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PALLADIUM(0) COMPLEXES COORDINATED WITH SUBSTITUTED OLEFINS AND TERTIARY PHOSPHINE LIGANDS

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Summary

New palladium(0) complexes with a variety of coordinated olefins, [Pd(olefin)($PMePh_2)_2$] (II) (olefin = styrene, ethyl methacrylate, methyl methacrylate, methyl acrylate, methacrylonitrile, and dimethyl maleate), were prepared by the reactions of [$PdEt_2(PMePh_2)_2$] (I) with corresponding olefins in toluene. These complexes were characterized by means of elemental analysis, IR and ^{1}H NMR spectroscopy and the chemical reactions. The dissociation of the coordinated olefin from complex II in solution was confirmed by spectroscopic studies of [Pd(mma)($PMePh_2)_2$] (mma = methyl methacrylate). From the variable temperature NMR study, kinetic parameters for the dissociation process were determined as E_a = 7 kcal/mol, and $\Delta S^{\ddagger}$(293 K) = —30 cal/deg · mol. Some new hydrido complexes, [Pd(H)ClL_2] (IV) (L = $PMePh_2$, $PEtPh_2$ and PEt_2Ph), were prepared by the reactions of [Pd(olefin)L_2] with dry HCl.

Introduction

A variety of transition metal—olefin complexes have been prepared and the nature of the bonding between central metal and olefin has been investigated extensively [1]. In the case of palladium, many stable palladium(II)—olefin complexes of the type [$PdCl_2$(olefin)] have been prepared and intensive studies have been carried out on their reactions with nucleophiles with special reference to the catalytic reactions such as the Wacker process [1,2]. On the other hand, studies of the olefin complexes of palladium(0) have been relatively limited and only [Pd(olefin)($PPh_3)_2$] (olefin = ethylene, dimethyl maleate, dimethyl fumarate, maleic anhydride, *p*-benzoquinone, 1,4-naphthoquinone, and octafluoro-2-butene) represents the isolated complexes reported until very recently [3—5]. The scarcity of the Pd(0)—olefin complexes may be due mainly to two reasons. The first is the low stability of the Pd(0)—olefin complex as compared to Ni(0)— and Pt(0)—olefin complexes. Since the stability of low valent group

VIII transition metal complexes is considered to depend on the extent of metal-to-olefin back donation, the reported increasing order of the ionization potential of Ni < Pt < Pd makes the back donation less favorable and renders the Pd(0)—olefin complexes less stable than the corresponding Ni(0) and Pt(0) analogs [6]. This view was supported by the result reported by Tolman et al. [7] who showed the decreasing order of equilibrium constant of eq. 1 as Ni >> Pt > Pd on the basis of the electronic spectroscopic evidence

$$ML_3 + C_2H_4 \rightleftharpoons (C_2H_4)ML_2 + L \qquad (1)$$

$(M = Ni, Pd, \text{ and } Pt;\ L = PPh_3)$

The second reason for the relative paucity of the Pd(0)—olefin complexes is the lack of an appropriate route to the Pd(0)—olefin complexes. For stabilizing zero valent transition metal complexes tertiary phosphines or organic nitrogen compounds are usually employed but these stabilizing ligands would compete with the olefin for coordination to the Pd(0) center and hinder the approach of the olefin. Recent isolation of [Pd(olefin)L_2] type complexes (olefin = maleic anhydride, dimethyl maleate, dimethyl fumarate, divinyl sulfone, acrylonitrile, tetracyanoethylene, and dimethyl fumarate; L = $\frac{1}{2}$(2,2′-bipyridine), P(OPh)$_3$, P(OMe)$_3$, $\frac{1}{2}$(*o*-phenanthroline), $\frac{1}{2}$(1,5-cyclooctadiene), $\frac{1}{2}$(norbornadiene), norbornene, and cyclopentene) with various olefins in the presence of suitable stabilizing ligands showed a new route to the Pd(0)—olefin complexes starting from a suitable Pd(0) complex containing a ligand which is easily replaced by an olefin [8,9].

We found that a diethylpalladium complex [$PdEt_2(PMePh_2)_2$] [10] can be used as a convenient precursor for the preparation of Pd(0)—olefin complexes because of its ready loss of the ethyl groups in solution in the presence of olefins. This provides a coordinatively unsaturated Pd(0) species capable of bonding with the olefins. A similar type of reaction has been reported for [$NiEt_2$(bipy)] (bipy = 2,2′-bipyridine) in its reactions with substituted olefins and a variety of [Ni(olefin)(bipy)] complexes has been isolated from this system [11].

The present olefin complexes are soluble in various organic solvents and amenable to NMR study, which provides information concerning the mode of olefin-coordination in such complexes. A similar NMR study of related Ni(0)—olefin complexes has been reported recently by our group [12].

We have found that the Pd(0)—olefin complexes react with dry hydrogen chloride to give new hydrido-chloropalladium complexes [Pd(H)ClL_2]. Our results are reported here together with details of the preparation and properties of [Pd(olefin)L_2] type complexes.

Results and discussion

Preparation of palladium(0)—olefin complexes

The reaction of [$PdEt_2(PMePh_2)_2$] (I) with olefins having electron-withdrawing substituents in a molar ratio of 1/2 in toluene under a nitrogen atmosphere afforded palladium(0)—olefin complexes II with the evolution of quantitative amounts of ethylene and ethane in a molar ratio of 1/1 (eq. 2).

$$[PdEt_2(PMePh_2)_2] + \text{olefin} \xrightarrow[\text{r.t.}]{\text{toluene}} [Pd(\text{olefin})(PMePh_2)_2] + C_2H_4 + C_2H_6 \qquad (2)$$

(I) (II)

olefin = styrene (st) (IIa), ethyl methacrylate (ema) (IIb), methyl methacrylate (mma) (IIc), methyl acrylate (ma) (IId), methacrylonitrile (man) (IIe), dimethyl maleate (dmm) (IIf)

On the other hand, similar reactions in toluene of I with olefins having electron-donating substituents, such as isobutyl vinyl ether, did not give type II complexes but evolved only one mol of ethane and about 0.1 mol of ethylene per mol of I.

It was reported that the decomposition of the diethyl complex (I) in solution affords the ethylene complex $[Pd(C_2H_4)(PMePh_2)_2]$, with the accompanying evolution of ethane, on the basis of the observation of the ^1H NMR spectrum [10], although the high lability of the ethylene complex prevented its isolation. In one experiment, an excess of dimethyl maleate was added to the solution of I after I had been completely decomposed by allowing it to stand at room temperature in the solution. Evolution of one mol of ethylene per mol of the complex was observed. The result indicates that II was formed by the ligand exchange reaction of the ethylene complex formed by the decomposition of I with the olefin having an electron-withdrawing substituent (eqs. 3 and 4).

$$[PdEt_2(PMePh_2)_2] \rightarrow [Pd(C_2H_4)(PMePh_2)_2] + C_2H_6 \qquad (3)$$

$$[Pd(C_2H_4)(PMePh_2)_2] + \text{olefin} \rightleftharpoons [Pd(\text{olefin})(PMePh_2)_2] + C_2H_4 \qquad (4)$$

In the case of olefins having electron-donating substituents, the equilibrium of eq. 4 may lie very far to the left, because of the poor coordinating ability of electron-rich olefins, hence the complexes of olefins with electron-donating substituents could not be obtained.

The results of the elemental analysis of the palladium(0)—olefin complexes (IIa—IIf) are listed in Table 1 together with decomposition points measured in vacuo. Complexes IIa—IIc and IIe are pale brown solids whereas complexes IId and IIf are pale yellow solids. They are diamagnetic and relatively insensitive to air in the solid state but decompose rapidly on contact with air in solution.

Complexes IIa—IIf release the corresponding olefin quantitatively on the addition of excess $PMePh_2$ to the ether solutions to give $[Pd(PMePh_2)_4]$. Table 1 shows that about one mol of the olefin per mol of the complexes was liberated by the treatment with $PMePh_2$. The reaction of II with CH_3I and CH_3COBr also released the corresponding olefin quantitatively, and formed $[Pd(Me)I(PMePh_2)_2]$ and $[Pd(COCH_3)Br(PMePh_2)_2]$, respectively (eq. 5).

$$[Pd(\text{olefin})(PMePh_2)_2] + RX \rightarrow [Pd(R)X(PMePh_2)_2] + \text{olefin} \qquad (5)$$

$(R = CH_3, X = I; R = CH_3CO, X = Br)$

These results support the view that one mol of olefin per mol of the complex is coordinated to palladium in these complexes.

In contrast to the reactions of the diethylpalladium complex with olefins, the reactions of dimethylpalladium complexes $[PdMe_2L_2]$ ($L = PEt_3$, IIIa, and

TABLE 1

ANALYTICAL DATA AND DECOMPOSITION POINTS OF [Pd(olefin)($PMePh_2$)$_2$]

Olefin	Elemental analysis; found (calcd. (%))			Olefin/ complex [a] (mol/mol of complex)	Dec. pt. [b] (°C)
	C	H	N		
Styrene IIa	67.5 (66.8)	5.9 (5.6)		[c]	[c]
Ethyl methacrylate IIb	62.0 (61.9)	6.2 (5.8)		0.93	110—116
Methyl methacrylate IIc	60.6 (61.3)	5.8 (5.7)		1.10	115—119
Methyl acrylate IId	60.6 (60.8)	5.9 (5.4)		0.80	88—90
Methacrylonitrile IIe	62.3 (62.8)	5.7 (5.4)	2.3 (2.4)	1.07	75—83
Dimethyl maleate IIf	59.3 (59.0)	5.4 (5.3)		0.89	116—119

[a] The amount of olefin released on addition of excess $PMePh_2$ to the complexes dissolved in Et_2O.
[b] Decomposition points were measured on a hot stage with a sample in a small capillary sealed under vacuum and are uncorrected. [c] Not measured.

$PMePh_2$, IIIb) [10], with substituted olefins (vinyl acetate, styrene, methyl methacrylate, ethyl methacrylate, methacrylonitrile, and acrylonitrile) without solvent or in solution (Et_2O and toluene) afforded the corresponding polymers accompanied by evolution of methane and/or ethane (see Experimental). The polymerization probably proceeds by a coordination-insertion mechanism as reported in the polymerization of vinyl compounds with various alkyl- and hydrido-transition metal complexes [13]. No palladium(0)—olefin complex has been obtained in these cases, although the reaction of IIIa with methyl acrylate without solvent afforded, in addition to poly(methyl acrylate), methyl crotonate (37% on the basis of the amount of initially used complex) with accompanying evolution of methane (81%). This result indicates that the methylation at the β-carbon of methyl acrylate took place in the reaction with the dimethylpalladium complex, presumably by an insertion-β-elimination mechanism.

Infrared spectra of the complexes

The characteristic infrared data of complexes IIa—IIf are listed in Table 2. The assignments were made by comparing the spectra with each other, and with those of [Pd($PMePh_2$)$_4$], *cis*-[$PdCl_2$($PMePh_2$)$_2$] and corresponding free olefins. The frequencies of the ν(C=O) and ν(C≡N) bands of the coordinated olefins decreased by 10—70 cm^{-1} ($\Delta\nu$(C=O) and $\Delta\nu$(C≡N)) compared with those of free olefins. On the other hand, the frequencies of the ν(C=C) of olefins decreased by as much as 170—180 cm^{-1} ($\Delta\nu$(C=C)) on coordination. These results suggest that the olefinic ligands in all complexes IIa—IIf are coordinated to the palladium atom only via the C=C bond and not through the C=O bond or C≡N bond. The participation of both C=C and C=O bonds of the olefin ligand in bonding to a metal has been reported to cause a large shift of ν(C=O) to lower frequency (157 cm^{-1} in the case of [Ni(acrolein)$_2$] [14]). The lowering of ν(C=O) by about 35 cm^{-1} has been reported for [Pd(olefin)(PPh$_3$)$_2$] (olefin = dimethyl fumarate and dimethyl maleate) in which a direct interaction between C=O group and Pd is not considered [4]. The value of $\Delta\nu$(C=C) of methyl methacrylate has been reported to be 132 cm^{-1} for [Fe(mma)(CO)$_4$] [15]. Furthermore, it has been recently confirmed by X-ray structural analysis that methyl acrylate (ma) in [Ni(ma)$_2$(bipy)] is coordinated to nickel only through the C=C double bond in the solid state [16].

The frequency of ν(C=O) or ν(C≡N) of the present complex in solution was found to be similar to that in the solid state. Thus, the frequency of ν(C=O) of IIc was observed at 1680 cm^{-1} in toluene and 1678 cm^{-1} in the solid state, indicating that there is no interaction between C=O or C≡N bond with palladium metal in solution as in the solid state.

The NMR spectra of the complexes [Pd(olefin)(PMePh$_2$)$_2$]

The results of the ^{1}H NMR measurements of the palladium(0)—olefin complexes IIa—IIf in toluene-d_8 at —20° C are listed in Table 3. The assignments of the signals were made by comparing the spectra with those of the corresponding free olefins measured in C$_6$D$_6$ at room temperature, of [Ni(olefin)(PR$_3$)$_2$] (olefin = ma, styrene, and acrylonitrile; R = —OC$_6$H$_4$CH$_3$) [17,18], and [Fe(olefin)(CO)$_4$] (olefin = ma and acrolein) [19].

As shown in Table 3, α-methyl protons of mma (H$_c$) in IIc appeared at 2.02 ppm as a doublet and β-olefinic protons of mma (H$_a$ and H$_b$) appeared at 3.73 and 3.01 ppm as triplets, respectively. These α-methyl and β-olefinic protons all appeared as singlets in the ^{31}P-decoupled ^{1}H NMR spectrum under the same conditions. This indicates that α-methyl and β-olefinic protons of IIc are split into the doublet and triplets due to the coupling with one and two phosphorus nuclei, respectively. Methyl protons of two phosphine ligands in IIc (P—Me) appeared at 1.69 and 1.38 ppm each as doublets due to the coupling with each phosphorus nucleus. The different chemical shifts between two phosphine methyl protons in IIc suggests that these two phosphine ligands are nonequivalent. This is supported by the observation of the ^{31}P{^{1}H} NMR spectrum of IIc, in which signals due to two phosphorus nuclei appeared as an AB quartet. This observation suggests that the C=C double bond of mma, an unsymmetric olefin, is involved in the plane containing the palladium atom and two phosphorus atoms in IIc, as shown in Fig. 1. The alternative way of coordination to this in which the C=C bond axis lies perpendicular to the MP$_2$ plane seems to be less probable in view of the observed large magnetic unequivalence of two phosphorus nuclei. The crystal and molecular structures have been investigated for several nickel(0)— and platinum(0)—olefin complexes and the C=C bond axis of olefinic group was found to lie close to the MP$_2$ plane in [(PPh$_3$)$_2$Ni(C$_2$H$_4$)] [20], [(PPh$_3$)$_2$Pt(C$_2$H$_4$)] [21] and [(PPh$_3$)$_2$Pt(fumaronitrile)] [22], in agreement with the present conclusion drawn from the NMR evidence.

As with the spectrum of IIc, the ^{1}H NMR spectrum of the methacrylonitrile complex IIe at —20° C consisted of a doublet at 1.51 ppm due to α-methyl protons of man and a pair of triplets at 3.10 and 2.67 ppm due to β-olefinic protons. On the other hand, α-methyl and/or olefinic protons in complexes IIa,

(Continued on p. 382)

TABLE 2

IR DATA OF [Pd(olefin)(PMePh$_2$)$_2$] (KBr DISK, cm^{-1})

Olefin	ν(C=O)	ν(C≡N)	ν(C=C)	ν(C—O)	$\Delta\nu$(C=O) [a]	$\Delta\nu$(C≡N) [a]	$\Delta\nu$(C=C) [a]
st IIa			[b]				
ema IIb	1670		1470	1144, 1270	−60		−182
mma IIc	1678		1470	1142, 1280	−54		−180
ma IId	1687		1465	1158, 1199	−51		−179
man IIe		2184	1462			−46	−172
dmm IIf	1730, 1670		[b]	1120, 1290	−10, −70		

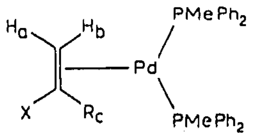
[a] $\Delta\nu = \nu_{coordinated} - \nu_{free}$. [b] Not discernible.

TABLE 3

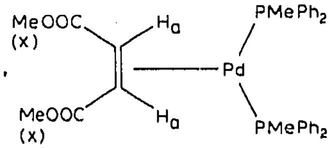
^{1}H NMR DATA OF [Pd(olefin)(PMePh$_2$)$_2$] [a,b]

Olefin	Olefin (Δδ) [c]				PMePh$_2$			
	a	b	c	X	Me		*m,p*-Ph	*o*-Ph
st IIa	3.52(br) (+2.08)	3.36(br) (+1.71)	4.82(br) (+1.78)	[d]	1.44(br)	1.28(br)	6.99(m)	7.32(m)
ema IIb	~3.8(br) (+2.4)	3.03(br) (+2.30)	2.02(br) (−0.16)	3.88(q) [e] 0.98(t) [e] (+0.14) (+0.03)	1.70(br)	1.40(br)	7.00(m)	7.38(m)
mma IIc	3.73(t) [f] (+2.41)	3.01(t) [f] (+2.29)	2.02(d) [g] (−0.18)	3.31(s) (+0.13)	1.69(d) [h]	1.38(d) [i]	6.99(m)	7.37(m)
ma IId	3.78(br) (+2.52)	2.93(br) (+2.48)	4.20(br) (+1.83)	3.27(s) (+0.18)	1.62(br)	1.38(br)	7.00(m)	7.33(m)
man IIe	3.10(t) [j] (+2.20)	2.67(t) [j] (+2.39)	1.51(d) [k] (−0.11)		1.74(d) [i]	1.35(d) [l]	7.04(m)	7.28(m)
dmm IIf	3.89(s) (+1.90)			3.21(s) (+0.19)	1.54(d) [l]		7.02(m)	7.33(m)

[a] In toluene-d_8, at −20°C, 100 MHz. Chemical shifts are in δ values (ppm) with respect to Si(Me)$_4$ as an internal standard (down field positive). Multiplicity abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. [b] Proton notations are made as follows:



for IIa - IIe ,



for IIf

[c] Values of Δδ(ppm) calculated from ($\delta_{free} - \delta_{coordinated}$) are in parentheses. [d] Not discernible. [e] ^3J(HH) = 7 Hz. [f] ^3J(HP) = 6 Hz. [g] ^4J(HP) = 7 Hz. [h] ^2J(HP) = 4 Hz. [i] ^2J(HP) = 5 Hz. [j] Apparent triplets whose coupling constants are obscure due to the secondary coupling with geminal proton. [k] ^4J(HP) = 8 Hz. [l] ^2J(HP) = 6 Hz.

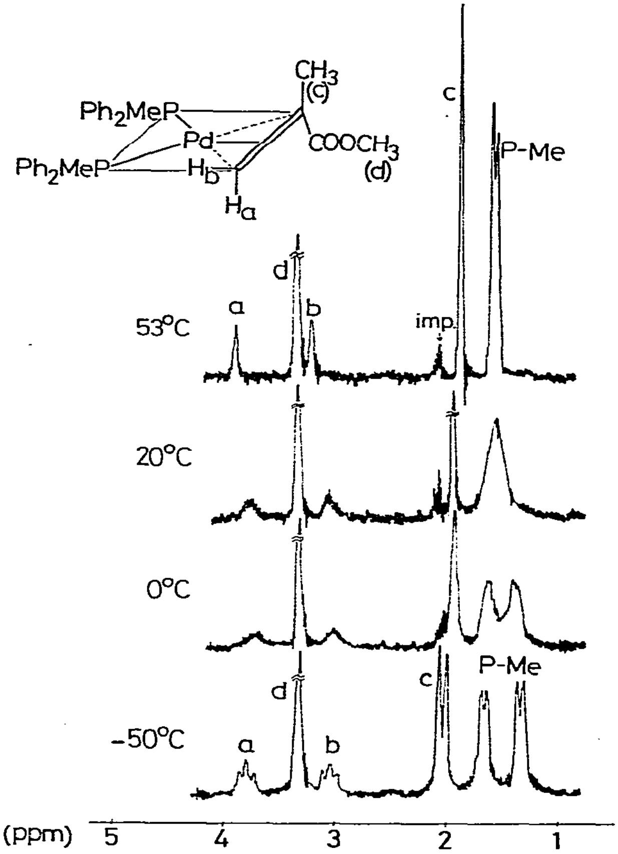


Fig. 1. Temperature dependence of ^{1}H NMR spectrum of [Pd(mma)(PMePh$_2$)$_2$] (100 MHz in toluene-d_8).

IIb, and IId each appeared as broad signals. These results, together with those described in the next section, suggest that the dissociation of the olefinic ligand in solution takes place at −20° C with complexes IIa, IIb, and IId, but not with IIc and IIe at the same temperature. Furthermore, from the degree of broadening of the olefinic protons and phosphine—methyl protons, it seems that the order of the ease of olefin dissociation was st > ema > ma > mma ≃ man. The spectrum of IIf was similar to that of [Pd(dmm)(PPh$_3$)$_2$], reported by Takahashi and Hagihara [4], i.e., two olefinic protons of dmm were observed as only one singlet at 3.89 ppm. In complex IIf, the coupling of olefinic protons with phosphorus atoms was not observed. Furthermore, methyl protons in two phosphine ligands were observed as only one doublet at 1.54 ppm. In view of the fact that dmm is, among olefins examined, the only such olefin that has two equivalent olefinic carbon atoms, these results further support the pseudo-square-planar structure for complexes II as described above.

In these complexes, upfield shifts of olefinic proton signals by 1.7—2.5 ppm, as compared with the signals of free olefins, were observed, suggesting that each olefin is coordinated to palladium through the C=C bond in accordance with the observation made using IR spectra.

The dynamic behavior of [Pd(mma)(PMePh$_2$)$_2$] in solution

The ^{1}H NMR spectrum of [Pd(mma)(PMePh$_2$)$_2$] (IIc) in toluene-d_8 was found to be temperature-dependent as shown in Fig. 1. Two phosphine methyl groups (P—Me), which appeared as a pair of doublets at —50° C, changed to a pair of broad signals at 0° C and then coalesced to a broad signal at 20° C. Furthermore, they appeared as a sharp doublet at 53° C. On the other hand, α-methyl groups (H$_c$) and β-olefinic protons (H$_a$ and H$_b$) were observed as a doublet and a pair of triplets, respectively, as a result of their coupling with the phosphorus nuclei at —50° C. On raising the temperature they all broadened at 0° C and then became sharp singlets at 53° C. Besides the changes in the signal pattern, it was observed that the β-olefinic signals shifted to the lower field slightly on raising the temperature (H_a = 3.73 ppm, H_b = 3.01 ppm at —50° C; H_a = 3.82 ppm, H_b = 3.19 ppm at 53° C).

To summarize these observations, the couplings of β-olefinic protons (H$_a$ and H$_b$) and α-methyl protons (H$_c$) with phosphorus nuclei disappear on raising the temperature and at the same time, two phosphine ligands, which are non-equivalent at low temperature due to the unsymmetrically substituted olefin, become equivalent. The results of the variable temperature ^{31}P{^{1}H} NMR spectra of IIc were also in line with these observations, i.e., two phosphorus atoms appeared as AB quartet signals at —32° C whereas they appeared as a singlet at 40° C.

As a possible explanation for the results of the dynamic NMR spectra of IIc, the following three cases may be considered; (i) the dissociation of mma ligand from IIc; (ii) the dissociation of PMePh$_2$ ligand from IIc; and (iii) the rotation of mma ligand about Pd—mma bond axis. Although a rotation of coordinated olefin about the metal—olefin bond (case (iii) above) has been amply precedented [23], it seems that the contribution of such process to the present system as a principal factor is less likely in view of the fact that protons H$_a$, H$_b$, and H$_c$ completely lose their coupling with phosphorus nuclei at the elevated temperature. If the averaging of two phosphine ligands in IIc were due solely to such rotation of olefin ligand, olefinic protons would maintain their couplings with ^{31}P. In order to distinguish between (i) and (ii) as a cause of the dynamic behavior of IIc in solution the following experiments were carried out.

The ^{1}H NMR spectra of IIc in toluene-d_8 solution containing an equimolar quantity of added mma at various temperatures are shown in Fig. 2. At —40° C, the signals of IIc in this system (β-olefinic protons = H$_a$, H$_b$; α-methyl protons = H$_c$; phosphine—methyl protons = P—Me; ester—methyl protons = H$_d$) were almost identical with the signals of IIc alone as shown in Fig. 1 (—50° C). Also, the signals due to free mma (β-olefinic protons = H$_a'$, H$_b'$; α-methyl protons = H$_c'$; ester—methyl protons = H$_d'$) were much the same as the spectrum of the free mma itself, which was measured at room temperature in C_6D_6. On raising the temperature, all signals of IIc and free mma broadened at 0° C and, at room temperature, signals due to H$_a$, H$_b$, H$_a'$ and H$_b'$ disappeared and signals due to H$_c$ and H$_c'$ appeared as a somewhat broad singlet. At the same time, P—Me signals collapsed to a broad singlet. At 60° C, pairs of H$_a$ and H$_a'$, H$_b$ and H$_b'$, and H$_c$ and H$_c'$ each collapsed to singlets and P—Me signal changed to a sharp doublet.

These spectral changes suggest that the ligand exchange reaction of the coordinated mma in IIc with free mma is taking place in such a rate as measur-

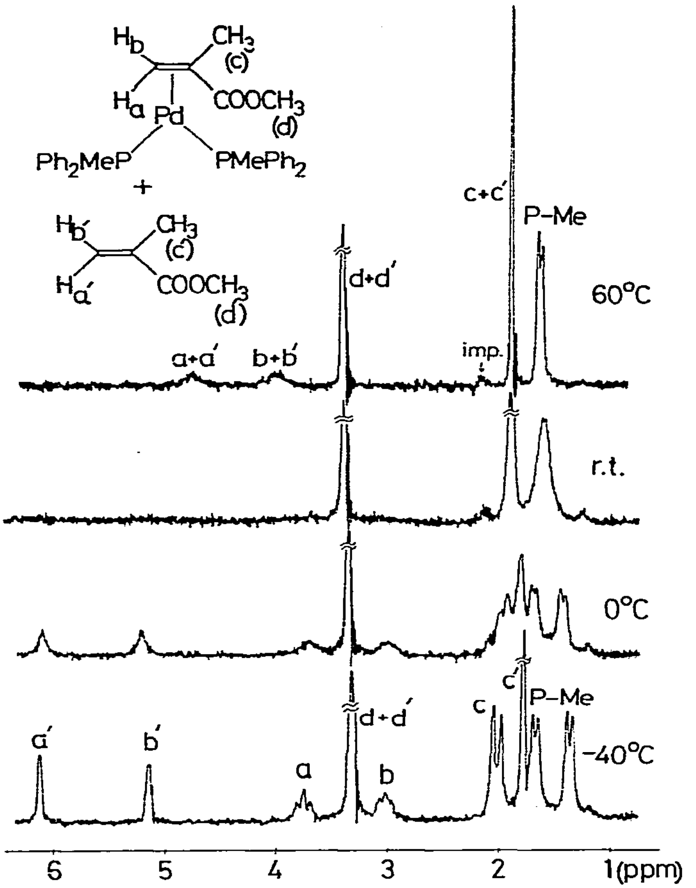


Fig. 2. Temperature dependence of ^1H NMR spectrum of [Pd(mma)$(PMePh_2)_2$] with an equimolar amount of mma (100 MHz in toluene-d_8).

able in an NMR time scale at elevated temperature (eq. 6).

$$[Pd(mma)(PMePh_2)_2] + mma^* \rightleftharpoons [Pd(mma^*)(PMePh_2)_2] + mma \qquad (6)$$

Furthermore, these results suggest that the averaging of two phosphine—methyl signals at the elevated temperature is due to the exchange of coordinated mma with free mma. In the variable temperature $^{31}P\{^1H\}$ NMR spectra, it was found that the signals of the phosphine ligands in IIc in the presence of an equimolar quantity of added mma were almost the same as those of IIc alone, i.e., two phosphorus atoms appeared as AB quartet signals at —40° C but as only one signal at 60° C. No signal due to free phosphine was observed. This ^{31}P NMR observation is in accordance with the ^1H NMR results and suggests that the cause for the changes in ^1H NMR spectra shown in Fig. 1 is ascribable to the reversible dissociation of mma ligand from IIc, process (i) being most important to account for the behavior of the present system. On the other hand, the importance of the process (ii) has been demonstrated by Minematsu et al. for the case of [Pd(maleic anhydride)$(PPh_3)_2$] [24] in which dissociation of PPh_3 in the presence of added PPh_3 was suggested by ^1H NMR measurements.

Most of the ligand exchange reactions in square planar complexes are known to proceed by S_N2 type pathways [25]. In order to see if the dissociation of mma from IIc and exchange reaction of coordinated mma with free mma described above also follow the S_N2 mechanism, the kinetic studies were attempted on the variable temperature ^1H NMR spectra using Gutowsky and Holm's equation [26]*. From the kinetic studies at the temperature of 10—20°C, the approximate activation energies of 7 kcal/mol for System I shown in Fig. 1 (without added mma) and 6 kcal/mol for System II shown in Fig. 2 (with added mma), and the activation entropies of —30 cal/deg · mol at 293 K for Systems I and II, were determined. The large negative values of the observed activation entropies suggest that the exchange of mma ligand in these systems containing IIc proceeds through an S_N2 mechanism. This result was further substantiated by the additional experiments in which two equivalents of γ-picoline were added to the toluene-d_8 solution of IIc. Two phosphine—methyl signals of this system coalesced at 0°C which is much lower than the coalescence temperature of 20°C in the absence of added γ-picoline (Fig. 1) indicating that the S_N2 type dissociation reaction was accelerated by addition of γ-picoline. Thus, the dissociation reaction of mma and the exchange reaction of coordinated mma with free mma in complex IIc is considered to proceed according to eq. 7.

$$\begin{aligned}[\mathrm{Pd(mma)(PMePh_2)_2}] + \mathrm{L} &\rightleftharpoons [\mathrm{Pd(mma)(L)(PMePh_2)_2}] \\ &\rightleftharpoons [\mathrm{Pd(L)(PMePh_2)_2}] + \mathrm{mma} \qquad (7)\end{aligned}$$

L = mma, solvent, etc.

In order to obtain some information on the relative coordination strength of olefins toward palladium(0) complex, ^1H NMR spectrum of $[Pd(mma)(PMePh_2)_2]$ (IIc) (mma = methyl methacrylate) in toluene-d_8 in the presence of an equimolar quantity of added methacrylonitrile (man) at —48° C was investigated. The signals of olefinic protons of mma and man appeared as broad signals at 6.14 ppm (H_a of mma), 5.16 ppm (H_b of mma), 3.08 ppm (H_a of man), and 2.66 ppm (H_b of man) in this spectrum. Comparison of the chemical shifts of the olefinic protons of mma and man in this spectrum with those of authentic free mma and man and those in the complexes, the latter of which are given in Table 3, revealed that the exchange reaction of coordinated mma with added man took place according to eq. 8 and that the equilibrium of eq. 8 was far to the right.

$$\underset{\text{(IIc)}}{[\mathrm{Pd(mma)(PMePh_2)_2}]} + \mathrm{man} \rightleftharpoons \underset{\text{(IIe)}}{[\mathrm{Pd(man)(PMePh_2)_2}]} + \mathrm{mma} \qquad (8)$$

The result indicates that man forms more stable olefin complexes than mma does. Similarly examined was the relative coordination strength in the systems of IIc and styrene (st), $[Pd(ma)(PMePh_2)_2]$ (IId) (ma = methyl acrylate) and man, and IId and dimethyl maleate (dmm). From these observations, the order of stability of palladium(0)—olefin complexes, $[Pd(olefin)(PMePh_2)_2]$, is dmm > ma > man > mma > st. This order of the stability indicates that the olefins having stronger electron-withdrawing substituents form more stable palladium(0)—olefin complexes.

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[*] A difference in the chemical shifts of two doublets due to P-Me protons (Figs. 1 and 2) was employed as a probe for the rate of olefin exchange process.

The relative stability of Ni(0)—olefin complexes with a variety of olefins has been studied by several workers [18,27,28] and it was established that the stability of Ni(0)—olefin complexes was related to the magnitude of back donation from Ni to olefin, i.e., the olefins having stronger electron-withdrawing substituents form more stable Ni(0)—olefin complexes. The order of the stability of the palladium(0)—olefin complexes determined as above in the present study agreed with that reported for Ni(0)—olefin complexes.

The examination of the ^{1}H and ^{31}P{^{1}H} NMR spectra of IIc in toluene-d_8 and toluene, respectively, in the presence of an equimolar quantity of added $PMePh_2$ at various temperatures revealed that the exchange reaction of coordinated mma with $PMePh_2$ to form, ultimately, the most stable Pd(0) complex of $[Pd(PMePh_2)_4]$ according to eq. 9 is taking place.

$$\begin{tikzcd}[column sep=small] 2[Pd(mma)(PMePh_2)_2] + PMePh_2 \arrow[r, shift left=0.5ex] & \arrow[l, shift left=0.5ex] [Pd(PMePh_2)_3] \arrow[d, shift right=0.5ex, "+PMePh_2"'] & + [Pd(mma)(PMePh_2)_2] + mma \\ & {[Pd(PMePh_2)_4]} \arrow[u, shift right=0.5ex, "-PMePh_2"'] & \end{tikzcd} \qquad (9)$$

The equilibration as expressed by eq. 9 still takes place in an NMR time scale even at −60°C. Furthermore, addition of two equivalents of $PMePh_2$ to the toluene-d_8 solution of IIc caused the complete displacement of the coordinated mma by $PMePh_2$ and the chemical shifts of β-olefinic protons of mma in this system were found to be very close to those of free mma taken at −50°C.

Reaction of palladium(0)—olefin complex with HCl gas

In contrast to a high reactivity of palladium(II)—olefin complexes towards nucleophilic reagents such as alcohols and amines [29], the present palladium(0)—olefin complexes did not react with nucleophilic reagents such as CH_3ONa. Higher electron densities at the metal centers in the Pd(0) complexes than in Pd(II) complexes may render the former more susceptible to the electrophilic attack than to the nucleophilic attack. In fact some reactions of Pt(0) or Pd(0) complex with protic acid such as CF_3COOH or HCl have been known [30—32].

$[Pd(mma)(PMePh_2)_2]$ (IIc) reacted with an excess of dry HCl gas at −70°C in toluene to form methyl isobutyrate (10% on the basis of starting complex IIc), methyl methacrylate (80%), hydrogen gas (90%), and *trans*-$[PdCl_2(PMePh_2)_2]$. $[Pd(ma)(PMePh_2)_2]$ (IId) reacted with two equivalents of CF_3COOH at room temperature in diethyl ether to form methyl propionate (20%), methyl acrylate (70%) and $[Pd(OCOCF_3)_2(PMePh_2)_2]$.

In contrast to these reactions, the monohydrido complex $[Pd(H)Cl(PMePh_2)_2]$ was obtained by the reaction of IIc with an equimolar amount of dry HCl gas. In this way, several new hydrido complexes of palladium(II) of the type $[Pd(H)ClL_2]$ were synthesized (eq. 10).

$$\underset{(I)}{[PdEt_2L_2]} + \text{olefin} \xrightarrow[\text{r.t.}]{\text{toluene}} \underset{(II)}{[Pd(\text{olefin})L_2]} \xrightarrow[-70^\circ C]{\text{dry HCl}} \underset{(IV)}{\textit{trans-}[Pd(H)ClL_2]}$$

olefin = styrene, methyl acrylate
L = $PMePh_2$ (IVa), $PEtPh_2$ (IVb), PEt_2Ph (IVc)

TABLE 4

IR AND ^{1}H NMR DATA OF [Pd(H)ClL$_2$] [a]

L	IR data [b]	^{1}H NMR data [c] (δ, ppm)				
	ν(Pd—H)	Pd—$\underline{\mathrm{H}}$	P—R			
			—CH$_3$	—CH$_2$—	*m,p*-Ph	*o*-Ph
PMePh$_2$ IVa	2030s	—12.36(t) [d]	2.17(br)		7.45(m)	7.69(m)
PEtPh$_2$ IVb	1999s	—12.80(t) [e]	1.20(qui) [e]	2.60(m)	7.44(m)	7.68(m)
PEt$_2$Ph IVc	2053s	—13.18(t) [f]	1.13(qui) [e]	2.21(m)	7.44(m)	7.78(m)

[a] s, strong; t, triplet; qui, quintet; m, multiplet; br, broad. [b] KBr disk, cm^{-1}. [c] In CDCl$_3$, at —40°C, 100 MHz. Si(Me)$_4$ as internal standard. [d] J = 7 Hz. [e] J = 8 Hz. [f] J = 6 Hz.

Complexes IV, which are all white crystals, were very sensitive to air and thermally unstable. The ^{1}H NMR data and ν(Pd—H) values in IR spectra of the isolated new hydrido complexes IV are summarized in Table 4. Similarly to the other monohydrido complexes of palladium(II) [31—33], complexes IV had a *trans* geometry which was deduced from the triplet patterns of Pd—H signals in their ^{1}H NMR spectra. In solution, complexes IV reacted with dry HCl gas very rapidly to yield hydrogen gas and *trans*-[PdCl$_2$L$_2$], quantitatively.

Experimental

All manipulations were carried out under an atmosphere of deoxygenated nitrogen or argon, or in vacuo. Solvents and olefins were dried in the usual manner, distilled, and stored under a nitrogen atmosphere.

Infrared spectra were recorded on a Hitachi 295 spectrometer using KBr pellets prepared under inert atmosphere. NMR spectra were measured on a JEOL PS-100 spectrometer. ^{1}H NMR signals are referred to tetramethylsilane as internal standard. Analysis of the gases evolved by the reaction was carried out by gas chromatography (Shimadzu GC-3BT) after collecting gases fractionally using a Toepler pump, by which the volumes of gases were also measured. Microanalysis (C, H, N, and halogen) were carried out by Mr. T. Saito of our laboratory using a Yanagimoto CHN Autocorder Type MT-2.

Diphenylmethylphosphine, diphenylethylphosphine, and diethylphenylphosphine were prepared by the reactions of PPh$_2$Cl (Strem Co.) and PPhCl$_2$ (Strem Co.) with RMgX (R = Me, X = I; R = Et, X = Br) in Et$_2$O, respectively. [PdEt$_2$(PMePh$_2$)$_2$], [PdMe$_2$(PEt$_3$)$_2$], and [PdMe$_2$(PMePh$_2$)$_2$] were prepared as previously reported [10]. The other diethyl complexes [PdEt$_2$L$_2$] (L = PEtPh$_2$ and PEt$_2$Ph) were prepared analogously from [Pd(acac)$_2$], tertiary phosphines, and AlEt$_2$(OEt) in Et$_2$O.

Preparation of (η^2-methyl methacrylate)bis(diphenylmethylphosphine)palladium(0), IIc

To a white heterogeneous mixture of toluene (5 ml) and [PdEt$_2$(PMePh$_2$)$_2$] (0.21 g, 0.37 mmol), methyl methacrylate (80 μl, 0.76 mmol) was added by means of a syringe. On stirring the system at room temperature for 5 h, it

TABLE 5

THE REACTIONS OF [$PdMe_2L_2$] WITH OLEFINS AT ROOM TEMPERATURE

Complex [a]	Olefin [b]	Solvent	Reaction time (h)	Evolved gas [c]		Product [c]	Polymer
				CH_4	C_2H_6		
IIIa	an	neat	4				yes
IIIa	man	neat	36	0.02	0.01	[e]	yes
IIIa	ma	neat	17	0.81		methyl crotonate (0.37)	yes
IIIa	ma	Et_2O	21	0.47		methyl crotonate (0.03)	yes
IIIa	mma	neat	12	0.03	trace		yes
IIIa	st	neat	48	[d]			yes
IIIa	vac	neat	20	0.07	trace		yes
IIIb	ma	neat	5	[d]	[d]	methyl crotonate (trace)	yes
IIIb	ema	neat	8	[d]	[d]	ethyl tiglate (trace)	yes
IIIb	vac	toluene	30	[d]	[d]	[e]	no

[a] IIIa, [$PdMe_2(PEt_3)_2$]; IIIb, [$PdMe_2(PMePh_2)_2$]. [b] an, acrylonitrile; man, methacrylonitrile; ma, methyl acrylate; mma, methyl methacrylate; ema, ethyl methacrylate; st, styrene; vac, vinyl acetate. [c] mol/mol of complex. [d] Gas evolution was observed qualitatively by means of GLC. [e] About 40% of dimethyl complex was recovered unreacted.

became a homogeneous yellow solution. The solution was concentrated to ca. 1 ml and 5 ml of hexane was added to the system. The mixture was stirred for 30 min at —70° C to precipitate pale brown powder, which was filtered, washed with a small amount of hexane and dried in vacuo. The product was recrystallized from hot acetone, containing an equimolar amount of methyl methacrylate, to yield a pale brown microcrystalline precipitate of [Pd(mma)($PMePh_2$)$_2$] (IIc) (0.18 g, 78% yield). Similarly obtained were [Pd(ema)($PMePh_2$)$_2$] (IIb) (79%), [Pd(man)($PMePh_2$)$_2$] (IIe) (85%), and [Pd(dmm)($PMePh_2$)$_2$] (IIf) (68%).

Preparation of (η^2-methyl acrylate)bis(diphenylmethylphosphine)palladium(0), IId

To a white heterogeneous mixture of toluene (7 ml) and [$PdEt_2$($PMePh_2$)$_2$] (0.46 g, 0.81 mmol), methyl acrylate (160 μl, 1.7 mmol) was added by means of a syringe. The system was stirred for 5 h at room temperature to give a homogeneous yellow solution. The solvent was evaporated from the solution to leave a yellow oil, which was dissolved in Et_2O (5 ml) containing an equimolar amount of methyl acrylate. The clear yellow solution was cooled to —70° C overnight to yield pale yellow micro crystals of [Pd(ma)($PMePh_2$)$_2$] (IId), which was filtered, washed with cold hexane and dried in vacuo (0.43 g, 90%). Similarly obtained was [Pd(st)($PMePh_2$)$_2$] (IIa) (32%).

Reaction of [Pd(ema)($PMePh_2$)$_2$], IIb, with methyl iodide

Methyl iodide (ca. 4 ml) was distilled over calcium hydride under vacuum into a flask containing [Pd(ema)($PMePh_2$)$_2$] (0.10 g, 0.17 mmol). On stirring the mixture at room temperature, the initial brown homogeneous solution turned to a clear yellow solution. No gas evolution was observed and the presence of ema (0.14 mmol, 83% on the basis of the initially used complex) in the system was observed by means of GLC. Concentration of the yellow solution to ca. 1 ml yielded a pale yellow precipitate which was filtered, and dried in vacuo. The pale yellow powder thus obtained was identified as [PdMe(I)($PMePh_2$)$_2$] on the basis of its IR spectrum (0.11 g, 100%).

Reaction of [Pd(mma)($PMePh_2$)$_2$], IIc, with acetyl bromide

To a brown heterogeneous mixture of Et_2O (2 ml) and [Pd(mma)($PMePh_2$)$_2$] (0.23 g, 0.38 mmol), acetyl bromide (60 μl, 0.74 mmol) was added by means of a syringe. The system was stirred for 1 h at room temperature to give a heterogeneous yellow mixture. No gas evolution was observed and mma (0.36 mmol, 95% on the basis of the initially used complex) was confirmed by means of GLC. The precipitate was filtered and recrystallized from acetone to yield yellow crystals of [Pd(CH_3CO)Br($PMePh_2$)$_2$] (0.20 g, 84% yield). $\nu(C{=}O) = 1670\ cm^{-1}$. Found: C, 52.7; H, 4.8; Br, 12.5. Calcd. for $PdC_{28}H_{29}BrOP_2$: C, 53.4; H, 4.6; Br, 12.7%.

Reaction of [Pd(mma)($PMePh_2$)$_2$], IIc, with excess dry HCl gas

To a clear brown solution (2 ml) of [Pd(mma)($PMePh_2$)$_2$] (0.059 g, 0.097 mmol) in toluene, dry HCl gas, which was produced from NaCl (0.031 g, 0.53 mmol) and excess conc. H_2SO_4, was introduced in vacuo at —198° C. The system was stirred at room temperature to yield a yellow precipitate. Evolution of

H_2 gas (0.089 mmol) was observed together with the formation of methyl isobutyrate (0.009 mmol, 9% on the basis of the initially used complex) and mma (0.076 mmol, 78%). The precipitate was filtered and dried in vacuo to yield $[PdCl_2(PMePh_2)_2]$ (0.056 g, 100%). Found: C, 53.4; H, 4.4; Cl, 11.8. Calcd. for $PdC_{26}H_{26}P_2Cl_2$: C, 54.0; H, 4.5; Cl, 12.3%.

Reaction of [Pd(ma)(PMePh₂)₂], IId, with excess CF₃COOH

To a yellow Et_2O solution of $[Pd(ma)(PMePh_2)_2]$ (0.076 g, 0.13 mmol), CF_3COOH (30 µl, 0.40 mmol) was added by means of a syringe. The system was stirred at room temperature to give a heterogeneous yellow mixture containing an orange precipitate. Methyl propionate (0.026 mmol, 20% on the basis of the complex initially used) and ma (0.090 mmol, 70%) were detected in the system by means of GLC. The precipitate was identified as $[Pd(OCOCF_3)_2(PMePh_2)_2]$ on the basis of the IR spectrum (ν(C—F) = 1193, ν(C—O) = 1420, ν(C=O) = 1686 cm^{-1}).

Preparation of chlorohydridobis(diphenylmethylphosphine)palladium(II), IVa

A solution of $[Pd(st)(PMePh_2)_2]$ (IIa) was prepared by the reaction of $[PdEt_2(PMePh_2)_2]$ (0.43 g, 0.75 mmol) and styrene (170 µl, 1.3 mmol) in toluene (8 ml). After the evolved gas was removed by pumping, dry HCl gas, which was produced from NaCl (0.063 g, 1.08 mmol) and excess conc. H_2SO_4, was introduced to the system in vacuo at —198° C. The solution was stirred at —78° C to yield a white precipitate instantly. The product was filtered, washed with cold hexane, dried at 0° C in vacuo and recrystallized from acetone to yield white crystals of $[Pd(H)Cl(PMePh_2)_2]$ (IVa) (0.19 g, 45%). Found: Pd, 19.7. Calcd. for $PdC_{26}H_{27}ClP_2$: Pd, 19.6%. Similarly obtained were $[Pd(H)Cl(PEtPh_2)_2]$ (IVb) (42%) and $[Pd(H)Cl(PEt_2Ph)_2]$ (IVc) (66%).

Reaction of dimethylpalladium complexes with olefins

Methyl acrylate (ma) (ca. 2 ml) was distilled over calcium hydride under vacuum into a flask containing $[PdMe_2(PEt_3)_2]$ (0.18 g, 0.49 mmol). On stirring the mixture at room temperature for 17 h, a yellow solution containing poly(methyl acrylate) was obtained. Evolution of gas (0.39 mmol, 80% on the basis of the initially used complex) was confirmed by means of GLC. The similar reactions of olefins with dimethylpalladium complexes IIIa and IIIb yielded the corresponding polymers as shown in Table 5.

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