

961. Transition Metal–Carbon Bonds. Part II.¹ π -Allylic and Related Complexes from Some Cyclic 1,3-Dienes.

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Chloro-bridged methoxy π -allylic palladium(II) complexes have been prepared from several cyclic 1,3-dienes. Cyclohepta- and cyclo-octa-dienyl-palladium(II) complexes and a methoxycyclo-octatrienylpalladium(II) complex have also been prepared. Metathetical replacement and bridge splitting reactions and conversion to mononuclear acetylacetonato and cyclopentadienyl complexes are described. Ultraviolet, infrared, and nuclear magnetic resonance (n.m.r.) properties are recorded.

In Part I¹ of this series we described the reactions of butadiene and several of its methyl derivatives with sodium chloropalladite in alcohols to give alkoxy- π -allylic palladium(II) complexes; thus, butadiene in methanol gave the chloro-bridged 4-methoxy- π -butenyl complex $[\text{Pd}_2\text{Cl}_2(\text{C}_4\text{H}_6\text{OCH}_3)_2]$ very readily. We also described several reactions of such complexes and the preparation of mononuclear derivatives. We have now investigated the reactions of cyclopenta-1,3-diene, cyclohexa-1,3-diene, cyclohepta-1,3-diene, and cyclo-octa-1,3-diene with sodium chloropalladite in methanol and similar reactions with cyclo-octa-1,5-diene and cyclo-octa-1,3,5,7-tetraene.

Cyclopenta-1,3-diene.—Addition of cyclopentadiene to a solution of sodium chloropalladite in methanol gave a yellow precipitate, but this darkened very rapidly and we have been unable to isolate the pure product or any of its derivatives.

Cyclohexa-1,3-diene.—On adding this diene to a solution of sodium chloropalladite in methanol, sodium chloride was rapidly precipitated and, on cooling the reaction mixture to -20° , di- μ -chlorodi-(4-methoxycyclohex-2-enyl)dipalladium, $[\text{Pd}_2\text{Cl}_2(\text{C}_6\text{H}_8\text{OCH}_3)_2]$ crystallised out. This compound was much less thermally stable than the analogous acyclic complexes described previously,¹ and on heating to 85° gave metallic palladium. Its solution in benzene at room temperature deposited a palladium mirror after a few hours. When cyclohexa-1,3-diene was added to a suspension of sodium chloropalladite tetrahydrate in methanol and the mixture warmed to 60° for 10 minutes, palladium was deposited and the known² di- μ -chlorodi(cyclohex-2-enyl)dipalladium, $[\text{Pd}_2\text{Cl}_2(\text{C}_6\text{H}_9)_2]$ was obtained and identified by means of its infrared absorption spectrum.³ Benzene was shown to be formed in this hydrogen transfer reaction by means of its characteristic ultraviolet absorption spectrum (benzene was similarly shown to be absent from the cyclohexa-1,3-diene used).

Cyclohepta-1,3-diene.—Similarly, cyclohepta-1,3-diene with sodium chloropalladite in methanol gave $[\text{Pd}_2\text{Cl}_2(\text{C}_7\text{H}_{10}\text{OCH}_3)_2]$ the chloro-bridged 4-methoxycyclohept-2-enyl complex. This compound was more thermally stable than the 4-methoxycyclohex-2-enyl complex, but slowly decomposed in solution to give a palladium mirror. When

¹ Part I, Robinson and Shaw, *J.*, 1963, 4806.

² Fischer and Werner, *Ber.*, 1962, 95, 695.

³ Fritz, *Ber.*, 1961, 94, 1217.

cyclohepta-1,3-diene was heated under reflux with sodium chloropalladite in methanol for 2 hours, it gave di- μ -chloro-di(cyclohepta-2,4-dienyl)dipalladium(II). This compound showed an extremely weak broad band at *ca.* 1625 cm^{-1} in its infrared absorption spectrum, but otherwise there were no bands between 1470 and 2800 cm^{-1} , suggesting the absence of an uncomplexed double bond. We think that the palladium atom may be associated with five carbon atoms of the cycloheptadienyl ligand in this complex, and we therefore represent the ligand by structure (I) rather than the $\alpha\beta$ -unsaturated π -allylic structure (II). The infrared absorption spectrum of this complex indicated the absence of a methoxyl group (see Table I), and the n.m.r. spectrum (Table 2), although very complex, had two bands, centred at 4.37 and 4.75 τ (total relative intensity five) and a band at 8.1 τ (relative intensity four) corresponding to hydrogens attached to unsaturated carbon atoms and saturated carbon atoms, respectively. An example of a metal atom being associated with five carbon atoms of a cyclohepta-2,4-dienyl ring is known *viz.* the cyclohepta-2,4-dienyl-(tricarbonyl)iron(II) cation.^{4,5} In contrast, the $\alpha\beta$ -unsaturated acyclic π -allylic complex di- μ -chlorobis(2,5-dimethylhexa-2,4-dienyl)dipalladium(II) showed a strong band at 1637 cm^{-1} attributed to the carbon-carbon stretching mode of vibration of the uncomplexed double bond. The palladium atoms in

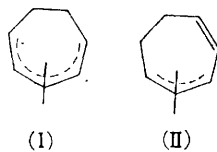


TABLE I.

Infrared absorption data for the methoxyl group in chloro-bridged methoxy complexes.

Complex	$\nu(\text{O}-\text{C})$ * cm^{-1}	$\nu(\text{C}-\text{H})$ † cm^{-1}
Di- μ -chlorodi-(4-methoxycyclohex-2-enyl)dipalladium(II)	1080	2817
Di- μ -chlorodi-(4-methoxycyclohept-2-enyl)dipalladium(II)	1091	2817
Di- μ -chlorodi-(4-methoxycyclo-oct-2-enyl)dipalladium(II)	1103	2821
Di- μ -chlorodi-(2-methoxycyclo-octa-3,5,7-trienyl)dipalladium(II) ...	1100	2817
Di- μ -chlorodi-(2-methoxycyclo-oct-5-enyl)dipalladium(II)	1081	2817

* As KBr disc or Nujol mull. † As hexachlorobutadiene mull.

this complex do not bond to five carbon atoms because of unfavourable steric and geometric factors. It is noteworthy that, of the two isomeric tricarbonyl(penta-1,3-diene)-iron(O) complexes, the *cis*-isomer reacts with triphenylmethyl fluoroborate to give the tricarbonyl(penta-2,4-dienyl)iron(II) cation but the *trans*-isomer does not.⁶

Cyclo-octa-1,3-diene.—Addition of this diene to a suspension of sodium chloropalladite tetrahydrate in methanol at 20° gave di- μ -chlorodi-(4-methoxycyclo-oct-2-enyl)dipalladium(II). This compound was formed more slowly than the six and seven membered ring analogues, and was much more stable. The rates of formation of these cyclic methoxy π -allylic complexes decreased as the ring size increased from six- to eight-membered, whilst the thermal stabilities of the resultant complexes showed a marked increase. When the sodium chloropalladite/methanol/cyclo-octa-1,3-diene reaction mixture was heated for two hours, the unsaturated complex di- μ -chlorodi-(cyclo-octa-2,4-dienyl)dipalladium(II) was formed. The infrared absorption spectrum of this complex showed the absence of a methoxyl group (see Table I) and, as above, favoured a structure in which the palladium was bonded to five carbon atoms, since apart from a very weak absorption at *ca.* 1660 cm^{-1} a band due to an uncomplexed double bond could not be observed. The n.m.r. spectrum (see Table 2) indicated that five hydrogens were attached to unsaturated carbon atoms and that the ligand was therefore monocyclic. Protonation of tricarbonyl(cyclo-octa-tetraene)iron(O) with fluoroboric acid gives a bicyclic ligand.⁷

Cyclo-octa-1,5-diene.—This diene is known⁸ to react with sodium chloropalladite in

⁴ Dauben and Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 497.

⁵ Burton, Pratt, and Wilkinson, *J.*, 1961, 594.

⁶ Mahler and Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3955.

⁷ Davison, McFarlane, and Wilkinson, *Chem. and Ind.*, 1962, p. 320.

⁸ Chatt, Vallarino, and Venanzi, *J.*, 1957, 3413.

n-propanol to give dichlorocyclo-octa-1,5-dienepalladium(II), which, with methanol and sodium carbonate, gives the 2-methoxycyclo-oct-5-enyl complex $[\text{Pd}_2\text{Cl}_2(\text{C}_8\text{H}_{12}\text{OCH}_3)_2]$, isomeric with the new complex described above. We found that this methoxy complex was unchanged by heating in methanol for two hours, whilst on heating in dilute methanolic hydrochloric acid, it was converted into dichlorocyclo-octa-1,5-dienepalladium(II).

TABLE 2.

Nuclear magnetic resonance data. Chemical shifts (τ) are relative to SiMe_4 as internal standard, the spectra being measured at 60 Mc./sec. and integrated.

Radical	τ_{OMe}	Acac.		$\pi\text{-C}_5\text{H}_5$ τ_{H}	Allylic and vinylic protons			Other protons		
		τ_{Me}	τ_{H}		Band centre	Relative intensity	Band width (c./sec.)	Band centre	Relative intensity	Band width (c./sec.)
Chloro-bridged complexes $[\text{Pd}_2\text{Cl}_2(\text{all})_2]$ in deuteriochloroform.										
4-Methoxycyclohex-2-enyl *	6.92	—	—	—	5.17	†	30	6.33	†	20
4-Methoxycyclohept-2-enyl	6.41	—	—	—	‡			8.9	†	110
Cyclohepta-2,4-dienyl	—	—	—	—	4.37	3	30	8.1	4	single peak ca. 25
					4.75	2	40			
4-Methoxycyclo-oct-2-enyl	6.42	—	—	—	4.65	1	triplet 20	6.3	1	
					5.33	2		30	8.53	8
Cyclo-octa-2,4-dienyl	—	—	—	—	4.6	§ 5	100	8.3	§ 6	75
2-Methoxycyclo-octa-3,5,7-trienyl	6.54	—	—	—	4.26	7	75	6.08	1	10
2-Methoxycyclo-oct-5-enyl	6.71	—	—	—	4.05	1	25	6.38	2	25
					4.46	1	20	7.88	8	95
Acetylacetonato-complexes $[\text{Pd}(\text{acac})(\text{all})]$ in carbon tetrachloride.										
Cyclohex-2-enyl	—	8.16	4.89	—	4.50	1	triplet 12	8.15	6	15
					5.17	2		15		
4-Methoxycyclohept-2-enyl	6.59	8.09	4.76	—	5.2	3	45	6.26	1	15
Cyclohepta-2,4-dienyl	—	8.12	4.80	—	4.00	1	10	8.2	§ 6	20
					5.08	2	20	8.0	§ 4	25
4-Methoxycyclo-oct-2-enyl	6.46	doublet 8.10 8.11	4.82	—	4.62	1	16	8.47	8	30
						5.7	2	25	¶	
Cyclo-octa-2,4-dienyl	—	8.16	4.88	—	4.8	†	125	8.3	†	80
Cyclopentadienyl complexes $[\text{Pd}(\text{C}_5\text{H}_5)(\text{all})]$ in carbon tetrachloride.										
4-Methoxycyclo-oct-2-enyl	6.38	—	—	4.27	4.95	1	triplet 15	8.55	8	45
					5.48	2		40	¶	
Cyclo-octa-2,4-dienyl	—	—	—	4.41	4.9	†	130	8.4	†	105
2-Methoxycyclo-oct-5-enyl	6.83	—	—	4.43	4.6	1	25	6.05	1	16
					5.47	1	20	7.5	ca. 1	20
								8.2	ca. 8	50

* Measurements in benzene. † These intensities could not be determined. ‡ This complex, which was too insoluble for n.m.r. measurements in benzene, decomposed slightly in deuteriochloroform and the spectrum was very complex and accompanied by much noise. § These intensities are of doubtful value because of either (a) poor signal: noise ratio or (b) the resonance was partly obscured by other absorptions. ¶ In these compounds the resonance due to tertiary hydrogen next to the methoxyl group could not be identified with certainty.

Cyclo-octatetra-1,3,5,7-ene.—Treatment of dichlorobisbenzotriplepalladium(II) with cyclo-octa-1,3,5,7-tetraene in benzene gave a good yield of dichlorocyclo-octa-1,3,5,7-tetraenepalladium(II).⁹ This complex, when suspended in methanol, rapidly solvolyzed to give di- μ -chlorodi-(2-methoxycyclo-octa-3,5,7-trienyl)dipalladium(II). This complex was also prepared by the action of cyclo-octa-1,3,5,7-tetraene on sodium chloropalladite in methanol.

⁹ Fritz and Keller, *Ber.*, 1962, **95**, 158.

Its infrared and n.m.r. spectra showed the presence of the methoxyl group (see Tables 1 and 2). We cannot say which carbon atoms or double bonds of the ring system are bonded to the palladium. The n.m.r. spectrum shows that seven hydrogens are attached to unsaturated carbon atoms and that the ligand is still therefore monocyclic.

Reactions of Chloro-bridged Cyclic π -Allylic Complexes.—In Part I of this series, we described several reactions of the halo-bridged acyclic π -allylic palladium complexes: *e.g.*, metathesis, splitting by pyridine and quinoline and the formation of mononuclear cyclopentadienyl and acetylacetonato complexes on treatment with cyclopentadienylsodium or thallos acetylacetonate, all of which were characteristic of the bridging groups. We have carried out these reactions with the analogous cyclic complexes. Thus, on treatment with lithium bromide in acetone, bridging chlorine atoms could be replaced by bridging bromine atoms, and fission with pyridine readily gave mononuclear complexes of the type $[\text{PdCl}(\text{all})\text{C}_5\text{H}_5\text{N}]$ (all = π -allylic ligand). Seven chloro-bridged complexes were converted into their mononuclear acetylacetonato derivatives on treatment with thallos acetylacetonate. These acetylacetonato derivatives were well crystallised and soluble, and the acetylacetonato ligand gave a very simple n.m.r. spectrum (Table 2). The chloro-bridged cyclo-octa-2,4-dienyl and 2-methoxycyclo-octa-3,5,7-trienyl complexes, $[\text{Pd}_2\text{Cl}_2(\text{all})_2]$ were converted into their cyclopentadienyl derivatives $[\text{Pd}(\text{all})(\text{C}_5\text{H}_5)]$ by treatment with cyclopentadienylsodium. A cyclopentadienyl derivative was similarly prepared from di- μ -chlorodi-(2-methoxycyclo-oct-5-enyl)dipalladium(II).

Spectroscopic Properties of the π -Allylic Palladium Complexes.—The infrared absorption spectra of all the methoxy cyclic π -allylic palladium complexes showed a strong absorption band(s) within the range 1080–1110 cm^{-1} due to the carbon–oxygen stretching mode of the ether linkage and a band in the range 2810–2840 cm^{-1} due to the carbon–hydrogen stretching mode of the methyl group (see Table 1); these bands were absent from the spectra of the non-methoxy complexes.

TABLE 3.

Ultraviolet absorption values for π -allylic palladium(II) complexes.

Radical	λ_{max} (m μ)	$\log \epsilon$	λ_{max}	$\log \epsilon$	λ_{max}	$\log \epsilon$
Chloro-bridged complexes $[\text{Pd}_2\text{Cl}_2(\text{all})_2]$ in chloroform.						
4-Methoxycyclohex-2-enyl	245	3.94	252 *	3.88	302	3.04
					338 *	2.95
4-Methoxycyclohept-2-enyl	249	3.90			297	3.11
					315 *	3.00
4-Methoxycyclo-oct-2-enyl.....	244	4.11	256	4.10	298 *	3.38
					339	3.10
Cyclohex-2-enyl	244	4.00	253 *	3.92	320	3.04
Cyclohepta-2,4-dienyl			264	4.05	291	3.58
Cyclo-octa-2,4-dienyl	232	3.93	259	4.09	285 *	3.87
					353 *	3.04
Acetylacetonato-complexes $[\text{Pd}(\text{acac})(\text{all})]$ in hexane.						
4-Methoxycyclo-oct-2-enyl.....	213 *	4.25	229	4.27	258 *	4.01
					292	3.91
2-Methoxycyclo-oct-5-enyl.....	205	4.38	227.5 *	4.27	306	3.93
Cyclohex-2-enyl			222	4.31	301	3.87
Cyclohepta-2,4-dienyl	211	4.12	265	4.04	291 *	3.93
Cyclo-octa-2,4-dienyl	221	4.24	250	4.20	286	4.18
Cyclopentadienyl complexes $[\text{Pd}(\text{C}_5\text{H}_5)(\text{all})]$ in hexane.						
4-Methoxycyclo-oct-2-enyl.....	199	4.23	229	4.01	270	4.33
					328	3.96
2-Methoxycyclo-oct-5-enyl.....	201.5	4.35	256	4.47	329	3.84
					410	2.40
2-Methoxycyclo-octa-3,5,7-trienyl...	200	4.33	223 *	4.13	312	4.49
					383 *	3.49
Cyclo-octa-2,4-dienyl	194	4.67	233	4.13	289	4.45
	203	4.22			348	4.01

* Shoulder.

The n.m.r. spectra of these compounds were very complex, but resonances due to methoxyl, cyclopentadienyl, and acetylacetonato groups were readily assigned (see Table 2). The remainder of the absorption was not assigned, but was found in two separated regions (1) 4—6 τ usually due to hydrogens attached to unsaturated carbon atoms and (2) 6—9 τ , due to hydrogens attached to saturated carbon atoms; thus, the integrated spectra gave the ratio of the two types of hydrogen, and were useful in confirming structure.

The ultraviolet absorption spectra of these cyclic π -allylic palladium complexes are very similar to those of their acyclic analogues and the values for chloro-bridged, acetylacetonato and cyclopentadienyl complexes are given in Table 3.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus and are corrected.

Di- μ -chlorodi-(4-methoxycyclohex-2-enyl)dipalladium(II).—Cyclohexa-1,3-diene (0.5 c.c.) was added to a suspension of sodium chloropalladite tetrahydrate (1.0 g.) in methanol (5 c.c.). When all the sodium chloropalladite tetrahydrate had reacted the mixture was cooled to -20° for 12 hr.; the resultant precipitate was washed with cold methanol, followed by water, to give the required product as pale yellow microcrystals (0.51 g.); m. p. $87-91^\circ$ (decomp.) (Found: C, 33.25; H, 4.3. $C_{14}H_{22}Cl_2O_2Pd_2$ requires C, 33.25; H, 4.4%).

Di- μ -chlorodi-(4-methoxycyclohept-2-enyl)dipalladium(II).—Cyclohepta-1,3-diene (0.7 c.c.) was added to a suspension of sodium chloropalladite tetrahydrate (1.0 g.) in methanol (5 c.c.). The mixture was shaken until all the sodium chloropalladite tetrahydrate had dissolved and a yellow precipitate formed. Cooling to -15° for 12 hr. and washing the resultant precipitate with methanol, followed by water, gave the required product as yellow microcrystals (0.443 g.), m. p. $108-112^\circ$ (decomp.) (Found: C, 36.2, 35.95; H, 5.05, 4.7; Cl, 13.45. $C_{16}H_{26}Cl_2O_2Pd_2$ requires C, 36.0; H, 4.9; Cl, 13.3%).

Di- μ -chlorodi-(4-methoxycyclo-oct-2-enyl)dipalladium(II).—Cyclo-octa-1,3-diene (1 c.c.) was added to a suspension of sodium chloropalladite tetrahydrate (1.0 g.) in methanol (10 c.c.). After 1 hr. water (5 c.c.) and light petroleum (5 c.c., b. p. $40-60^\circ$) were added and the mixture cooled to 0° for 12 hr. Recrystallisation of the resultant precipitate from benzene-methanol gave the required product as yellow needles (0.32 g.), decomposing without melting at 140° (Found: C, 38.55; H, 5.6; Cl, 12.3. $C_{18}H_{30}Cl_2O_2Pd_2$ requires C, 38.45; H, 5.4; Cl, 12.6%).

Dichloro-(cyclo-octa-1,3,5,7-tetraene)palladium(II).—Cyclo-octa-1,3,5,7-tetraene (0.3 c.c.) was added to a solution of dichlorobisbenzonnitripalladium(II) (0.5 g.) in benzene (15 c.c.). The required product separated immediately as orange needles (0.314 g.), which were filtered off and washed with light petroleum (b. p. $60-80^\circ$) (Found: C, 34.5; H, 3.0. Calc. for $C_8H_8Cl_2Pd$: C, 34.1; H, 2.85%).

Di- μ -chlorodi-(2-methoxycyclo-octa-3,5,7-trienyl)dipalladium(II) from Dichloro-(cyclo-octa-1,3,5,7-tetraene)palladium(II).—A suspension of dichloro-(cyclo-octa-1,3,5,7-tetraene)palladium (0.33 g.) in methanol (20 c.c.) was heated on a steam-bath for 30 min. The resultant yellow suspension was cooled and filtered, and the precipitate recrystallised from benzene-methanol to give the required product as yellow microcrystals (0.20 g.) decomposing $130-135^\circ$ (Found: C, 38.85; H, 4.0. $C_{18}H_{22}Cl_2O_2Pd_2$ requires C, 39.0; H, 4.0%).

Di- μ -chlorodi-(2-methoxycyclo-octa-3,5,7-trienyl)dipalladium(II) from Sodium Chloropalladite Tetrahydrate.—Cyclo-octa-1,3,5,7-tetraene (1.0 c.c.) was added to a suspension of sodium chloropalladite tetrahydrate (1.0 g.) in methanol (10 c.c.). After 10 min. the mixture was cooled to 0° and the resultant precipitate filtered off and washed with water followed by cold methanol. Recrystallisation from benzene-methanol gave the required product identical with that prepared above.

Di- μ -chlorodi-(cyclohex-2-enyl)dipalladium(II).—Cyclohexa-1,3-diene (0.75 c.c.) was added to a suspension of sodium chloropalladite tetrahydrate (0.5 g.) in methanol (10 c.c.). The resultant yellow solution was warmed to 60° for 10 min., metallic palladium was deposited and the solution rapidly turned greenish yellow. The mixture was then evaporated to dryness and the required product isolated with benzene. It formed yellow microcrystals (0.16 g.), m. p. $80-83^\circ$ (decomp.) from methylene chloride-light petroleum (b. p. $40-60^\circ$) (Found: C, 32.3; H, 4.05. Calc. for $C_{12}H_{18}Cl_2Pd_2$, C, 32.3; H, 4.05%).

Di- μ -chlorodi-(cyclohepta-2,4-dienyl)dipalladium(II).—Cyclohepta-1,3-diene (0.5 c.c.) was

added to a suspension of sodium chloropalladite tetrahydrate (1.0 g.) in methanol (15 c.c.). The mixture was heated under reflux for 2 hr. on a steam-bath, and the resultant brown solution evaporated to dryness under reduced pressure. The required product was isolated with benzene and formed orange yellow microcrystals (0.25 g.), from methylene chloride–light petroleum (b. p. 80–100°), decomposing without melting above 150° (Found: C, 35.8; H, 3.95. $C_{14}H_{18}Cl_2Pd_2$ requires C, 35.8; H, 3.85%).

Di-μ-chlorodi-(cyclo-octa-2,4-dienyl)dipalladium(II).—Cyclo-octa-1,3-diene (1.5 c.c.) was added to a suspension of sodium chloropalladite tetrahydrate (0.60 g.) in methanol (15 c.c.). The mixture was heated under reflux for 2 hr., evaporated to dryness under reduced pressure and the residue recrystallised from benzene–light petroleum (b. p. 80–100°) and formed yellow microcrystals (0.26 g.) decomposing without melting above 160° (Found: C, 38.75; H, 4.6; Cl, 13.75. $C_{16}H_{22}Cl_2Pd_2$ requires C, 38.6; H, 4.4; Cl, 14.25%).

Di-μ-bromodi-(4-methoxycyclo-oct-2-enyl)dipalladium(II).—The corresponding chloro-complex (0.200 g.) suspended in acetone (15 c.c.) was treated with lithium bromide (0.07 g.) and the mixture warmed for 5 min., filtered and the filtrate evaporated under reduced pressure. Recrystallisation of the residue from benzene–methanol gave the required compound as yellow needles (0.180 g.), decomposing without melting above 130° (Found: C, 33.6; H, 4.6. $C_{18}H_{30}Br_2O_2Pd_2$ requires C, 33.2; H, 4.65%).

Di-μ-bromodi-(cyclo-octa-2,4-dienyl)dipalladium(II).—The corresponding chloro complex (0.152 g.) was suspended in acetone (20 c.c.), lithium bromide (0.100 g.) added and the mixture warmed to ca. 40°; the resultant orange red solution was evaporated to dryness under reduced pressure and the product isolated with benzene. It formed orange yellow microcrystals (0.10 g.) from benzene–light petroleum (b. p. 40–60°), which decomposed without melting above 160° (Found: C, 33.25; H, 3.85. $C_{16}H_{22}Br_2Pd_2$ requires C, 32.75; H, 3.8%).

Chloro(4-methoxycyclo-oct-2-enyl)pyridinepalladium(II).—A solution of di-μ-chlorodi-(4-methoxycyclo-oct-2-enyl)dipalladium (0.100 g.) in methylene chloride (2 c.c.) was treated with pyridine (0.1 c.c.) then diethyl ether (5 c.c.) and the solution cooled to –20°. The resultant precipitate was washed with light petroleum (b. p. 30–40°) to yield the required product as yellow prisms (0.060 g.) (Found: C, 46.45; H, 5.3; N, 3.6. $C_{14}H_{20}ClNOPd$ requires C, 46.7; H, 5.6; N, 3.9%).

Preparation of Acetylacetonato(π-allylic)palladium(II), Complexes.—General method. A solution of the chloro-bridged palladium complex (0.10–0.25 g.), in benzene or methylene chloride (5 c.c.), was treated with a solution of thallos acetylacetonate (5% excess) in warm benzene or methylene chloride (20 c.c.). The precipitate of thallos chloride was filtered off, the filtrate evaporated to dryness and the residue recrystallised from light petroleum (b. p. 40–60°) to give the required product. The following seven complexes were prepared in this manner.

Acetylacetonato(4-methoxycyclohept-2-enyl)palladium(II), as yellow microcrystals (yield 31%), m. p. 80–84° (Found: C, 46.95; H, 6.15. $C_{13}H_{20}O_3Pd$ requires C, 47.2; H, 6.1%).

Acetylacetonato(4-methoxycyclo-oct-2-enyl)palladium(II), as pale yellow needles (yield 40%), m. p. 120–125° (decomp.) (Found: C, 48.9; H, 6.25. $C_{14}H_{22}O_3Pd$ requires C, 48.8; H, 6.45%).

Acetylacetonato(2-methoxycyclo-oct-5-enyl)palladium(II) as cream-coloured microcrystals (yield 23%), m. p. 96–98° (Found: C, 48.85; H, 6.45. $C_{14}H_{22}O_3Pd$ requires C, 48.8; H, 6.45%).

Acetylacetonato(2-methoxycyclo-octa-3,5,7-trienyl)palladium(II), as yellow microcrystals (yield 5%), m. p. 84–88° (Found: C, 48.85; H, 5.15. $C_{14}H_{18}O_3Pd$ requires C, 49.35; H, 5.35%).

Acetylacetonato(cyclohex-2-enyl)palladium(II), as cream-coloured microcrystals (yield 43%), m. p. 78–81° (decomp.) (Found: C, 46.15; H, 5.55. $C_{11}H_{16}O_2Pd$ requires C, 46.1; H, 5.65%).

Acetylacetonato(cyclohepta-2,4-dienyl)palladium(II), as orange microcrystals (yield 35%), m. p. 95–100° (Found: C, 48.6; H, 5.6. $C_{12}H_{16}O_2Pd$ requires C, 48.25; H, 5.4%).

Acetylacetonato(cyclo-octa-2,4-dienyl)palladium(II), as yellow needles (yield 62%), m. p. 93–95° (Found: C, 49.85; H, 5.8. $C_{13}H_{18}O_2Pd$ requires C, 49.95; H, 5.8%).

Cyclopentadienyl(2-methoxycyclo-octa-3,5,7-trienyl)palladium(II).—Di-μ-chlorodi-(2-methoxycyclo-octa-3,5,7-trienyl)dipalladium (0.235 g.) suspended in tetrahydrofuran (5 c.c.) under nitrogen, was treated with a solution of cyclopentadienylsodium in tetrahydrofuran (5% excess). The resultant red solution was evaporated to dryness under reduced pressure and the product isolated with light petroleum (b. p. 40–60°). It formed dark red microcrystals (0.060 g.), m. p. 100–105° (decomp.) from light petroleum (b. p. 40–60°) (Found: C, 54.85; H, 5.15. $C_{14}H_{16}OPd$ requires C, 54.85; H, 5.25%).

Cyclo-octa-2,4-dienyl(cyclopentadienyl)palladium(II).—Di- μ -chlorodi(cyclo-octa-2,4-dienyl)-dipalladium (0.32 g.) suspended in tetrahydrofuran (5 c.c.) under nitrogen was treated with a solution of cyclopentadienylsodium in tetrahydrofuran (5% excess). The red solution was evaporated under reduced pressure and the product isolated with light petroleum (b. p. 30—40°). It was purified by vacuum sublimation (40—60° bath temperature/ 10^{-2} mm.) and formed dark red microcrystals (0.265 g.), m. p. 83—87° (Found: C, 56.1; H, 5.65. $C_{13}H_{16}Pd$ requires C, 56.05; H, 5.8%).

Cyclopentadienyl(2-methoxycyclo-oct-5-enyl)palladium(II).—The corresponding chloro-complex (0.49 g.) suspended in tetrahydrofuran under nitrogen was treated with a solution of cyclopentadienylsodium in tetrahydrofuran (5% excess). The yellow solution was treated with water (5 c.c.) and diethyl ether (10 c.c.). The product was isolated from the ether and recrystallised from light petroleum (b. p. 30—40°) to give pale orange needles (0.376 g.), m. p. 62—64° (Found: C, 54.0; H, 6.3. $C_{14}H_{20}OPd$ requires C, 54.05; H, 6.5%).

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