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UNUSUAL REARRANGEMENT OF σ-VINYLPALLADIUM COMPLEXES INTO η^2-OLEFIN COMPLEXES. THE STRUCTURE OF (η^2-1-TRIPHENYLPHOSPHONIUM-2-CARBOMETHOXYETHYLENE)-(TRIPHENYLPHOSPHINE)IODOPALLADATE

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Summary

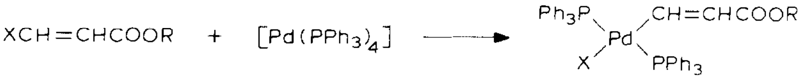
β-Substituted σ-vinylpalladium complexes $[\mathrm{Pd}(\sigma\text{-CH=CHCOOR})(\mathrm{PPh_3})_2(\mathrm{X})]$ (I) (X = Cl, I; R = Me, Et) have been obtained by interaction of the *E*- and *Z*-β-halogen acrylates with tetrakis(triphenylphosphine)palladium. On heating complexes I rearrange into isomeric η^2-olefin-ylidepalladium complexes $[\overline{\mathrm{Pd}\{\mathrm{CH(COOR)}\overset{+}{\mathrm{C}}}\mathrm{HPPh_3}\}(\mathrm{PPh_3})(\mathrm{X})]$ (II). The structure of these complexes has been established by X-ray study of the compound with X = I, R = Me.

Introduction

The synthesis of σ-vinylpalladium(II) complexes, based preferentially on the reactions of halogenolefins with palladium(0) compounds, has been described in a series of papers [1–9]. However, the properties of these complexes have been insufficiently studied. The studies of such complexes concerned mainly their thermal decomposition [6], or decomposition induced by various reagents, in order to use these reactions in organic synthesis [5,6,8]. This paper reports a new type of isomerization of the σ-β-alkoxycarbonylvinylpalladium complexes, $[\mathrm{Pd}(\sigma\text{-CH=CHCOOR})(\mathrm{PPh_3})_2(\mathrm{X})]$ (I) and X-ray studies of the resulting olefinphosphonium-ylide-palladium complexes $[\overline{\mathrm{Pd}\{\mathrm{CH(COOR)}\overset{+}{\mathrm{C}}}\mathrm{HPPh_3}\}(\mathrm{PPh_3})(\mathrm{X})]$ (II).

Results and discussion

Continuing the studies of reactions of the σ-vinylmetal derivatives with iron carbonyls [10] we examined the behaviour of the σ-vinylpalladium complexes (Ia–If) in these reactions. These were prepared by interaction of β-halogen acrylates with tetrakis(triphenylphosphine)palladium (eq. 1). The synthesis and thermal decomposition of the complexes Ia and Ib have been described earlier [6].


(1)

(Ia–If)

	X	R	Configuration of the σ-vinyl ligand
a	Cl	Me	*E*
b	Cl	Me	*Z*
c	I	Me	*E*
d	I	Me	*Z*
e	I	Et	*E*
f	I	Et	*Z*

The NMR spectral data for compounds Ia–If (Table 1) are in full agreement with the square-planar structure of *trans*-σ-vinylpalladium complexes and suggest retention of the geometrical configuration of the vinyl moiety by palladium insertion into the C–halogen bond. The IR spectra for all complexes I reveal the double C=C bond absorption bands at 1565–1570 cm^{-1} and the ester bands at 1695–1705 cm^{-1}, which are in good agreement with the published data [6].

To find out the possibility of the iron carbonyl group being coordinated at the double bond of the vinyl ligand in complexes I, we treated these compounds with $Fe(CO)_5$ under ultraviolet irradiation and with $Fe_2(CO)_9$ with heating in benzene. The reactions proved to be very complicated, and the only iron carbonyl products isolated were the phosphine derivatives $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$. Formation of these complexes suggested ready triphenylphosphine abstraction from the initial compounds I. The ready substitution and elimination of the phosphine ligands in the square-planar palladium(II) complexes are also reported by other authors [6,7,11].

The reactions of complexes I with iron carbonyls were carried out by heating or by UV irradiation in benzene, therefore it was necessary to determine the transformations of the σ-β-alkoxycarbonylvinyl palladium complexes themselves under these conditions. These studies were started with thermal conversions of complexes I. It

TABLE 1

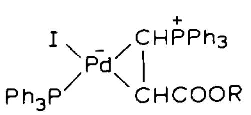
NMR [a] SPECTRAL DATA FOR COMPLEXES I

Compound	^1H [b] ($CDCl_3$)			^{31}P (CH_2Cl_2)		
	$\delta(H_\alpha)$	$\delta(H_\beta)$	$J_{\alpha\beta}$	$J(P-H_\alpha)$	$J(P-H_\beta)$	δ
Ia	7.89	5.16	16.1	8.3	1.7	23.99
Ic	7.90	5.02	16.2	8.5	1.7	22.82
Id	[c]	5.03	10.7	–	2.2	22.24
Ie	7.91	5.07	16.2	8.6	1.8	22.71
If	[c]	5.05	9.2	–	0.5	22.27

[a] Chemical shifts in ppm, coupling constants in Hz. [b] For the olefinic protons only. [c] The H_α resonance falls in the phenyl proton region.

should be noted that on reflux in solvents such as benzene, chloroform, dioxane or toluene the complexes Ia and Ib yield mainly dimethylmuconate [6]. The only palladium compound isolated was [Pd(PPh$_3$)$_2$Cl$_2$]. Apart from these results we have found that the iodine containing complexes (Ic–If), on heating in benzene at 75–80°C, resulted in the new palladium complexes II being isomeric to the initial complexes. Heating the chlorine-containing complex Ia under similar conditions also resulted in its isomerization to IIa. The thermally unstable chlorine-containing complex Ib with the *Z*-configuration for the vinyl ligand underwent rapid decomposition in benzene solution even at room temperature with no corresponding isomeric complex (IIb) being produced.

The IR and NMR spectral data * suggested the isomerization of complexes I into II causing to the disappearance of the free double bond and the change of the bonding mode of one of the PPh$_3$ groups. Moreover, complexes II obtained from *E*- and *Z*-isomeric complexes I differ in their spectra. In order to determine the structure of complexes II unequivocally, compounds IIc (X = I, R = Me) were studied by X-ray. It was found to contain a 1-triphenylphosphonium-2-carbomethoxyethylene ligand PH$_3\overset{+}{\text{P}}$CH=CHCOOMe coordinated with the metal by the C=C double bond:



In this ylide metallate structure the palladium atom in IIc acquires its usual 16-electron configuration. It should be noted that only one structural study of the ylide-palladium complex has been reported in the literature [12].

Thus, on heating the σ-β-alkoxycarbonylvinylpalladium complexes (I) their rearrangement takes place to η^2-olefin complexes with the phosphine ligand migrating from the metal to the vinyl α-carbon atom (IIa, IIc–IIf).

(Ia, Ic-If)

(IIa, IIc-IIf)

Recently a similar rearrangement has been observed in vinyl-molybdenum and -tungsten complexes [13].

The structure of molecule IIc together with the main geometrical parameters is shown in Fig. 1, bond lengths and angles are listed in Tables 2 and 3. The distortions of the palladium square-planar coordination are due to the rigidity of the geometry of coordinated ethylene and the steric effect of the bulky PPh$_3$ ligand. The dihedral angle between the IPdP(1) and C(1)PdC(2) planes is 5.2°.

The geometry of the 1-triphenylphosphonium-2-carbomethoxyethylene ligand is of considerable interest. The P(2)–C(Ph) bond lengths, 1.795(5), 1802(5), 1.794(5) Å (the mean value being 1.797(5) Å), are typical of triphenylphosphonium groups

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* Their detailed discussion will be made in a separate paper.

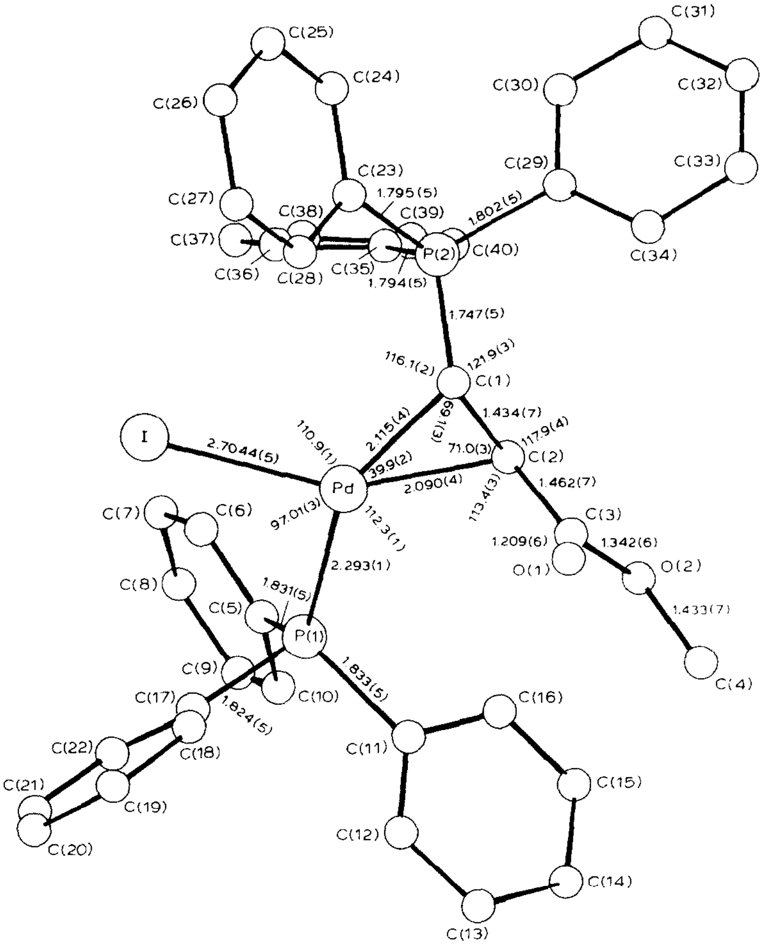


Fig. 1. Molecular structure of complex IIc.

TABLE 2

BOND DISTANCES, *d* (Å)

Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
Pd–I	2.7044(5)	C(4)–O(2)	1.433(7)	C(15)–C(16)	1.375(7)	C(28)–C(23)	1.381(7)
Pd–P(1)	2.293(1)	C(1)–C(2)	1.434(7)	C(16)–C(11)	1.407(7)	C(29)–C(30)	1.404(7)
Pd–C(1)	2.115(4)	C(2)–C(3)	1.462(7)	C(17)–C(18)	1.401(8)	C(3)–C(31)	1.396(7)
Pd–C(2)	2.090(4)	C(5)–C(6)	1.388(7)	C(18)–C(19)	1.379(8)	C(31)–C(32)	1.361(7)
P(1)–C(5)	1.831(5)	C(6)–C(7)	1.386(8)	C(19)–C(20)	1.383(8)	C(32)–C(33)	1.378(8)
P(1)–C(11)	1.833(5)	C(7)–C(8)	1.376(9)	C(20)–C(21)	1.375(9)	C(33)–C(34)	1.402(7)
P(1)–C(17)	1.824(5)	C(8)–C(9)	1.379(9)	C(21)–C(22)	1.385(8)	C(34)–C(29)	1.372(7)
P(2)–C(1)	1.747(5)	C(9)–C(10)	1.378(8)	C(22)–C(17)	1.388(7)	C(35)–C(36)	1.395(7)
P(2)–C(23)	1.795(5)	C(10)–C(5)	1.387(8)	C(23)–C(24)	1.400(7)	C(36)–C(37)	1.389(7)
P(2)–C(29)	1.802(5)	C(11)–C(12)	1.378(7)	C(24)–C(25)	1.379(8)	C(37)–C(38)	1.357(8)
P(2)–C(35)	1.794(5)	C(12)–C(13)	1.374(8)	C(25)–C(26)	1.384(8)	C(38)–C(39)	1.414(8)
C(3)–O(1)	1.209(6)	C(13)–C(14)	1.372(8)	C(26)–C(27)	1.382(8)	C(39)–C(40)	1.384(8)
C(3)–O(2)	1.342(6)	C(14)–C(15)	1.385(8)	C(27)–C(28)	1.383(8)	C(40)–C(35)	1.383(7)

TABLE 3

BOND ANGLES, ω (°)

Angle	ω	Angle	ω	Angle	ω
IPdP(1)	97.01(3)	C(34)P(2)C(35)	111.8(2)	C(21)C(22)C(17)	120.0(5)
IPdC(1)	110.9(1)	C(29)P(2)C(35)	105.3(2)	P(2)C(23)C(24)	120.3(4)
PIdC(2)	150.6(1)	P(1)C(5)C(6)	118.0(4)	P(2)C(23)C(28)	120.3(4)
P(1)PdC(1)	152.0(1)	P(1)C(5)C(10)	122.7(4)	C(28)C(23)C(24)	119.4(4)
P(1)PdC(2)	112.3(1)	C(10)C(5)C(6)	119.2(5)	C(23)C(24)C(25)	119.9(5)
C(1)PdC(2)	39.9(2)	C(5)C(6)C(7)	120.3(5)	C(24)C(25)C(26)	120.3(5)
PdC(1)C(2)	69.1(3)	C(6)C(7)C(8)	119.9(5)	C(25)C(26)C(27)	120.0(5)
PdC(1)P(2)	116.1(2)	C(7)C(8)C(9)	120.2(5)	C(26)C(27)C(28)	120.0(5)
P(2)C(1)C(2)	121.9(3)	C(8)C(9)C(10)	120.1(6)	C(27)C(28)C(23)	120.5(5)
PdC(2)C(1)	71.0(3)	C(9)C(10)C(5)	120.4(5)	P(2)C(29)C(30)	118.6(4)
PdC(2)C(3)	113.4(3)	P(1)C(11)C(12)	124.1(4)	P(2)C(29)C(34)	120.7(4)
C(1)C(2)C(3)	117.9(4)	P(1)C(11)C(16)	117.3(4)	C(34)C(29)C(30)	120.7(4)
O(1)C(3)O(2)	122.3(9)	C(16)C(11)C(12)	118.6(5)	C(29)C(30)C(31)	118.9(5)
O(1)C(3)C(2)	126.1(4)	C(11)C(12)C(13)	121.5(5)	C(30)C(31)C(32)	119.9(5)
PdP(1)C(11)	118.6(2)	C(15)C(16)C(11)	119.4(5)	P(2)C(35)C(36)	118.9(4)
PdP(1)C(17)	114.9(2)	P(1)C(17)C(18)	117.9(4)	P(2)C(35)C(40)	120.7(4)
C(5)P(1)C(11)	102.5(2)	P(1)C(17)C(22)	123.1(4)	C(40)C(35)C(36)	120.4(5)
C(5)C(1)C(17)	102.2(2)	C(22)C(17)C(18)	119.0(5)	C(35)C(36)C(37)	118.8(5)
C(11)P(1)C(17)	101.3(2)	C(17)C(18)C(19)	120.4(5)	C(36)C(37)C(38)	121.1(5)
C(1)P(2)C(23)	107.6(2)	C(18)C(19)C(20)	119.9(5)	C(37)C(38)C(39)	120.7(5)
C(1)C(2)C(29)	111.9(2)	C(19)C(20)C(21)	120.1(6)	C(38)C(39)C(40)	118.4(5)
C(1)C(2)C(35)	111.8(2)	C(20)C(21)C(22)	120.5(6)	C(39)C(40)C(35)	120.7(5)
C(23)P(2)C(29)	108.3(2)				

(1.78–1.81 Å [14]) and close to those found in the zwitter-ionic molybdenum complex, $[\overset{-}{\text{Mo}}\text{CH(CN)C(CN)}(\overset{+}{\text{P}}\text{Ph}_3)\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ (III) [13]. At the same time, the P(2)–C(1) bond (1.747(5) Å), is considerably shorter than the P(2)–C(Ph) bonds in IIc and the analogous bonds in the molybdenum complex III (1.802 Å). Shortening of the P(2)–C(1) bond is indicative of a significant contribution of the ylene form $\text{Ph}_3\text{P=C(R)C(M)HR}$. The contribution of this form is also manifested in the lengthening of the Pd–C(1) as compared with the Pd–C(2) bond length (2.115(4) vs. 2.090(4) Å).

A number of ethylenepalladium(II) complexes have as yet been studied. In such complexes the coordinated C=C double bond is usually normal to the coordination plane of the palladium atom. Complex IIc with the olefinic ligand in the metal coordination plane can be formally regarded as a palladium(0) compound and this is the first example of the structural investigation of an ethylenepalladium(0) complex.

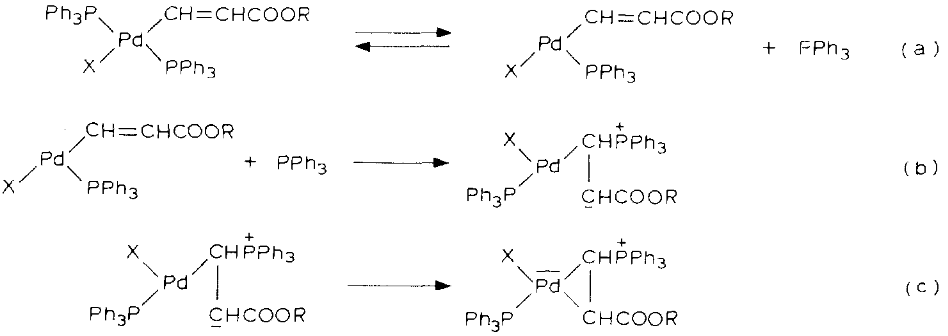
The C(1)–C(2) bond length 1.434(7) Å in molecule IIc is somewhat larger than the values typical for the π-ethylene palladium(II) complexes (1.34–1.42 Å) [15–17], whereas, the Pd–C(1) and Pd–C(2) bonds are somewhat shorter than the usual Pd–C(ethylene) distances, 2.18–2.20 Å in the ethylene palladium(II) complexes [15–17] and are close to the Pd–C(sp^3) σ-bonds, 2.04–2.084 Å [18–20]. This suggests a significant contribution of back-donation, which plays a more important role in IIc, than in the similar palladium(II) complexes.

The Pd–I bond in IIc, 2.7044(5) Å, is apparently the longest among the known Pd–I bonds in palladium complexes (2.577–2.658 Å [21–24]).

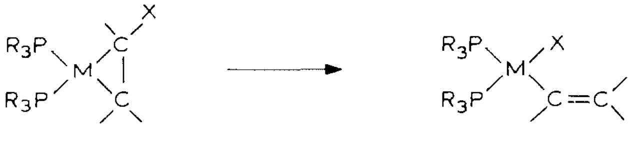
The C(2)–C(3) bond length, 1.462(7) Å, coincides within the limits of experimental error with the mean statistical value of the ordinary $C(sp)^2$–$C(sp^2)$ bond length of 1.476 Å [26], the geometrical parameters of the methoxycarbonyl group are also close to the standard values [27]. This suggests only a small participation of this group in the charge delocalization in complex IIc, which is also corroborated by the distortion of planarity of the P(2)C(1)C(2)C(3)O(1)O(2) group (torsion angles: P(2)C(1)C(2)C(3) 144.5(5)°, C(1)C(2)C(3)O(1) 16.7(5)°, C(1)C(2)C(3)O(2) 161.6(7)°). Nevertheless, the transposition of the substituents is quite natural in view of the fact that compound IIc is derived from complex Ic, in which the vinyl ligand has *E*-configuration.

Interestingly, the I → II rearrangement is suppressed by triphenylphosphine. Thus complexes IIa, IIe were not found in the reaction products after heating the σ-vinyl complexes Ia and Ie in benzene in the presence of 2 equivalents of PPh_3. This result and the fact of this reaction being stereospecific allows some conclusions about the mechanism of isomerization to be drawn. It seems likely that there occurs initial abstraction of the phosphine ligand (Scheme 1, step a) and its addition to the double bond of the alkoxycarbonylvinyl ligand (Scheme 1, step b). The interaction of the coordinatively unsaturated palladium atom with the carbanion C_β centre (step "c") gives complex II. But one cannot exclude the possibility that steps 'a' and 'b' or 'b' and 'c' proceed simultaneously.

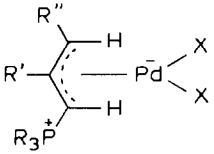
SCHEME 1



It should be noted that the established rearrangement of the σ-alkenyl complexes I into the π-olefinic complexes II proved surprising as a reverse process is usually observed, i.e. conversion of π-olefinic into σ-alkenyl complexes. This has been well studied on platinum complexes (cf., e.g., [1,28–30]) and some palladium complexes [2]:



The zwitter-ionic olefin-ylide complexes II obtained by us were previously unknown in organopalladium chemistry. The η^3-allyl-ylide metallate complexes (IV) [31] with the π-ligands also containing phosphonium groups seem to be the closest analogues among the known ylide-palladium complexes.



(IV)

However, some differences between these ylide π-complexes can be noted. The η^3-allyl complexes IV are palladium(II) complexes, whereas complexes II are considered to be η^2-olefinic complexes, which can be attributed to palladium(0) complexes.

Experimental

All reactions were carried out under argon. β-Halogen acrylates ROCOCH=CHX were prepared as described elsewhere [32] for R = Me, X = Cl and [33] for R = Me, Et, X = I. $[Pd(PPh_3)_4]$ was also obtained by a published method [34]. IR spectra were taken on an UR-20 spectrometer in KBr pellets, ^1H and ^{31}P NMR spectra were recorded on a WP-200 SY instrument (operating frequencies at 200.13 and 80.01 MHz). Chemical shifts are measured relative to an internal $SiMe_4$ for ^1H and relative to 85% H_3PO_4 for ^{31}P.

Preparation of [Pd(σ-CH=CHCOOMe-E)(PPh$_3$)$_2$(Cl)] (Ia)

Complex Ia was synthesized by a known method [6] from 0.24 g (2 mmol) of *E*-CHCl=CHCOOMe and $[Pd(PPh_3)_4]$ *. Yield: 1.30 g (85%), m.p. 121–123°C (dec.), (lit. 125–127°C [6]). Found: C, 63.63; H, 4.68; Pd, 14.41. $C_{10}H_{35}ClO_2P_2Pd$ calcd.: C, 63.92; H, 4.69; Pd, 14.16%.

Preparation of [Pd(σ-CH=CHCOOMe-Z)(PPh$_3$)$_2$(Cl)] (Ib)

Complex Ib was synthesized as decribed for Ia from 0.24 g (2 mmol) of Z-CHCl=CHCOOMe and $[Pd(PPh_3)_4]$. Yield: 1.25 g (82%), m.p. 110–112°C (dec.). Found: C, 65.75; H, 4.89; Pd, 12.96. $C_{40}H_{35}ClO_2P_2Pd \cdot 0.5C_6H_6$ calcd.: C, 65.32; H, 4.84; Pd, 13.46%.

Preparation of [Pd(σ-CH=CHCOOMe-E)(PPh$_3$)$_2$(I)] (Ic)

0.43 g (2 mmol) of *E*-CHI=CHCOOMe in 10 ml of benzene was added to a solution of $[Pd(PPh_3)_4]$ in 50 ml of benzene. The mixture was stirred at room temperature for 8 h. The benzene was then removed in vacuo to 1/3 of the initial volume. The precipitate was filtered off, and washed with benzene and hexane. Yield: 1.05 g (66%), as lightly coloured fine crystals, m.p. 150–153°C (dec.). Found: C, 57.22; H, 4.24; I, 15.22; Pd 12.53; P, 7.30. $C_{40}H_{35}IO_2P_2Pd$ calcd.: C, 56.99; H, 4.18; I, 15.06; Pd, 12.62; P, 7.35%.

Preparation of [Pd(σ-CH=CHCOOMe-Z)(PPh$_3$)$_2$(I)] (Id)

Complex Id (a bright-cream powder) was prepared as described for Ic by interacting $[Pd(PPh_3)_4]$ with 0.4 g (2 mmol) of *Z*-CHI=CHCOOMe. Yield: 1.43 g

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* Obtained from 0.36 g (2 mmol) of $PdCl_2$, here and in some other experiments.

TABLE 4

YIELDS, ANALYTICAL AND ^{31}P NMR DATA FOR COMPLEXES II

Compound	M.p. (dec.) (°C)	Yield (%)	Analysis (Found (Calcd.) (%))					Molecular formula	^{31}P NMR (CH_2Cl_2)	
			C	H	Hal	Pd	P		δ(ppm)	*J*(Hz)
IIa	152–156	35	63.90 (63.92)	4.73 (4.69)	4.32 (4.72)	14.16 (14.16)	8.12 (8.24)	$C_{40}H_{35}ClO_2P_2Pd$	26.25(d) 22.32(d)	7.9
IIc	138–142	83	57.73 (56.99)	4.09 (4.18)	14.81 (15.06)	12.77 (12.62)		$C_{40}H_{35}IO_2P_2Pd$	26.33(d) 22.99(d)	7.0
IId	128–132	90	59.78 (59.98)	4.37 (4.49)	14.68 (13.78)	10.98 (11.55)		$C_{40}H_{35}IO_2P_2Pd$ $\cdot C_6H_6$	27.35(d) 24.19(d)	8.5
IIe	158–162	77	60.96 (60.37)	4.84 (4.63)	13.60 (13.57)	11.32 (11.38)	6.55 (6.63)	$C_{41}H_{37}IO_2P_2Pd$ $\cdot C_6H_6$	26.77(d) 23.02(d)	6.7
IIf	156–161	75	61.04	4.69	14.05	11.52		$C_{41}H_{37}IO_2P_2Pd$ $\cdot C_6H_6$	27.81(d) 24.45(d)	8.9

(80%), m.p. 156–158°C (dec.). Found: C, 60.27; H, 4.68; I, 14.45. $C_{40}H_{35}IO_2P_2Pd \cdot C_6H_6$ calcd.: C, 59.98; H, 4.49; I, 13.78%.

Preparation of [Pd(σ-CH=CHCOOEt-E)(PPh$_3$)$_2$(I)] (Ie)

0.46 g (2 mmol) of *E*-CHI=CHCOOEt in 10 ml of benzene was added to a solution of $[Pd(PPh_3)_4]$ in 50 ml of benzene. The mixture was stirred at room temperature for 5 h. The precipitate was filtered off and crystallized from CH_2Cl_2 (without heating). Yield: 1.5 g (80%), m.p. 158–162°C (dec.). Found: C, 56.60; H, 4.47; Hal, 16.37; P, 12.24. $C_{41}H_{37}IO_2P_2Pd \cdot 0.25CH_2Cl_2$ calcd.: C, 56.41; H, 4.30; Hal, 16.47; Pd, 12.12%.

Preparation of [Pd(σ-CH=CHCOOEt-Z)(PPh$_3$)$_2$(I)] (If)

Complex If was obtained, as described for Ie by interacting $[Pd(PPh_3)_4]$ with *Z*-CHI=CHCOOEt, as fine crystals, which were twice reprecipitated by hexane from CH_2Cl_2. Yield: 1.2 g (66%), m.p. 118–122°C (dec.). Found: C, 56.05; H, 4.35; Hal, 17.78. $C_{41}H_{37}IO_2P_2Pd \cdot 0.5CH_2Cl_2$ calcd.: C, 55.41; H, 4.26; Hal, 18.06%.

Preparation of $[\overset{-}{P}d\{CH(COOMe)CH(\overset{+}{P}Ph_3)\}(PPh_3)(Cl)]$ *(IIa)*

1.4 g (1.75 mmol) of complex Ia was heated in 30 m of benzene at 75°C for 15 min. The solution was cooled to room temperature and 60 ml of hexane were added. The precipitate was filtered off and extracted with dichloromethane. The insoluble residue, 0.2 g of $[Pd(PPh_3)_2Cl_2]$, was identified by the IR spectrum, m.p. 280–285°C (lit. 288–290°C [35]). The extract was treated with hexane and the precipitated yellow crystals were twice reprecipitated by hexane from CH_2Cl_2, washed with pentane and dried in vacuo. Yields, melting points, elemental analysis, ^{31}P NMR data for complexes II are listed in Table 4.

Preparation of $[\overset{-}{P}d\{CH(COOMe)CH(\overset{+}{P}Ph_3)\}(PPh_3)(I)]$ *(IIc)*

0.83 g (1 mmol) of complex Ic was heated in 30 ml of benzene at 75°C for 30 min. The reaction mixture was cooled to room temperature to give bright yellow crystals of the complex IIc. They were filtered off, washed with benzene, hexane and dried in vacuo.

Complexes IId–IIf were obtained as described for IIc. To isolate complex IId the benzene was evaporated to 1/3 of the initial volume.

X-ray study of complex IIc. The crystals of IIc, $C_{40}H_{35}IO_2P_2Pd$, are monoclinic, at −120°C a 11.649(5), b 13.380(7), c 22.63(1) Å, β 95.85(4)°, V 35.08(3) Å^3, $Z = 4$, $d_{\text{calcd.}}$ 1.54 g/cm^3, space group $P2_1/n$.

The unit cell parameters and intensities of 6489 reflections with $I > 2\sigma$ were measured with a four circle automatic diffractometer Syntex $P2_1$ (at −120°C, graphite monochromator, $\lambda(\text{Mo-}K_\alpha)$ $\theta/2\theta$ scan, $2\theta_{\text{max}}$ 60°). No absorption correction was applied ($\mu(\text{Mo-}K_\alpha)$ 15.3 cm^{-1}).

The structure was solved by the heavy atom method, refined by a block-diagonal least-squares technique first in isotropic and then in anisotropic approximation.

Hydrogen atoms at the ethylene carbon atoms C(1) and C(2), of the Me group were located on a difference map. The final refinement in the anisotropic approximation with allowance for the contribution of all hydrogen atoms (the position of hydrogen atoms in the phenyl groups were calculated geometrically) with fixed

TABLE 5

ATOMIC COORDINATES $\times 10^4$ (for the I, Pd, P atoms $\times 10^5$, for H atom $\times 10^3$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS $B_{iso}^{equiv} = 1/3\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$ OF THE NON-HYDROGEN ATOMS

Atom	x	y	z	B_{iso}^{equiv}	Atom	x	y	z	B_{iso}^{equiv}
I	16774(3)	76251(2)	24871(1)	1.57(1)	C(21)	4387(4)	8578(5)	882(3)	2.6(2)
Pd	−588(3)	75197(3)	15998(2)	1.24(1)	C(22)	3444(4)	7942(4)	806(2)	1.9(1)
P(1)	10722(10)	75017(10)	8275(6)	1.19(3)	C(23)	−1451(4)	6983(3)	3169(2)	1.1(1)
P(2)	−19290(10)	65617(9)	24320(6)	0.92(3)	C(24)	−1693(4)	6421(4)	3663(2)	1.7(1)
O(1)	−2312(3)	9086(3)	1093(2)	1.9(1)	C(25)	−1365(5)	6772(5)	4228(3)	2.3(2)
O(2)	−2661(3)	7917(3)	391(2)	1.53(9)	C(26)	−791(4)	7674(5)	4309(2)	2.3(1)
C(1)	−1683(4)	7528(4)	1942(2)	1.2(2)	C(27)	−550(4)	8231(4)	3823(2)	1.9(1)
C(12)	−1814(4)	7388(3)	1310(2)	1.1(1)	C(28)	−872(4)	7881(4)	3255(2)	1.5(1)
C(3)	−2263(4)	8223(4)	939(2)	1.3(1)	C(29)	−3438(4)	6247(3)	2404(2)	1.2(1)
C(4)	−3024(5)	8684(5)	−29(3)	2.4(2)	C(30)	−3754(4)	5372(4)	2689(2)	1.4(1)
C(5)	1660(4)	6277(4)	660(2)	1.4(1)	C(31)	−4920(4)	5122(4)	2667(2)	1.6(1)
C(6)	1937(4)	5623(4)	1130(2)	1.8(1)	C(32)	−5730(4)	5726(4)	2375(2)	1.8(1)
C(7)	2485(5)	4726(4)	1036(3)	2.3(2)	C(33)	−5428(4)	6590(4)	2097(2)	1.9(1)
C(8)	2726(5)	4469(4)	473(3)	2.3(2)	C(34)	−4261(4)	6851(4)	2111(2)	1.5(1)
C(9)	2430(5)	5104(4)	2(3)	2.6(2)	C(35)	−1219(4)	5428(3)	2251(2)	1.1(1)
C(10)	1911(5)	6009(4)	96(3)	2.3(2)	C(36)	−9(4)	5257(4)	2501(2)	1.5(1)
C(11)	447(4)	7932(4)	96(2)	1.3(1)	C(37)	471(4)	4396(4)	2344(3)	1.9(1)
C(12)	814(4)	8768(4)	−187(2)	1.7(1)	C(38)	−56(5)	3732(4)	1952(3)	2.2(1)
C(13)	328(5)	9042(4)	−742(3)	2.1(1)	C(39)	−1194(5)	3902(4)	1692(2)	2.1(1)
C(14)	−547(5)	8480(4)	−1025(2)	2.0(1)	C(40)	−1758(4)	4756(4)	1849(2)	1.7(1)
C(15)	−938(4)	7641(4)	−749(2)	2.0(1)	H(1)	−180	819	210	
C(16)	−458(4)	7360(4)	−193(2)	1.7(1)	H(2)	−201	676	114	
C(17)	2370(4)	8270(4)	939(2)	1.5(1)	H(1.4)	−340	833	−39	
C(18)	2265(4)	9237(4)	1165(2)	1.9(1)	H(2.4)	−255	897	−3	
C(19)	3205(5)	9868(4)	1228(3)	2.4(2)	H(3.4)	−350	900	12	
C(20)	4269(5)	9533(5)	1091(3)	2.8(2)					

coordinates and temperature parameters (B_{iso} 4 Å^2) converged at $R = 0.0373$, $R_w = 0.0418$ for 6282 reflections with $F^2 > 3\sigma$.

The coordinates of the nonhydrogen atoms, hydrogen atoms directly located in the difference synthesis and the isotropic equivalent temperature parameters (B_{iso}^{equiv}) for the nonhydrogen atoms are given in Table 5. All calculations were performed with an Eclipse S/200 computer using INEXTL programs [36].

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