Carbene Complexes. Part I. Electron-rich Olefins as a Source of Carbene Complexes of Platinum(II) and Palladium(II); and Some Experiments with $(CF_3)_2CN_2$

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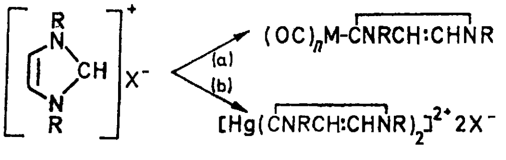
The reactions of electron-rich olefins with di-μ-chloro-dichlorobis(phosphine)diplatinum(II) (and bromo-, arsine-, and Pd^{II} analogues) have been investigated. In general, the product is the *trans*-Pt^{II} or Pd^{II} carbene complex, or the *cis*-isomer, or a mixture of these compounds, depending on the reagents, solvent, and reaction conditions. The compounds are stable, crystalline, and monomeric. Bis(trifluoromethyl)diazomethane reacts with (i) di-μ-chloro-dichlorobis(triethylphosphine)diplatinum(II) to give the product of insertion only into the terminal Pt–Cl bonds, and (ii) tris(triphenylphosphine)platinum(0) to furnish the adduct $Pt[(CF_3)_2CN_2{\cdot}(CF_3)_2C](PPh_3)_2$. Structures and mechanisms are discussed.

CARBENE complexes, LM–CYZ (I) have an extensive chemistry[1] and are involved as intermediates in many transition metal-promoted organic reactions.[2] Various synthetic methods are available: most of these are based on reactions of co-ordinated carbonyls[3] or of pseudo-isoelectronic compounds such as metal isonitriles, acyls, imidoyls, or acetylenes; additionally, some metal carbene complexes are derived from others by substitution or addition reactions. The only organic precursors which had previously been used as a source of co-ordinated carbene were the *gem*-dichloride $PhC{\cdot}CCl_2{\cdot}CPh$ [with $Na_2Cr(CO)_5$ [4] or Pd [5]] or imidazolium salts (II) [equations (1a) [5,6] and (1b) [7]].



(1)

(II)

(a) $X = [HM(CO)_n]^-$, R = Me ($M = Cr$ and $n = 5$,[4] or $M = Fe$ and $n = 4$[6])

(b) $+ HgCl_2$
$X = ClO_4$ and R = Ph

An objective of our work was to explore the possibility of (i) trapping free carbenes as metal complexes, and (ii) finding *organic* starting materials which might provide rather more general syntheses than those currently available. In this paper, which is confined to Pd^{II} and Pt^{II} complexes, we report on the following classes of compound: electron-rich olefins, including (III) and (IV); the imidazolidine (V); and the diazomethane (VI). The metal substrates which were used are (VII) (L = a tertiary phosphine or arsine, X = Cl or Br, and M = Pd or Pt) and (VIII). A preliminary account of some of these results has been published.[8] Reagents (III)—(V) were chosen as potential sources of complexes of nucleophilic carbenes, whereas (VI) could in principle yield a complex of the electrophilic carbene $(CF_3)_2C$. Structurally authenticated complexes known to date are of the former type. Compounds (VII) and (VIII) are known to be susceptible to nucleophilic and electrophilic attack, respectively.

The reactions of (III) with (VII) afforded the new carbene complexes of Pd^{II} or Pt^{II}, (IX) or (X), details for which [and others from (IV) with (VII)] are shown in Table 1. It will be noted that in some cases only the *trans*-complex (IX) was obtained, in others only the rearranged *cis*-isomer (X), whereas the formation of a mixture of (IX) and (X) was also sometimes found. As briefly described, *cis*-isomers, which are the thermo-

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[1] *Cf.* D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[2] *Cf.* D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, in the press.

[3] *Cf.* E. O. Fischer and A. Maasböl, *Angew. Chem. Internat. Edn.*, 1964, **3**, 580, and later papers.

[4] K. Öfele, *Angew. Chem. Internat. Edn.*, 1969, **8**, 916.

[5] K. Öfele, *J. Organometallic Chem.*, 1970, **22**, C9.

[6] K. Öfele and C. G. Kreiter, *Chem. Ber.*, 1972, **105**, 529.

[7] H. J. Schönherr and H.-W. Wanzlick, *Chem. Ber.*, 1970, **103**, 1037.

[8] D. J. Cardin, B. Çetinkaya, M. F. Lappert, Lj. Manojlovic-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.

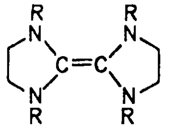
TABLE 1

Pt^{II} and Pd^{II} carbene complexes from electron-rich olefins (III) or (IV) with halogen-bridged metal complexes (VII), and their characterisation

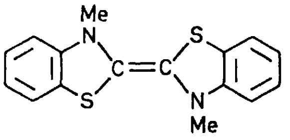
Compound	No.	M.p. (°C)	Yield (%)	Colour	Found (Required) (%)				Found (Required)
					C	H	N	Cl	*M*
trans-$\mathrm{PtCl_2(CNPhCH_2CH_2NPh)(PEt_3)}$	1	201—205 [a]	50	Pale yellow	41·5 (41·6)	5·0 (4·8)	4·6 (4·6)	11·7 (11·7)	597 (606) [b]
trans-$\mathrm{PtBr_2(CNPhCH_2CH_2NPh)(PEt_3)}$	2	187—190	64	Yellow	36·9 (36·3)	4·2 (4·2)	4·1 (4·0)		
trans-$\mathrm{PtCl_2(CNPhCH_2CH_2NPh)(PBu^n_3)}$	3	130—132	73	Yellow	45·4 (46·9)	5·8 (5·9)	4·0 (4·1)		
trans-$\mathrm{PtCl_2(CNPhCH_2CH_2NPh)(PMe_2Ph)}$	4	197—199 [c]	16	Pale yellow	43·9 (44·1)	4·1 (3·7)	4·3 (4·5)	11·9 (11·35)	
trans-$\mathrm{PtCl_2(CNPhCH_2CH_2NPh)(AsEt_3)}$	5	188—190 [a]	37	Pale yellow	38·8 (38·8)	4·3 (4·5)	4·4 (4·3)		620 (650) [b]
trans-$\mathrm{PdCl_2(CNPhCH_2CH_2NPh)(PEt_3)}$	6	197—200	17	Pale yellow	48·7 (48·7)	5·8 (5·6)	5·5 (5·6)		
trans-$\mathrm{PdCl_2(CNPhCH_2CH_2NPh)(PBu^n_3)}$	7	145—146	44	Yellow	54·0 (53·9)	7·0 (6·8)	4·7 (4·7)		615·8 (601·5) [b]
trans-$\mathrm{PtCl_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PEt_3)}$	8	156—158	25 [d]	Yellow	31·7 (31·5)	4·2 (4·1)	2·7 (2·6)		531 (533) [e]
cis-$\mathrm{PtCl_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PEt_3)}$	9	280—290 [f]	46 [d]	Pink [g]	31·7 (31·5)	3·9 (4·1)	3·0 (2·6)		
trans-$\mathrm{PtBr_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PEt_3)}$	10	172—173	20 [d]	Yellow	27·8 (27·0)	3·6 (3·5)	2·4 (2·3)		
cis-$\mathrm{PtBr_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PEt_3)}$	11	250—275 [f]	50 [d]	Pink [g]	28·1 (27·0)	3·5 (3·5)	2·4 (2·3)		
trans-$\mathrm{PtCl_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PBu^n_3)}$	12	89—93	58 [d]	Yellow	38·9 (38·9)	5·6 (5·5)	2·2 (2·3)		
cis-$\mathrm{PtCl_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PBu^n_3)}$	13	256—258	18 [d]	Pink [g]	38·6 (38·9)	5·4 (5·5)	2·3 (2·3)		
cis-$\mathrm{PtCl_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PMe_2Ph)}$	14	259—260	43	Pink [g]	34·6 (34·8)	3·3 (3·3)	2·5 (2·5)		
cis-$\mathrm{PdCl_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PEt_3)}$	15	200—255 [f]	57	Buff [g]	38·4 (37·8)	5·0 (5·0)	3·5 (3·2)	153 (16·0)	
cis-$\mathrm{PdCl_2(CNMe{\cdot}C_6H_4{\cdot}S\text{-}}$*o*$\mathrm{)(PBu^n_3)}$	16	210—270 [f]	67	Buff [g]	45·8 (45·4)	6·5 (6·4)	3·0 (2·7)		
trans-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$	17	183—185	82 [d]	Pale yellow	27·9 (27·4)	5·3 (5·2)	5·7 (5·8)		482 (482) [e]
cis-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$	18	*ca.* 280 [f]	4 [d]	White	28·0 (27·4)	5·3 (5·2)	6·0 (5·8)		672 (482) [e]
trans-$\mathrm{PtBr_2(CNMeCH_2CH_2NMe)(PEt_3)}$	19	172—175	26 [d]	Yellow	23·7 (23·1)	4·4 (4·4)	4·8 (4·9)		543 (571) [e]
cis-$\mathrm{PtBr_2(CNMeCH_2CH_2NMe)(PEt_3)}$	20	268—273	23 [d]	White	23·8 (23·1)	4·5 (4·4)	4·8 (4·9)		
trans-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PPr^n_3)}$	21	133—134	15 [d]	Pale yellow	32·6 (32·1)	6·2 (5·9)	5·2 (5·35)		
cis-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PPr^n_3)}$	22	188—195	21 [d]	White	32·3 (32·1)	6·2 (5·9)	5·4 (5·35)		
trans-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PBu^n_3)}$	23	95—96	33 [d]	Yellow	35·2 (36·0)	6·5 (6·5)	4·8 (4·9)		556 (566) [e]
cis-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PBu^n_3)}$	24	167—168	15	White	35·1 (36·0)	6·4 (6·5)	4·9 (4·9)		735 (566) [e]
cis-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(PMe_2Ph)}$	25	240—246 [f]	42	White	31·1 (31·1)	4·3 (4·3)	5·5 (5·6)	15·0 (14·15)	
trans-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(AsEt_3)}$	26	138—150 [f]	30 [d]	Yellow	25·1 (25·1)	4·7 (4·8)	5·8 (5·3)		
cis-$\mathrm{PtCl_2(CNMeCH_2CH_2NMe)(AsEt_3)}$	27	200—240 [f]	16 [d]	White	25·0 (25·1)	4·8 (4·8)	6·1 (5·3)		866 (526) [e]
cis-$\mathrm{PdCl_2(CNMeCH_2CH_2NMe)(PEt_3)}$	28	*ca.* 245 [h]	24	White	33·5 (33·5)	6·4 (6·3)	7·8 (7·1)		
cis-$\mathrm{PdCl_2(CNMeCH_2CH_2NMe)(PBu^n_3)}$	29	186—188	25	White	43·2 (42·8)	8·1 (7·8)	5·8 (5·9)		

[a] Partial melt. [b] In C_6H_6 solution. [c] Resolidifies at 200°. [d] These yields are misleading: the *cis* and *trans*-complexes were separated from a mixture of isomers. [e] In $CHCl_3$ solution. [f] Decomposes. [g] Should be white; the colour is probably due to intensely coloured impurity. [h] Decomposes without melting.

dynamically more stable, may be formed by thermolysis of *trans*-complexes;[9] this aspect, as well as other features of the chemistry of carbene complexes, is described in Part II.[10] All compounds have been identified by spectroscopic means; single crystal *X*-ray data (obtained by Drs. Lj. Manojlović-Muir and K. W. Muir) of an example of each of (IX) and (X) (L = PEt$_3$, X = Cl, M = Pt, and R = Ph) are available.[9] I.r., ^{1}H, and ^{31}P n.m.r. spectroscopic results for all compounds (including those reported in Part II), especially features relevant to discussions of the *trans*-influence of the carbene ligand, are discussed in Part IV,[11] and data from ^{13}C n.m.r. spectra are presented in Part III.[12]



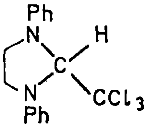
(IIIa) R = Me
(IIIb) R = Ph



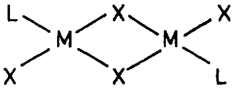
(IV)

$(CF_3)_2CN_2$

(VI)



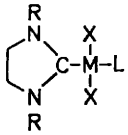
(V)



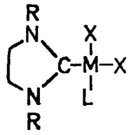
(VII)

$(Ph_3P)_3Pt$

(VIII)



(IX)



(X)

Reactions of Electron-rich Olefins and an Imidazoline.— Electron-rich olefins, such as (III) or (IV), are good reducing agents and have a weak C=C bond.[13] Consistent with this, they have an exceptionally low first vertical ionisation potential (*ca.* 6 eV; *cf.* Na, 5·1 eV)[14] and are expected to be good nucleophiles. At one time they were thought to dissociate into two nucleophilic carbene fragments in solution,[15] but this has been discounted by negative cross-over experiments using two different olefins (III; R = Ph or *p*-Me·C$_6$H$_4$);[16] nevertheless, cross-over is achieved catalytically, *e.g.*, using certain Rh^I complexes, but a Pt^{II} compound (IX; L = PEt$_3$, X = Cl, M = Pt, and R = Ph) was inactive.[17]

When heated under reflux in xylene (10 min) with di-μ-chloro-dichlorobis(triethylphosphine)diplatinum(II), (VII; L = PEt$_3$, X = Cl, M = Pt), the CC double bond in 1,1′,3,3′-tetraphenyl-2,2′-bi-imidazolidinylidene (IIIb), was cleaved to afford the *trans*-carbene complex (IX; L = PEt$_3$, X = Cl, M = Pt, and R = Ph). This complex was also obtained from the reaction of the same platinum dimer (VII) and the imidazoline (V). The latter is, however, known to yield the olefin (IIIb) when heated in xylene under reflux.[18] When a platinum dimer (VII) was heated with the olefin (IIIb) an insoluble solid, believed to be (on grounds of insolubility and i.r. spectrum) the salt [PtXL$_2$]$^+$[PtX$_3$(IIIb)]$^-$, separated out; this was a minor product (the carbene complex remains in solution). The *trans*-palladium complexes (IX; L = PEt$_3$ or PBu^n$_3$, X = Cl, M = Pd, R = Ph) were prepared using the appropriate olefin (IIIb) and dimer (VII). In the preferred procedure for the preparation of *trans*-complexes (IX; R = Ph), a hot solution of the chosen dimer (VII), in xylene, was added dropwise to a refluxing solution of the olefin (IIIb) in xylene, in 1 : 1 stoicheiometry. For the Pd compounds, the yields were low (*ca.* 20%) probably owing to thermal decomposition. However, unless heated at 140° for 10—20 min, carbene complexes were not isolated using this olefin. It is noteworthy that with the latter only *trans*-isomers (IX) were obtained, whereas (IIIa) or (IV) gave *cis*-complexes (X), or mixtures of isomers, (IX) and (X). The ratio of *cis*- to *trans*-isomers markedly depends on the temperature of reaction. *cis*-Isomers are soluble in chloroform (except for compounds 9, 14, and 15, see Table 1) but insoluble in benzene and they are much less soluble than their *trans*-analogues.[10]

For the preparation of carbene complexes, the choice of solvent is important. For example, the olefin (IV) with a platinum dimer (VII; M = Pt) in xylene at *ca.* 90° invariably afforded a *cis*- and *trans*-mixture. However, when the same olefin and a palladium dimer (VII; M = Pd) were heated in xylene, no carbene product was identified, whereas in DMF at *ca.* 90°, *cis*-$PdCl_2(\overline{CNMe{\cdot}C_6H_4{\cdot}S}\text{-}o)L$ (L = PEt$_3$ or PBu^n$_3$) was obtained in high yield.

These reactions were extended to other olefins in order to determine the scope of the reactions and also to prepare more soluble *cis*-derivatives for spectroscopic studies.[11,12] In order to overcome the solubility problem ligands containing long alkyl chains were employed. Triethylarsine complexes were made in order to avoid the complication of phosphorus coupling in the n.m.r. spectra.

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[9] D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *J. Organometallic Chem.*, 1972, **44**, C59.

[10] Part II, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, in the press.

[11] Part IV, D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, in the press.

[12] Part III, D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, in the press.

[13] *Cf.* R. W. Hoffmann, *Angew. Chem. Internat. Edn.*, 1968, **7**, 754; N. Wiberg, *ibid.*, p. 766.

[14] B. Çetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Chem. Comm.*, 1971, 1370.

[15] H.-W. Wanzlick, *Angew. Chem. Internat. Edn.*, 1962, **1**, 75.

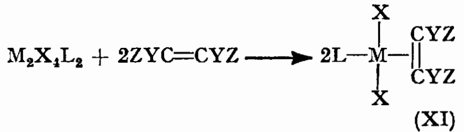
[16] D. M. Lemal, R. A. Lovald, and K. I. Kawano, *J. Amer. Chem. Soc.*, 1964, **86**, 2518.

[17] D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 927.

[18] H.-W. Wanzlick and E. Schikora, *Chem. Ber.*, 1961, **94**, 2389.

Several observations (i)—(iii) were made regarding the variations in the olefin and the dimer. (i) Among the olefins, reactivity decreases in the order (IIIa) > (IV) > (IIIb), which reflects the progressive decrease in electron-richness of the olefin. As an example, although (IIIa) reacts with (VII) at ambient temperature, (IV) reacts with (VII) only at or above 90°. On the other hand, (IIIb) does not yield carbene complexes unless heated at 140° (*ca.* 10 min). The solubility for the resulting carbenes (*cis* or *trans*) increases in the order (IIIb) < (IV) < (IIIa). A further point relates to the isomer specificity for the initially formed reaction product from treatment of (VII) and the olefin in refluxing xylene. Thus (IIIa) and (IV) gave *cis*- and *trans*-mixtures of carbene complexes, whereas (IIIb) gave only the *trans*-isomer. (ii) Among the dimers (VII), palladium species appear to be more reactive than the platinum analogues. The yield and solubility is greater for bromo- rather than chloro-complexes, but no clear distinction in reactivity was noted between them. (iii) Dimethylphenylphosphine is the least reactive of all the ligands (L) and it also differs from the others by not giving *trans*-carbenes when the dimer (VII; M = Pt, L = PMe_2Ph) is treated with the olefins (III) or (IV).

It is known that ethylene and $Pt_2Cl_4(PEt_3)_2$ yield the π-complex *cis*-$PtCl_2(C_2H_4)PEt_3$.[19] It seems possible, therefore, that co-ordination of the electron-rich olefin is the initial step in the formation of a carbene complex, as shown in Scheme 1. Attempts to isolate such an intermediate π-complex (XI), by using a (2—3) fold excess of (IIIa) with $Pt_2Cl_4(PEt_3)_2$ at 20°, gave *cis*- and *trans*-carbene complexes, (IX) and (X), as the only isolable products. But almost all reactions involving electron-rich olefins and cleavage of the bridged dimers, proceeded through highly coloured stages, suggesting intermediate(s).

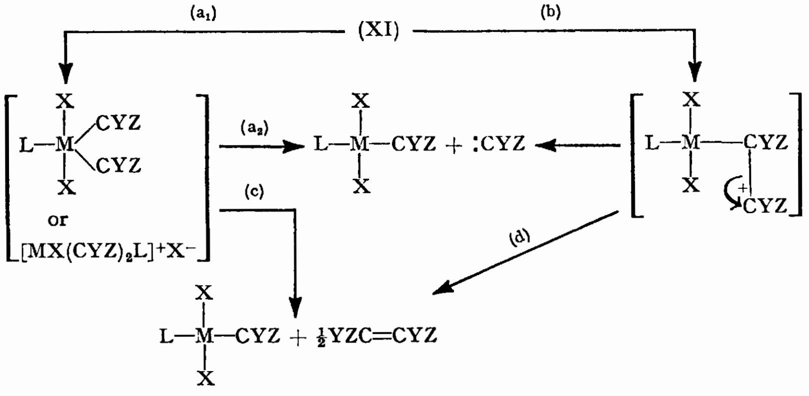


$$M_2X_4L_2 + 2ZYC{=}CYZ \longrightarrow 2L{-}\overset{X}{\underset{X}{M}}{-}\left\|\begin{matrix}CYZ\\CYZ\end{matrix}\right.$$

(XI)

SCHEME 1

A π-complex (XI) could decompose to furnish a carbene complex by one or other of the reaction paths (a)—(d) shown in Scheme 2; (c) and (d) require a bimolecular mechanism and free carbene is not implicated. Trapping experiments at present provide no evidence for the participation of a free carbene :CYZ.



SCHEME 2

The compounds shown in Table 1 are stable towards air and water, whereas the parent olefins are extremely sensitive to oxygen and moisture. The complexes were characterised by analysis, molecular weight determination, i.r., ^1H, ^{13}C, and ^{31}P n.m.r., and mass spectra.[11,12] They are diamagnetic and their ^1H n.m.r. spectra in $CDCl_3$ showed the expected patterns with satisfactory integration. All the complexes gave parent molecular ions in the mass spectra. The monomeric formulation for the complexes was confirmed by osmometric molecular weight determination. It is surprising that the *cis*-isomers have high (up to 50%) molecular weights; we note that (X; L = PEt_3, X = Cl, M = Pt, R = Ph) is a monomer in the crystal.[9]

Reactions of Bis(trifluoromethyl)diazomethane.—Diazoalkanes, $ZYCN_2$, are well known as precursors of the carbenes :CYZ. Their decomposition may be catalysed by transition metal salts. Copper compounds have often been employed. There is much evidence that metal carbene complexes are intermediates.[2] Bis(trifluoromethyl)diazomethane has frequently been used.[20] Insertion of $(CF_3)_2C$: into an M–X bond was found for $(OC)_5Mn$–H, *trans*-$(Et_3P)_2ClPt$–H, $(OC)_4Co$–$Co(CO)_4$, or $Cl(PhCN)_2Pd$–Cl,[21] whereas with *trans*-$IrCl(CO)(PPh_2Me)_2$ the adduct was believed to be the carbene complex $IrCl(CO)(PPh_2Me)_2[C(CF_3)_2]$. Reactions of diazoalkanes with inorganic compounds have been reviewed.[22]

Bis(trifluoromethyl)diazomethane reacted with (i) di-μ-chloro-dichlorobis(triethylphosphine)diplatinum(II) in

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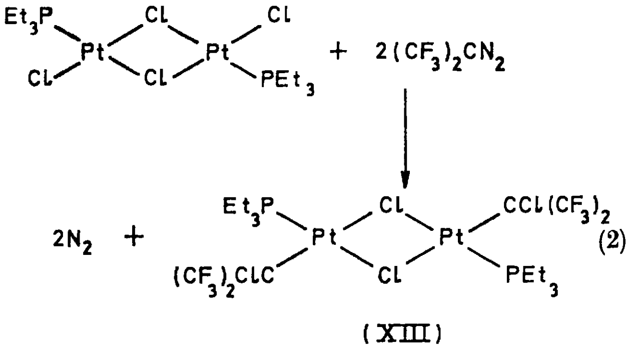
[19] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662.

[20] J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1872.

[21] J. Ashley-Smith, J. Clemens, M. Green, and F. G. A. Stone, *J. Organometallic Chem.*, 1969, **17**, P23.

[22] M. F. Lappert and J. S. Poland, *Adv. Organometallic Chem.*, 1970, **9**, 397.

ether at 20° to give the insertion product (XIII) [equation (2)], and (ii) the Pt^0 complex (VI) in benzene at −15° to give the adduct (XIV) [equation (3)]. Compound


(2)

(XIII)

$$\mathrm{Pt(PPh_3)_3 + 3(CF_3)_2CN_2 \longrightarrow Pt[(CF_3)_2CN_2(CF_3)_2C](PPh_3)_2 + Ph_3P{\cdot}N_2C(CF_3)_2 + N_2} \quad (3)$$

(XIV)

(XIII), the first example of the series $Pt_2Cl_2R_2L_2$, was characterised by its i.r., ^{19}F n.m.r., and mass spectra (Table 2). The mass spectrum (100°) showed the highest peak at $m/e = 534$, which corresponds to the monomer $PtCl[ClC(CF_3)_2]PEt_3$. However, there were other peaks above that of the monomer ion, when the spectrum was run at lower temperature, although the parent ion for the dimer was not observed. Molecular weight determination of a benzene solution of (XIII) confirmed the dimeric formulation.

TABLE 2

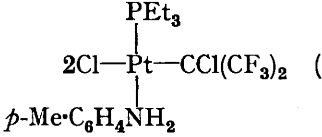
Some data on the platinum(II) complexes from bis(trifluoromethyl)diazomethane

Compound	Appearance	M.p. (°C)	Yield (%)	M [a,b]	Selected i.r. data [c]	Selected ^{19}F n.m.r. data [d]
(XIII)	Yellow crystals	163—165	74	1076 (1068)	ν(PtCl) 308—265	61·38 [s, J(Pt–F) 78 Hz]
(XV) [e]	White crystals	96—97	72		ν(NH) 3372, 3204, 3188, 3150, 3118 ν(PtCl) 307	
(XIV)	Orange cubes	200 (dec.)	50	1067 (1047)	ν(CN) 1560	59·45 [d, J(P–F) 10 Hz, J(Pt–F) 77 Hz]; 63·52 (m, unresolved); 65·82 [q, J(app) 6 Hz]

[a] Calculated values in parentheses. [b] In C_6H_6, isopiestically. [c] Max. in cm^{-1} for Nujol mulls. [d] Chemical shifts expressed in δ (p.p.m.) (rel. to $CFCl_3$). [e] Stereochemistry has not been determined but chloro-bridged platinum(II) dimers are known to react with amines to give complexes of the type $PtCl_2(amine)(PR_3)$, which invariably have the *trans*-configuration (J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 3858).

The bridge-splitting reaction [equation (4)] of (XIII) with *p*-toluidine to give (XV) (for details, see Table 2), provides further evidence for structure (XIII). The

$2p\text{-}\mathrm{Me{\cdot}C_6H_4{\cdot}NH_2} + \mathrm{(XIII)} \longrightarrow$



$$\mathrm{2Cl{-}\overset{\displaystyle PEt_3}{\underset{\displaystyle \mathit{p}\text{-}Me{\cdot}C_6H_4NH_2}{Pt}}{-}CCl(CF_3)_2} \quad (4)$$

(XV)

insertion product (XIII) was also treated with bromine in the expectation of obtaining $(CF_3)_2CBrCl$ by cleavage of the Pt–C bond. This product was not detected in the mass spectrum, but the residue afforded bromo-bridged complex (VII; L = PEt_3, X = Br, M = Pt).

There are indications that di-μ-chloro-dichlorobis(dimethylphenylphosphine)diplatinum(II) reacts in the same manner with $(CF_3)_2CN_2$ to give bis(trifluoromethyl)methylene insertion into the terminal Pt–Cl bonds. The reactions of other diazoalkanes, such as trimethylsilyldiazomethane, phenyltrimethylsilyldiazomethane, and diazoacetic ester with $Pt_2Cl_4(PEt_3)_2$ were also examined; nitrogen was evolved at 20°, but no products were characterised. Polymethylene was obtained from this platinum complex and diazomethane.

Compound (XIV), the characterisation of which initially established merely its composition as $Pt[(CF_3)_2CN_2{\cdot}(CF_3)_2C](PPh_3)_2$, was then examined by spectroscopic (Table 2) and X-ray diffraction methods. However, we became aware of its preparation, from different starting materials, by colleagues at Bristol, who had completed a single crystal X-ray analysis (XVI).[23] Spectroscopic and preliminary X-ray data (Table 3) confirmed that the two compounds were identical and further investigation at Sussex ceased.

The mechanism of formation of (XVI) may involve initial electrophilic carbene complex formation

TABLE 3

Crystal data for three samples of compound (XIV)

Sample	System	Space-group	a	b	c	beta	Z
A [a]	Monoclinic	$P2_1/c$	12·64	23·51	15·76	119·5	4
B [b]	Monoclinic	[c]	30·9	13·01	21·5	109	[c]
C [d]	Monoclinic	$C2/c$	31·155	13·091	21·828	109·24	8

[a] Data obtained by Dr. K. W. Muir on a sample prepared as indicated in the text and recrystallised from $CHCl_3$–n-C_6H_{14}. [b] Data obtained by Dr. K. W. Muir on a sample prepared as indicated in the text and recrystallised from CH_2Cl_2. [c] These were left incomplete when it became apparent that samples B and C were identical (also indicated by data of Table 2 and comparison with results from Bristol). [d] Data obtained by Prof. R. E. Davis (personal communication to Dr. K. W. Muir) on a sample prepared by Dr. M. Green, Prof. F. G. A. Stone, and their co-workers, and crystallised from CH_2Cl_2.

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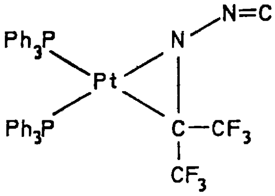
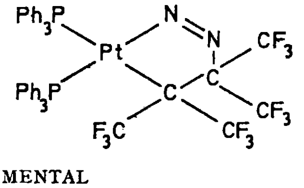
[23] J. Clemens, R. E. Davis, M. Green, J. D. Oliver, and F. G. A. Stone, *Chem. Comm.*, 1971, 1095.

$[Pt(PPh_3)_2C(CF_3)_2]$, subsequent 1,3-dipolar addition thereto of $(CF_3)_2CN_2$ to give (XVII) (this structure had been considered [22]), and finally re-arrangement to (XVI).


(XVI)


(XVII)

EXPERIMENTAL

General Procedures.—Carbon, hydrogen, and nitrogen analyses were carried out in our Microanalytical Laboratory by Mr. and Mrs. A. Olney. Chlorine, fluorine, and phosphorus analyses were by the Bernhardt Microanalytical Laboratory, Hohenweg, West Germany. Infrared (to 250 cm^{-1}) spectral samples were examined as Nujol or hexachlorobutadiene mulls, or solutions in organic solvents, using Perkin-Elmer 337 (4000—400 cm^{-1}) and 457 (4000—250 cm^{-1}) grating spectrophotometers. ^1H N.m.r. spectra were recorded on Varian Associates HA 100 or T 60, spectrometers, using saturated solutions for sparingly soluble compounds or solutions of *ca.* 1 mmol in 10 ml concentration. Mass spectra were obtained with an A.E.I. MS 9 double-focussing instrument. M.p.s were taken in capillary tubes, *in vacuo* for air- or moisture-sensitive compounds, and readings are uncorrected. Molecular weights were determined either isopiestically in benzene or chloroform using a Mechrolab 301A vapour pressure osmometer, or mass spectrometrically from parent ion peaks. Hydrocarbon and ether solvents were dried over fine sodium wire, chlorinated solvents by distillation from phosphorus pentoxide, and alcohols by distillation from their corresponding magnesium alkoxides. Dimethylamine was dried over sodium wire at −15°.

Due to the oxygen- and moisture-sensitivity of many of the compounds used, reactions were performed under pure dry nitrogen, and apparatus was 'flamed out' before use and allowed to cool under vacuum, and then filled with pure dry nitrogen.

Starting materials were prepared and purified according to literature methods: $Pt(PPh_3)_3$,[24] $Pd_2Cl_4(PR_3)_2$,[25] $Pt_2Cl_4(PR_3)_2$,[26,27] $(CF_3)_2CN_2$,[28] $(PhNCH_2CH_2PhNC)_2$,[29] $PhNCH_2CH_2PhNC(CCl_3)H$,[18] $(MeNCH_2CH_2MeNC)_2$,[30] $(o\text{-}S\cdot C_6H_4\cdot MeNC)_2$,[31] $[(Me_2N)_2C]_2$.[32] Since 1,1′,3,3′-tetramethyl-2,2′-bi-imidazolidinylidene is solid at room temperature, it was warmed to 60° before use and dispensed by means of a warm syringe.

Reactions of 1,1′,3,3′-*Tetraphenyl*-2,2′-*bi-imidazolidinylidene* (III; R = Ph).—(a) *With di-μ-chloro-dichlorobis-(triethylphosphine)diplatinum*(II). The olefin (0·4620 g, 1·04 mmol) and the platinum complex (0·7680 g, 1·00 mmol) were heated under reflux in xylene (40 ml) for 10 min; the colour lightened and heating was continued for another 50 min. The mixture was allowed to cool, and then filtered. The yellow residue [Found: C, 45·7; H, 4·5; N, 6·1%; ν(PtCl) 330, 275 cm^{-1}; insoluble in organic solvents and not further identified] was washed with benzene (25 ml). The benzene and xylene solutions were combined and evaporated to *ca.* 15 ml. Methanol was added to obtain crystals, which were recrystallised (MeOH) to give trans-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*) (*triethylphosphine*)*platinum*(II) (0·6100 g).

(b) *With di-μ-bromo-dibromobis*(*triethylphosphine*)*diplatinum*(II). Using a similar procedure, the platinum complex (0·9460 g, 1·00 mmol) and the olefin (0·4440 g, 1 mmol) afforded trans-*dibromo*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (0·8920 g).

(c) *With di-μ-chloro-dichlorobis*(*tri-n-butylphosphine*)-*diplatinum*(II). A hot solution of the platinum complex (0·9360 g, 1·00 mmol) in xylene (15 ml) was added to a hot solution of the olefin (0·4440 g, 1·00 mmol) in xylene (20 ml). A dark orange solution formed. Upon heating (20 min, reflux) it became yellow, and after a further 10 min the solution became cloudy. The mixture was allowed to cool to 20°; the yellow solid (0·2600 g) [Found: C, 45·0; H, 5·7; N, 4·0%; ν(PtCl) 330, 270 cm^{-1}] was filtered off and dried. The yellow filtrate was evaporated to *ca.* 4 ml and ether (10 ml) was added. Filtration followed by cooling gave a solid which was recrystallised ($CHCl_3$–Et_2O) to obtain trans-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)-(*tri-n-butylphosphine*)*platinum*(II) (1·0120 g).

(d) *With di-μ-chloro-dichlorobis*(*dimethylphenylphosphine*)-*diplatinum*(II). The platinum complex (0·4040 g, 0·50 mmol) and the olefin (0·2220 g, 0·50 mmol) were mixed in xylene (25 ml). The mixture was heated under reflux for 1 h. The clear, hot supernatant liquor was decanted and the solvent was removed *in vacuo*. The residue was purified by treatment with aqueous methanolic hydrogen chloride and by washing with ether. Finally, it was recrystallised ($CHCl_3$–Et_2O) to obtain trans-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*dimethylphenylphosphine*)-*platinum*(II) (0·1002 g).

(e) *With di-μ-chloro-dichlorobis*(*triethylarsine*)*diplatinum*(II). A hot solution of the platinum complex (0·6257 g, 0·73 mmol) in xylene (15 ml) was added to a boiling (reflux) solution of the olefin (0·3241 g, 0·73 mmol) in xylene (25 ml). A dark red solution formed, which turned black after 5 min; the mixture was allowed to cool and was then filtered. The volume of the filtrate was reduced to *ca.* 15 ml and hexane (20 ml) was added to obtain a solid, which was washed with a solution of hydrogen chloride in ether (15 ml). Recrystallisation ($CHCl_3$–Et_2O) gave trans-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylarsine*)-*platinum*(II) (0·3528 g).

When the xylene-insoluble dark residue was treated with

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[24] R. Ugo, F. Cariati, and G. La Monica, *Inorg. Synth.*, 1968, **11**, 105.

[25] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2351.

[26] R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.*, 1965, 7533.

[27] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

[28] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1966, **88**, 3617.

[29] H.-W. Wanzlick, *Org. Synth.*, 1967, **47**, 14.

[30] H. E. Winberg, *Chem. Abs.*, 1966, **64**, 15,854h; H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *J. Amer. Chem. Soc.*, 1965, **87**, 2055.

[31] H.-W. Wanzlick, H.-J. Kleiner, I. Lasch, H. U. Füldner, and H. Steinmaus, *Annalen*, 1967, **708**, 155.

[32] R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Amer. Chem. Soc.*, 1950, **72**, 3646.

chloroform (10 ml) it gave a dark yellow filtrate, from which a yellow solid [0·210 g; ν(PtCl) 328, 270 cm^{-1}] was precipitated by addition of ether (15 ml).

(f) *With di-μ-chloro-dichlorobis(triethylphosphine)dipalladium*(II). The palladium complex (0·5908 g, 1·00 mmol) and the olefin (0·4440 g, 1·00 mmol) were heated in xylene (30 ml). When the temperature reached *ca.* 110° some decomposition set in, but heating was continued up to 140°. The mixture was allowed to cool, was then filtered, and the filtrate was evaporated to dryness. The residue was washed several times with ethereal hydrogen chloride and then methanol to yield trans-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*palladium*(II) (0·1762 g).

(g) *With di-μ-chloro-dichlorobis(tri-n-butylphosphine)dipalladium*(II). A hot solution of the palladium complex (1·5200 g, 2·00 mmol) in xylene (40 ml) was added to a boiling (reflux) solution of the olefin (0·8880 g, 2·00 mmol) in xylene (35 ml); a red solution was formed. Immediately after the addition was completed, the solution became dark and opaque. During heating under reflux (8 min), the colour became yellow and a black precipitate was formed. After cooling to 20°, the volume of the solution was reduced to *ca.* 30 ml. Filtration gave a xylene-insoluble yellow solid (0·2796 g) (Found: C, 55·7; H, 7·2; N, 5·8%).

The yellow filtrate was evaporated to dryness. The oily residue was washed with light petroleum (b.p. 40—60°, 20 ml), then with ether (2 × 15 ml). The residue was dissolved in chloroform and ether was added. Crystals (0·7351 g) were formed and were filtered off, washed with ether, and identified as trans-*dichloro*(1,3-*diphenylimidazolidin*-2-*ylidene*)(*tri-n-butylphosphine*)*palladium*(II). The filtrate yielded further crystals (0·3329 g) at −20°.

The yellow light petroleum and ether washings were combined. Solvents were removed *in vacuo* and the residue was dissolved in the minimum volume of methanol to yield *trans*-dichlorobis(tri-n-butylphosphine)palladium(II) (0·2000 g) (Found: C, 50·4; H, 9·6. Calc. for $C_{24}H_{54}Cl_2P_2Pd$: C, 49·55; H, 9·3%).

Reaction of 1,3-*Diphenyl*-2-*trichloromethylimidazolidine*, (V), *with Di-μ-chloro-dichlorobis(triethylphosphine)diplatinum*(II).—The imidazolidine (1·0073 g, 2·95 mmol) and the platinum compound (0·7060 g, 0·92 mmol) were heated in xylene (40 ml) under reflux for 1·5 h. After cooling to 20°, the reaction mixture was filtered and the filtrate was evaporated to dryness. The brownish residue was washed with a mixture of methanol (15 ml) and ether (15 ml saturated with HCl). Recrystallisation (MeOH, 70 ml) afforded needles of *trans*-dichloro(1,3-diphenylimidazolidin-2-ylidene)(triethylphosphine)platinum(II) (0·5640 g, 50%) (Found: C, 41·9; H, 4·9; N, 4·9%).

Reactions of Bis(N-*methylbenzothiazolinylidene*) (IV).—(a) *With di-μ-chloro-dichlorobis(triethylphosphine)diplatinum*(II). The olefin (0·1490 g, 0·50 mmol) and the platinum complex (0·3840 g, 0·50 mmol) were heated in xylene (30 ml). A dark red precipitate was formed at *ca.* 100°, but heating was continued at 140° for 10 min. After cooling to 20°, the precipitate was filtered off and washed with acetone and ether to give cis-*dichloro*(N-*methylbenzothiazolinylidene*)(*triethylphosphine*)*platinum*(II) (0·2241 g).

Addition of n-hexane to the xylene filtrate caused precipitation of crystals of the trans-*isomer* (0·1330 g), which were recrystallised (Me_2CO).

(b) *With di-μ-bromo-dibromobis(triethylphosphine)diplatinum*(II). From the platinum complex (0·9480 g, 1·00 mmol) and the olefin (0·2980 g, 1·00 mmol) using the procedure of (a), cis- (0·6200 g) and trans- (0·2490 g) *dibromo*(N-*methylbenzothiazolinylidene*)(*triethylphosphine*)*platinum*(II) were obtained.

(c) *With di-μ-chloro-dichlorobis(tri-n-butylphosphine)diplatinum*(II). The mixture of platinum complex (0·9360 g, 1·00 mmol) and olefin (0·2980 g, 1·00 mmol) was heated (10 min) under reflux in xylene (25 ml). The hot solution was decanted to remove matter which adhered to the reaction vessel. Upon cooling, the liquor gave crystals, which were recrystallised (Me_2CO at −20°) and identified as cis-*dichloro*(N-*methylbenzothiazolinylidene*)(*tri-n-butylphosphine*)*platinum*(II) (0·2250 g). The filtrate was evaporated and the residue was dissolved in benzene and passed through an alumina column. A yellow eluate was collected, benzene was removed *in vacuo*, and recrystallisation (MeOH) gave the trans-*isomer* (0·7200 g).

(d) *With di-μ-chloro-dichlorobis(dimethylphenylphosphine)diplatinum*(II). The platinum complex (0·4040 g, 0·50 mmol) and the olefin (0·1490 g, 0·50 mmol) were mixed in xylene (35 ml). The flask containing this solution was plunged into an oil-bath at 120°, which was further heated to 140° and kept at this temperature for 3—5 min. A dark sticky solid and an orange-red solution were formed. The solution was immediately decanted off to yield a precipitate upon cooling. This was recrystallised ($CHCl_3$–Et_2O) to afford cis-*dichloro*(N-*methylbenzothiazolinylidene*)(*dimethylphosphine*)*platinum*(II) (0·1964 g).

(e) *With di-μ-chloro-dichlorobis(triethylphosphine)dipalladium*(II). The palladium complex (0·2955 g, 0·50 mmol) and the olefin (0·1550 g, 0·52) were gradually heated in DMF (5 ml). When the temperature reached 90°, a dark red solution was formed. Upon cooling this gave cis-*dichloro*(N-*methylbenzothiazolinylidene*)(*triethylphosphine*)*palladium*(II) (0·2520 g), purified by washing with ether.

(f) *With di-μ-chloro-dichlorobis(tri-n-butylphosphine)dipalladium*(II). By using the procedure (e) (but inducing crystallisation by adding ether), the palladium complex (0·3800 g, 0·5 mmol) and the olefin (0·1490 g, 0·50 mmol) gave cis-*dichloro*(N-*methylbenzothiazolinylidene*)(*tri-n-butylphosphine*)*palladium*(II) (0·3550 g).

Reactions of 1,1′,3,3′-*Tetramethyl*-2,2′-*bi-imidazolidinylidene*) (IIIa).—(a) *With di-μ-chloro-dichlorobis(triethylphosphine)diplatinum*(II). The olefin (0·7 ml) was added to a suspension of the platinum complex (1·4733 g, 1·92 mmol) in benzene (25 ml). A red solution formed within about 10 min. The colour gradually faded and a small amount of solid formed after agitation (3 h at 20°). This was filtered off, washed with ether, and identified as cis-*dichloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (0·0760 g).

The benzene-soluble fraction was evaporated to *ca.* 10 ml and n-hexane (20 ml) was added. The precipitate was crystallised [$CHCl_3$ (10 ml)–n-C_6H_{14} (20 ml)] to yield the trans-*isomer* (1·5200 g).

(b) *With di-μ-bromo-dibromobis(triethylphosphine)diplatinum*(II). The olefin (0·3 ml) was added to a solution of the platinum complex (0·9460 g, 1·00 mmol) in benzene (30 ml) and the mixture heated under reflux (15 min). After cooling to 20°, the precipitate was filtered off and washed with ether. Recrystallisation ($CHCl_3$–Et_2O) gave cis-*dibromo*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*platinum*(II) (0·2613 g).

The filtrate was evaporated to dryness. The residue was recrystallised (Me_2CO–Et_2O) to yield the trans-*isomer* (0·3000 g).

(c) *With di-μ-chloro-dichlorobis(tri-n-propylphosphine)diplatinum*(II). The olefin (0·5 ml) was added to a solution of the platinum complex (1·6942 g, 2·00 mmol) in benzene (35 ml). A red solution formed which lightened upon stirring (2 h at 20°) and yielded a white solid. The volume of the solution was reduced to *ca.* 20 ml, and the solid was filtered off and washed with ether (10 ml). It was identified as cis-*dichloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*tri-n-propylphosphine*)*platinum*(II) (0·4376 g).

The benzene solution was evaporated to *ca.* 3 ml and passed through an alumina column. The pale yellow fraction was removed; the residue was recrystallised (n-C_6H_{14}, 20 ml) and identified as the trans-*isomer* (0·3200 g).

(d) *With di-μ-chloro-dichlorobis(tri-n-butylphosphine)diplatinum*(II). The olefin (0·3 ml) was added to a solution of the platinum complex (0·9360 g, 1 mmol) in benzene (2·5 ml) and the mixture was agitated (3 h at 20°). The volume of benzene was reduced to *ca.* 5 ml and ether was added. Upon cooling, an oily solid separated. This was twice crystallised (MeOH–C_6H_6–n-C_6H_{14} and $CHCl_3$–Et_2O) to yield cis-*dichloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*tri-n-butylphosphine*)*platinum*(II) (0·1700 g).

The trans-*isomer* (0·3796 g) was purified as in (c).

(e) *With di-μ-chloro-dichlorobis(dimethylphenylphosphine)diplatinum*(II). The olefin (0·3 ml) was added to the platinum complex (0·8080 g, 1·00 mmol) in benzene (35 ml), and the mixture was heated under reflux for 20 min. During heating a sticky oil separated out. The mixture was set aside for 30 h at 20°. An off-white precipitate had formed. This was filtered off, treated several times with warm acetone, and the washings were cooled. The precipitated solid was recrystallised ($CHCl_3$–Et_2O) to yield cis-*dichloro*-(1,3-*dimethylimidazolidin*-2-*ylidene*)(*dimethylphenylphosphine*)*platinum*(II) (0·4210 g).

This compound was also obtained (in 45% yield) by stirring (25 h) the platinum complex (0·8080 g, 1·00 mmol) and the olefin (0·3 ml) in benzene (30 ml) at 20°.

(f) *With di-μ-chloro-dichlorobis(triethylarsine)diplatinum*(II). The olefin (0·3 ml) was added to the platinum complex (0·8560 g, 1·00 mmol) in benzene (25 ml). The mixture was agitated (16 h at 20°). A sticky solid formed. This was filtered off and washed with acetone. The solid was extracted with chloroform (*ca.* 6 ml). Addition of ether to the extract gave cis-*dichloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylarsine*)*platinum*(II) (0·1630 g).

The benzene-soluble part was evaporated to dryness and washed with n-hexane. The residue was crystallised (twice from Me_2CO, 8 ml) to yield the trans-*isomer* (0·3180 g).

(g) *With di-μ-chloro-dichlorobis(triethylphosphine)dipalladium*(II). The olefin (0·2 ml) was added to a solution of the palladium complex (0·4000 g, 0·68 mmol) in benzene (20 ml), and the mixture was heated under reflux (15 min). A black precipitate formed. The mixture was allowed to cool and was then filtered. The precipitate was heated with charcoal under reflux in chloroform (15 ml). Filtration (57°) provided a yellow filtrate. This was evaporated to *ca.* 5 ml and addition of n-hexane gave cis-*dichloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triethylphosphine*)*palladium*(II) (0·1302 g).

The benzene-soluble fraction from the black precipitate was evaporated to dryness and dissolved in ether. Upon cooling to −20°, yellow crystals of *trans*-dichlorobis(triethylphosphine)palladium(II) (0·063 g) (Found: C, 35·6; H, 7·6. Calc. for $C_{12}H_{30}Cl_2P_2Pd$: C, 35·4; H, 7·4%) were obtained.

(h) *With di-μ-chloro-dichlorobis(tri-n-butylphosphine)dipalladium*(II). The olefin (0·6 ml) was added to a solution of the palladium complex (1·5200 g, 2 mmol) in benzene (35 ml), and the mixture was heated under reflux for 15 min. A black precipitate had formed. After cooling to 20°, benzene was removed *in vacuo*. The residue was treated with charcoal in hot chloroform (15 ml) and was then filtered. The filtrate was evaporated to dryness, washed several times with ether (3 × 10 ml), and the combined washings yielded *trans*-dichlorobis(tri-n-butylphosphine)-palladium(II) (0·1900 g) (Found: C, 49·85; H, 9·7. Calc. for $C_{24}H_{54}Cl_2P_2Pd$: C, 49·5; H, 9·3%).

The ether-insoluble residue was dissolved in chloroform. Addition of ether gave cis-*dichloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*tri-n-butylphosphine*)*palladium*(II) (0·4830 g).

Attempted Reactions with Other Olefins.—(a) *N,N'*-Dimethylbiacridylidene (0·0425 g, 0·11 mmol) (from Dr. F. McCapra) and di-μ-chloro-dichlorobis(triethylphosphine)-diplatinum(II) (0·1587 g, 0·21 mmol) were heated under reflux in xylene (15 ml) for 2 h. There was no colour change. The mixture was cooled, the product filtered off and dried.

(b) Tetraphenylethylene (0·1450 g, 0·44 mmol) and di-μ-chloro-dichlorobis(triethylphosphine)diplatinum(II) (0·3350 g, 0·44 mmol) were heated under reflux in xylene (20 ml) for 3 h.

The reactants in (a) and (b) were recovered essentially quantitatively, and identified by their i.r. spectra, after removal of xylene and separation ($CHCl_3$) of the two components (the Pt complex is $CHCl_3$-soluble).

Reaction of Bis(trifluoromethyl)diazomethane with Di-μ-chloro-dichlorobis(triethylphosphine)diplatinum(II).—The diazomethane (0·4 ml, 0·6 g, 3·3 mmol) was distilled into the suspension of the complex (0·9173 g, 1·2 mmol) in ether (20 ml) at −196°. The mixture was allowed to warm to room temperature and was stirred for 2 h to afford a pale yellow solution. Filtration and cooling to −20° produced pale yellow crystals of *di-μ-chloro-di[chlorobis(trifluoromethyl)-methyl]bis(triethylphosphine)diplatinum*(II) (0·9510 g) (Found: C, 20·0; H, 2·9; Cl, 13·0; F, 21·6; P, 5·8. $C_{18}H_{30}Cl_4F_{12}P_2Pt_2$ requires C, 20·2; H, 2·8; Cl, 13·3; F, 21·3; P, 5·8%).

Reaction of Di-μ-chloro-di[bis(trifluoromethyl)chloromethyl]-bis(triethylphosphine)diplatinum(II), (XIII).—(a) *With* p-*toluidine*. The insertion product (XIII) (0·5561 g, 0·5 mmol) and *p*-toluidine (0·1525 g, 1·4 mmol) were stirred in benzene (20 ml) for 5 h. The solvent was removed and the residue was crystallised from light petroleum (b.p. 60—80°). Recrystallisation from the same solvent yielded crystals of [*bis(trifluoromethyl)chloromethyl*]*chloro*(*triethylphosphine*)(p-*toluidine*)*platinum*(II), (XV) (0·4630 g) (Found: C, 30·2; H, 3·9; N, 2·3. $C_{16}H_{24}Cl_2F_6NPPt$ requires C, 30·0; H, 3·7; N, 2·2%).

(b) *With bromine*. The insertion product (XIII) (0·5553 g, 0·5 mmol) and bromine (0·1 ml, 0·3 g, 1·9 mmol) were heated (½ h) in ether (25 ml) under reflux. Volatile material was removed *in vacuo*. The dark residue was washed with ether and then extracted with benzene. Ether addition to the benzene solution afforded orange crystals of di-μ-bromo-dibromobis(triethylphosphine)diplatinum(II) (0·2246 g, 45%) (Found: C, 15·1; H, 3·3. Calc. for $C_{12}H_{30}Br_4P_2Pt$: C, 15·2; H, 3·2%).

Reaction of Tris(triphenylphosphine)platinum(0) with Bis-(trifluoromethyl)diazomethane.—The diazomethane (1·3 ml, 2·1 g, 10 mmol) was distilled onto a frozen solution of tris(triphenylphosphine)platinum(0) (3·1096 g, 3·16 mmol) in benzene (25 ml) at −196°. The mixture was allowed to warm to room temperature; at *ca.* −20°, gas evolution was observed and lasted for *ca.* 5 min. The amount of gas evolved was 104% of the calculated quantity (a gas burette was used). The solution was stirred (2 h) at 20°. The volume of the solution was reduced to *ca.* 5 ml *in vacuo* and was then passed through a Florisil packed column. The main fraction was crystallised by adding n-hexane to the benzene eluent. The yellow crystalline solid was sublimed at 90°, 0·01 mmHg for 30 h to isolate the phosphazine, identified by comparison with an authentic sample of $(CF_3)_2CN_2{\cdot}PPh_3$. The residue was recrystallised ($CHCl_3$–n-C_6H_{14}) to obtain *orange cubes* (1·6 g) (Found: C, 47·6; H, 2·9; N, 2·6. $C_{42}H_{30}F_{12}N_2P_2Pt$ requires C, 48·1; H, 2·9; N, 2·7%).

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