Preparation and Nuclear Magnetic Resonance Studies of the Dynamic Processes in α,1,2-η-Triphenylmethyl- and Monosubstituted-α,1,2-η-triphenylmethyl-palladium and -platinum Complexes

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Reaction of the zerovalent palladium or platinum complexes $[M_2(dba)_3(s)]$ (dba = PhCH=CHCOCH=CHPh; s = dba or solvent) with Ph_3CCl gives $[\{M(CPh_3)Cl\}_n]$ (*n* probably 2) which are converted into the pentane-2,4-dionates $[M(CPh_3)(acac)]$ [M = Pd (3a) or Pt (3b); acac = MeCOCHCOMe] by reaction with Tl(acac). The CPh_3 ligands in complexes (3a) and (3b) are η^3-benzylically bound to the metal. Three different dynamic processes of progressively higher $\Delta G^\ddagger$ are undergone by complex (3a) and have been studied by n.m.r. spectroscopy: (A), where the metal moves between two η^3-positions on a single phenyl *via* a suprafacial [1,5]-sigmatropic shift; (B), where the metal moves from one phenyl ring to another ($\Delta G^\ddagger$ = 13.8 kcal mol^{-1} at 300 K); and (C), where the ends of the acac ligand also become equilibrated [after remaining distinct during processes (A) and (B)]. Process (A) [but not (B) or (C)] also occurs in (3b) ($\Delta G^\ddagger$ = *ca.* 6.4 kcal mol^{-1} at 187 K) within the accessible temperature range, but it could not be frozen out for either (3a) or (3b). A *p*-substituent in one phenyl ring has a small effect on the rate of process (B), but the metal shows definite site preferences and favours the phenyl bearing the more electron-releasing substituent.

THE possibility that the benzyl group could be η^3- (rather than σ-) bonded was first suggested by King and Fronzaglia[1] for the complex $[Mo(\eta^5\text{-}C_5H_5)(CH_2Ph)(CO)_2]$ obtained by decarbonylation of $[Mo(\eta^5\text{-}C_5H_5)(\sigma\text{-}CH_2Ph)(CO)_3]$. This was confirmed by an *X*-ray structure determination of $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2C_6H_4Me\text{-}4)(CO)_2]$ carried out by Cotton and La Prade.[2] Cotton and Marks[3] later reported an elegant ^1H n.m.r. investigation of the dynamic processes which occur in such molecules and concluded that they proceeded *via* 16-electron σ-benzylic intermediates of the type $[Mo(\eta\text{-}C_5H_5)(\sigma\text{-}CH_2R)(CO)_2]$ (R = aryl) with E_{act} = 19 kcal mol^{-1}.† Since then a number of η^3-benzyl complexes of other metals have been prepared including $[Pd(\eta^3\text{-}CH_2Ph)(PEt_3)_2]^+$,[4] $[\{Pd(\eta^3\text{-}CH_2Ph)Cl\}_2]$,[5] and $[Co(\eta^3\text{-}CH_2Ph)\{P(OMe)_3\}_3]$.[6] Wilke and Schott[7] have reported the preparation of $[Ni(CPh_3)_2]$ and $[\{Ni(CPh_3)Cl\}_n]$ but the structures have not been elucidated.[8]

In connection with our interest in the use of the zerovalent palladium and platinum olefin complexes $[M_2(dba)_3(s)]$ [M = Pd (1a) or Pt (1b); dba = 1,5-diphenylpenta-1,4-dien-3-one, PhCH=CHCOCH=CHPh; s = solvent or dba][9,10] as synthetic precursors, we have examined their reactions with a number of organic halides, in particular those likely to give η^3-bonded complexes.[11,12] We here report the reactions of (1a) and (1b) with chlorotriphenylmethane, and with some mono-*p*-substituted chlorotriphenylmethanes, to give η^3-triphenylmethyl complexes of Pd^{II} and Pt^{II} and also the dynamic behaviour that these complexes show. A preliminary communication on part of this work has appeared,[13] and details of the crystal structures of two complexes are given in the following paper.[14]

RESULTS AND DISCUSSION

Preparation of the Complexes.—Complexes (1a) and (1b) reacted with Ph_3CCl in chloroform to give the chloro-complexes (2a) and (2b) in virtually quantitative and 44% yield, respectively. The yield of (2b) was improved (to 81%) if $[Pt(dba)_3]$ was used in place of (1b). The yield of (2a) was unchanged when the reaction was carried out in the presence of 1 equivalent of 2,6-di-t-butyl-4-methylphenol (ionol) as a radical-trapping agent. This suggests that the free triphenylmethyl radical is not formed in the reaction and that the complex arises either *via* a caged radical intermediate or by an S_N2 reaction path. Free, unchanged dba ligand was recovered from these reactions. Reaction of complexes (3a) or (3b) with HCl regenerated complexes (2a) or (2b) respectively.

$$\underset{(1)}{[M_2(dba)_3(s)]} + 2Ph_3CCl \longrightarrow [\{M(CPh_3)Cl\}_n] \qquad s = \text{solvent or dba}$$

$$\underset{(2)}{[\{M(CPh_3)Cl\}_n]} + Tl(acac) \longrightarrow \underset{(3)}{[M(CPh_3)(acac)]}$$

(a, M = Pd; b, M = Pt)

Complexes (2a) and (2b) were rather insoluble and molecular-weight determinations were not possible; some samples gave low C and H and high Cl analyses suggesting the presence of excess of $PdCl_2$. In order to investigate the complexes of the CPh_3 ligand further the more soluble pentane-2,4-dionate (acac) complexes (3a) and (3b) were prepared. *X*-Ray structure determinations on complexes (3a) and (3b)[14] showed that the two complexes were isostructural and that both contained the CPh_3 ligand η^3-co-ordinated to the metal which was also *OO'*-bonded to the acac ligand. The n.m.r. spectra of (3a) and (3b) showed that a variety of dynamic processes was occurring; in order to study these in more detail a series of η^3-triphenylmethylpalladium complexes bearing one *p*-substituent, $[\{Pd[CPh_2(C_6H_4X\text{-}4)]Cl\}_2]$ (4) and $[Pd[CPh_2(C_6H_4X\text{-}4)(acac)]$ (5) [(a) X = F, (b) X = Me, or (c) X = OMe], as also prepared by similar routes from the substituted chlorotriphenylmethane.

The chloro-complexes (4) were more soluble than (2a) and molecular-weight determinations showed them to be dimeric. The presence of a strong band in the far-i.r.

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† Throughout this paper: 1 kcal = 4.187 kJ.

spectrum of (2a) at 288 cm^{-1} is consistent with the presence of bridging chlorines, and we therefore presume these complexes to have dimeric structures with Pd_2Cl_2 bridges similar to those found for $[Pd_2(allyl)_2Cl_2]$.[15]

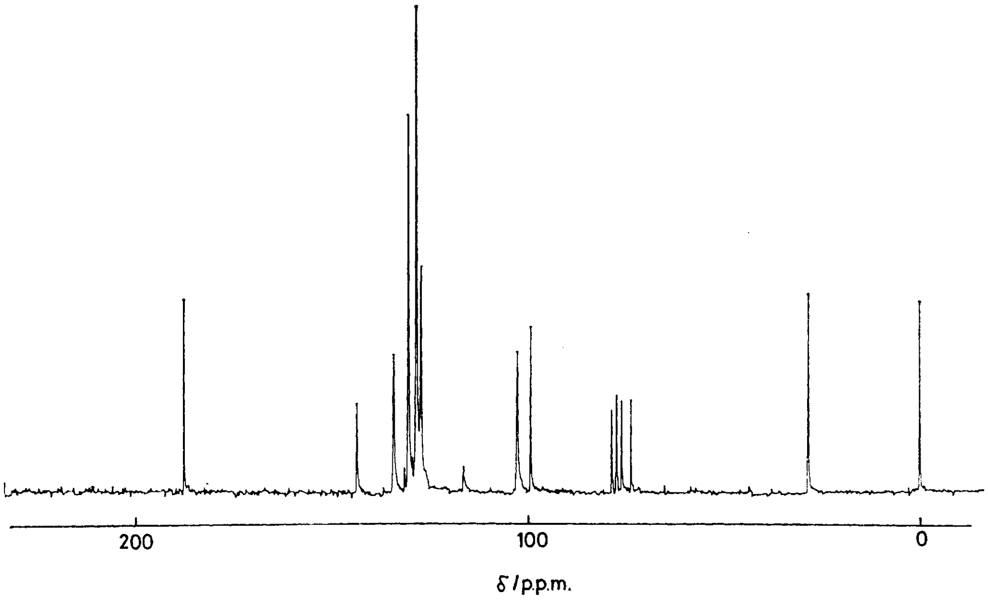

FIGURE 1 ^{13}C N.m.r. spectrum of $[Pd(\eta^3\text{-}CPh_3)(acac)]$ in $CDCl_3$ at −30 °C

N.M.R. Spectra of Complexes (3a) *and* (3b).—The ^{13}C n.m.r. spectra of neither (3a) (at −30 °C) nor of (3b) (at 20 °C) were consistent with the solid-state structures shown by the *X*-ray determination.* In particular, in place of the 15 signals expected for the η^3-CPh_3 ligand in (3a) (assuming free rotation of unco-ordinated phenyls), only eight could be observed (Figure 1). This may be explained by assuming a rapid fluxional process (A) such that the molecule appears to have a plane of symmetry through C(4)–C(1)–C(α). This should give rise to nine rather than eight CPh_3 signals but we find that there is additional accidental degeneracy between C(4) and C(3′ + 5′ + 3″ + 5″). The assignments of the acac carbons as well as of C(α), C(1), C(1′), and C(1″) are straightforward; the other carbons were assigned with the help of the higher-temperature spectra.

TABLE 1

^1H N.m.r. spectra in $CDCl_3$ at 30 °C

			acac	
	Compound	aryl	CH	CH_3
	Ph_3CCl	7.30		
(3a)	$[Pd(\eta^3\text{-}CPh_3)(acac)]$	7.00—7.60	5.08	1.76, 1.84
(3b)	$[Pt(\eta^3\text{-}CPh_3)(acac)]$	7.19, 7.33, 7.46	5.31	1.78, 1.90
		6.14 [H(2), *J*(H–Pt) 27 Hz]		
	$[4\text{-}FC_6H_4)Ph_2CCl$ [a]	6.7—7.5		
(5a)	$[Pd\{\eta^3\text{-}CPh_2(C_6H_4F\text{-}4)\}(acac)]$ [b]	6.8—7.6	5.06	1.74, 1.82
	$(4\text{-}MeC_6H_4)Ph_2CCl$ [c]	7.1, 7.25		
(5b)	$[Pd\{\eta^3\text{-}CPh_2(C_6H_4Me\text{-}4)\}(acac)]$ [d]	7.0—7.6	5.08	1.76, 1.84
	$(4\text{-}MeOC_6H_4)Ph_2CCl$ [e]	6.7—7.3		
(5c)	$[Pd\{\eta^3\text{-}CPh_2(C_6H_4OMe\text{-}4)\}(acac)]$ [f]	6.7—7.4	5.07	1.75, 1.83

[a] $\delta(^{19}F)$ = −115.8 p.p.m. with respect to $CFCl_3$. [b] $\delta(^{19}F)$ = −126.5 p.p.m. for forms 5aX and 5aY. [c] $\delta(^{19}F)$ = −115.4 for form 5aZ; δ(Me) = 2.30 p.p.m. [d] δ(Me) = 2.20 p.p.m. [e] δ(Me) = 3.72 p.p.m. [f] δ(Me) = 3.77 p.p.m.

Above −30 °C a second fluxional process (B) was observed for complex (3a). The only carbons unaffected by this are C(α) and the acac carbons. The signal at δ 102.3 p.p.m. can be assigned as the averaged C(2 + 6) signal since C(6) is expected to be at *ca.* δ 130 and C(2) at *ca.* 70 p.p.m. The remaining signals were assigned by a qualitative application of the Forsén–Hoffman spin-saturation method at −14 °C (Figure 2). Thus, irradiation at δ 116.0 p.p.m. [C(1)] caused the signal at 143.1 p.p.m. [C(1′ + 1″)] to vanish; irradiation

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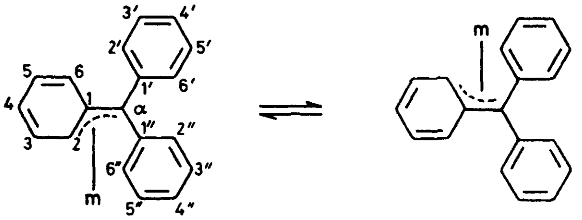
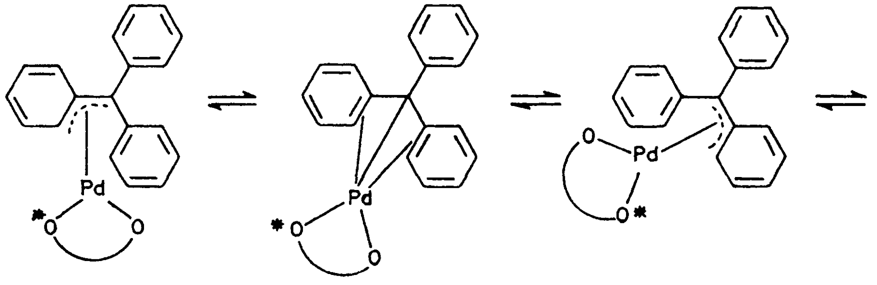
* The aromatic region of the ^1H spectra of complex (3b) at 30 °C and of (3a) at −30 °C showed two multiplets in the ratio of 13 : 2. The lower-frequency band of intensity 2 arises from H(2 + 6); at higher temperatures exchange occurs of the aromatic protons to produce a complex multiplet for (3a).



[m = Pd(acac) or Pt(acac)]
Process (A)

at δ 102.3 p.p.m. [C(2 + 6)] caused the signal at 129.9 p.p.m. to decrease markedly and allowed its assignment to C(2' + 2'' + 6' + 6''). On the basis of their intensities the signals at δ 133.7 and 127.9 p.p.m. were assigned to C(3 + 5) and C(3' + 3'' + 5' + 5'') respectively. This last assignment is consistent with the normal position of a *m*-carbon in a monosubstituted phenyl ring, between δ 127.5 and 129.5 p.p.m. Confirmation of these assignments came from the observation that irradiation at δ 133.7 p.p.m. caused a decrease in the intensity of the signal at 127.9 p.p.m. However, the decrease was not as much as that observed for C(2' + 2''+6'+6'') when the C(2+6) signal was irradiated; this suggests that the missing C(4) signal is also at δ 127.9 p.p.m. and leaves only the signal at 126.7 p.p.m. to C(4' + 4''). The behaviour of these resonances at higher temperatures was in agreement with these assignments (see below).



Process (B)

The ^{13}C n.m.r. spectrum of the platinum complex (3b) showed the nine resonances expected for the fluxional molecule. They were assigned by analogy with those of (3a) and with the help of *J*(Pt–C). Attempts to freeze out process (A) were unsuccessful. However, at −86 °C the signal at δ 92.9 p.p.m., due to C(2 + 6) in complex (3b), is broad, while the remaining signals are still sharp. This behaviour is consistent with process (A) beginning to slow down on the n.m.r. time scale. Following the argument developed above, if C(6) in (3b) resonates at *ca.* δ 130 p.p.m., C(2) should then be observed at *ca.* 54 p.p.m. From the difference (*ca.* 1 840 Hz) an exchange rate of 1.3×10^5 s^{-1} may be estimated which gives a value for $\Delta G^{\ddagger}$ of *ca.* 6.4 kcal mol^{-1} at 187 K. No similar broadening could be detected for the palladium complex (3a), implying a still lower $\Delta G^{\ddagger}$.

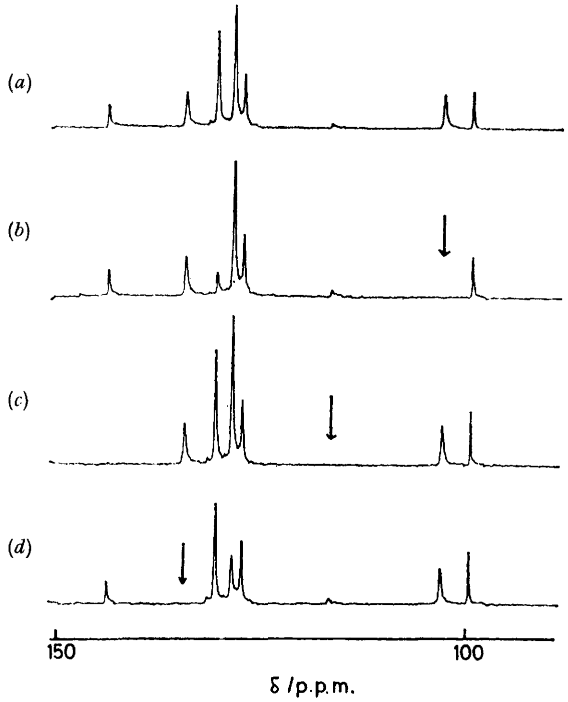


FIGURE 2 Partial ^{13}C n.m.r. spectra of [Pd(η^3-CPh_3)(acac)] in $CDCl_3$ at − 14°C; (*a*) unperturbed spectrum, (*b*) irradiation at δ 102.3, (*c*) irradiation at 116.0, (*d*) irradiation at 133.7 p.p.m.

The partial variable-temperature ^{13}C n.m.r. spectrum of the palladium complex (3a) is shown, together with a computer simulation, in Figure 3. The computer simulation is based on process (B) as shown. Good agreement is found especially around δ 128 p.p.m. where any mis-assignment of C(4), C(4'), or C(4'') would have produced significant discrepancies between the observed and computed spectra. The rates of process (B) for (3a) are 24 (263), 77 (273), 143 (282), 605 (302), 1 600 (316), 3 850 (326), and 5 500 s^{-1} (334 K). These values give activation parameters $\Delta G^{\ddagger} = 13.79 \pm 0.19$ kcal mol^{-1} (at 300 K), $\Delta H^{\ddagger} = 12.63 \pm 0.13$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -3.85 \pm 0.44$ cal K^{-1} mol^{-1}. By contrast, the platinum complex (3b) showed no evidence for process (B) even at 58 °C, giving a lower limit of 19.4 kcal mol^{-1} for $\Delta G^{\ddagger}$.

During processes (A) and (B) the two methyls of the acac in complex (3a) remained inequivalent in the ^1H spectrum,* but at 50 °C exchange [process (C)] between

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* The ^{13}C spectra of complexes (3) and (5) frequently showed only singlets for the acac CO and CH resonances owing to accidental equivalence; the two CH signals were, however, clearly distinguished in the ^1H spectra (Table 1).

the two sites became significant. The rate of process (C) is much less than that of (B); for example, when that of (B) is 605 s^{-1} the rate of (C) is only *ca.* 8 s^{-1}, for the same concentration at 30 °C. In contrast to process (B), which was independent of solvent and concentration, process (C) was somewhat concentration dependent; thus, when a solution at 15 °C was diluted seven-fold the rate changed from *ca.* 10 to *ca.* 3 s^{-1}.

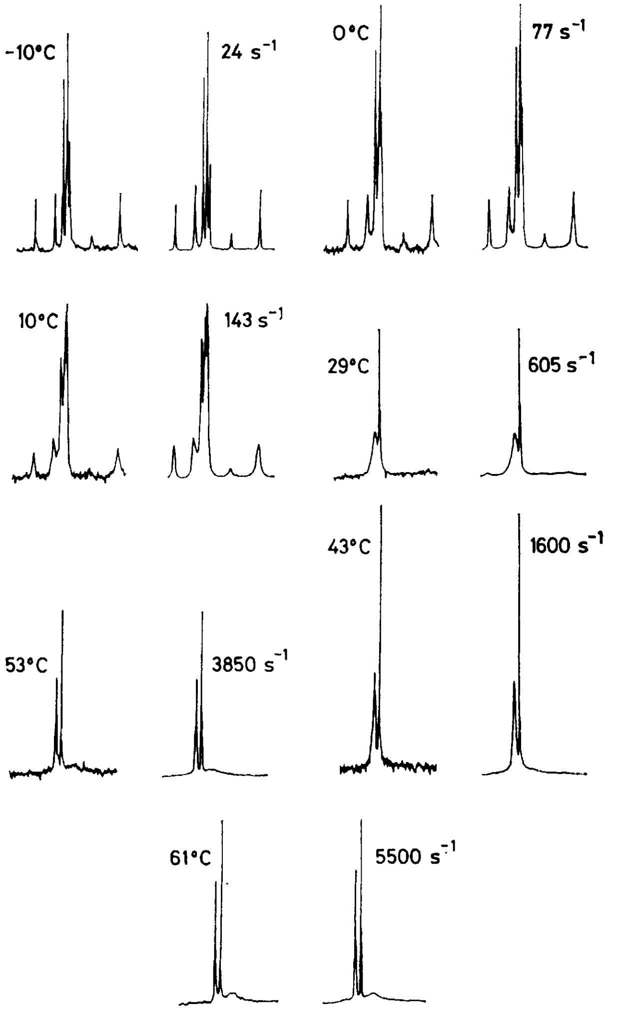
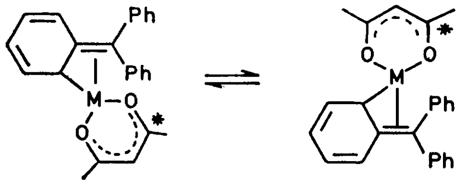
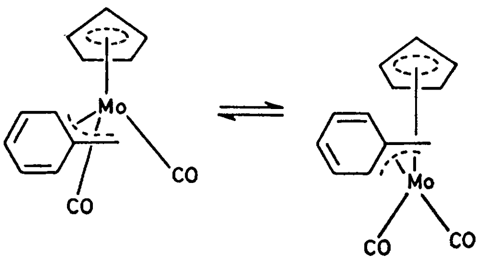


FIGURE 3 Partial variable-temperature ^{13}C n.m.r. spectra (δ 100 — 140) of [Pd(η^3-CPh_3)(acac)] in $CDCl_3$ at various temperatures and the computer-simulated spectra for various rates of exchange

Similarly ready fluxional processes to that described by (A) here have been observed for the other η^3-benzylic complexes;[4-6] however, for [Mo(η^5-C_5H_5)(η^3-CH_2R)$(CO)_2$] (R = aryl) the activation energies were found to be substantially higher. Process (A) may be interpreted in terms of a symmetry-allowed suprafacial sigmatropic [1,5]-shift, following the application of Woodward–Hoffman rules to fluxional molecules by Mingos.[16] The crystal structures of (3a) and (3b) show that the metal would need to move by some 2.35 Å from one η^3-benzylic position to the other equivalent one during process (A); it is likely that the actual movement required is less and that some compensation is provided by a twisting about the C(α)–C(1) bond. This process implies that the ends of the acac remain inequivalent, as is observed. An alternative mechanism, involving a 14-electron transition state in which the metal was σ-bonded only to C(α), should allow free rotation about the Pd–C(α) bond making the ends of the acac equivalent. Since no movement of the acac methyls is detected during process (B) this mechanism can be excluded.



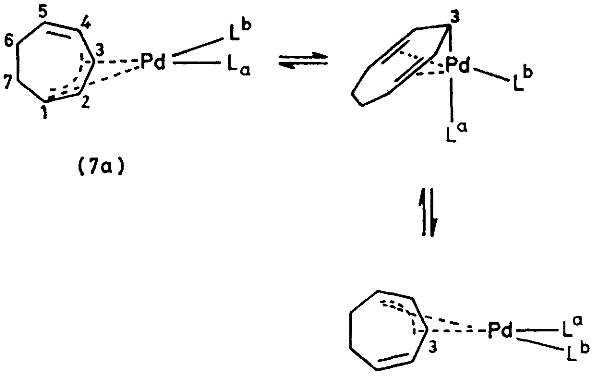
For [Co(η^3-CH_2Ph){$P(OR)_3$}$_3$] a fluxional process corresponding to (A) is also observed since two of the three phosphite ligands exchange, giving rise to an AB_2 pattern in the ^{31}P n.m.r. spectrum.[6] However, the higher activation energies found for the molybdenum complexes [Mo(η^5-C_5H_5)(η^3-CH_2R)$(CO)_2$] (6; R = aryl) arise from a process other than a [1,5]-shift and which has been characterised as proceeding through a 16-electron σ-benzyl intermediate.[3] In these molecules a [1,5]-shift does not result in the interconversion of C(2) and C(6) but in the interconversion of isomers (6a) $\rightleftharpoons$ (6b) in which the η^3-benzyl remains bound to the metal by the same face. This latter process can in practice not be observed. Infrared spectra showed that only one isomer was present for [Mo(η^5-C_5H_5)(η^3-CH_2R)$(CO)_2$],[3] presumably (6a), the form present in the crystal; the other isomer (6b) is probably strongly disfavoured for steric reasons. We postulate that the interconversion (6a) $\rightleftharpoons$ (6b) is fast and comparable in rate to process (A) but that the equilibrium concentration of (6b) is very small. Both isomers have been detected for the less-hindered η^3-allyl complex [Mo(η^5-C_5H_5)(η^3-C_3H_5)$(CO)_2$] [17] and for related complexes.[18]



(6a) (6b)

The fluxional behaviour shown by complex (3a) and characterised as process (B) has been observed in other systems, in particular for [Pd(η^3-cycloheptadiene-2,4-diyl)L_2]$^+$ and [Pd(η^3-cyclo-octadiene-2,4-diyl)L_2]$^+$, where the 1,3-shift was shown to proceed *via* an 18-electron transition state, *e.g.* (7a) $\rightleftharpoons$ (7b).[19] Again here the two L ligands remain inequivalent. An analogous proposal has been made by Rinze to account for the dynamic behaviour of the 18-electron complex, [Co(η^3-C_7H_9)$(CO)_2$(PPh_3)].[20] A related transition state as shown above is suggested for process (B) for complex (3a).

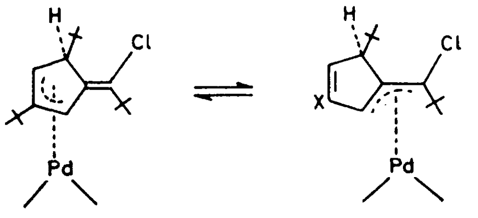
No conclusion can, however, be drawn about the detailed path of the interconversion since a second path



(7a)

(7b)

is also possible and has been shown to take place for (8a) ⇌ (8b)[21] where the C–C single bond between the



(8a) (8b)

double bond and the allylic ligand in (8a) has the *s-trans* arrangement, rather than the *s-cis* arrangement in (7).

TABLE 2

Carbon-13 n.m.r. spectra in $CDCl_3$ [$J(^{195}Pt-^{13}C)$ {and $J(^{19}F-^{13}C)$} are in H2]

		(4-XC_6H_4)Ph_2C carbons													acac		
Compound	θ_c/°C	α	1	2,6	3,5	4	1′	2′,6′	3′,5′	4′	1′′	2′′,6′′	3′′,5′	4′′	CH_3	CH	CO
[Pd(η^3-CPh_3)(acac)]	−19 (3a)	73.3	116.0	102.3	133.7	127.9	143.1	129.9	127.9	126.7	143.1	129.9	127.9	126.7	28.3	98.8	187.1
[Pt(η^3-CPh_3)(acac)]	(3b)	56.8	104.0	92.9	135.8	125.3	144.9	129.7	128.1	125.8	144.9	129.7	128.1	125.8	28.1	100.6	183.6
			(91)	(66)	(14)		(41)	(15)			(41)	(15)			27.5	(83)	184.4
[Pd{η^3-CPh_2(C_6H_4F-4)}(acac)]	−41 (5aX + Y)	72.4	116.1	99.4	133.7	128.1	142.9	129.8	128.1	126.9	139.1	131.7	114.9	161.3			
				104.9	134.1						{3.0}	{7.6}	{21.4}	{247.2}	28.3	98.9	187.1
	(5aZ)				120.3		142.9	129.8	128.1	126.9	142.9	129.8	128.1	126.9			187.2
					{24.0}												
[Pd{η^3-CPh_2(C_6H_4Me-4)}(acac)] [a]	−40 (5bX + Y)	73.6	115.8	99.4	133.5	128.0	143.1	129.9	128.0	126.6	140.4	128.0	128.6	136.4			
				104.9	134.0										28.5	99.0	187.0
	(5bZ)	72.3	113.8	102.9	134.0	138.1	143.2	129.9	128.0	126.6	143.2	129.9	128.0	126.6			187.2
[Pd{η^3-CPh_2(C_6H_4OMe-4)}(acac)] [b]	−45 (5cX + Y)	73.5	115.8	98.0	133.9	128.0	143.1	129.8	128.0	126.6	135.2	131.2	113.0	158.0			
				106.0	135·2										28.4	98.9	187.1
	(5cZ)	71.5	109.2	105.5	117.3	158.8	143.3	129.8	128.0	126.6	143.3	129.8	128.0	126.6			187.3
Ph_3CCl		81.2	145.1	129.5	127.5	127.5	145.1	129.5	127.5	127.5							
(4-FC_6H_4)Ph_2CCl [c]		80.7	141.0	131.5	114.5	162.0	145.0	129.5	127.7	127.7							
				{7.6}	{23.0}	{248.7}											
(4-MeC_6H_4)Ph_2CCl [d]		81.4	142.4	127.7	128.4	137.5	145.4	129.6	127.6	127.6							
(4-$MeOC_6H_4$)Ph_2CCl [e]		81.5	137.4	130.9	112.9	158.9	145.4	129.6	127.7	127.7							

[a] δ(Me) = 21.4 and 22.4 p.p.m. [b] δ(Me) = 55.1 and 55.4 p.p.m. [c] ^{19}F n.m.r.: δ(F) = −115.8 p.p.m. [d] δ(Me) = 21.0 p.p.m. [e] δ(Me) = 55.2 p.p.m.

N.M.R. Spectra of the Substituted Complexes (5a)—(5c).—The ^{13}C n.m.r. spectra of [Pd{η^3-CPh_2(C_6H_4X-4)}(acac)] (5; X = F, Me, or OMe) are considerably more complex than those of (3a) (Figure 4) but they show similar fluxional processes to those described for (3a) over the same temperature range. The extra complexity arises from there being three different species in solution, (5X), (5Y), and (5Z), in different concentrations. Although process (A) interconverts (5X) and (5Y) rapidly on the n.m.r. time scale, there are unequal populations of the two species. Consequently, since rotation about the C(1)–C(α) bond in (5X) and (5Y) is slow on the n.m.r. time scale, C(2), C(3), C(5), and C(6) give four, not two, signals. The signals were assigned on the basis of the signals for (4-XC_6H_4)Ph_2CCl, using the methods described above for the elucidation of the spectrum of [Pd(η^3-CPh_3)(acac)] (3a), and the ^{13}C n.m.r. data are given in Table 2.

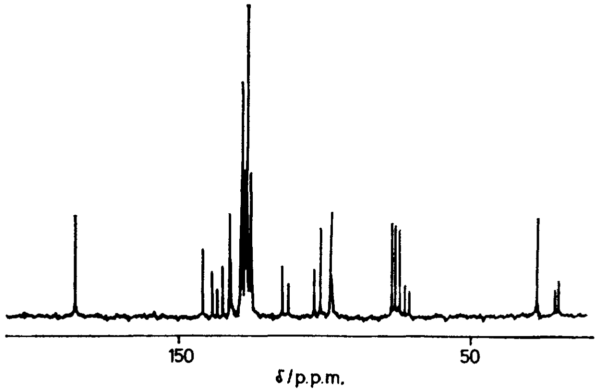


FIGURE 4 The ^{13}C n.m.r. spectrum of [Pd{CPh_2(C_6H_4Me-4)}(acac)] in $CDCl_3$ at −40 °C

At −30 °C, process (B) for these complexes is slow and it was possible to determine the relative concentrations of (5X) + (5Y) compared to (5Z); these are given in Table 3. Since there are two phenyl groups and only one substituted phenyl group, the combined concentration of (5X) + (5Y) is favoured by a factor of two over the concentration of (5Z). The equilibrium constants and $\Delta G^\ominus$ were calculated after dividing the combined concentration of (5X) + (5Y) by two. $\Delta G^\ominus$ then gives a measure of how much the 4-X substituent favours binding to the substituted rather than the unsubstituted ring. It is clear that the electron-releasing substituents (MeO, Me) favour the binding of the metal to the phenyl on which they are situated; fluoride similarly disfavours the binding of the metal. This is a not unexpected result since it is generally agreed that the σ- (ligand to metal) donation is more important in metal(II) d^8 complexes than the π-back bonding. Any effect which increases the tendency of electronic charge to be donated to the metal will therefore be expected to stabilise the bonding and *vice versa.*

Although the substituent, X, has an effect on the bonding preference of the palladium atom, it has very little effect on the rate of process (B), as shown by the marked similarity of the room-temperature ^{13}C n.m.r. spectra of complexes (3a), (5a), (5b), and (5c) (Figure 5).

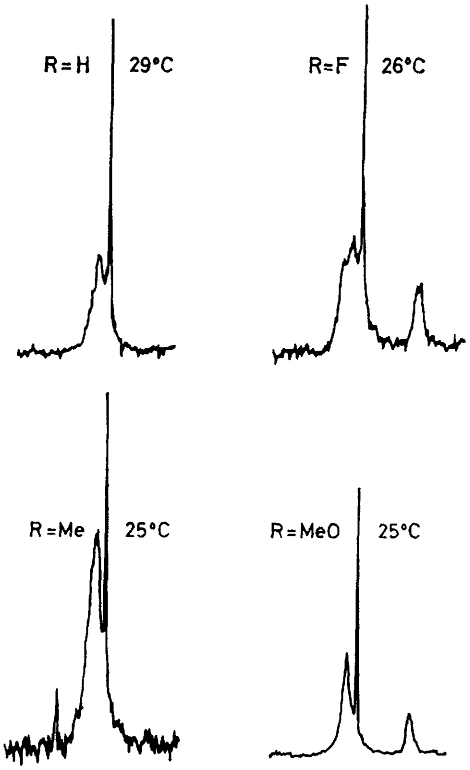
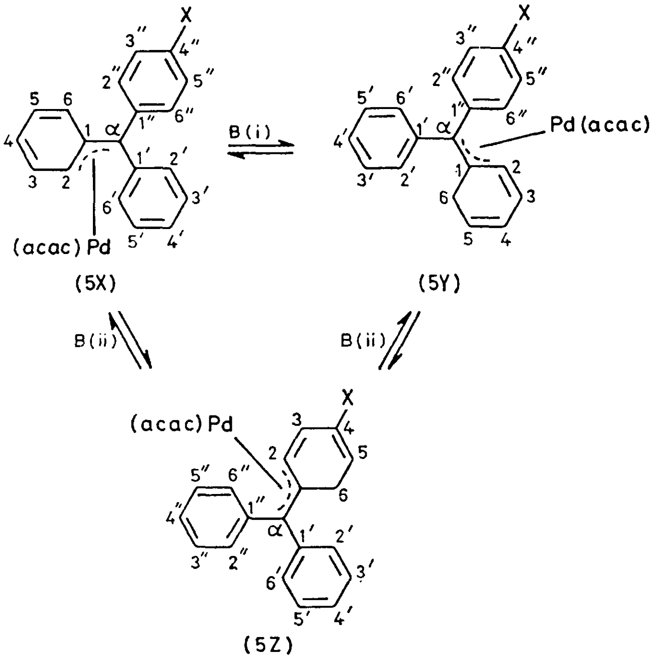


FIGURE 5 Partial (aromatic region) ^{13}C n.m.r. spectra of $[Pd\{CPh_2(C_6H_4R\text{-}4)\}(acac)]$ in $CDCl_3$

Only for (5a; X = F) was there any difference in lineshape and this system was analysed in detail. For these molecules, process (B) leads to two independent rates. In one, B(i), the palladium atom moves between the two unsubstituted rings while in the second, B(ii), it moves between the substituted and an unsubstituted ring:



For (5a) the second process could be conveniently investigated by use of ^{19}F n.m.r. spectroscopy. Between −58.5 and −4.3 °C, the relative concentrations of (5aX) + (5aY) with respect to (5aZ) were determined by a combination of integration and lineshape fitting. These values were used to calculate $\Delta H^\ominus = 0.74 \pm 0.14$ kcal mol^{-1} and $\Delta S^\ominus = -0.9 \pm 0.6$ cal K^{-1} mol^{-1} for the equilibrium after allowing for the factor of two favouring (5aX) and (5aY). These values were then used to estimate the concentration of the two forms at higher temperatures for use in the lineshape analysis. It was observed that the separation of the two ^{19}F resonances decreased from 580.6 to 562.5 Hz between −58.5 and −4.3 °C. A linear dependence on temperature was assumed and the separation was extrapolated to higher temperature. Lineshape analysis (Figure 6) at higher temperature yielded rates and hence activation parameters for exchange between the substituted and unsubstituted rings. The relative concentrations of (5aX) + (5aY) with respect to (5aZ) derived from the ^{19}F n.m.r. study were then used in the analysis of the ^{13}C n.m.r. spectra where rates were derived for both processes B(i) and B(ii) (Figure 7). Use of the Eyring equation to analyse these rates yielded activation parameters for the interchange of the unsubstituted rings of $\Delta G^\ddagger_{300} = 14.22 \pm 0.39$ kcal mol^{-1}, $\Delta H^\ddagger = 12.76 \pm 0.27$ kcal mol^{-1}, and $\Delta S^\ddagger = -4.9 \pm 0.9$ cal K^{-1} mol^{-1}, and for the interchange of the substituted and unsubstituted rings, using the rate of leaving the unsubstituted ring, $\Delta G^\ddagger = 13.74 \pm 0.37$ kcal mol^{-1}, $\Delta H^\ddagger = 14.13 \pm 0.31$ kcal mol^{-1}, and $\Delta S^\ddagger = 1.3 \pm 1.4$ cal K^{-1} mol^{-1}. Since

TABLE 3

Site preferences of the η^3-benzyl–metal bond in the substituted $[Pd\{\eta^3\text{-}CPh_2(C_6H_4X\text{-}4)\}(acac)]$ (5a)—(5c)

	Relative observed populations		Relative site preference		
Substituent	(5X) + (5Y)	(5Z)	C_6H_5[(5X) + (5Y)]	RC_6H_4(5Z)	Free-energy difference at 230 K, $\Delta G^\ominus\{(5Z) - [(5X) + (5Y)]\}$/kcal mol^{-1}
F	1.0	0.31	1.0	0.26	−0.6
H	1.0	0.50	1.0	1.0	0.0
Me	1.0	0.71	1.0	1.42	0.15
OMe	1.0	1.43	1.0	2.86	0.5

these results were not significantly different to those found for the unsubstituted derivative no further detailed studies of complexes (5b) and (5c) were carried out.

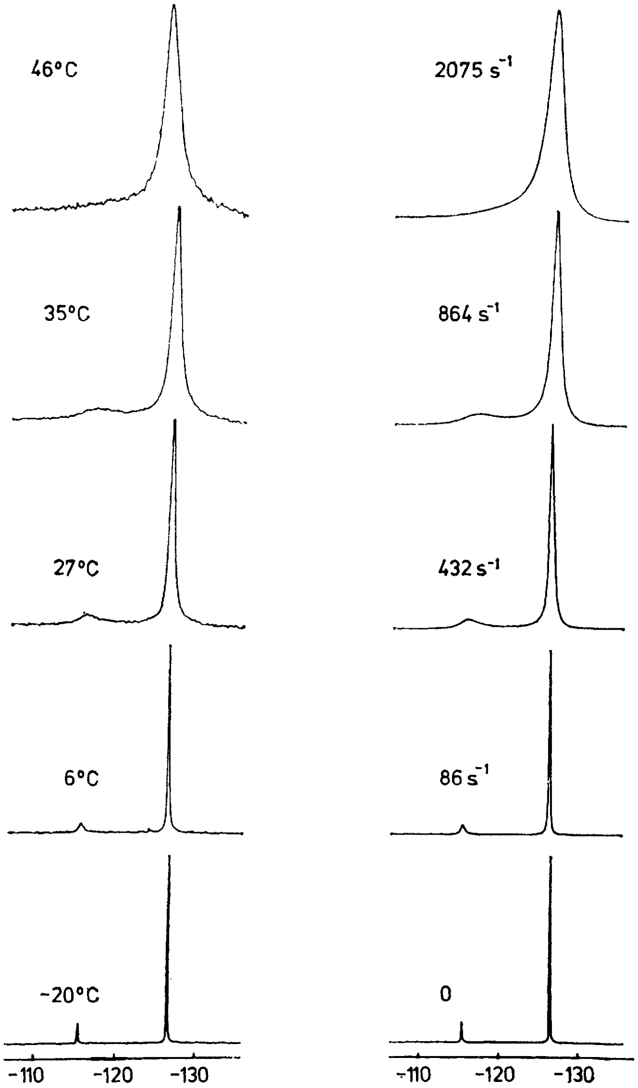


FIGURE 6 Variable-temperature ^{19}F n.m.r. spectra of $[Pd\{CPh_2(C_6H_4F\text{-}4)\}(acac)]$ in $CDCl_3$ and the computer-simulated spectra for various rates of exchange

The low-temperature ^{13}C n.m.r. spectra of (5a), (5b), and (5c) showed the somewhat surprising feature that two resonances could be distinguished for both C(2 + 6) and C(3 + 5). This shows that the relative populations of (5X) and (5Y) were significantly different from each other in all three complexes. The explanation of this very long-range effect can only be guessed at: it might be due to a long-range intramolecular electronic effect of the 4-X substituent or it could arise from a preferential solvation of one form.*

EXPERIMENTAL

Microanalytical data, molecular weights, and yields are collected in Table 4. Molecular weights were determined in chloroform using a Mechrolab 301A vapour-pressure osmometer. ^1H N.m.r. spectra (Table 1) were recorded on a Perkin-Elmer R12B or Varian HA-100 spectrometer, ^{13}C (Table 2) and ^{19}F n.m.r. spectra on a JEOL PFT-100 spectrometer. In each case $CDCl_3$ was used as solvent.

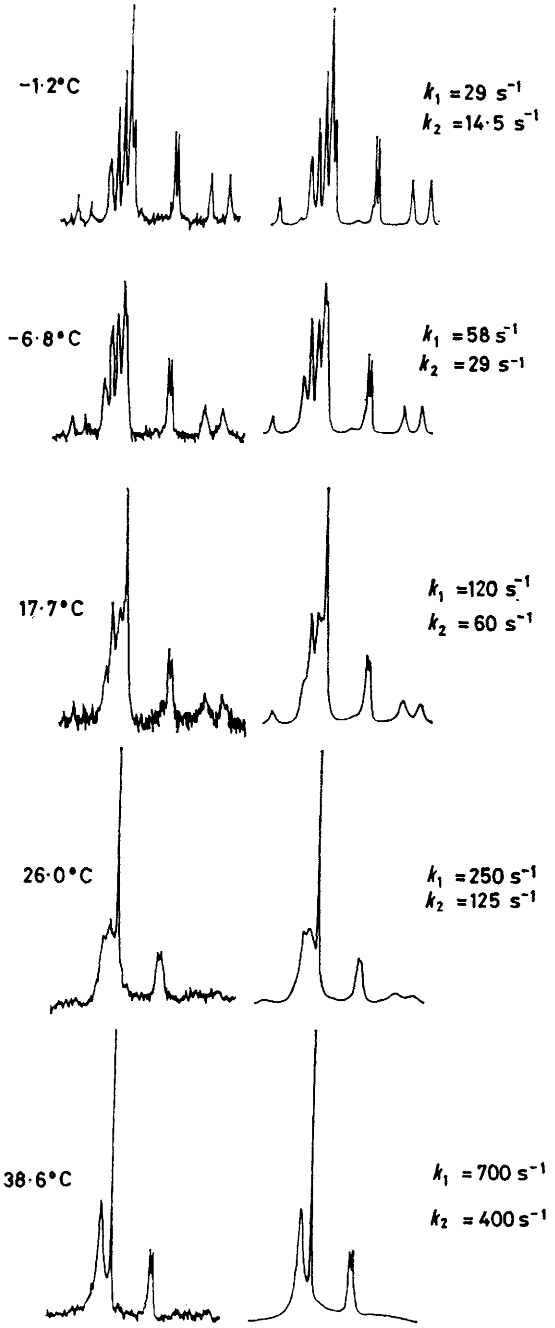


FIGURE 7 Partial variable-temperature ^{13}C n.m.r. spectra (δ 100—140) of $[Pd\{CPh_2(C_6H_4F\text{-}4)\}(acac)]$ in $CDCl_3$ and the computer-simulated spectra; k_1 is the rate of motion between unsubstituted rings and k_2 is the rate of motion from the unsubstituted to substituted ring

The I.U.P.A.C. recommended sign convention that high frequency is positive is used with $SiMe_4$ (^1H,^{13}C) and $CFCl_3$

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* *Note added in proof.* We also draw attention to the recent paper by Y. Becker and J. K. Stille (*J. Amer. Chem. Soc.*, 1978, **100**, 845) on dynamic η^1- and η^3-benzylbis(triethylphosphine)-palladium cations.

TABLE 4

Analytical data, melting points, yields, and molecular weights

	Complex	Analysis (%) [a] C	H	Cl		Yield (%)	Decomposition point (°C)
(2a)	$[\{Pd(\eta^3\text{-}CPh_3)Cl\}_2]$	59.1	4.2	9.3		95	104—106
		(59.2)	(3.9)	(9.2)			
(2b)	$[\{Pt(\eta^3\text{-}CPh_3)Cl\}_2]$	51.0	3.7	7.7		44 (81) [b]	170—179
		(51.0)	(3.7)	(7.5)			
(4a)	$[\{Pd[\eta^3\text{-}CPh_2(C_6H_4F\text{-}4)]Cl\}_2]\cdot 2Me_2CO$ [c]	57.4	4.5	7.4		86	135—140
		(57.3)	(4.4)	(7.7)			
(4b)	$[\{Pd[\eta^3\text{-}CPh_2(C_6H_4Me\text{-}4)]Cl\}_2]$	60.4	4.7	8.6		86	165—168
		(60.2)	(4.3)	(8.9)			
(4c)	$[\{Pd[\eta^3\text{-}CPh_2(C_6H_4OMe\text{-}4)]Cl\}_2]$	58.1	4.5	8.7	772	91	140—144
		(57.9)	(4.1)	(8.5)	(830)		
(3a)	$[Pd(\eta^3\text{-}Ph_3)(acac)]$	64.6	5.3		470	46	176—178
		(64.3)	(4.9)		(490)		
(3b)	$[Pt(\eta^3\text{-}PPh_3)(acac)]$	53.2	4.4		557	80	175—178
		(53.6)	(4.1)		(538)		
(5a)	$[Pd\{\eta^3\text{-}CPh_2(C_6H_4F\text{-}4)\}(acac)]\cdot 2C_5H_{12}$ [c]	63.0	5.3		475	44	140—142
		(63.3)	(5.4)		(502)		
(5b)	$[Pd\{\eta^3\text{-}CPh_2(C_6H_4Me\text{-}4)\}(acac)]$	64.7	5.3		473	37	125—128
		(64.9)	(5.2)		(462)		
(5c)	$[Pd\{\eta^3\text{-}CPh_2(C_6H_4OMe\text{-}4)\}(acac)]$	62.5	5.4		468	48	160—163
		(62.7)	(5.0)		(478)		

[a] Calculated values are given in parentheses. [b] Using $[Pt(dba)_3]$ as starting material. [c] Solvent confirmed by ^1H n.m.r. spectroscopy.

(^{19}F) as reference compounds. The quoted errors are for one standard deviation.

The compound Ph_3CCl (m.p. 113—115 °C) is commercially available; $[M_2(dba)_3]$ (M = Pd or Pt),[9] $(4\text{-}FC_6H_4)Ph_2CCl$ (m.p. 87—89 °C),[22] $(4\text{-}MeC_6H_4)Ph_2CCl$ (m.p. 96—98 °C),[23] and $(4\text{-}MeOC_6H_4)Ph_2CCl$ (m.p. 120—121 °C)[24] were all prepared by literature methods. Representative preparations are given.

$[\{Pd(\eta^3\text{-}CPh_3)Cl\}_2]$ (2a).—Solid $[Pd_2(dba)_3]$ (1.6 g, 3.4 mmol) was added to a solution of chlorotriphenylmethane (2.6 g, 9.3 mmol) in dry chloroform (50 cm^3) and the mixture was stirred for 2 h at 20 °C. The reaction mixture was filtered, and the filtrate concentrated (to 5 cm^3) on a rotary evaporator. Acetone (15 cm^3) was added and the solution was set aside for 15 min. The orange-yellow microcrystalline powder was filtered off, washed with acetone, and dried (yield 1.3 g). When the acetone washings were concentrated and pentane was added, free dba crystallised out (87%, m.p. 102—108 °C). Far-i.r. spectra: (2a), 326w,br, 288s, 262ms, and 234ms cm^{-1}; (5a), 303mw, 268ms, 248vs, and 211m cm^{-1}.

A number of variations were found to be equally successful; $[Pd(dba)_2] = [Pd_2(dba)_3(dba)]$ was used in place of $[Pd_2(dba)_3]\cdot CHCl_3$, and dichloromethane was used as solvent in place of chloroform for the syntheses of (4a), (4b), and (4c).

$[Pd(\eta^3\text{-}CPh_3)(acac)]$ (3a).—Thallium(I) pentane-2,4-dionate (1.3 g, 4.3 mmol) was added in portions to a suspension of (2a) (1.5 g, 2 mmol) in dry toluene (50 cm^3), under nitrogen. The suspensions were stirred (16 h at 20 °C) and then filtered to remove precipitated TlCl and to leave a clear amber solution from which the solvent was removed *in vacuo*. The residue was crystallised from benzene–light petroleum (b.p. 60—80 °C) to give orange-yellow crystals (0.90 g, 50%).

Complexes (5a), (5b), and (5c) were prepared similarly and crystallised from diethyl ether–hexane.

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