408. *Organopalladium Compounds.*

By G. Calvin and G. E. Coates.

Methyl- and some aryl-palladium compounds have been prepared by the action of Grignard or organolithium reagents on complex halides, commonly containing tertiary phosphines. Ethyl and propyl derivatives appear to be formed but could not be isolated on account of their instability. All aryl-palladium compounds prepared have a *trans*-structure. Complexes with chelate ligands never yielded *cis*-diaryl derivatives, but several *cis*-dimethyls were prepared. The tertiary arsine complex $(AsEt_3)_2PdMe_2$ has a *cis*-structure, but its phosphine analogue appears to exist in benzene solution as a mixture of isomers. Reactions between $(PEt_3)_2PdMe_2$ and ethanol and some other weakly acidic substances are reported.

Several years ago one of us began a study of the possibility of preparing normal (sigma-bonded) organic derivatives of transition metals by reactions between organolithium or Grignard reagents and transition-metal co-ordination complexes. These methods were suggested by the substantial improvements in yield resulting from the use of dichlorodipyridinegold(III) chloride and *cis*-tetrachlorodipyridineplatinum(IV), in place of uncomplexed halides, for the preparation of organic gold(III) and platinum(IV) compounds.[1] We were interested mainly in nickel, palladium, and platinum in their +2 oxidation level, and therefore gave most attention to complexes of halides of these metals with tertiary phosphines, which are about the strongest donors to these elements in that oxidation level (particularly platinum [2]).

When this work was in progress and we had prepared a number of organic compounds of these elements co-ordinated to tertiary phosphines, we learned that Dr. J. Chatt and his colleagues were working on similar lines and thereafter confined our own work on this group to palladium.

Most of the organopalladium compounds we obtained, which were generally of the type L_2PdRX and L_2PdR_2 (L = tertiary phosphine, R = Me, aryl, or Ph·C:C, X = Br, I, SCN), are unstable, and few of them can be kept undecomposed for long periods at room temperature. Most but not all of them are colourless and slowly turn grey and eventually black, owing to formation of elemental palladium. Usually it was necessary to purify products by crystallization at low temperature.

Reaction between dihalides, for instance, dibromo(bistriethylphosphine)palladium, $(PEt_3)_2PdBr_2$, and a Grignard reagent resulted in the rapid replacement of one halogen, but a large excess was necessary to replace both. Organolithium reagents replace both halogens, usually quite rapidly below room temperature, and these were the preferred reagents for the preparation of dimethyl or diaryl derivatives.[3]

Donor Groups.—Though triethylphosphine appeared to have a stronger stabilizing effect than other donor substances investigated, organopalladium compounds were also prepared from palladium halides co-ordinated to tertiary arsines, sulphides, a diene, and bipyridyl.

Reaction between $(PEt_3)_2PdBr_2$ and methyl-lithium yielded $(PEt_3)_2PdMe_2$, but a single strong donor co-ordinated to palladium is inadequate to stabilize a methyl derivative since treatment of the binuclear complex $Bu^n{}_3P(Cl)PdCl_2Pd(Cl)PBu^n{}_3$ with methyl-lithium resulted in rapid decomposition (formation of metallic palladium) even at −45°. If the bridge chlorine atoms are replaced by ethylthio-groups,[4] the metal then being co-ordinated to three quite strongly donor groups (I), a dimethyl derivative (II) can then be isolated. No significance should be attached to the *cis*-formulation of (II) No organopalladium

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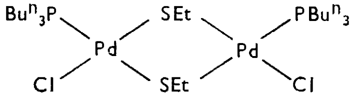
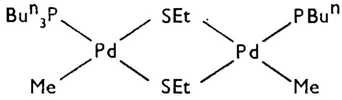
[1] Foss and Gibson, *J.*, 1951, 299.
[2] Chatt, *J.*, 1951, 652.
[3] Calvin and Coates, *Chem. and Ind.*, 1958, 160.
[4] Chatt and Mann, *J.*, 1938, 1949.

compounds could be prepared from *trans*-$(Et_2S)_2PdCl_2$, but the chelate complex $(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)PdCl_2$ afforded a dimethyl derivative which was liquid at room temperature and difficult to purify. Reaction with phenyl-lithium resulted in complete decomposition at —50° with formation of biphenyl. A crystalline dimethyl compound was obtained from the higher-melting complex $(MeS{\cdot}CH_2{\cdot}CH_2{\cdot}SMe)PdCl_2$. Olefins have relatively weak σ- but strong π-bonding character to transition metals,[5] and, since cycloocta-1,5-diene seems to form the most stable olefin complexes, the preparation of $C_8H_{12}PdMe_2$ was attempted. This compound was obtained but only in low yield, and it was very unstable indeed.



(I)



(II)

The only aryl derivatives prepared were derived from tertiary phosphine complexes, and tertiary phosphines appear also to have the best stabilizing effect on σ-bonded organic compounds of nickel,[6] palladium, platinum,[7] and possibly cobalt.[6] The most stable σ-bonded organic compounds of elements near the middle of the transition series are, so far, those in which the metals form six or more bonds and are in combination with ligands such as carbonyl and cyclopentadienyl [examples are $MeMn(CO)_5$ [8] and $C_5H_5W(CO)_3Me$ [9]].

Organic Groups.—Comparisons between organopalladium compounds (L_2PdRX or L_2PdR_2) containing a variety of organic groups suggest that the most stable compounds are formed when R is methyl, phenylethynyl, or phenyl bearing an electron-attracting substituent. The difference between methyl and higher alkyls is striking; whereas $(PEt_3)_2PdMeBr$ and $(PEt_3)_2PdMe_2$ are two of the few compounds that melted without decomposition, there was evidence from characteristic colour changes during reaction that $(PEt_3)_2PdEtBr$ and $(PEt_3)_2PdPr^nBr$ were formed from the dibromide and a Grignard reagent, but they were too unstable to be isolated. In contrast, nickel [6] yielded no methyl derivatives, but a variety of stable platinum [7] alkyls, from methyl to butyl, has been prepared.

All the phenyl derivatives prepared in this work were derived from $(PEt_3)_2PdBr_2$; all other palladium complexes that were treated with phenyl-lithium decomposed to palladium even at low temperatures. The diphenyl compound $(PEt_3)_2PdPh_2$ darkens at room temperature during a week or more. The di-*p*-tolyl compound appeared to be considerably less stable and was not isolated. Both $(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}CF_3)Br$ and the mixed diaryl $(PEt_3)_2PdPh(p\text{-}C_6H_4{\cdot}CF_3)$ prepared from it seem to be indefinitely stable at room temperature [this is also true of the compounds $(PEt_3)_2PdBr(p\text{-}C_6H_4Cl)$, $(PEt_3)_2Pd(p\text{-}C_6H_4Cl)_2$, and $(PEt_3)_2Pd(p\text{-}C_6H_4Br)_2$, which will be reported later]. The dimethylaminophenyl derivative $(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}NMe_2)_2$ is so unstable that its purification is difficult, but its dimethiodide $[(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}NMe_3)_2]I_2$, in which electron-attracting replace electron-releasing groups, does not readily decompose in solution and remains unchanged in the air during long periods. Attempts to prepare mixed alkyl-aryl compounds, for example, by reaction between $(PEt_3)_2PdMeBr$ and phenyl-lithium, resulted in complete decomposition, and reaction with phenylethynyl-lithium yielded $(PEt_3)_2Pd(C{\vdots}CPh)_2$ as the only organometallic product.

Aryl derivatives of platinum bearing *ortho*-substituents are more stable than those without,[7] and in the case of nickel [6] the stabilizing effect of *ortho*-substituents is so marked

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[5] Chatt. Duncanson, and Venanzi, *J.*, 1955, **4456**, **4461**.

[6] Chatt and Shaw, *Chem. and Ind.*, 1959, 675, *J.*, in the press.

[7] *Idem, J.*, 1959, 705, and in the press.

[8] Closson, Kozikowski, and Coffield, *J. Org. Chem.*, 1957, **22**, 598; Hieber and Wagner, *Z. Naturforsch.*, 1957, **12**, *b*, 478.

[9] Piper and Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104; Fischer, Hafner, and Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.

that these are the only aryl compounds to be isolatable pure. Palladium must surely occupy an intermediate position in this respect, but it seems that inductive or electromeric effects are even more pronounced. We believe this *ortho*-effect stabilizes *trans*-$(PEt_3)_2Pd(mesityl)Br$, which remained undecomposed in the air, but is not so stable as its nickel analogue since it decomposes on melting (the nickel compound can be sublimed even at atmospheric pressure).

The only other stable complexes prepared were the *trans*-diethynyl compounds $(PEt_3)_2Pd(C⋮CPh)_2$ and $(PEt_3)_2Pd(C⋮C{\cdot}C_6H_4{\cdot}NO_2\text{-}p)_2$. The relatively high stability of *trans*-diethynyl-nickel compounds (complexed with phosphines) is reasonably attributed to reduction of energy of the metal d_{xy} and d_{yz} orbitals by conjugation with ethynyl, the d_{xz} level being already strongly stabilized by π bonding to the phosphines (the plane of the complex is taken as xy with the phosphorus atoms on the x axis). The same effect could help to stabilize ethynylpalladium compounds, but in view of our observations on the effect of polar substituents on the relative stability of the phenylpalladium compounds, we are inclined to attribute part at least of this stability to the electronegative character of acetylenic carbon atoms. The stretching frequencies of the ethynyl groups are not markedly reduced in either the palladium or the nickel compounds, but they are slightly reduced in accordance with partial occupation of the acetylenic antibonding orbitals.

Structure.—In view of the lability of palladium complexes (relative to platinum) we were not surprised to find no evidence of isomerism except in the case of the dimethyl, $(PEt_3)_2PdMe_2$. The dipole moment of this compound appears to change with the time elapsing since its preparation (decomposition was not involved since all measurements were made on colourless specimens). The highest moment recorded was 4·68 D, and freshly prepared material, m. p. 46—47°, generally had a moment near this. The lowest value was 1·4 D, for a specimen, m. p. 66—67°, which had been stored for six months under nitrogen and then crystallized from hexane. At present we conclude only that freshly prepared material has a largely *cis*-structure,* as the dipole moment of *cis*-$(PEt_3)_2PtMe_2$ is 5·65 D and the *trans*-dimethyl-platinum is rather difficult to obtain. Addition of triethylphosphine to a freshly prepared solution of the dimethylpalladium compound did not result in any significant change during three days at room temperature. The certainly *cis*-compound $(MeS{\cdot}CH_2{\cdot}CH_2{\cdot}SMe)PdMe_2$ had a moment of 6·4 D. The unstable triphenylphosphine complex, $(PPh_3)_2PdMe_2$, has a moment of 4·6 D, so appears to be mainly *cis* [compare *cis*-$(PPh_3)_2PtMe_2$, 5·45 D [7]]. The triethylarsine complex $(AsEt_3)_2PdMe_2$ has a dipole moment, 5·4 D, which indicates a *cis*-structure. The monomethyl compounds have *trans*-structures; this is expected as the *trans*-monomethyl platinum compounds are evidently considerably more stable than their *cis*-isomers, into which they rapidly and almost completely change in the presence of a trace of free phosphine.[7]

All the aryl compounds prepared, and $(PEt_3)_2Pd(C⋮CPh)_2$, have *trans*-structures like the parent dihalides. The *cis*- or *trans*-structures of non-chelate complexes of this group of elements depend on the balance between an electrostatic factor favouring the *trans*- and a π-bonding factor favouring the *cis*-form.[10] An additional factor which could stabilize *trans*-diaryl compounds is the ring-to-ring conjugation which could take place through the d_{yz} metal orbital if the rings are in the xy plane of the complex, or through the d_{xy} orbital if they are at right angles to it.

The *instability* of the *cis*-diaryls is striking; every chelate *cis*-dihalide decomposed when treated with phenyl-lithium. For example, the diphosphine complex $C_2H_4(PPh_2)_2PdCl_2$ gave no arylpalladium compound on treatment with phenyl-lithium, nor did dichlorobipyridylpalladium on treatment with mesityl-lithium. This could be due to the absence of ring-to-ring conjugation, or to a low energy gap between the ground

* Its infrared spectrum was very similar to that of a specimen of *cis*-$(PEt_3)_2PtMe_2$ kindly given to us by Dr. J. Chatt.

[10] Chatt and Wilkins, *J.*, 1952, 273, 4300; 1953, 70; 1956, 525.

state of a *cis*-diaryl compound and a transition state leading to biphenyl formation and decomposition of the complex.

The relatively high stability of the bright orange bipyridyl complex, (bipy)$PdMe_2$, is surprising; it shows no signs of darkening after six months at room temperature. The bipyridyl molecule being taken as co-planar with the xy plane of the complex, it would then be able to interact only with the d_{xz} and d_{yz} metal orbitals. The highest-energy non-bonding metal orbital is very likely to be d_{xy}, and to achieve stability in a covalently bonded complex it is necessary that the energy difference between the highest occupied non-bonding orbital (d_{xy}) and the lowest antibonding orbital should be large.[6,7] We are unable to account for the stability of the bipyridyl complex other than on the basis of a reduction of the energy of the important d_{xy} orbital by hyperconjugation with the methyl groups. Conditions for hyperconjugation should be favourable in view of the rather large metal d orbitals and consequent good overlap with the methyl groups. We believe this effect to be important in stabilizing platinum(II) complexes with ammonia (relative to amines) as suggested by Chatt and Gamlen,[11] and other ammonia complexes of metals with occupied d orbitals such as the cobaltammines.

Reactions.—The monomethyl complex $(PEt_3)_2PdMeBr$ undergoes exchange reactions with, for example, potassium thiocyanate, giving $(PEt_3)_2PdMeSCN$. Similar reactions have been reported in connection with platinum.[7] Attempts to prepare a nitro-derivative resulted in decomposition of the complex, but a monomeric cyanide $(PEt_3)_2PdMeCN$ was obtained.

Dimethyl derivatives were converted into dihalides by ethanolic hydrochloric or hydrobromic acid, and this was a useful reaction for the identification of the least stable organic compounds. Since $(PEt_3)_2PdMe_2$ is prepared in nearly 90% yield by a method involving a hydrolysis step, we were surprised to find that it reacts rapidly with ethanol below room temperature, with evolution of 1 mol. of methane but without deposition of metallic palladium. In this reaction the ethanol appears to act as an acid, forming an ethoxide; the process is unaffected by the presence of styrene. The evolution of 1 mol. of methane is followed by a second much slower reaction accompanied by evolution of more methane together with ethane and ethylene and with deposition of palladium. The second stage is evidently a decomposition involving formation of methyl radicals since acetaldehyde was detected among the volatile products (attack of $CH_3\cdot$ on ethanol), and addition of styrene almost entirely suppressed the formation of C_2 gases as well as giving polystyrene. The reaction sequence (in the absence of styrene) is probably

$$\begin{aligned}(PEt_3)_2PdMe_2 + EtOH &= (PEt_3)_2Pd(OEt)Me + CH_4\\ (PEt_3)_2Pd(OEt)Me &= 2PEt_3 + Pd + EtO\cdot + Me\cdot\\ 2EtO\cdot &= CH_3{\cdot}CHO + C_2H_5{\cdot}OH\\ EtO\cdot + Me\cdot &= CH_4 + CH_3{\cdot}CHO, \text{ etc.}\end{aligned}$$

Since ethanol attacks $(PEt_3)_2PdMe_2$, the effect of a few other very weak acids was studied. Thiophenol reacts rapidly, giving $(PEt_3)_2Pd(SPh)_2$, and *p*-nitrophenylacetylene much more slowly, forming $(PEt_3)_2Pd(C{:}C{\cdot}C_6H_4{\cdot}NO_2\text{-}p)_2$.

The dimethyl compound sublimes without decomposition at 40—50° in vacuum, but completely decomposes when heated for several hours at 100° in a sealed tube, giving a mixture of ethane and ethylene (in one experiment 92 and 8%, respectively) with only a trace of methane.

In decompositions leading to deposition of metallic palladium, the metal is likely to be present transiently in a nascent or atomic state which must be the most reactive form of the element. In fact, it reacts in this state with triphenylphosphine, forming $(PPh_3)_4Pd$

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[11] Chatt and Gamlen, *J.*, 1956, 2371.

which had previously been prepared by other methods.[12] No blackening was observed when $(PEt_3)_2PdMe_2$ decomposed in ethanol in the presence of excess of triphenylphosphine.

Infrared Spectra.—Spectra of methyl complexes are so very similar to those of the parent halides that bands due to methyl bound to palladium are easily recognized. Spectra were taken by using the potassium bromide or iodide disc method, since these generally unstable compounds lasted longer in this form than in solution in organic solvents.

In the CH stretching region the spectrum of $(bipy)PdMe_2$ was very similar to that of $(bipy)PdCl_2$ except for two strong additional bands at 2919 and 2842 cm.$^{-1}$. Similarly, $(PPh_3)_2PdMe_2$ had bands at 2945 and 2876 cm.$^{-1}$, absent from $(PPh_3)_2PdCl_2$. Most complexes prepared were not suitable for study in this region owing to the presence of many ethyl groups (PEt_3 complexes), but a rather low-frequency band, 2854 cm.$^{-1}$, was observed with o-$C_6H_4(AsMe_2)_2PdMe_2$ and was absent from the corresponding dibromide.

At lower frequencies the two major features of the spectra of methyl complexes were a single sharp band at 1129—1180 cm.$^{-1}$, which by analogy to methyl compounds of other heavy metals we assign to a symmetrical methyl deformation. The bisarsine compound $(AsEt_3)_2PdMe_2$ was exceptional in having two bands (1152 and 1124 cm.$^{-1}$) in this region. The methyl complexes also had absorption bands in the range 435—534 cm.$^{-1}$. Both these features are absent from the parent halides. Two low-frequency bands were observed in dimethyl and only one in monomethyl complexes, and we assign them to $Pd-CH_3$ stretching, regarding the methyl group as if it were an atom of atomic weight 15. The lower frequencies of $(PEt_3)_2PdMe_2$ (457 and 491 cm.$^{-1}$) compared with *cis*-$(PEt_3)_2PtMe_2$ (523 and 506 cm.$^{-1}$) reflect the lower force constant of the Pd–C bond, in accordance with the chemical evidence of weaker Pd–C bonding.

In the Table, only those infrared bands are included which are absent from the parent halides. The methyl deformation band in the 1150 cm.$^{-1}$ region is omitted in the case of $(bipy)PdMe_2$ because of the complexity of the spectrum of $(bipy)PdCl_2$ in this region.

Organopalladium compounds prepared in the course of this work are listed in the Table.

Methyl derivatives	M. p.*	Infrared bands (cm.$^{-1}$)	Dipole moment (D)
$(PEt_3)_2PdMeBr$	73—74°	1162, 510	4·0
$(PEt_3)_2PdMeSCN$	86—87	1180, 526	
$(PEt_3)_2PdMeCN$	78	(2127, 2117 CN), 1161, 502	4·75
$(PEt_3)_2PdMe_2$	47—49	1164, 491, 457	See text)
$(AsEt_3)_2PdMe_2$	49 *	1152, 1124, 498, 479	5·4
$(PPh_3)_2PdMe_2$	197—198 *	1129, 529, 482	4·6
$(bipy)PdMe_2$	155 *	534, 522	
$PBu^n_3(Me)Pd(SEt)_2Pd(Me)PBu^n_3$	51—53	1148, 501	
$(MeS{\cdot}CH_2{\cdot}CH_2{\cdot}SMe)PdMe_2$	75 *	1168, 525, 512	
$(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)PdMe_2$	Oil	1160, 518, 502	
$(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)PdMe_2$	166—168 *	1149	
o-$C_6H_4(AsMe_2)_2PdMe_2$	105 *	1160, 498, 435	
o-$C_6H_4(AsMe_2)(PEt_2)PdMeBr$	98—100		
(cyclo-octa-1,5-diene)$PdMe_2$	Too unstable to obtain these data		

Aryl derivatives	M. p.*	Dipole moment (D)	Aryl derivatives	M. p.*	Dipole moment (D)
trans-$(PEt_3)_2PdPhBr$	89° *	3·6	$(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}NMe_2)_2$	99—100° *	
trans-$(PEt_3)_2PdPh_2$	95 *	0	$[(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}NMe_3)_2]I_2$	140 *	
trans-$(PEt_3)_2Pd$(mesityl)Br	162 *	3·52	*trans*-$(PEt_3)_2Pd(C{\vdots}CPh)_2$	162—164 *	0
$(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}CF_3)Br$	145—146·5		$(PEt_3)_2Pd(p\text{-}NO_2{\cdot}C_6H_4{\cdot}C{\vdots}C)_2$	123—125 *	
$(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}CF_3)Ph$	74—75 *				

* With decomposition.

EXPERIMENTAL

Microanalyses (C, H, and F) are by Mr. A. Wiper, of these laboratories.

Combustion analyses presented difficulties in many instances, partly because several of the compounds were so unstable that some decomposition took place before analysis, and partly

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[12] Malatesta and Angoletta, *J.*, 1957, 1186.

because the combustion residue often retained carbon. At a relatively late stage experiments on the combustion of stable palladium complexes showed that better and more reproducible results were obtained when, at the end of a combustion, the boat containing the residue was heated with an oxygen-enriched flame. In view of these difficulties we commonly used a gravimetric procedure in which an organopalladium compound was converted back into a halide which was identified by mixed m. p. and infrared spectrum.

Palladium was determined as its dimethylglyoxime complex after cautious destruction of the organopalladium compound by nitric acid.

Infrared spectra were measured with a Grubb-Parsons GS2A spectrometer, generally in potassium iodide discs.

Methyl Derivatives.

trans-*Bromo(methyl)bistriethylphosphinepalladium*, [$(PEt_3)_2PdMeBr$].—The dibromide $(PEt_3)_2PdBr_2$ (10 g., 0·02 mole) in ether (200 c.c.) was cooled to −65° and methylmagnesium bromide (0·045 mole) in ether (40 c.c.) was added with stirring during 30 min. The reaction mixture was stirred for 15 min. at −65° and then for 30 min. as it was allowed to reach room temperature; the colour changed from yellow to white. After hydrolysis at 0° with water (100 c.c.) the ether phase was separated from the filtered mixture, and the crude product from evaporation of the solvent was crystallized from hexane, yielding 6·7 g. (78%) of colourless *complex*. It is readily soluble in acetone, ethanol, and hydrocarbons (Found: C, 35·0; H, 7·4; Pd, 24·7, 24·6. $C_{13}H_{33}BrP_2Pd$ requires C, 35·6; H, 7·6; Pd, 24·4%).

Thiocyanato(methyl)bistriethylphosphinepalladium, [$(PEt_3)_2PdMeSCN$].—Potassium thiocyanate (0·089 g.) was added to $(PEt_3)_2PdMeBr$ (0·40 g.) in ethanol (5 c.c.). A white solid was precipitated and after the addition of more ethanol the suspension was warmed. Solvent was removed at the pump, and the pale yellow residue was washed with water, dried in air, and crystallized from methanol–water, forming long needles (Found: C, 40·4; H, 8·1. $C_{14}H_{33}NPPdS$ requires C, 40·4; H, 8·0%).

trans-*Cyano(methyl)bistriethylphosphinepalladium*, [$(PEt_3)_2PdMeCN$].—The bromo(methyl) compound $(PEt_3)_2PdMeBr$ (1 g.) was dissolved in methanol (~10 c.c.) and excess of potassium cyanide was added. After 16 hr. at room temperature the product was precipitated as an oil at 0° by addition of water. After about an hour, scratching induced crystallization, and the white solid was dried and crystallized from hexane (Found: C, 43·7; H, 8·5%; *M*, cryoscopically in 1·72 and 3·90% benzene solution, 395, 395. $C_{14}H_{33}NP_2Pd$ requires C, 43·8; H, 8·65%; *M*, 384).

Dimethyl(bistriethylphosphine)palladium, [$(PEt_3)_2PdMe_2$].—To the dibromide $(PEt_3)_2PdBr_2$ (10·0 g., 0·02 mole) were added ether (200 c.c.) and a trace of triethylphosphine, and to the cooled mixture (−60°) was added methyl-lithium (0·045 mole) in ether (38 c.c.) during 15 min. Stirring was continued for 15 min. after the reaction mixture had reached room temperature. Evaporation (by pumping) of the ether phase, after hydrolysis at 0°, afforded a crude *complex*, which was crystallized from hexane (7·4 g., 90%) (Found: C, 44·6; H, 9·6; Pd, 28·0, 27·9. $C_{14}H_{36}P_2Pd$ requires C, 45·1; H, 9·7; Pd, 28·6%).

Reactions of Dimethyl(bistriethylphosphine)palladium.—Thermal decomposition. The dimethyl compound (0·1566 g., 0·4196 mmole) was heated for 16 hr. in a sealed tube at 100°. The sealed tube was then connected to a vacuum system, the seal broken, and volatile matter pumped off through two traps at −196° into a gas burette. Only 0·028 c.c. (*i.e.*, c.c. corrected to S.T.P., as for all later values) of gas was collected, and this could only be hydrogen or methane. A further 12·1 c.c. of gas were pumped off when the traps were allowed to warm to −96°, and this was shown by combustion analysis and infrared spectrum to consist of 92% ethane and 8% ethylene.

Ethanolic hydrobromic acid. To the dimethyl compound (0·0953 g., 0·255 mmole) was added degassed aqueous-ethanolic hydrobromic acid. The gaseous reaction product after passage through two traps at −196°, amounted to 11·1 c.c. (theoretical for 2 mols. of methane, 11·4 c.c.).

Ethanol. Degassed ethanol (10 c.c.) was added at room temperature to the dimethyl compound (0·1341 g., 0·3593 mmole), and the rapid reaction was allowed to continue until the first sign of darkening, at which stage the vessel was cooled in liquid air and 8·53 c.c. of methane (identified by combustion analysis) were pumped off. Volatile material which had condensed in liquid-air traps was then condensed back in the reaction vessel, and the second stage of decomposition allowed to proceed for 3 hr. at room temperature. Fractional condensation of the volatile products yielded methane (4·57 c.c.) and mixed gases (2·60 c.c.) in which ethylene and acetaldehyde were identified by infrared spectra.

Ethanol and styrene. Freshly distilled styrene was condensed on another sample of the dimethyl compound (0·1256 g., 0·3365 mmole), and degassed ethanol added at room temperature. The initial rapid reaction yielded methane (7·2 c.c., 0·322 mmole), and the subsequent slow reaction (overnight at room temperature) yielded methane (4·9 c.c., 0·219 mmole) and only a trace (0·13 c.c.) of C_2 gases. Polystyrene (0·38 g.) was recovered when the filtered product was poured into methanol.

Ethanol and triphenylphosphine. When the dimethyl compound was added to excess of triphenylphosphine in ethanol, a yellow precipitate, m. p. 95—105° (decomp.), separated and was identified as tetrakistriphenylphosphinepalladium(0), since its infrared spectrum was identical with that of a specimen prepared by Malatesta and Angoletta's method. There was no deposition of palladium in this reaction.

Thiophenol. To the dimethyl compound (0·58 g.) in hexane (10 c.c.) was added thiophenol (2·12 mol.). Gas was evolved and the solution became yellow. Next day the orange-yellow crystalline *diphenylthio(bistriethylphosphine)palladium* was collected and crystallized from hexane, m. p. 141° (Found: C, 51·3; H, 7·2. $C_{24}H_{40}P_2PdS_2$ requires C, 51·0; H, 7·2%).

p-*Nitrophenylacetylene.* To the dimethyl compound (0·5 g.) in benzene (10 c.c.) was added *p*-nitrophenylacetylene (1·98 mol.) in benzene (10 c.c.). The solution rapidly darkened and after 2 days at room temperature was chromatographed through alumina. Elution with hexane and then benzene yielded the yellow *complex* (Found: C, 52·6; H, 6·0. $C_{28}H_{38}N_2O_4P_2Pd$ requires C, 52·9; H, 6·0%).

Dimethyl(bistriphenylphosphine)palladium, $[(PPh_3)_2PdMe_2]$.—To the dichloride $[(PPh_3)_2PdCl_2]$ (14·0 g., 0·02 mole) suspended in ether (200 c.c.) at −50° was added methyl-lithium (0·044 mole) in ether (75 c.c.). The mixture was then allowed to warm to room temperature and more methyl-lithium was added to the cooled mixture until a positive colour test (Michler's ketone) was obtained at room temperature. A total of 3 mol. was required. The *complex* obtained after hydrolysis at 0° was very unstable and decomposed when warmed to 35—40° in the presence of solvents; it was crystallized by cooling to −78° its solution in tetrahydrofuran or ethyl methyl ketone (Found: C, 71·3; H, 6·0. $C_{38}H_{36}P_2Pd$ requires C, 69·0; H, 5·5. 0·4871 mole of product, when treated in benzene solution with hydrochloric acid, yielded 0·4316 mmole of dichloride).

Bipyridyl(dimethyl)palladium, $[C_{10}H_8N_2PdMe_2]$.—To dibromobipyridylpalladium (10·0 g.) suspended in ether (200 c.c.) at −60° was added methyl-lithium (2·7 mol.), and the mixture was allowed to attain room temperature. 3·0 mol. of methyl-lithium were required before a positive colour test was obtained. After hydrolysis of the mixture, the *complex* was dried and crystallized from acetone, forming orange needles (4 g., 57%) (Found: C, 48·8, 48·8; H, 5·1, 4·9. $C_{12}H_{14}N_2Pd$ requires C, 49·2; H, 4·8%. 0·2112 g. afforded 0·2363 g. of dichloride on treatment with ethanolic hydrochloric acid; $C_{12}H_{14}N_2Pd$ requires 0·240 g.). The solubility of this compound in benzene was too low to allow its dipole moment to be measured.

1,2-*Di(methylthio)ethane(dimethyl)palladium,* $[C_2H_4(SMe)_2PdMe_2]$.—To the dichloride $C_2H_4(SMe)_2PdCl_2$ (12·0 g.) suspended in ether (175 c.c.) methyl-lithium was added until a positive colour test was obtained, 3 mol. being required. No reaction appeared to take place below −10°. After hydrolysis at 0°, evaporation of the ether phase afforded a buff-coloured crude *complex* which was crystallized from acetone [0·0520 g. of complex afforded the dichloride, (0·0604 g.) and methane (8·72 c.c.), when treated with aqueous ethanolic hydrochloric acid. $C_6H_{16}PdS_2$ requires dichloride, 0·0604 g.; methane, 8·99 c.c.].

1,2-*Di(ethylthio)ethane(dimethyl)palladium,* $[C_2H_4(SEt)_2PdMe_2]$.—Prepared similarly this was an unstable oil, which could not be purified but was identified by conversion into the dichloride and by the characteristic Pd–Me infrared absorptions observed at 518 and 502 cm.$^{-1}$.

1,2-*Bis(diphenylphosphino)ethane(dimethyl)palladium,* $[C_2H_4(PPh_2)_2PdMe_2]$.—The dichloride $C_2H_4(PPh_2)PdCl_2$ (8·1 g.), treated with methyl-lithium until a positive colour test was obtained, yielded after hydrolysis a crude *complex* (6·7 g.), which was thrice crystallized from acetone (by cooling) [Found: C, 61·5; H, 5·6. $C_{28}H_{30}P_2Pd$ requires C, 62·8; H, 5·65%. 0·1930 g. afforded the dichloride (0·2040 g.) when treated with ethanolic hydrochloric acid. $C_{28}H_{30}P_2Pd$ requires 0·2080 g.].

*Dimethyl-*o*-phenylenebisdimethylarsinepalladium,* $[C_6H_4(AsMe_2)_2PdMe_2]$.—From the dibromide $C_6H_4(AsMe_2)_2PdBr_2$ and methyl-lithium, a crude product was obtained that appeared to remain unchanged for 3 weeks at room temperature (some free diarsine was present). The *complex* was crystallized by cooling its solution in acetone, but as its purification progressed, so apparently did its tendency to decompose. A specimen of the best product, which was colourless, turned brown when kept overnight in a refrigerator [Found: Pd, 24·85. $C_{12}H_{22}As_2Pd$ requires Pd, 25·35%. 0·2894 g. afforded the dibromide (0·3574 g.) when treated with aqueous-ethanolic hydrobromic acid. $C_{12}H_{22}As_2Pd$ requires 0·3732 g.].

*Bromo-{*o*-dimethylarsinophenyl)diethylphosphine}(methyl)palladium,* [(o-C_6H_4·$AsMe_2PEt_2$)PdMeBr].—From the dibromide o-C_6H_4·$AsMe_2PEt_2PdBr_2$ (10·7 g.) and methyl-lithium, there was obtained a white crystalline *complex* (6 g., 64%) (from acetone). This material was much more stable than the diarsine derivative described above [Found: C, 33·5; H, 4·8. $C_{13}H_{23}AsBrPPd$ requires C, 33·1; H, 4·9%. 0·3301 g. afforded the dibromide (0·3760 g.) when treated with aqueous-ethanolic hydrobromic acid. $C_{13}H_{23}AsBrPPd$ requires 0·3756 g.].

Bistri-n-butylphosphine(dimethyl)-μμ′-bisethylthiodipalladium (II).—The dichloride (I) (16·2 g.), after treatment with methyl-lithium, yielded crude *complex* (13·0 g., 84%), which was purified by cooling its solution in acetone (Found: C, 74·1; H, 9·1. $C_{30}H_{70}P_2Pd_2S_2$ requires C, 46·8; H, 9·1%).

*Cyclo-octa-*1,5-*diene(dimethyl)palladium,* [$C_8H_{12}PdMe_2$].—To the dichloride $C_8H_{12}PdCl_2$ (8·5 g.) suspended in ether (150 c.c.) at −40° was added methyl-lithium (2·2 mol.). The mixture became black as it warmed to room temperature. Evaporation of the ether phase, after separation of palladium from the hydrolyzed mixture, yielded a small amount of white solid which darkened at room temperature. This material was dissolved in ether under nitrogen and filtered into a receiver at −78°. The white crystalline *complex* was separated, washed with cold ether, pumped dry, and stored at −78°. All operations were carried out as quickly as possible [Found: Pd, 43·2. $C_{10}H_{18}Pd$ requires Pd, 43·55%. 0·4790 g. afforded the dichloride (0·5400 g.) when treated with aqueous ethanolic hydrochloric acid. $C_{10}H_{18}Pd$ requires 0·5592 g.].

cis-*Bistriethylarsine(dimethyl)palladium,* [$(AsEt_3)_2PdMe_2$].—This was prepared from the dibromide $(AsEt_3)_2PdBr_2$ and methyl-lithium by the procedure used to obtain dimethylbis(triethylphosphine)palladium. It was crystallized by cooling its solution in hexane containing a trace of triethylarsine (Found: C, 36·4; H, 8·1. $C_{14}H_{36}As_2Pd$ requires C, 36·4; H, 7·8%).

Aryl Derivatives.

trans-*Bromo(phenyl)bistriethylphosphinepalladium,* [$(PEt_3)_2PdPhBr$].—To the dibromide $(PEt_3)_2PdBr_2$ (10·0 g.) in ether (200 c.c.) at −60° was added phenylmagnesium bromide (1·1 mol.) in ether (75 c.c.). No reaction was apparent at −60° but the solution darkened at −40°. The mixture was stirred for 30 min. at room temperature, cooled to 0°, and hydrolyzed. Evaporation of the ether phase yielded 7 g. of yellow product which contained starting material. The colourless *complex* was separated chromatographically on alumina, the yellow dibromide being eluted first, by hexane (Found: C, 42·2; H, 7·0. $C_{18}H_{35}BrP_2Pd$ requires C, 43·2; H, 7·1%).

trans-*Diphenyl(bistriethylphosphine)palladium,* [$(PEt_3)_2PdPh_2$].—To the dichloride $(PEt_3)_2PdCl_2$ (7·04 g.) in ether (200 c.c.) at −75° was added phenyl-lithium (2 mol.) during 35 min., after which the mixture was stirred for 40 min. at −75° and then allowed to warm to room temperature. After hydrolysis at 0°, evaporation of the ether phase yielded a yellowish-green crude product (7·8 g.) which was washed with a little methanol and crystallized by cooling its solution in acetone, giving colourless *complex* (4·7 g., 55%) (Found: C, 58·4; H, 8·3; Pd, 21·9, 21·5. $C_{24}H_{40}P_2Pd$ requires C, 58·0; H, 8·1; Pd, 21·5%).

trans-*Bromo(mesityl)bistriethylphosphinepalladium,* [$(PEt_3)_2Pd$(mesityl)Br].—To the dibromide $(PEt_3)_2PdBr_2$ (10·0 g.) in ether (175 c.c.) at −50° was added mesitylmagnesium bromide (2·2 mol.) during 10 min. The mixture darkened as it warmed to room temperature. After hydrolysis at 0°, the ether phase was evaporated and yielded a pale yellow solid which gradually became black on continued pumping. The crude product was dissolved under nitrogen in ethyl methyl ketone, filtered from finely divided metallic palladium, and crystallized by cooling the solution. Repetition of this procedure yielded colourless *complex* (2·05 g., 19%) (Found: C, 46·4; H, 7·7; Pd, 19·5, 19·3. $C_{21}H_{41}BrP_2Pd$ requires C, 46·5; H, 7·6; Pd, 19·7%).

Addition of aqueous ethanolic hydrobromic acid to an ethanol solution of the monomesityl compound caused no apparent reaction, and the substance is stable to the air.

*Bromo(bistriethylphosphine)-(*p*-trifluoromethylphenyl)palladium,* [$(PEt_3)_2Pd(p$-C_6H_4·$CF_3)Br$].

—Reaction between the dibromide and *p*-trifluoromethylphenylmagnesium bromide (1·1 mol.) yielded a mixture of starting material and colourless product. These were separated chromatographically on alumina, the dibromide being eluted first (hexane). The *complex* was sufficiently stable to be recrystallized in the normal way (Found: C, 39·5; H, 6·2; Br, 13·7; F, 9·9. $C_{19}H_{34}BrF_3P_2Pd$ requires C, 40·2; H, 6·0; Br, 14·1; F, 10·0%).

*Phenyl(bistriethylphosphine)-(*p*-trifluoromethylphenyl)palladium,* $[(PEt_3)_2PdPh(p\text{-}C_6H_4{\cdot}CF_3)]$.—The monobromide (6·8 g.) just described was treated with phenyl-lithium (1·2 mol.) in ether, and yielded colourless *complex* (5·8 g., 85%), which was crystallized by cooling its solution in acetone (Found: C, 53·2; H, 7·5; Pd, 18·8. $C_{25}H_{39}F_3P_2Pd$ requires C, 53·1; H, 6·7; Pd, 18·9%).

*Bis-(*p*-dimethylaminophenyl)(bistriethylphosphine)palladium,* $[(PEt_3)_2Pd(p\text{-}C_6H_4{\cdot}NMe_2)_2]$.—The dichloride $(PEt_3)_2PdCl_2$ (12·4 g.) was treated with *p*-dimethylaminophenyl-lithium (2·1 mol.) in ether at −65°. The mixture was allowed to warm to room temperature, and a colour test was then positive but weak. After hydrolysis at 0°, the mixture was brown-black. Evaporation of the filtered ether phase yielded an unstable white product (14 g., 80%). About 2 g. of this were recrystallized twice by cooling the solution in hexane, and this was done as quickly as possible since the *complex* readily decomposes (Found: Pd, 18·0. $C_{28}H_{50}N_2P_2Pd$ requires Pd, 18·8%).

The remainder of the base (12 g.) was dissolved in ether, and excess of methyl iodide added. After 4 hr. the white precipitate of *dimethioide* was collected and recrystallized from methanol (Found: Pd, 12·9; I, 30·0. $C_{30}H_{56}I_2N_2P_2Pd$ requires Pd, 12·3; I, 29·3%).

trans-*Di(phenylethynyl)bistriethylphosphinepalladium,* $[(PEt_3)_2Pd(C{:}CPh)_2]$.—The dibromide $(PEt_3)_2PdBr_2$ and phenylethynylmagnesium bromide (2·2 mol.) afforded a colourless *complex* (66% yield) which was crystallized by cooling its solution in toluene (Found: C, 61·6; H, 7·7; Pd, 20·0. $C_{28}H_{40}P_2Pd$ requires C, 61·7; H, 7·4; Pd, 19·6%).

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