

The Preparation, Structures, and Reactions of the Metallacyclobutenyl Complexes $[M_3\{C_3R^1R^2\}_2X_2]$ Derived from Addition of Triarylcyclopropenium Salts to Zerovalent Palladium and Platinum Compounds †

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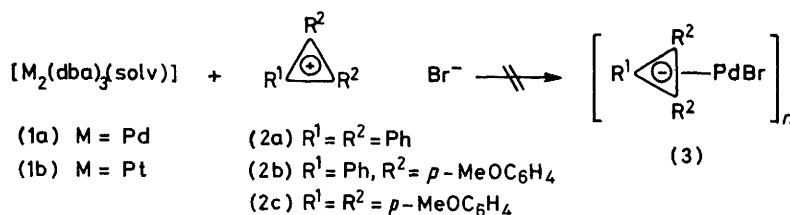
Reaction of $[M_2(dba)_3(CHCl_3)]$ ($M = Pd$ or Pt ; $dba = PhCH=CHCOCH=CHPh$) with $[C_3R^1R^2]Br$ gave $[M_3(C_3R^1R^2)_2Br_2]$ ($M = Pd$, $R^1 = R^2 = Ph$; $M = Pd$, Pt , $R^1 = R^2 = p\text{-MeOC}_6\text{H}_4$; $M = Pd$ or Pt , $R^1 = Ph$, $R^2 = p\text{-MeOC}_6\text{H}_4$), which reacted with $Tl(acac)$ to give the corresponding $[M_3(C_3R^1R^2)_2(acac)_2]$ [$acac = \text{pentane-2,5-dionato}$]. The platinum complex $[Pt_3\{C_3(p\text{-MeOC}_6\text{H}_4)_3\}_2Br_2]$ was also converted into $[Pt_3\{C_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(\eta^5\text{-C}_5\text{H}_5)_2]$, $[Pt_3\{C_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(S_2CNPr^i)_2]$, and $[Pt_3\{C_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(L_2)_2] \cdot [PF_6]_2$ [$L = PPh_3$, $L_2 = \text{cyclo-octa-1,5-diene (cod)}$, bipyridyl , or $o\text{-phenanthroline}$]. The n.m.r. spectra showed that the unusual structure, which had been determined for $[Pd_3\{C_3Ph(p\text{-MeOC}_6\text{H}_4)_2\}_2(acac)_2]$, was present in all the other complexes, and that they each possessed a bent trimetallic framework composed of two metallacyclobutenyl units $\{M(C_3R^1R^2)\}$ each π^4 -bonded to the central metal, each terminal metal bearing in addition $acac$, C_5H_5 , S_2CNPr^i , or L_2 ligands. The complexes exhibited dynamic behaviour in solution and ΔG^\ddagger values were determined from the n.m.r. spectra. The process involves a racemisation about the central metal atom and may also be viewed as arising from a movement of the two metallacyclobutenyl units with respect to each other between two equivalent positions about the central metal atom.

THE 1,5-diphenylpenta-1,4-dien-3-one (dibenzylideneacetone, dba) complexes of zerovalent palladium and platinum $[M_2(dba)_3(\text{solvent})]$ and $[M(dba)_3]$ ($M = Pd$ or Pt)¹⁻⁶ have been shown to be valuable starting materials for the synthesis of organo-palladium and -platinum complexes. In particular they undergo oxidative addition reactions with allylic^{1,3} and benzylic halides^{7,8} to give η^3 -allylic- or η^3 -benzylic-(halogeno)metal complexes, with displacement of dba .

products was obtained. A preliminary communication on part of this work has appeared.⁹

RESULTS AND DISCUSSION

Preparation and Structures of the Complexes.—Initial experiments showed that reaction occurred readily between (1a) and $[C_3Ph_3]Cl$ to give a product of low solubility which it was not possible to purify. The bromide (2a) also reacted with (1a) to give a more



tractable material, (4), which was converted into the pentanedionato-derivative (7) on reaction with $Tl(acac)$. The 1H n.m.r. spectrum of (4) only showed phenyl resonances, but that of (7) was more informative since it showed $acac$ as well as phenyl resonances in the expected intensity ratio. However, the $acac$ methyls appeared

† No reprints available.
¹ Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, *Chem. Comm.*, 1970, 1065.
² K. Moseley and P. M. Maitlis, *Chem. Comm.*, 1971, 983.
³ T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organometallic Chem.*, 1974, **65**, 253.
⁴ C. G. Pierpont and M. C. Mazza, *Inorg. Chem.*, 1974, **13**, 1891.
⁵ M. C. Mazza and C. G. Pierpont, *Inorg. Chem.*, 1973, **12**, 2955.

⁶ A. Keasey, B. E. Mann, A. Yates, and P. M. Maitlis, *J. Organometallic Chem.*, 1978, **152**, 117.

⁷ A. Sonoda, B. E. Mann, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1975, 108.

⁸ A. Sonoda, P. M. Bailey, and P. M. Maitlis, *J.C.S. Dalton*, in the press.

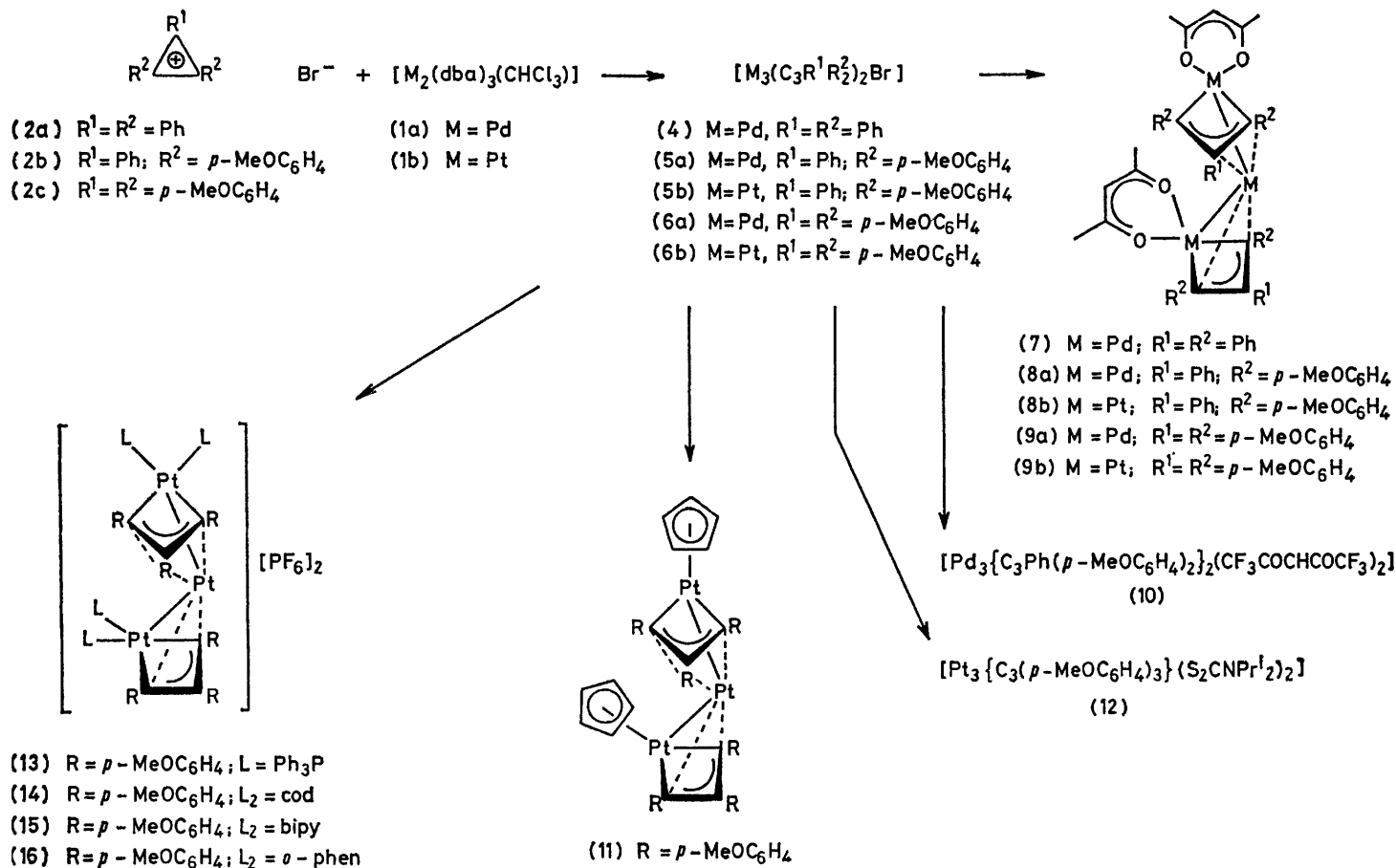
⁹ A. Keasey, P. M. Bailey and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1977, 178.

as two singlet resonances indicating that the molecule lacked a plane of symmetry. This ruled out any structure based on formula (3) (acac in place of Br). Elemental analyses and osmometric molecular-weight measurements for (4) and (7) were also incorrect for structure (3) or a derivative thereof, but fitted the formula $[\text{Pd}_3(\text{C}_3\text{Ph}_3)_2\text{X}_2]$ ($\text{X} = \text{Br}$ or acac).

In order to improve the solubility of the complexes and to provide a suitable group which would make the n.m.r. spectra of the organic C_3 ligand easier to interpret,

π -bonded to a central Pd(2). The two (equivalent) halves of the molecule are related by a two-fold symmetry axis through Pd(2).

From this structure it can be seen that (8 α) has arisen by the addition of a ring-opened ($\text{C}_3\text{R}^1\text{R}^2$) ligand to Pd(1), a ring-opening which can occur by cleavage of either the $\text{R}^2\text{C}-\text{CR}^2$ or a $\text{R}^1\text{C}-\text{CR}^2$ bond. In fact the crystal of (8 α) studied was found not to be a single isomer and oxygen electron density (corresponding to a total of two *p*-methoxy-substituents) in the ratio 0.97 :



SCHEME

complexes were prepared from the *p*-methoxyphenyl-cyclopropenium salts (2b) and (2c). The palladium complexes (5 α) and (6a), and (8 α) and (9a) [corresponding to (4) and (7)] were prepared from (1a), and the analogous platinum complexes (5 β), (6b), (8 β), and (9b) were obtained in a similar manner from the platinum(0) complex (1b) (Scheme).

The compound (8 α) was also found to provide crystals suitable for a single crystal X-ray diffraction study, details of which are given in the preceding paper.¹⁰

The X-ray determination of (8 α) revealed a structure which is most easily visualised¹⁰ as consisting of two palladiacyclobutenyl units $\{(\text{acac})\text{Pd}(\text{C}_3\text{R}^1\text{R}^2)_2\}$ each

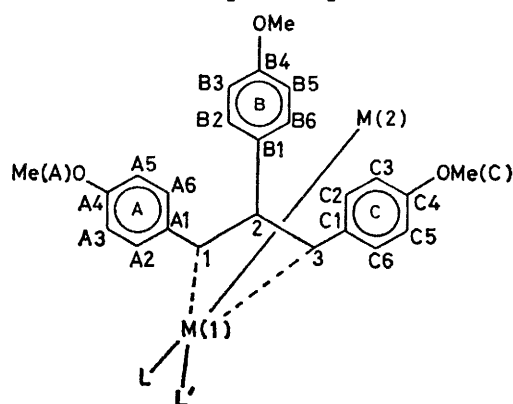
* Although we have no direct evidence, we presume that the bromo-complexes (5 α) and (5 β) are composed of isomers in similar ratios to those found for the acac compounds.

0.33 : 0.70 was present on the *para*-positions of all three phenyl rings, (A), (B) and (C), attached to each C_3 ligand. This implies that the major ring-opening path is cleavage of $\text{R}^2\text{C}-\text{CR}^2$ giving as major product the isomer shown as (8a), where the terminal carbons [C(1) and C(3)] of the C_3 ligand bear *p*-methoxyphenyl and the central carbon bears a phenyl group. In addition, minor isomers derived from combination of the units (i) (67%), (ii) (30%), and (iii) (3%) (the last two arising by cleavage of $\text{R}^1\text{C}-\text{CR}^2$ bonds) are also present in (8 α).*

The existence of isomers of (8a) was also confirmed by the ¹H n.m.r. spectra (see below) which showed some extra peaks. Very similar results were obtained for the

¹⁰ P. M. Bailey, A. Keasey, and P. M. Maitlis, *J.C.S. Dalton*, preceding paper.

TABLE I
¹H n.m.r. spectroscopic data



Complex	Field strength (MHz) and solvent	Aromatic H's ^a				acac		
		Ring A H(2 + 6)		Ring C H(3 + 5)		CH	Methyl	
[C ₃ Ph ₃]Br (2a) [Pd ₃ (C ₃ Ph ₃) ₂ (acac) ₂] (7)	60; (C ² H ₅) ₂ SO 60; C ² HCl ₃	7.2—8.5(m) ^c 6.5—8.0(m) ^c				5.3	1.84, 1.97	
[C ₃ Ph(<i>p</i> -MeOC ₆ H ₄) ₂]Br (2b) [Pd ₃ {C ₃ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ (acac) ₂] (8a)	60; CF ₃ CO ₂ H 100; C ² HCl ₃	Ring B 7.9(m) 6.5— 7.1(m)	Ring A H(2 + 6) 8.55 ^a 8.00 7.5(m), 8.0(m), 8.6(m)	Ring C H(3 + 5) 7.40 6.7— 7.1(m)	Me(A), Me(C) 4.10 3.76, 3.80 3.50, 3.80	5.16	1.76, 1.98	
[Pt ₃ {C ₃ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ (acac) ₂] (8b)	220; C ² HCl ₃	6.3—7.9				5.32	1.78, 1.93	
[Pd ₃ {C ₃ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ (hfac) ₂] (10)	100; ^d C ² HCl ₃	7.5(m), 8.0(m), 8.6(m)				3.81	5.83	
[C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃]Br (2c)	100; CF ₃ CO ₂ H	H(2 + 6)	8.52	H(3 + 5)	7.47	4.16	acac	
[Pd ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (acac) ₂] (9a)	100; C ² HCl ₃	Ring B 6.5— 6.8(m)	Rings A and C 7.42, 7.94	Ring B 6.5—6.8(m)	Rings A and C 6.54, 6.66	Me(A), Me(B), Me(C) 3.76— 3.80 3.73, 3.75 3.78	CH 5.18 5.35	methyls 1.80, 2.00 1.71, 1.95
[Pt ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (acac) ₂] (9b)	220; C ² HCl ₃	6.67	7.34, 7.78	6.48	6.54, 6.66	3.72, 3.77	CH 4.45(m)	η ⁵ -C ₅ H ₅ 5.54[16] ^b methyls 1.48(m)
[Pt ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (η ⁵ -C ₅ H ₅) ₂] (11)	220; C ² HCl ₃	6.77	7.07	6.45	6.62	3.72, 3.77	CH 4.45(m)	η ⁵ -C ₅ H ₅ 5.54[16] ^b methyls 1.48(m)
[Pt ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (S ₂ CNPr ¹ ₂) ₂] (12)	220; C ² HCl ₃	6.70	6.93, 7.95	6.46	6.54, 6.70	3.71, 3.72, 3.74	CH 4.45(m)	η ⁵ -C ₅ H ₅ 5.54[16] ^b methyls 1.48(m)
[Pt ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (PPh ₃) ₄] ²⁺ (13)	220; (C ² H ₅) ₂ CO	6.9—7.8(m)		5.64, 6.38 6.9—7.8(m)		3.40, 3.88, 3.92	CH 4.45(m)	PPh ₃ 7.1—7.44(m)
[Pt ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (cod) ₂] ²⁺ (14)	220; (C ² H ₅) ₃ CO	7.05	7.25, 7.77	6.83	6.93, 7.05	3.82, 3.88, 3.94	CH 5.2 (2 H) [60], 5.8 (1 H), 6.1 (1 H)	cod =CH —CH ₂ 2.45 (8 H) (m)
[Pt ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (bipy) ₂] ²⁺ (15)	220; C ² H ₃ CN	6.95	7.15, 7.96	6.34	6.60, 6.88	3.64, 3.75, 3.84	bipy 7.40 (t), 7.62 (q), 8.10 (d), 8.25 (m) 8.40 (2 × d)	
[Pt ₃ {C ₃ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (phen) ₂] ²⁺ (16)	220; C ² H ₃ CN	7.00	7.20, 7.90	6.74	5.88, 6.92	3.45, 3.78, 3.87	phen 7.55 (m), 8.12 (s), 8.30 (d), 8.68 (t)	

^a All protons 2 + 6 and 3 + 5 show coupling, $J(\text{H-H}) = 9$ Hz. ^b [] indicates coupling to ¹⁹⁵Pt. ^c (m) = multiplet. ^d Fourier-transform ¹H spectrum at 100 MHz.

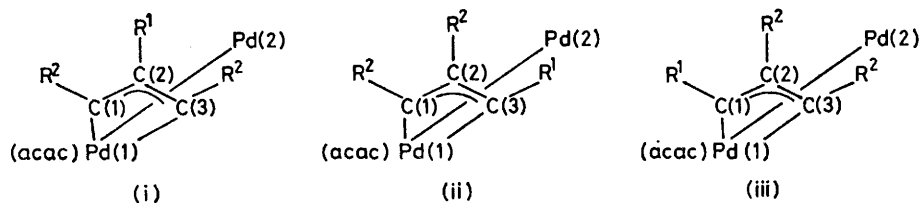
platinum complex (8β), derived from (2b) and (1b), which was likewise found to be a mixture but with isomer (8b) as the major component.*

No such isomerism can exist for the complexes derived from the tri-*p*-methoxyphenyl compound (2c) and since

* See footnote on page 1831.

this series presented fewer experimental problems, its chemistry, and particularly that of the more stable platinum complexes (6b) and (9b), was more extensively investigated. The compounds prepared are summarised in the Scheme.

Bidentate monoanionic ligands other than acac formed stable derivatives, one of which, the di-isopropyl-dithiocarbamate (12), was fully characterised. The diethyl- and dimethyl-dithiocarbamate complexes were rather insoluble and proved difficult to purify.



It was also found that reaction of the bromide (6b) with $\text{Ag}[\text{PF}_6]$ in the presence of triphenylphosphine or the bidentate ligands cyclo-octa-1,5-diene, bipyridyl, or *o*-phenanthroline gave the cationic complexes (13) and (14)—(16) respectively.

One other derivative of some note was obtained when the platinum bromide complex (6b) was treated with $\text{Tl}(\text{C}_5\text{H}_5)$. The bis- η^5 -cyclopentadienyl (11) may be regarded as a quadruple-decker sandwich complex, albeit a bent one.

All the complexes were fully characterised by elemental analyses and molecular weights (Table 4) and by n.m.r. spectroscopy (Tables 1 and 2).

N.M.R. Spectroscopic Studies.—The crystal structure shows that (8a) has a two-fold symmetry axis through Pd(2) and, therefore, the unprimed atoms in one half of the molecule and the symmetry-related primed atoms in the other half are expected to be equivalent. However, since the environment of C(1) is different from that of C(3) in each half of the molecule, these atoms and their substituents should be different. Similarly, the acac ligands in complexes (7)—(8) will have no plane of symmetry and two methyl signals are therefore expected in the ^1H n.m.r. spectrum. This argument not only applies to the complexes derived from (2b) but also to those [(9)—(16)] with three *p*- MeOC_6H_4 substituents. Since such effects are observed in solution the molecular geometry found for complex (8a) cannot be the result of intermolecular packing forces in the crystal.

For example, complexes (8a) and (8b) each showed two methoxy-signals [δ 3.76, 3.80 (8a) and 3.50, 3.80 (8b)] and two acac methyl signals [δ 1.76, 1.98 (8a) and 1.78, 1.93 (8b)] in their ^1H n.m.r. spectra. Similarly the complex (9b) derived from (2c) showed three methoxy-resonances [δ 3.73, 3.75, 3.78] and two acac methyl resonances [δ 1.71, 1.95]. In some cases this asymmetry was only resolved at very high resolution, thus two of the three methoxy-resonances in (9a) were coincident in both $[\text{D}_2\text{O}]$ chloroform and $[\text{D}_6]$ benzene at 100 MHz; however, in this case the more anisotropic

solvent $[\text{D}_6]$ nitrobenzene caused a splitting into three equal intensity resonances even at 100 MHz.

As mentioned above the complex (8 α) obtained from (2b) has, as the major component, isomer (8a) in which C(1) and C(3) of the C_3 ligand bear *p*-methoxyphenyl substituents. Smaller amounts of isomers, where C(2) has a *p*-methoxyphenyl substituent, are also formed; the presence of these isomers in solutions of (8 α) is seen in the 220 MHz ^1H n.m.r. spectrum which shows small peaks around the main methoxy and methyl resonances

arising from (8a). These extra peaks were more easily seen in the platinum compound (8 β), which had one main set of resonances which we assign to (8b), the platinum analogue of (8a), and again the minor isomers are presumably due to the analogues of (ii) and (iii). It was not possible to estimate the amounts of these other isomers with any degree of reliability owing to overlapping peaks but it appeared that more of the minor compounds were present in (8 β) than in (8 α).

In the complexes derived from the tri-*p*-methoxyphenyl salt (2c) the three different *p*-disubstituted phenyls are expected to give rise to three different sets of AB quartets in the ^1H n.m.r. spectra, assuming free rotation about the *p*- MeOC_6H_4 -C bonds. For the platinum complex (9b) six doublets were observed (all $J = 9$ Hz) which were assigned by decoupling experiments and on chemical-shift arguments (see below) as shown in Table 1. This analysis was also possible for complexes (11), (12), and (14)—(16).

The asymmetry was also reflected in the other ligands attached to the terminal metal atoms in complexes (12)—(16). Thus at +25 °C the methyl protons of the di-isopropyl groups of (12) were observed as a broad multiplet and the resonances of bipyridyl and *o*-phenanthroline ligands in (15) and (16) were extremely complex. In all these cases this complexity is caused by the absence of a plane of symmetry for the L_2 ligand. More interesting was the cod complex (14) where the ^1H spectrum showed three olefinic CH resonances (in the ratio of 1 : 1 : 2). Given the asymmetry of the molecule, each of the four =CH- groups that are co-ordinated to each Pt should be different from the others. The accidental degeneracy of two of the CH groups is removed in the ^{13}C spectrum where four separate =CH- resonances are observed.

Although the ^1H spectrum showed the inequivalence of the three *p*-methoxy-groups in the triphenylphosphine complex (13), the aromatic region could not be analysed because of the coincidence of the various phenyl resonances. The ^{31}P n.m.r. spectrum however showed the

presence of two inequivalent phosphorus atoms [δ 6.6 and 14.6, * $J(\text{P-P}) = 11$ Hz] which were also coupled to Pt(1) [$J(\text{P-Pt}) = 3\,514$ and $3\,286$ Hz respectively]. Additional fine splitting was also observed resulting from coupling to the central Pt(2). This was not analysed in detail but it was clearly different for each phosphorus. This implies that there is a small difference in the orientation of Pt(2) with respect to the two phosphorus atoms, in other words that the plane perpendicular to the bisector of the angle P(1)Pt(1)P(2)

three methoxy-carbons are coincident. Although the couplings of platinum to carbon [particularly to C(1), C(2), and C(3)] should have been very informative we were usually unable to detect them owing to poor signal-to-noise levels in the spectra.

The 25 °C ^1H n.m.r. spectrum of the cyclopentadienyl complex (11) showed that an exchange process was occurring. Two of the methoxy-groups were equivalent, and in the phenyl region only four doublets were observed. On cooling the resonances broadened and

TABLE 2

^{13}C N.m.r. spectroscopic data [chemical shifts in δ (p.p.m.); coupling to ^{195}Pt (Hz) shown in parentheses; labelling as for Table 1]

	C(A1, B1, C(1—3))	C(A4, C4)	C(A2, A6, C(C2, C6))	C(B3, B5)	C(A3, A5, C(C3, C5))	C(B4)	C(A4, C4)	Me(A, Me(C))	Me	acac CH	CO
$[\text{C}_3\text{Ph}(p\text{-MeOC}_6\text{H}_4)_2]\text{Br}$ (2b) ^a	148.7, 150.1	111.8, 120.1	135.5	139.4	131.0	117.0	137.5	168.0	57.0		
$[\text{Pd}_3\{\text{C}_3\text{Ph}(p\text{-MeOC}_6\text{H}_4)_2\}_2\text{-}$ (acac) ₂] (8a)	127.5, 128.5, 129.7, 134.1, 134.9, 142.7	131.4, 132.6, 133.1,			113.8	n.a.	160.2, 160.9	55.2, 55.4	28.0	99.3	186.6
$[\text{Pt}_3\{\text{C}_3\text{Ph}(p\text{-MeOC}_6\text{H}_4)_2\}_2\text{-}$ (acac) ₂] (8b) ^b	127.4, 128.3, 129.8,	131.0, 131.8			112.9	n.a.	159.1, 159.8	55.0	27.8	101.1 (58)	185.2
$[\text{Pd}_3\{\text{C}_3\text{Ph}(p\text{-MeOC}_6\text{H}_4)_2\}_2\text{-}$ (hfac) ₂] (10) ^b	125.8, 128.4, 129.2, 132.9, 133.6, 134.4,	129.7, 1304, 137.7, 143.4	131.2,		111.9, 113.9	n.a.	159.5, 161.7	55.1, 55.5	<i>f</i>	89.4	174.3, 175.7
$[\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3]\text{Br}$ (2c) ^c	149.5	C(A1, B1, C1) 113.9 or 117.0	C(A2, 6; B2, 6; C2, 6) 139.5	C(A3, 5; B3, 5; C3, 5) 113.9 or 117.0	C(A4, B4, C4) 166.1	Me(A, B, C) 57.8					
$[\text{Pd}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(\text{acac})_2]$ (9a) ^b	129.8, 134.4, 142.5	126.7, 131.4, 132.3	129.8, 133.0	113.4, 113.9	158.8, 160.0, 160.8	55.0, 55.2		28.0	99.3	186.7	
$[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(\text{acac})_2]$ (9b) ^b	127.6— 132.1, 137.8(20)	127.6, 129.2, 131.8, 132.1	130.0, 131.0,	113.0, 113.5	158.4, 159.0, 159.7	55.0		27.8 (26)	101.1 (61)	185.1, 185.3 (26)	
$[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2\text{-}$ ($\eta^5\text{-C}_5\text{H}_5$) ₂] (11) ^b	100.3, 120.7, 132.6, 133.7	129.4, 131.0, 131.6,		112.2, 113.3	158.1, 159.8	55.0, 55.2				$\eta^5\text{-C}_5\text{H}_5$ 90.4(15)	
$[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2\text{-}$ {S ₂ CNPr ¹ ₂ } ₂] (12) ^b	126.2, 129.8, 131.5, 134.6	133.0, 133.4,		113.0, 113.3	158.4, 158.7, 159.5	54.9, 55.1		Me 19.8	CH 51.0, 51.2	S ₂ CN 211.8 (90)	
$[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2\text{-}$ (PPh ₃) ₄] ²⁺ (13) ^d	128.7, 129.1, 129.4, 131.9, 132.3, 135.2,	129.8, 130.3, 135.6		113.9, 115.1, 115.4,	161.2, 161.5, 162.1	55.6, 55.9				128.7—135.6	
$[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(\text{cod})_2]$ ²⁺ (14) ^d	129.7, 132.0, 132.3,	132.9		115.8, 116.1, 118.5	162.8, 163.2	56.1			cod =CH 103.7, 104.7, 105.1, 105.9	—CH ₂ 30.0, 31.0	
$[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(\text{bipy})_2]$ ²⁺ (15) ^e	124.5, 127.8, 138.0, 131.6, 132.1, 132.7	129.4, 131.0,		114.4, 114.7, 115.2, 117.9	161.0, 161.4, 161.7	55.8			bipy 140.9, 141.6, 149.0, 150.9, 155.9, 156.2		
$[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(\text{phen})_2]$ ²⁺ (16) ^e	124.3, 126.7, 129.7, 133.1	131.5, 132.4,		114.2, 115.4, 118.0	161.2, 161.4, 162.0	55.8, 56.1			phen 140.0, 146.5, 147.1, 149.3, 151.7		

Solvents: ^a C₂H₂Cl₂; ^b C²HCl₃; ^c H₂SO₄; ^d (C²H₅)₂CO; ^e C²H₃CN. *f* Carbons of CF₃ groups not observed.

passes to one side of Pt(2). Such an asymmetry is also revealed in the crystal structure of compound (8 α).

The ^{13}C n.m.r. spectra (Table 2) confirm the ^1H spectra but provide only limited extra information. In general we find that, since the carbons are more shielded from their surroundings than their attached hydrogens, they are less sensitive indicators of asymmetry. Thus, for example while the methoxy-protons of rings (A) and (C) are almost invariably resolved, the carbons are not; indeed in the compounds (8b), (15) and (16) all

* $^{31}\text{P}\{^1\text{H}\}$ N.m.r. spectrum at 40.48 MHz, δ with respect to H₃PO₄ as external reference.

then sharpened again at -60 °C. At this temperature the phenyl protons were seen as six pairs of doublets (with two resonances accidentally overlapping) and the methoxy-resonances were again seen as two singlets but with the relative intensities inverted by comparison with the $+25$ °C spectrum; we ascribe this latter effect to an accidental coincidence at the lower temperature since the pattern of the phenyl resonances clearly indicates that the asymmetry demanded by structure (8a) is still present.

The C₅H₅ groups in (11) gave rise to sharp resonances throughout the temperature range, and showed coupling

to Pt(1). The magnitude of this coupling [$J(\text{H-Pt}) = 16$ Hz] indicates that the cyclopentadienyls are most probably η^5 -bonded since the value is in the middle of the range (11–19 Hz) for known $\eta^5\text{-C}_5\text{H}_5\text{-Pt}^{\text{II}}$ complexes and much lower than those found for fluxional $\eta^1\text{-C}_5\text{H}_5\text{-Pt}^{\text{II}}$ (26–39 Hz).¹¹ This conclusion is also supported by the ¹³C spectra which showed a single sharp C₅H₅ resonance [$J(\text{C-Pt}) = 15$ Hz] over the range –90 to +40 °C.

Dynamic Behaviour of the Complexes.—Dynamic behaviour, very similar to that shown by the cyclopentadienyl complex (11), was exhibited by the other complexes when their solutions were heated; on cooling the original spectra were regenerated. Thus, when the di-*p*-methoxyphenyl complex (8a)* was heated in [²H₅]nitrobenzene the two separate ¹H methoxy-resonances coalesced at +50 °C; on further heating to +100 °C the acac methyls also coalesced. This indicated that the aryl rings (A) and (B) were becoming equivalent on the n.m.r. time scale.

A similar result was obtained when the tri-*p*-methoxyphenyl complex (9a) was heated in [²H₅]nitrobenzene. In this case two of the three methoxy-resonances coalesced at +50 °C, the third one remaining distinct; at +90 °C the resonances in the phenyl region also broadened and the methyls of the acac coalesced into a single peak. No further changes occurred on heating the solution to +170 °C and the methoxy-protons remained as two resonances of intensity 1:2 over the temperature range +50 °C to +170 °C; above this temperature rapid decomposition occurred. The coalescence temperatures for (9a) were the same in [²H₅]nitrobenzene (dielectric constant, 34.8) as in [²H₆]benzene (dielectric constant, 2.3); furthermore when a solution of (9a) in [²H₅]nitrobenzene at +100 °C was diluted by a factor of 4 no change in the degree of broadening of the phenyl region at 220 MHz was observed. These two observations suggested that the dynamic process did not proceed *via* a highly polar or an ionic intermediate and that the process was first order and intramolecular.

The platinum complex (9b) showed very similar behaviour to that of (9a) except that coalescence occurred at higher temperatures. Similar results were also obtained for the dithiocarbamate complex (12) and the cationic complexes (14)–(16). However, for the latter complexes significantly higher temperatures were required before broadening and coalescence occurred. Thus the *o*-phenanthroline complex required heating to 180 °C before the high-field methoxy-resonance had coalesced with one of the two low-field methoxy-resonances, while the other low-field methoxy-resonance remained sharp. The n.m.r. spectrum of the triphenylphosphine complex (13) did not show any signs of

coalescence below the decomposition temperature (+100 °C).

The coalescence of Me(A) and Me(C), as well as the coalescence of two of the aryl resonances that was observed in some of the complexes, allowed an unambiguous assignment of Me(B) [and of the phenyl ring (B)] in all the complexes derived from (2c). The activation energies (ΔG^\ddagger) for the fluxional process for the complexes (8a), (9a), (9b), (11), (12), and (16) were estimated from the rates of exchange of Me(A) and Me(C) at coalescence given by the following relationships, where

$$k_c = \pi(\nu_A - \nu_B)/\sqrt{2} \text{ and } k_c = (\kappa T_c/h)\exp(-\Delta G^\ddagger/RT_c)$$

ν_A and ν_B are the frequencies of the two lines which coalesce in the absence of exchange and T_c is the temperature at which coalescence occurs.¹² In order to check these values, the ΔG^\ddagger values were also evaluated from coalescence data on the aryl protons as well as on the acac methyls for the (acac) complexes (9a) and (9b). Good agreement was obtained.

No coalescence data could be obtained for the cod complex (14) but since broadening of the aryl doublets was observed at +150 °C, indicating a slow exchange, the rate at this temperature was estimated from the empirical relationship, $k = \pi\Delta\nu$, where $\Delta\nu$ is the observed line broadening due to exchange. This rate was used to derive a minimum value of ΔG^\ddagger for (14).

A line-shape analysis was carried out for part of the aryl resonances of the cyclopentadienyl complex (11) near the coalescence temperature. Using a program with a graphical output, an input rate of 708 s^{–1} gave a calculated line shape in very good agreement to the observed spectrum at 0 °C. This rate gave a value of ΔG^\ddagger (52 kJ mol^{–1}) in reasonable agreement with that obtained (48 kJ mol^{–1}) from the coalescence of the methoxy-protons at lower temperatures. We may conclude that the ΔG^\ddagger values obtained from coalescence data are reasonably accurate.

The results (Table 3) show the following trends.

(i) The platinum compound (9b) requires a significantly higher ΔG^\ddagger than the palladium analogue (9a). This is in agreement with the general observation that platinum is usually more kinetically inert than palladium.¹³

(ii) There is no significant difference between the ΔG^\ddagger values for compounds (8a) and (9a).

(iii) There is quite a range of ΔG^\ddagger values for the platinum complexes derived from (2c) with the cyclopentadienyl having the lowest (50 kJ mol^{–1}) and the cationic compounds (14) and (16) the highest values (95–97 kJ mol^{–1}). The acac (9b) and the dithiocarbamate complex (12) are nearer the higher end of the range (87–89 kJ mol^{–1}).

Since the equilibration process only exchanges two (A and B) of the three methoxy and aryl groups in the complexes derived from (2c) it is clear that the process

* This, and subsequent, discussion of the spectra of (8 α) and (8 β) is concerned only with the behaviour of the major isomers (8a) and (8b) since lack of sensitivity precluded any observation of the much lower intensity signals of the minor isomers.

¹¹ R. J. Cross and R. Wardle, *J. Chem. Soc. (A)*, 1971, 2000.

¹² I. O. Sutherland, *Ann. Reports N.m.r. Spectroscopy*, 1971, 4, 71.

¹³ P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. 1, p. 36.

does not involve reversible ring-closure since this would result in the equilibration of all three groups.

The observation that ΔG^\ddagger is the same (within experimental error) for the equilibration of the aryls as for the acac methyls in both (9a) and (9b) suggests that the same process is responsible for both. It is, therefore, unlikely that an interconversion just of the M(acac) part of the molecule is proceeding either by a twisting about M(1) or by a decomplexing of one end of the acac ligand.

A more plausible explanation is that a twisting about

chelate π -ligand to Pd(2) and their motion relative to each other can be likened to a type of 'Bailar twist'.¹⁴

The motion of two η^3 -allylic groups relative to each other is also a feature of a variety of bis- η^3 -allylic complexes.¹⁵ In the bis- η^3 -allylic complexes of Ni, Pd, and Pt it is a *cis,trans*-isomerisation; in complexes of the form $[M(A)_2XY]$ ($A = \eta^3$ -allylic ligand; $X, Y =$ unidentate ligands, $M = Ru$ or Fe , etc.) the motion may be described in terms of a *syn, syn-anti, anti*-equilibration of the allylic substituents.

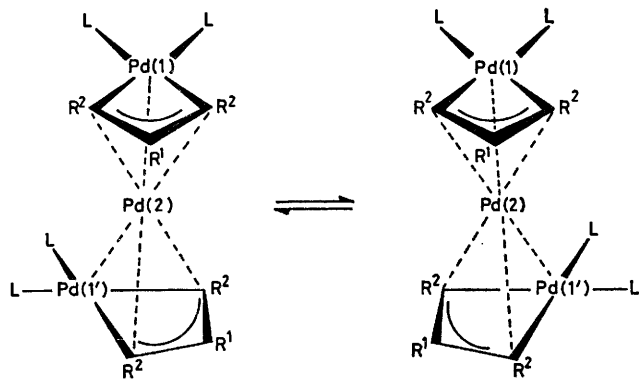
TABLE 3

Free energies of activation for the dynamic processes in the trinuclear complexes ^a

	Field strength (MHz) and solvent	Observed signals	Signal separation (Hz) in absence of exchange	Coalescence temp. (K)	Exchange rate at coalescence (s^{-1})	Free energy of activation (ΔG^\ddagger) (kJ mol ⁻¹)
$[Pd_3\{C_3Ph(p-MeOC_6H_4)_2\}_2(acac)_2]$ (8a)	100; C ₆ H ₅ NO ₂	acac methyls	17	363	38	78
$[Pd_3\{C_3(p-MeOC_6H_4)_3\}_2(acac)_2]$ (9a)	(i) 100; C ₆ H ₅ NO ₂	acac methyls	6	353	13	79
	(ii) 100; C ₆ H ₅ NO ₂	(i) acac methyls	15	363	33	79
		(ii) phenyl ring protons	140	403	311	81
$[Pt_3\{C_3(p-MeOC_6H_4)_3\}_2(acac)_2]$ (9b)	100; C ₆ H ₅ NO ₂	(i) acac methyls	5	383	11	87
		(ii) methoxy-protons	5	383	11	87
$[Pt_3\{C_3(p-MeOC_6H_4)_3\}_2(\eta^5-C_5H_5)_2]$ (11)	(i) 220; C ² HCl ₃	phenyl ring protons	line-shape analysis at 273 K		708	52
	(ii) 220; C ² HCl ₃	methoxy-protons	25	228	56	48
$[Pt_3\{C_3(p-MeOC_6H_4)_3\}_2(S_2CNPr'_2)_2]$ (12)	100; C ₆ H ₅ NO ₂	phenyl ring protons	150	443	338	89
$[Pt_3\{C_3(p-MeOC_6H_4)_3\}_2(cod)_2]^{2+}[PF_6]_2^-$ (14)	220; C ₆ H ₅ NO ₂	phenyl ring protons	line broadening below coalescence at 423 K		16	95
$[Pt_3\{C_3(p-MeOC_6H_4)_3\}_2(phen)_2]^{2+}[PF_6]_2^-$ (16)	100; C ₆ H ₅ NO ₂	methoxy-protons	28	453	62	97

^a The temperatures are accurate to ± 5 K (± 1.5 to 2%) and thus the ΔG^\ddagger values based on coalescence data are accurate to ± 2 to 3 kJ mol⁻¹, whilst the value derived from the line-shape analysis has an accuracy of ± 1 to 2 kJ mol⁻¹.

M(2) is occurring which has the effect of creating an apparent plane of symmetry in the molecule on the n.m.r. time scale. This racemisation process can be visualised as follows. The crystal structure of (8a) shows that the co-ordination about Pd(2) may be described in terms of a distorted octahedron, four sites of which are taken up by the two η^3 -allylic groups and two by Pd(1) and



Pd(1') respectively. Each η^3 -allylic group and its associated palladium atom thus forms a tridentate

In the systems investigated here a substantial part of the barrier to rotation probably arises from the mutual interactions of the aryl substituents on the two allylic ligands. The crystal structure shows that these mesh together in the manner of three pairs of cogs on two gear-wheels and the racemisation can be viewed simply as a movement by which the two gear-wheels ($C_3R^1R^2_2$ units) are displaced by one cog relative to each other.

The reason for the large difference in ΔG^\ddagger between the η^5 -cyclopentadienyl platinum complex (11) and the other platinum complexes is not clear. However, Pt(1) and Pt(1') are both formally 17-electron centres in (11) whereas they are 15-electron centres in the other molecules and it is possible that the Pt(1)-Pt(2) bonds in (11) are, therefore, weaker and allow an easier racemisation.

The racemisation of another bent trinuclear complex $[(C_5H_5)Fe(CO)(\mu-CO)(\mu-PAr_2)_2Rh]^+$ has very recently been reported;¹⁶ however, the mechanism is quite different from that which occurs for the trinuclear palladium and platinum complexes described here since the racemisation of the $[RhFe_2]^+$ complex is solvent

¹⁴ R. H. Holm, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' ed. L. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 340 *et seq.*

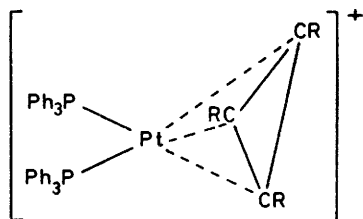
¹⁵ K. Vrieze, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' ed. L. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 457, *et seq.*

¹⁶ A. Agapion, S. E. Pedersen, L. A. Zyzyck, and J. R. Norton, *J.C.S. Chem. Comm.*, 1977, 393.

dependent and occurs *via* an intermediate of type $[(C_5H_5)Fe(CO)_2(\mu-Par_2)_2RhL_2]^+$ [L = solvent].

Far-infrared Studies.—The structures of the bromide complexes (4)—(6) are not known, but according to molecular-weight measurements the compounds (5 α), (5 β), (6a), and (6b) are monomeric in solution. The far-i.r. spectra of these complexes show weak, broad bands which are difficult to assign; however, a general feature appears to be a broad band at 150—200 cm^{-1} which is not inconsistent with the presence of a bridging M_2Br unit.

A number of related chloride complexes were also examined and these also showed rather broad weak absorptions in the region characteristic of M—Cl bridging bands (240—280 cm^{-1} for M = Pd, 200—230 cm^{-1} for M = Pt). In view of their high insolubility, however, it is not clear whether they have the same structures as the bromides or whether a polymeric chloride-bridged structure is indicated.



(17a) R = Ph

(17b) R = *p*-MeOC₆H₄

Other Reactions.—The relation between the mononuclear platinum complex (17a)¹⁷ and the trinuclear clusters prepared here has already been commented on.¹⁰

20 °C) or toluene (at 110 °C). In both cases the starting complex (13) was recovered in better than 90% yield. Attempts to carry out the reverse reaction, by treating complex (17a) with zerovalent platinum olefin complexes, were similarly unsuccessful. It is very interesting that two such closely related species as (13) and (17b) should be able to exist independently and we ascribe this to the very high kinetic inertness of both complexes which does not allow an interconversion.

An early view of these complexes, which are formally 46-electron species, by contrast with the linear 44-electron trimetallic complexes $[Pd_3(RNC)_6(Ph_3P)_2]^{2+}$,¹⁸ suggested that the observed bend in the Pd₃ framework in (8 α) might be due to the two extra electrons being localised in a 'lone pair' at Pd(2). In fact, the complexes appear to have little or no Lewis basicity associated with the metal atoms. Thus, when the platinum compound (9b) was treated with trifluoroacetic acid at 50 °C, complete decomposition to metal occurred immediately. Clearly the salts of any such cation must be exceedingly unstable.

There was no reaction of the platinum complex (9b) with H₂ in [²H₆]benzene at 20 °C. Although carbon monoxide did react with (9b) in [²H₆]benzene at 20 °C to give a brown solid showing $\nu(CO)$ at 2 060 cm^{-1} , the n.m.r. spectrum of the compound was very broad and no pure material could be isolated from the reaction mixture.

EXPERIMENTAL

¹H and ¹³C N.m.r. data are collected in Tables 1—3 and microanalytical and molecular-weight data are given in Table 4. N.m.r. spectra were measured on Perkin-Elmer

TABLE 4
Microanalytical data

Compound	Microanalytical [Found(Calc.)]			Molecular weight ^a [Found(Calc.)]	Decomp. point (°C)
	C	H	Br[N]		
[Pd ₃ (C ₆ Ph ₅) ₂ Br ₂] (4)	50.3 (49.76)	2.95 (2.98)			150
[Pd ₃ (C ₆ Ph ₅) ₂ (acac) ₂] (7)	59.0 (59.36)	4.55 (4.22)		1 098 (1 052)	220
[Pd ₃ {C ₆ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ Br ₂] (5 α)	48.25 (48.72)	3.1 (3.36)	14.03 (14.11)	1 090 (1 133)	210
[Pd ₃ {C ₆ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ (acac) ₂] (8 α)	56.9 (57.38)	4.8 (4.47)		1 220 (1 171)	170
[Pd ₃ {C ₆ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ (hfac) ₂] (10)	48.55 (48.45)	3.05 (2.90)		1 307 (1 387)	
[Pd ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ Br ₂] (6a)	48.0 (48.28)	3.35 (3.54)	13.15 (13.40)	1 095 (1 194)	190
[Pd ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (acac) ₂] (9a)	56.65 (56.53)	4.85 (4.57)		1 268 (1 232)	220
[Pt ₃ {C ₆ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ Br ₂] (5 β)	39.6 (39.47)	2.7 (2.73)	11.38 (11.43)	1 520 (1 399)	220
[Pt ₃ {C ₆ Ph(<i>p</i> -MeOC ₆ H ₄) ₂ } ₂ (acac) ₂] (8 β)	47.2 (46.77)	3.9 (3.64)		1 399 (1 438)	
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ Br ₂] (6b)	39.55 (39.48)	3.1 (2.91)	11.10 (10.96)	1 470 (1 460)	230
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (acac) ₂] (9b)	46.5 (46.50)	3.65 (3.77)		1 522 (1 498)	240
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (η^5 -C ₅ H ₅) ₂] (11)	49.05 (48.71)	3.65 (3.66)		1 320 (1 430)	
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (S ₂ CNPr ₂) ₂ ·2H ₂ O] ^b (12)	43.8 (44.11)	4.0 (4.42)		1 464 (1 688)	
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (PPh ₃) ₄] ²⁺ [PF ₆] ₂ ⁻ (13)	55.1 (54.61)	4.0 (3.90)	[1.80 (1.66)]		260
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (cod) ₂] ²⁺ [PF ₆] ₂ ⁻ (14)	42.55 (42.52)	3.7 (3.65)			m.p. 240—242
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (bipy) ₂] ²⁺ [PF ₆] ₂ ⁻ ·(CH ₃) ₂ CO ^c (15)	43.8 (43.51)	3.3 (3.29)	[2.91 (2.88)]		m.p. 252—255
[Pt ₃ {C ₆ (<i>p</i> -MeOC ₆ H ₄) ₃ } ₂ (phen) ₂] ²⁺ [PF ₆] ₂ ⁻ ·(CH ₃) ₂ CO ^c (16)	44.75 (44.86)	3.05 (3.21)	[2.67 (2.79)]		m.p. 191—194
					m.p. 224—227

^a Osmometric determination in chloroform. ^b An OH band was observed in the i.r. spectrum. ^c A resonance due to acetone was observed in the ¹H n.m.r. spectrum at δ 2.20.

Since the *p*-MeOC₆H₄ analogue (17b) ought to be easily accessible from (13), a number of attempts were made to degrade (13) to (17b), for example, by refluxing (13) with an excess of triphenylphosphine in either acetone (at

R-12B (60 MHz) and R-34 (220 MHz), and JEOL PFT-100 (¹³C and Fourier-transform ¹H) spectrometers. Typical preparations are described. All reactions were carried out under nitrogen atmospheres.

¹⁷ M. D. McLure and D. L. Weaver, *J. Organometallic Chem.*, 1973, **54**, C59.

¹⁸ A. L. Balch, J. R. Boehm, H. Hope, and M. M. Olmstead, *J. Amer. Chem. Soc.*, 1976, **98**, 7431.

The cyclopropenium bromides were prepared by literature methods: 19 $[\text{C}_3\text{Ph}_3]\text{Br}$, m.p. 250–253 °C (lit.,¹⁹ 253–255 °C); $[\text{C}_3\text{Ph}(\textit{p}\text{-MeOC}_6\text{H}_4)_2]\text{Br}$, m.p. 180–182 °C (lit.,¹⁹ 178–179 °C); $[\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3]\text{Br}$, m.p. 212–214 °C (lit.,¹⁹ 210–212 °C), after recrystallisation from acetonitrile–diethyl ether. Light petroleum is that fraction with b.p. 40–60 °C.

$[\text{Pd}_3(\text{C}_3\text{Ph}_3)_2\text{Br}_2]$ (4).—A suspension of $[\text{C}_3\text{Ph}_3]\text{Br}$ (1.0 g, 2.9 mmol) in dichloromethane (20 ml) was added to a stirred solution of $[\text{Pd}_2(\text{dba})_3\text{CHCl}_3]$ (1.0 g, 0.97 mmol) in dichloromethane (100 ml) at 25 °C; an immediate colour change from maroon to amber occurred. The reaction was continued for 1 h, the solution was filtered and the solvent evaporated to give a red oil. Diethyl ether was added to give an orange solid which was filtered off and washed with methanol (25 ml), diethyl ether (3 × 25 ml), and light petroleum (25 ml). The sample was further purified by dissolving it in dichloromethane (25 ml), filtering, removing the solvent, adding diethyl ether to the residue and repeating the wash sequence as above. The brick-red solid was dried *in vacuo*; yield 0.60 g (92%).

$[\text{Pd}_3\{\text{C}_3\text{Ph}(\textit{p}\text{-MeOC}_6\text{H}_4)_2\}_2\text{Br}_2]$ (5 α), (88%); $[\text{Pt}_3\{\text{C}_3\text{Ph}(\textit{p}\text{-MeOC}_6\text{H}_4)_2\}_2\text{Br}_2]$, (5 β), (77%); $[\text{Pd}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2\text{Br}_2]$, (6a) (65%); $[\text{Pt}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2\text{Br}_2]$ (6b), (65%) were all prepared in a similar manner. Since these complexes were appreciably more soluble they were purified by filtering a chloroform solution through a 15-cm Florisil column. Removal of the solvent from the eluate left a residue which gave the analytically pure sample after washing with diethyl ether. Far-i.r. spectra: Complex (4): 250m, br cm^{-1} ; (5 α): 150w, 212m, and 245m cm^{-1} ; (5 β): 200w, br cm^{-1} ; (6a): 150w, 210w, 230w, 260w, and 290w cm^{-1} (all broad); (6b): 150s, 180s, 210s, and 230m cm^{-1} .

$[\text{Pd}_3(\text{C}_3\text{Ph}_3)_2(\text{acac})_2]$ (7).— $\text{Ti}(\text{acac})$ (0.60 g, 1.97 mmol) was added to a stirred suspension of the complex $[\text{Pd}_3(\text{C}_3\text{Ph}_3)_2\text{Br}_2]$ (0.70 g, 0.69 mmol) in toluene (50 ml) at 25 °C. Thallium bromide was immediately deposited and the reaction was continued for 2 h. The solution was filtered and the solvent removed to give an amber oil which, on the addition of diethyl ether, gave the crude product as an orange solid.

The solid was dissolved in dichloromethane (10 ml) and carefully chromatographed on a 20-cm Florisil column in light petroleum–diethyl ether (1 : 1 v/v). A pale orange band was first eluted from the column with diethyl ether; this was found to contain only a mixture of organic products and was discarded. A red band at the top was then eluted with dichloromethane and collected. The volume of the solvent was reduced (to 10 ml) and diethyl ether was slowly added until a red solid began to form. The sample was then allowed to crystallise overnight at 0 °C to give a solid which was filtered off and washed with diethyl ether and light petroleum before being dried *in vacuo*; yield 0.30 g (41%).

$[\text{Pd}_3\{\text{C}_3\text{Ph}(\textit{p}\text{-MeOC}_6\text{H}_4)_2\}(\text{acac})_2]$ (8 α).— $\text{Ti}(\text{acac})$ (0.46 g, 1.5 mmol) was added to a stirred suspension of the bromide complex (5 α) (0.70 g, 0.62 mmol) in toluene (100 ml) at 20 °C. After 3 h, the solution was filtered and reduced in volume (to 5 ml). This solution was chromatographed on a 20-cm Florisil column made up in light petroleum. After a fore-run of organic materials, which were eluted in light petroleum, the main red fraction was eluted with diethyl ether and collected.

¹⁹ R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, 1961, **83**, 2367.

The volume of the solvent was reduced under reduced pressure (to 10 ml) and n-hexane was carefully added until crystallisation commenced. The solution was set aside overnight at 0 °C to give red–brown crystals which were filtered off and washed with light petroleum before being dried *in vacuo*; yield 0.52 g (72%).

A sample of compound (8 α) was recrystallised from chloroform (5 ml)–diethyl ether (5 ml)–light petroleum (10 ml) to give crystals for the X-ray diffraction study.

The following complexes were prepared in the same manner as (8 α): $[\text{Pt}_3\{\text{C}_3\text{Ph}(\textit{p}\text{-MeOC}_6\text{H}_4)_2\}_2(\text{acac})_2]$ (8 β), 54%; $[\text{Pd}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2(\text{acac})_2]$ (9a), 70%; $[\text{Pt}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2(\text{acac})_2]$ (9b), 49%; $[\text{Pd}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2(\text{CF}_3\text{COCHCOCF}_3)_2]$ (10), 53%.

$[\text{Pt}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2(\eta^5\text{-C}_6\text{H}_5)_2]$ (11).—Cyclopentadienylthallium (0.40 g, 1.08 mmol) was added to a solution of complex (6b) (0.58 g, 0.4 mmol) in acetone (50 ml) at 20 °C. After 2 h, the solution was filtered through a 5-cm layer of Hyflo Supercel and the solvent was evaporated to leave a dark maroon oil. This was dissolved in dichloromethane (5 ml) and carefully chromatographed on a 15-cm Florisil column made up in diethyl ether. A dark purple band that was eluted with dichloromethane was collected and the solvent volume was reduced (to ca. 10 ml) under reduced pressure. n-Hexane was slowly added and the mixture set aside overnight at 0 °C to give a dark crystalline material. The mother liquor was decanted and the dark purple crystals were washed with light petroleum before being dried *in vacuo* to give a pure sample of complex (11); yield 0.28 g (49%).

$[\text{Pt}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2(\text{S}_2\text{CNPr}_2)_2]$ (12).— $\text{Na}[\text{S}_2\text{CNPr}_2] \cdot 2\text{H}_2\text{O}$ (0.10 g, 0.43 mmol) was added to a stirred solution of complex (6b) (0.29 g, 0.2 mmol) in acetone (30 ml) at 20 °C. Stirring was continued for 3 h, the solution was filtered, and the solvent evaporated to leave a red–brown oil. This was dissolved in dichloromethane (5 ml) and chromatographed on a 20-cm Florisil column made up in diethyl ether. A red band moved down the column and was collected. The solvent volume was reduced (to 5 ml) under reduced pressure and n-hexane was slowly added until a solid started to form. The solution was set aside overnight at 0 °C and the resulting red–brown crystals were filtered off, washed with light petroleum and dried *in vacuo*; yield 0.15 g (45%).

$[\text{Pt}_3\{\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_3\}_2(\text{PPh}_3)_4]^{2+}2[\text{PF}_6]^-$ (13).—Silver hexafluorophosphate (0.10 g, 0.40 mmol) was added to a stirred solution of complex (6b) (0.29 g, 0.20 mmol) in acetonitrile (25 ml) at 20 °C in the dark. A clear red–brown solution containing a dark suspension was immediately formed. The reaction was allowed to continue for 0.25 h and the mixture was then filtered through a 5 cm layer of Hyflo Supercel into a stirred solution of triphenylphosphine (0.36 g, 1.4 mmol) in acetonitrile (25 ml) at 20 °C.

A red solution containing a fine white suspension was formed and the mixture was stirred for 2 h before being filtered. The filtrate was collected and the solvent evaporated to leave a red–brown oil. The addition of diethyl ether gave an orange solid which was filtered off and washed with diethyl ether (3 × 25 ml) and light petroleum before being dried *in vacuo*.

This crude material was dissolved in dichloromethane, filtered, and diethyl ether was slowly added to the filtrate to form a flocculent white precipitate $\{[\text{C}_3(\textit{p}\text{-MeOC}_6\text{H}_4)_2]\text{-}[\text{PF}_6]\}$ in a clear red solution. The precipitate was filtered off and diethyl ether was slowly added to the filtrate. The

clear red solution was set aside for 18 h at 0 °C to give bright orange-red crystals which were filtered off and washed with diethyl ether and light petroleum before being dried *in vacuo*; yield 0.21 g (40%).

The complexes $[\text{Pt}_3\{\text{C}_3(p\text{-MeOC}_6\text{H}_4)_3\}_2(\text{L}_2)_2][\text{PF}_6]_2$ were prepared in the same manner except that compounds (14) or (15) ($\text{L}_2 =$ bipyridyl or *o*-phenanthroline) were crystallised from acetone-diethyl ether. Yields were (14; $\text{L}_2 =$

cod) 42%, (15; $\text{L}_2 =$ bipyridyl) 45%, and (16; $\text{L}_2 =$ *o*-phenanthroline) 46%.

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