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PREPARATION OF COMPLEXES CONTAINING Pt—C BONDS BY USE OF (CROWN ETHER)POTASSIUM HYDROXIDE *

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Summary

The complexes $[PtR_2L_2]$ and $[PtR(Cl)L_2]$ containing phosphines (L) and the σ-carbyl ligands R (R = CH_2NO_2, C≡CPh, CH_2CN, CH_2COPh, $CH_2COC_6H_4$-NO_2-4, $CH_2COC_6H_4OMe$-2, CH_2COMe) have been prepared from $[PtCl_2L_2]$, RH and KOH in the presence of 18-crown-6. Some complexes containing hydroxo-ligands were also formed. Structures have been determined from the ^{31}P-$\{^1H\}$ and ^1H NMR spectra.

Introduction

Recent work has shown that platinum(II) complexes with terminal hydroxo ligands react with acidic C—H bonds with the elimination of H_2O and formation of organoplatinum(II) complexes with functional groups in the organo-ligand [1,2]. Such ligands cannot be introduced into platinum(II) complexes by conventional organolithium or Grignard methods and the methods involving hydroxo-platinum complexes are severely limited because they have been isolated with terminal OH ligands only in complexes of the type $[Pt(OH)RL_2]$ (R = CH_3 or C_6F_5, L = phosphine). Dixon et al. [3] have shown that the isolation of hydroxy-complexes is unnecessary if chloro-complexes are treated with Ag_2O in presence of the acidic C—H compound. The Ag_2O provides both the halide abstracting agent (Ag^+) and a strong base (O^{2-}) and the complexes *cis*-$[PtCl(CH_2COCH_3)(PEt_3)_2]$, *cis*-$[PtCl(CH_2NO_2)(PEt_3)_2]$ and *trans*-$[Pt(C{\equiv}CPh)_2(PEt_3)_2]$ have been prepared by this method. Since work in this group [4] has shown that Pt—Cl bonds can be converted to Pt—OH bonds by use of KOH in organic solvents containing crown ethers, we have investigated the applicability of this method to the synthesis of organoplatinum(II) complexes from compounds containing acidic C—H bonds.

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Results and discussion

The stoichiometry of the reaction between a Pt—Cl bond and an acidic C—H bond in RH in presence of KOH is represented by equation 1. Since the organoplatinum product is, therefore, of the same electrical charge as the starting chloroplatinum(II) complex, an uncharged platinum complex dissolved in RH or an organic solvent can be treated with KOH in water in presence of the crown-ether 18-crown-6 to act as a phase transfer catalyst. This procedure was successful with several systems and it was usually possible to replace only one Cl of a dichloro-complex by use of equimolar proportions of KOH and complex. However, in some instances ^{31}P-{^1H} NMR spectra of product mixtures showed the presence of several complexes, so alternative procedures were investigated with the aim or providing more efficient methods of preparation of the complexes [PtR_2L_2] and [$PtR(Cl)L_2$].

$$\text{Pt—Cl} + \text{RH} + \text{KOH} \rightarrow \text{Pt—R} + H_2O + \text{KCl} \qquad (1)$$

(a) Complexes with $R = CH_2NO_2$

The phase-transfer method, in which *cis*-[$PtCl_2(PPh_3)_2$] in nitromethane was treated with 18-crown-6 and an excess of KOH (2.5 mol) in water (Method I), gave an oily residue after evaporation of the organic layer. Recrystallisation of this residue from dichloromethane/ether gave pale yellow crystals of the bis-(nitromethyl) complex [$Pt(CH_2NO_2)_2(PPh_3)_2$]. This was characterised by elemental analysis (Table 1), and by IR and NMR spectroscopy (Table 2). The ^{31}P-{^1H} NMR spectrum comprised a singlet with $^1J(PtP)$ 2388 Hz. The magnitude of the coupling constant $^1J(PtP)$ usually provides a sufficient basis for the assignment of configuration of complexes [$PtX_2(PR_3)_2$], but for alkyl groups with electronegative substituents, the coupling constants for *cis* complexes are expected to be larger than in *cis*-[$PtMe_2(PPh_3)_2$] [$^1J(PtP)$ 1898 Hz] and may be of similar magnitude to those found for *trans* complexes [$^1J(PtP)$ ca. 2400—3200 Hz]. The ^1H NMR spectrum, however, provides unequivocal evidence for the *cis* configuration, since the spectrum of the nitromethyl protons comprises a triplet with relative peak heights ca. 0.2 : 1 : 0.2 and with additional coupling to ^{195}Pt (Table 2). The unusual intensity pattern of the triplet must derive from an $A_2XX'A'_2$ spin system with the separation of the outer (broad) lines corresponding to the sum of the coupling constants between the CH_2 protons (A, A') and the phosphorus nuclei (X, X') $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ 16 Hz.

The complex [$Pt(CH_2NO_2)_2(DPPE)$] [DPPE = 1,2-bis(diphenylphosphino)-ethane], which was obtained by a similar method (Tables 1 and 2), gave a ^{31}P-{^1H} NMR spectrum with $^1J(PtP)$ 2356 Hz. Coupling constants $^1J(PtP)$ are generally slightly larger in complexes of PPh_3 than in those of DPPE [5], so the magnitudes of $^1J(PtP)$ are consistent with the *cis* configuration assigned to the PPh_3 complex.

The complex *cis*-[$Pt(CH_2NO_2)Cl(PPh_3)_2$] was obtained by treatment of a suspension of *cis*-[$PtCl_2(PPh_3)_2$] in dichloromethane/nitromethane with an equimolar proportion of KOH in water in presence of 18-crown-6 (Method II). The complex was isolated after this mixture had been stirred vigorously for 24 h at room temperature. The ^{31}P-{^1H} NMR spectrum comprised the pair of doublets

TABLE 1

COMPLEXES $[\mathrm{PtR_2L_2}]$ AND $[\mathrm{PtR(Cl)L_2}]$

Complex	Method	M.p. (°C)	Yield	Analysis (Found (calcd.) (%))		
				C	H	N
cis-$[\mathrm{Pt(CH_2NO_2)_2(PPh_3)_2}]$	I[a]	181—182	65	54.1 (54.3)	4.2 (4.1)	3.2 (3.4)
$[\mathrm{Pt(CH_2NO_2)_2(DPPE)}]$	I	210(dec)	59	47.5 (47.1)	4.1 (3.8)	1.8 (2.0)
cis-$[\mathrm{Pt(CH_2NO_2)Cl(PPh_3)_2}]$	II[a]	220(dec)	73	54.3 (54.5)	4.4 (4.0)	1.6 (1.7)
cis-$[\mathrm{Pt(CH_2NO_2)Cl(PEtPh_2)_2}]$	III	172—173	67	48.5 (48.4)	4.6 (4.5)	1.9 (1.9)
cis-$[\mathrm{Pt(CH_2NO_2)Cl(PMe_2Ph)_2}]$	III	114—115	62	36.3 (36.0)	4.5 (4.3)	2.5 (2.5)
cis-$[\mathrm{Pt(CH_2NO_2)Cl(PEt_2Ph)_2}]$	III[a]	n.r.[b]	n.r.	40.5 (39.8)	5.2 (5.6)	2.4 (1.9)
cis-$[\mathrm{Pt(CH_2NO_2)Cl(PEt_3)_2}]$[c]	III	166—167	42	28.4 (29.6)	6.0 (6.1)	1.3 (2.7)
$[\mathrm{Pt(C{\equiv}CPh)_2(DPPE)}]$	I	210—212	70	63.8 (63.4)	4.4 (4.3)	
trans-$[\mathrm{Pt(C{\equiv}CPh)_2(PMe_2Ph)_2}]$	I[a]	177	68	56.4 (57.1)	5.0 (4.8)	
trans-$[\mathrm{Pt(C{\equiv}CPh)_2(PEt_3)_2}]$	I	164	66	53.1 (52.1)	6.2 (6.3)	
$[\mathrm{Pt(CH_2CN)_2(DPPE)}]$	I[a]	n.r.	low	53.4 (53.5)	5.1 (4.2)	4.1 (4.2)
cis-$[\mathrm{Pt(CH_2CN)Cl(PPh_3)_2}]$	II	176	low	57.9 (57.3)	4.3 (4.3)	1.8 (1.8)
cis-$[\mathrm{Pt(CH_2COPh)_2(PPh_3)_2}]$	I	160(dec)	73	65.1 (65.2)	4.6 (4.6)	
$[\mathrm{Pt(CH_2COPh)_2(DPPE)}]$	I	175(dec)	61	60.6 (60.8)	4.6 (4.7)	
cis-$[\mathrm{Pt(CH_2COPh)Cl(PPh_3)_2}]$	I	190(dec)	45	59.9 (60.4)	4.3 (4.3)	
cis-$[\mathrm{Pt(CH_2COPh)Cl(PEtPh_2)_2}]$	III	230(dec)	75	56.1 (55.6)	5.2 (4.8)	
cis-$[\mathrm{Pt(CH_2COPh)Cl(PMe_2Ph)_2}]$	III	136	57	45.7 (46.0)	4.6 (4.6)	
cis-$[\mathrm{Pt(CH_2COC_6H_4NO_2\text{-}4)Cl(PMe_2Ph)_2}]$	II[a]	164	63	43.2 (43.0)	4.9 (4.2)	2.2 (2.1)
cis-$[\mathrm{Pt(CH_2COC_6H_4NO_4\text{-}4)Cl(PPh_3)_2}]$	II	120	54	48.0 (48.1)	7.8 (7.6)	1.8 (1.7)
cis-$[\mathrm{Pt(CH_2COCH_3)(PEtPh_2)_2}]$	III	84	62	51.9 (52.1)	4.9 (4.9)	
cis-$[\mathrm{Pt(CH_2COCH_3)(PMe_2Ph)_2}]$	II	130	32	40.3 (40.5)	4.9 (4.7)	

[a] Method described in Experimental section. [b] n.r. = not recorded. [c] Unsatisfactory elemental analysis: spectroscopic parameters in good agreement with those of ref. 4.

with ^{195}Pt satellites expected for a complex of *cis* configuration and the coupling constants ^1J(PtP) follow a well-established pattern for complexes of this type [5]. Thus, the coupling *trans* to $\mathrm{CH_2NO_2}$ (2122 Hz) is smaller than in *cis*-$[\mathrm{Pt(CH_2NO_2)_2(PPh_3)_2}]$ (2388 Hz) and the coupling *trans* to Cl (4082 Hz) is larger than in *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (3679 Hz), and the alkyl ligand may be said to have a lower *cis*-influence than Cl. The ^{1}H NMR spectrum shows a single $\mathrm{CH_2}$

TABLE 2

SPECTROSCOPIC PROPERTIES OF COMPLEXES $[PtR_2L_2]$ AND $[PtRClL_2]$

Complex	$^{31}P-\{^1H\}$ NMR parameters [a]			^1H NMR parameters of $PtCH_2$ [b]			IR Bands (cm^{-1})	
	$-\delta$ (ppm)	$^1J(PP)$ (Hz)	$^2J(PP)$ (Hz)	δ (ppm)	$^2J(PtH)$ (Hz)	$^3J(PH)$ (Hz)		
cis-$[Pt(CH_2NO_2)_2(PPh_3)_2]$	119.5	2388		4.7	80	16	$\nu(NO)$	1510
$[Pt(CH_2NO_2)_2(DPPE)]$	92.8	2356					$\nu(NO)$	1495
cis-$[Pt(CH_2NO_2)Cl(PPh_3)_2]$	121.3	2122	17	4.52	72	8, 5	$\nu(NO)$	1510
	122.7	4082					$\nu(PtCl)$	300
cia-$[Pt(CH_2NO_2)Cl(PEtPh_2)_2]$	125.8	2146	17	4.97	72	9, 5	$\nu(NO)$	1500
	128.1	3999					$\nu(PtCl)$	300
cis-$[Pt(CH_2NO_2)Cl(PMe_2Ph)_2]$	151.7	2108	18	5.05	74	9, 5	$\nu(NO)$	1400
	155.2	3860						1510
							$\nu(PtCl)$	290
cis-$[Pt(CH_2NO_2)Cl(PEt_2Ph)_2]$	134.7	2119	17	4.95	72	9, 5	$\nu(NO)$	1505
	137.5	3857					$\nu(PtCl)$	301
cis-$[Pt(CH_2NO_2)Cl(PEt_3)_2]$	130.9	2129	17				$\nu(NO)$	1500
	134.7	3801					$\nu(PtCl)$	208
$[Pt(C\equiv CPh)_2(DPPE)]$	99.1	2270					$\nu(C\equiv C)$	2110
trans-$[Pt(C\equiv CPh)_2(PMe_2Ph)_2]$	152.8	2400		[f]			$\nu(C\equiv C)$	2100
trans-$[Pt(C\equiv CPh)_2(PEt_3)_2]$	128.6	2370						
$[Pt(CH_2CN)_2(DPPE)]$	93.8	2293		1.74	84	7, 9	$\nu(CN)$	2200
cis-$[Pt(CH_2CN)Cl(PPh_3)_2]$	96.8	2086	4				$\nu(CN)$	2210
	98.1	4008						
cis-$[Pt(CH_2COPh)_2(PPh_3)_2]$	117.8	2397						
$[Pt(CH_2COPh)_2(DPPE)]$	92.7	2358						

cis-[Pt(CH$_2$COPh)Cl(PPh$_3$)$_2$]	118.7	1997	15				ν(CO)	1630
	120.7	4292					ν(PtCl)	1650
[Pt(CH$_2$COPh)Cl(DPPE)]	96.4	2107	4					
	97.3	4027						
cis-[Pt(CH$_2$COPh)Cl(PEtPh$_2$)$_2$]	123.6	2065	17					
	127.1	4189						
cis-[Pt(CH$_2$COPh)Cl(PMe$_2$Ph)$_2$]	148.9	2078	17	3.55 ^{g}	84	11, 5	ν(CO)	1585
	153.6	4033						1630
							ν(PtCl)	280
cis-[Pt(CH$_2$COC$_6$H$_4$NO$_2$-4)Cl(PMe$_2$Ph)$_2$]	148.6	2137	17	3.50 ^{h}	84	11, 5	ν(CO)	1610
	153.4	3978						1630
							ν(NO)	1525
							ν(PtCl)	280
cis-[Pt(CH$_2$COC$_6$H$_4$NO$_2$-4)Cl(PBu$_3$)$_2$]	139.6	2100	15	3.32	70	11, 4	ν(CO)	1600
	141.9	3940						1625
							ν(NO)	1510
							ν(PtCl)	290

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[a] In dichloromethane; positive shifts are to high frequency of the external reference (MeO)$_3$P in C$_6$D$_6$; upper entry assigned to P *trans* to C. [b] In CDCl$_3$. [c] From Nujol mulls. [d] A$_2$XX'A$_2$' spectrum $|{}^3J(\mathrm{PH})_{trans} + {}^3J(\mathrm{PH})_{cis}|$. [e] δ(PCH_3) 1.85, 1.62 ppm. [f] δ(PCH_3) 2.10 ppm, ^3J(PtH) 31 Hz, $|{}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})|$ 8 Hz. [g] δ(PCH_3) 1.80 ppm, ^2J(PH) 12 Hz, ^3J(PtH) 42 Hz; δ 1.43 ppm, ^2J(PH) 10 Hz, ^3J(PtH) 18 Hz. [h] δ(PCH_3) 1.80 ppm, ^2J(PH) 12 Hz, ^3J(PtH) 42 Hz; δ(PCH_3) 145 ppm, ^2J(PH) 9 Hz, ^3J(PtH) 19 Hz. [i] δ (OCH_3) δ 3.90 ppm; δ(PCH_3) 1.84 ppm, ^2J(PH) 12 Hz, ^3J(PtH) 40 Hz; δ(PCH_3) 1.39 ppm, ^2J(PH) 10 Hz, ^3J(PH) 20 Hz. [j] CH$_3$CO resonance obscured. [k] δ(CH_3CO) 2.34 ppm; δ(PCH_3) 1.77 ppm, ^2J(PH) 12 Hz, ^3J(PtH) 46 Hz; δ(PCH_3) 1.46 ppm, ^2J(PH) 8 Hz, ^3J(PtH) 24 Hz.

group coupled to ^{195}Pt and two non-equivalent ^{31}P nuclei.

With dichloro-complexes of the phosphines (L) $PEtPh_2$, PMe_2Ph, PEt_2Ph and PEt_3, the phase-transfer procedure gave unsatisfactory results (vide infra), but the use of an equimolar proportion of KOH dissolved in methanol instead of water led to the isolation of the complexes *cis*-$[Pt(CH_2NO_2)ClL_2]$ (Method III, Table 1). These had ^{31}P parameters similar to those of the PPh_3 complex (Table 2), and our results for *cis*-$[PtCl(CH_2NO_2)(PEt_3)_2]$ differ from those reported by Dixon et al. [δ —130 ppm, $^1J(PtP)$ 2098 Hz; δ —134.6 ppm, $^1J(PtP)$ 3818, ^2J 18 Hz] only by amounts attributable to concentration or solvent effects [6].

The phase-transfer method with an excess of KOH gave products with elemental analysis consistent with the formula *cis*-$[PtCl(OH)L_2]CH_3NO_2$ (L = PPh_2Et, $PPhMe_2$, $PPhEt_2$) (see Experimental section), and the ^{31}P-{^1H} NMR spectra showed the presence of non-equivalent phosphines with coupling constants $^1J(PtP)$ (ca. 3.7 and 2.8 kHz) of magnitude compatible with the presence of *trans* Cl and OH ligands. These complexes and the complexes *cis*-$[Pt(CH_2NO_2)ClL_2]$ were shown by ^{31}P-{^1H} NMR spectroscopy to be present in the organic layer of mixtures obtained by the phase transfer method with an equimolar proportion of KOH, and for L = PEt_3 and an excess of KOH the complex assigned the structure *cis*-$[PtCl(OH)(PEt_3)_2]$ was present together with another *cis*-bis(phosphine) complex [δ —126.7 ppm, $^1J(PtP)$ 2417 Hz; δ —140.9 ppm, $^1J(PtP)$ 3102 Hz, $^2J(PP)$ 18.3 Hz]. On the basis that couplings *trans* to OH are normally smaller than those *trans* to Cl [1,4], this complex is tentatively formulated *cis*-$[Pt(CH_2NO_2)(OH)(PEt_3)_2]$ by comparison with the parameters of *cis*-$[Pt(CH_2NO_2)Cl(PEt_3)_2]$ (Table 2).

(b) Complexes with R = C≡CPh

A good example of the care required in the assignment of structures on the basis of the magnitude of $^1J(PtP)$ is provided by the complexes $[Pt(C{\equiv}CPh)_2L_2]$ (L = DPPE/2, PMe_2Ph, PEt_3). These were obtained from phenylacetylene by the phase transfer method and were the only products even when the KOH was used in equimolar proportion. The DPPE complex, which must have P *trans* to C≡CPh has $^1J(PtP)$ 2270 Hz, only slightly smaller than the complex of PMe_2Ph which is shown to have P *trans* to P by the virtually coupled form of the P—*Me* portion of the ^1H NMR spectrum (Table 2). The complex of PEt_3 is also known to be *trans* [3,7].

(c) Complexes with R = CH_2CN

The complex *cis*- and *trans*-$[Pt(CH_2CN)Cl(PPh_3)_2]$ have been obtained with solvent of crystallisation from reactions between $ClCH_2CN$ and $[Pt(PPh_3)_4]$ [8]. The *cis* complex (see Table 2) was obtained with some difficulty and in low yield from acetonitrile by the phase transfer method with an equimolar proportion of KOH (Method II). The phase transfer method with an excess of KOH gave $[Pt(CH_2CN)_2(DPPE)]$ in low yield and it was clear that extensive side reactions occurred in these systems.

(d) Complexes with R = CH_2COR

The complexes $[Pt(CH_2COPh)_2(PPh_3)_2]$ and $[Pt(CH_2COPh)_2(DPPE)]$ were obtained from acetophenone by the phase-transfer method with an excess of KOH. These complexes have ^{31}P NMR parameters that are very similar to those of the corresponding nitromethyl complexes (Table 2), so the PPh_3 complex is almost certainly *cis*.

Although the ^{31}P-{^1H} NMR spectra of the organic layer showed that the complexes [$Pt(CH_2COAr)ClL_2$] were formed from acetophenone by the phase-transfer method with an equimolar proportion of KOH, a substantial proportion of a second complex was also present and the mixture was not easily separated by fractional crystallisation. The complexes [$Pt(CH_2COPh)ClL_2$] were, however, obtained easily when the KOH was added in methanol (Method III). The complexes [$Pt(CH_2COAr)ClL_2$] ($Ar = C_6H_4X$, $X = NO_2$-4, OMe-2) were obtained by the phase-transfer method using a solution of the ketone in dichloromethane. The complexes had similar ^{31}P-{^1H} NMR spectra which established their *cis* configuration in solution (Table 2), and the ^1H NMR spectra, which were recorded for several of the complexes, displayed resonances for the Pt—CH_2 protons with coupling from platinum and two non-equivalent ^{31}P nuclei (Table 2).

The additional complexes present in the organic layer from the phase-transfer method had *cis*-configurations and parameters [$L = PPh_3$, δ —117.0 ppm, ^1J(PtP) 2373 Hz; δ —124.9 ppm, ^1J(PtP) 3506; ^2J(PP) n.r. * Hz. L = DPPE/2: δ —101.1 ppm, ^1J(PtP) 2532 Hz; δ —104.8 ppm, ^1J(PtP) 3223; ^2J(PP) n.r. Hz] which are rather similar to those assigned to *cis*-[$Pt(CH_2NO_2)(OH)(PEt_3)_2$] in section (a) above. We, therefore, tentatively assign the formulae *cis*-[$Pt(CH_2COPh)(OH)L_2$] to these complexes. The formulae are consistent with the view that stable platinum(II) phosphine complexes with terminal hydroxo ligands are readily formed when the remaining ligands are not easily displaced by ligand hydroxide with formation of hydroxo-bridged complexes [4].

The reactions with acetone followed a similar pattern: although *cis*-[$Pt(CH_2COMe)Cl(PMe_2Ph)_2$] was obtained by the phase-transfer method (Tables 1 and 2), *cis*-[$Pt(CH_2COMe)(OH)(PMe_2Ph)_2$] [$\delta$ —140.9 ppm, ^1J(PtP) 2397 Hz; δ —161.0 ppm, ^1J(PtP) 3235; ^2J(PP) 17 Hz] was present in substantial proportion in the organic phase, and the method in which KOH was added in methanol gave a good yield of *cis*-[$Pt(CH_2COMe)Cl(PPh_2Et)_2$] (Tables 1 and 2). Complexes of DPPE and PEt_2Ph were also prepared, but were not fully characterised (Table 2).

Conclusions

The use of KOH to introduce alkyl ligands derived from weakly acidic C—H groups has been shown to be successful for a range of phosphine complexes, though careful choice of conditions is sometimes necessary. The products are easily monitored by ^{31}P-{^1H} NMR spectroscopy and the method avoids the additional complications occasioned by the precipitation of AgCl in the procedure based on Ag_2O [4]. The relative ease with which complexes [PtMe(R)-(DPPE)] are obtained from [PtMe(OH)(DPPE)] [1,2] probably derives at least

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* Not recorded.

in part from the fact that three of the coordination sites are securely blocked by the phosphine and methyl ligands.

Experimental

Reactions were carried out under an atmosphere of dry nitrogen. Dichloromethane was distilled from phosphorus pentoxide, and methanol was distilled from magnesium methoxide. Melting points were determined from a Kofler block or a Gallenkamp Electrothermal apparatus. Infra-red spectra were recorded as Nujol mulls. The ^1H NMR spectra were recorded on a Perkin-Elmer R 32 instrument at 90 MHz or a Varian T 60 spectrometer at 60 MHz; tetramethylsilane was used as the internal standard in deuteriochloroform solutions. The $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded at 40.48 MHz with a JEOL PFT-100 Fourier Transform spectrometer using a solution of $P(OMe)_3$ in deuteriobenzene as the ^2D-lock and external standard. Positive shifts are to high frequency of the reference. Elemental analyses were obtained from the Microanalytical Laboratory of this School.

Preparation of $[Pt(CH_2NO_2)_2(PPh_3)_2]$ *(Method I)*

This complex was obtained by the phase-transfer method with an excess of KOH. A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.2 g, 2.5×10^{-4} mol) in nitromethane (5 cm^3) was treated with KOH (6.3×10^{-4} mol) in the form of a standardized aqueous solution (ca. 0.1 *M*). After addition of 18-crown-6 (0.1 g) the mixture was stirred vigorously at room temperature for 24 h. The aqueous layer was discarded and the organic layer was evaporated under reduced pressure to leave a yellow oil. This was washed with diethyl ether and recrystallised from dichloromethane/ether to give the product as pale yellow crystals. Similarly obtained was $[Pt(CH_2NO_2)_2(DPPE)]$.

The products obtained with this procedure from the *cis*-dichloro-complexes of $PPhMe_2$, $PPhEt_2$ and PEt_3 are tentatively formulated *cis*-$[PtCl(OH)L_2]CH_3NO_2$ on the basis of the ^{31}P NMR parameters discussed in the text and the following elemental analysis results [L = $PPhMe_2$, $\nu(PtCl)$ 315 cm^{-1} (Found: C, 35.1; H, 5.3; N, 1.8. $C_{17}H_{34}ClNO_2P_2Pt$ calcd.: C, 34.9; H, 4.4; N, 2.4%.); L = $PPhEt_2$, $\nu(PtCl)$ 315 cm^{-1} (Found: C, 39.1; H, 4.7; N, 2.0. $C_{21}H_{34}ClNO_3P_2Pt$ calcd.: C, 39.3; H, 5.3; N, 2.2.); L = PEt_3, $\nu(PtCl)$ 310 cm^{-1} (Found: C, 27.9; H, 5.8; N, 2.9. $C_{13}H_{34}ClNO_3P_2Pt$ calcd.: C, 28.6; H, 6.2; N, 2.6%.)].

Preparation of $[Pt(CH_2NO_2)Cl(PPh_3)_2]$ *(Method II)*

This complex was obtained by the phase-transfer method with an equimolar proportion of KOH. A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.2 g, 2.5×10^{-4} mol) in a mixture of nitromethane (2 cm^3) and dichloromethane (4 cm^3) was treated with aqueous KOH (2.5×10^{-4} mol) and 18-crown-6 (0.05 g) and the mixture was stirred vigorously at room temperature for 24 h. The organic layer was treated as described above and the product was obtained as pale yellow crystals.

Preparation of cis-$[Pt(CH_2NO_2)Cl(PEtPh_2)_2]$ *(Method III)*

A suspension of *cis*-$[PtCl_2(PEtPh_2)_2]$ (0.2 g) in nitromethane (4 cm^3) was treated with KOH (0.02 g) in methanol (0.5 cm^3) and 18-crown-6 (0.05 g). The mixture was stirred vigorously at room temperature for 24 h, filtered, and the filtrate evaporated under reduced pressure. The yellow residue was washed with diethyl ether and recrystallised from dichloromethane/diethyl ether to give the product as pale yellow crystals.

Preparation of trans-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$

A suspension of *cis*-$[PtCl_2(PPhMe_2)_2]$ (0.2 g, 3.7 × 10^{-4} mol) in phenylacetylene (3 cm^3) was treated with an excess of aqueous KOH (1.7 × 10^{-3} mol) and 18-crown-6 (0.05 g). The mixture was stirred at 50°C for 2 h. The resulting solution was evaporated to dryness. The residue was dissolved in benzene and treated with diethyl ether to give the product as a pale yellow precipitate.

Preparation of cis$[Pt(CH_2CN)_2(DPPE)]$

A suspension of $[PtCl_2(DPPE)]$ (0.2 g, 3 × 10^{-4} mol) in acetonitrile (5 cm^3) was treated with KOH (0.044 g, 8 × 10^{-4} mol) and 18-crown-6 (0.1 g) in methanol (0.5 cm^3). The mixture was stirred vigorously at room temperature and the complex dissolved gradually to form a green-yellow solution after 36 h. The mixture was then evaporated to dryness and recrystallised from dichloromethane/diethyl ether to give the product as colourless crystals.

Preparation of cis-$[Pt(CH_2COC_6H_4NO_2\text{-}4)Cl(PMe_2Ph)_2]$

A solution of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (0.2 g, 3.7 × 10^{-4} mol) in dichloromethane, (4 cm^3) was treated with $CH_3COC_6H_4NO_2$-4 (0.13 g), 18-crown-6 (0.1 g) and KOH (0.023 g, 4 × 10^{-4} mol) in water (0.5 cm^3), and the mixture was stirred vigorously at room temperature for 24 h. The organic layer was separated and evaporated to dryness. The residue was washed with diethyl ether and recrystallised from dichloromethane/diethyl ether to give the product as pale yellow crystals.

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