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Dialkylpalladium(II) Complexes. Syntheses, Characterizations, and Reactions with CO, I_2, and CH_3I

Takashi Ito, Hirotaka Tsuchiya, and Akio Yamamoto

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The reaction of bis(acetylacetonato)palladium(II), $[Pd(acac)_2]$ with $AlR_2(OEt)$ in the presence of tertiary phosphine, L, in diethyl ether yields a series of dialkylpalladium(II) complexes, $[PdR_2L_2]$, where R=Me, Et, and Pr^n; L=PEt_3, PPh_2Me, and $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$ (dpe). These complexes were characterized by means of elemental analysis, IR and ^{1}H-NMR spectra and of some decomposition reaction such as thermolysis and acidolysis. The *trans-* and *cis*-configurations of $[PdMe_2L_2]$ (L=PEt_3 and PPh_2Me, respectively) in solution were established on the basis of the ^{1}H-NMR spectra. The examination of ^{1}H-NMR spectra in the presence of tertiary phosphine suggests the ligand exchange processes promoted by the added phosphine. $[PdR_2L_2]$ (L=PEt_3 and PPh_2Me) reacted with CO in toluene to yield the quantitative amounts of the corresponding dialkyl ketones. The reactions of the complexes $[PdR_2L_2]$ with iodine afforded $[PdI_2L_2]$ and RI, and of $[PdR_2(dpe)]$ with MeI gave CH_3H, CH_3CH_3, R(−H), RH, R·CH_3, R·R, and RI together with $[PdI_2L_2]$, suggesting the presence of a quadrivalent, six-coordinate intermediate palladium species.

Among the transition elements, palladium and its compounds are known to show the most versatile catalytic activities, which include olefin oxidation (Hoechst-Wacker process), oligomerization, carbonylation, vinylation, acetoxylation, isomerization, and hydrogenation of olefins, dienes and acetylenes.[1] In most of these catalytic reactions, formation of the intermediate species possessing an unstable palladium-carbon σ-bond is thought to constitute one of the key steps.[1] In this respect, the systematic studies of the alkylpalladium complexes are expected to provide the useful information related to the mechanistic aspect of the catalytic reactions and to the exploitation of the new catalytic processes.

Since the first syntheses of the methylpalladium complexes by Calvin and Coates in 1960,[2] various kinds of methylpalladium complexes have been prepared:[3] the preparation method includes alkylation of halogenopalladium(II) complex with methyl Grignard reagent or methyllithium,[2] and with dimethyl(1,5-cyclooctadiene)platinum(II),[4] and oxidative addition of methyl halide to the palladium(0) complex.[5,6] The isolation of the ethylpalladium complex, on the other hand, has been limited to only one example: diethyl{1,2-bis(dicyclohexylphosphino)ethane}palladium(II) which was prepared by the reaction of $[Pd(acac)_2]$ (acac=acetylacetonato) with diethylaluminum monoethoxide in the presence of a tertiaryphosphine ligand under the atmosphere of ethylene.[7] Following our systematic studies on the preparations of series of alkyl complexes of Cr,[8] Fe,[9] Co,[10] Ni,[11] and Cu[12] by the use of alkylaluminum compounds as the alkylating agent, we succeeded in the isolation of the series of dialkylpalladium complexes by the analogous method. Alkylation of bis(acetylacetonato)palladium by alkylaluminum compounds has the advantage over the conventional alkylation reaction using palladium halides and alkyllithium or Grignard reagent in that the product can be isolated simply by the filtration and washing with some organic solvents such as hexane. This merit enables the reaction product isolable even if it is susceptible to water and is stable only at the low temperature.

Here we report the preparation, characterization and some reactions of the series of dialkylpalladium complexes with tertiary phosphine ligands. Zerovalent complexes, such as $[Pd(PPh_3)_4]$,[13] $[Pd(CO)(PPh_3)_3]$,[14] $[Pd(CO)PPh_3]_n$,[14] $[Pd_3(CO)_3(PPh_3)_4]$,[14] $[Pd(C_2H_4)(PPh_3)_2]$,[7] and $[Pd\{P(C_6H_{11})_3\}_2]$,[15] and diethyl and dihydrido complexes, $[PdEt_2\{(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2\}]$[7] and $[PdH_2\{P(C_6H_{11})_3\}_2]$,[15] have been hitherto reported as reaction products between palladium acetylacetonate and alkylaluminum compounds.

Results and Discussion

Preparation of Dialkylpalladium Complexes. The reaction of $[Pd(acac)_2]$, tertiary phosphine, L, and dialkylaluminum monoethoxide (molar ratio, 1 : 2 : 3—5) in diethyl ether under a nitrogen atmosphere afforded a series of dialkylpalladium complexes.

$$[Pd(acac)_2] + 2L + AlR_2(OEt) \rightarrow [PdR_2L_2]$$

L = PEt_3, R = Me, **1a**; Et, **2a**; and Pr^n, **3a**.

L = PPh_2Me, R = Me, **1b**; Et, **2b**; and Pr^n, **3b**;

L = $\frac{1}{2}$dpe, R = Me, **1c**; Et, **2c**; and Pr^n, **3c**.

(dpe=$Ph_2PCH_2CH_2PPh_2$)

The results of the elemental analysis for these complexes are listed in Table 1 together with their decomposition points measured *in vacuo*. Among the complexes, $[PdMe_2(PEt_3)_2]$(**1a**)and $[PdMe_2(dpe)]$(**1c**) have been already prepared by Calvin and Coates by the method employing methyllithium as an alkylating agent.[2] The complexes, white solid except for complex **2c**, which is yellow, are diamagnetic and mostly sensitive to air. When L=PEt_3, ethyl and propyl complexes, **2a** and **3a**, are thermally unstable and decompose at room temperature even under a nitrogen atmosphere. Thermal stability increases in the order of PEt_3<PPh_2Me<dpe for the complexes with the same alkyl groups, and of $Pr^n(n\text{-}C_3H_7)$<Et<Me for those with the same phosphine ligands. The latter series of stability suggests that the mechanism involving β-hydrogen abstraction[16] is operative in the thermal decomposition of these complexes *(vide infra)*. The solubility of the complexes depends mostly on the phosphine ligand. On the whole the complexes with PEt_3 are soluble in most organic

Table 1. Analytical data and decomposition points of $[PdR_2L_2]$

Compounds		Analysis (%)[a] C	H	Pd	Dec. pt.[b] °C
$[PdMe_2(PEt_3)_2]$	**1a**	44.7(45.1)	10.4(9.7)	28.7(28.5)	56—64
$[PdEt_2(PEt_3)_2]$	**2a**	——[c]	——[c]	26.9(26.5)	<20
$[PdPr^n_2(PEt_3)_2]$	**3a**	——[c]	——[c]	24.4(24.8)	<20
$[PdMe_2(PPh_2Me)_2]$	**1b**	63.2(62.6)	6.5(6.0)	19.0(19.8)	110—115
$[PdEt_2(PPh_2Me)_2]$	**2b**	64.5(63.8)	7.2(6.4)	18.7(18.8)	73—76
$[PdPr^n_2(PPh_2Me)_2]$	**3b**	63.9(64.9)	6.9(6.8)	17.8(18.0)	58—63
$[PdMe_2(dpe)]$	**1c**	62.3(62.9)	6.0(5.6)	19.6(19.9)	166—168
$[PdEt_2(dpe)]$	**2c**	62.6(64.0)	6.3(6.1)	19.2(18.9)	144—148
$[PdPr^n_2(dpe)]$	**3c**	64.6(65.0)	7.1(6.5)	18.4(18.0)	132—140

a) Calculated values are in parentheses. b) Decomposition points were measured on a hot stage with a sample in a small capillary sealed under vacuum and are uncorrected. c) The complexes were too unstable to obtain good micro-analytical results.

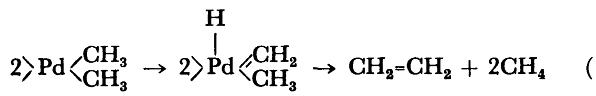
Table 2. Gases evolved by the decomposition of $[PdR_2L_2]$

Compounds $[PdR_2L_2]$ R	L		Thermolysis[a] Temp °C	Evolved gases, Molar ratio R(−H)	RH	R·R	others	$\sum R$[c] %	Acidolysis[b] Evolved gases Molar ratio	$\sum R$[c] %
Me	PEt_3	**1a**	70	—	trace[f]	0.90[f]	C_2H_4(0.10)[f]	130	d)	
Et	PEt_3	**2a**	35	0.38	0.62	0	—	80	C_2H_6(1.0)	40
Pr^n	PEt_3	**3a**	40	0.50	0.50	d)	—	55[g]	C_3H_8(1.0), C_2H_6 (trace)[h]	25
Me	PPh_2Me	**1b**	100	0	0	1.00	—	75	d)	
Et	PPh_2Me	**2b**	70	0.50	0.50	0	—	95	C_2H_6(1.0)	60
Pr^n	PPh_2Me	**3b**	70	0.50	0.50	d)	—	85[g]	C_3H_8(1.0), C_2H_6 (trace)[h]	35
Me	$\frac{1}{2}$dpe	**1c**	170	—	0.01	0.92	C_2H_4(0.07)	70	CH_4(1.0)	100
Et	$\frac{1}{2}$dpe	**2c**	145	0.31	0.22	0.47	—	45	C_2H_6(1.0)	65
Pr^n	$\frac{1}{2}$dpe	**3c**	220	0.30	0.20	d)	C_2H_4(0.50)	10[g]	C_3H_8(0.8), C_3H_6(0.2) C_2H_6 (trace)[e],[h]	15

a) Thermolysis *in vacuo*. b) Acidolysis by concd H_2SO_4. c) $\sum R = \{\text{moles}(R(-H)+RH+2R\cdot R+\text{others})/2\text{mol (complex)}\}\times 100$. d) Not investigated. e) Besides the hydrocarbons, the evolved gas contained H_2 (0.54 mol/mol of the complex). f) The similar results have been reported by Calvin and Coates, see Ref. 2. g) The figures do not include the possible non-gaseous product, R·R (hexane). h) Ethane might have come from the trace amounts of diethylpalladium impurities possibly produced by $AlEt_2(OEt)$ contaminated in $AlPr^n_2(OEt)$.

solvents while those with dpe are scarcely soluble. Thus, complex **1a** was recrystallized from hexane and **2a**, **3a**, **1b**, **3b**, and **1c** from acetone. The rest failed to be recrystallized.

Decomposition of the Complexes. Thermolysis of the dialkyl complexes released the corresponding alkene (R(–H)) and alkanes (RH and R·R) as are shown in Table 2. The formation of ethylene and methane in the thermolysis of dimethyl complexes, **1a** and **1c**, suggests the possibility of occurrence of the following α-elimination reaction as has been reported for $[FeMe_2(dpe)_2]$.[17]



$$2\rangle Pd\langle{}^{CH_3}_{CH_3} \rightarrow 2\rangle \overset{H}{\underset{|}{Pd}}\langle{}^{CH_2}_{CH_3} \rightarrow CH_2{=}CH_2 + 2CH_4 \quad (1)$$

As the alternative source of ethylene, the alkyl groups in the tertiary phosphine ligand cannot be ruled out at present. In fact a high value of $\sum R$ in the case of **1a** (130%) may be ascribed to the decomposition of triethylphosphine which might be catalyzed by Pd moiety.

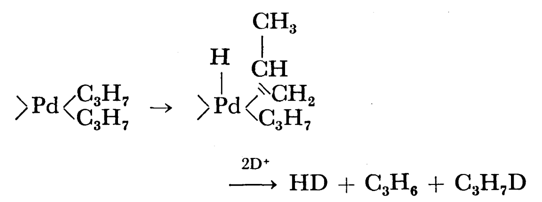
Decomposition of the complexes with concd H_2SO_4 evolved mainly the corresponding alkane (R·H). The results are included in Table 2. The reason for evolution of smaller amounts of the gases as compared with the theoretical amount (except for methyl complex **1c**) may be ascribed to the dissolution of the product gases into sulfuric acid. The acidolysis of propyl complex **3c** evolved H_2 and propene, together with propane. The decomposition of **3c** with D_2SO_4 evolved hydrogen gas which was consisted mainly of HD (0.84) together

Table 3. IR[a] and ^{1}H-NMR[b] spectral data of [PdR$_2$L$_2$]

Compounds		IR data			^{1}H-NMR data[g]			
		νC-H[c]	δC-H[d]	νPd-C	Solvent	Temp/°C	Rd-R signals	PR$_3$′ signals
[PdMe$_2$(PEt$_3$)$_2$]	**1a**	2900 s	1130 m	455 s	(CD$_3$)$_2$CO	25	−0.61 (t; J=5.5, 6H, Pd-C$\underline{\mathrm{H}}_3$)	1.75 (m, 12H, P-C$\underline{\mathrm{H}}_2$-) 1.10 (qu; J=8.0, 18H, P-C-C$\underline{\mathrm{H}}_3$)
[PdEt$_2$(PEt$_3$)$_2$]	**2a**	2875 s 2825 s	1145 s 1360 m	455 s	(CD$_3$)$_2$CO	25	0.33 (q; J=8.0, 4H, Pd-C$\underline{\mathrm{H}}_2$-) 1.12 (qu; J=8.0, 24H, Pd-C-C$\underline{\mathrm{H}}_3$+P-C-C$\underline{\mathrm{H}}_3$)	1.82 (m, 12H, P-C$\underline{\mathrm{H}}_2$-)
[PdPr$^n_2$(PEt$_3$)$_2$]	**3a**	2855 s 2805 s	1125 s 1360 m 785 m	(560 s)[e]	(CD$_3$)$_2$CO	25	0.32 (m, Pd-C-(C$\underline{\mathrm{H}}_2$-) 1.19 (qu; J=8.0, Pd-C$\underline{\mathrm{H}}_2$-C-C$\underline{\mathrm{H}}_3$+P-C-C$\underline{\mathrm{H}}_3$)	1.75 (m, P-C$\underline{\mathrm{H}}_2$-)
[PdMe$_2$(PPh$_2$Me)$_2$]	**1b**	2860 s	1125 s	475 s	(CD$_3$)$_2$CO	25	0.10 (q,[h] 6H, Pd-C$\underline{\mathrm{H}}_3$)	1.58 (d; J=5.0, 6H, P-C$\underline{\mathrm{H}}_3$)
[PdEt$_2$(PPh$_2$Me)$_2$]	**2b**	2890 s 2830 s	1140 m 1355 m	455 s	C$_6$D$_5$CD$_3$	−40	1.04 (br, Pd-C$_2\underline{\mathrm{H}}_5$)	1.83 (s, P-C$\underline{\mathrm{H}}_3$)
[PdPr$^n_2$(PPh$_2$Me)$_2$]	**3b**	2880 s 2850 w 2810 s	1120 s 1360 m	(560 s)[e]	(CD$_3$)$_2$CO	−40	0.27 (br, Pd-C$\underline{\mathrm{H}}_2$-C-C$\underline{\mathrm{H}}_3$) 0.90 (br, Pd-C-C$\underline{\mathrm{H}}_2$-)	1.70 (br, P-C$\underline{\mathrm{H}}_3$)
[PdMe$_2$(dpe)]	**1c**	2845 m	1130 m	f)	CH$_2$Cl$_2$	25	0.31 (t; J=7.0, 6H, Pd-C$\underline{\mathrm{H}}_3$)	2.26 (d; J=18, 4H, P-C$\underline{\mathrm{H}}_2$-)
[PdEt$_2$(dpe)]	**2c**	2900 s 2815 s	1140 s 1360 m	f)	C$_5$H$_5$N	25	1.96 (br, Pd-C$\underline{\mathrm{H}}_2$-) 1.72 (br, Pd-C-C$\underline{\mathrm{H}}_3$)	2.31 (d; J=18, P-C$\underline{\mathrm{H}}_2$-)
[PdPr$^n_2$(dpe)]	**3c**	2900 s 2850 s 2810 m	1135 m 1360 w 785 m	f)	C$_6$D$_5$CD$_3$	−40	1.23 (br, Pd-C-C$\underline{\mathrm{H}}_2$-C$\underline{\mathrm{H}}_3$) 0.90 (br, Pd-C$\underline{\mathrm{H}}_2$-)	1.68 (d; J=18, P-C$\underline{\mathrm{H}}_2$-)

a) KBr disc, in cm^{-1}. b) 100 MHz, chemical shifts are in δ values (ppm) with respect to tetramethylsilane as an external standard (down field positive). Coupling constants, J, are in Hz. c) ν(C-H) of the coordinated alkyl group. d) The band due to the C-H deformation of the palladium-bonded methyl group and may contain contribution due to the other vibrations. e) The assignments are not certain, see text. f) ν(Pd-C) were not discernible from the complicated bands due to dpe. g) Multiplicity abbreviations are: s, singlet; t, triplet; q, quartet; qu, quintet, m, multiplet; br, broad singlet. h) An abnormal quartet, see Fig. 1 and text.

with minor amounts of H_2 (0.05) and D_2 (0.11) as analyzed by mass spectrometry. These results suggest the presence of such a β-elimination process as shown in Eq. 2, in addition to the normal protonation of propyl group with D_2SO_4 to yield propane-d_1.



$$>\mathrm{Pd}\begin{matrix}C_3H_7\\C_3H_7\end{matrix} \rightarrow >\overset{H}{\mathrm{Pd}}\begin{matrix}CH(CH_3)\cdots CH_2\\C_3H_7\end{matrix} \xrightarrow{2D^+} HD + C_3H_6 + C_3H_7D \qquad (2)$$

Infrared Spectra of the Complexes. [PdR_2L_2]. The representative absorption assignable to ν(C–H), δ(C–H) *etc.* of the coordinated alkyl group are listed in Table 3 together with Pd–C stretching vibrations. These assignments were made by comparing the spectra each other and with those of the corresponding dichloro complexes, [$PdCl_2L_2$].

Somewhat different frequencies from those observed for our complexes were reported by Calvin and Coates for the methyl complex **1a**,[2] *i. e.*, δ(C–H)$=1164$ and ν(Pd–C)$=491$ and 457 cm^{-1}. The difference in the configuration of the complex might have caused such differences (as for the discussion about the configurations of the complexes, see the following section). The palladium-carbon stretching frequencies of the dimethyl and diethyl complexes with L$=PEt_3$ and $P(Ph_2Me)_3$ are observed in the region of 455—475 cm^{-1} which is lower than those of the corresponding Pt complexes (495—525 cm^{-1}),[18] reflecting the weaker Pd–C bond than Pt–C.

The ^{1}H-NMR Spectra of the Complexes, [PdR_2L_2]. The results of the ^{1}H-NMR measurements of the dialkyl complexes are included in Table 3. Some complexes are unstable in the solution even at low temperatures making their assignments somewhat tentative. The spectra of [$PdEt_2(PPh_2Me)_2$] (**2b**) and [$PdPr^n{}_2L_2$] (L$=PEt_3$, **3a** and PPh_2Me, **3b**) accompanied the weak signals due to ethane and propane, respectively, which may be formed by partial decomposition of the original complexes in solution. For the dimethyl complexes, [$PdMe_2L_2$], well resolved spectra were obtained and are reproduced in Fig. 1 for L$=PEt_3$ (**1a**) and PPh_2Me (**1b**).

The apparent doublet of the phosphine–methyl signal in **1b** suggests that the complex is in *cis* configuration.[19,20] This is further supported by observation of the complicated pattern of Pd–C$\underline{H}_3$ signal centered at 0.10 ppm, the pattern of which is very close to those of Pt–C$\underline{H}_3$ signals reported for *cis*-[$PtMe_2L_2$].[21–25] In contrast to the *cis* configuration of [$PdMe_2(PPh_2Me)_2$], **1b**, the triethylphosphine complex, [$PdMe_2(PEt_3)_2$], **1a**, was found to possess trans configuration. As is shown in Table 3 and Fig. 1, palladium-bonded methyl protons in **1a** resonates at -0.61 ppm as a triplet due to the coupling with two equivalent phosphorus atoms present in mutually trans positions. The apparent quintet pattern of the methyl protons in the phosphine ligand is also characteristic of the *trans*-bis(triethylphosphine) complexes.[26]

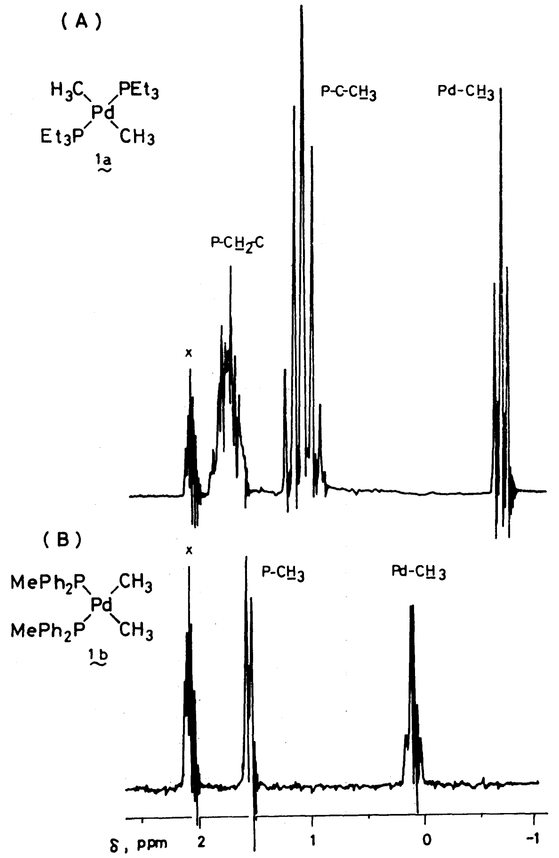


Fig. 1. ^{1}H-NMR spectra (100 MHz, methyl and methylene region) of the complexes, [$PdMe_2L_2$], L$=PEt_3$ **1a** (A) and PPh_2Me **1b** (B) in $(CD_3)_2CO$ at 25 °C. The sign x refers to the solvent impurities.

The same dimethyl complex as **1a** has been prepared by Calvin and Coates *via* methylation of [$PdCl_2(PEt_3)_2$] with methyllithium.[2] Although no ^{1}H-NMR spectral data have been reported, they assumed *cis* configuration for the complex through the dipole moment measurement. Furthermore, a slow isomerization in the solution from *cis* to trans as monitored by a decrease in the dipole moment has been suggested. In fact, the ^{1}H-NMR spectrum taken in $(CD_3)_2CO$ by us for [$PdMe_2(PEt_3)_2$] prepared by Calvin and Coates' method[2] showed two sets of Pd–C$\underline{H}_3$ signals, one at 0.01 ppm as a deformed quartet characteristic of the *cis*-dimethyl complex *(vide supra)* and the other at -0.67 ppm as a triplet corresponding to the *trans*-dimethyl isomer. These findings indicate that the product contains both cis and trans isomers in accord with the observation by Calvin and Coates.[2]

The ^{1}H-NMR spectra of the solutions of diethyl complexes, either after being heated at *ca.* 40 °C (for **2a**) or kept at room temperature for several days (for **2b**), indicated the formation of the ethylene-coordinated complex with the accompnaying evolution of ethane. As is shown in Fig. 2, the very small signals at 0.86 and 2.90 ppm observed in the spectrum of the freshly prepared acetone-d_6 solution of **2a** (Fig. 2A) grew considerably on heating the solution at the expense of the quartet at 0.33 ppm assigned to the palladium-attached methylene protons (Fig. 2B). A sharp singlet at 0.86 ppm in Fig. 2B can be assigned to ethane evolved

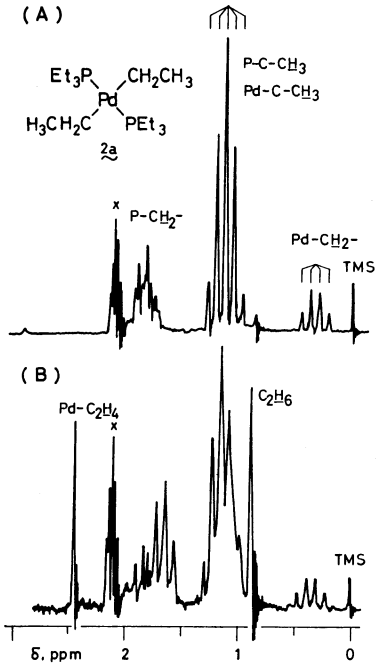
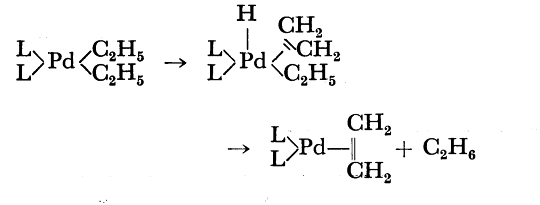


Fig. 2. ^{1}H-NMR spectra of $[PdEt_2(PEt_3)_2]$ **2a** in $(CD_3)_2CO$ at 25 °C. (A) Freshly prepared sample solution. (B) After being heated at 40 °C. The signals x refer to the solvent impurities.

whereas the one at 2.42 ppm (shifted upfield from the initial position of 2.90 ppm in Fig. 2A) to the coordinated ethylene protons. The similar values of the chemical shifts of the coordinated ethylene protons have been reported for $[Ni(C_2\underline{H}_4)(PPh_3)_2]$ (2.55 ppm in toluene-d_8)[27] and $[Pt(C_2\underline{H}_4)(PPh_3)_2]$ (2.41 ppm in toluene-d_8).[27] $[Pd(C_2\underline{H}_4)(PPh_3)_2]$ prepared by the method reported by van der Linde and de Jongh[7] had the value of 2.88 ppm in acetone-d_6 at 25 °C. In the case of PPh_2Me complex **2b**, the proton resonance of the coordinated ethylene appeared at 3.64 ppm as a broad singlet, which is somewhat lower than the other coordinated ethylenes. The complete absence of the signal in the region of free ethylene (5.35 ppm in toluene-d_8)[27] suggests that ethylene, evolved by the decomposition of the diethyl complex according to the following equation, coordinates to palladium preferentially to form the zero-valuent ethylene complex.



$$\begin{matrix}L\\L\end{matrix}\!\!>\!Pd\!<\!\begin{matrix}C_2H_5\\C_2H_5\end{matrix} \rightarrow \begin{matrix}L\\L\end{matrix}\!\!>\!\overset{\overset{H}{|}}{Pd}\!<\!\begin{matrix}CH_2\\ \cdot\!\cdot CH_2\\C_2H_5\end{matrix} \rightarrow \begin{matrix}L\\L\end{matrix}\!\!>\!Pd\!-\!\begin{matrix}CH_2\\ \|\\CH_2\end{matrix} + C_2H_6 \qquad (3)$$

Attempted isolation of the ethylene complex by treatment of **2b** with excess ethylene in toluene failed.

Some evidence for the ligand exchange in the dimethyl complexes **1a** and **1b** was obtained by measuring the ^{1}H-NMR spectra in the presence of added phosphine ligand. Addition of PEt_3 to the solution of $[PdMe_2(PEt_3)_2]$ **1a** caused the ^{1}H-NMR spectral change from the triplet to a singlet for the $Pd–C\underline{H}_3$ signal, from the multiplet to a quartet for the $P–C\underline{H}_2–$ signal and from the quintet to a triplet for the $P–C–C\underline{H}_3$ signal. The existence of a rapid exchange between the coordinated and dissociated PEt_3 has been demonstrated for $[CoMe_2(acac)(PEt_3)_2]$, where triplet, quintet and multiplet signals of the protons due to, respectively, $Co–C\underline{H}_3$, $P–C–C\underline{H}_3$, and $P–C\underline{H}_2–$, at −20 °C changes to singlet, triplet, and quartet, respectively, at 0 °C.[10c] The similar dissociation-exchange process has been observed for $[NiMe_2(PEt_3)_2]$ whose NMR at 25 °C consists of a siglet due to $Ni–C\underline{H}_3$, a triplet due to $P–C–C\underline{H}_3$, and a quartet assignable to $P–C\underline{H}_2$-protons.[28] The monomethyl complex $[PdMeCl(PEt_3)_2]$ also behaves quite similarly.

The ^{1}H-NMR spectrum of a mixture of $[PdMe_2(PPh_2Me)_2]$ and PPh_2Me at −40 °C in acetone-d_6 showed the resonances of the methyl protons of free $PPh_2\underline{Me}$ at 1.66 ppm as a singlet, of coordinated $PPh_2\underline{Me}$ at 1.49 ppm as a doublet (J=5 Hz) and of $Pd–C\underline{H}_3$ at 0.0 ppm, which appears as a distorted quartet as mentioned previously but is somewhat ill-resolved in the present spectrum. The reason for the absence of phosphorus coupling in the methyl proton signal of free PPh_2Me is uncertain. On raising the temperature to 25 °C, the methyl protons of the coordinated and uncoordinated PPh_2Me collapsed to a broad singlet at 1.6 ppm and the resonance due to $Pd–C\underline{H}_3$ also changed to a broad singlet at 0.04 ppm. The existence of the free phosphine ligand may be accelerating the exchange of the phosphine ligand and the exchange rate may be enhanced at the higher temperature. The similar ligand exchange process has been reproted for $[NiR(acac)(PPh_3)_{1\text{ or }2}]$.[29]

Reactions of Dialkylpalladium Complexes with Carbon Monoxide. Booth and Chatt have reported that the reaction of carbon monoxide with monomethyl complex, $[PdMeCl(PEt_3)_2]$, afforded the acyl complex $[Pd(COMe)Cl(PEt_3)_2]$, while the reactions with dimethyl complexes $[PdMe_2L_2]$ either gave uncharacterizable product ($L=PEt_3$) or led to decomposition ($L=\frac{1}{2}$ dpe).[30]

Introduction of carbon monoxide into the toluene solution of dialkyl complexes $[PdR_2L_2]$ ($L=PEt_3$ and PPh_2Me; R=Me, Et, and Pr^n) at *ca.* 1 atm afforded immediately a red clear solution, whose GLC analysis indicated the formation of a quantitative amount of the corresponding dialkyl ketone. None of alkanes, alkenes and α-diketones were detected in the system. The red solution was unstable in the absence of carbon monoxide and the removal of the solvent by evaporation *in vacuo* left a viscous yellow oil whose IR spectra showed the characteristic C≡O stretching band at 1800 and 1805 cm^{-1} for the PEt_3 and PPh_2Me complexes, respectively. This result suggests formation of carbonyl complexes, which may possibly be related to the reported palladium-carbonyl complexes, $[Pd(CO)(PPh_3)_3]$, $[Pd(CO)PPh_3]_n$ or $[Pd_3(CO)_3(PPh_3)_4]$[14]. However, purification and characterization of the complexes were not successful. Monitoring the reaction of $[PdEt_2(PPh_2Me)_2]$ with CO in toluene-d_8 by means of ^{1}H-NMR spectroscopy also supported the formation of a zero-valent palladium carbonyl complex as well as of diethyl ketone, since the spectrum consisted of the signals due to diethyl ketone (0.90 ppm, triplet, $J\approx7$ Hz, 4H, $–C\underline{H}_2–$ and 1.87 ppm, quartet, $J\approx7$ Hz, 6H, $–C\underline{H}_3$) and the coordinated PPh_2Me (1.59 ppm, doublet, $J\approx7$ Hz, 6H, $P–C\underline{H}_3$).

$$[PdR_2L_2] + CO \rightarrow \{Pd(COR)RL_2\} \xrightarrow{CO} R_2CO + [Pd_x(CO)_yL_z]$$

Dialkylcobalt(III) complexes $[CoR_2(acac)(PR'_3)_2]$, have also been found to give the corresponding dialkyl ketones, $R_2C{=}O$, in a quantitative yield on the reaction with carbon monoxide,10) while $[CuR(PR_3)_n]$ and $[NiR_2(bpy)]$ (bpy=2,2′-bipyridine) afforded ketones and/or diketones whose relative yield depended on the conditions employed.12a,31) The formation of biacetyl by the reaction of CO with $[PtMe_2(PEt_3)_2]$ has been reported.30) The acyl complexes which are considered to be the intermediates of the ketone or α-diketone formation have been isolated when $[NiR(acac)(PPh_3)_2]$,32) $[CoMe(dpe)_2]$,10a,33) and $[MRX(PEt_3)_2]$ (M=Pd and Pt, X=halogen, NCS, NO_2, and NO_3)30) were allowed to react with carbon monoxide.

The reactions of $[PdR_2(dpe)]$ with carbon monoxide led to the decomposition of the complex evolving ethane (when R=Me) and ethylene and ethane (when R=Et). When R=Pr^n, dipropyl ketone was formed in 17% yield with concomitant evolution of propane.

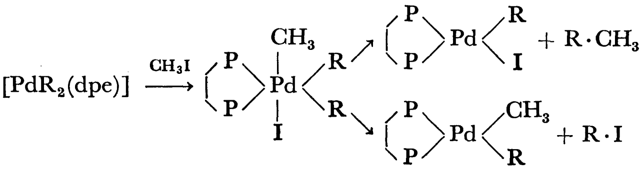
Reactions of Dialkyl Palladium Complexes with Iodine. Diethyl and dipropyl complexes of palladium $[PdR_2L_2]$ in benzene reacted with excess amounts of iodine at room temperature to yield di-iodo complex $[PdI_2L_2]$ (as analyzed by IR spectra and elemental analyses), the corresponding alkyl iodide, RI, and the gases such as ethylene and ethane when R=Et and propylene and propane when R=Pr^n (Table 4). The analogous reaction involving dimethyl(bipyridine)palladium and iodine to produce methyl iodide and $[PdI_2(bpy)]$ has been reported by Maitlis and Stone.34)

TABLE 4. THE REACTION PRODUCTS OF $[PdR_2L_2]$ AND I_2

Compounds		Molar ratio		$\sum R$a)	RI
		R(−H)	R·H	%	%
$[PdEt_2(PEt_3)_2]$	**2a**	0.42	0.58	30	trace
$[PdPr^n_2(PEt_3)_2]$	**3a**	0.06	0.94	3	54
$[PdPr^n_2(PPh_2Me)_2]$	**3b**	0.33	0.67	9	37
$[PdEt_2(dpe)]$	**2c**	0.40	0.60	10b)	74
$[PdPr^n_2(dpe)]$	**3c**	c)	c)	c)	18

a) $\sum R = \{mol(R(-H) + R\cdot H)/2\,mol(complex)\} \times 100$ where R(−H) corresponds to C_2H_4 (R=Et) and C_3H_6 (R=Pr^n) and R·H to C_2H_6 (R=Et) and C_3H_8 (R=Pr^n). b) R contained a trace amount of C_4H_{10}. c) Not measured.

Reactions of $[PdR_2(dpe)]$ with Methyl Iodide. Addition of methyl iodide to $[PdR_2(dpe)]$(R=Me, **1c**; Et, **2c**; and Pr^n, **3c**) *in vacuo* yielded a clear red solution from which a yellow solid precipitated with the accompanying evolution of gases and alkyl iodides. The yellow powder thus obtained was identified as $[PdI_2(dpe)]$ by means of IR spectroscopy. When R is CH_3, the evolved gas was mainly ethane containing a trace of methane. The amount of the produced RI (CH_3I) could not be measured because of the presence of the unreacted CH_3I. As is shown in Table 5, the gases evolved by the reactions of diethyl and dipropyl complexes (**2c** and **3c**) with CH_3I contained C_1 to C_4 hydrocarbons. The formation of propane as well as ethyl iodide in the case of diethyl complex and of ethane, butane, and propyl iodide in the case of dipropyl complex by the reactions with CH_3I, suggest the formation of intermediate Pd(IV) species as shown below.



(5)

Beside the above equation, a number of processes may be postulated as the routes to yield the products listed in Table 5. Whichever process the reaction may follow, the six-coordinate palladium(IV) species seems to play an important role in these reactions. Although little has been known about the palladium(IV) compounds, quadrivalent platinum compounds have been amply reported including $[PtMe_2I_2(PEt_3)_2]$,35) $[Pt(tolyl)RI_2(py)_2]$,36) $[PtMeRX_2(PMe_2Ph)_2]$,23,37) and $[PtMe_2RX(PMe_2Ph)_2]$23,37,38) which were prepared by the oxidative addition of alkyl or aryl halide to the corresponding bivalent platinum-dialkyl or -alkyl halide complexes. Furthermore, the products of the thermal decomposition of series of platinum(IV) alkyl halide complexes have been studied38,39) and the formation of ethane, methyl chloride and $[PtClMe(PMe_2Ph)_2]$ has

TABLE 5. THE REACTION PRODUCTS OF $[PdR_2(dpe)]$ AND EXCESS CH_3I

Compounds		Products						
		CH_4	Molar ratio					RI
		mol/mol·Pd	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	mol/mol·Pd
$[PdMe_2(dpe)]$	**1c**	trace	0	1.00 (R·R)	0	0	0	a)
$[PdEt_2(dpe)]$	**2c**	0.52	0.23 (R(−H))	0.36 $\begin{pmatrix}R\cdot H\\CH_3\cdot CH_3\end{pmatrix}$	0	0.35 ($R\cdot CH_3$)	0.06 (R·R)	0.22
$[PdPr^n_2(dpe)]$	**3c**	0.19	0	0.12 ($CH_3\cdot CH_3$)	0.34 (R(−H))	0.21 (R·H)	0.33 ($R\cdot CH_3$)	0.26

a) Not measurable, see text.

been observed when $[PtClMe_3(PMe_2Ph)_2]$ was heated at 170 °C.[39] The attempted isolation of the intermediate Pd(IV) species in the reaction of $[PdEt_2(dpe)]$ **2c** with CH_3I by quenching the red clear solution by the addition of Et_2O was not successful, but the orange powder which may be a mixture of several kinds of Pd complexes including $[PdI_2(dpe)]$ was obtained. Evolution of CH_4 as well as C_2H_6 on decomposition of the orange powder with H_2SO_4 indicates the presence of $Pd–CH_3$ species in the mixture as the result of oxidative addition of CH_3I to **2c**.

In the metathesis reaction of $[PdMe_2(bpy)]$ with perfluoropropyl iodide to yield either $[PdMe(C_3F_7)(bpy)]$ (when equimolar amount of n-C_3F_7I was employed) or $[Pd(C_3F_7)_2(bpy)]$(excess C_3F_7I), Maitlis and Stone postulated the quadrivalent six-coordinate palladium intermediate, $[PdMe_2(C_3F_7)I(bpy)]$,[34] although the other possible by-products, MeI, $Me\cdot C_3F_7$, *etc.* have not been detected.

Experimental

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

Infrared spectra were recorded on Hitachi EPI–G3 and 295 spectrometers using KBr pellets prepared under an inert atmosphere. NMR spectra were measured on JEOL PS–100 spectrometer by Mr. Y. Nakamura of our reseach laboratory to whom we are indebted. ^{1}H-NMR signals are referred to tetramethylsilane as internal standard unless otherwise stated. Analysis of the gases evolved by the reaction or decomposition of the alkyl complexes was carried out by mass spectrometry and/or gas chromatography (Shimadzu GC–3BT) after collecting gases fractionally using a Toepler pump, by which the volumes of gases were also measured. Micro analyses (C, H, and halogens) were carried out by Mr. T. Saito of our laboratory using Yanagimoto CHN Autocorder Type MT-2 (for C and H analyses). Analysis of palladium content was performed by EDTA-back titration method using $Zn(NO_3)_2$ aqueous solution. The complete ionization of the palladium metal in the complex was achieved by treating the sample with a hot aqua regia.

Triethylphosphine (Strem) was used as purchased. Diphenylmethylphosphine[40] and 1,2-bis(diphenylphosphino)-ethane[41] were prepared by the literature method starting from PPh_2Cl (Strem) and PPh_3 (kindly donated by Ihara Chemical Industry Co. Ltd.), respectively. Dialkylmonoethoxyaluminums, $AlR_2(OEt)$ ($R=Me$, Et, and Pr^n), were prepared by the reactions of the corresponding trialkylaluminums and the equimolar amount of ethanol at a low temperature. $[PdCl_2L_2]$ ($L=PEt_3$ and PPh_2Me) were prepared by the analogous way as reported for $[PdCl_2\{tris(dimethylamino)phosphine\}_2]$.[42] $[PdCl_2(dpe)]$ was obtained from $PdCl_2$ and dpe according to the method described in the literature.[30] The monomethyl complex, $[PdMeCl(PEt_3)_2]$ was prepared by the methylation of $[PdCl_2(PEt_3)_2]$ with MeMgBr in Et_2O.[2]

*Preparation of Dimethylbis(triethylphosphine)palladium(II), **1a**.* To a yellow heterogeneous mixture of $[Pd(acac)_2]$ (1.5 g, 5.0 mmol), PEt_3 (1.5 cm^3, 10 mmol) and 30 ml of diethyl ether cooled at −70 °C, $AlMe_2(OEt)$ (3.0 cm^3, 18 mmol) was added dropwise. On raising the temperature of the mixture gradually, it became homogeneous at −30 °C. The solution was stirred for several hours at 0 °C. Cooling the clear solution at −70 °C overnight yielded a white precipitate, which was filtered off, washed with a small amount of Et_2O at the same temperature and dried *in vacuo*. The product was recrystallized from cold hexane to yield colorless needles of $[PdMe_2(PEt_3)_2]$ **1a** (0.71 g, 40%). Similarly obtained were $[PdEt_2(PEt_3)_2]$ **2a** and $[PdPr^n{}_2(PEt_3)_2]$ **3a** by the use of, respectively, $AlEt_2(OEt)$ and $AlPr^n{}_2(OEt)$ in place of $AlMe_2(OEt)$. Complexes **2a** and **3a** were crystallized quickly from acetone at low temperatures. The low yields of crystallized complexes **2a** and **3a** (less than 15%) may be accounted for instability of the complexes in solution.

*Preparation of Dimethylbis(diphenylmethylphosphine)palladium(II) **1b**.* To the heterogeneous yellow mixture of $[Pd(acac)_2]$ (1.5 g, 5 mmol), PPh_2Me (2.3 cm^3, 12 mmol) and diethyl ether (30 cm^3) cooled at −70 °C, was added 3 cm^3 (25 mmol) of $AlMe_2(OEt)$ dropwise. Gradual warming of the system to −20 °C with stirring afforded a clear red solution, and the solution was further stirred at 0 °C for several hours. Cooling the solution at −70 °C overnight yielded a white precipitate which was filtered off, washed with Et_2O and hexane at low temperature and dried *in vacuo*. The product was crystallized from cold acetone to give white crystals of $[PdMe_2(PPh_2Me)_2]$, **1b**, (0.23 g, 10%).

Similarly obtained were its ethyl and propyl analogs, **2b** and **3b**, using $AlEt_2(OEt)$ and $AlPr^n{}_2(OEt)$, respectively, in place of $AlMe_2(OEt)$. Crude complex **2b** (0.70 g, 25%) could not be crystallized due to its poor solubility. White crystals of **3b** (0.33 g, 10%) were obtained by the careful, low temperature crystallization from acetone.

*Preparation of Dimethyl{1,2-bis(diphenylphosphino)ethane} palladium(II), **1c**.* Into the cooled (−70 °C) heterogeneous mixture of $[Pd(acac)_2]$ (1.5 g, 5 mmol), 1,2-bis(diphenylphosphino)ethane (dpe, 2.2 g, 5.5 mmol), and Et_2O (30 cm^3), was added dropwise 3 cm^3 (16 mmol) of $AlMe_2(OEt)$. Stirring the mixture at −20 to −30 °C yielded, at first, a sticky solid, and then finally a white precipitate, which was filtered off, washed with Et_2O and hexane, and dried *in vacuo*. Recrystallization of the product from acetone yielded white crystals of $[PdMe_2(dpe)]$ **1c** (1.6 g, 45%).

The analogous complexes, $[PdEt_2(dpe)]$ **2c** and $[PdPr^n{}_2(dpe)]$ **3c** were obtained by the similar method as above using $AlEt_2(OEt)$ and $AlPr^n{}_2(OEt)$, respectively, as alkylating agents in place of $AlMe_2(OEt)$. Complexes **2c** (2.1 g, 75%) and **3c** (2.5 g, 85%) could not be crystallized due to their poor solubility.

Reactions of Dialkylpalladium Complexes with Carbon Monoxide. To the pre-evacuated flask containing the mixture of $[PdMe_2(PEt_3)_2]$ **1a** (46.5 mg, 0.125 mmol) and toluene (1 cm^3) freezed at −198 °C, carbon monoxide was introduced. The system turned red instantly on melting by raising the temperature under carbon monoxide. At room temperature, a clear red solution resulted. No gas evolution was observed in the system. The formation of acetone (0.108 mmol, 90% on the basis of the amount of **1a** used) in the solution was confirmed by means of GLC.

The similar reactions of CO with complexes **2a**, **3a**, **1b**, **2b**, and **3b** yielded the corresponding ketones as shown in Table 6.

*Reactions of Dialkylpalladium Complexes with Iodine. $[PdEt_2(dpe)]$ (**2c**):* Into the Schlenk flask fitted with a side arm, 74.1 mg (0.132 mmol) of $[PdEt_2(dpe)]$ was placed. The benzene (2 cm^3) solution of iodine (1.0 g) in a L-shaped tube was connected to the side arm of the flask. After being evacuated by freeze-thaw method, the contents were mixed together by rotating the L-shaped tube. The mixture was stirred at room temperature for several hours. The gases evolved by the reaction are listed in Table 4. From the solution, all volatile liquid was removed by a trap-to-trap distillation

Table 6. The amount of dialkylketones formed by the reactions of $[PdR_2L_2]$ with carbon monoxide

Complexes		mg	(mmol)	Dialkylketones	mmol	(%)
$[PdMe_2(PEt_3)_2]$	**1a**	46.5	(0.125)	Me_2CO,	0.108	(85)
$[PdEt_2(PEt_3)_2]$	**2a**	52.1	(0.130)	Et_2CO,	0.144	(110)
$[PdPr^n_2(PEt_3)_2]$	**3a**	21.1	(0.049)	Pr^n_2CO,	0.046	(95)
$[PdMe_2(PPh_2Me)_2]$	**1b**	77.0	(0.143)	Me_2CO,	0.129	(90)
$[PdEt_2(PPh_2Me)_2]$	**2b**	49.9	(0.088)	Et_2CO,	0.088	(100)
$[PdPr^n_2(PPh_2Me)_2]$	**3b**	25.2	(0.042)	Pr^n_2CO,	0.042	(100)

to leave a residual orange solid. The presence of methyl iodide (0.196 mmol, 74% on the basis of the amount of initially used complex) was confirmed by means of GLC. Recrystallization of the residue from acetone–hexane yielded orange crystals of $[PdI_2(dpe)]$ (Found: C, 41.6; H, 3.8; I, 33.0%. Calcd for $C_{26}H_{24}I_2P_2Pd$: C, 41.2; H, 3.2; I, 33.5%).

Similarly carried out were the reactions of $[PdEt_2(PEt_3)_2]$ and $[PdPr^n_2L_2]$ ($L=PEt_3$, PPh_2Me, and 1/2dpe) with iodine.

Reactions of $[PdR_2(dpe)]$ with methyl iodide. $[PdMe_2(dpe)]$: Methyl iodide (*ca.* 2 cm^3) was distilled over calcium hydride under a vacuum into a flask containing $[PdMe_2(dpe)]$ (69.6 mg, 0.13 mmol). On stirring the mixture at room temperature, the initial white suspension turned to a clear red solution and then finally to the suspension containing a yellow precipitate which was identified as $[PdI_2(dpe)]$ on the basis of the IR spectrum. The evolution of ethane containing a trace of methane was observed as analyzed by GLC. The amount of ethane can not be measured due to the coexistence of unreacted CH_3I. The reactions of diethyl and dipropyl complexes with methyl iodide were carried out similarly.

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