Preparation and Spectroscopic Properties of Electroneutral Alkoxy(organo)carbene Complexes of Platinum(II) and the Crystal and Molecular Structure of *cis*-[Benzyl(ethoxy)carbene]dichloro(dimethylphenylphosphine)platinum(II)

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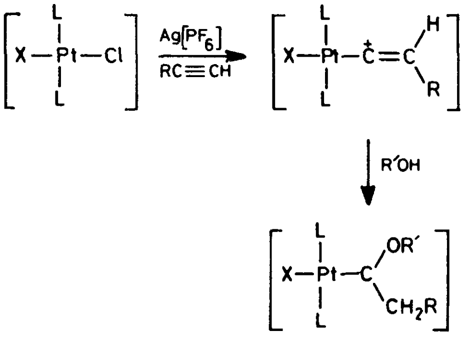
A series of electroneutral alkoxy(organo)carbene complexes of platinum(II), *cis*-$[PtX_2L\{C(OR')(CH_2R)\}]$, has been prepared by reaction of the halide-bridged dimer $[Pt_2X_4L_2]$ (X = Cl, Br, or I; L = PMe_2Ph or PEt_3) with monosubstituted acetylenes RC≡CH(R = Ph, Me, or Et) and alcohols R'OH (R' = Me, Et, or Pr^n). The complexes have been characterised analytically, by ^1H and ^{31}P n.m.r. and i.r. spectroscopy, and by *X*-ray analysis of a typical member of the series. Crystals of the title complex are monoclinic, space group $P2_1/n$, with a = 15.084(2), b = 8.419(3), c = 15.801(3) Å, β = 92.93(2)°, and Z = 4. The structure has been solved by the heavy-atom method and refined by full-matrix least squares to R = 0.036 for 2 166 diffractometric intensity data corrected for absorption. The crystals are built of discrete molecules with *cis* square-planar geometry. Selected bond lengths are: Pt–P 2.240(3), Pt–Cl(*trans* to P) 2.355(3), Pt–Cl(*trans* to C) 2.375(3), and Pt–C 1.920(9) Å. The molecular structure displays a Pt · · · H contact of 2.6(1) Å to a hydrogen atom of the ethoxy CH_2 group. The ^1H n.m.r. spectra indicate that this Pt · · · H interaction persists in solution, and is a general feature of these neutral complexes.

WELL characterised alkoxy(organo)carbene complexes are now known for many transition metals.[1] In the case of platinum, however, only cationic species have so far been reported. They were prepared either by the reaction of acetylenes and alcohols with platinum(II) halide complexes[2] or by the action of alcohols on platinum(II) acetylides or α-chlorovinyls.[3] A reaction mechanism involving cationic platinum(II) vinylidene intermediates has been proposed [equation (1)].[3] The use of non-co-ordinating anions, such as $[PF_6]^-$, is necessary to prevent nucleophilic attack at the co-ordinated carbene, leading to decomposition.

Our interest in the effect of the positive charge on the stability of these complexes, on the intermediates leading to them, and on the course of their reactions led us to prepare and examine spectroscopically a corresponding series of electroneutral alkoxy(organo)carbene derivatives of Pt^{II}. A typical member of the series, *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$, has been subjected to *X*-ray diffraction analysis in order to provide an unequivocal structural basis for the interpretation of the chemistry and spectroscopic properties of the new complexes.[4] The structure determination also enables us to extend our previous studies of the *trans* influence and bonding to Pt^{II} of different types of carbene ligands.[5,6]

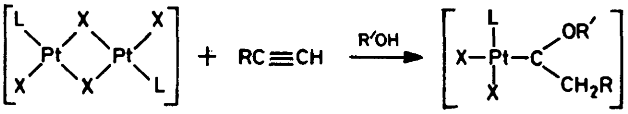


(1)

The reactions of the electroneutral alkoxy(organo)carbene complexes of Pt^{II} are compared with those of the cationic species in the following paper.[7]

RESULTS AND DISCUSSION

Preparation of $[PtX_2L\{C(OR')(CH_2R)\}]$ *Complexes*.—Treatment, at room temperature, of chloroform solutions of binuclear halide-bridged platinum complexes, $[Pt_2X_4L_2]$ (X = Cl, Br, or I; L = PMe_2Ph or PEt_3), with monosubstituted acetylenes, RC≡CH (R = Ph, Me, or Et), and alcohols, R'OH (R' = Me, Et, or Pr^n), led to the formation of electroneutral alkoxy(organo)carbene derivatives [equation (2)]. Reactions with acetylene itself (R = H) were unsuccessful, presumably owing to competing side reactions.[2]



(2)

The yields of the complexes varied between 30 and 70%, being highest in the cases where X = Br. The reaction rates and yields were generally increased if at least a 50% excess of the acetylene was employed, suggesting that the first step of the reaction is formation of a platinum–acetylene complex by halide-bridge cleavage [equation (3)]. Thus it is apparent that a

$$[Pt_2X_4L_2] + 2RC{\equiv}CH \rightleftharpoons 2[PtX_2L(RC{\equiv}CH)] \quad (3)$$

positive charge is not necessary either for the formation of platinum(II) carbene complexes from acetylenes and alcohols, or for their subsequent stabilisation. Moreover, if a route analogous to that of equation (1) is followed, the vinylidene intermediates must exist in a neutral form as well. Such a possibility has recently been suggested.[3]

The complexes are colourless crystalline solids, stable to air and moisture; the melting points and analytical data are listed in Table 1. They are soluble in chloroform and methylene chloride, but only sparingly so in benzene, acetone, or methanol. The solutions in chloroform survive for several days at room temperature with little decomposition. Those of the chloro-complexes decompose to the extent of *ca.* 20% over 24 h at 60 °C, while those of the bromide complexes appear to be more resistant to thermal decomposition.

TABLE 1

Characterisation data

Complex	M.p. (θ_c/°C)	Analysis (%)						ν(Pt–Cl) (cm^{-1})	*J*(Pt–P)/Hz
		Found			Calc.				
		C	H	X	C	H	X		
$[PtCl_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$	118—119	37.84	3.90	13.77	37.92	3.93	13.18	312, 289	3 754
$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$	124—125	39.24	4.24	12.88	39.13	4.20	12.84	317, 288	3 764
$[PtCl_2(PMe_2Ph)\{C(OPr^n)(CH_2Ph)\}]$	144—145	40.09	4.32		40.29	4.45		312, 287	
$[PtCl_2(PMe_2Ph)\{C(OMe)Et\}]$	122—123	30.50	3.97	15.30	30.25	4.02	14.89	312, 289	3 763
$[PtCl_2(PMe_2Ph)\{C(OEt)Et\}]$	139—141	32.19	4.46		31.84	4.32		311, 288	
$[PtCl_2(PMe_2Ph)\{C(OEt)Pr^n\}]$	128—129	33.39	4.63	13.81	33.33	4.60	14.07	313, 283	3 778
$[PtCl_2(PEt_3)\{C(OMe)(CH_2Ph)\}]$	122—123	34.55	4.73		34.75	4.86		312, 285	3 690
$[PtCl_2(PEt_3)\{C(OEt)Pr^n\}]$	150—151	29.83	5.32		29.75	5.62		311, 286	3 726
$[PtBr_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$	126—127	32.41	3.27	25.54	32.54	3.38	25.49		3 723
$[PtBr_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$	137—138	33.74	3.59	24.84	33.70	3.62	24.93		3 733
$[PtBr_2(PMe_2Ph)\{C(OMe)Et\}]$	126—127	25.56	3.26	28.22	25.49	3.39	28.28		
$[PtBr_2(PMe_2Ph)\{C(OEt)Et\}]$	130—131	27.17	3.64	27.44	26.94	3.66	27.60		
$[PtBr_2(PEt_3)\{C(OMe)(CH_2Ph)\}]$	124—125	29.61	3.73		29.65	4.15			
$[PtI_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$	121—122	27.99	2.69		28.22	2.93			3 589
$[PtI_2(PMe_2Ph)\{C(OMe)Et\}]$	120—121	21.50	2.79	38.79	21.79	2.90	38.70		3 596
$[PtI_2(PEt_3)\{C(OMe)(CH_2Ph)\}]$	116	25.49	3.61	35.99	25.68	3.59	36.23		

TABLE 2

Proton n.m.r. data ($CDCl_3$ solution)

	Phosphine methyls			α-Alkoxy protons			α-Carbene protons		
Complex	δ(Me) [a]	*J*(P–H) [b]	*J*(Pt–H)	δ(OCH_2R)	*J*(Pt–H)	*J*(CH_2–CH_2R')	δ(CH_2R)	*J*(H–H′)	*J*(CH_2–CH_2R')
$[PtCl_2(PMe_2Ph)$-$\{C(OMe)(CH_2Ph)\}]$ [c]	1.80 1.76	11.5	45.0	4.92	8.2		4.11 3.73	17.7	
$[PtCl_2(PMe_2Ph)$-$\{C(OEt)(CH_2Ph)\}]$ [d,e]	1.78 1.73	11.7	44.6	5.73 5.11	8.6	7.2	4.11 3.77	17.6	
$[PtCl_2(PMe_2Ph)\{C(OPr^n)(CH_2Ph)\}]$	1.77 1.73	11.5	46.0	5.53 4.91	*f*	*f*	4.09 3.72	18.0	
$[PtCl_2(PMe_2Ph)\{C(OMe)Et\}]$	2.07 2.00	11.7	44.8	4.92	8.2		2.64		7.0
$[PtCl_2(PMe_2Ph)\{C(OEt)Et\}]$	2.05 1.97	11.7	45.0	*f*	*f*	7.2	2.75		7.0
$[PtCl_2(PMe_2Ph)\{C(OEt)Pr^n\}]$	2.05 1.96	12.0	44.2	5.67 5.10	*f*	7.0	2.62		*f*
$[PtCl_2(PEt_3)\{C(OMe)(CH_2Ph)\}]$				4.95	8.2		4.35 4.00	18.0	
$[PtCl_2(PEt_3)\{C(OEt)Pr^n\}]$ [e,g]				5.89 5.30	*f*	7.2	*f*		7.0
$[PtBr_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$	1.86 1.84	12.0	46.0	4.88	8.5		4.29 3.81	17.8	
$[PtBr_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$	1.83 1.79	11.5	47.0	*f*	*f*	7.0	4.25 3.83	17.8	
$[PtBr_2(PMe_2Ph)\{C(OMe)Et\}]$	2.15 2.09	11.5	46.0	4.88	8.2		2.70		7.0
$[PtBr_2(PMe_2Ph)\{C(OEt)Et\}]$	2.12 2.05	11.5	46.0	*f*	*f*	7.0	2.70		7.0
$[PtBr_2(PEt_3)\{C(OMe)(CH_2Ph)\}]$				4.83	8.5		4.47 4.07	18.0	
$[PtI_2(PMe_2Ph)\{C(OMe)(CH_2Ph)\}]$	1.92	11.5	45.5	4.71	8.5		4.54 3.97	18.5	
$[PtI_2(PMe_2Ph)\{C(OMe)Et\}]$	2.19 2.12	11.5	44.5	4.72	8.0		2.83		7.0
$[PtI_2(PEt_3)\{C(OMe)(CH_2Ph)\}]$				4.73	*h*		4.78 4.29	18.0	

[a] Shifts in p.p.m. downfield of $SiMe_4$. [b] Coupling constants in Hz. [c] 100-MHz spectrum. [d] 220-MHz spectrum. [e] α-Alkoxy protons, *J*(H–H′) 10.5 Hz. [f] Unresolved. [g] 90-MHz spectrum. [h] Unresolved due to overlap of CH_2 signal.

N.M.R. and I.r. Spectra.—The ^{31}P n.m.r. spectra of the neutral complexes all show $^1J(^{195}Pt-^{31}P)$ coupling constants around 3 600 Hz (Table 1). These values are typical for tertiary phosphines *trans* to halides in platinum(II) species,[8] and thus indicate a *cis* geometry for the complexes. The *cis* configuration is also apparent from the far-i.r. spectra of the chloro-complexes: two ν(Pt–Cl) stretching bands of equal intensity are found at *ca.* 310 and 290 cm^{-1} (Table 1). These values are similar to those reported for other *cis*-carbenedichloroplatinum(II) species,[9] and also for *cis*-$[PtCl_2(PEt_3)_2]$ (305 and 283 cm^{-1}).[10]

The ^1H n.m.r. spectra reveal a number of interesting features (Table 2). The benzyl methylene groups of the alkoxy(benzyl)carbene complexes give rise to AB patterns, and the phosphine methyl groups of the PMe_2Ph complexes are non-equivalent (double doublets with ^{195}Pt satellites).* Both these features are indicative of hindered rotation about the Pt–C bond in solution. The OCH_2 protons of the ethoxy- and propoxy-carbene complexes are also non-equivalent. For each complex the chemical-shift difference between the two methylene protons is substantial (*ca.* 0.6 p.p.m., Table 2), suggesting that on average they occupy very different magnetic environments.

Long-range coupling of ^{195}Pt to the alkoxy-groups is present in all the complexes, but can only be clearly resolved in the methoxycarbene derivatives. Irradiation of the ethyl CH_3 groups in *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$ and *cis*-$[PtCl_2(PEt_3)\{C(OEt)Pr^n\}]$ results in each of the OCH_2CH_3 signals collapsing to a broadened doublet [due to $^2J(H-H')$], but $^4J(Pt-H)$ coupling is still not fully resolved. Similarly, the α-carbene-carbon proton signals of the benzyl, ethyl, and propyl groups are broadened by coupling to platinum, but $^3J(Pt-H)$ values have not been obtained.

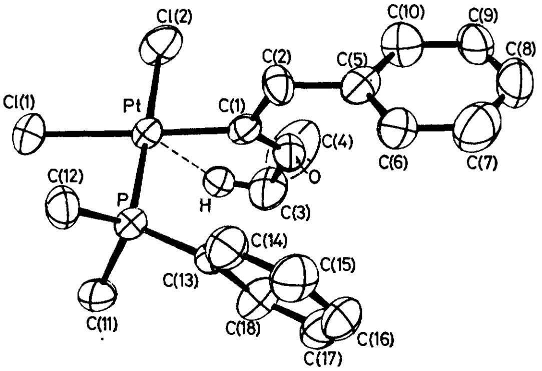


FIGURE A view of the molecular structure of *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$. The thermal vibration ellipsoids display 50% probability. Hydrogen atoms are omitted for clarity, apart from that involved in the Pt ··· H contact of 2.59(8) Å. The corresponding C(1)–Pt–H and P–Pt–H angles are respectively 64 and 104° and the deviations of the atoms Pt, O, C(1), C(3), and H from their common plane do not exceed 0.08 Å

The Crystal and Molecular Structure of cis-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$.—The crystals are built of discrete monomeric molecules. The shortest distances between atoms in different molecules are close to the sums of the appropriate van der Waals radii.

The molecules adopt a *cis* square-planar configuration (Figure, Table 3), as expected from the ^{31}P n.m.r. and i.r. spectra of the complex. The rotational orientation of the phosphine ligand around the Pt–P bond is such that the α-carbon atom C(13) lies only 0.09 Å away from the co-ordination plane of platinum, and consequently forms a rather close approach, 3.23 Å, to the carbenoid carbon, C(1). Steric interaction between the bulky phosphine and carbene ligands is further apparent from the opening of the Pt–P–C(13) angle to 116.9(3)°, as compared with the values [111.2(4) and 112.7(4)°] for the other Pt–P–C angles; it also leads to opening of the P–Pt–C(1) angle to 94.5(3)°, mainly at the expense of the C(1)–Pt–Cl(2) and P–Pt–Cl(1) angles of 86.9(3) and 87.9(1)°, respectively (Table 3). The individual displacements of the Pt, Cl(1), Cl(2), P, and C(1) atoms from their least-squares plane do not exceed ±0.002 Å. Thus the co-ordination geometry of the metal atom is closely similar to those found in the complexes *cis*-$[PtCl_2(PEt_3)L]$ [L = C(OEt)(NHPh)[5] and $C(NPhCH_2)_2$].[6] All these complexes are characterised by a close contact between one of the α-carbon atoms of the phosphine ligand and the carbenoid carbon (*ca.* 3.2 Å), a P–Pt–C angle of 94—95°, and an almost exact coplanarity of the metal and ligand donor atoms.

TABLE 3

Selected interatomic distances and angles

(*a*) Bond lengths (Å)

Pt–Cl(1)	2.375(3)	C(5)–C(6)	1.39(2)
Pt–Cl(2)	2.355(3)	C(5)–C(10)	1.40(2)
Pt–P	2.240(3)	C(6)–C(7)	1.39(2)
Pt–C(1)	1.920(9)	C(7)–C(8)	1.37(2)
P–C(11)	1.798(11)	C(8)–C(9)	1.37(2)
P–C(12)	1.808(11)	C(9)–C(10)	1.35(2)
P–C(13)	1.821(9)	C(13)–C(14)	1.38(2)
O–C(1)	1.283(11)	C(13)–C(18)	1.40(2)
O–C(3)	1.509(15)	C(14)–C(15)	1.37(2)
C(1)–C(2)	1.490(15)	C(15)–C(16)	1.34(2)
C(2)–C(5)	1.524(14)	C(16)–C(17)	1.36(2)
C(3)–C(4)	1.506(22)	C(17)–C(18)	1.38(2)

(*b*) Bond angles (°)

Cl(2)–Pt–Cl(1)	90.7(1)	C(1)–O–C(3)	121.4(8)
C(1)–Pt–Cl(1)	177.6(3)	Pt–P–C(11)	111.2(4)
C(1)–Pt–Cl(2)	86.9(3)	Pt–P–C(12)	112.7(4)
P–Pt–Cl(1)	87.9(1)	Pt–P–C(13)	116.9(3)
P–Pt–Cl(2)	178.6(1)	C(11)–P–C(12)	105.1(5)
C(1)–Pt–P	94.5(3)	C(11)–P–C(13)	105.4(5)
Pt–C(1)–O	127.5(8)	C(12)–P–C(13)	104.6(5)
Pt–C(1)–C(2)	120.4(7)	O–C(3)–C(4)	105.9(12)
O–C(1)–C(2)	111.6(8)	C(1)–C(2)–C(5)	118.8(8)

(*c*) Torsion angles (°)

C(1)–Pt–P–C(11)	−118(1)
C(1)–Pt–P–C(12)	125(1)
C(1)–Pt–P–C(13)	3(1)
Pt–C(1)–C(2)–C(5)	178(1)
C(2)–C(1)–O–C(3)	−174(1)
C(1)–C(2)–C(5)–C(6)	−98(1)
C(1)–C(2)–C(5)–C(10)	82(1)
Pt–C(1)–O–C(3)	−2(1)
C(1)–O–C(3)–C(4)	119(1)

The orientation of the carbene ligand around the Pt–C(1) bond is such as to make the plane through the C(1), Pt, C(2), and O atoms almost normal to the co-ordination plane of platinum, the dihedral angle being 85°. Similar values for such angles, 70—90°, have been observed in other platinum(II) complexes containing non-chelating carbene ligands.[5,6] The co-ordination geometry around the carbenoid carbon atom is distorted trigonal planar. The individual displacements of the Pt, C(1), C(2), and O atoms from their least-squares plane are within ±0.05 Å. The substantial deviations from 120° of the valency angles subtended at C(1) are not unusual; thus the C(2)–C(1)–O angle of 111.6(8)° compares well with the N–C–O angle of 110(2)° in *cis*-

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* Changing the solvent can sometimes simplify this feature, presumably by coincidental chemical shifts of the methyl groups.

$[PtCl_2(PEt_3)\{C(OEt)(NHPh)\}]$.[5] The C(1)–C(2), C(2)–C(5), O–C(3), and C(3)–C(4) distances (Table 3) are indicative of single-bond character. The C(1)–O distance [1.283(11) Å] is somewhat shorter than the value (1.33 Å) found in *cis*-$[PtCl_2(PEt_3)\{C(OEt)(NHPh)\}]$,[5] *trans*-$[PtMe(PMe_2Ph)_2\{C(OMe)Me\}]^+$,[11] and in alkoxy(organo)carbene derivatives of $[Cr(CO)_5]$, and believed to reflect a bond order of 1.3.[1b] It is therefore apparent that, in the *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$ complex, donation of lone-pair electron density by the oxygen atom to the carbenoid carbon atom contributes considerably to stabilisation of the carbene ligand. The ligand displays a *trans* configuration about the multiple C(1)–O bond, as evident from the C(2)–C(1)–O–C(3) torsion angle of −174(1)°.

The Pt–C(1) bond length [1.920(9) Å] may be compared with the corresponding distances [1.96(2) and 2.009(13) Å] in *cis*-$[PtCl_2(PEt_3)L]$ complexes, where L = C(OEt)(NHPh) [5] and $C(NPhCH_2)_2$,[6] respectively, and also with our estimate of 2.02 Å for the length of a single Pt^{II}–$C(sp^2)$ bond subject to low *trans* influence.[12] We believe that the variations in these bond lengths reflect small changes in the extent of Pt→C backbonding and thus lead to the π-acidity series of the carbene ligands: $C(OEt)(CH_2Ph) > C(OEt)(NHPh) > C(NPhCH_2)_2$. This series is related to the number of α-carbene heteroatoms having lone-pair electrons capable of interacting with the formally empty *p* orbital of the carbenoid carbon, and also to the electronegativity of the heteroatoms. A similar conclusion has been drawn from structural studies of chromium(0) carbene complexes.[1b] The Cr–C bond lengths, however, display a greater range than the Pt–C distances [2.04(3) Å for C(OR)R ligands, 2.16(1) Å for $C(NR_2)R$ ligands (R = alkyl or aryl), and 2.21(2) Å for a single Cr^0–$C(sp^2)$ bond [1b]]. This is not unexpected, since the π basicity of Pt^{II} is unlikely to be as high as that of Cr^0. The shortening of the C(1)–O bond in *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$, with respect to C–O distances in alkoxy(organo)carbenechromium(0) species, is consistent with the above view of the relative π-donor abilities of the metal atoms.

The Pt–Cl(*trans* to C) distances in the $C(OEt)(CH_2Ph)$, C(OEt)(NHPh),[5] and $C(NPhCH_2)_2$ [6] complexes [respectively 2.375(3), 2.361(5), and 2.362(3) Å] indicate that the three carbene ligands exert comparable *trans* influence on Pt–Cl bonds. This result is in apparent conflict with our view that increasing π acidity, evident in the series $C(NPhCH_2)_2 < C(OEt)(NHPh) < C(OEt)(CH_2Ph)$, should lead to diminishing *trans* influence.[13] However, in the $C(OEt)(CH_2Ph)$ complex there is a short intramolecular Pt · · · H(carbene) contact (see below), not present in the C(OEt)(NHPh) or $C(NPhCH_2)_2$ complexes, which could perturb the *trans* Pt–Cl bond length. Such an effect is not unprecedented: differences in the Rh–Cl bond lengths in the two isomers of $[RhCl(PPh_3)_3]$ have been rationalised in terms of the different natures of the intramolecular *trans* Rh · · · H interactions.[14,15]

The Pt–Cl(*trans* to P) and Pt–P distances [respectively 2.355(3) and 2.240(3) Å] agree well with the corresponding values in the C(OEt)(NHPh) and $C(NPhCH_2)_2$ complexes.[5,6] The former distance is comparable with the Pt–Cl(*trans* to C) bond length, implying that the PMe_2Ph and $C(OEt)(CH_2Ph)$ ligands exert similar *trans* influences on Pt–Cl bonds. The geometry of the dimethylphenylphosphine ligand is normal (Table 3).

Perhaps the most interesting feature of the molecular structure is the short intramolecular Pt · · · H contact [2.59(8) Å] * involving a hydrogen atom bonded to the α-carbon of the ethoxy-group, C(3) (Figure). [The next shortest Pt · · · H distances, 2.94 and 3.00 Å, are to the protons attached to C(2).] Shorter metal–hydrogen contacts have been reported for complexes of the earlier transition metals: 2.2 Å in a ruthenium carbene derivative [16] and *ca.* 2.0 Å in two molybdenum pyrazolylborate complexes.[17] In square-planar d^8 species, notably in the red and orange forms of Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, metal–hydrogen contacts as long as 2.8 Å are considered to be of structural and chemical significance. It has been suggested that they represent *non-primary valence interactions* formally providing a noble gas configuration at the metal atom.[14] In *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$ the Pt–C(1)–O–C(3) and C(1)–O–C(3)–H torsion angles are −2(1) and 11(4)°. Thus the geometry of the co-ordinated carbene is such as to direct one of the C(3)–H bonds towards the metal atom; it can be considered that the C–H electron pair approaching the valence shell of the metal atom enables it to achieve, at least in a formal sense, an 18-electron configuration.

As noted above, the ^1H n.m.r. spectra of *cis*-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$ and of related complexes indicate that rotation about the Pt–C bond is restricted in solution and, furthermore, that the magnetically non-equivalent ethoxy methylene protons are in very different environments. The intramolecular Pt · · · H interaction we report here may thus be a general feature of this series of complexes, persisting in solutions at ambient temperatures as well as in the solid state.

EXPERIMENTAL

Spectra.—Infrared spectra of solid products as KBr discs were recorded on Perkin-Elmer 225 and 580 spectrophotometers. Proton n.m.r. spectra were obtained on Varian T-60, Varian HA-100, and Perkin-Elmer R32 spectrometers, ^{31}P n.m.r. spectra on a Varian XL-100 spectrometer.

Preparations.—All the neutral carbene complexes were prepared by similar procedures. A typical example is given below.

cis-*[Benzyl(ethoxy)carbene]dibromo(dimethylphenylphosphine)platinum*(II). Di-μ-bromo-bis[bromo(dimethylphenylphosphine)platinum(II)] (0.630 g) was dissolved in pure chloroform (50 cm^3) under nitrogen and ethanol (4 cm^3) was added. Phenylacetylene (0.20 cm^3, 3 mol. equivalents) was introduced and the solution was stirred for 8 h at room temperature. The solvent was then removed to leave a light brown solid which was dried *in vacuo* to remove trace

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* Obtained from the refined co-ordinates of the hydrogen atom; calculation based on an assumed C–H bond length of 1.08 Å leads to a value of 2.57 Å.

amounts of unchanged phenylacetylene. This solid was stirred vigorously in benzene and the solution was filtered to remove brown, soluble, organic materials. The nearly white solid was recrystallised from methylene chloride–diethyl ether giving *cis*-$[PtBr_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$ as fine white *crystals* (0.459 g, 56%).

In those preparations where methyl- or ethyl-acetylene was used, the gas was bubbled through the chloroform solution containing the dimeric platinum species and the alcohol.

Determination of the Crystal Structure of cis-$[PtCl_2(PMe_2Ph)\{C(OEt)(CH_2Ph)\}]$.—*Crystal data*. $C_{18}H_{23}Cl_2OPPt$, $M = 552.4$. Monoclinic, $a = 15.084(2)$, $b = 8.419(3)$, $c = 15.801(3)$ Å, $\beta = 92.93(2)°$, $U = 2\,004$ Å^3, $Z = 4$, $D_c = 1.830$ g cm^{-3}, $F(000) = 1\,064$, space group $P2_1/n$ (C^5_{2h}, no. 14), Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 74.2 cm^{-1}.

Measurements. A crystal of dimensions *ca*. 0.05 × 0.09 × 0.17 mm was chosen for the analysis and its faces, representing all members of the forms {101}, {111}, and {001}, were identified by optical goniometry and *X*-ray measurements.

The crystal symmetry and preliminary unit-cell dimensions were determined from oscillation and Weissenberg photographs. Final values of the unit-cell parameters and the intensities of all the independent reflections with θ(Mo-K_α) $\leqslant 27°$ were measured on a Hilger and Watts Y290 four-circle diffractometer, equipped with a graphite monochromator and a pulse-height analyser. A symmetrical θ—2θ scan technique was employed. Each reflection was scanned through a θ range of 0.5°, with a scan step of 0.02° and a counting time of 4 s per step; the local background was counted for 15 s at each end of the scan range. The intensities of two strong reflections, periodically remeasured throughout the experiment, varied by $< \pm 6\%$ of their mean values.

The integrated intensities, I, and their standard deviations, $\sigma(I)$, were determined as described earlier, and using a value of 0.04 for the parameter q.[18] They were corrected for instability of the incident *X*-ray beam and for Lorentz, polarisation, and absorption effects. The transmission factors on F^2, calculated by Gaussian integration, varied between 0.57 and 0.74.

The subsequent calculations proceeded with 2 166 reflections for which $I \geqslant 3\sigma(I)$.

Structure analysis. The position of the platinum atom was determined from a Patterson function and the positions of the remaining atoms, including hydrogens, were obtained from the subsequent difference syntheses.

The structure was refined by full-matrix least-squares minimisation of the function $\Sigma w\Delta^2$, where $w = 1/\sigma^2(F_o)$ and $\Delta = |F_o| - |F_c|$. The atomic scattering factors were taken from ref. 19 apart from that for hydrogen.[20] The anomalous scattering of Pt, Cl, and P atoms was taken into account.[19]

Refinement of an overall scale factor and of the positional and thermal parameters of all the atoms, assuming isotropic and anisotropic vibrations for hydrogen and non-hydrogen atoms, respectively, converged at $R = 0.036$ and $R' = 0.041$. It led to hydrogen-atom positions which, although not accurately determined, are in agreement with the established stereochemistry of the trigonal and tetrahedral carbon atoms. Thus the C–H bond lengths range from 0.9(1) to 1.1(1) Å, apart from a C(4)–H distance of 0.6(1) Å in the ethoxy methyl group which displays a relatively high degree of thermal motion (Figure).

In the last cycle of refinement all the parameters shifted by $\leqslant 0.19\sigma$. The standard deviation of an observation of unit weight was 1.17, indicating that the w values were on a scale close to absolute. The mean values of $w\Delta^2$ showed little variation with either $|F_o|$ or sin θ. The extreme function values in the final difference synthesis, 1.1 and -1.4 e Å^{-3}, were at positions close to that of the platinum atom.

The final positional and thermal parameters of the hydrogen atoms and the thermal parameters of non-hydrogen atoms are listed in Supplementary Publication No. SUP 22413 (12 pp.),* together with the observed and calculated structure amplitudes. Fractional co-ordinates of the non-hydrogen atoms and the selected molecular geometry functions derived from these co-ordinates are presented in Tables 3 and 4. The computer programs used were those listed in ref. 21.

TABLE 4

Fractional co-ordinates of non-hydrogen atoms (× 10^4)

Atom	x	y	z
Pt	3 708.9(2)	1 764.3(5)	1 636.9(3)
Cl(1)	2 395(2)	0 278(4)	1 324(2)
Cl(2)	3 571(2)	3 002(5)	0 300(2)
P	3 809(2)	0 552(3)	2 900(2)
O	5 540(4)	2 739(8)	1 580(5)
C(1)	4 764(6)	3 010(13)	1 845(6)
C(2)	4 716(6)	4 595(13)	2 260(7)
C(3)	5 728(8)	1 281(15)	1 064(9)
C(4)	6 020(10)	1 883(26)	0 225(10)
C(5)	5 574(7)	5 517(14)	2 445(7)
C(6)	5 981(7)	5 456(16)	3 250(8)
C(7)	6 745(10)	6 338(19)	3 427(9)
C(8)	7 101(8)	7 263(17)	2 813(12)
C(9)	6 716(8)	7 273(14)	2 007(9)
C(10)	5 968(8)	6 440(15)	1 829(7)
C(11)	3 942(7)	−1 557(13)	2 783(8)
C(12)	2 820(7)	0 790(14)	3 487(7)
C(13)	4 712(6)	1 173(12)	3 635(6)
C(14)	4 595(7)	2 166(14)	4 314(7)
C(15)	5 304(9)	2 592(16)	4 842(7)
C(16)	6 125(9)	2 052(17)	4 717(8)
C(17)	6 265(7)	1 060(16)	4 054(7)
C(18)	5 567(7)	0 618(16)	3 504(7)

We thank Johnson, Matthey and Co. Ltd. for a loan of platinum halides, and the S.R.C. for the award of a maintenance grant (to G. K. A.).

[8/811 *Received, 2nd May*, 1978]

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