The Reaction of Metal-ion Complexes with Hydrocarbons. Part 4.[1] Formation of Complexes of the Types Di-μ-acetato-bis[(η^3-allyl)palladium] and Tetra-μ-acetato-di(η^3-allyl)tripalladium by Reaction of Mono-olefins and 1,3-Dienes with Palladium Acetate

By **Robert G. Brown, Raghunath V. Chaudhari,** and **John M. Davidson,*** Department of Chemical Engineering, School of Engineering Science, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JL

Trimeric palladium acetate, $[Pd_3(O_2CMe)_6]$, reacts with mono-olefins such as cyclohexene, hex-1-ene, *cis*-hex-2-ene, oct-1-ene, *cis*-pent-2-ene, propene, and 2,3,3-trimethylbut-1-ene in acetic acid solution by loss of acetic acid and with formation of $[Pd_3(\eta^3\text{-allyl})_2(\mu\text{-}O_2CMe)_4]$ which reacts further to yield $[Pd_2(\eta^3\text{-allyl})_2(\mu\text{-}O_2CMe)_2]$. Perchloric acid catalyses these reactions, suggesting that they involve electrophilic attack of Pd^{II} on the olefin with loss of a proton from the allylic carbon. The ^1H and ^{13}C n.m.r. spectra in $CDCl_3$ solution show that the complexes are fluxional due to the acetato-bridging arrangement which allows interconversion of different conformations of the allyl group. Exchange experiments with acetic acid show that Pd–O bonds *trans* to the allyl group are more labile than those attached to the central palladium with four oxygen donors in the trinuclear complex. Hexa-2,4-diene undergoes an addition reaction with $[Pd_3(O_2CMe)_6]$ to yield di-μ-acetato-bis[(2—4-η-5-acetoxyhex-2-enyl)-palladium] which also yields a trinuclear complex on further reaction with $[Pd_3(O_2CMe)_6]$. N.m.r. spectra show that this binuclear complex exchanges with acetic acid in $CDCl_3$ solution, the μ-acetate being more labile to exchange than the organic acetate, while the trinuclear complex does not exchange under these conditions.

OUR interest in the oxidation of olefins catalysed by palladium(II) has led us into the current study of η^3-allylic complexes because many such species are formed from hydrocarbons during catalytic reactions. These η^3-allylic complexes are usually stable towards solvolysis and reductive elimination of metal and are not the immediate precursors of oxidised organic products, although an exception is η^3-cyclohex-2-en-1-ylpalladium acetate which decomposes readily to cyclohex-2-en-1-yl acetate.[1-3]

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[1] Part 3, R. G. Brown and J. M. Davidson, *J. Chem. Soc. (A)*, **1971**, 1321. For a preliminary account see R. G. Brown and J. M. Davidson, *Adv. Chem. Ser.*, 1974, **132**, 49.

[2] S. Wolfe and P. G. C. Campbell, *J. Amer. Chem. Soc.*, **1971**, **93**, 1497.

[3] S. Wolfe and P. G. C. Campbell, *J. Amer. Chem. Soc.*, **1971**, **93**, 1499.

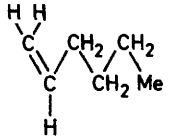
This paper describes the direct formation of η^3-allylic palladium acetate complexes by the reaction of $[Pd_3(O_2CMe)_6]$ with mono- and di-olefins in acetic acid solution. Hitherto, it has not been possible to prepare η-allylic complexes in good yield from linear alkenes because oxidation predominates,[4] but in our system correct choice of reaction conditions allows isolation of the pure complexes in high yields. We describe a new series of trinuclear species, $[Pd_3(allyl)_2(O_2CMe)_4]$, and report the use of ^{13}C as well as ^1H n.m.r. in the elucidation of their structures and fluxional behaviour.

TABLE 1

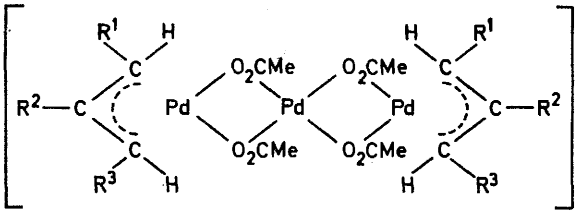
Analytical and molecular-weight data

	Analysis (%)						
	Found			Calc.			
	C	H	Pd	C	H	Pd	M [a]
Ligand in complexes $[Pd_3(\eta^3\text{-allyl})_2(\mu\text{-}O_2CMe)_4]$							
$CH_2{-}CH{-}CH_2$	27.2	3.50		26.4	3.35		
$CH_2{-}CH{-}CH{-}Pr$	33.4	5.10	43.9	33.2	4.70	44.2	629 [b] (720)
$MeCH{-}CH{-}CH{-}Et$	33.8	4.85		33.2	4.70		765 [b] (720)
$MeCH{-}CH{-}CHMe$	31.0	4.20		31.2	4.35		
$CH_2{-}CBu^t{-}CH_2$	35.5	4.95	42.7	35.2	5.02	42.6	
$CH_2{-}CH{-}CH{-}C_5H_{11}$	37.6	5.50	41.8	37.0	5.45	41.2	
$MeCH(O_2CMe){-}CH{-}CH{-}Me$	34.1	4.50		34.4	4.55		
Ligand in complexes $[Pd_2(\eta^3\text{-allyl})_2(\mu\text{-}O_2CMe)_2]$							
$CH_2{-}CH{-}CH{-}Pr$	38.8	5.65	43.0	38.6	5.70	42.9	
$Me{-}CH{-}CH{-}CH{-}Et$	38.5	5.70		38.6	5.70		515 [c] (496)
$Me{-}CH{-}CH{-}CH{-}Me$	35.5	5.20		35.8	5.15		
$MeCH(O_2CMe){-}CH{-}CH{-}Me$	38.9	5.35		39.2	5.20		556 [b] (613)

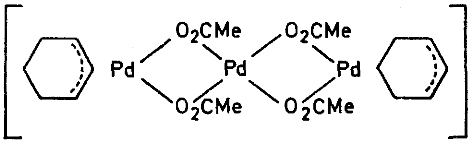
[a] Calculated values are given in parentheses. [b] Determined by osmometry in $CHCl_3$. [c] Determined by osmometry in C_6H_6.



(1)



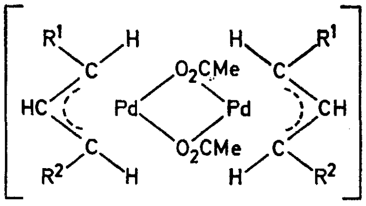
	R^1	R^2	R^3
(2a)	H	H	Pr
(2c)	Me	H	Et
(2d)	H	H	C_5H_{11}
(2e)	Me	H	Me
(2f)	H	H	H
(2g)	H	Bu^t	H



(2b)

RESULTS

Reactions of Mono-olefins.—Trimeric palladium acetate reacted with two molecules of a mono-olefin in acetic acid at 25 °C, the initial product still being trinuclear. After 6 h, hex-1-ene (1) yielded the brown complex tetra-μ-acetato-di(1—3-η-hex-2-enyl)tripalladium, (2a) [reaction (1)]. When the reaction was carried out *in vacuo* some palladium precipitated, but in the presence of dioxygen which reoxidises the palladium the yield of (2a) based on $[Pd_3(O_2CMe)_6]$ was quantitative. Similar reactions were carried out with cyclohexene, *cis*-hex-2-ene, oct-1-ene, *cis*-pent-2-ene, propene, and 2,3,3-trimethylbut-1-ene yielding the complexes (2b)—(2g). All the complexes are stable and easily recrystallised with the exception of the very labile 1—3-η-cyclohex-2-enyl complex which decomposed at 0—10 °C. Analytical and molecular-weight data are given in Table 1.



	R^1	R^2
(3a)	H	Pr
(3c)	Me	Et
(3e)	Me	Me
(3f)	H	H

After the formation of (2a) from hex-1-ene, the reduction of Pd^{II} was very slow and in the absence of dioxygen a further reaction led to the formation of di-μ-acetato-bis[(1—3-η-hex-2-enyl)palladium], (3a), which is complete at *ca.* 150 h [reaction (2)]. Similarly *cis*-hex-2-ene, (4),

$$[Pd_3(O_2CMe)_6] + 2C_6H_{12} \longrightarrow [Pd_3(\eta^3\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4] + 2MeCO_2H \quad (1)$$

$$2[Pd_3(\eta^3\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4] + 2C_6H_{12} \longrightarrow 3[Pd_2(\eta^3\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_2] + 2MeCO_2H \quad (2)$$

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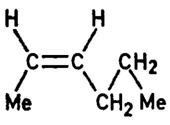
[4] H. C. Volger, *Rec. Trav. chim.*, 1968, **87**, 225.

gave (2c) and then (3c). The course of these reactions may be followed semiquantitatively by means of the following bands in the i.r. spectra obtained from Nujol mulls of the mixed solids: $[Pd_3(O_2CMe)_6]$ 1 600 and 700; (2a) and (2c) 1 560 and 700; (3a) and (3c) 1 560 and 675 cm^{-1}.

A few of the reactions of the complexes were studied.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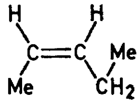
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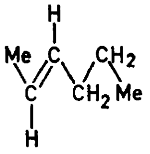
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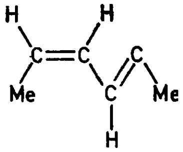
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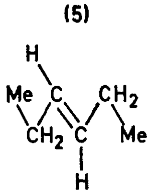
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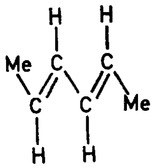
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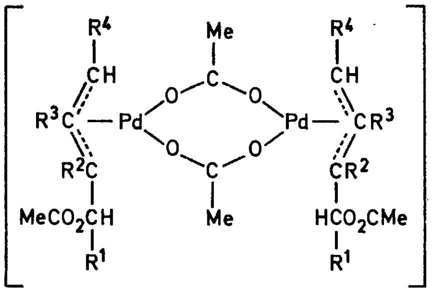
Thus hydrogenation of (2a) in dioxan solution served to confirm the stoicheiometry of the trinuclear complex since n.m.r. analysis showed the presence of n-hexane and acetic acid in the molar ratio 1 : 2.0. On shaking with aqueous sodium cyanide and ethylbenzene the complexes decomposed yielding n-hexenes. The 1—3-η complexes (2a) and (3a) gave hex-1-ene, *cis*-hex-2-ene, and *trans*-hex-2-ene, (5), in the ratio 9 : 7 : 9, and the 2—4-η complexes (2c) and (3c) gave (1), (4), (5), and *trans*-hex-3-ene, (6), in the ratio 14 : 25 : 33 : 28. Reaction (2) is reversible, for when nitrogen was bubbled slowly through an acetic acid solution of (3a) to remove all the hexenes formed the trinuclear complex (2a) crystallised. The trinuclear complexes are also readily prepared by reaction of the binuclear species with palladium acetate [equation (3)].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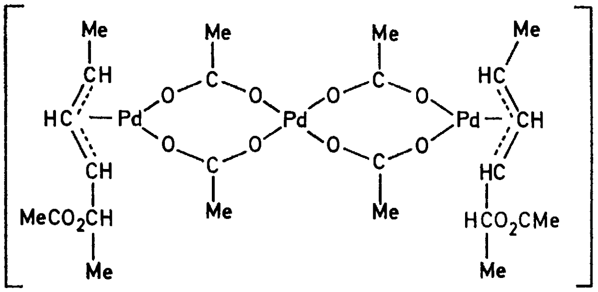
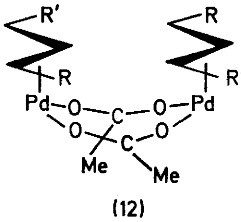

(11)

$$[Pd_2(\eta^3\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_2] + \tfrac{1}{3}[Pd_3(O_2CMe)_6] \longrightarrow [Pd_3(\eta^3\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4] \quad (3)$$

These preparative reactions may be modified by addition of solvent acid or base. Solid palladium acetate dissolved very rapidly in 0.5 mol dm^{-3} $HClO_4$ in acetic acid containing an excess of an olefin. Some Pd^{II} was reduced and olefins such as (1) and (4) were isomerised to equilibrium mixtures. The pale straw-coloured solutions contained allyl complexes and the binuclear complexes (3c), *etc.* could be isolated after neutralisation with sodium acetate. Thus propene gave (3f) whilst (1), (4), and *cis*-pent-2-ene, (7), all gave 2—4-η complexes which were shown by ^{13}C n.m.r. spectroscopy to contain a little of the terminal 1—3-η species. However, n.m.r. spectra also show that a terminal allylic species such as (3a) does not isomerise to the internal allylic isomer even in the presence of $HClO_4$, contrary to our earlier findings.[5] Although palladium acetate reacted with olefins in acetic acid containing 0.5 mol dm^{-3} $Na(O_2CMe)$, (2) and (3) were not formed and the actual product was not investigated further.

Reactions of Diolefins.—Conjugated dienes reacted with palladium acetate in acetic acid solution at 25 °C in the absence of O_2 to give 1-acetoxyalkyl-η³-allylic complexes, (10). Both *cis,trans*-hexa-2,4-diene, (8), and ***trans,trans***-hexa-2,4-diene, (9), gave yellow crystalline di-μ-acetato-bis[(2—4-η-5-acetoxyhex-3-en-2-yl)palladium], (10; $R^1 = R^4 = Me$, $R^2 = R^3 = H$). The dienes (8) and (9) underwent only very slow isomerisation in the presence of this complex. Although an excess of (8) or (9) reacted to give the complex (10), the latter reacted with 1 mol of palladium acetate to give tetra-μ-acetato-di(2—4-η-5-acetoxyhex-3-en-2-yl)tripalladium, (11). 2,3-Dimethylbuta-1,3-diene and 5,5-dimethyl-2-t-butylhexa-1,3-diene reacted similarly to give oils that were characterised by n.m.r. and i.r. spectroscopy as dimeric (10; $R^1 = R^4 = H$, $R^2 = R^3 = Me$) and (10; $R^1 = R^3 = Bu^t$, $R^2 = R^4 = H$).

N.M.R. Spectra of the Complexes.—There have been a number of papers [6-8] describing the ^1H n.m.r. spectra of acetato-bridged complexes of the type $[Pd_2(\eta^3\text{-allyl})_2(O_2CMe)_2]$ which exist in solution as two conformers (12) and (13). At low temperatures in $CDCl_3$ solution (12; R = R′ = H) undergoes intramolecular exchange of the ' head-in ' and ' head-out ' allyl groups by cleavage of one of the acetate bridges followed by rearrangement and collapse. At higher temperatures the allylic fragments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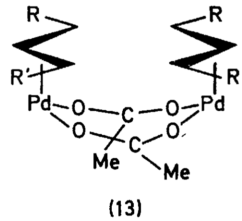
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[5] R. G. Brown, J. M. Davidson, and C. Triggs, Amer. Chem. Soc. Div. Petroleum Chem., preprinted papers, 1966, vol. 13, p. 66.

[6] J. Powell, *J. Chem. Soc.* (*A*), 1971, 2233.

[7] J. Powell and T. Jack, *Inorg. Chem.*, 1972, **11**, 103.

[8] P. W. N. M. Van Leeuwen and A. P. Praat, *Rec. Trav. chim.*, 1970, **89**, 321.

TABLE 2

N.m.r. data for allylic complexes

Allyl	Solvent	^{13}C Resonances [a](δ/p.p.m.)							^{1}H Resonances [b](τ)						Comment
		θ_c/°C	C^1	C^2	C^3	CH_3 (*syn*)	O–C–O	CH_3 Acetate	θ_c/°C	C^1–H (*anti*)	C^2–H	C^3–H (*anti*)	C^1–CH_3 (*syn*)	CH_3 (acetate bridge)	
$[Pd_2(\eta^3\text{-allyl})_2(\mu\text{-}O_2CMe)_2]$ complexes															
C^1H_2–C^2H–C^3H_2	CD_3CO_2D								28	70.7 (d) (12) [c]	4.45 [d]	7.07 (d) (12)			C^1–H (*syn*): τ 6.07 (d) (7.0)
	$CDCl_3$	16	54.8	110.5	54.8		179.4	22.9							
	$CDCl_3$	−53	3 lines [−14] [e]	3 lines [−14]			2 lines [−5]	br							
MeC^{1}H–C^2H–C^3HMe	CD_3CO_2D								28	6.30 (10.5, 6.5)	4.70 (t) (10.5)		8.90 (d) (6.5)		
	$CDCl_3$	40 [f]	70.7	113.0	70.7	17.0	179.5	24.0	55	6.52 (dq) [g] (10.5, 6.5)	4.91 (t) (10.5)		8.87 (d) (6.5)	8.06 (s)	
	$CDCl_3$	−60	3 lines [−20]	3 lines [−20]	3 lines [−20]	2 lines [−40]	br	br	−60	3 (dq) [g] [−25, 5]	3 (t) [g] [25, 5]		2 (d) [h] [−25]	7.92 (s)	
MeC^{1}H–C^2H–C^3HEt	$CDCl_3$	40 [i]	71.3	111.0	77.6	17.1	179.6	24.1	35	6.5 (m) (br)	4.88 (t) (11.0)	6.5 (m) (br)	8.86 (d) (6.5)	8.03 (s)	C^3Et: δ 12.8 (CH_2) and 24.9 (CH_3) and τ 8.51 (q) (7.0) and 8.92 (t) (7.0)
	$CDCl_3$	−40	vbr	2 br lines	vbr	2 lines	br	24.6br	−60	br [j]	3 (t) [g] [−20.0]	br			C^3Et: 2 lines from CH_2 (δ 13.9); a br line (δ 24.6) overlapped acetate (CH_3?)
C^1H_2–C^2H–C^3HPr	$CDCl_3$								35	7.44 (d) (12.0)	4.80 (dt) (12.0, 7.0)	6.4 (m) (br)		8.07 (s)	C^3Pr: m at τ 8.50 (complex) and 9.13 (t) C–H (*syn*): τ 6.38 (7.0)
	$CDCl_3$								−50	2 (d) (7.0)	2 (m) [−20]	br			
MeC^{1}H–C^2H–C^3H–C^4HMe(O_2CMe)	CD_3CO_2D								28	6.15 (dq) (7.0)	4.50 (t) (11.0)	6.69 (2d) (11.0, 8.0)	8.90(d) (6.0)		C^4HMe(O_2CMe): τ 5.08 (qnt) (7.0) and 8.71 (d) (7.0) from CH_3
	$CDCl_3$	48	73.0	110.3	70.3 [k]	16.5	179.4	23.5	55	6.30 (m)	4.60 (t) (10.0)	6.84 (t)	8.83(d) (6.0)	8.07 (s)	C^4HMe(O_2CMe): δ19.0 (CH_3), 69.8 [k] (CH) 20.6, (CH_3 in acetate), and 169.7 (carboxyl) τ 5.01 (qnt) (7.0), 8.73 (7.0) (from CH_3) 7.99 (s) (from acetate)
	$CDCl_3$	−57	br	3 lines	br	3 lines	4 lines	br	−40	br	br	br	8.79(d)	5 lines	C^4HMe(O_2CMe): 2 lines from carboxyl (δ 170.7, and 170.0) τ 8.59 (d) [l] (CH_3) and 2 lines from acetate
C^1H_2–C^2Me–C^3MeCH_2(O_2CMe)	CD_3CO_2D								30	Unsymmetrical m at 5.9 and 6.7					CH_3: τ 7.75 (s) and 8.78 (s)
	$CDCl_3$								40	Unsymmetrical m at 5.9, 6.1, and 6.8				7.99 (s) [m]	Acetate ester: τ 7.99; [m] other (CH_3) at 7.79(s) and 8.78 (s)
	$CDCl_3$								−50	br	br	br		7.90 [m]	Each CH_3 gave 2 lines of equal intensity τ 7.74 and 8.75 [−20]
C^1HBu^t–C^2H–C^3Bu^t–CH_2(O_2CMe)	CD_3CO_2D								30	Unsymmetrical m at 5.8 and 6.7					Bu^t: τ 8.69 (s) and 9.10 (s); 6 weak lines at 8.7—9.15
	$CDCl_3$								30	Unsymmetrical m at 4.5—5.7				8.10 (5lines)	Bu^t: 8.59 (s), and 8.82 (s). 6 weak lines at s 8.4—9.2
$[Pd_3(\eta\text{-}^3\text{allyl})_2(\mu\text{-}O_2CMe)_4]$ complexes															
C^1H_2–C^2H–C^3H_2	$CDCl_3$								50	6.31 (d) (br)	4.1 (vbr)		8.12 (s)		C^1–H (*syn*): τ 5.74 (d) (7.0)
	$CDCl_3$								−30	6.1—6.6 3 (d)	4.1 (vbr)		8.05 (s)		C^1–H (*syn*): τ 5.64 (d) 7.0) (br)
MeC^{1}H–C^2H–C^3HMe	$CDCl_3$								60 [h,n]	6.0 (vbr)	4.2 (vbr)		8.75 (d) (7.0)	8.17	
	$CDCl_3$								−40	6.15 (2d), 5.5 (br)	4.16 (t) (13.0), 4.5 (m) *ca.* [40]		(2d) [h] [10]	8.10 (br)	
MeC^{1}H–C^2H–C^3HEt	$CDCl_3$								65 [h]	5.82(br)	4.28 (t) (10.0) (10.0)		8.77 (d) (6.5)	8.20 (s)	C^3Et: τ 8.92 (t) (7.0) from CH_3 and br unresolved resonances from CH_2
	$CDCl_3$								−45	(2m)	(4t)		br	br	
C^1H_2–C^2H–C^3HPr	$CDCl_3$								60 [h]	5.58 (br)	4.26 (br)	6.64 (t) (br)		8.11 (s)	C^3Pr: br resonances C–H (*syn*): τ 5.98 (d) (6.0)
	$CDCl_3$								−45	5.28 (br)	(4t)	(4d) [h]		br	C^1–H (*syn*): τ 5.87 (br unsymmetrical d)
C^1H_2–C^2H–$C^3HC_5H_{11}$	$CDCl_3$								35	5.22 (br)	4.38 (br)	6.32 (d) (br)		8.11 (s)	C^1–H (*syn*): 5.91 (d) (6.0). Resonances from alkyl groups not resolved)
1—3-η-Cyclohex-2-enyl	$CDCl_3$ [o]								10	4.99 (br)	4.60 (t) (6.0)			8.10	
	$CDCl_3$ [o]								−70	br	(t + m)				
MeC^{1}H–C^2H–C^3H–C^4HMe(O_2CMe)	$CDCl_3$								40	4.0 — 6.5(br m)			8.76 (d) (6.0)	8.15 (br)	C^4HMe(O_2CMe): τ 8.64 (d) (7.0) (CH_3) and 8.01 (CH_3 in acetate)
	$CDCl_3$								−20	3.9—6.6 (m)			(6d)	(4s)	2CHMe groups gave overlapping pattern of at least 6 doublets

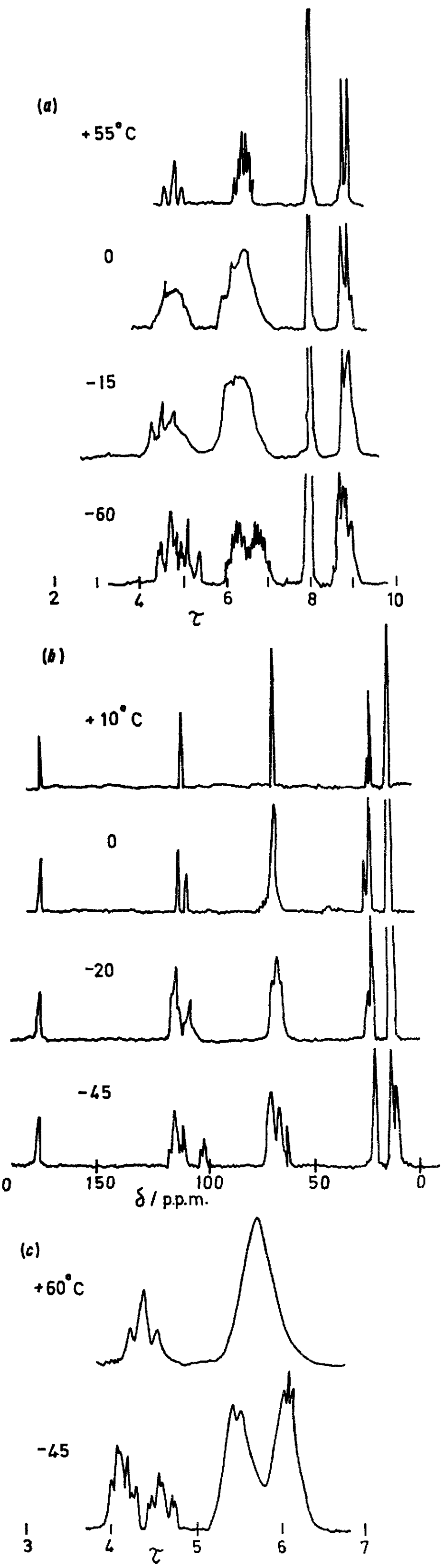
[a] Varian Xl-100 spectra at 25.2 MHz; δ values relative to $SiMe_4$. [b] Varian HA-100 spectra at 100 MHz; τ values relative to $SiMe_4$. [c] Coupling constants (J/Hz) are given in parentheses. [d] Symmetrical seven-line multiplet from a triplet of triplets. [e] Coalescence temperatures (°C) are given in square brackets. [f] Spectrum showed the presence of some 1-3-η-isomer, *e.g.* C^1 had δ 52.7 p.p.m. [g] Overlapping multiplets. [h] Incompletely resolved [i] Spectrum showed the presence of some 1—3-η-isomer, *e.g.* C^1 had δ 53.3 p.p.m. [j] Hydrogen at C^1 and C^3 barely resolved from each other. [k] Resonances from C^3 and C^4 overlapped. [l] At least five overlapping doublets from the CH_3 (*syn*) and the methyl at C^4. [m] Broad overlapping singlets at low temperature which coalesced to one broad singlet at 40 °C. [n] Sharpened by the addition of acetic acid. [o] Contained a trace amount of acetic acid from preparation.

exchange between (12) and (13). Coalescence temperatures are lowered by bridge-splitting ligands, especially acetic acid. Hence spectra observed in acetic acid show fast exchange and, while these give information concerning positional isomerism of the allyl fragment, they do not help to elucidate the structures of the complexes themselves *in acetic acid*.

Thus most spectra were recorded in $CDCl_3$ at 50 to −65 °C (Table 2). Proton-decoupled ^{13}C n.m.r. spectra were used to obtain further information about the dimers, *e.g.* they confirm that complex (3f) exists as a 2 : 1 mixture of (12) and (13) ($R = R' = H$). At 16 °C four sharp lines were observed. At −5 °C the line at δ 179.4 p.p.m. (carboxyl carbon) collapsed and the lines at δ 110.5 (central allylic carbon) and 54.8 p.p.m. (terminal allylic carbon) became broad. Below −14 °C the carboxylate carbon gave two lines (δ 179.1 p.p.m.) with an intensity ratio of 2 : 1. Although the resonance of the methyl of the acetate group remained sharp at −24 °C, the allylic carbons were nearly resolved. Below −36 °C the allylic carbons appeared as three lines of nearly equal intensity from the central carbon and three lines of approximately double this intensity from the terminal carbon.

Hydrogen-1 n.m.r. spectra of the *syn*-substituted η^3-allylic complexes (3c) and (3e) show that they have similar fluxional behaviour to (3f), and that in general the resonances due to the hydrogen on the allylic carbons give well resolved apparent first-order spectra. At 55 °C complex (3e) showed a triplet, a double quartet (*anti*-protons), a doublet (methyl groups), and a singlet (acetate) [Figure 1(*a*)]. The 'allylic' resonances coalesced at just above 6 °C, and on cooling to −10 °C the resonance of the central hydrogen was resolved into a triplet overlying a broad peak. At −60 °C this part of the spectrum showed three triplets with intensity ratio 5 : 1 : 5 in agreement with the predominant existence of Powell's 'head-in, head-out' conformer. Corresponding changes occurred in the double quartet and doublet, and similar spectra were obtained from (3c). These results were confirmed by ^{13}C n.m.r. spectroscopy. Thus the terminal carbons of the allyl group in (3e) [Figure 1(*b*)] (δ 70.7 p.p.m. at 40 °C) gave a sharp peak (δ 66.1 p.p.m.; head-in,head-in) and two broad peaks (δ 71.4 and 70.1 p.p.m.; head-in,head-out) at −60 °C. The central carbon showed a similar effect. The resonances of the *syn*-methyl groups were only partly resolved. The unsymmetrical complex (3c) showed similar behaviour to (3e). Since large samples were required for ^{13}C n.m.r. spectroscopy they were crystallised fewer times than were those for ^1H n.m.r. As a consequence, impurities such as 1—3-η-allyls could be detected, *e.g.* δ *ca.* 53 p.p.m. at 40 °C for $=CH_2$ in the pent-2-enyl and hex-2-enyl complexes.

The trinuclear complexes were much less soluble than the binuclear species and ^{13}C n.m.r. spectra were not run. The ^1H n.m.r. spectra are surprisingly similar to those of the binuclear complexes. Complex (3f) had a sharp doublet (τ 5.74, *syn*-hydrogen) and a broad doublet (τ 6.3, *anti*-hydrogen) at 50 °C. On cooling to −20 °C the broad doublet sharpened and two additional doublets of lower intensity appeared at τ 6.13 and 6.72, all three doublets having coupling constants of 12 Hz. At *ca.* −30 °C crystallisation commenced but the resonance due to acetate was still a sharp singlet. Complex (2c) gave only broad resonances from the allylic protons even at 60 °C, while the methyl groups gave rise to one strong sharp doublet overlapping another much weaker one. The trinuclear com-



Variable-temperature n.m.r. spectra of: (*a*) (2e), ^1H; (*b*) (2e), ^{13}C; and (*c*) (2c), ^1H

plexes do not appear to reach the fast-exchange limit below 60 °C unless a little acetic acid is added. At −60 °C complex (2e) gave the expected triplet plus double quartet overlying weaker multiplets. The related complex (2c) gave a better resolved spectrum in which a pattern of two strong triplets and two weak triplets was observed from the central allylic hydrogen.

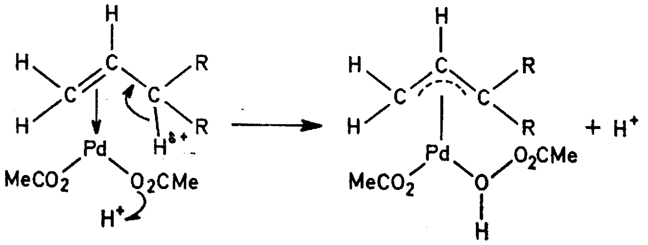
Acetic acid lowers the coalescence temperature of the exchange processes by *ca.* 25 °C. However, it is interesting that the exchange of acetic acid with the bridging acetate groups is faster for the binuclear than for the trinuclear species. For example at 28 °C complex (2f) in $CDCl_3$ solution gave acetate resonances due to the complex as well as those due to added acetic acid, while for (3f) the acetate resonances collapsed to a singlet together with those of the free acetic acid. The unstable complex from cyclohexene did not show exchange with acetic acid at 10 °C and is presumably trimeric $[Pd_3(C_6H_9)_2(O_2CMe)_4]$.

Due to the lack of symmetry, the complex (10; $R^1 = R^4 =$ Me, $R^2 = R^3 =$ H) potentially has six forms (excluding optical isomers). If the head-in,head-in isomer is sterically forbidden the number is reduced to four which have a total of seven environments for the μ-acetate and six for the organic acetate. In fact the ^{1}H n.m.r. spectrum at −40 °C showed four resolved peaks and two shoulders near τ 8.07 from the μ-acetate and a very broad unsymmetrical peak from the organic acetate. If all the possible arrangements of the methyl groups from C^1 and C^6 of the hexa-2,3-diene are distinguishable, 16 doublets should be seen but in fact only five were observed at −40 °C (see Discussion section). In the ^{13}C n.m.r. spectrum at −57 °C the carboxyl carbon of the μ-acetate gave four lines and the organic acetate two. As was the case with the other acetate-bridged binuclear complexes, the central carbon of the allyl group gave three lines in the ^{13}C spectrum. Addition of 1 equivalent of acetic acid caused a sharpening of most of the resonances in the ^{13}C n.m.r. spectrum but those of the μ-acetate became broad. In the ^{1}H n.m.r. spectrum at −40 °C the four resonances from the μ-acetate collapsed together with that of the acetic acid into a singlet and began to coalesce with that of the organic acetate, and at 0 °C these resonances became a sharp singlet. Thus the μ-acetate exchanges with acetic acid at a lower temperature than does the organic acetate.

The trinuclear complex (11) was again insufficiently soluble to allow the ^{13}C n.m.r. spectrum to be obtained, but the ^{1}H spectrum was quite informative. At 40 °C the resonances were sharp and included singlets with an intensity ratio 2 : 1 (acetates) and two doublets (methyls). At −20 °C five lines due to the μ-acetate and three due to the organic acetate were observed, together with doublets from the two methyl groups.

DISCUSSION

It is apparent that under the conditions of our experiments the cyclic trimer of palladium acetate,[9] which undergoes slow cleavage reactions in acetic acid at 25 °C,[10] reacts with mono-olefins, presumably *via* a η^2 complex, to yield the series of trinuclear allylpalladium complexes, (2a)—(2g). A further slow reaction yields the binuclear species (3a), *etc.* Both of these steps involve loss of acetic acid from a η^2 complex and it is therefore surprising to find that perchloric acid catalyses this process.* This suggests that palladium acts as an electrophile towards the olefin, removing charge and ultimately polarising the C–H bond from which a proton is lost. This process would be enhanced by protonation of an acetate ligand.



It is noteworthy that the 1—3-η complexes (2a) and (3a) are formed from hex-1-ene despite extensive isomerisation of the olefin to *cis*- and *trans*-hex-2-ene. Apparently (1) is very much more reactive than (4) and kinetic control leads to essentially pure products. The reaction of 1,3-dienes with palladium acetate to yield acetoxyalkylpalladium complexes is to be expected, although only hexa-2,4-diene gave a crystalline solid that could be crystallised readily. The interest in these complexes lies in their powerful action as oxidation catalysts.[12]

In his original study on the fluxional behaviour of $[Pd_2(1\text{—}3\text{-}\eta\text{-allyl})_2(\mu\text{-}O_2CMe)_2]$ Powell[6] concluded that the conformers (12) and (13) ($R = R' =$ H) exist in solution and that the head-in,head-in conformer should be absent because of steric hindrance at the central allylic carbon. Our new series of trinuclear complexes presents rather similar possibilities [(14), (15), and (16)] but the steric hindrance to the head-in allyl group is of a different type. The general appearance of the low-temperature ^{1}H n.m.r. spectra of the trinuclear complexes is very similar to that of the binuclear species suggesting that the head-in,head-out conformer (14) predominates. But since the environment of the head-in groups in (14) and (15) is very similar, there seems to be little reason why the latter should not exist. In fact the central allylic carbon of complex (2c) gives rise to four triplets at −45 °C confirming the existence of all the three conformers. When the allylic group in both series of complexes is substituted unsymmetrically in the *syn* position by alkyl groups as in (2c) and (3c), the number of conformers is much increased and there are many possible environments for some of the atoms which might be distinguished by ^{1}H or ^{13}C n.m.r. spectroscopy. Apparently the chemical-shift differences are very small because the resonances are generally not resolved in the manner of those due to hydrogen attached to the allylic carbons. Perhaps the largest shifts might

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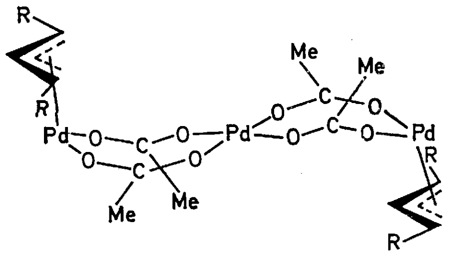
* It is possible that the binuclear complex is a by-product of reduction of the trinuclear species.[11]

[9] A. C. Skapsky and M. L. Smart, *Chem. Comm.*, 1970, 658.

[10] R. N. Pandey and P. M. Henry, *Canad. J. Chem.*, 1974, **52**, 1241.

[11] R. G. Brown, R. V. Chaudhari, and J. M. Davidson, following paper.

[12] R. V. Chaudhari and J. M. Davidson, unpublished work.



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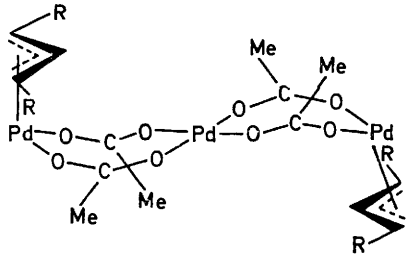

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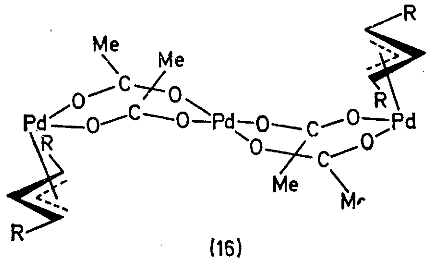

(16)

have been expected for the ^{13}C resonances of the carboxylate carbon of the acetate bridge and these do give two lines for the conformers (12) and (13) ($R = R' = H$). However, when the *syn*-substituent bears an organic acetate group as in the diene complexes (10; $R^1 = R^4 =$ Me, $R^2 = R^3 = H$) and (11) the chemical-shift differences are larger, perhaps due to the magnetic anisotropy associated with the carbonyl group, and some details of the fluxional behaviour are revealed. In order to account for the observed number of lines it becomes necessary to take account of the disposition of the *syn*-substituents with respect to the plane which passes through the palladium atoms and bisects the acetate bridges. Since the head-in,head-in conformation is sterically forbidden in complex (10; $R^1 = R^4 =$ Me, $R^2 = R^3 = H$), the observed six ^{1}H resonances from the μ-acetate group are close to the seven required by all the possible arrangements of the substituents on the same or different 'sides' of the molecule. However, the methyl substituents themselves give only five doublets in the ^{1}H spectrum at −40 °C and likewise in the ^{13}C spectrum at low temperature there are only four lines from the carboxylate carbons. Both of these resonances have chemical shifts that are sensitive only to the head-in or head-out arrangement. In the corresponding trinuclear complex (11) the spectra are best explained by the existence of all the three head-in,head-out conformers but the *syn*-substituents are too distant for mutual disposition to show any effects.

The ^{1}H studies of the exchange of acetate ions between the complexes and free acetic acid in $CDCl_3$ show that the binuclear series exchange at lower temperature than the trinuclear complexes. It seems likely that a *trans* effect of the allyl groups renders the Pd–O bonds labile to exchange. In the trinuclear complexes the central palladium atom experiences no such labilising influence and thus all the four acetate groups are bound by relatively inert bonds. Exchange of the organic acetate in the diene complexes must involve prior dissociation of Pd–O bonds in the bridges since it only occurs in the dimer and then at a higher temperature than exchange of the bridging acetate.

EXPERIMENTAL

Palladium acetate and other reagents were purified by the methods described in the following paper. Reactions of the olefins were carried out in sealed evacuated tubes at 25 °C. Hydrogen-1 and ^{13}C n.m.r. spectra were recorded on Varian HA-100 and XL-100 spectrometers with variable-temperature probes. Olefins were analysed by g.l.c. at 50 °C using a column (12 m × 6 mm) packed with polypropylene glycol LB-500-x on Chromosorb W and a Perkin-Elmer model 451 fractometer. Routine identification of complexes was made by i.r. and n.m.r. spectroscopy.

*Reaction of Hex-*1*-ene with Palladium Acetate.*—Hex-1-ene (0.67 g) was shaken with palladium acetate (0.41 g) in acetic acid (30 cm^3) for 6 h *in vacuo*. The precipitate of palladium (0.040 g) was filtered off and crude tetra-μ-acetato-di(1—3-η-hex-2-enyl)tripalladium, (2a), was obtained as a residue after removal of all the volatile material at 10^{-6} mmHg.* The trinuclear complex (0.48 g) was recrystallised from diethyl ether. A similar reaction carried out for 144 h afforded di-μ-acetato-bis[(1—3-η-hex-2-enyl)palladium], (3a) (0.36 g), which was recrystallised from light petroleum (b.p. 40—60 °C). The hexenes were recovered from the volatile fraction after both reactions by use of fractional condensation at −45 °C (10^{-6} mmHg) to remove acetic acid and hexenyl acetates. Analysis by g.l.c. showed hex-1-ene, *cis*-hex-2-ene, *trans*-hex-2-ene, *cis*-hex-3-ene, and *trans*-hex-3-ene in the ratio 15 : 13 : 65 : 3 after 6 h and 7 : 14 : 74 : 1 : 4 after 144 h. Similar reactions were carried out with the other olefins listed in the Results section.

Reaction of cis*-Pent-*2*-ene with Palladium Acetate in Acetic Acid–Perchloric Acid.*—Palladium acetate (0.75 g) and *cis*-pent-2-ene (2.0 cm^3) were shaken with 60% perchloric acid (5% v/v, 20 cm^3) in acetic acid. After 1 h the slight precipitate of palladium was removed from the

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 atm = 101 325 Pa.

straw-coloured solution which was then mixed with 0.46 mol dm^{-3} sodium acetate (20 cm^3) in acetic acid. Volatile materials were removed at 10^{-6} mmHg and di-μ-acetato-bis[(2—4-η-pent-3-en-2-yl)palladium], (3e), was extracted from the residue with diethyl ether from which it was also crystallised at −10 °C.

Preparation of Tetra-μ-acetato-di(2—4-η-hex-3-en-2-yl)tripalladium, (2c).—Di-μ-acetato-bis[(2—4-η-hex-3-en-2-yl)-palladium] (0.0246 g), palladium acetate (0.0059 g), and acetic acid (0.793 g) were allowed to react in a sealed evacuated tube at 25 °C. The trinuclear *complex* (2c) crystallised slowly and after 2 d the yield was 0.0161 g. Complex (2c) was also obtained after 12 h by slow crystallisation when nitrogen gas was bubbled slowly through an acetic acid solution (1 cm^3) of complex (3c) (0.058 g).

Preparation of Di-μ-acetato-bis[(2—4-η-5-acetoxyhex-3-en-2-yl)palladium] (10; $R^1 = R^4 =$ Me, $R^2 = R^3 =$ H).—A solution of *trans,tran*-hexa-2,4-diene (0.239 g) in acetic acid (10 cm^3) was shaken with palladium acetate (0.62 g). The solid dissolved slowly (4 d) to give a clear yellow solution. Volatile compounds were removed at 10^{-6} mmHg to give a quantitative yield of the desired acetoxyalkyl *complex* which was recrystallised from light petroleum (b.p. 60—80 °C). *cis,trans*-Hexa-2,4-diene afforded the same complex, but other dienes generally gave oily substances that could not be crystallised.

Reactions of Complex (2c).—A mixture of (2c) (0.051 g) and a few milligrams of PtO_2 was treated with hydrogen (20 atm) for 24 h in the presence of dioxan as solvent. The filtered solution was transferred to an n.m.r. tube and the integrated intensities of the resonances due to the methyl groups in acetic acid and n-hexane was noted. These had the intensity ratio 1 : 2.0.

Complex (2c) (0.37 g) was also treated with aqueous Na[CN] in the presence of ethylbenzene (1 cm^3) until the colour of the complex disappeared. The ethylbenzene solution was analysed directly by g.l.c. and contained n-hexanes as described above.

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