# **919.** *Transition Metal–Carbon Bonds. Part I. π-Allylic Palladium Complexes from Butadiene and its Methyl Derivatives.*

By S. D. Robinson and B. L. Shaw.

Butadienepalladous chloride is shown to have the chloro-bridged π-allylic structure, [$Pd_2Cl_2$(4-chlorobutenyl)$_2$]. Butadiene and several of its methyl derivatives react with sodium chloropalladite in methanol to give stable chloro-bridged π-allylic complexes [$Pd_2Cl_2(C_xH_{2x-2}\cdot OMe)_2$]. Metathetical replacement, bridge splitting, and acid-catalysed alcoholysis are described for these complexes, also their conversion into mononuclear acetylacetonato- and cyclopentadienyl complexes. Ultraviolet, infrared, and nuclear magnetic resonance properties are recorded and various types of isomerism and rotational effects are discussed.

As part of a general study of compounds containing metal–carbon bonds we have re-investigated butadienepalladous chloride.[1] This complex, prepared by treating dichlorobisbenzonitrilepalladium(II) in benzene with butadiene [Kharasch's method for palladium(II)–olefin complexes] was previously thought to be a true olefin complex, for which structures such as (I) [1] and (II) [2] have been suggested. These structures, however, do not explain why the compound is so much paler than other olefin–palladous chloride complexes, *e.g.*, ethylenepalladous chloride, or why it is more stable than butadieneplatinous chloride [platinum(II)–olefin complexes are usually much more stable than their palladium(II) analogues]. The chemical and physical evidence presented below shows that butadienepalladous chloride has the chloro-bridged π-4-chlorobutenyl structure [$Pd_2Cl_2(C_4H_6Cl)_2$] (III; X = Cl); this explains the stability and pale yellow colour; other chloro-bridged π-allylic palladium complexes, *e.g.*, [$Pd_2Cl_2(C_3H_5)_2$], are pale yellow and have considerable thermal stability. It is possible that in a solution of butadienepalladous chloride small amounts of true olefin complexes such as (I) and (II) are present. Butadienepalladous chloride was rapidly solvolysed by methanol, giving the more stable methoxy-analogue [$Pd_2Cl_2(C_4H_6\cdot OMe)_2$] (III; X = OMe), whose nuclear magnetic resonance (n.m.r.) spectrum showed a strong peak due to the methoxyl protons though the rest of the spectrum was similar to that of butadienepalladous chloride and there can be little doubt that the two compounds have analogous structures. This methoxy-analogue was more conveniently prepared by passing butadiene into a methanolic suspension of sodium chloropalladite; the mixture rapidly became paler, sodium chloride was precipitated, followed on cooling to −10° by the pale yellow π-methoxybutenyl complex (III; X = OMe). A preliminary account of this work has been published.[3] This reaction has been

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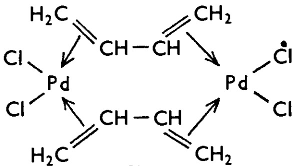
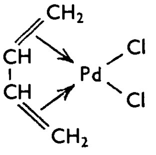
[1] Slade and Jonassen, *J. Amer. Chem. Soc.*, 1957, **79**, 1277.

[2] Coates in " Organometallic Compounds," Methuen, London, 1960, 2nd edn., p. 339.

[3] Shaw, *Chem. and Ind.*, 1962, 1190.

extended to several methyl derivatives of butadiene which, when added to a suspension of sodium chloropalladite in methanol, rapidly gave stable yellow chloro-bridged methoxy-π-allylic complexes, $[Pd_2Cl_2(C_xH_{2x-2}\cdot OMe)_2]$, namely, those from isoprene (IV), 4-methylpenta-1,3-diene (V), 2,3-dimethylbuta-1,3-diene (VI) or (VII), 2,4-dimethylpenta-1,3-diene (VIII), and 2,5-dimethylhexa-2,4-diene (IX); *trans*-piperylene gave a mixture of isomers. The complexes were yellow and many melted without


(I)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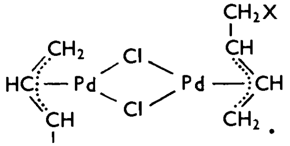
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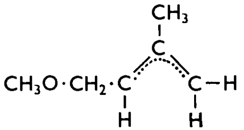
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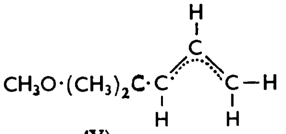
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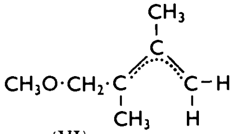
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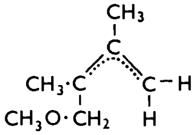
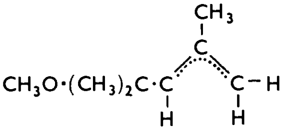
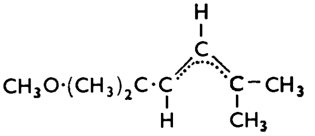
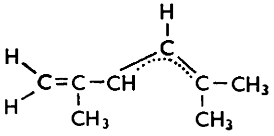
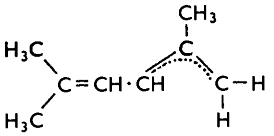
(VII)



(VIII)

decomposition. In ethanol the corresponding chloro-bridged ethoxy-π-allylic complexes $[Pd_2Cl_2(C_xH_{2x-2}\cdot OEt)_2]$ were formed. A suspension of sodium chloropalladite in propan-2-ol, when treated with isoprene, gave the isopropoxy-π-allylic complex, $[Pd_2Cl_2(C_5H_8\cdot OPr^i)_2]$, but similar treatment with 2,5-dimethylhexa-2,4-diene gave an αβ-unsaturated π-allylic complex $[Pd_2Cl_2(C_8H_{13})_2]$. The last compound gave a strong infrared band at 1637 cm.$^{-1}$ due to a stretching vibration of a polar C=C bond, and ultraviolet maxima and inflections at longer wavelengths than in the chloro-bridged alkoxy-π-allylic complexes. The n.m.r. spectrum of the π-allylic ligand in this complex excluded the isopropenyl structure (X), formed simply by loss of methanol from structure (IX),


(IX)


(X)


(XI)

but favoured the isobutenyl structure (XI) formed from (IX) by a 1,3-shift of the palladium atom, the methyl protons of the isobutenyl group having τ 8·39, and the vinylic proton, τ 4·42, coupled with the adjacent proton of the allylic system with $J = 11{\cdot}0$ c./sec. Similar results were obtained for the acetylacetonato- and cyclopentadienyl derivatives of this αβ-unsaturated π-allylic complex. In spite of repeated purification, these αβ-unsaturated π-allylic complexes showed in their n.m.r. spectra a few weak bands which were not assigned. These extra bands were probably due to the presence of small quantities of isomers, which could have been geometrical, positional, or rotational (see below) and may have been formed only when the compounds were dissolved.

Molecular-weight determinations (cryoscopic in benzene) indicated a binuclear structure for these chloro-compounds and reactions confirming the chloro-bridged structure include fission by bridge-splitting ligands such as pyridine, metathesis of the bridging chloro-ligands by other bridging ligands such as bromo, iodo, and thiocyanato, and reactions with thallous acetylacetonate and cyclopentadienylsodium. The evidence for the π-allylic nature of the organic ligands comes from n.m.r. spectra and confirmation from their similarity to known π-allylic palladium systems.

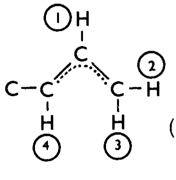
*Reactions involving the Bridging Chloro-groups.*—A characteristic of chloro-bridged complexes of palladium(II) is the bridge-splitting reaction with amines,[4,5] and on addition of pyridine or quinoline, solutions of our chloro-bridged π-allylic-palladium complexes became almost colourless and complexes of the type [PdCl(all)L] (L = pyridine or quinoline; all = allylic ligand) were isolated. These complexes readily lost amine when heated, giving back the chloro-bridged complex. *p*-Toluidine complexes dissociated even more readily and could not be obtained pure.

Bromo-, iodo-, and thiocyanato-bridged complexes were readily prepared by treating an acetone solution of the chloro-bridged complex with lithium bromide, sodium iodide, or potassium thiocyanate, respectively.

A new and probably general way of characterising these binuclear complexes, $[Pd_2Cl_2(all)_2]$, was by conversion into the mononuclear acetylacetonato-complexes, [Pd(all)(acac)], by treatment with a slight excess of thallous acetylacetonate in benzene; thallous chloride was precipitated and the new complex was readily isolated from the mother-liquor. These acetylacetonato-derivatives were crystalline and readily purified and some had definite melting points. The acetylacetonato-group has a very simple n.m.r. spectrum and did not usually interfere with the assignment of the various peaks in the spectrum of the π-allylic ligand. Treatment of dichlorobisbenzonitrile-palladium(II) with thallous acetylacetonate gave a good yield of bisacetylacetonato-palladium(II) and is a much improved route to this compound.

Since the preparation of allylcyclopentadienylpalladium(II)[6] many mixed π-allylic cyclopentadienylpalladium(II) complexes have been prepared and another good method of characterising halogeno-bridged π-allylic palladium complexes, $[Pd_2Cl_2(all)_2]$, is by conversion into their cyclopentadienyl derivatives by treatment with cyclopentadienyl-sodium. Several of our new complexes underwent this reaction, but most of the products did not crystallise. They could readily be distilled, however, and their n.m.r., ultraviolet, and infrared spectra were determined.

*Structure and Properties of the Allylic Ligands.*—The detailed structures of the various allylic ligands follow from their n.m.r. (proton) spectra, and chemical shift (τ values) and coupling constants (*J* values) are given in Tables 1—3. The structures and (in some cases) configurations of the more complex allylic ligands are shown in formulæ (III)—(XI) and the various types of protons are numbered as in (XII) and (XIII). The system $CH_2X{\cdot}CH=$ (X = Cl or $OCH_3$) present in butadienepalladous chloride or its methoxy-analogue gave a complex resonance pattern which was not analysed. The ethoxy-π-allylic palladium complexes had n.m.r. spectra practically identical with those of the corresponding methoxy-complexes, except that the resonance pattern characteristic of the ethoxy-group replaced the single peak for the methoxy-group. Similar remarks apply to the isopropoxy-complex.



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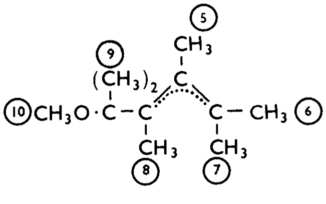

(XIII)

Three lines of evidence support our assignment of the τ and *J* values shown in Tables

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[4] Chatt and Venanzi, *J.*, 1957, 2445.
[5] Chatt, Vallarino, and Venanzi, *J.*, 1957, 3413.
[6] Shaw, *Proc. Chem. Soc.*, 1960, 247.

TABLE 1.

Nuclear magnetic resonance date for bridged complexes $[Pd_2Y_2(all)_2]$ in chloroform. In this and other Tables chemical shifts ($\tau$) are relative to $SiMe_4$ as internal standard, coupling constants ($J$) are in c./sec., the spectra being measured at 60 Mc./sec. and integrated.

| Radical | Y | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ | $\tau_5$ | $\tau_{10}$ | $\tau$ (others) | $J_{12}$ | $J_{13}$ | $J_{14}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Allyl .................. | Cl | 4·57 | 5·93 | 6·91 | | | | | 6·9 | 12·0 | |
| $CH_2{:}CMe{\cdot}CH_2$ ...... | Cl | | 6·15 | 7·12 | | 7·86 | | | | | |
| But-2-enyl ......... | Cl | 4·73 | 6·10 | 7·18 | | | | $\tau_7$ 8·65 | 6·5 | 12·1 | |
| (III; X = Cl) ...... | Cl | 4·55 | 5·98 | 6·97 | | | | | 6·9 | 12·0 | |
| (III; X = OMe) * | Cl | 4·50 | 6·00 | 7·03 | | | 6·58 | | 6·9 | 12·2 | |
| (III; X = OMe) ... | Br | 4·50 | 5·93 | 6·99 | | | 6·58 | | 6·8 | 11·9 | |
| (IV) .................. | Cl | | 6·16 | 7·12 | 6·37 | 7·83 | 6·59 | 6·37 ($CH_2$) | | | |
| (IV) .................. | Br | | 6·11 | 7·12 | 6·30 | 7·92 | 6·59 | 6·30 ,, | | | |
| (IV) * ............... | I | | 5·96 | 7·17 | † | 8·07 | 6·60 | † ,, | | | |
| (IV) * ............... | SCN | | 6·22 | 7·24 | 6·37 | 7·98 | 6·62 | 6·37 ,, | | | |
| (V) . .................. | Cl | 4·53 | 6·00 | 7·02 | 6·25 | | 6·70 | $\tau_9$ 8·60 | 6·8 | 11·6 | 11·4 |
| (V) . .................. | Br | 4·56 | 5·96 | 7·08 | 6·14 | | 6·70 | $\tau_9$ 8·57 | 6·9 | 12·3 | 11·4 |
| (V) .................... | I | 4·64 | 5·87 | 7·10 | 5·96 | | 6·71 | $\tau_9$ 8·50, 8·55 | 7·0 | 12·2 | 12·2 |
| (VI) or (VII) * ...... | Cl | | | | | 7·86 | 6·79 | $\tau_8$ 8·60 ‡ | | | |
| ,, * ...... | Br | | | | | 7·92 | 6·81 | $\tau_8$ 8·46 ‡ | | | |
| (VIII) .............. | Cl | | 6·28 | 7·21 | 6·55 | 7·76 | 6·67 | $\tau_9$ 8·53, 8·62 | | | |
| (IX) .................. | Cl | 4·93 | | | 6·18 | | 6·70 | $\tau_9$ 8·61<br>$\tau_6/\tau_7$ 8·61 or 8·77 | | | 11·9 |
| (IX) .................. | I | 4·89 | | | 5·93 | | 6·70 | { 8·13, 8·48, 8·54, 8·67 ** | | | 11·9 |
| (XI) .................. | Cl | | 6·39 | 7·29 | | 7·86 | | | | | |

* In deuterochloroform. † Complex resonance pattern. ‡ Tentative assignment. ** Not assigned but due to one methyl group of type 6, one of type 7, and two of type 9 (split by rotational isomerism).

TABLE 2.

Acetylacetonato-complexes [Pd(acac)(all)] in carbon tetrachloride.

| Radical | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ | $\tau_5$ | $\tau_9$ | $\tau_{10}$ | acac | | $J_{12}$ | $J_{13}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $\tau_{Me}$ | $\tau_H$ | | |
| Allyl .................. | 4·53 | 6·26 | 7·20 | | | | | 8·12 | 4·83 | 6·5 | 11·8 |
| $CH_2{:}CMe{\cdot}CH_2$ ......... | | 6·48 | 7·34 | | 7·79 | | | 8·13 | 4·83 | | |
| (IV) ..................... | | 6·48 | 7·33 | | 7·82 | | 6·64 | 8·14 | 4·84 | | |
| (VIII) ................. | | 6·53 | 7·36 | 6·93 | 7·69 | 8·53, 8·63 | 6·71 | 8·12 | 4·82 | | |
| (XI) ..................... | | 6·62 | 7·44 | | 7·69 | | | 8·18 | 4·90 | | |

TABLE 3.

Cyclopentadienyl complexes $[Pd(C_5H_5)(all)]$ in carbon tetrachloride.

| Radical | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ | $\tau_5$ | $\tau_9$ | $\tau_{10}$ | $C_5H_5$ $\tau_H$ | $J_{12}$ | $J_{13}$ | $J_{14}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (IV) ..................... | | § | § | | 8·03 | | 6·70 | 4·45 | | | |
| (V) ..................... | 5·17 | 6·55 | 7·88 | 6·9 | | 8·66, 8·75 | 6·85 | 4·38 | 6·4 | 10·5 | § |
| (VIII) ................. | | | | | 7·93 | 8·63 | 6·76 | 4·40 | | | |
| (IX) ..................... | 5·22 | | | 6·62 | | 8·65, 8·75 | 6·85 | 4·50 | | | 10·4 |
| (XI) ..................... | | 6·76 | 7·84 | | 7·96 | | | 4·51 | | | |

§ Resonance obscured.

1—3 to protons 3 and 4 in *trans*-position to proton 1, and to proton 2 in *cis*-position to proton 1. (*a*) The coupling constants $J_{13}$ and $J_{14}$ are within the range 10·4—12·3 c./sec., nearly twice the coupling constants $J_{12}$ (6·4—7·0 c./sec.). It is well established that in unsaturated organic systems the coupling constants between *trans*-protons are larger, often nearly twice the coupling constants between *cis*-protons. A similar argument based on the relative strength of *cis*- and *trans*-coupling constants was used in determining the configuration of the two geometrical isomers of structure $[Co(\pi\text{-butenyl})(CO)_3]$.[7] (*b*) In cyclic $\pi$-allylic palladium complexes, *e.g.*, the $\pi$-cyclohexenyl complex $[Pd_2Cl_2(C_6H_9)_2]$,

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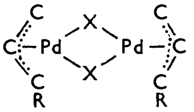
[7] Moore, Jonassen, Joyner, and Bertrand, *Chem. and Ind.*, 1960, 1304.

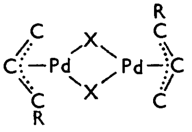
protons of types 3 and 4 are absent and the chemical shifts for protons of type 2 lie close to those assigned to protons of type 2 in our acyclic systems and are well removed from the chemical shifts of protons of type 3.[8] (*c*) The *X*-ray structure[9] of di-μ-chloro-diallyldipalladium(II) strongly suggests that protons of type 3 are nearer to the palladium than protons of type 2 and therefore, in agreement with our assignment, one might expect them to show the larger τ values. Dehm and Chien[10] assumed that protons of type 2 are nearer to the palladium atom than protons of type 3, and their assignment of τ and *J* values to these protons was therefore the opposite of ours; this assignment has also been made in a recent review.[11] However, other published n.m.r. assignments[7,8,12] for π-allylic complexes allot, as we do, the larger values of τ and *J* to protons of type 3, rather than to those of type 2, and there can be little doubt than this is correct.

Unsymmetrical dienes could give π-allylic ligands showing positional isomerisation; thus isoprene could give 4-methoxy-2-methylbut-2-enyl- and/or 4-methoxy-3-methylbut-2-enyl-palladium complexes. However, only one isomer was obtained from isoprene, and this in very good yield. The n.m.r. data in Tables 1—3 are in good agreement with the first possibility, *i.e.*, structure (IV) for this allylic ligand. This ligand has been tentatively assigned a *trans*-configuration because the allylic proton (starred) of the system $CH_3O\cdot CH_2\cdot {}^*CH\colon$ in this ligand has τ values similar to protons of type 4 in other ligands. For ligands derived from 4-methylpenta-1,3-diene and 2,5-dimethylhexa-2,4-diene, the n.m.r. data show *trans*-configurations (V) and (IX), respectively. By analogy, ligand (VIII) has been assigned the *trans*-configuration as shown. In Tables 1—3, for complexes derived from 2,3-dimethylbutadiene, only the τ values for methyl protons are given; the other peaks could not be assigned with certainty and the spectra did not distinguish between configurations (VI) and (VII) for the allylic radical. The spectra contained some extra peaks of low intensity, possibly due to an effect of restricted rotation (see below) and/or to the presence of small quantities of isomers (these isomers may have been formed only when the compounds were dissolved). The configuration (*i.e.*, whether *cis* or *trans*) of the αβ-unsaturated ligand (XI) was not determined from n.m.r. spectra: the allylic proton on the carbon atom next to the isobutenyl side-chain had τ values of 5·55, 5·89, and 6·26 for the chloro-bridged, the acetylacetonato-, and the cyclopentadienyl complex, respectively; τ values for the protons of the isobutenyl side-chain have been given above.

In addition to the geometrical and positional isomers, other types of isomerism are possible for bridged alkoxy-π-allylic palladium complexes. The unsymmetrical π-allylic ligands could be arranged in the *syn*- or the *anti*-form as shown (*e.g.*, R = $CH_2\cdot OMe$). No evidence for such isomerism has yet been obtained but by using a very strong bridging group, *e.g.*, methylthio, it might be possible to isolate such isomers. Orientation of the allylic ligands such that the centrally bonded carbon atoms would both lie on the same or on opposite sides of the plane formed by the two palladium and two bridging atoms, could also give rise to isomers; but this type of isomerism has also not been observed.



*syn*



*trans*

*Restricted Rotation in π-Allylic Palladium Complexes.*—The n.m.r. spectra of several complexes containing the group $MeO\cdot CMe_2$ showed the *C*-methyl groups numbered 9

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[8] Shaw and Sheppard, *Chem. and Ind.*, 1961, 517.

[9] Rowe, *Proc. Chem. Soc.*, 1962, 66.

[10] Dehm and Chien, *J. Amer. Chem. Soc.*, 1960, **82**, 4429.

[11] Miller, *Adv. Inorg. Chem. Radiochem.*, 1962, **4**, 133.

[12] Impastato and Ihrman, *J. Amer. Chem. Soc.*, 1961, **83**, 3726.

(cf. XIII) to have protons with two different $\tau$ values, caused by restricted rotation about the carbon–carbon single bond joining this group to the allylic system. The effect was greatest in cyclopentadienyl- and iodo-complexes, especially with benzene as solvent.

TABLE 4.

Ultraviolet absorption data for $\pi$-allylic palladium(II) complexes.

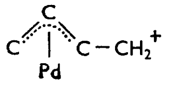
| Halogen | Radical | $\lambda_{max.}$ (m$\mu$) | log $\varepsilon$ | $\lambda_{max.}$ | log $\varepsilon$ | $\lambda_{max.}$ | log $\varepsilon$ |
|---|---|---|---|---|---|---|---|
| *Halogen-bridged complexes* [$Pd_2(hal)_2(all)_2$] *in methanol* | | | | | | | |
| Cl | Allyl | 207 * | 4·03 | 227 * | 3·94 | 320 | 3·03 |
| Cl | $CH_2$:CMe·$CH_2$ | 204 | 4·14 | 224 * | 3·83 | 339 | 2·90 |
| Cl | Butenyl | 206 | 4·29 | 228 * | 3·84 | 331 | 3·03 |
| Cl | (III; X = OMe) | 208 | 4·19 | 229 * | 3·86 | 330 | 2·98 |
| Cl | (IV) | 207 | 4·44 | 229 * | 4·16 | 331 | 2·97 |
| Br | (IV) | 208 | 4·25 | 237 | 3·99 | 334 | 3·07 |
| Br | (V) | 212 | 4·20 | 243 | 3·99 | 332 | 3·17 |
| Cl | (VI) or (VII) | 210 | 4·40 | 240 * | 3·96 | 333 | 3·00 |
| Cl | (IX) | 212 | 4·46 | 236 | 4·04 | 320 | 3·16 |
| *Acetylacetonato-complexes* [Pd(acac)(all)] *in hexane* | | | | | | | |
| | (IV) | | | 220 | 4·48 | 303 | 4·03 |
| | (VIII) | | | 220 | 4·28 | 320 | 3·93 |
| | (XI) | 210 | 4·54 | 266 | 4·25 | 286,* 357 * | 4·24, 3·38 |
| *Cyclopentadienyl complexes* [Pd($C_5H_5$)(all)] *in hexane* | | | | | | | |
| | (IV) | 217 | 4·04 | 259 | 4·38 | 316 | 3·94 |
| | (V) | 223 | 3·95 | 264 | 4·48 | 323 | 3·36 |
| | (VIII) | 219 * | 4·01 | 263 | 4·32 | 319 | 3·88 |
| | (IX) | 225 | 4·13 | 272 | 4·33 | 330 | 3·90 |
| | (XI) | 240 | 4·22 | 291 | 4·14 | 352 | 4·03 |

* Shoulder.

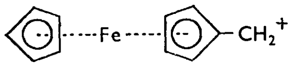
For example, in the cyclopentadienyl complex [Pd($C_5H_5$)(all)] {all = (IX)} the $\tau$ values for the *C*-methyl groups were 8·45, 8·59, 8·74, and 8·88 in benzene. We hope to make a more detailed study of these rotational effects at different temperatures.

*Ultraviolet Absorption Spectra.*—The ultraviolet absorption maxima (see Table 4) were rather broad for the halogen-bridged and acetylacetonato-complexes but were much sharper for the cyclopentadienyl complexes. In the acetylacetonato- and cyclopentadienyl complexes containing the $\alpha\beta$-unsaturated $\pi$-allylic ligand (XI) the various maxima were shifted to longer wavelengths by up to 40 m$\mu$.

*Interconversion of Methoxy- and Ethoxy-groups.*—Treatment with ethanol $10^{-2}$—$10^{-3}$M in hydrochloric acid readily replaced a methoxy-group in one of the $\pi$-allylic ligands by an ethoxy-group. Thus, the methoxy-complex [$Pd_2Cl_2(all)_2$] {all = (V)} was converted by hot ethanolic $10^{-2}$M-hydrochloric acid in 30 sec. into the ethoxy-complex. The reversed transformation was similarly very readily carried out. Similar conversions were slower for the complex [$Pd_2Cl_2(all)_2$] {all = (IV)} which contains only primary ether linkages; boiling with ethanolic $10^{-3}$M-hydrochloric acid for 2 hr. gave the optimum yield. These extremely easy alkoxy-exchanges suggest that allyl carbonium ions of the type (XIV) may have considerable stability. In this respect $\pi$-allylic complexes are analogous to cyclopentadienyl complexes: the extremely rapid solvolysis of the acetoxymethyl derivative of ferrocene, which occurs at about the same rate as that of triphenylmethyl acetate, was thought to be due to the considerable stability of the intermediate carbonium ion (XV);[13] the diferrocenylcarbonium ion can be isolated as its perchlorate.[14]



(XIV)



(XV)

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[13] Richards and Hill, *J. Amer. Chem. Soc.*, 1959, **81**, 3484; 1961, **83**, 3840, 4216.

[14] Jutz, *Tetrahedron Letters*, 1959, No. 21, p. 1.

## EXPERIMENTAL

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

*Action of Methanol on Butadienepalladous Chloride.*—Di-μ-chlorodi-(4-chlorobut-2-enyl)-dipalladium(II) (butadienepalladous chloride, 0·232 g.) was treated with warm methanol (15 c.c.), giving an acidic brown solution. This was cooled to *ca.* 15°, anhydrous sodium carbonate (0·1 g.) added, and after 2 min. the solid was filtered off and the filtrate evaporated to dryness. Recrystallisation of the residue from methanol gave *di-μ-chlorodi-(4-methoxybut-2-en-1-yl)dipalladium*(II) as yellow prisms (0·119 g.), m. p. 97·5—99·5° (Found: C, 26·5; H, 3·9%; *M*, cryoscopically in 1·2% benzene solution, 452. $C_{10}H_{18}Cl_2O_2Pd$ requires C, 26·5; H, 4·0%; *M*, 454).

*Di-μ-chlorodi-(4-methoxybut-2-enyl)dipalladium*(II) *from Sodium Chloropalladite Tetrahydrate.*—A solution of sodium chloropalladite tetrahydrate (1·00 g.) in methanol (8 c.c.) was saturated with butadiene; anhydrous sodium carbonate (0·5 g.) was then added. After the mixture had been shaken for *ca.* 1 min. the solid was filtered off and the residue obtained by evaporating the filtrate to dryness was recrystallised from methanol to give the product (0·472 g.), identical with that prepared as above.

*Di-μ-chlorobis-(4-methoxy-2,3-dimethylbut-2-enyl)dipalladium*(II).—2,3-Dimethylbuta-1,3-diene (2·0 c.c.) was added to a suspension of sodium chloropalladite tetrahydrate (1·00 g.) in methanol (10 c.c.). Anhydrous sodium carbonate (0·3 g.) was added and after 2 min. the whole was filtered and evaporated. The residue was washed with water and recrystallised from methanol, to give the required *product* as yellow prisms (0·52 g.), m. p. 110—113° (Found: C, 33·1; H, 5·25. $C_{14}H_{26}Cl_2O_2Pd_2$ requires C, 33·0; H, 5·15%).

*Other Chloro-bridged Methoxy-π-allylic Palladium*(II) *Complexes.—General method.* A suspension of sodium chloropalladite tetrahydrate (0·5—1·0 g.) in methanol (4—6 c.c.) was treated with the diene (1—2 c.c.). When all the sodium chloropalladite tetrahydrate had dissolved the mixture was cooled to −20° for 3 hr., water (5 c.c.) and light petroleum (5 c.c., b. p. 30—40°) were added, and the mixture was kept at 0° for 5 min. Recrystallisation of the resultant precipitate from methanol gave the product. The following were thus prepared:

*Di-μ-chlorodi-(4-methoxy-2-methylbut-2-enyl)dipalladium*(II) (81%), pale yellow needles, m. p. 145—146° (decomp.) (Found: C, 30·15; H, 4·7%; *M*, cryoscopically in 1·35% benzene solution, 460. $C_{12}H_{22}Cl_2O_2Pd$ requires C, 29·9; H, 4·6%; *M*, 482).

*Di-μ-chlorodi-(4-methoxy-4-methylpent-2-enyl)dipalladium*(II) (80%), yellow needles, m. p. 152—153·5° (Found: C, 32·75; H, 5·0. $C_{14}H_{26}Cl_2O_2Pd_2$ requires C, 32·95; H, 5·15%).

*Di-μ-chlorobis-(4-methoxy-2,4-dimethylpent-2-enyl)dipalladium*(II) (68%), yellow, m. p. 155—160° (decomp.) (Found: C, 35·55; H, 5·6. $C_{16}H_{30}Cl_2O_2Pd_2$ requires C, 35·7; H, 5·6%).

*Di-μ-chlorobis-(4-methoxy-1,1,4-trimethylpent-2-enyl)dipalladium*(II) (74%), yellow prisms, m. p. 170—175° (decomp.) (Found: C, 37·9; H, 6·0. $C_{18}H_{34}Cl_2O_2Pd_2$ requires C, 38·2; H, 6·0%).

*Di-μ-chlorodi-(4-ethoxy-2-methylbut-2-enyl)dipalladium*(II).—A suspension of sodium chloropalladite tetrahydrate (0·50 g.) in ethanol (5 c.c.) was treated with 2-methylbuta-1,3-diene (0·5 c.c.), a precipitate being formed rapidly. After 30 min. the mixture was cooled to −30°, water (5 c.c.) added, and the precipitate filtered off and recrystallised from ethanol, to give the *product* as yellow needles (0·254 g.), m. p. 122—125° (Found: C, 33·2; H, 5·3. $C_{14}H_{26}Cl_2O_2Pd_2$ requires C, 33·0; H, 5·15%).

Similarly prepared were: *di-μ-chlorodi-(4-ethoxy-4-methylpent-2-enyl)dipalladium*(II), yellow prisms (from ethanol) (37%), m. p. 137—139° (Found: C, 35·85; H, 5·7. $C_{16}H_{30}Cl_2O_2Pd_2$ requires C, 35·7; H, 5·6%); *di-μ-chlorobis-(4-ethoxy-1,1,4-trimethylpent-2-enyl)dipalladium*(II) as yellow prisms (from ethanol) (57%), m. p. 167—170° (decomp.) (Found: C, 40·15; H, 6·35. $C_{20}H_{38}Cl_2O_2Pd_2$ requires C, 40·4; H, 6·45%).

*Di-μ-chlorodi-(4-isopropoxy-2-methylbut-2-en-1-yl)dipalladium*(II).—A suspension of sodium chloropalladite tetrahydrate (1·0 g.) in propan-2-ol (4 c.c.) was treated with 2-methylbuta-1,3-diene (1·2 c.c.) and put aside for 24 hr. Water (5 c.c.) and light petroleum (5 c.c., b. p. 30—40°) were then added and the mixture was cooled to 0°. Recrystallisation of the precipitate from benzene–light petroleum (b. p. 80—100°) gave the pale yellow *product* (0·155 g.), m. p. 110—122° (Found: C, 35·4; H, 5·3. $C_{16}H_{30}Cl_2O_2Pd_2$ requires C, 35·7; H, 5·6%).

*Di-μ-chlorobis-(2,5-dimethylhexa-2,4-dienyl)dipalladium*(II).—A suspension of sodium chloropalladite tetrahydrate (1·0 g.) in propan-2-ol (8 c.c.) was treated with 2,5-dimethylhexa-2,4-diene (1·5 c.c.) and set aside for 12 hr. Recrystallisation of the precipitate from acetone gave the deep yellow *product* (0·290 g.), decomp. >160°, $\nu_{max.}$ (in KCl) 1637s cm.$^{-1}$ (C=C) (Found: C, 38·9, 39·15; H, 5·2, 5·3. $C_{16}H_{26}Cl_2Pd_2$ requires C, 38·3; H, 5·2%).

*Metathetical Reactions.*—The chloro-complex was treated with a 10% excess of the appropriate alkali-metal salt (lithium bromide, sodium iodide, potassium thiocyanate) in acetone solution at room temperature. After 10 min. the solvent was removed under reduced pressure, and the residue washed with water and recrystallised from methanol. Prepared in this manner were: *di-μ-bromodi-(4-methoxybut-2-enyl)dipalladium*(II), as yellow prisms (83%), m. p. 93—94° (Found: C, 22·35; H, 3·35. $C_{10}H_{18}Br_2O_2Pd_2$ requires C, 22·1; H, 3·35%); *di-μ-bromodi-(4-methoxy-2-methylbut-2-enyl)dipalladium*(II), pale yellow needles (84%), m. p. 136° (Found: C, 25·35; H, 3·7. $C_{12}H_{22}Br_2O_2Pd_2$ requires C, 25·25; H, 3·9%); *di-μ-iododi-(4-methoxy-2-methylbut-2-enyl)dipalladium*(II), yellow needles (56%), m. p. 110—111° (slight decomp.) (Found: C, 21·5; H, 3·2. $C_{12}H_{22}I_2O_2Pd_2$ requires C, 21·7; H, 3·3%); *di-μ-thiocyanatodi-(4-methoxy-2-methylbut-2-enyl)dipalladium*(II), cream needles (63%), m. p. 144—145° (Found: C, 32·3; H, 4·05; N, 5·45. $C_{14}H_{22}N_2O_2Pd_2S_2$ requires C, 31·9; H, 4·2; N, 5·3%); *di-μ-bromodi-(4-methoxy-4-methylpent-2-enyl)dipalladium*(II), yellow prisms (79%), m. p. 142—144°, which then solidified and remelted at 155—156° (Found: C, 28·3; H, 4·45. $C_{14}H_{26}Br_2O_2Pd_2$ requires C, 28·1; H, 4·4%); *di-μ-iododi-(4-methoxy-4-methylpent-2-enyl)dipalladium*(II), deep yellow prisms (75%), m. p. 135—142° (decomp.) (Found: C, 24·75; H, 3·85. $C_{14}H_{26}I_2O_2Pd_2$ requires C, 24·25; H, 3·8%); *di-μ-bromobis-(4-methoxy-2,3-dimethylbut-2-enyl)dipalladium*(II), yellow prisms (50%), m. p. 110—114° (Found: C, 28·05; H, 4·4. $C_{14}H_{22}Br_2O_2Pd_2$ requires C, 28·05; H, 4·4%); *di-μ-bromobis-(4-methoxy-1,1,4-trimethylpent-2-enyl)dipalladium*(II), yellow prisms (38%), m. p. 170—171° (decomp.) (Found: C, 33·3; H, 5·25. $C_{18}H_{34}Br_2O_2Pd_2$ requires C, 33·0; H, 5·25%); *di-μ-iodobis-(4-methoxy-1,1,4-trimethylpent-2-enyl)dipalladium*(II), yellow plates (51%), m. p. 157—160° (decomp.) (Found: C, 28·7; H, 4·45. $C_{18}H_{34}I_2O_2Pd_2$ requires C, 28·85; H, 4·6%).

*Chloro-(4-methoxybut-2-enyl)pyridinepalladium*(II).—Di-μ-chlorodi-(4-methoxybut-2-enyl)dipalladium(II) (0·195 g.) was dissolved in a minimum of warm dichloromethane (*ca.* 2 c.c.), and pyridine (0·2 c.c.) followed by diethyl ether (4 c.c.) were then added. The yellow precipitate formed on cooling to 20° was filtered off and washed with diethyl ether, to give the *product* as pale yellow needles (0·141 g.) (Found: C, 39·5; H, 4·7; N, 4·9. $C_{10}H_{14}ClNOPd$ requires C, 39·25; H, 4·6; N, 4·6%).

*Chloro-(4-methoxy-4-methylpent-2-enyl)quinolinepalladium*(II).—This *complex* was similarly prepared from di-μ-chlorodi-(4-methoxy-4-methylpent-2-enyl)dipalladium(II) (0·100 g.) and quinoline and formed pale yellow prisms (0·065 g.) (Found: C, 49·75; H, 5·25; N, 3·8. $C_{16}H_{20}ClNOPd$ requires C, 50·0; H, 5·25; N, 3·65%).

*Chloro-(4-methoxy-1,1,4-trimethylpent-2-enyl)pyridinepalladium*(II).—Di-μ-chlorodi-(4-methoxy-1,1,4-trimethylpent-2-enyl)dipalladium(II) (0·211 g.) was suspended in benzene (2 c.c.) and light petroleum (b. p. 60—80°; 2 c.c.). Pyridine (0·1 c.c.) was added and the mixture warmed gently for 2 min., then filtered. The cream precipitate formed on cooling was washed with cold light petroleum (b. p. 30—40°), to give the cream-coloured *product* (0·136 g.) (Found: C, 46·55; H, 6·05; N, 3·7. $C_{14}H_{22}ClNOPd$ requires C, 46·45; H, 6·1; N, 3·85%). This was non-conducting in acetone solution.

*Preparation of Acetylacetonato-(π-allylic)palladium*(II) *Complexes.*—*General method.* The chloro-bridged π-allylic palladium complex (0·15—0·25 g.), dissolved in warm benzene (5 c.c.), was treated with a solution of thallous acetylacetonate (5% excess) in warm benzene (20 c.c.). Thallous chloride was filtered off, the filtrate evaporated to dryness, and the residue recrystallised from light petroleum (b. p. 40—60°). The following were thus prepared.

*Acetylacetonato(allyl)palladium*(II), pale yellow needles (52%), m. p. 72—75° (decomp.) (Found: C, 39·0; H, 5·05. $C_8H_{12}PdO_2$ requires C, 39·0; H, 4·9%).

*Acetylacetonato-(2-methylallyl)palladium*(II), cream needles (62%), m. p. 122—125° (Found: C, 41·25; H, 5·4. $C_9H_{14}PdO_2$ requires C, 41·5; H, 5·4%).

*Acetylacetonato-(4-methoxy-2-methylbut-2-enyl)palladium*(II), cream needles (54%), m. p. 111—114° (decomp.) (Found: C, 43·65; H, 5·9%; *M*, cryoscopically in 1·8% benzene solution, 286. $C_{11}H_{18}PdO_3$ requires C, 43·4; H, 6·0%; *M*, 305).

*Acetylacetonato-(4-methoxypent-2-enyl)palladium*(II), pale yellow needles (42%), m. p. 65—75° (decomp.) (Found: C, 43·75; H, 5·9. $C_{11}H_{18}PdO_3$ requires C, 43·4; H, 6·0%).

*Acetylacetonato-(4-methoxy-2,3-dimethylbut-2-enyl)palladium*(II), pale yellow prisms (20%), m. p. 97—103° (Found: C, 45·45; H, 6·25. $C_{12}H_{20}PdO_3$ requires C, 45·25; H, 6·3%).

*Acetylacetonato-*(4-*methoxy*-2,4-*dimethylpent*-2-*enyl*)*palladium*(II), pale yellow plates (55%), m. p. 120—123° (Found: C, 46·9; H, 6·65. $C_{13}H_{22}PdO_3$ requires C, 46·95; H, 6·65%).

*Acetylacetonato*-(2,5-*dimethylhexa*-2,4-*dienyl*)*palladium*(II), yellow needles (46%), m. p. 115—118° (decomp.) (Found: C, 49·25; H, 6·25. $C_{13}H_{20}PdO_2$ requires C, 49·6; H, 6·4%), $\nu_{max.}$ (in $CCl_4$) 1650m cm.$^{-1}$ (C=C).

*Di*(*acetylacetonato*)*palladium*(II).—Dichlorobisbenzonitrilepalladium(II) (0·387 g.) in warm benzene (15 c.c.) was treated with a solution of thallous acetylacetonate (5% excess) in warm benzene (25 c.c.). Thallous chloride was filtered off, the filtrate evaporated to dryness, and the residue recrystallised from benzene, to give the product as orange-yellow needles (0·150 g.), volatalising 220—230° with complete decomp. (Found: C, 39·5; H, 4·4. Calc. for $C_{10}H_{14}PdO_4$: C, 39·45; H, 4·65%). The n.m.r. spectrum in deuterochloroform showed two peaks $\tau$ 7·93 (methyl protons) and 4·58 (single proton).

*Preparation of π-Allylic Cyclopentadienylpalladium*(II) *Complexes.—General method.* The corresponding chloro-bridged π-allylic palladium complex (0·25—0·45 g.), suspended in tetrahydrofuran (7—15 c.c.) under nitrogen was treated with a tetrahydrofuran solution of cyclopentadienylsodium (5% excess). The resultant red solution was evaporated to dryness after 5 min. and the product isolated with light petroleum (15 c.c.; b. p. 30—40°). Solid products were recrystallised from light petroleum (b. p. 40—60°) or sublimed in a vacuum. Liquid products, which were not analysed, were purified by distillation on to a cold finger and characterised by their ultraviolet and nuclear magnetic resonance spectra (see above). Prepared in this manner were:

Cyclopentadienyl-(4-methoxy-2-methylbut-2-enyl)palladium(II), deep red viscous liquid, b. p. 35°/10$^{-2}$ mm.

Cyclopentadienyl-(4-methoxy-4-methylpent-2-enyl)palladium(II), deep red viscous liquid, b. p. 25°/10$^{-2}$ mm.

Cyclopentadienyl-(4-methoxy-2,4-dimethylpent-2-enyl)palladium(II), deep red viscous liquid, b. p. 25°/10$^{-2}$ mm.

*Cyclopentadienyl*-(4-*methoxy*-1,1,4-*trimethylpent*-2-*enyl*)*palladium*(II), deep red prisms, m. p. 57—58° (from light petroleum, b. p. 30—40°) (70%) (Found: C, 53·85; H, 6·8. $C_{14}H_{22}OPd$ requires C, 53·8; H, 7·1%).

*Cyclopentadienyl*-(2,5-*dimethylhexa*-2,4-*dienyl*)*palladium*(II) sublimed at 35°/10$^{-2}$ mm. as deep red prisms, m. p. 48—54° (30%) (Found: C, 55·75; H, 6·5. $C_{13}H_{18}Pd$ requires C, 55·65; H, 6·45%).

*Interconversion of Di-μ-chlorodi*-(4-*methoxy*-2-*methylbut*-2-*enyl*)*dipalladium*(II) *and di-μ-chlorodi*-(4-*ethoxy*-2-*methylbut*-2-*enyl*)*dipalladium*(II).—(*A*) *Methoxy to ethoxy.* Di-μ-chloro di-(4-methoxy-2-methylbut-2-enyl)dipalladium(II) (0·060 g.) was suspended in ethanolic 10$^{-3}$M-hydrochloric acid (5 c.c.). The mixture was heated under reflux for 2 hr., filtered from traces of palladium, and cooled, to give di-μ-chlorodi-(4-ethoxy-2-methylbut-2-enyl)dipalladium(II) (0·035 g.), identical with that described above.

(*B*) *Ethoxy to methoxy.* Similarly, di-μ-chlorodi-(4-ethoxy-2-methylbut-2-enyl)dipalladium was converted into di-μ-chlorodi-(4-methoxy-2-methylbut-2-enyl)dipalladium in 60% yield by using methanolic 10$^{-3}$M-hydrochloric acid.

*Interconversion of Di-μ-chlorodi*-(4-*methoxy*-4-*methylpent*-2-*enyl*)*dipalladium and Di-μ-chlorodi*-(4-*ethoxy*-4-*methylpent*-2-*enyl*)*dipalladium.*—(*A*) *Methoxy to ethoxy.* Di-μ-chlorodi-(4-methoxy-4-methylpent-2-enyl)dipalladium(II) (0·053 g.) was suspended in ethanolic 10$^{-2}$M-hydrochloric acid (2 c.c.). The mixture was boiled for 30 sec., then cooled to give di-μ-chlorodi-(4-ethoxy-4-methylpent-2-enyl)dipalladium (0·040 g.), identical with that described above.

(*B*) *Ethoxy to methoxy.* Similarly the ethoxy-compound was converted into the methoxy-analogue in 80% yield by using methanolic 10$^{-2}$M-hydrochloric acid.

*Interconversion of Di-μ-chlorobis*-(4-*methoxy*-1,1,3-*trimethylpent*-2-*enyl*)*dipalladium and the Ethoxy-analogue.*—(*A*) *Methoxy to ethoxy.* The methoxy-complex (0·121 g.) was suspended in ethanolic 10$^{-2}$M-hydrochloric acid (6 c.c.) and boiled for 1 min., then cooled to give the ethoxy-complex (0·120 g.).

(*B*) *Ethoxy to methoxy.* Similarly the ethoxy-compound was converted into the methoxy-compound in 85% yield by using ethanolic 10$^{-2}$M-hydrochloric acid.

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