Reactivity of Co-ordinated Ligands. Part XV.[1] Formation of Complexes containing Group V Donor Atoms and Metal–Carbon σ-bonds

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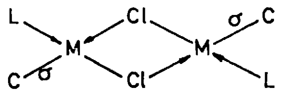
The reactions of various palladium(II) and platinum(II) species with a number of ligands which may function as electron pair donors while simultaneously forming metal–carbon σ-bonds have been examined. Compounds containing metal–carbon σ-bonds have been obtained for *NN*-2-trimethylbenzylamine, *N*-benzylpiperid-4-one, 1-phenyl-*NN*-dimethylcyclohexylamine, triphenylmethylamine, *N*-methyltriphenylmethylamine, benzophenone phenylhydrazone, and benzo[*h*]quinoline. Various substitution and displacement reactions of some similar derivatives have also been examined.

As part of our investigation into the reactions of co-ordinated ligands, we became interested in complexes of type (I), in which the ligand is bound to the metal through both a donor atom L (L = Group V or Group VI element) and a carbon–metal σ-bond. Cope *et al.*[2] have shown that such compounds are readily formed by the reaction of azobenzene, *NN*-dimethylbenzylamine, or certain substituted *NN*-dimethylbenzylamines[3] with the appropriate palladium(II) or platinum(II) compound in the presence of either an excess of ligand or some non-co-ordinating base such as tri-n-butylamine [*e.g.* reaction (I)]. They found, however, that such reactions are not general, and outlined three requirements that must be met by the ligand before this reaction will proceed: (i) the nitrogen must be tertiary, (ii) it must be possible

(I)



M = Pd or Pt

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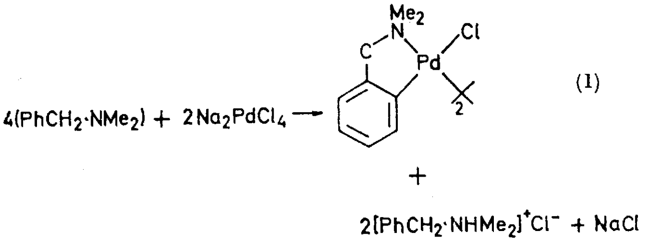
[1] Part XIV, J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.

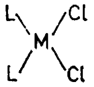
[2] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

[3] A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1968, **90**, 909.

to form a planar five-membered ring containing the metal, and (iii) the metal must displace a hydrogen ion from an aromatic carbon atom that is not highly deactivated towards electrophilic attack.

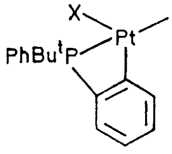


If these conditions are not met a bis(ligand)metal dichloride complex (II) is formed. More recently other workers have used reactions similar to those employed by Cope to prepare a range of complexes of type (I). The ligands employed have, in general, conformed to Cope's three requirements. A few exceptions have, however, been recorded. These include the platinum and palladium complexes of 8-methylquinoline in which the metal is bonded to an aliphatic carbon [4] and some related complexes, *e.g.* (III), in which the metal is part of a four-membered ring.[5] We have investigated the reactions of some palladium(II) and platinum(II) compounds with a variety of ligands which have the potential of forming carbon–metal σ-bonds in order to investigate the scope of Cope's reaction and test more fully his three criteria. In addition, we have prepared some derivatives of type (I) complexes in which the metal–carbon σ-bond has been retained. These include compounds in which the halogen-bridged dimers have been bridge split by the addition of various monodentate ligands, compounds in which the bridging chlorides have been exchanged for other anionic ligands, and cationic complexes in which the bridging chlorides have been exchanged for various neutral ligands.



M = Pd or Pt

(II)



(III)

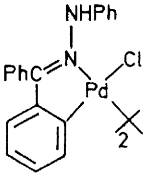
RESULTS AND DISCUSSIONS

The complexes prepared in this work are given in the Tables. The assignment of their structures [*i.e.* type (I) or type (II)] is based principally on the results of elemental analyses which are given in the Tables. The compounds are not, in general, sufficiently volatile to permit mass spectroscopic examination, and it is difficult or impossible to distinguish between the two structural types directly from ^{1}H n.m.r. or i.r. spectroscopic data.

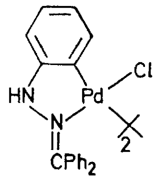
Reactions of Substituted Benzylamines.—Previous workers have examined the reactions of a number of ring-substituted *NN*-dimethylbenzylamines and have shown that the nature of the ring substituent affects the course of the reaction.[3] We have also found this to be the case. The slightly activated *NN*-2- and 4-trimethylbenzylamines both react with sodium chloropalladite in methanol to give complexes of type (I). The same type of complex is formed under these conditions by *NN*-dimethylnaphthylmethylamine, which can be considered to be a ring-substituted benzylamine. The reaction of the highly hindered *NN*-3,5-tetramethylbenzylamine, however yields a type (II) complex. This behaviour contrasts with that of the similarly hindered but more highly activated *NN*-dimethyl-3,5-dimethoxybenzylamine, which has been reported to form a type (I) complex.[3]

We have also investigated the reactions of various other *N*-substituted and α-substituted benzylamines. Replacement of one or both *N*-methyl groups with other substituents does not appear to affect the course of the reaction. Both *N*-methyl-*N*-phenylbenzylamine and *N*-benzylpiperidin-4-one react with sodium chloropalladite to give type (I) complexes. The substitution of the α-benzyl position with bulky groups, however, favours the formation of type (I) complexes. Not only does the tertiary amine, 1-phenyl-*NN*-dimethylcyclohexylamine form a type (I) palladium complex but so do the primary and secondary amines, triphenylmethylamine and *N*-methyltriphenylmethylamine. These are the first examples of primary and secondary amines to form such complexes with palladium.

Reaction of Ligands containing Acyclic Unsaturated Nitrogen Atoms.—It is well established that azobenzene readily forms complexes of type I.[2] It was, therefore, of some interest to examine the reactions of organic molecules which are stereochemically and electronically similar to azobenzene. Within this class the first compounds investigated were phenylhydrazones, and it was found that benzophenone phenylhydrazone readily forms a type (I) complex. This species, however, offers two potential sites [see (IV) and (Va)] for σ-bond formation both of which satisfy all Cope's criteria. In order to distinguish between these two possibilities, the reaction of sodium chloropalladite with cyclohexanone phenylhydrazone was investigated since this compound



(IV)



(Va)

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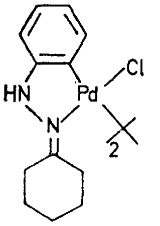
[4] G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Comm.*, 1970, 912.

[5] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. (A)*, 1971, 3833.

offers only *one* potential site for σ-bond formation. If the benzophenone phenylhydrazone complex has structure (Vb) then it is reasonable to assume that the cyclohexanone phenylhydrazone would be of the same type involving metal–carbon σ-bond formation with the aromatic ring [see (Va)]. If, on the other hand, σ-bond formation takes place with one of the two alternative aromatic rings in the benzophenone phenylhydrazone complex [*i.e.* structure (IV)], then one would expect cyclohexanone phenylhydrazone to form a type (II) complex. Cyclohexanone phenylhydrazone does form a type (II) palladium complex which suggests that the type (I) complex of benzophenone phenylhydrazone has structure (IV). The reactions of two oximes, those of benzaldehyde and benzophenone, were also examined: in both cases type (II) complexes were formed.



(Vb)

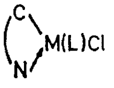
Palladium complexes of the Schiff bases benzylideneaniline and a number of substituted benzylideneanilines have been reported previously to be of type (I).[6] These complexes were reported as the products of the reaction of bis(benzonitrile)palladium dichloride and a large excess of the Schiff base in methanol under reflux. McQuillin *et al.*[7] have subsequently reported that this reaction yields the related bis(aniline)palladium dichloride species. If the reaction is carried out in dichloromethane, however, certain benzylideneanilines form the corresponding type (II) Schiff base complex. We had undertaken an investigation of these reactions prior to the publication of McQuillin's work. In general, our results agree with those of McQuillin. Seven different Schiff bases (Table 3) were treated with an excess of bis(benzonitrile)palladium dichloride in aqueous methanol. In all but one case, the related bis(aniline)-palladium dichloride is produced. The Schiff base *m*-nitrobenzylideneaniline, however, reacts with bis(benzonitrile)palladium dichloride to give a material which appears to be a mixture of bis(aniline)palladium dichloride and *cis*-bis-(*m*-nitrobenzylideneaniline)palladium dichloride. The i.r. spectrum of this mixture contains all the bands found in the spectrum of pure bis(aniline)-palladium dichloride as well as those in the spectrum of pure *cis*-bis-(*m*-nitrobenzylidinaniline)palladium dichloride (*vide infra*).

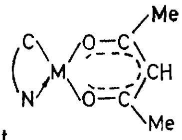
We have also investigated the reactions of benzylideneaniline and *m*-nitrobenzylideneaniline with several palladium(II) species under other conditions. The reaction of benzylideneaniline with sodium chloropalladite in basic aqueous methanol yields a material (VI) which does not contain any bis(aniline)palladium dichloride although it does appear to contain a small amount of palladium. The results of the elemental analysis of this material are reasonably consistent with those expected for bis(benzylideneaniline)palladium dichloride and it has been assigned a *cis*-structure based on its i.r. spectrum in the region 300—400 cm^{-1} (ν_{M-Cl} 357, 345, and 332 cm^{-1}). If this material is extracted with boiling toluene, a second compound (VII) is obtained whose i.r. spectrum differs slightly from that of (VI); the compound is, however, also free from hydrolysis products. This material has an analysis fairly close to that expected for bis(benzylideneaniline)palladium dichloride and it has been assigned a *trans*-structure (ν_{M-Cl} 344 cm^{-1}). Similar results were obtained with *m*-nitrobenzylideneaniline. The reaction of benzylideaniline with bis-(benzonitrile)palladium dichloride in dichloromethane or strictly anhydrous methanol produces materials which are mixtures of (VI) and (VII). This result, coupled with the fact that benzaldehyde is the by-product of this reaction rather than the dimethyl acetal of benzaldehyde, indicates that the formation of bis(aniline)palladium dichloride reaction arises from a hydrolysis reaction, not an alcoholysis as reported by McQuillin. Finally we have found that our palladium complexes, which are apparently similar to those obtained by McQuillin, are relatively stable towards hydrolysis once they have been formed.

The reactions of a number of ligands in which the nitrogen is part of a heterocyclic system have also been investigated. A type (I) platinum complex of benzo-[*h*]quinoline which is analogous to the previously reported palladium complex[4] can be prepared by the reaction of benzo[*h*]quinoline with potassium chloroplatinite in methanol. If, however, 2,5-diphenyloxazole is treated with sodium chloropalladite, a type (II) complex is the only product.

Reactions with Ligands containing Sulphur and Arsenic Donor Atoms.—Attempts to prepare type (I) complexes with benzyldimethylarsine and benzyl methyl sulphide were unsuccessful. Only type (II) complexes are obtained.

Reactions of Type (I) *Complexes.*—A number of the halogen-bridged dimers easily undergo cleavage reactions with ligands such as pyridine, triphenylphosphine, triphenylarsine, or triphenylstibine and substitution reactions with the conjugate base of acetylacetone to produce the monomeric species (VIII) and (IX). These are more soluble than the corresponding dimeric com-





M=Pd or Pt

(VIII) (IX)

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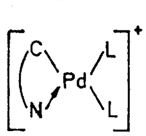
[6] S. P. Molnar and M. Orchin, *J. Organometallic Chem.*, 1969, **16**, 196.

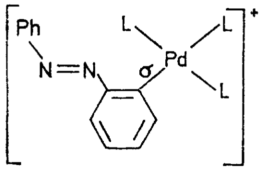
[7] I. Jardine and F. J. McQuillin, *Tetrahedron Letters*, 1972, **6**, 459.

pounds and as a consequence more amenable to spectroscopic study. The type (IX) compound, acetylacetonato(benzo[*h*]quinolin-10-yl-*N*)palladium reacts with triphenylphosphine to form a five-co-ordinate species. This can also be prepared by the reaction of (benzoquinolin-10-yl-*N*)chlorotriphenylphosphinepalladium with acetylacetonatothallium.

The acetylacetonates (IX) also serve as convenient precursors to a number of cationic derivatives. Treatment of these complexes with Ph_3CBF_4 followed by the addition of the appropriate ligand, L, leads to the formation of cations of the type (X). With acetylacetonato[2-(phenylazo)phenyl-*N*]palladium, it was found necessary to employ three moles of unidentate ligand in order to isolate a stable complex. Although these complexes may involve five-co-ordinate palladium(II), it is possible that they possess structure (XI) which involves a unidentate 2-(phenylazo)phenyl-*N* ligand bonded to four-co-ordinate palladium *via* a single σ-bond.[8] Cationic species are also the products of the reaction of the bidentate ligands 1,2-diaminoethane and 1,2-bis(diphenylphosphino)ethane with the halogen-bridged complexes. These are also of the type (X). The dimers also undergo metathetical reactions with SCN^-, $CH_3CO_2^-$, and $CF_3CO_2^-$ to produce the corresponding thiocyanato- and carboxylato-bridged complexes. The ^1H n.m.r. spectra of the di-μ-acetato and di-μ-trifluoroacetato[(dimethylaminophenyl)phenyl-*N*]dipalladium and -diplatinum exhibit two N–Me resonances and the methylene protons appear as an AB quartet. This indicates that those species have a ' folded ' structure similar to that of di-μ-acetatobisallyldipalladium.[8]



(X)



(XI)

EXPERIMENTAL

Preparation of Type (I) *and Type* (II) *Complexes.*—The majority of the reactions used to prepare the type (I) and type (II) complexes were performed using the same basic technique. The method used was a variation of that of Cope *et al.*[2] and involved the reaction of a methanol solution containing 2 equivalents of the appropriate ligand with a methanol solution of 1 equivalent of Na_2PdCl_4. Full experimental details for two typical preparations and exceptions to the standard preparations are given below. The results of other preparations and analytical data are given in Tables 1 and 2. The ligands used were either obtained commercially or prepared using standard procedures. The purity of the ligands was checked using i.r., n.m.r., and mass spectroscopy.

(a) *Di-μ-chloro-bis*[2-(*dimethylaminomethyl*)-5-*methylphenyl*-N]*dipalladium*. A solution of *NN*,3-trimethylbenzylamine (0·30 g, 2 mmol) in methanol (10 ml) was added to Na_2PdCl_4 (0·31 g, 1 mmol) in methanol (20 ml) and the mixture was shaken for 12 h. The yellow solid was filtered off and washed with methanol and ether. Recrystallization from benzene yielded the product as yellow crystals (0·25 g, 85%).

(b) *Dichlorobis*(NN,3,4-*tetramethylbenzylamino*)*palladium*. A solution of Na_2PdCl_4 (0·50 g, 1·82 mmol) in methanol (30 ml) was added with stirring to a solution of *NN*,3,4-tetramethylbenzylamine (0·60 g, 3·64 mmol) and the mixture was set aside for 12 h; tan needles separated. These were filtered off, washed with methanol (10 ml), and dried at room temperature *in vacuo* (yield 0·50 g, 53%). Recrystallization from acetone yielded the pure product as orange needles.

(c) *Reaction of Benzo*[h]*quinoline with Potassium Tetrachloroplatinite*. A mixture of K_2PtCl_4 (0·42 g, 1 mmol) in water (50 ml) and benzo[*h*]quinoline (0·36 g, 2 mmol) in methanol (50 ml) was heated under reflux for 1 h, and then cooled. The yellow precipitate was filtered off and washed with dichloromethane. Soxhlet extraction of this solid for 24 h with dichloromethane gave the pure *product* (0·16 g, 40%) as a yellow powder.

(d) *Preparation of* cis-*dichlorobis*(*benzylideneaniline*)*palladium* (VI). A solution of Na_2PdCl_4 (0·29 g, 1·00 mmol) in methanol (30 ml) was added to a solution of benzylideneaniline (0·36 g, 2·00 mmol) and triethylamine (0·020 g, 0·20 mmol) in methanol (20 ml). The mixture was shaken for 12 h to give a grey-black precipitate. This was filtered off, washed with pentane, and dried at 60° *in vacuo* to give (VI) (0·42 g, 78%).

(e) *Preparation of* trans-*dichlorobis*(*benzylideneaniline*)-*palladium* (VII). A sample of (VI) (0·10 g, 0·19 mmol) was extracted for 60 h with benzene (15 ml) using a Soxhlet apparatus to yield (VII) (0·096 g, 0·17 mmol, 90%).

(f) *Preparation of* cis-*dichlorobis*(m-*nitrobenzylideneaniline*)*palladium*. This material was prepared in exactly the same manner as compound (VI) in 70% yield.

(g) *Preparation of* trans-*dichlorobis*(m-*nitrobenzylideneaniline*)*palladium*. A solution of dichlorobis(benzonitrile)-palladium (0·39 g, 1·0 mmol) and *m*-nitrobenzylideneaniline (0·68 g, 3·0 mmol) in benzene (50 ml) which had been dried over Na–K alloy was heated at 100° in a sealed tube for 24 h. A yellow solid slowly separated leaving a colourless solution. The solid (0·55 g, 0·88 mmol, 88%) was filtered off, washed with methanol, ether, acetone, and pentane, and dried *in vacuo*.

Reactions of Benzylideneanilines with Dichlorobisbenzonitrilepalladium in Methanol.—(a) *Reaction of benzylideneaniline with dichlorobis*(*benzonitrile*)*palladium under anhydrous conditions*. All the glassware used for this reaction was flamed out. Methanol was dried by distillation from $Mg(OMe)_2$. All operations were carried out either under dry nitrogen or *in vacuo*.

A solution of benzylideneaniline (0·45 g, 2·5 mmol) and dichlorobis(benzonitrile)palladium (0·19 g, 0·50 mmol) in methanol (100 ml) was heated at 65° for 3 h and then cooled to room temperature. Tan crystals, which had separated during the course of the reaction were filtered off, washed with methanol, and dried *in vacuo*. The i.r. spectrum of

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[8] M. R. Churchill and R. Mason, *Nature*, 1964, **204**, 777.

this material (yield 0·17 g, 0·32 mmol, 64%) indicates that it is a mixture of (VI) and (VII).

(b) *Reaction of benzylideneaniline with dichlorobisbenzonitrilepalladium.* A solution of benzylideneaniline (0·905 g, 5·00 mmol) and dichlorobis(benzonitrile)palladium (0·395 g, 1·04 mmol) in AnalaR grade methanol (200 ml) was heated at reflux under nitrogen for 3 h and then cooled to room temperature. Tan crystals, which had separated during the course of the reaction, were filtered off, washed with methanol and ether, and dried *in vacuo* at 50° to yield dichlorobisanilinepalladium (0·245 g, 0·67 mmol, 67%). This material was identified by its elemental analysis (Table 3) and by comparison of its i.r. spectrum with that of an authentic sample.

TABLE 1

Chloro-bridged complexes containing a carbon–metal σ-bond

	Yield		Analyses							
			Calculated (%)				Found (%)			
Ligand	Metal	(%)	C	H	N	Cl	C	H	N	Cl
NN,2-Trimethylbenzylamine	Pd	85	41·4	4·9	4·8		41·4	4·9	4·7	
NN,4-Trimethylbenzylamine	Pd	85	41·4	4·9	4·8		41·3	4·9	4·8	
NN-Dimethyl-1-naphthylmethylamine	Pd	80	47·9	4·3	4·3	10·9	47·8	4·6	4·3	12·1
N-Methyl-*N*-phenylbenzylamine	Pd	51	49·7	4·2	4·2	10·5	48·8	4·4	4·0	10·9
N-Benzylpiperidin-4-one	Pd	22	43·6	4·3	4·2		43·0	4·3	4·5	
1-Phenyl-*NN*-dimethylcyclohexylamine	Pd	83	48·9	5·9	4·1	10·3	48·5	6·4	3·9	10·2
Triphenylmethylamine [a]	Pd	56	52·9	3·9	3·2	16·0	53·4	4·1	3·3	15·8
N-Methyltriphenylmethylamine	Pd	60	58·0	4·4	3·4		58·1	4·6	3·2	
Benzophenone phenylhydrazone	Pd	56	55·2	3·6	6·8	8·6	55·2	4·0	6·6	8·8
Benzo[*h*]quinoline	Pt	40	37·8	2·0	3·7	8·7	38·2	2·0	3·4	8·7
2-Phenylpyridine	Pd	60	44·6	2·7	4·7		43·7	2·9	4·3	

[a] The calculated analytical figures are for a species containing one mole of dichloromethane of crystallization per mole of dimer.

TABLE 2

Dichlorobis(ligand)palladium species

		Analyses							
		Calculated (%)				Found (%)			
Ligand	Yield (%)	C	H	N	Cl	C	H	N	Cl
NN,3,5-Tetramethylbenzylamine	60	52·4	6·8	5·6		52·0	5·7	5·6	
Cyclohexanonephenylhydrazone	79	52·1	5·8	10·1		52·5	6·1	9·7	
Benzaldehyde oxime	58	40·1	3·4	6·7		40·3	4·1	6·1	
Benzophenone oxime	67	54·6	3·9	4·9		54·6	4·3	5·2	
2,5-Diphenyloxazole	84	57·9	3·6	4·5		57·8	3·8	4·3	
2-Phenylpyridine	30	54·1	3·7	5·7		53·2	4·0	5·2	
Benzyldimethylarsine	64	38·0	4·6		12·5	37·8	4·7		11·9
Benzyl methyl sulphide	74	42·3	4·4			42·0	4·6		
Benzylideneaniline [a]	80	57·9	4·1	5·2		56·5	4·8	5·6	
Benzylideneaniline [b]	90	57·9	4·1	5·2		58·9	4·3	4·8	
m-Nitrobenzylideneaniline [a]	54	49·6	3·2	8·9		48·3	3·2	8·4	
m-Nitrobenzylideneaniline [b]	87	49·6	3·2	8·9		49·4	3·4	8·9	

[a] Complex to which a *cis*-structure has been assigned. [b] Complex to which a *trans*-structure has been assigned.

(c) *Reactions of substituted benzylideneanilines with dichlorobisbenzonitrilepalladium.* The reactions of various substituted benzylideneanilines with dichlorobis(benzonitrile)palladium were carried out in a similar manner. The products obtained from those reactions were identified by their elemental analyses (Table 3 and by comparison of their i.r. spectra with those of authentic samples of the corresponding dichlorobis(aniline)palladium species.

(d) *Reaction of benzylideneaniline with methanol.* A solution of benzylideneaniline (0·45 g, 2·5 mmol) in AnalaR grade methanol (100 ml) was heated under nitrogen at a reflux temperature for 3 h. Examination of the reaction mixture by g.l.c. showed no hydrolysis products. The solvent was then removed *in vacuo* until *ca.* 10 ml of solution remained. This was cooled at 0° to give colourless crystals (0·40 g, 90%). The i.r. spectrum and m.p. of this material were identical with that of an authentic sample of benzylideneaniline.

Reactions of the Type (I) *Complexes with Lewis Bases.*—(a) *Chloro*[2-(1-*dimethylaminomethylnaphthyl*)-N]*triphenylphosphinepalladium.* Triphenylphosphine (0·52 g, 2 mmol) was dissolved in a solution of di-μ-chloro-bis[2-(1-dimethylaminomethylnaphthyl)-*N*]dipalladium (0·64 g, 1 mmol) in dichloromethane (25 ml). The yellow solution became paler, and addition of light petroleum (b.p. 100—120°), followed by concentration, gave an off-white solid. Recrystallization of this solid from benzene–light petroleum (b.p. 100—120°) gave the pure *product* as pale yellow crystals (0·91 g, 78%).

(b) 1,2-*Bisdiphenylphosphinoethane*[2-(*dimethylaminomethyl*)*phenyl*-N]*palladium hexafluorophosphate.* Di-μ-chloro-bis[2-(dimethylaminomethyl)phenyl-*N*]dipalladium (0·55 g, 1 mmol) was suspended in methanol (25 ml) and the diphosphine ligand (0·87 g, 2·2 mmol) was added to it. When the solution had become clear an aqueous solution of ammonium hexafluorophosphate (15%) was added dropwise till there was no further precipitation of the white product. The white (1·4 g, 95%) powder was washed with water, methanol, and ether.

Other complexes of this type were prepared using these basic methods; they are listed in Table 4 with their analytical data.

Metathetical Ligand Exchange Reactions.—(a) *Di-μ-thiocyanato-bis*[2-(*dimethylaminomethyl*)*phenyl*-N]*dipalladium.*

TABLE 3

Products from the reactions of Schiff bases with dichlorobisbenzonitrilepalladium in aqueous methanol

		Analyses											
		Calc. for type (I) complex (%)			Calc. for type (II) complex (%)			Calc. for corresponding dichlorobis(aniline)-palladium (%)			Found (%)		
Schiff base	Yield (%)	C	H	N	C	H	N	C	H	N	C	H	N
Benzylideneaniline	80	48·4	3·2	4·3	57·9	4·1	5·2	39·6	3·9	7·7	39·7	4·1	7·4
Benzylidene-*p*-toluidine	48	50·0	3·6	4·2	59·2	4·6	4·9	42·9	4·6	7·2	42·9	4·8	7·0
Benzylidene-*m*-nitroaniline	70	42·5	2·5	7·6	49·6	3·2	8·9	31·8	2·6	12·4	32·7	3·1	13·6
m-Nitrobenzylideneaniline [a]		42·5	2·5	7·6	49·6	3·2	8·9	39·6	3·9	7·7	45·1	3·5	8·6
p-Chlorobenzylideneaniline	65	43·8	2·5	3·9	51·3	3·3	4·6	39·6	3·9	7·7	40·9	4·1	7·2
Benzylidene-*p*-chloroaniline	68	43·8	2·5	3·9	51·3	3·3	4·6	33·3	2·8	6·5	33·4	3·0	6·3
p-Chlorobenzylidene-*p*-chloroaniline	50	39·9	2·1	3·6	46·1	2·7	4·1	33·3	2·8	6·5	35·3	2·8	5·6

[a] The i.r. spectrum of the product from this reaction indicates that it is a mixture of dichlorobisanilinepalladium and *cis*-bis(*m*-nitrobenzylideneaniline)dichloropalladium.

TABLE 4

Products from the reactions of neutral ligands with the halide-bridged dimers

			Analyses							
			Calc. (%)				Found (%)			
Complex [a]		Yield (%)	C	H	N	Cl	C	H	N	Cl
(dmp)PdCl	Ph_3Sb	67	47·4	4·8	7·9	10·0	47·1	5·0	7·9	10·2
(dmp)Pd(SCN)	Ph_3P	92	60·0	4·8	5·0		60·0	5·2	4·7	
(dan)PdCl	Ph_3P	73	62·9	4·7	2·9	6·2	62·5	4·7	2·3	6·6
	Ph_3AS	57	58·5	4·5	2·3	5·7	57·9	4·7	1·9	5·7
	C_5H_5N	90	52·2	4·4	7·2		52·4	4·5	6·7	
(dmn)PdCl	Ph_3P	78	63·2	5·0	2·4	6·0	63·1	5·2	2·0	7·1
	Ph_3AS	85	59·1	4·6	2·2		59·1	4·8	2·0	
	C_5H_5N	76	53·3	4·7	6·9	8·8	53·3	5·0	7·1	8·9
(bq)PdCl	Ph_3P	74	63·9	4·0	2·4	6·1	64·2	4·3	2·3	6·4
	C_5H_5N	82	54·1	3·3	7·0		54·1	3·5	6·5	
(bq)PtCl	Ph_3P	64	55·5	3·5	2·1	5·3	55·1	4·1	2·5	4·8
[(bq)Pd(diphos)]$^+$[PF$_6$]$^-$		95	56·5	3·9	1·7		56·5	4·5	1·7	

[a] dmp = 2-(dimethylaminomethylphenyl)-*N*; dmn = 2-[1-(dimethylaminomethyl)naphthyl]-*N*; dan = 2-[1-(dimethylamino)-naphthyl]-*N*; bq = benzo[*h*]quinolin-10-yl-*N*; diphos = bis(diphenylphosphino)ethane.

TABLE 5

Products from the reactions of anionic ligands with the chloro-bridged dimers

	Analyses							
	Calc. (%)				Found (%)			
Complex [a]	C	H	N	F	C	H	N	F
[(dmp)Pd(SCN)]$_2$	40·2	4·0	9·4		39·9	4·3	9·1	
[(dmp)Pd(MeCO$_2$)]$_2$	43·9	5·0	4·7		44·0	4·4	4·6	
[(dmp)Pd(CF$_3$CO$_2$)]$_2$	37·7	3·4	4·0	16·1	38·0	3·7	4·1	16·2
[(dmp)Pt(CH$_3$CO$_2$)]$_2$	34·1	3·9	3·6		34·9	4·2	3·5	
(dmp)Pd(acac)	49·6	5·6	4·1		49·8	5·8	4·0	
(dmn)Pd(acac)	55·5	5·4	3·6		55·3	5·3	3·7	
(bq)Pd(acac)	56·4	3·9	3·6		56·4	4·1	3·5	
(bq)Pt(acac)	45·8	3·2	3·0		45·8	3·4	2·9	

[a] dmp = 2-(dimethylaminomethylphenyl)-*N*; dmn = 2-[1-(dimethylaminomethyl)-naphthyl]-*N*; bq = benzo[*h*]quinolin-10-yl-N; acac = acetylacetonato-.

TABLE 6

Cationic complexes containing a carbon–metal σ-bond

	Analyses										
	Calculated (%)					Found (%)					Λ_M
Complex [a]	C	H	N	P	F	C	H	N	P	F	Ω^{-1} cm^2 mol^{-1} [b]
[(bq)Pd(diphos)]$^+$[BF$_4^-$]	60·8	4·9	1·8	8·0	9·9	61·1	4·6	1·8	7·9	10·1	83
[bq)Pd(PPh$_3$)$_2$]$^+$[BF$_4$]$^-$	65·7	4·3	1·6	6·9	8·5	64·9	4·7	1·5	7·1	8·8	93
[(dmp)Pd(diphos)]$^+$[BF$_4$]$^-$	57·9	4·9	1·9	8·5	10·6	57·2	5·5	1·9	8·4	10·3	78
[(dmp)Pd(PMePh$_2$)$_2$]$^+$[BF$_4$]$^-$	57·7	5·2	1·9	8·5	10·6	57·4	5·6	1·9	8·7	10·7	98
[(azb)Pd(diphos)]$^+$[BF$_4$]$^-$	59·1	4·3	3·6	8·0		59·7	4·2	3·4	8·0		84
[(azb)Pd(PMePh$_2$)$_3$]$^+$[BF$_4$]$^-$	62·8	4·9	2·9	9·5	7·8	62·9	5·3	2·7	9·6	8·5	95
[(azb)Pd(PEt$_3$)$_3$]$^+$[BF$_4$]$^-$	49·5	7·4	3·8	12·8	10·4	49·5	7·4	3·8	12·7	10·3	80

[a] diphos = Bis(diphenylphosphino)ethane; bq = benzo[*h*]quinolin-10-yl-*N*; dmp = 2-(dimethylaminomethylphenyl)-*N*; azb = 2-(phenylazo)phenyl-*N*. [b] Λ_M Determined at 25° in nitromethane.

Di-μ-chloro-bis[2-(dimethylaminomethyl)phenyl-*N*]dipalladium (0·55 g, 1 mmol) was suspended in acetone (30 ml) *and an* excess of lithium thiocyanate (0·27 g, 4 mmol) was added to it. This mixture was refluxed for 1 h after which the pale yellow product was filtered off and washed several times with water and methanol (0·45 g, 73%).

(b) *Di-μ-acetato-bis*[2-*dimethylaminomethyl*)*phenyl*-N]*dipalladium*. Di-μ-chloro-bis[2-(dimethylaminomethyl)-phenyl-*N*]dipalladium (0·55 g, 1 mmol) was suspended in acetone (30 ml) and potassium acetate (0·39 g, 4 mmol) was added to it. The mixture was refluxed for 1 h and then evaporated to dryness. The product was extracted with benzene and recrystallized from benzene–petroleum (b.p. 80—100°) as yellow crystals (0·45 g, 75%).

(c) *Acetylacetonato*[1-(2-*dimethylaminomethyl*)*phenyl*-N]-*palladium*. A suspension of acetylacetonatothallium (0·61 g, 2 mmol) in a solution of the di-μ-chloro-bis[2-(dimethylaminomethyl)phenyl-*N*]dipalladium (0·55 g, 1 mmol) was shaken for 1 h at room temperature. The off-white precipitate of thallous chloride was filtered off to leave a bright yellow solution; addition of light petroleum (b.p. 100—120°) to this, followed by concentration, gave yellow crystals of the pure *product* (0·31 g, 46%).

Other complexes of this type were prepared using the same basic methods, and are listed in Table 5 with their analytical data.

(d) *Acetylacetonato*(*benzo*[h]*quinolin*-10-*yl*-N)(*triphenylphosphine*)*palladium*. Chloro(benzo[h]quinolin-10-yl-*N*)triphenylphosphinepalladium (0·2 g, 0·34 mmol) was dissolved in benzene and acetylacetonatothallium (0·11 g, 0·36 mmol) was added to it. After being shaken for 20 min, the mixture was filtered to give a pale yellow solution. Addition of light petroleum (b.p. 100—120°) to this gave the *product* (0·15 g, 67%) as yellow crystals (Found: C, 66·7; H, 5·1; N, 2·2. $C_{36}H_{30}NO_2PPd$ requires C, 66·9; H, 4·7; N, 2·2%).

Acetylacetonato(benzo[*h*]quinolin-10-yl-*N*)palladium (0·16 g, 0·4 mmol) was suspended in dry ether (50 ml) under nitrogen, and triphenylphosphine (0·44 g, 1·7 mmol) was added to it; after being stirred for 3 h, the pale yellow solid was filtered off and recrystallized from benzene–light petroleum (b.p. 100—120°) to give the pure *product* as yellow microcrystals (0·23 g, 90%).

Electrophilic Reactions with Trityl Tetrafluoroborate.—(a) *Bistriphenylphosphine*(*benzo*[h]*quinolin*-10-*yl*-N)*palladium tetrafluoroborate*. Acetylacetonato(benzo[*h*]quinolin-10-yl-*N*)palladium (0·38 g, 1 mmol) was dissolved in dichloromethane (25 ml) and trityl tetrafluoroborate (0·33 g, 1 mmol) was added to it. The mixture was shaken for a few seconds to give a deep red solution. This was diluted with ether and triphenylphosphine was added to it. The solution became colourless and on addition of more ether white crystals were produced. The product (0·42 g, 48%) was recrystallised from acetone–light petroleum (b.p. 80—100°).

(b) *Tristriethylphosphine*[2-(*phenylazo*)*phenyl*-N]*palladium tetrafluoroborate*. Acetylacetonato[2-(phenylazo)phenyl-*N*]palladium (0·39 g, 1 mmol) was dissolved in dichloromethane (25 ml) and trityl tetrafluoroborate (0·33 g, 1 mmol) was added to it. After dilution of the mixture with ether, triethylphosphine (0·35 g, 3 mmol) was added to it; further ether was then added to give a red oil from which crystals formed overnight. On recrystallization from acetone–light petroleum (b.p. 80—100°) the product was obtained as orange-red crystals (0·51 g, 70%).

The other compounds described in Table 6 were prepared by one of the above methods, depending on the ratio of phosphine to complex required to give a crystalline product.

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