Synthesis, Characterization, and Thermolytic Behaviour of η^3-Allyl(methyl)(tertiary phosphine)palladium(II), and *X*-Ray Structure of the Cluster $[Pd_4(\mu\text{-}C_3H_5)_2(\mu\text{-}Cl)_2(\mu\text{-dppm})_2]\cdot4C_4H_8O$ (dppm = $Ph_2PCH_2PPh_2$)†

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Complexes of the type $[Pd(\eta^3\text{-allyl})Me(L)]$ [allyl = C_3H_5 or 2-MeC_3H_4; L = $P(C_6H_{11})_3$, PPh_3, PPh_2Me, $PPhMe_2$, or $PBu^n{}_3$] have been synthesized and characterized by ^1H, ^{13}C n.m.r. and mass spectroscopy. The $[Pd(\eta^3\text{-}C_3H_5)Me(L)]$ complexes thermally decompose with preferential evolution of ethane rather than but-1-ene, the allylic alkylation product. The participation of the binuclear methyl-bridged intermediate $[Pd_2(\eta^3\text{-allyl})_2(\mu\text{-Me})_2]$ (**3**) is supposed. Indirect support for this is given by the thermolysis of a toluene solution of (**3**). The effects of phosphines, alkenes, and other additives on the thermolysis products are discussed. The structure of a complex isolated from the $[Pd_2(\eta^3\text{-allyl})_2(\mu\text{-Cl})_2]$–LiMe–$Ph_2PCH_2PPh_2$ (dppm) reaction system in tetrahydrofuran was revealed by *X*-ray analysis as two μ-chloro-μ-allyl-dipalladium(I) units bridged by two dppm ligands.

Palladium-catalysed reactions involving allyl–alkyl coupling have become of great interest in recent years.[1–4] Complexes containing both η^3-allyl and other organic groups on a palladium atom are of especial importance as models of the intermediates involved in those catalytic reactions. As such models, η^3-allyl(aryl)(tertiary phosphine)palladium(II) complexes were first synthesized by Kurosawa and co-workers[5,6] and a series of mechanistic studies has been performed on reductive elimination of the organic groups.[6,7] However, the corresponding methyl complexes have not been reported so far. In contrast with palladium, methylnickel complexes of the same type have been synthesized by Bogdanovic *et al.*[8] and by Schenkluhn *et al.*,[9] independently, each using methyl Grignard reagents. We here describe the synthesis and characterization of the first methyl complexes of η^3-allylpalladium(II) to be isolated, a novel intermolecular coupling reaction observed during their thermolysis, and an *X*-ray crystal structure of the tetranuclear palladium(I) cluster isolated from the related reaction system. A preliminary account of the thermolytic behaviour of the triphenylphosphine complex has previously been reported.[10]

Experimental

Air-sensitive compounds were handled in an atmosphere of nitrogen unless otherwise stated, using solvents and reagents which were redistilled under and purged with argon, respectively. The diethyl ether solution of LiMe (0.89 mol dm^{-3}) was a gift from Toyo Stauffer Chemical Co., Ltd. The starting complexes $[Pd_2(\eta^3\text{-allyl})_2(\mu\text{-Cl})_2]$ (**1**) were synthesized according to the literature.[11] The mononuclear complexes $[Pd(\eta^3\text{-allyl})Cl(L)]$ (**2**) were produced in solution by the reactions of (**1**) with tertiary phosphines (L) and used in subsequent reactions *in situ*. Tertiary phosphines and other reagents were purchased and used without further purification. Standard gases were also purchased.

Synthesis of $[Pd(\eta^3\text{-}C_3H_5)Me\{P(C_6H_{11})_3\}]$ (**4**).—*Method* (*a*). Tricyclohexylphosphine (0.449 g, 1.60 mmol) was added to a suspension of complex (**1**) (0.293 g, 0.800 mmol) in tetrahydrofuran (thf) (5 cm^3) and the mixture was stirred for 10 min to prepare complex (**2**). After cooling to −70 °C, a diethyl ether solution of LiMe (1.60 mmol) was added dropwise. The mixture was gradually warmed to 0 °C and the solvent removed to leave a white residue which was extracted with pentane and the extract again evaporated to dryness to leave a white solid.

Method (*b*). A diethyl ether solution of LiMe (1.60 mmol) was added to a suspension of complex (**1**) (0.293 g, 0.800 mmol) in thf (5 cm^3) at −80 °C. To the resulting deep red solution was added a solution of $P(C_6H_{11})_3$ (0.449 g, 1.60 mmol) in thf (5 cm^3) at −65 °C, and the mixture was warmed slowly to 0 °C. The solvent was removed at this temperature and the residue was extracted with pentane. The extract was evaporated to dryness to leave a white solid.

Synthesis of $[Pd(\eta^3\text{-}C_3H_5)Me(PPh_3)]$ (**5**).—*Method* (*c*). The mononuclear complex (**2**) was prepared by the reaction of (**1**) (1.02 g, 2.78 mmol) with PPh_3 (1.46 g, 5.55 mmol) in thf (30 cm^3) at −65 °C. The solution of (**2**) thus prepared was cooled to −78 °C and allowed to react with LiMe (5.55 mmol). The mixture was warmed slowly to 0 °C and the resulting solution was concentrated to dryness to leave an oily substance. The crude product was extracted with toluene and the extract was completely evaporated to leave a pale yellow solid, which was washed with pentane and dried *in vacuo*.

Method (*d*). To a suspension of complex (**1**) (0.358 g, 0.979 mmol) in thf (6 cm^3) precooled to −95 °C was added dropwise a diethyl ether solution of LiMe (1.96 mmol). As the mixture was warmed slowly to −70 °C the yellowish orange suspension changed to a deep red solution. After the addition of PPh_3 (0.436 g, 1.66 mmol), the resulting solution was warmed to 0 °C and the solvent was evaporated to dryness to leave an oily substance. The crude product was treated as done in (*c*).

Synthesis of the Complexes $[Pd(\eta^3\text{-allyl})Me(L)]$ [*allyl* = C_3H_5, L = PPh_2Me (**6**), $PPhMe_2$ (**7**), *or* $PBu^n{}_3$ (**8**); *allyl* =

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† Di-μ-bis(diphenylphosphino)methane-bis[μ-allyl-C^1C^3-μ-chloro-dipalladium (*Pd–Pd*)]-tetrahydrofuran(1/4).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

Table 1. Analytical and physical data for the complexes [Pd(η^3-allyl)Me(L)]

Complex				Yield	I.r. data (cm^{-1})		Analysis (%)[a]	
	Allyl	L	Nature	(%)	δ(C–H)	ν(Pd–C)	C	H
(4)[b]	C_3H_5	$P(C_6H_{11})_3$	White solid	27	1 132	494	58.0 (59.7)[c]	9.1 (9.3)[c]
(5)[d]	C_3H_5	PPh_3	Pale yellow solid	94	1 139	473	62.6 (62.2)	5.5 (5.5)
(6)	C_3H_5	PPh_2Me	Yellow oil	90	1 135	*e*	56.3 (56.3)	5.7 (5.8)
(7)	C_3H_5	$PPhMe_2$	Yellow oil	98	*f*	*f*	49.3 (47.9)[c]	6.4 (6.4)[c]
(8)	C_3H_5	$PBu^n{}_3$	Yellow oil	93	1 137	470	52.6 (52.7)	9.8 (9.7)
(9)	2-MeC_3H_4	$P(C_6H_{11})_3$	Pale yellow solid	64	1 138	493	58.3 (60.5)[c]	9.2 (9.5)[c]
(10)	2-MeC_3H_4	PPh_3	Yellow solid	88	*e*	482	53.4 (63.0)	5.7 (5.7)
(11)	2-MeC_3H_4	PPh_2Me	Pale yellow solid	79	*e*	*e*	57.3 (57.4)	6.1 (6.2)
(12)	2-MeC_3H_4	$PPhMe_2$	Yellow-orange oil	60	*f*	*f*	44.6 (49.6)[c]	6.0 (6.7)[c]
(13)	2-MeC_3H_4	$PBu^n{}_3$	Yellow-orange oil	99	1 137	490	53.5 (53.9)	9.9 (9.8)

[a] Calculated values in parentheses. [b] Synthesized by method (*a*). [c] Too thermally unstable to give satisfactory elemental analysis. [d] Synthesized by method (*c*). [e] Obscured by L. [f] Decomposed during the measurement.

2-MeC_3H_4, L = $P(C_6H_{11})_3$ (**9**), PPh_3 (**10**), PPh_2Me (**11**), $PPhMe_2$ (**12**) *or* $PBu^n{}_3$ (**13**)].—All the complexes except (**10**) and (**11**), in the case of which method (*c*) was employed, were synthesized according to method (*a*).

Analytical and some physical data of these complexes are summarized in Table 1, while ^1H and ^{13}C n.m.r. data are collected in Tables 2 and 3, and mass spectral data in Table 4.

Thermolysis Experiments.—A solid or solution sample was placed in a Schlenk tube and degassed several times by the freeze–pump–thaw method. A standard gas of constant volume was introduced to the tube through a manometer, and then the sample was thermolysed and the evolved gases analysed by gas chromatography. Propane was used as an internal standard and diphenylmethane or toluene as a solvent. The area of a gas chromatographic peak in comparison with that of a standard was used for quantitative purposes. The area was corrected for the solubility of a particular gas relative to propane in the solvent employed. A YANACO G-180 gas chromatograph was used for the gas analysis. Porapak Q (89—100 mesh, 2 m), TCP C-22 (60—80 mesh, 8 m), or molecular sieves type 5A (80—100 mesh, 1.5 m) were used as packings.

Gas analytical data obtained by the thermolysis experiments are given in Tables 5 and 6.

Preparation and Thermolysis of a Toluene Solution of [$Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Me)_2$].—A diethyl ether solution of LiMe (0.180 mmol) was added to a suspension of complex (**1**) (36.6 mg, 0.100 mmol) in toluene (1 cm^3) precooled to −90 °C. As the temperature was raised to −78 °C the reaction proceeded slowly, giving a deep red solution containing (**3**), together with a small amount of a precipitate of LiCl. The solution thus obtained was subjected to thermolysis after the treatment described above. The thermolysis was performed by allowing the solution to warm slowly to 0 °C.

Isolation of [{$Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}Cl)$}$_2$($\mu$-dppm)$_2$]·$4C_4H_8O$ (**15**) *from Complex* (**1**), LiMe *and* $Ph_2PCH_2PPh_2$(dppm) *in* thf.—A thf solution of [$Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Me)_2$] was prepared, under argon, similarly to that of the toluene solution described above. To a suspension of complex (**1**) (0.201 g, 0.550 mmol) in thf (4 cm^3) precooled to −80 °C was added dropwise a diethyl ether solution of LiMe (1.10 mmol), and then the mixture was warmed to −65 °C, resulting in a deep red solution. A solution of dppm (0.210 g, 0.550 mmol) in thf (10 cm^3) was added slowly keeping this temperature, when the deep red solution gradually turned through a yellow suspension to a yellow solution. The solution was warmed slowly to −50 °C, resulting in evolution of CH_4 (98.4%) and C_2H_6 (1.6%). The solvent was removed at 0 °C and the residue extracted with toluene. The extract was again dried to leave a pale yellow solid, which was washed successively with diethyl ether and pentane, and dried *in vacuo*. Recrystallization from thf gave pale yellow crystals of complex (**15**). On air-drying, the crystals lost the thf molecules with devitrification to give [{$Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}Cl)$}$_2$($\mu$-dppm)$_2$] (Found: C, 49.45; H, 4.15. $C_{28}H_{27}ClP_2Pd_2$ requires C, 49.90; H, 4.05%).

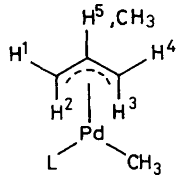
Measurements.—I.r. (Nujol or neat) spectra were recorded on a JASCO DS-701G spectrometer. Proton n.m.r. spectra at 100 and 400 MHz respectively were recorded on JEOL JNM MH-100 and GX-400 instruments, carbon-13 n.m.r. spectra at 100.5 MHz on a JEOL JNM GX-400 spectrometer, both with $SiMe_4$ as internal standard. Mass spectra were measured with a JEOL JMS-D300 spectrometer (electron-impact type) by means of the direct injection method at ionization potentials of 20—30 eV.

Crystal Structure Determination of Compplex (**15**).—*Crystal data.* $C_{72}H_{86}Cl_2O_4P_4Pd_4$, M = 1 635.9, triclinic, space group $P\bar{1}$, a = 14.599(9), b = 12.385(5), c = 11.627(5) Å, α = 101.32(3), β = 101.38(3), γ = 89.86(3)°, Z = 1, D_c = 1.34 g cm^{-3}, μ(Mo-K_α) = 10.4 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å, U = 2 019(2) Å^3, F(000) = 828.

The crystals (0.25 × 0.25 × 0.55 mm) was sealed in a capillary tube and was mounted in an arbitrary orientation on a Philips PW1100 automated diffractometer. The PW1100 program obtained the triclinic cell. The unit-cell dimensions with standard deviations were derived from a least-squares fit from the angular positions of 20 centred reflections. The intensity data ($4 \leqslant 2\theta \leqslant 50°$) were collected at ambient temperature by the use of graphite-monochromated Mo-K_α radiation. The ω-scan method was employed. The scan range was $(1.2 + 0.3 \tan\theta)°$ and the scan speed 0.05° s^{-1}; the background was counted for 10 s at each side of the scan range. Intensities of three check reflections showed a decay of 5% during data collection and a linear correction was applied. A total of 4 192 reflections [$F_o{}^2 > 3\sigma(F_o{}^2)$] were considered as observed. The intensities were corrected for Lorentz polarization[12] and absorption (maximum and minimum correction coefficients 1.31 and 1.24).

The positions of two palladium atoms were obtained from the Patterson synthesis. Subsequent least-squares refinement followed by Fourier difference syntheses revealed the positions of all non-hydrogen atoms. The least-squares refinement gave R = 0.066 and $R' = (\Sigma w\Delta F^2/\Sigma wF_o{}^2)^{\frac{1}{2}}$ = 0.094. Two thf molecules were disordered and their parameters were

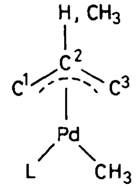
Table 2. Proton n.m.r. data for the selected [Pd(η^3-allyl)Me(L)] complexes[a]



Complex	H^1	H^2	H^3	H^4	H^5	CH_3	Pd–CH_3
(**4**)	3.58 (d) (6.6)	2.51 (d) (13.7)	2.78 (t) (11.1) [11.1]	3.64 (t) (6.2) [6.2]	5.08 (m)		0.73 (d) [4.9]
(**5**)	3.59 (d) (7.6)	2.76 (d) (13.9)	2.88 (dd) (11.4) [10.9]	3.69 (t) (5.7) [5.7]	5.17 (m)		0.81 (d) [6.1]
(**6**)	3.48 (dd) (7.6) [2.2]	2.58 (d) (13.9)	2.81 (dd) (11.8) [10.4]	3.69 (t) (6.3) [6.3]	5.10 (m)		0.80 (d) [6.4]
(**6**)[b]	3.46 (d) [2.2]	2.57 (s)	2.79 (d) [9.3]	3.67 (d) [4.2]			
(**12**)	3.30 (d) [2.7]	2.45 (s)	2.76 (d) [10.0]	3.49 (br)		1.62 (s)	0.76 (d) [6.1]
(**13**)	3.32 (s)	2.42 (s)	2.75 (d) [8.8]	3.47 (s)		1.65 (s)	0.69 (d) [4.4]

[a] 400 MHz. Chemical shifts (δ) from $SiMe_4$ as internal standard in C_6D_6, $J(H^5–H)$ and $J(PH)$ values (Hz) in parentheses and square brackets, respectively. [b] Homodecoupled on irradiation at δ 5.10.

Table 3. Carbon-13 n.m.r. data for the selected [Pd(η^3-allyl)Me(L)] complexes[a]



Complex	C^1	C^2	C^3	CH_3	Pd–CH_3
(**4**)	60.8 (s)	117.9 (d) (2.9)	57.5 (d) (36.7)		–16.2 (d) (13.2)
(**7**)	61.9 (s)	117.9 (s)	55.7 (d) (38.2)		–15.3 (d) (10.3)
(**8**)	58.9 (s)	117.3 (s)	56.1 (d) (25.0)		–17.0 (d) (13.2)
(**8**)[b]	dt	d	dt		dq
(**10**)	66.6 (s)	130.6 (d) (4.4)	56.8 (d) (39.6)	24.6 (s)	–12.8 (d) (11.7)
(**10**)[b]	t	s	dt	q	q
(**11**)	64.6 (s)	131.1 (d) (4.4)	56.7 (d) (41.1)	64.6 (s)	–15.3 (d) (13.2)

[a] 100.5 MHz. Chemical shifts (δ) from $SiMe_4$ as internal standard in C_6D_6, $J(PC)$ values (Hz) in parentheses. [b] Multiplicities in the ^1H gated-decoupled spectrum.

isotropically refined. In the final cycles of the refinement, hydrogen atoms fixed at idealized positions (C–H 0.95 Å, B = 6.0 $Å^2$) were included, but their parameters were not refined. The thf hydrogen atoms were excluded in the refinement. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w = 1.0. All the parameter shifts were less than 0.3σ. The highest peak in the final Fourier difference synthesis was 1.9 e $Å^{-3}$. Atomic scattering factors for Pd, Cl, P, O, and C atoms were taken from ref. 13, with corrections for anomalous scattering ($\Delta f'$) for Pd, Cl, and P. Final atomic co-ordinates are given in Table 7. The computer programs used in the calculations were a local version of UNICS (RSLC-3, HBLS-IV, RSSFR-5, and DAPH).[14] Calculations were performed on a HiTAC M-660K computer at Osaka City University.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Synthesis and Characterization.—We have recently reported the complexes [$Pd_2(\mu$-$Cl)_2Me_2L_2$] (L = tertiary phosphine).[15] The complex (L = $PBu^n{}_3$) readily reacts with an allyl Grignard reagent and allyl-lithium, giving in each case [Pd(η^3-allyl)-Me($PBu^n{}_3$)] (**8**) in solution. We confirmed this on the n.m.r. basis, but could not isolate (**8**) as a pure substance. However, the following two methods using complex (**1**) as a starting material led to the synthesis and isolation of the pure [Pd(η^3-allyl)Me(L)] complexes (**4**)—(**13**): (*a*) the bridge-splitting reaction of (**1**) with L, followed by methylation with LiMe, (*b*) the reaction of (**1**) with LiMe to afford (**3**) and the subsequent bridge-splitting reaction with L (Scheme 1). As shown in Table 1, these complexes are isolated as oily substances or as crystalline or amorphous solids, and are moderately stable without appreciable change in air at ambient temperature for 1—3 d, except those with L = $P(C_6H_{11})_3$ and $PPhMe_2$. The complexes exhibit an i.r. absorption owing to δ(C–H) of the co-ordinated methyl group together with a Pd–C stretching vibration (Table 1).[15]

Apart from the signals for L, the ^1H n.m.r. spectra of the complexes (Table 2) consist of six signals, of which the intensity ratios are 1:1:1:1:1:3 for (**4**)—(**8**) and 1:1:1:1:3:3 for (**9**)—(**13**). The highest-field signal appears as a doublet due to *cis* coupling to the phosphorus atom and is assigned to the methyl group directly bonded to the metal. Five other signals, except that of the methyl substituent in (**9**)—(**13**), are in the range of normal chemical shifts for allylic protons and can be assigned as shown in Table 2 according to the literature.[6,16] Application of a homodecoupling technique to the H^5 signal of complex (**6**) served to evaluate each of the $J(H^5–H)$ and $J(PH)$ values. The ^{13}C n.m.r. spectra of the complexes consist of four or five signals owing to the methyl and allyl groups. They can be assigned as shown in Table 3, with the assistance of a ^1H gated-decoupling technique applied to (**8**) and (**10**). The highest-field signal appears as a doublet with *cis* coupling to phosphorus, again indicating that the methyl group is directly bonded to the metal.

Complexes (**6**), (**7**), and (**9**)—(**12**) show the molecular-ion peak in their mass spectra (Table 4), while the others do not. It is noteworthy that three particular fragments are detected, especially in the following order of intensity; $[Pd(allyl)L]^+ > [PdL]^+ < [PdL - 1]^+$. The last fragment corresponds to loss of both the methyl radical and propene molecule from the molecular ion. Thus the complexes lose the methyl group in preference to but-1-ene or 2-methylbut-1-ene, the allyl–alkyl coupling product, and the allyl group in the remaining $[Pd(allyl)L]^+$ abstracts a H radical from the co-ordinated phosphine ligand to give propene or 2-methylpropene. More remarkable is the appearance of $[Pd(allyl)]^+$ and $[PR_3Me]^+$

Table 4. Characteristic mass spectral data (*m*/*z*) for the selected $[Pd(\eta^3\text{-allyl})Me(L)]$ complexes *

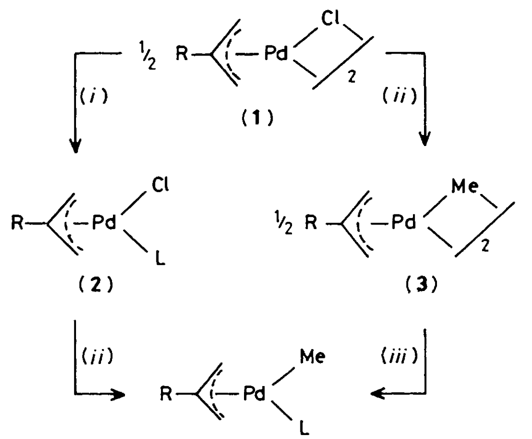
(**6**)	360—366 (M^+, 7), 345—351 [100, $Pd(allyl)L^+$], 304—310 (56, PdL^+), 303—309 [94, $(PdL - 1)^+$], 215 (≫100, $PPh_2Me_2^+$), 145—151 [≫100, $Pd(allyl)^+$]
(**7**)	298—304 (M^+, 11), 283—289 [100, $Pd(allyl)L^+$], 242—248 (84, PdL^+), 241—247 [>100, $(PdL - 1)^+$], 153 (34, PMe_3Ph^+), 145—151 [9, $Pd(allyl)^+$]
(**9**)	454—460 (M^+, 2), 439—445 [100, $Pd(allyl)L^+$], 384—390 (29, PdL^+), 383—389 [94, $(PdL - 1)^+$], 295 [53, $P(C_6H_{11})_3Me^+$], 159—165 [10, $Pd(allyl)^+$]
(**10**)	436—442 (M^+, 42), 421—427 [100, $Pd(allyl)L^+$], 366—372 (44, PdL^+), 365—371 [72, $(PdL - 1)^+$], 272 (≫100, PPh_3Me^+), 159—165 [>100, $Pd(allyl)^+$]
(**11**)	374—380 (M^+, 8), 359—365 [100, $Pd(allyl)L^+$], 304—310 (42, PdL^+), 303—309 [>100, $(PdL - 1)^+$], 215 (>100, $PMe_2Ph_2^+$), 159—165 [40, $Pd(allyl)^+$]
(**12**)	312—318 (M^+, 13), 297—303 [100, $Pd(allyl)L^+$], 242—248 (44, PdL^+), 241—247 [>100, $(PdL - 1)^+$], 159—165 [88, $Pd(allyl)^+$], 153 (>100, PMe_3Ph^+)

* For convenience the peak intensity (%) of the $[Pa(allyl)L]^+$ fragment is used as a base. Omitted for complexes which do not show the molecular-ion peak.

Table 5. Gases evolved in the thermolysis of $[Pd(\eta^3\text{-}C_3H_5)Me(L)]$ complexes in the solid state[a]

Complex	Total mol per Pd	Evolved gas ratio			
		Methane	Ethane	Propene	But-1-ene
(**4**)	0.47	3.2	35.3	29.0	32.6
(**5**)	0.42	3.2	77.5	3.3	16.1
(**6**)	0.57	9.5	40.5	47.8	2.2
(**8**)[b]	0.41	4.6	45.4	31.6	17.2

[a] In an evacuated tube at 100 °C for 40 min. [b] Propane (1.3%) was also detected.



	R	L		R	L
(**4**)	H	$P(C_6H_{11})_3$	(**9**)	Me	$P(C_6H_{11})_3$
(**5**)	H	PPh_3	(**10**)	Me	PPh_3
(**6**)	H	PPh_2Me	(**11**)	Me	PPh_2Me
(**7**)	H	$PPhMe_2$	(**12**)	Me	$PPhMe_2$
(**8**)	H	PBu^n_3	(**13**)	Me	PBu^n_3

Scheme 1. (*i*) L, 0 °C; (*ii*) MeLi, -LiCl, −78 °C; (*iii*) L, −60 °C

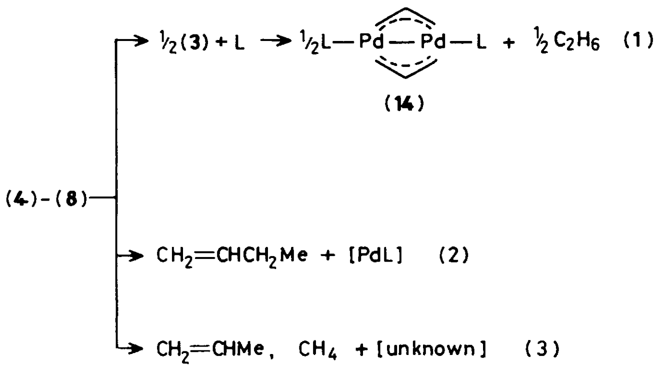
Table 6. Gases evolved in the thermolysis of the $[Pd(\eta^3\text{-allyl})Me(L)]$ complexes in solution[a]

Entry	Complex	Temp. / °C	Time / min	Additive[b] / mol dm^{-3}	Total mol per Pd	Evolved gas ratio			
						Methane	Ethane	Propene	But-1-ene
1	(**4**)	50	60	None	0.13	4.0	85.5	0.8	9.7
2	(**5**)	50	60	None	0.36	4.2	79.7	12.9	3.2
3	(**5**)	70	10	PPh_3 (0.3)	1.01	17.0	25.0	4.8	53.2
4	(**5**)	50	60	Ph_2C_2 (0.1)	0.69	2.5	33.9	7.8	55.8
5	(**5**)	75	60	C_6Cl_6 (0.2)	0.59	5.8	47.0	8.2	39.0
6	(**5**)	25	60	ma (0.1)	0.49	2.0	0.8	4.8	92.4
7	(**6**)	50	60	None	0.33	33.2	56.9	7.8	2.2
8	(**8**)	50	60	None	0.12	8.9	76.4	13.0	1.7
9	(**10**)[c]	60	60	ac (0.1)	0.97	7.6	36.7	2.4	46.4

[a] In degassed Ph_2CH_2 (0.1 mol dm^{-3}). [b] ma = maleic anhydride; ac = allyl chloride. [c] 2-Methylbut-1-ene (6.9%) was also detected.

Table 7. Fractional atomic co-ordinates for complex (**15**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Pd(1)	0.132 22(9)	0.455 92(11)	0.548 80(10)
Pd(2)	−0.006 26(9)	0.644 87(10)	0.633 31(10)
P(1)	0.236 9(3)	0.535 9(4)	0.713 4(4)
P(2)	0.111 9(3)	0.738 4(4)	0.773 4(4)
Cl	0.031 2(3)	0.302 5(3)	0.565 2(3)
C(1)	0.058 6(13)	0.446 1(15)	0.257 4(14)
C(2)	0.143 7(13)	0.453 1(16)	0.340 4(14)
C(3)	0.181 5(14)	0.541 5(16)	0.434 9(15)
C(51)	0.228 3(12)	0.684 7(13)	0.767 7(13)
C(11)	0.357 9(12)	0.524 6(15)	0.688 5(12)
C(12)	0.385 0(15)	0.419 3(18)	0.647 2(18)
C(13)	0.470 8(17)	0.400 4(22)	0.625 5(19)
C(14)	0.533 5(15)	0.487 7(25)	0.642 9(18)
C(15)	0.508 6(14)	0.591 6(22)	0.684 1(19)
C(16)	0.421 4(13)	0.613 5(18)	0.707 9(17)
C(21)	0.248 5(12)	0.479 3(13)	0.851 0(13)
C(22)	0.326 9(14)	0.505 3(18)	0.942 4(15)
C(23)	0.331 7(17)	0.467 9(21)	1.044 5(17)
C(24)	0.264 1(17)	0.405 3(19)	1.061 4(15)
C(25)	0.186 9(17)	0.375 1(18)	0.974 3(17)
C(26)	0.179 0(14)	0.413 6(15)	0.866 4(15)
C(31)	0.133 0(12)	0.880 4(13)	0.763 3(13)
C(32)	0.085 2(14)	0.924 6(15)	0.668 5(15)
C(33)	0.100 9(16)	1.034 3(16)	0.657 5(17)
C(34)	0.165 5(15)	1.101 0(15)	0.739 9(18)
C(35)	0.214 1(15)	1.059 0(16)	0.836 8(19)
C(36)	0.197 0(14)	0.950 9(15)	0.849 0(16)
C(41)	0.099 2(12)	0.754 7(14)	0.930 0(13)
C(42)	0.139 6(17)	0.688 9(17)	1.004 8(15)
C(43)	0.118 6(20)	0.699 5(20)	1.118 4(18)
C(44)	0.061 0(16)	0.777 8(18)	1.158 5(15)
C(45)	0.022 3(15)	0.840 5(19)	1.086 3(18)
C(46)	0.038 8(14)	0.829 6(18)	0.969 9(16)
O(1)	0.238(3)	0.155(3)	0.406(3)
C(61)	0.169(3)	0.101(3)	0.300(3)
C(62)	0.215(3)	0.105(4)	0.197(4)
C(63)	0.307(3)	0.154(4)	0.244(4)
C(64)	0.314(3)	0.192(4)	0.349(4)
O(2)	0.405(3)	0.857(4)	0.447(4)
C(71)	0.319(4)	0.794(5)	0.416(5)
C(72)	0.269(4)	0.838(4)	0.495(4)
C(73)	0.345(4)	0.900(5)	0.601(5)
C(74)	0.432(5)	0.927(5)	0.576(6)



Scheme 2.

(R = C_6H_{11}, Ph, Me, or Bu^n) peaks, in certain cases with intensity exceeding that of the $[PdL]^+$ fragment. The methyl–phosphorus coupling rather than the methyl–allyl coupling seems to be the preferred decomposition process.

Thermolytic Experiments.—Table 5 shows that ethane rather than but-1-ene, the allylic alkylation product, is a major organic product in the thermolysis of the $[Pd(\eta^3\text{-}C_3H_5)Me(L)]$ complexes in the solid state. This tendency was more clearly observed in thermolysis in Ph_2CH_2 (Table 6, entries 1, 2, 7, and 8). These observations are in marked contrast to those for the aryl analogues,[6] as well as those for (η^3-1,3- dimethylallyl)-methylnickel–ligand complexes,[9] and suggest that thermolysis primarily takes place intermolecularly through the binuclear methyl-bridged intermediate formed by phosphine dissociation [equation (1) in Scheme 2]. To confirm this hypothesis, we prepared a toluene solution of $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Me)_2]$ below −78 °C and examined the gases evolved on warming the solution to 0 °C. The relative amounts of gases liberated were as follows: methane:ethane:propene:but-1-ene:others = 12.6:74.5:7.0:3.4:2.1; total mol per 2Pd = 1.26. Thus, the intermediate $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Me)_2]$ decomposed liberating ethane almost quantitatively (0.94 mol per 2Pd). Furthermore, the relative amounts show a close resemblance to those for entry 2 in Table 6. These results indicate that the process represented by equation (1) in Scheme 2 is predominant for the thermolysis of $[Pd(\eta^3\text{-}C_3H_5)Me(L)]$.

When a $[^2H_6]$benzene solution of complex (**5**) was heated to 50 °C for 10 min in a degassed sealed tube the formation of $[Pd_2(\mu\text{-}C_3H_5)_2(PPh_3)_2]$ (*Pd–Pd*) (**14**) with the concomitant evolution of ethane was observed by the appearance of four new ^1H n.m.r. signals (Figure 1).[10] The formation of (**14**) was recognized more clearly in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the solution under similar conditions (50 °C, 3 h).[10] Unfortunately, our attempts to isolate the product (**14**) after thermolysis conducted under milder conditions (*e.g.* 20 °C, 3 d) were not successful, possibly because some side reactions took place even under these conditions.

Complexes of type (**14**) are now generally accepted to be generated by the reaction of $[Pd(\eta^3\text{-allyl})_2]$ with $[PdL_2]$.[17] In such the case free phosphine cannot be present, and hence the intermediate formation of $[Pd(\eta^3\text{-allyl})(\sigma\text{-allyl})L]$ has been excluded. However, it was recently found that complexes of type (**14**), *e.g.* $[Pd_2(\mu\text{-allyl})_2(PPh_3)_2]$, can also be synthesized from $[Pd(\eta^3\text{-allyl})(\sigma\text{-allyl})(PPh_3)]$ according to equation (4).[18] This

$$2\,[Pd(\eta^3\text{-allyl})(\sigma\text{-allyl})(PPh_3)] \longrightarrow [Pd_2(\mu\text{-allyl})_2(PPh_3)_2] + C_6H_{10} \quad (4)$$

fact also supports our proposal for the formation of (**14**) from $[Pd(\eta^3\text{-allyl})Me(L)]$ [equation (1) in Scheme 2] and the involvement of $[Pd(\eta^3\text{-allyl})_2]$ need not be taken into account in the present case. The involvement of a $Pd(\eta^5\text{-}C_5H_5)L$ radical is also proposed for the reaction of $[Pd(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)L]$ to give $[Pd_2(\mu\text{-}C_5H_5)_2L_2]$.[19]

In general, but-1-ene was liberated only as a minor product. It can be formed by reductive elimination, directly from complexes (**4**)—(**8**) [equation (2) in Scheme 2] or through (**3**). Propene, one of the other products, probably originates from complexes (**4**)—(**8**) [equation (3)] and (**14**), methane from (**4**)—(**8**) [equation (3)]. Hydrogen abstraction can occur from the phosphine ligand or the solvent. Compared to the case in the solid state, the amount of but-1-ene liberated on thermolysis in solution is significantly decreased. This tendency was also observed for the amount of propene, with the exception of complex (**5**). These

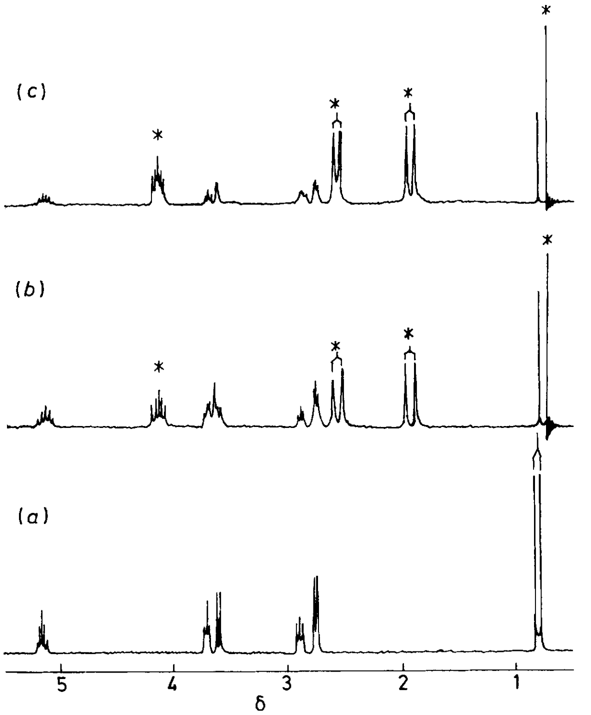


Figure 1. Time-dependent decomposition of complex (**5**). Proton n.m.r. spectra (100 MHz, C_6D_6) in a degassed sealed tube, δ from $SiMe_4$ as internal standard: (*a*) at 33 °C; (*b*) after decomposition at 50 °C for 10 min; (*c*) for 30 min. Asterisk shows signals of complex (**14**) and ethane [δ 1.96 (d, *J* 12, μ-allyl), 2.56 (d, *J* 8 Hz, μ-allyl), 4.15 (m, μ-allyl), and 0.76 (s, C_2H_6)]

results indicate that in the solid state the thermolysis process through equation (1) is somewhat suppressed compared with that in solution. However, these relations cannot rationalize the details of the data obtained for all of the complexes. The stability of the complexes [Pd(η^3-allyl)Me(L)] and [Pd_2(μ-allyl)$_2L_2$] in the solid state and in solution depends on the nature of the phosphine, and hence this subtly alters the proportions of pathways (1)—(3).

For ease of preparation and greater tendency to prefer the pathway (1), the triphenylphosphine complexes (**5**) and (**10**) were chosen as samples appropriate for further studies on the effect of alkenes and other additives on the thermolysis products. The addition of Pd^0-stabilizing ligands like phosphines and alkenes is known to be effective in preventing the deposition of palladium(0) species and these additives allow clear and complete reductive elimination of η^3-allyl(aryl)-palladium complexes.[6,7] In the present case, the addition of 3 equivalents of PPh_3 per complex (**5**) caused an increased evolution of but-1-ene (up to 50%), but a significant amount of ethane (25%) was still liberated (entry 3 in Table 6). This means that phosphine dissociation from (**5**) to form (**3**) is appreciably suppressed so that the two decomposition pathways (1) and (2) become of comparable importance. The addition of maleic anhydride was more effective in causing the preferential formation of but-1-ene, but the yield still remained less than 0.5 mol per mol Pd under the conditions shown in Table 6. Diphenylacetylene and hexachlorobenzene are not so effective for the elimination of but-1-ene as is maleic anhydride, but their effect seems to be comparable to those of phosphines. Interestingly, when the 2-methylallyl complex (**10**) was subjected to thermolysis in the presence of allyl chloride in Ph_2CH_2 its major coupling product was not 2-methylbut-1-ene but but-1-ene. This result may be explained by the involvement of palladium(IV) species formed by oxidative addition of the allylic chloride to (**10**).[7b]

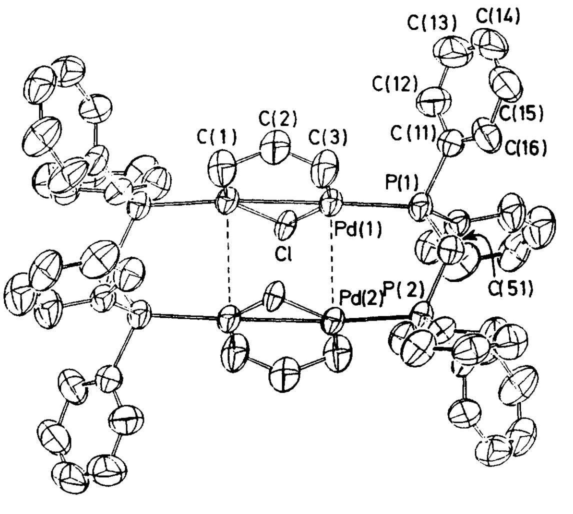


Figure 2. An ORTEP view of the complex ($Pd_4(\mu\text{-}C_3H_5)_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2$] (**15**) with the atomic numbering scheme

Molecular Structure of [$Pd_4(\mu\text{-}C_3H_5)_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2$]·$4C_4H_8O$ (**15**).—Our attempt to synthesize a methylene-bridged dipalladium complex according to equation (5) was not successful, although the evolution of methane was recognized.

$$[Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Cl)_2] \xrightarrow{2LiMe} [Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}Me)_2] + 2LiCl \xrightarrow{dppm} [Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}CH_2)(\mu\text{-}dppm)] + CH_4 \quad (5)$$

Instead of the complex, the Pd_4 cluster [$Pd_4(\mu\text{-}C_3H_5)_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2$] containing four molecules of thf as solvent of crystallization was isolated. The formation of such a chlorine-containing cluster suggests the participation of the thf-soluble LiCl in this reaction. An ORTEP view of the molecular structure of (**15**) is shown in Figure 2, together with the numbering scheme used in the crystallographic work. Bond distances and angles are reported in Table 8.

The complex is composed of two μ-chloro-μ-allyl-dipalladium units bridged by two dppm and has a crystallographically imposed centre of symmetry. The Pd(1) ··· Pd(2) distance of 3.223(2) Å excludes any metal–metal interaction, but the Pd(1)–Pd(2^I) ($-x$, $1 - y$, $1 - z$) distance of 2.619(2) Å is indicative of a metal–metal interaction, so the complex constitutes a novel 10-membered ring (see Figure 2). A similar 10-membered ring structure has recently been found for the related complex cation [$Pd_4(\mu\text{-}Cl)_2(\mu\text{-}dppm)_4$]$^{2+}$.[20]

The bridging chlorine atom is at nearly equivalent distances from the palladium atoms and forms a triangular plane, which makes an angle of 87.0° with the plane defined by the four palladium atoms. The allyl group is bonded to the palladium atoms from the side opposite to the chlorine atom, the interplanar angle between the Pd_2Cl plane and the least-squares plane Pd(1), C(3), C(1), Pd(2) ($-x$, $1 - y$, $1 - z$) being 172.8°. The plane of the allyl group is inclined from the plane parallel to that of Pd_4 by 14.3° in such a direction that the central carbon atom comes closer to the Pd_4 plane and is situated outside the Pd–Pd bond [the distances from the Pd_4 plane to C(1), C(2), and C(3) are 2.096, 1.933, and 2.073 Å, respectively]. The allyl group is internally symmetrical and symmetricaly bonded to the two palladium atoms. The C–C distances [1.43(3) and 1.42(3)

Table 8. Selected bond lengths (Å) and angles (°) for complex (**15**) with e.s.d.s in parentheses

Pd(1)–P(1)	2.256(5)	Pd(2)–C(2^{I})	2.45(2)
Pd(1)–Cl	2.467(5)	P(1)–C(51)	1.839(18)
Pd(1)–C(2)	2.46(3)	P(1)–C(11)	1.846(19)
Pd(1)–C(3)	2.08(2)	P(1)–C(21)	1.848(18)
Pd(2)–P(2)	2.265(5)	P(2)–C(51)	1.832(18)
Pd(1) · · · Pd(2)	3.223(2)	P(2)–C(31)	1.817(18)
Pd(1)–Pd(2^{I})	2.619(2)	P(2)–C(41)	1.839(19)
Pd(2)–Cl^{I}	2.478(4)	C(1)–C(2)	1.41(3)
Pd(2)–C(1^{I})	2.10(2)	C(2)–C(3)	1.42(3)
P(1)–Pd(1)–Cl	117.9(2)	C(1)–C(2)–C(3)	129(2)
P(1)–Pd(1)–C(3)	94.8(6)	Pd(1)–C(3)–C(2)	87(2)
Cl–Pd(1)–C(3)	146.5(6)	Pd(1)–P(1)–C(51)	117.1(6)
Pd(1)–Pd(2)–Pd(1^{I})	86.17(5)	Pd(1)–P(1)–C(11)	111.79(6)
Pd(2)–Pd(1)–Pd(2^{I})	93.83(5)	Pd(1)–P(1)–C(21)	119.1(6)
Pd(1)–Pd(2^{I})–Cl	57.8(1)	C(11)–P(1)–C(21)	100.4(8)
Cl–Pd(2^{I})–C(1)	146.0(6)	Pd(2)–P(2)–C(51)	115.1(6)
Pd(1)–Pd(2^{I})–C(1)	88.8(6)	Pd(2)–P(2)–C(31)	115.8(6)
Pd(2^{I})–C(1)–C(2)	86(2)	Pd(2)–P(2)–C(41)	116.3(6)
P(2^{I})–Pd(2^{I})–C(1)	98.2(6)	C(31)–P(2)–C(41)	101.3(8)
P(1)–Pd(1)–Pd(2^{I})	176.1(2)	P(1)–C(51)–P(2)	118(1)
P(2^{I})–Pd(2^{I})–Pd(1)	172.7(2)		

Symmetry equivalent: I, $-x$, $1 - y$, $1 - z$.

Å] are slightly shorter than the single-bond distance, being indicative of delocalization of the π electrons in the allyl group. The terminal carbon–palladium distances [2.10(2) and 2.08(2) Å] do not differ significantly from those (2.05—2.19 Å, ref. 21) observed for the Pd–C σ bonds. The central carbon–palladium distances [2.46(3) and 2.45(2) Å] suggest that there is a weak π-metal interaction between allyl and palladium atoms. These results are different from those obtained for the dinuclear complexes [$Pd_2(\mu\text{-allyl})(\mu\text{-I})(PPh_3)_2$][22] and [$Pd_2(\mu\text{-allyl})_2(PPh_3)_2$],[18] which showed different bond distances between the two C–C bonds of the allyl group.

Each palladium atom has a square-planar co-ordination geometry, but the angle P–Pd–Cl is considerably distorted from 90° because of bridging of the chlorine atom to the second palladium. The two phosphorus atoms of the dppm ligand are also situated significantly apart from the Pd_4 plane in opposite directions to each other [the distances from the Pd_4 plane to P(1) is 0.152 Å and that to P(2) is 0.269 Å].

Acknowledgements

We thank Professor Akio Yamamoto and Dr. Fumiyoshi Ozawa of Tokyo Institute of Technology for invaluable suggestions on thermolysis experiments. We also thank Toyo Stauffer Chemical Co., Ltd. for a gift of the diethyl ether solution of LiMe. This work was partially supported by a Grant-in-Aid for Scientific Research No. 63470040 from the Ministry of Education, Science and Culture.

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Received 3*rd October* 1988; *Paper* 8/03921F