc.	Found	Calc.	Found	Calc.
4 (Y = 5'OCH_3)	72.05	72.07	5.95	6.05	4.93	4.94
5 (Y = 5'–OCH_3)[a])	62.99	63.07	4.63	4.65	2.15	2.23
$[PdCl(\mathbf{1a})]_2$[b])	48.91	49.21	3.78	3.85	3.84	3.83
$[PdCl(\mathbf{1b})]_2$[c])	51.31	51.46	4.09	4.03	3.80	4.00
$[PdCl(\mathbf{1f})]_2$[d])	45.15	45.38	3.05	2.99	3.68	3.78
[PdCl(**1a**)(py)][e])	53.73	53.95	4.15	4.30	6.10	6.29
[PdCl(**1b**)(py)][f])	55.89	55.96	4.47	4.46	6.48	6.53
$[PdCl(\mathbf{1a})(NHEt_2)]$[g])	51.97	51.95	5.67	5.74	6.23	6.38
6 (Y = 5'OCH_3)	69.28	69.44	5.64	5.50	4.54	4.50
7	76.80	77.08	8.09	8.02	10.32	10.79
8	64.14	64.41	5.07	5.01	1.77	1.83
9	74.50	74.51	7.10	6.88	8.31	8.69
12a	48.43	48.62	3.79	3.89	5.29	5.40
b	48.14	48.62	3.98	3.89	5.19	5.40
c	49.52	49.63	3.78	3.97	2.65	2.76
d	49.54	49.63	3.91	3.97	2.79	2.76
e	52.38	52.45	4.72	4.60	2.90	2.78

[a]) Cl [%]: found, 5.60; calc., 5.64. [b]) Cl [%]: found, 9.83; calc., 9.68. [c]) Cl [%]: found, 9.95; calc., 10.13. [d]) Cl [%]: found, 18.93; calc., 19.14. [e]) Cl [%]: found, 7.96; calc., 8.51. [f]) Cl [%]: found, 8.27; calc., 8.26. [g]) Cl [%]: found, 8.33; calc., 8.07.

The UV/VIS spectra were measured on a *Umicon 410* instrument. IR measurements were made using *Beckmann 4250* and *Perkin-Elmer 1430* spectrophotometers. ^{1}H- and ^{13}C-NMR spectra were obtained on a *Bruker WM-250* spectrometer, whereas the ^{31}P-NMR spectra were measured on a *Bruker HX-90* instrument. A compilation of ^{1}H-NMR data may be found in *Table 4*. ^{13}C-NMR data for **12b–e** are given in *Table 5*. MS, molecular-weight determinations, and microanalyses were provided by the analytical services of the ETH.

*Determination and Refinement of the Structure of [Pd(OAc)(***1a***)]$_2$.* Orange crystals of the complex were prepared by slow crystallization from CH_2Cl_2/hexane, and are unstable in the air with loss of solvent. A crystal of approximate prismatic habit was sealed under N_2 in a glass capillary and used for the data collection (CAD4).

Crystal data and data collection parameters are listed in *Table 6*. The cell parameters were obtained by least-squares fit of the 2Θ values of 25 higher order reflections ($16.0 \leq 2\Theta \leq 24.0$). No absorption correction was deemed necessary, and structure factors were calculated in the usual way (Lp corrections applied). The structure was solved by standard *Patterson* and *Fourier* methods and refined by block diagonal least-squares using a *Cruickshank* weighting scheme [24]. Anisotropic temp. factors were used for the refinement of all atoms, with scattering factors taken from [25] with anomalous dispersion correction taken into account.

A *Fourier* difference at the end of the refinement revealed a disordered molecule of solvent (CH_2Cl_2). The two Cl-atoms are related by the symmetry operation $-x, y, 1/2-2z$. It proved impossible to fit a model for the disorder; therefore, only the contribution of the Cl-atoms were taken into account and refined.

Final positional and equivalent temperature factors [26] are given in *Table 7*[5]).

*Carbonylation of [PdCl(***1a***)]$_2$.* A suspension of $[PdCl(\mathbf{1a})]_2$ (50 mg, 0.07 mmol) in MeOH (50 ml) was treated with CO (1 atm) for 20 h at r.t. The resulting dark suspension was filtered through *Celite* to remove Pd metal and then concentrated on a rotary evaporator. Extraction with Et_2O gave a soln. which was allowed to slowly evaporate at r.t. The product crystallized during this process and was collected by filtration: 30 mg (78%), m.p. = 98°. IR(KBr): 1695 (C=O). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 166.81, 164.07 (C=O, C(5')); 142.49; 135.26; 135.08; 129.88 (C(3)); 125.76; 125.59; 122.00 (C(2)); 116.94; 108.40; 87.32 (C(7')); 56.05 (C(5')–O*C*H$_3$); 49.30 (C(7')–O*C*H$_3$); 21.16 (C(4)–*C*H$_3$). MS: 283 ($C_{17}H_{17}NO_3^+$).

[5]) Tables of final observed and calculated structure factors *etc.* are available from the authors upon request.

Table 4. *^{1}H-NMR*[a]) *Data for the Products*

Compound	H–C(3′)	H–C(4′)	H–C(6′)	H–C(7′)	H_3CO–C(5′)	H_3C–C(4)	Others
4 (Y = 5′–OCH_3)	7.82	7.06 –	7.09	6.36	3.92	2.37	H_3CO–C(7′) = 2.93
5 (Y = 5′–OCH_3)	6.36	6.24	6.99	8.21	3.69	2.34	^4J(P,H–C(7′)) = 6.7
[PdCl(**1a**)]$_2$	*ca.* 7.25	6.71	6.90	7.91	3.77	2.40	
[PdCl(**1a**)(py)][b])	6.06	6.64	c)	8.01	3.77	2.37	
	7.96	c)	c)	8.07	3.81	2.24	
[PdCl(**1a**)($NHEt_2$)][b])	7.91	*ca.* 6.80	6.95	7.97			
	ca. 6.95	*ca.* 6.80	7.03	7.99	(3.78, 3.81)	(2.36, 2.42)	
6 (Y = 5′–OCH_3)	7.85	7.05 –	7.09	5.68	3.91	2.36	H_3CO_2C = 3.70
7	7.01	6.87	6.13	–	3.39	2.34	$(H_3C)_3CN$ = 1.76
							$(H_3C)_3CN$ = 1.42
8	c)	6.43	7.15	8.22	3.73	2.19	
9	7.65	6.94	5.97	–	3.50	2.38	$(H_3C)_3CN$ = 1.82
10	7.58	7.02	7.66	8.86	3.90	2.39	HC = C*H*–C(2′) = 6.32
							*H*C=CH–C(2′) = 8.32
							^3J(H,H) = 15.8
							CH_3CH_2O = 4.27
							CH_3CH_2O = 1.34
11	7.60	7.13	7.36	10.33[d])	3.88		HC=C*H*–C(2′) = 6.31
							*H*C=CH–C(2′) = 8.43
							^3J(H,H) = 15.8
							CH_3CH_2O = 4.27
							CH_3CH_2O = 1.33
2′-I-5′-OCH_3–C_6H_3CHO	7.81	6.93	7.44	10.03[d])		3.85	
12a	7.34	8.01	8.22	8.31		2.42	3.89, 3.88, 3.72 5′-O*C*H_3
12b	7.99	7.98[e])	7.53	8.31		2.42	4.04, 3.89, 3.73 5′-O*C*H_3
12c	7.08	7.16	7.38	8.15		2.41	3.87, 3.85, 3.71 5′-O*C*H_3
12d[c])				8.17		2.40	3.93, 3.87, 3.71 5′-O*C*H_3
12e	7.03	6.81	7.01	8.15		2.40	3.86, 3.86, 3.80,
							3.70 5′-O*C*H_3

[a]) Chemical shifts in ppm, coupling constants in Hz. $CDCl_3$ solns. All the aromatic protons of the imine ring show normal ^3J(H,H) vicinal coupling constants, 7–9 Hz, and ^4J(H,H) values of 1–3 Hz.

[b]) Two geometric isomers.

[c]) Signals overlap and prevent assignment.

[d]) Aldehyde proton.

[e]) H–C(5′).

Preparation of the Double-Insertion Product **6**. Ph_3P (67 mg, 0.26 mmol) was added to a soln. of [Pd(OAc)(**1a**)]$_2$ (100 mg, 0.13 mmol) in CH_2Cl_2 (2 ml). The resulting soln. was concentrated to give crude [Pd(OAc)(**1a**)(Ph_3P)] which was then dissolved in MeOH (100 ml). Treatment of this soln. with CO (1 atm) at r.t. for 1.5 h was followed by filtration through *Celite*. Removal of the MeOH was followed by washing with Et_2O (1 ml). The resulting crude product was then recrystallized twice from Et_2O, to afford 31 mg (38%) of the product, m.p. = 184°. IR(KBr): 1750 (CO_2CH_3) 1695 (C=O). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 169.22, 167.43, 163.78 (2 C=O, C(5′)); 142.55; 136.08; 135.11; 130.07 (C(3)); 126.18; 125.08; 121.41 (C(2)); 116.49; 107.59; 63.81 (C(7′)); 56.09, 53.33 (2 CH_3O); 21.14 (C(4)-CH_3). MS: 311 ($C_{18}H_{17}NO_4^+$).

*[PdCl(***1a***)]*$_2$. A soln. of LiCl (2.5 g, 59 mmol) in H_2O (15 ml) was added in a dropwise fashion to a soln. of the 5′-OCH_3 acetate-bridged dimer (0.520 g, 0.670 mmol) in acetone (100 ml). After stirring for 30 min at r.t. the resulting yellow suspension was filtered and the solid product washed twice with 5 ml of acetone/H_2O 1:1. Drying gives the product (485 mg, 99%) as a yellow powder. The 4′-CH_3 and other analogs were prepared in a similar fashion. IR(KBr): 1605 (C=N). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 174.04 (C(7′)); 157.69 (C(5′)); 146.34; 146.17; 144.12; 138.17; 134.15; 129.56 (C(3)); 123.15 (C(2)); 116.70; 113.59; 55.71 (C(5′)-OCH_3); 21.39 (C(4)-CH_3).

Table 5. *^{13}C-NMR Data for the Products* **12b–e**

	12a	**12b**	**12c**	**12d**	**12e**[a])
C(1′)	148.24[b])	153.39[b])[c])	148.96	146.13[b])	148.08
C(2′)	163.17	153.10[b])	149.11	153.40[b])	140.93
C(3′)	135.16	129.00	135.66	134.69	135.08
C(4′)	125.05	148.16	131.02	137.69	117.18
C(5′)	145.89[b])	120.13	130.71	124.84	157.64
C(6′)	123.02	128.67	128.99	130.08	115.67
C(7′)	169.76	169.53	170.25	170.34	171.16
C(1)	145.65	145.53	145.92	146.07	146.23
C(2)	122.42	122.36	122.36	122.36	122.38
C(3)	129.89	129.79	129.73	129.69	129.65
C(4)	138.90	139.01	138.31	138.05	137.90
Pd–*C*(R)=C(R)OCH_3	153.57	153.39	154.48	154.37[b])	155.41
Pd–C(R)=*C*(R)OCH_3	145.19[b])	144.79	144.76	144.63[b])	144.55
C=O	177.22	177.09	176.83	176.96	176.65
	174.18	174.02	174.49	174.26	174.69
CH_3O	60.91	60.84	60.89	60.84	60.89
	54.34	54.35	54.17	54.18	55.66
	51.66	52.14	51.57	51.62	54.01
					51.48
C(4′)–*C*H_3	21.35	21.40	21.33	21.32	21.33

[a]) Assignment based on the ^{13}C-^1H-coupled spectrum. [b]) Tentative assignment. c) Two quaternary ^{13}C signals, as judged by the integral.

Table 6. *Crystal Data, Data Collection Parameters, and Data Refinement for [Pd(OAc)(***1a***)]$_2$*

Formula	$[PdO_3NC_{17}H_{17}]_2 \cdot CH_2Cl_2$
Mol.wt.	864.39
Crystal dimensions [mm]	0.40 × 0.45 × 0.35
Crystal system	Monoclinic
Space group	*C*2/*c*
a [Å]	24.212(4)
b [Å]	7.458(4)
c [Å]	20.207(3)
β [deg]	102.89(1)
V [Å^3]	3557.3
Z	4
ρ [calc. g·cm^{-3}]	1.613
μ[cm^{-1}]	11.92
Radiation	Mo$K_{\bar{a}}$ (λ = 0.71069 Å)
2 θ range [deg]	$2.5 \leqslant \theta \leqslant 19.0$
Scan type	$\omega/2\theta$
Receiving aperture	2.0 + tan θ
Max. scan speed [deg min^{-1}]	10.5
Max. counting time [sec]	55
Scan width [deg]	1.10 + 0.35 tan θ
Background time	0.5 × scan time
Prescan rejection limit	0.5 (2σ)
Prescan acceptance limit	0.03 (33σ)
No. of measured reflections	3220 ($\pm h, k, l$)
No. of obs. data ($I_{net} \geqslant 3\sigma(I)$)	2171
Standard reflections	3 (measured every hours), no variation
Function minimized	$\Sigma_w(\|F_o\| - (1/k)\|F_c\|)^2$
$R\Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.050
$R_w(\Sigma\|\Delta F\|/\Sigma_w\|F_o\|^2)^{1/2}$	0.058

Table 7. *Final Positional and Thermal Factors.* E.s.d.'s on the last significant digit are given in parentheses.

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Pd	0.1367(2)	0.14775(8)	0.17832(3)	3.32
O(1)	0.0667(2)	−0.0530(7)	0.2358(3)	4.30
O(2)	0.0509(2)	−0.0311(7)	0.3407(3)	4.19
O(3)	−0.1042(2)	0.7190(10)	−0.0231(3)	5.44
C(B1)	0.0745(3)	−0.0996(10)	0.2962(4)	3.73
C(B2)	0.1147(4)	−0.2527(14)	0.3198(6)	5.61
N	0.0740(3)	0.3413(8)	0.1836(3)	3.24
C(1)	0.1319(3)	0.3361(11)	0.2213(4)	3.56
C(2)	0.1430(3)	0.2916(11)	0.2892(4)	3.86
C(3)	0.1989(4)	0.3014(13)	0.3275(5)	4.43
C(4)	0.2429(4)	0.3500(12)	0.2963(5)	4.48
C(5)	0.3041(4)	0.3640(15)	0.3405(6)	6.19
C(6)	0.2310(4)	0.3865(13)	0.2287(5)	4.88
C(7)	0.1760(3)	0.3817(12)	0.1898(4)	4.15
C(7′)	0.0574(3)	0.4817(11)	0.1482(4)	3.73
C(1′)	0.0003(3)	0.4786(11)	0.1077(4)	3.28
C(2′)	−0.0293(3)	0.3185(11)	0.1136(4)	3.69
C(3′)	−0.0842(3)	0.2980(12)	0.0712(4)	3.95
C(4′)	−0.1069(4)	0.4346(12)	0.0267(4)	4.15
C(5′)	−0.0768(4)	0.5942(13)	0.0226(4)	4.16
C(6′)	−0.0224(3)	0.6201(11)	0.0633(4)	3.84
C(8′)	−0.0758(5)	0.8867(14)	−0.0244(5)	5.78
Cl(1)	0.2667(3)	0.5673(14)	0.5231(5)	20.44

*[PdCl(py)(***1a***)].* Addition of pyridine (33 ml, 0.44 mmol) to a suspension of the Cl-bridged dimer in CH_2Cl_2 (5 ml) results in a yellow soln. After stirring at r.t. for 5 min, 15 ml of petroleum ether were added and the soln. cooled to 0°. The yellow crystalline material which precipitated was collected by filtration and dried, from 150 mg (10.20 mmol) of starting material we obtained 165 mg (90%) of product. The 4′-CH_3 analog was prepared in a similar fashion in 94% yield. IR (KBr): 1600 (C=N). ^{13}C-NMR (62.9 MHz, $CDCl_3$), two isomers): 175.72 (2 C(7′); 157.66 (2C(5′)); 153.58; 150.99; 146.99; 146.78; 146.47; 138.14; 137.82; 137.28; 132.79; 129.46; 129.11; 125.67; 124.51; 123.58; 122.38; 117.22; 117.06; 113.91; 55.67 (2C(5′)–OCH_3); 21.34, 21.13 (2 C(4)–CH_3).

*[Pd(***1a***)(diphos)]Cl.* Addition of solid $Ph_2PCH_2CH_2PPh_2$ (102 mg, 0.26 mmol) to a suspension of [PdCl(**1a**)]$_2$ (94 mg, 0.13 mmol) in CH_2Cl_2 (3 ml) afforded a clear soln. Stirring at r.t. for 10 min was followed by addition of 15 ml of pentane. The product precipitated and was collected by filtration. Recrystallization from CH_2Cl_2/hexane gave 186 mg (96%) of the cationic complex. IR (KBr): 1618 (C=N). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 179.16 (*m*, C(7′)); from 158.14 to 116.27 (30 signals); 55.65 (C(5′)–OCH_3); 31.53–30.69, 28.09–27.47 (*m*, PCH_2CH_2P, PCH_2CH_2P); 21.10 (C(4)–CH_3). ^{31}P-NMR (36.4 MHz, $CDCl_3$): 60.92 (^2J(P,P) = 26,8, N–Pd–P); 42.03 (^2J(P,P) = 26.8, C–Pd–P).

The Et_2NH and Ph_3P complexes were prepared in an analogous fashion. The ^{1}H-NMR data are listed in *Table 4*. IR and ^{13}C-NMR data for [PdCl(**1a**)(Et_2NH)] IR(KBr) 1610 (C=N), ^{13}C-NMR (62.9 MHz, $CDCl_3$, two isomers): 176.83, 175.08 (2 C(7′)); 157.58, 157.46 (2 C(5′)); 147.79; 147.31; 146.73; 146.26; 145.31; 138.26; 137.67; 137.47; 131.08; 130.61; 129.02; 123.58; 122.55; 117.44; 116.79; 114.40; 113.82; 55.71 (C(5′)–OCH_3); 48.60, 45.83 (2 NCH_2CH_3); 21.36 (C(4)–CH_3); 16.14, 15.16 (2 NCH_2CH_3).

Data *for [PdCl(***1a***)(PPh$_3$)].* IR (KBr): 1610 (C=N). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 175.50 (C(7′)); 156.82 (C(5′)); 148.93–114.69 (17 signals); 55.43 (C(5′)–OCH_3); 21.30 (C(4)–CH_3). ^{31}P-NMR (36.4 MHz, $CDCl_3$): 43.89 (N–Pd–*P*).

Preparation of the Ketenimine **7**. To a soln. containing diphos (205 mg, 0.52 mmol) and [Pd(μ-Cl)(**1a**)]$_2$ (94 mg, 0.13 mmol) in CH_2Cl_2 (1.5 ml) was injected Bu^{t}N≡C (60 µl, 0.52 mmol) and the soln. stirred for 20 min. During this period a yellow-red solid precipitated. Addition of hexane (5 ml) completes the precipitation. Evaporation of the solvent was followed by extraction with 5 × 30 ml of hexane. Concentration of the hexane gives the crude product: 110 mg (95% by ^{1}H-NMR). The compound can be obtained analytically pure by suspending the crude material in MeOH (1.5 ml) and allowing the suspension to stand at −20° for one day. Decantation of the solvent

followed by drying affords the product: 61 mg (60%), m.p. = 134°. IR(KBr): 2010 (N=C=C); 1630 (N=C). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 190.38 (N=*C*=C); 157.89, 151.03 (C(5'), C=N); 149.28; 131.34; 131.00; 129.86; 129.76 (C(3)); 121.56 (C(2)); 119.54; 118.68; 109.63; 62.62 (N=C=*C*); 58.14 (2 N–*C*–(CH_3)); 55.19 (C(5')–O*C*H_3); 30.11, 29.06 (2 N–C–(*C*H_3)$_3$); 20.99 (C(4)-*C*H_3). MS: 389 ($C_{25}H_3N_3O^+$).

Preparation of **9**. To compound **7** (0.020 g, 0.05 mmol) in acetone (10 ml) was added conc. HCl (1 ml) in a dropwise fashion. During this period the yellow soln. became colorless. Removal of the acetone was followed by extraction with CH_2Cl_2/H_2O, 1:1. The CH_2Cl_2 layer was dried ($MgSO_4$) and the solvent removed. The crude oil was chromatographed on silica gel using CH_2Cl_2 as eluent. The product is eluted whereas the remaining components required acetone as eluent to remove them from the column. Removal of the CH_2Cl_2 and recrystallization from toluene gave 0.005 g (30%), m.p. = 117°. IR(KBr): 1730 (C=O); 1650 (C=N). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 168.90 (C=O); 162.97 (C(5')); 152.36 (C=N); 147.08; 133.22; 131.52; 130.15 (C(3)); 125.96; 124.42; 119.40 (C(2)); 118.03; 110.40; 58.84 (*C*(CH_3)$_3$); 55.46 (C(5')–O*C*H_3); 29.89 (C(*C*H_3)$_3$); 21.06 (C(4)–*C*H_3). MS: 322 ($C_{20}H_{22}N_2O_2^+$).

Synthesis of **10**. Ethylacrylate (332 µl, 3.0 mmol) was injected into a suspension containing [PdCl(**1a**)]$_2$ (110 mg, 0.15 mmol) and Et_3N (420 µl, 3.0 mmol) in benzene (12 ml). Refluxing for 19 h was followed by hot filtration. The residue was washed with CH_2Cl_2 and the combined filtrates concentrated *i.v.* The crude product, 19.5 mg, was found to be 90% pure (^{1}H-NMR) with the impurity essentially Et_3N. ^{13}C-NMR (62.9 MHz, $CDCl_3$): 167.07 (C=O); 161.32 (C(5')); 156.60 (C(7')); 149.55; 140.82 (C–*C*H=CHCO$_2$CH$_2$CH$_3$); 136.55; 130.06 (C(3)); 129.12; 128.38; 121.20 (C(2)); 119.91 (C–CH=*C*HCO$_2$CH$_2$CH$_3$); 118.71; 111.91; 60.72 (CO$_2$*C*H$_2$CH$_3$); 55.83 (C(5')–O*C*H_3); 21.22 (C(4)–*C*H_3); 14.57 (CO$_2$CH$_2$*C*H$_3$).

2'(–CH=CHCO$_2$CH$_2$CH$_3$)5'–OCH$_3$C$_6$H$_3$CHO (**11**). [PdCl(**1a**)]$_2$ (146 mg, 0.20 mmol), ethyl acrylate (0.4 ml, 3.6 mmol), and Et_3N (0.3 ml, 2.2 mmol) were dissolved in toluene (7.5 ml) and then heated under reflux for 20 h. After cooling to r.t. the mixture was filtered through *Celite* which was washed with CH_2Cl_2. Removal of the solvents was followed by extraction with toluene and then concentration of the toluene soln. The red-brown oil which resulted was then treated with conc. HCl (6 ml) dissolved in acetone (40 ml) over a 20 h period. Addition of 3N HCl (50 ml) was followed by extraction with CH_2Cl_2 and the org. phase then washed with aq. $NaHCO_3$. Removal of the CH_2Cl_2 gives the crude product which was dissolved in CH_2Cl_2 (1 ml) and chromatographed on silica gel (42 g) using exane/Et_2O 2:1 as eluent. The product **11** was obtained as a yellow oil: 36 mg (39%). IR(film): 1720 (C=O). MS: 234 ($C_{13}H_{14}O_4^+$).

2'-I-5'-OCH$_3$–C$_3$H$_6$CHO. A soln. of I_2 (70 mg, 0.27 mmol) in MeOH (10 ml) was cooled to 0° and added to a previously cooled (0°) suspension of [Pd(OAc)(**1a**)]$_2$ (108 mg, 0.14 mmol) in MeOH (40 ml). Stirring for 5 min was followed by warming to 40° and stirring for an additional 2 h. Then, the resulting dark suspension was filtered to remove Pd metal and the solvent concentrated. The crude *Schiff*'s base was dissolved in acetone (10 ml) and then treated with conc. HCl (2 ml). Stirring for 2 h was followed by extraction of the product with CH_2Cl_2. Drying ($MgSO_4$), filtration, and concentration of the solvent gave the crude aldehyde which was recrystallized from Et_2O/hexane: 37.8 mg (52%). IR(KBr): 1680 (C=O). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 195.91 (C(7')); 160.52 (C(5')); 141.26 (C(3')); 135.94 (C(1')); 123.70 (C(4')); 113.81 (C(6')); 89.98 (C(2')); 55.86 (C(5')–O*C*H_3). MS: 262 ($C_8H_7D_2I^+$).

*[Pd(**1c**){C(CO$_2$CH$_3$)=C(OCH$_3$)COOCH$_3$}]* (**12**). Dimethylacetylene dicarboxylate (300 µl, 2.4 mmol) was injected into a suspension of [Pd(OAc)(**1a**)]$_2$ (50 mg, 0.06 mmol) in MeOH (10 ml) and the resulting suspension stirred at 40° for 21 h (higher temp. resulted in poorer yields and difficulty in isolation). Concentration of the soln. was followed by washing with Et_2O. The solid product which remained was dried *i.v.*: 57 mg (88%). IR(KBr): 1698 (C=O) 1612 (C=N). The 4'-NO_2-5'-Cl-, and 5'-OCH_3-substituted compounds **12b**, **c**, and **e**, resp., were obtained in a similar fashion. See *Table 5* for ^{13}C-NMR data.

CH$_3$O$_2$C(OCH$_3$)C=CH(CO$_2$CH$_3$) (**14**). [Pd(OAc)(**1a**)]$_2$ (0.050 g, 0.05 mmol) was suspended in glacial AcOH (10 ml) and stirred for 3 days at r.t. Filtration of [Pd(OAc)(**1c**)]$_2$ (which is only slightly soluble in AcOH) was followed by removal of the solvent. The yellow oil which results is pure **14** as shown by ^{1}H-NMR. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.20 (*s*, H–C=); 3.96, 3.86, 377 (*s*, 2 CO$_2$*C*H$_3$, *C*H$_3$O). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 165.02, 163.59 (2 *C*O$_2$CH$_3$): 155.13 (*C*=CH); 108.19 (C=*C*H); 61.30 (*C*H$_3$O); 53.03, 51.91 (2 CO$_2$*C*H$_3$). MS: 174 ($C_7H_{10}O_5^+$).

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