

Reactions of Co-ordinated Ligands. Part V.¹ Reactions of Triphenylmethyl Tetrafluoroborate and Fluoroboric Acid with a Variety of Enyl Metal Complexes

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The electrophilic reagents triphenylmethyl tetrafluoroborate and fluoroboric acid react with the enyl complexes $(C_8H_{12}acac)M(acac)$ ($M = Pd$ and Pt), $(C_8H_{12}ba)Pt(ba)$ and $(C_8H_{12}dbm)M(dbm)$ ($M = Pd$ and Pt) to give the cations $[C_8H_{12}M(acac)]^+$, $[C_8H_{12}Pt(ba)]^+$, and $[C_8H_{12}M(dbm)]^+$ ($acac$, ba , and dbm are the conjugate bases of acetylacetone, benzoylacetone, and dibenzoylmethane). Other cations $[(diene)M(diketone)]^+$ ($diene = C_7H_8$ or $C_{10}H_{12}$, $diketone = acac$, ba , and dbm) are produced similarly. Electrophilic attack by triphenylmethyl tetrafluoroborate is selective and in the reaction with the isomers $(C_8H_{12}acac)Pd(dbm)$ and $(C_8H_{12}dbm)Pd(acac)$ the same cation $[C_8H_{12}Pd(dbm)]^+$ is obtained. The halogen-bridged complexes $(C_8H_{12}R)_2M_2Cl_2$ ($R = CH(COMe)_2$ or OMe) react with thallous cyclopentadienide ($TlCp$) to give the orange oils $(C_8H_{12}R)M(\pi-C_5H_5)$ and with various phosphine ligands (L) to give $(C_8H_{12}R)M(L)Cl$. These complexes also react with triphenylmethyl tetrafluoroborate to give the cations $[C_8H_{12}M(\pi-C_5H_5)]^+$ and $[C_8H_{12}M(L)Cl]^+$.

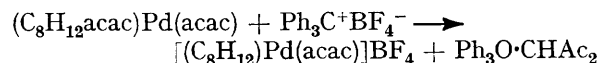
COMPLEXES of the type $[(diene)MX_2]$ ($diene =$ cyclo-octa-1,5-diene (C_8H_{12}), norbornadiene (C_7H_8), and dicyclopentadiene ($C_{10}H_{12}$); $M = Pd$ and Pt ; $X = Cl$, Br , and I) readily undergo nucleophilic attack, at the co-ordinated olefin, by the conjugate bases of alcohols,² keto-esters,³ malonic esters,³ β -diketones,⁴ carboxylic acids,⁵ and amines,⁶ to give complexes containing enyl-type ligands. Many of these enyl compounds have been shown to regenerate the complexes $(diene)MX_2$ on treatment with hydrohalic acids. We report now the reactions of several enyl-complexes with the electrophiles triphenylmethyl tetrafluoroborate and fluoroboric acid.

The Complexes (Enyl-diketone)palladium(diketone).—

¹ Part IV, B. F. G. Johnson, T. Keating, J. Lewis, M. S. Subramanian, and D. A. White, *J. Chem. Soc. (A)*, 1969, 1793.

² K. A. Hoffman and J. von Narbutt, *Ber.*, 1908, **41**, 1625; J. R. Doyle and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1956, **78**, 3965; J. Chatt, L. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2496, 3413; J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, 1966, **88**, 5135; J. K. Stille and J. R. Doyle, *J. Amer. Chem. Soc.*, 1965, **87**, 3282; R. G. Schultz, *J. Organometallic Chem.*, 1966, **6**, 435.

The complex $(C_8H_{12}acac)Pd(acac)$ reacts with triphenylmethyl tetrafluoroborate, to give the cation $[(C_8H_{12})Pd(acac)]^+$ and 3-triphenylmethylpentane-2,4-dione. This



cation has also been derived from the compounds $(C_8H_{12}\cdot OR)Pd(acac)$ ($R = H$ and Me) (see Scheme 1). Other similar compounds yield cations of the type $[(diene)M(diketone)]^+$ [$diene = C_8H_{12}$, C_7H_8 , and $C_{10}H_{12}$; $M = Pd$ and Pt ; $diketone =$ conjugate bases of acetylacetone($acac$), benzoylacetone(ba), or dibenzoylmethane(dbm)] on reaction with triphenylmethyl tetrafluoroborate (see Table 1). In contrast with the compounds containing the diketonates ba and dbm the

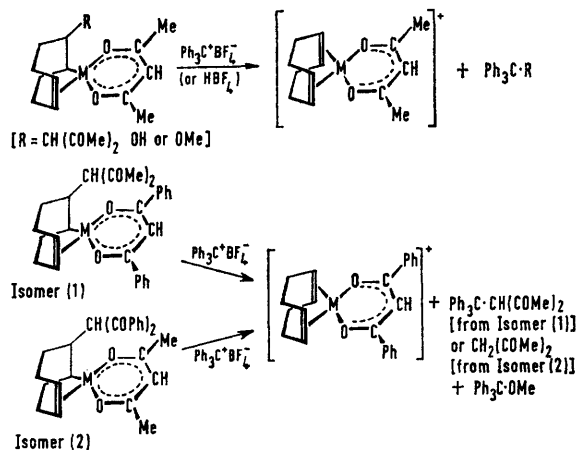
³ J. Tsuji and M. Takahashi, *J. Amer. Chem. Soc.*, 1965, **87**, 3275.

⁴ B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *J. Chem. Soc. (A)*, 1968, 1993.

⁵ G. B. Anderson and B. J. Burreson, *Chem. and Ind.*, 1967, 620.

⁶ G. Riario, A. Dehenzi, and R. Palumbo, *Chem. Comm.*, 1967, 1150.

organic product is a mixture of triphenylmethanol and the parent β -diketone (Hba or Hdbm). The same cations are also produced on treatment of the enyl compounds with fluoroboric acid and in this case the organic product is the β -diketone only. For the compounds containing the diketones ba and dbm, the reactive species must therefore be fluoroboric acid



SCHEME 1

(produced by reaction of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ with water in the solvents used) and the triphenylmethyl cation does not appear to attack these two β -diketonates (probably because of the bulky phenyl substituents). For the acetylacetone compounds attack occurs directly on the C-bonded acac, as shown by the isolation of 3-triphenylmethylpentane-2,4-dione. This is a primary product as we have been unable to obtain this compound either by the reaction of triphenylmethanol with acetylacetone alone or in the presence of fluoroboric acid or organic bases.

Selectivity of electrophilic attack by triphenylmethyl tetrafluoroborate on β -diketonates appears to be shown by its reactions with the isomers $(\text{C}_8\text{H}_{12}\text{acac})\text{Pd}(\text{dbm})$ and $(\text{C}_8\text{H}_{12}\text{dbm})\text{Pd}(\text{acac})$ which both yield the cation $[\text{C}_8\text{H}_{12}\text{Pd}(\text{dbm})]^+$ (see Scheme 1). The former isomer gave 3-triphenylmethylpentane-2,4-dione as the organic product but with the latter isomer the organic product was a mixture of triphenylmethanol and acetylacetone indicating that fluoroboric acid is the reactive species. This indicates that the C-bonded acac is more reactive towards the triphenylmethyl cation than the O-bonded group. The two isomers also undergo selective electrophilic attack by hydrochloric acid to yield $(\text{C}_8\text{H}_{12}\text{dbm})_2\text{Pd}_2\text{Cl}_2$. This would suggest that in the reaction with $(\text{C}_8\text{H}_{12}\text{acac})\text{Pd}(\text{acac})$ to give $(\text{C}_8\text{H}_{12}\text{acac})_2\text{Pd}_2\text{Cl}_2$ it is not necessarily the O-bonded acac which undergoes attack.

The Complexes $(\text{Enyl-diketone})_2\text{M}_2\text{Cl}_2$.—The halogen-bridged dimers $(\text{C}_8\text{H}_{12}\text{acac})_2\text{M}_2\text{Cl}_2$ ($\text{M} = \text{Pd}$ and Pt) do not react with triphenylmethyl tetrafluoroborate. The palladium compound does, however, react with fluoro-

boric acid to give $\text{C}_8\text{H}_{12}\text{PdCl}_2$, which is also obtained from the reaction of $(\text{C}_8\text{H}_{12}\cdot\text{OMe})_2\text{Pd}_2\text{Cl}_2$ with that acid. It is presumably formed by electrophilic attack at the

TABLE 1

Some physical data for new compounds

No.	Compound	Colour	$\nu(\text{CO})^a$ (β -diketonate)	Λ_M^b
Complexes: $[(\text{diene})\text{M}(\text{diketone})]\text{BF}_4$				
(1)	$\text{C}_8\text{H}_{12}\text{Pd}(\text{acac})^+$	Deep yellow	1522 1553	161
(2)	$\text{C}_8\text{H}_{12}\text{Pd}(\text{dbm})^+$	Orange	1520	
(3)	$\text{C}_8\text{H}_{12}\text{Pt}(\text{acac})^+$	Cream	1533 1558	168
(4)	$\text{C}_8\text{H}_{12}\text{Pt}(\text{ba})^+$	Pale yellow	1530 1540sh	154
(5)	$\text{C}_8\text{H}_{12}\text{Pt}(\text{dbm})^+$	Yellow	1535	
(6)	$\text{C}_7\text{H}_8\text{Pt}(\text{ba})^+$	Yellow	1530 1537sh	152
(7)	$\text{C}_{10}\text{H}_{12}\text{Pt}(\text{acac})^+$	Cream	1530 1550	148
(8)	$\text{C}_{10}\text{H}_{12}\text{Pt}(\text{ba})^+$	Yellow	1520 1547	154
Complexes: Isomer (1) and (2) (see scheme 1)				
(9)	$\text{C}_8\text{H}_{12}(\text{acac})\text{Pd}(\text{dbm})$	Yellow	1690 1510 1542	
(10)	$\text{C}_8\text{H}_{12}(\text{dbm})\text{Pd}(\text{acac})$	White	1647 1518 1572	
Complexes: $[\text{C}_8\text{H}_{12}\text{M}(\pi\text{-C}_5\text{H}_5)]\text{BF}_4$				
(11)	$\text{C}_8\text{H}_{12}\text{Pd}(\pi\text{-C}_5\text{H}_5)^+$	Violet		148
(12)	$\text{C}_8\text{H}_{12}\text{Pt}(\pi\text{-C}_5\text{H}_5)^+$	Cream		155
Complexes: $\text{C}_8\text{H}_{12}\text{PtCl}(\text{L})$				
(13)	$\text{L} = \text{Bu}_3\text{P}$	White	1690	
(14)	PhEt_2P	White	1688	
(15)	Ph_2EtP	White	1690	
(16)	py	White	1686	
Complexes $[\text{C}_8\text{H}_{12}\text{Pt}(\text{L})\text{X}]\text{BF}_4$				
$\text{X} = \text{Cl}$				
(17)	$\text{L} = \text{Et}_3\text{P}$	White		168
(18)	Bu_3P	White		160
(19)	PhEt_2P	White		162
(20)	Ph_2EtP	White		154
(21)	Ph_3P	White		147
(22)	Ph_3P	White		157
$\text{X} = \text{Br}$				
(23)	$\text{L} = \text{Ph}_3\text{P}$	White		
(24)	Ph_3As	White		

^a In cm^{-1} ; measured in Nujol. ^b Conductivity ($\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$) of ca. 10^{-3}M -acetone solutions.

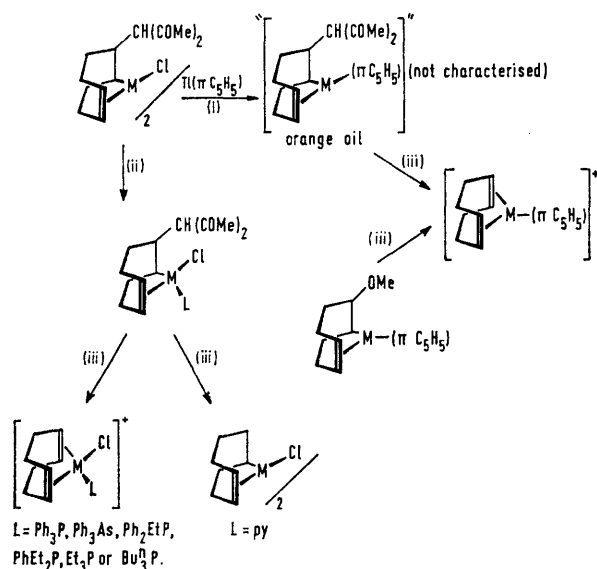
substituent (acac or OMe) followed by disproportionation.

The Complexes $(\text{C}_8\text{H}_{12}\text{acac})\text{M}(\pi\text{-C}_5\text{H}_5)$.—Reaction of the dimers $(\text{C}_8\text{H}_{12}\text{acac})_2\text{M}_2\text{Cl}_2$ ($\text{M} = \text{Pd}$ and Pt) with cyclopentadienylthallium(I) gives unstable orange oils, presumably the monomeric cyclopentadienyl derivatives. These oils react with triphenylmethyl tetrafluoroborate to give the cations $[\text{C}_8\text{H}_{12}\text{M}(\pi\text{-C}_5\text{H}_5)]^+$. The palladium compound has been reported previously.⁷ The same products are obtained on reaction of the compounds $(\text{C}_8\text{H}_{12}\cdot\text{OMe})\text{Pd}(\pi\text{-C}_5\text{H}_5)$ with triphenylmethyl tetrafluoroborate (see Scheme 2).

The Complexes $(\text{C}_8\text{H}_{12}\text{acac})\text{Pt}(\text{L})\text{Cl}$.—The compound $(\text{C}_8\text{H}_{12}\text{acac})_2\text{Pt}_2\text{Cl}_2$ reacts with triphenyl-phosphine or -arsine to give the monomers $(\text{C}_8\text{H}_{12}\text{acac})\text{Pt}(\text{L})\text{Cl}$. Similar monomers have been obtained with $\text{L} = \text{PEt}_3$, PBU_3 , PET_2Ph , and PETPh_2 (Scheme 2). All of these compounds react with triphenylmethyl tetrafluoroborate

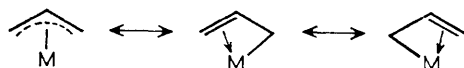
⁷ P. M. Maitlis, A. Efraty, and M. L. Games, *J. Organometallic Chem.*, 1964, **2**, 284.

to give the compounds $[\text{C}_8\text{H}_{12}\text{Pt}(\text{L})\text{Cl}]\text{BF}_4$. The organic product from these reactions is 3-triphenylmethylpentane-2,4-dione. However, the compound $(\text{C}_8\text{H}_{12}\text{acac})\text{Pt}(\text{py})\text{Cl}$ (py = pyridine) behaves differently yielding a 2 : 1 molar mixture of pyridine tetrafluoroborate



and $(\text{C}_8\text{H}_{12}\text{acac})_2\text{Pt}_2\text{Cl}_2$; in this case triphenylmethanol was formed. Thus attack occurs at the pyridine rather than at the enyl ligand; similar behaviour has been observed on treatment of the compounds $\text{CH}_3\text{COMn}(\text{CO})_4(\text{amine})$ with acid.⁸ Also the reaction of tricarbonyl(5-morpholinocyclohexa-1,3-diene)iron with triphenylmethyl tetrafluoroborate yields a 1 : 1 mixture of tricarbonyl π -cyclohexadienyliron tetrafluoroborate and morpholinium tetrafluoroborate.⁹

Reactions of some π -Allylpalladium Compounds.—The π -allyl ligand can be described in valence-bond terms as a hybrid of two enyl canonical forms (see Scheme 3).

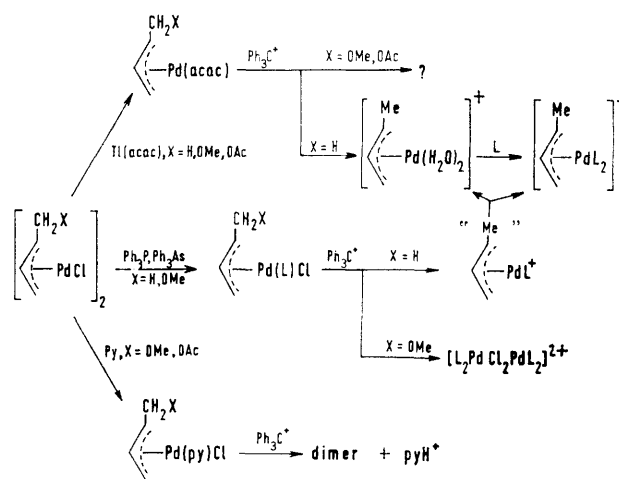


This formal similarity to the enyl compounds above prompted an investigation of the similar reactions of some allylpalladium compounds. The compounds used were derived from the π -allyl compounds $(\pi\text{-C}_4\text{H}_6\text{X})_2\text{Pd}_2\text{Cl}_2$ ($\text{X} = \text{H}$,¹⁰ OMe ,¹¹ and OAc ¹²) (see Scheme 4). Like the compounds $(\text{C}_8\text{H}_{12}\text{acac})_2\text{Pd}_2\text{Cl}_2$, these dimeric π -allyl complexes do not react with the triphenylmethyl cation. However the monomer $(\pi\text{-CH}_2\text{-CH=CH-CH}_3)\text{-Pd}(\text{acac})$ reacts with triphenylmethyl cation to yield a yellow oil. Although this oil has not been characterized, subsequent reaction with donor ligands gave the pure,

⁸ K. A. Kebly and A. H. Filbey, *J. Amer. Chem. Soc.*, 1960, **82**, 4204.

⁹ A. W. Parkins, Ph.D. Thesis, University of Manchester, 1968.

crystalline compounds $[(\pi\text{-C}_4\text{H}_7)\text{PdL}_2]\text{BF}_4$ ($\text{L} = \text{Ph}_3\text{P}$ and Ph_3As). This behaviour, together with the observation that the BF_4^- ion but no acetylacetonate is present (i.r. data) leads to the suggestion that the oils are the diaquo salts $[(\pi\text{-C}_4\text{H}_7)\text{Pd}(\text{H}_2\text{O})_2]\text{BF}_4$. The compounds $[(\pi\text{-C}_4\text{H}_7)\text{PdL}_2]\text{BF}_4$ are also obtained on treatment of the compounds $(\pi\text{-C}_4\text{H}_7)\text{Pd}(\text{L})\text{Cl}$ with triphenylmethyl tetrafluoroborate. Presumably the Pd-Cl bond is cleaved in this case to produce an intermediate of the type $[(\pi\text{-C}_4\text{H}_7)\text{Pd}(\text{L})\text{H}_2\text{O}]\text{BF}_4$ which then disproportionates to yield $[(\pi\text{-allyl})\text{Pd}(\text{H}_2\text{O})_2]^+$ and $[(\pi\text{-allyl})\text{Pd}(\text{L})_2]^+$. In neither of these types of reaction is there any evidence of attack at the π -but-2-enyl ligand. No identifiable palladium compounds could be isolated on reaction of the compounds $(\pi\text{-C}_4\text{H}_6\text{X})\text{Pd}(\text{acac})$ ($\text{X} = \text{OMe}$ and OAc) with the triphenylmethyl cation but $(\pi\text{-C}_4\text{H}_6\text{X})\text{Pd}(\text{L})\text{Cl}$ ($\text{X} = \text{OMe}$; $\text{L} = \text{Ph}_3\text{P}$ and Ph_3As) gave the dimeric cations $[\text{L}_2\text{PdCl}_2\text{PdL}_2]^{2+}$. Here initial



attack must occur at the organic ligand. The complexes $(\pi\text{-C}_4\text{H}_6\text{X})\text{Pd}(\text{py})\text{Cl}$ ($\text{X} = \text{OMe}$ and OAc) behaved like the enyl complexes, on treatment with triphenylmethyl tetrafluoroborate to yield the dimers $(\pi\text{-C}_4\text{H}_7)\text{-Pd}_2\text{Cl}_2$ and pyridinium tetrafluoroborate. Thus none of these π -allyl compounds yield the 1,3-diene complexes on treatment with triphenylmethyl tetrafluoroborate but there is some indication of attack at the π -allyl ligand in the reactions of the methoxy-substituted compounds. In order to obtain more information about this system we have prepared the complex $[\pi\text{-PhC}_4\text{H}_4(\text{OMe})\text{Ph}]_2\text{PdCl}_2$ and the derivatives $[\pi\text{-PhC}_4\text{H}_4(\text{OMe})\text{Ph}]\text{Pd}(\text{acac})$ and $[\pi\text{-PhC}_4\text{H}_4(\text{OMe})\text{Ph}]\text{Pd}(\text{Ph}_3\text{As})\text{Cl}$. The acetylacetonate reacts with triphenylmethyl tetrafluoroborate to give a brown solid and methyl triphenylmethyl ether (see Scheme 5). On the basis of analytical and i.r. data the brown compound appears to be $\{\pi\text{-PhC}_4\text{H}_4[\text{CH}(\text{Ac})\text{Ph}]\text{Pd}(\text{H}_2\text{O})\}\text{BF}_4$. With the tri-

¹⁰ W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1964, 1585.

¹¹ S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806.

¹² J. M. Rowe and D. A. White, *J. Chem. Soc. (A)*, 1967, 1451.

phenylarsine compound, the compound $[(\text{Ph}_3\text{As})_2\text{PdCl}_2\text{-Pd}(\text{Ph}_3\text{As})_2](\text{BF}_4)_2$ was obtained. The organic product from this reaction was identified as a mixture of methyltriphenylmethylether and *trans,trans*-1,4-diphenylbutadiene. These results imply that, as with the enyl

triphenylarsine compound the 1,3-diene is liberated from the metal.

In view of the apparent instability of these intermediate 1,3-diene complexes we have investigated the reactions of a similar cyclic π -allyl complex. This instability may be associated with the formation of the diene in a *transoid* rather than a *cisoid* form. For this purpose there are three suitable compounds *viz.* the 4-methoxycyclo-oct-2-enyl compound¹³ and the *exo*- and *endo*-isomers of $(\text{Ph}_4\text{C}_4\cdot\text{OEt})_2\text{Pd}_2\text{Cl}_2$.¹⁴⁻¹⁹ The latter two compounds were prepared and from them the monomeric compounds $(\text{Ph}_4\text{C}_4\cdot\text{OEt})\text{Pd}(\text{acac})$. However on reaction of either of these compounds with triphenylmethyl tetrafluoroborate cleavage of the chelated acetylacetonate occurred. In the case of the *endo*-isomer addition of cyclo-octa-1,5-diene gave the compound $[(\text{endo-Ph}_4\text{C}_4\cdot\text{OEt})\text{Pd}(\text{C}_8\text{H}_{12})]\text{BF}_4$.

N.m.r. spectra.—The spectra of the neutral compounds $\text{C}_8\text{H}_{12}\text{M}(\text{diketone})$ ($\text{M} = \text{Pd}$ and Pt ; diketone = acac, ba, and dbm) are listed in Table 2. The spectra of the cationic complexes are listed (Tables 3—5). In all cases they are consistent with the suggested structure. Comparison of the spectra of the compounds $[(\text{C}_8\text{H}_{12})\text{M}(\text{diketone})]\text{BF}_4$ ($\text{M} = \text{Pd}$ and Pt ; diketone = acac, ba, and dbm) with those of their isoelectronic neutral

TABLE 2

N.m.r. spectra (τ values) of $\text{C}_8\text{H}_{12}\text{M}(\text{diketone})$ complexes (in CDCl_3)

Compound	Olefin protons *		Diketone protons *	
	Olefinic	Methylenic	C—H	Me and Ph
$\text{C}_8\text{H}_{12}\text{Rh}(\text{acac})$	6.00(4)	7.2—8.5(8)	4.78(1)	8.12(6)
$\text{C}_8\text{H}_{12}\text{Rh}(\text{ba})$	5.87(4)	7.1—8.5(8)	4.06(1)	2.1—2.9(5)
$\text{C}_8\text{H}_{12}\text{Rh}(\text{dbm})$	5.70(4)	7.1—8.4(8)	3.36(1)	2.0—2.8(10)
$\text{C}_8\text{H}_{12}\text{Ir}(\text{acac})^\dagger$	6.26(4)	7.4(8)	4.36(1)	7.86(6)
$\text{C}_8\text{H}_{12}\text{Ir}(\text{dbm})$	5.79(4)	7.5—8.4(8)	3.12(1)	1.9—2.7(10)

* Relative intensities are in parentheses. † Measured by Robinson and Shaw,²¹ the value of τ 4.26 for the olefinic protons, quoted in this reference, is assumed to be a misprint for 6.26.

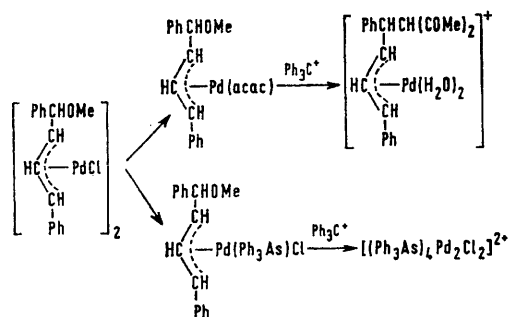
TABLE 3

N.m.r. spectra of $[\text{C}_8\text{H}_{12}\text{M}(\text{diketone})]\text{BF}_4$ Complexes

No.	Compound	Solvent	Olefin protons *		Diketone C—H	Protons * Me and Ph
			Olefinic	Other		
(1)	$\text{C}_8\text{H}_{12}\text{Pd}(\text{acac})^+$	CDCl_3	3.78(4)	6.8—7.4(8)	4.39(1)	7.88(6)
(2)	$\text{C}_8\text{H}_{12}\text{Rh}(\text{dbm})^+$	SO_2	3.59(4)	6.7—7.4(8)	3.02(1)	1.8—2.6(10)
(3)	$\text{C}_8\text{H}_{12}\text{Pt}(\text{acac})^+$	CDCl_3	4.25(4)	6.9—7.6(8)	4.15(1)	7.81(6)
(4)	$\text{C}_8\text{H}_{12}\text{Pt}(\text{ba})^+$	SO_2	J (PtH), 70 4.05(4)	6.9—7.6(8)	J (PtH), 9 3.38(1)	J (PtH), 4.5 1.9—2.5(5), 7.62(3)
(6)	$\text{C}_7\text{H}_8\text{Pt}(\text{ba})^+$	SO_2	J (PtH), 70 4.19(4)	5.37(2), 8.20(2) t, J (HH), 1	J (PtH), 9 3.46(1)	J (PtH), 4.5 1.9—2.6(5), 7.69(3)
(7)	$\text{C}_{10}\text{H}_{12}\text{Pt}(\text{acac})^+$	CDCl_3	J (PtH), 78 2.5—4.3(4)br	6.0—8.0(8)	4.15(1)	J (PtH), 5.5 7.80(6)
(8)	$\text{C}_{10}\text{H}_{12}\text{Pt}(\text{ba})^+$	SO_2	2.5—4.3(4)br	6.0—8.0(8)	J (PtH), 8 3.48(1) J (PtH), 8	1.9—2.6(5), 7.65(3)

* Chemical shift (τ); relative area in parenthesis; coupling constants (Hz). d = Doublet; t = triplet; qa = quartet; q = quintet; br = broad.

compounds electrophilic attack by triphenylmethyl cation does occur at the organic ligand but that the 1,3-diene complexes produced undergo further reactions.



SCHEME 5

With the acetylacetonate the β -diketonate attacks the 1,3-diene to reform a π -allyl system, whereas in the

¹³ S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1964, 5002.

¹⁴ A. T. Bloomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1962, **84**, 2329.

¹⁵ L. Malalita, G. Santarella, L. Vallarino, F. Zingalis, and L. Cambi, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1959, **27**, 230.

ba, and dbm) are listed in Table 2. The spectra of the cationic complexes are listed (Tables 3—5). In all cases they are consistent with the suggested structure. Comparison of the spectra of the compounds $[(\text{C}_8\text{H}_{12})\text{M}(\text{diketone})]\text{BF}_4$ ($\text{M} = \text{Pd}$ and Pt ; diketone = acac, ba, and dbm) with those of their isoelectronic neutral

TABLE 4

N.m.r. spectra of $[\text{C}_8\text{H}_{12}\text{M}(\pi\text{-C}_5\text{H}_5)]\text{BF}_4$ compounds

No.	M	Solvent	Olefin protons *		$(\pi\text{-C}_5\text{H}_5)$ protons *
			Olefinic	Methylenic	
(11)	Pd	CDCl_3	3.93(4)	7.2—7.5(8)	3.75(5)
(12)	Pt	CDCl_3	4.39(4)	7.4—7.7(8)	3.74(5)
			J (PtH), 83		J (PtH), 17

* Relative intensities are in parentheses

analogues shows that a considerable deshielding of the protons occurs. This is particularly evident for the protons of the co-ordinated double bonds and is of the

¹⁶ P. M. Maitlis and M. L. Games, *Canad. J. Chem.*, 1964, **42**, 183.

¹⁷ L. M. Vallarino and G. Santarella, *Gazzetta*, 1964, **94**, 252.

¹⁸ W. E. Oberhansli and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 629.

¹⁹ P. M. Maitlis, A. Efraty, and M. L. Games *J. Amer. Chem. Soc.*, 1965, **87**, 719.

TABLE 5
 N.m.r. spectra of $[\text{C}_8\text{H}_{12}\text{Pt}(\text{L})\text{X}]\text{BF}_4$ compounds

No.	L	X	Olefinic		Methylenic	Ligand (L) protons*		Solvent
			<i>trans</i> to L	<i>cis</i> to L				
(17)	Et_3P	Cl	3.74(2) <i>J</i> (PtH), 42 <i>J</i> (PH), 3	4.56(2) <i>J</i> (PtH), 67	7.0—7.8(8)	7.5—8.0(6)	8.74(9) d, t <i>J</i> (PH), 18 <i>J</i> (HH), 7	CDCl_3
(18)	Bu_3P	Cl	3.82(2) <i>J</i> (PtH), 45 <i>J</i> (PH), 3	4.78(2) <i>J</i> (PtH), 65	6.7—7.8(8)	7.6—8.8(18)	9.03(9) t, <i>J</i> (HH), 5	CDCl_3
	Bu_3P	Cl	3.77(2) <i>J</i> (PtH), 42 <i>J</i> (PH), 3	4.75(2) <i>J</i> (PtH), 68	6.7—7.9(8)	7.6—8.8(18)	9.03(9) t, <i>J</i> (HH), 5	SO_2
(19)	PhEt_2P	Cl	3.77(2) <i>J</i> (PtH), 46 <i>J</i> (PH), 3	5.02(2) <i>J</i> (PtH), 64	6.7—7.9(8)	2.4(5)	ca. 7.5(4) 8.73(6) d, t <i>J</i> (PH), 18 <i>J</i> (HH), 7	CDCl_3
(20)	Ph_2EtP	Cl	3.62(2) <i>J</i> (PtH), 46 <i>J</i> (PH), 3	5.29(2) <i>J</i> (PtH), 65	6.7—7.8(8)	2.4(10)	ca. 7.5(2) 8.49(3) d, t <i>J</i> (PH), 20 <i>J</i> (HH), 7	CDCl_3
(21)	Ph_3P	Cl	3.53(2) <i>J</i> (PtH), 50 <i>J</i> (PH), 3	5.24(2) <i>J</i> (PtH), 65	6.7—7.8(8)		2.4(15)	SO_2
(22)	Ph_3As	Cl	3.59(2) <i>J</i> (PtH), 55	5.01(2) <i>J</i> (PtH), 65	6.8—7.8(8)		2.4(15)	SO_2
(23)	Ph_3P	Br	3.42(2) <i>J</i> (PtH), 50 <i>J</i> (PH), 3	5.15(2) <i>J</i> (PtH), 65	6.9—8.0(8)		2.4(15)	SO_2
(24)	Ph_3As	Br	3.53(2) <i>J</i> (PtH), 56	4.93(2) <i>J</i> (PtH), 66	6.9—7.8(8)		2.4(15)	SO_2

* See footnotes to Table 3.

order of 2.0—2.2 p.p.m. Similarly a comparison of the spectra of $[(\text{C}_8\text{H}_{12})\text{M}(\pi\text{-C}_5\text{H}_5)]\text{BF}_4$ ($\text{M} = \text{Pd}$ and Pt) and $\text{C}_8\text{H}_{12}\text{M}(\pi\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Rh}^{20}$ and Ir^{21}) shows a chemical shift difference of ca. 2 p.p.m. for the double-bond protons but ca. 1 p.p.m. for the protons of the cyclopentadienyl ring. These large shift differences for the double-bond protons may be associated with a decreased amount of back-bonding to the olefin, which might be expected in the positively charged olefin complexes.

The compounds $[\text{C}_8\text{H}_{12}\text{Pt}(\text{PR}_3)\text{Cl}]\text{BF}_4$ shows two resonances for the double-bond protons, the signal to lower field shows coupling to phosphorus and on this basis it can be assigned to the protons of the double bond *trans* to the phosphine. The lower field position of these resonances is presumably due to the competition of the phosphine with the olefin for metal *d*-electron density. A comparison with the spectrum of $\text{C}_8\text{H}_{12}\text{Ir}(\text{PPh}_3)\text{Cl}^{22}$ shows that the deshielding of the double-bond protons *trans* to the phosphine is smaller than that for those *trans* to chlorine. This is consistent with the rationalization of large chemical-shift differences as being due to decreased back-bonding in the positively charged species, since this decrease in back-bonding would be less marked for double bonds *trans* to phosphorus which must compete with the phosphine for *d*-electron density.

In the series of compounds $[\text{C}_8\text{H}_{12}\text{Pt}(\text{L})\text{Cl}]\text{BF}_4$ and $\text{C}_8\text{H}_{12}\text{Rh}(\text{L})\text{Cl}^{23}$ the signal attributed to the protons of the double bond *trans* to the phosphine moves to higher field as L is changed along the series Ph_3P , Ph_2EtP , PhEt_2P , and Bu_3P .

I.r. Spectra.—The i.r. spectra of the cationic complexes are in all cases in agreement with their formulation above. They all show a strong band at ca. 1060 cm^{-1} , characteristic of the BF_4^- ion. Other significant peaks such as $\nu(\text{C}=\text{O})$, of the β -diketonates are noted in Table 1.

The compounds $[(\text{C}_8\text{H}_{12})\text{Pt}(\text{L})\text{Cl}]\text{BF}_4$ show a doublet for the $\nu(\text{Pt}-\text{Cl})$ mode whereas a singlet might be expected. We have observed similar behaviour with the compounds $(\pi\text{-C}_3\text{H}_5)\text{Pd}(\text{L})\text{Cl}$.

 TABLE 6
 Olefin n.m.r. chemical shifts for $\text{C}_8\text{H}_{12}\text{Rh}(\text{L})\text{Cl}$ complexes

L	τ (H_a) (<i>trans</i> to L)	τ (H_b) (<i>cis</i> to L)
Ph_3P	4.43	6.85
Ph_2EtP	4.52	6.95
PhEt_2P	4.66	6.78
Et_3P	4.63	6.40
Bu_3P	4.73	6.50
Ph_3As	4.60	6.55
py	5.30	6.33
pip	5.51	6.28

 TABLE 7
 N.m.r. chemical shift differences

L	$\text{H}(\text{Rh}) - \text{H}(\text{Pt})$ Protons <i>trans</i> to L	$\text{H}(\text{Rh}) - \text{H}(\text{Pt})$ Protons <i>cis</i> to L
Ph_3P	0.90	1.61
Ph_2EtP	0.90	1.66
PhEt_2P	0.89	1.76
Et_3P	0.91	1.72
Bu_3P	0.89	1.84
Ph_3As	1.01	1.54

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 237 and 257 machines and in the far i.r. region on a Grubb-Parsons DM4. U.v. spectra were obtained on a Perkin-Elmer 137 machine and n.m.r. spectra on Varian A60, Perkin-Elmer R10 and Varian HA100 spectrometers.

Only representative examples of reactions are given in full detail.

Enyl Complexes

(a) *Preparation of Starting Materials.*—The cyclo-enyl β -diketonate complexes shown in Scheme 1 were prepared by the literature method¹¹ with only slight modifications.

²³ T. Keating, University College, London, unpublished observations.

²⁰ J. Lewis and A. W. Parkins, to be published.

²¹ S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1965, 4997.

²² G. Winkhaus and H. Singer, *Chem. Ber.*, 1966, **99**, 3610.

The complexes $[(C_8H_{12} \cdot OMe)PdCl]_2$,²⁴ $(C_8H_{12} \cdot OMe)Pd(acac)$,¹¹ $(C_8H_{12} \cdot OMe)M(\pi-C_5H_5)$, ($M = Pd$ and Pt),²⁵ $[(C_8H_{12} \cdot OAc)PdX]_2$, ($X = Cl$ and OAc)²⁶ and *exo*- and *endo*- $[(Ph_4C_4 \cdot OEt)PdCl]_2$ ¹⁴ were prepared by published procedures.

(i) 1,3-Diphenylpropan-1,3-dionato 2-(3-pentan-2,4-dionato)-cyclo-oct-5-enylpalladium, $(C_8H_{12} \cdot acac)Pd(dbm)$. The dimer, di- μ -chloro-bis 2-(3-pentan-2,4-dionato)cyclo-oct-5-enyldipalladium, $[(C_8H_{12}acac)PdCl]_2$ (698 mg., 1.0 mmole) was suspended in chloroform and the suspension was cooled to -5° , whilst being stirred. To this, 1,3-diphenylpropan-1,3-dionatothallium(I), $Tl(dbm)$, (856 mg.; 2.0 mmoles) was added and the mixture was stirred at -5° for 1 hr. After removal of the precipitated thallium(I) chloride, the clear solution was evaporated to dryness, then taken up in ether and filtered through a short (ca. 15 cm. 1 cm.^2) column of alumina (Spence, grade 'H'). Elution of the column with ether (ca. 300 ml.) gave, on evaporation, the *product*, as white crystals (882 mg., 1.64 mmoles, 82%).

Filtration through short columns of alumina was found to be a very effective method of purifying complexes containing chelated β -diketonates and was employed for all such complexes. The complexes were usually obtained analytically pure after such treatment. Ether was usually used as solvent but where solubility required it, a 1:1 mixture of ether and methylene chloride was used.

The isomeric $(C_8H_{12}dbm)Pd(acac)$ was similarly prepared.

(ii) Pentan-2,4-dionato(2-hydroxycyclo-oct-5-enyl)-palladium. The dimer, di- μ -chloro-bis(2-acetoxycyclo-oct-5-enyl)dipalladium, $[(C_8H_{12} \cdot OAc)PdCl]_2$ (618 mg.; 1.0 mmole) was treated with pentan-2,4-dionatothallium(I), $Tl(acac)$, (606 mg., 2.0 mmoles) in chloroform. Isolation and purification as in (i) gave a white solid, which on addition of ether was seen to be only partly soluble. Filtration gave the *product* as white microcrystals (60 mg., 0.15 mmole, 7.5%). Evaporation of the filtrate gave an oil (120 mg.) identified by its i.r. spectrum.

The mechanism of the formation of the product is not clear and has not been investigated.

(iii) $(C_8H_{12} \cdot acac)Pt(L)Cl$. This is exemplified for the compound with $L = Bu_3P$. The dimer di- μ -chloro-bis 2-(3-pentan-2,4-dionato)cyclo-oct-5-enyldiplatinum, $[(C_8H_{12} \cdot acac)PtCl]_2$, (656 mg., 0.75 mmole) was suspended in acetone and tributylphosphine (306 mg., 1.50 mmoles) was added. Most of the solid dissolved when the mixture was shaken and the small amount that did not was filtered off. Evaporation of the filtered solution gave an oil which crystallized on being pumped at 0.05 mm.Hg pressure for several hours. The solid was dissolved in hot acetone-light petroleum (b.p. 100–120) (1:1) and the solution was cooled and evaporated until an oil began to separate. A little acetone was then added and the solution was set aside at ambient temperature for 24 hr., during which time white *needles* were formed. These were filtered off (804 mg., 1.25 mmoles, 83%) and were washed with pentane and finally dried *in vacuo*.

(b) *Reactions with Triphenylmethyl Tetrafluoroborate*.—In many cases it was found convenient to prepare the substrate and react it immediately rather than to isolate it as a pure crystalline solid. Thus, some of the yields quoted are based on the (diene) MX_2 complex.

(i) *Preparation of pentan-2,4-dionato(cyclo-octa-1,5-diene)-*

palladium tetrafluoroborate. Dichloro(cyclo-octa-1,5-diene)-palladium (572 mg., 2.0 mmoles) was suspended in chloroform (ca. 40 ml.) and the solution was cooled to -5° . To this solution pentan-2,4-dionatothallium(I) (1.212 g., 4.0 mmoles) was added and the mixture was stirred at -5° for 1 hr. during which time it became colourless. Filtration and evaporation yielded a colourless oil which was taken up in ether and washed through a column of alumina with ether. Evaporation yielded $(C_8H_{12}acac)Pd(acac)$ as an oil, which was dissolved in methylene chloride and treated with triphenylmethyl tetrafluoroborate (660 mg., 2.0 mmoles). Addition of ether to the reaction mixture gave a deep yellow precipitate which was filtered off, dried; it was purified by dissolution in chloroform followed by careful addition of ether until crystallization occurred. This gave the product as deep yellow *plates* (677 mg., 1.69 mmoles, 84.5%). The product was stable when stored *in vacuo* below 0° , but decomposed slowly in air.

The filtrate from the reaction mixture after removal of the complex was evaporated to dryness to give a yellow solid, which on recrystallization from ethanol gave 3-triphenylmethylpentan-2,4-dione as white *needles*, m.p. 170–111.5° (409 mg., 1.20 mmoles, 60%) [Found: C, 83.7; H, 6.3; O, 9.9%; M (mass spec.), 342. $C_{24}H_{20}O_2$ requires C, 84.1; H, 6.5; O, 9.4%; M , 342.] The n.m.r. spectrum of this compound, at 60 MHz., showed resonances at τ 2.3–2.9(15), 4.36(1), and 8.14(6), which show it to be entirely in the diketone-form. This conclusion was confirmed by its i.r. spectrum which showed only two carbonyl absorptions (at 1685 and 1722 cm^{-1} , the latter being broader and more intense) in the region characteristic of the diketone-form.

The palladium complex was also obtained from $(C_8H_{12} \cdot OMe)Pd(acac)$ as follows. The complex, pentan-2,4-dionato(2-methoxycyclo-oct-5-enyl)palladium (344 mg., 1.0 mmole) was treated with triphenylmethyl tetrafluoroborate (330 mg., 1.0 mmole) in methylene chloride. Addition of ether gave a yellow precipitate, which was purified as above to yield the *product* (362 mg., 0.91 mmole, 91%). Evaporation of the filtrate gave an off-white solid which was taken up in benzene and eluted through a column of alumina with the same solvent. Evaporation of the benzene gave an oil which on crystallization from methanol gave methyl triphenylmethyl ether (131 mg., 0.48 mmole, 48%), m.p. 95–96.5° (lit., 96–96.5°) which was identical with an authentic sample, prepared by reaction of triphenylmethyl tetrafluoroborate with methanol.

The other compounds listed (Table 1) were similarly obtained.

(ii) *Cyclopentadienyl(cyclo-octa-1,5-diene)palladium tetrafluoroborate*. The dimer, $[(C_8H_{12}acac)PdCl]_2$ (349 mg., 0.50 mmole) was suspended in methylene chloride (25 ml.) and cyclopentadienylthallium(I) (296 mg., 1.1 mmoles) was added. The mixture was shaken for 15 min. during which time it became deep orange in colour. The solid was centrifuged off and triphenylmethyl tetrafluoroborate (330 mg., 1 mmole) was added to the clear orange solution. Addition of ether gave a violet solid which was dissolved in methylene chloride; addition of ether to the solution gave the *product* as a violet powder (188 mg., 0.51 mmole, 51%).

The platinum analogue was prepared similarly but it was found that if the reaction was not carried out sufficiently rapidly $[C_8H_{12}Pt(acac)]BF_4$ was also formed; thus, the

²⁴ C. B. Anderson and B. J. Bunson, *J. Organometallic Chem.*, 1967, 7, 181.

²⁴ R. G. Schultz, *J. Organometallic Chem.*, 1966, 6, 435.

²⁵ C. C. Hunt and J. R. Doyle, *Inorg. and Nuclear Chem. Letters*, 1966, 2, 282.

reaction time with $\text{Ti}(\text{C}_6\text{H}_5)_3$ was reduced to *ca.* 2 min. and the remaining operations were carried out as rapidly as possible.

(iii) $[\text{C}_8\text{H}_{12}\text{Pt}(\text{L})\text{Cl}]\text{BF}_4$. This is exemplified for the compound with $\text{L} = \text{Bu}_3\text{P}$. Chloro(tributylphosphine)-2-(3-pentan-2,4-dionato)-cyclo-oct-5-enyl)platinum (640 mg., 1.0 mmole) was treated with triphenylmethyl tetrafluoroborate in methylene chloride. Ether was added to the mixture and the sides of the reaction vessel were scratched to give a white solid; this recrystallized from chloroform-ether to give chloro(tributylphosphine)cyclo-octa-1,5-dieneplatinum tetrafluoroborate as white needles (552 mg., 0.88 mmole, 88%).

(iv) *Di-μ-chloro-bis(2-methoxycyclo-oct-5-enyl)dipalladium*. The complex (421 mg., 0.75 mmole) was dissolved in methylene chloride and an equimolar quantity of triphenylmethyl tetrafluoroborate was added. A yellow precipitate was formed immediately which was filtered off under nitrogen and washed with methylene chloride (yield 207 mg.) (Found: C, 29.8; H, 3.6; Cl, 9.1. $\text{C}_9\text{H}_{16}\text{BClF}_4$ -OPd requires C, 29.3; H, 4.4; Cl, 9.6%). The reactions of this compound indicate that protonation has occurred.

(c) *Reactions with Fluoroboric Acid*.—(i) *Pentan-2,4-dionato-2-(3-pentan-2,4-dionato)-cyclo-oct-5-enyl platinum*. The complex (100 mg., 0.20 mmole) was dissolved in acetone (2 ml.) and the acid (one drop of 40% aqueous solution) was added. The solution was then diluted with water and the white precipitate so formed was filtered off and dried *in vacuo*. Recrystallization of this from chloroform-ether gave *pentan-2,4-dionato(cyclo-octa-1,5-diene)-platinum tetrafluoroborate* (61 mg., 61%).

The analogous palladium compound behaved similarly.

(ii) *1,3-Diphenylpropan-1,3-dionato-2-(3-pentan-2,4-dionato)cyclo-oct-5-enylpalladium*. A similar treatment to that used above gave on precipitation with ether (not water) *1,3-diphenylpropan-1,3-dionato(cyclo-octa-1,5-diene)-palladium tetrafluoroborate* as an orange solid (83%).

The same compound was obtained from the isomeric $(\text{C}_8\text{H}_{12}\text{dbm})\text{Pd}(\text{acac})$ and both isomers also gave this product on reaction with triphenylmethyl tetrafluoroborate. Further, treatment of both isomers with an equimolar amount of hydrochloric acid (added as *N*-hydrochloric acid to an acetone solution) gave $[(\text{C}_8\text{H}_{12}\text{dbm})\text{PdCl}]_2$ in yields of *ca.* 90%.

π-Allyl Complexes

(a) *Preparation of Starting Materials*.—The chlorobridged dimers ($\text{X} = \text{H}$,¹⁰ OMe,¹¹ and OAc¹²) were prepared by established methods. From these the monomeric acetylacetonates were prepared by reaction with $\text{Ti}(\text{acac})$ in chloroform. The triphenyl-phosphine and -arsine compounds ($\text{X} = \text{H}$ and OMe) were prepared by reaction of the dimers with stoichiometric quantities of the ligand in acetone and were recrystallized from benzene or benzene-light petroleum (100:120). The pyridine complexes ($\text{X} = \text{OMe}$ and OAc) were similarly prepared and purified.

(i) *Di-μ-chloro-bis(1-syn-phenyl-3-syn-phenylmethoxymethyl-π-allyl)dipalladium*. Palladium chloride (1.77 g., 10 mmoles) and sodium chloride (1.170 g., 20 mmoles) were dissolved in hot methanol and *trans,trans*-1,4-diphenylbutadiene (4.12 g., 20 mmoles) was added to the solution. The mixture was then stirred at room temperature for 2 weeks to give a yellow solid; this was filtered off and repeatedly recrystallized by dissolution in chloroform and addition of methanol until it was free from the diene, as

judged by its u.v. spectrum. The product was obtained as small yellow crystals (695 mg., 0.90 mmole, 18%) [Found: C, 53.8; H, 4.5; Cl, 9.4; O, 4.2%; M (1.73% solution in chloroform), 724. $\text{C}_{34}\text{H}_{34}\text{Cl}_2\text{O}_2\text{Pd}_2$ requires C, 53.8; H, 4.5; Cl, 9.4; O, 4.2%; M , 755.8].

(b) *Reactions with Triphenylmethyl Tetrafluoroborate*.—

(i) *Pentan-2,4-dionato(1-syn-methyl-π-allyl)palladium*, ($\text{X} = \text{H}$). The complex (260 mg., 1.0 mmole) was dissolved in methylene chloride and treated with triphenylmethyl tetrafluoroborate (330 mg., 1.0 mmole). Dilution of the reaction mixture with ether failed to give a precipitate and upon evaporation to dryness it yielded an uncrystallizable yellow oil. Addition of triphenylphosphine (524 mg., 2.0 mmoles) to an ether suspension of the oil gave a white solid, which was recrystallized from methylene chloride-ether to give *1-syn-methyl-π-allyl(bistriphenylphosphine)-palladium tetrafluoroborate* (690 mg., 0.89 mmole; 98%).

(ii) *Chloro(triphenylphosphine)(1-syn-methyl-π-allyl)-palladium*, ($\text{X} = \text{H}$). The complex (459 mg., 1 mmole) was treated with triphenylmethyl tetrafluoroborate in methylene chloride. Addition of ether to the reaction mixture failed to give a precipitate; however upon evaporation to dryness followed by addition of ether a yellow precipitate was obtained. This was recrystallized from methylene chloride-ether to give *bis-triphenylphosphine-(1-syn-methyl-π-allyl)palladium tetrafluoroborate* (361 mg., 0.47 mmole, 94%).

The corresponding triphenylarsine compound behaved similarly.

(iii) *Chloro(triphenylarsine)(1-syn-methoxymethyl-π-allyl)-palladium* ($\text{L} = \text{Ph}_3\text{As}$, $\text{X} = \text{OMe}$). The complex (533 mg., 1.0 mmole) was treated with triphenyl tetrafluoroborate in methylene chloride. Addition of ether to the reaction mixture gave a red oil, which settled out. Decantation of the supernatant liquid and titration of the oil with ether gave *di-μ-chloro-tetrakis(triphenylarsine)dipalladium ditetrafluoroborate* as an orange-brown solid.

The triphenylphosphine analogue of this di-cation was similarly obtained from ($\text{L} = \text{Ph}_3\text{P}$; $\text{X} = \text{OMe}$).

(iv) *Chloro(pyridine)(1-syn-acetoxymethyl-π-allyl)palladium* ($\text{X} = \text{OAc}$). The complex (334 mg., 1.0 mmole) was treated with triphenylmethyl tetrafluoroborate (330 mg., 1.0 mmole) in methylene chloride. A white precipitate formed instantaneously and this was filtered off and recrystallized from acetone-ether to give *pyridinium tetrafluoroborate* (149 mg., 0.89 mmole, 89%) [Found: C, 36.0; H, 3.6; N, 8.3. Calc. for $\text{C}_5\text{H}_6\text{BF}_4\text{N}$: C, 36.0; H, 3.6; N, 8.4%].

Evaporation of the methylene chloride solution and recrystallization of the yellow solid obtained, gave the *dimer* ($\text{X} = \text{OAc}$) as yellow needles from benzene-light petroleum (b.p. 100–120°) m.p. 135–136° (Found: C, 28.3; H, 3.6. Calc. for $\text{C}_{12}\text{H}_{18}\text{Cl}_2\text{O}_4\text{Pd}_2$: C, 28.2; H, 3.6%).

(v) *Derivatives of compound (XX)*. Acetylacetonate. The complex (188 mg.) was treated with triphenylmethyl tetrafluoroborate (150 mg.) in methylene chloride and the brown precipitate which formed immediately was filtered off and dried *in vacuo*. The yield was 150 mg. (Found: C, 48.2; H, 3.2. Calc. for the monohydrate $\text{C}_{21}\text{H}_{23}\text{BF}_4\text{O}_3\text{Pd}$: C, 48.8; H, 4.5%. Calc. for the dihydrate $\text{C}_{21}\text{H}_{25}\text{BF}_4\text{O}_4\text{Pd}$: C, 47.2; H, 4.7%). The organic product was found to be methyl triphenylmethyl ether.

Triphenylarsine adduct. The complex (171 mg.) was treated with triphenylmethyl tetrafluoroborate (83 mg.)

and gave (in methylene chloride solution) an orange precipitate identified as *di-μ-chloro-tetrakis(triphenylarsine)dipalladium ditetrafluoroborate* (82 mg.) (Found: C, 50.7; H, 3.4. Calc. for $C_{72}H_{60}As_4B_2Cl_2F_8Pd_2$: C, 51.4; H, 3.6%), the i.r. spectrum of which was identical with that of the compounds obtained from the simpler triphenylarsine complexes. The n.m.r. spectrum showed only one resonance at *ca.* τ 2.5.

Tetraphenylcyclobutenyl Complexes

Pentan-2,4-dionato(*endo*-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)palladium, $(Ph_4C_4 \cdot OEt)Pd(acac)$ (202 mg., 0.33 mmole) was treated with triphenylmethyl tetrafluoroborate (110 mg., 0.33 mmole) in methylene chloride.

Addition of ether to the mixture failed to give a precipitate but on subsequent addition of cyclo-octa-1,5-diene resulted in the precipitation of the orange complex *endo-ethoxytetraphenylcyclobutenyl(cyclo-octa-1,5-diene)palladium tetrafluoroborate* (130 mg., 6%) (Found: C, 64.1; H, 4.6. $C_{38}H_{37}BF_4OPd$ requires C, 64.9; H, 5.3%).

The *exo*-isomer behaved similarly but the cyclo-octadiene complex was obtained in only very low yield and was characterized only by i.r. spectroscopy. It was also considerably less stable than the *endo*-isomer.

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