Stability of (Chloromethyl)platinum(II) Complexes

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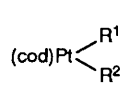
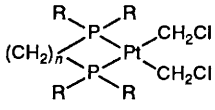
The stabilities of $[Pt(CH_2Cl)_2(cod)]$, $[Pt(CH_2Cl)Cl(cod)]$ (cod = cycloocta-1,5-diene) and a range of phosphine-containing mono- and *cis*-bis-(chloromethyl)platinum(II) complexes have been investigated in deuteriochloroform at room temperature. Some of the bis(chloromethyl) derivatives appear to be indefinitely stable (cod and chelating arylphosphines), others suffer very slow decomposition to the dichlorides (non-chelating arylphosphines), and the remainder decompose relatively rapidly, and cleanly, to the dichlorides plus ethylene (alkylphosphines, non-chelating faster than chelating). Rapid decomposition of the arylphosphine complexes can be induced by adding hexafluoroisopropyl alcohol to the deuteriochloroform solutions. Attempts to generate $[Pt(CH_2Cl)_2\{P(C_6H_{11})_3\}_2]$ by addition of $P(C_6H_{11})_3$ to $[Pt(CH_2Cl)_2(cod)]$ resulted in the formation of *cis*-$[Pt^-\{CH_2CH_2P^+(C_6H_{11})_3\}Cl_2\{P(C_6H_{11})_3\}]$; a mechanism is proposed. All *cis*-mono(chloromethyl) derivatives studied appear to be indefinitely stable. In contrast, the *trans*-mono(chloromethyl) complexes, although stable in very dry solvent, undergo decomposition in the presence of moisture to the corresponding hydrides plus formaldehyde; a mechanism is proposed. The hydrides undergo subsequent conversion into a mixture of *cis* and *trans* dichlorides.

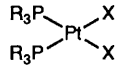
In the course of our studies[1] of the preparation of (halogenomethyl)platinum(II) complexes it became clear that some of the products showed a much greater tendency than others to decompose when left standing in solution. Thus, as a part of a general investigation of the chemistry of these complexes, a study of their solution stabilities at room temperature was initiated in the hope of determining the mode(s) of such decomposition. Prior to the 1980s α-halogenomethyl derivatives of transition metals had the reputation of being 'notoriously unstable',[2] although many members of this class are now known.[3] Some of these compounds have been reported to be labile, readily losing the CH_2 moiety to give the corresponding metal halides. In most of these cases[4] there is no mention of the fate of this moiety but in one case[5] (Pt^{II}) it was presumed to be lost as ethylene while in another[6] (Ir^{I}) it was shown that polymethylene was the major product. The present investigation has dealt with both mono- and bis-(chloromethyl)platinum(II) complexes, the latter representing, to our knowledge, the only known derivatives of this type for the transition metals.



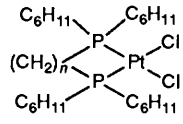
1 $R^1 = R^2 = CH_2Cl$
2 $R^1 = CH_2Cl$, $R^2 = Cl$



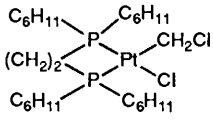
	n	R
3	2	Ph
4	3	Ph
5	4	Ph
12	2	C_6H_{11}
13	3	C_6H_{11}
14	4	C_6H_{11}



	R	X
6	Ph	CH_2Cl
7	Ph	Cl
8	*p*-$MeOC_6H_4$	CH_2Cl
9	*p*-$MeOC_6H_4$	Cl
10	*p*-FC_6H_4	CH_2Cl
11	*p*-FC_6H_4	Cl
19	Et	CH_2Cl
20	Et	Cl
24	C_6H_{11}	CH_2Cl



	n
15	2
16	3
17	4



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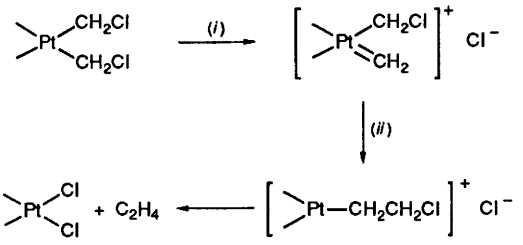
Results and Discussion

During this investigation certain experimental results provided a forceful reminder that the presence of small amounts of impurities may have a marked effect on the apparent stability of a transition-metal compound. In several instances, chloromethyl complexes freshly generated in reactions with diazomethane underwent fairly rapid decomposition in the reaction medium but decomposed much more slowly in a similar solvent after purification. In general, cleaner products, more amenable to further purification, are generated by ligand displacement from $[Pt(CH_2Cl)_2(cod)]$ **1** or $[Pt(CH_2Cl)Cl(cod)]$ **2** (cod = cycloocta-1,5-diene) both of which can be purified readily and are quite stable when pure. This route was used to produce the phosphine-containing complexes studied and, indeed, provides access to compounds which are either inaccessible by, or only minor products of, direct insertion of methylene into a Pt–Cl bond by diazomethane. The stability of the complexes was examined for samples stored in the dark at room temperature, usually in deuteriochloroform solution.

cis-Bis(chloromethyl) Complexes.—All but one of the complexes of this type studied were bis(phosphine) complexes, the other being $[Pt(CH_2Cl)_2(cod)]$ **1**. The last, when monitored by ^1H NMR spectroscopy, showed no evidence of decomposition



Scheme 1 Proposed mechanism for the production of ethylene from the bis(chloromethyl) complexes

when kept in solution for a month in acid-free solvent. In some experiments slow conversion into $[Pt(CH_2Cl)Cl(cod)]$ **2** was observed, but this could be avoided by running the solvent through a short column of anhydrous potassium carbonate before making up the solution.

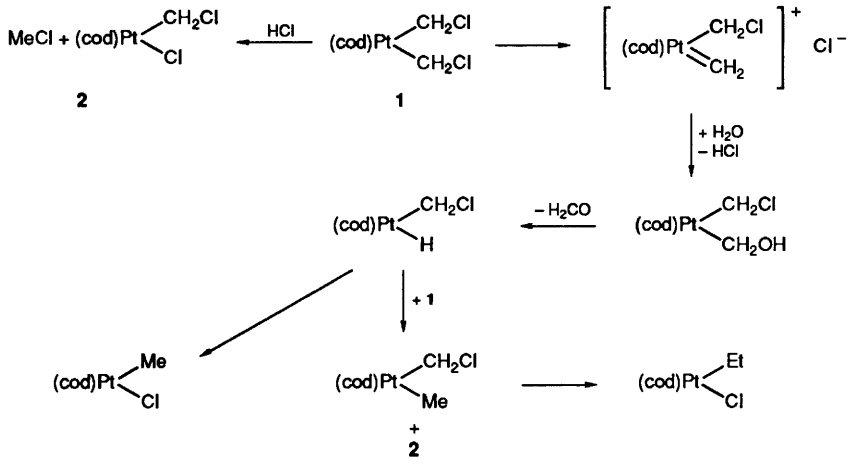
The three chelating aryl phosphine complexes **3**–**5**, when carefully purified, are also quite stable in solution at room temperature, remaining apparently intact for three months (sealed tubes *in vacuo*). When stored under air in capped tubes $[Pt(CH_2Cl)_2(PPh_3)_2]$ **6** yielded a small amount (less than 1%) of the corresponding dichloride **7** during 2 weeks. In analogous experiments the corresponding *p*-methoxy- and *p*-fluoro-phenyl derivatives, **8** and **10**, also produced small amounts of the corresponding dichlorides, **9** and **11** slowly (*ca.* 5 and 2% during 1 week). The fate of the CH_2 moiety has not been investigated in these cases. The three chelating alkyl phosphine complexes **12**–**14** are substantially less stable than the compounds discussed above, undergoing complete conversion into the dichlorides **15**–**17** during about 2 weeks. No significant peaks attributable to products from the CH_2 moieties could be found in the ^1H NMR spectra of these solutions, but analysis of the head-space gases by GLC showed ethylene accompanied by a little methane. Since in this (see below), and earlier [7] work we have found that some reactions in deuteriochloroform result from the presence of water in the solvent, the decomposition of complex **12** was monitored for a solution in deuteriochloroform that had been saturated with water. However, no obvious change in either the rate or the course of the reaction was observed. When tetrabutylammonium chloride (4 molar equivalents), rather than water, was added to a solution of **12** the rate of decomposition to **15** almost doubled. Even more rapid decomposition of **12** was observed when 1,1,1,3,3,3-hexafluoropropan-2-ol (4 molar equivalents) was substituted for the ammonium salt, conversion into **15** being complete within 1 d. Indeed, the three chelating aryl phosphine complexes **3**–**5** also suffered quantitative conversion into the corresponding dichlorides (^1H NMR spectroscopy tubes sealed *in vacuo*) within 1 d under similar conditions [$CDCl_3$–$(CF_3)_2CHOH$, 9:1]. Exposure of a solution of complex **12** to room light had no apparent effect on its rate of decomposition; however, irradiation with 300 nm light accelerated the production of **15** and yielded a new product, the mono(chloromethyl) derivative **18**. The bis(triethylphosphine) complex **19** proved to be the most labile of all the compounds of this type studied, producing the dichloride **20** within 1 d. When this decomposition was allowed to proceed in a sealed NMR tube the ^1H spectrum contained a signal attributable to ethylene. An estimate of the ethylene present in the tube was made based on the intensity of the signal, the volume of both the solvent and of the free space in the tube, and the solubility of ethylene in the solvent.[8] This indicated that essentially all of the methylene moiety lost in the production of **20** could be accounted for as ethylene.

The decomposition of these bis(chloromethyl)phosphine complexes to the dichlorides and ethylene may proceed *via* a reaction pathway (Scheme 1)* analogous to that proposed [9] for the conversion of $[PtMe(CH_2Cl)(cod)]$ into $[PtEt(Cl)(cod)]$, *viz.* by ionisation to a cationic carbene intermediate, followed by migration of the remaining CH_2Cl moiety, and then β elimination of chloride.† Certainly, some of the observations reported here could be taken as evidence for the involvement of such a pathway. The more strongly electron-donating alkyl phosphine ligands lead to faster decomposition than their aryl counterparts, presumably by facilitating ionisation of the halide ion (and possibly also migration of the chloromethyl group), while the acceleration in the rate of decomposition effected by the addition of 1,1,1,3,3,3-hexafluoropropanol would result from this compound's ability to assist heterolysis of the CH_2–Cl bond. With this latter effect in mind, $[Pt(CH_2Cl)_2(cod)]$ was allowed to stand in $CDCl_3$–$(CF_3)_2CHOH$. Disappearance of the starting complex occurred slowly, and after 3 weeks a ^1H NMR spectrum showed that about half of the substrate had reacted to give three major products, $[PtMe(Cl)(cod)]$, $[Pt(CH_2Cl)Cl(cod)]$ and chloromethane, along with a minor quantity of $[PtEt(Cl)(cod)]$. The formation of the products found can be rationalised on the basis of initial carbene-cation generation if this undergoes attack by adventitious water rather than chloromethyl migration, as indicated in Scheme 2. The absence of significant amounts of the dichloride $[PtCl_2(cod)]$ in the product mixture indicates that if a cationic carbene intermediate is formed (Scheme 2) then the chloromethyl group is reluctant to migrate.

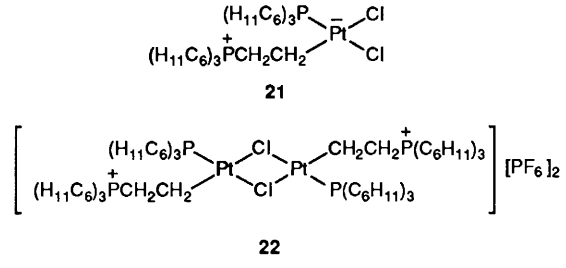
A new type of product was formed [11] rapidly when $[Pt(CH_2Cl)_2(cod)]$ was treated with 2 molar equivalents of tricyclohexylphosphine, $P(C_6H_{11})_3$, in deuteriochloroform in an attempt to generate the phosphine complex **24**. Proton and ^{31}P NMR spectra of the resulting solution revealed the presence of essentially a single platinum-containing species, the phosphonioethyl complex **21**, the proposed structure of which was supported by conversion into the hexafluorophosphate **22** whose structure has been established by X-ray crystallography.[11] Thus, tricyclohexylphosphine promotes coupling of the two methylene moieties in the chloromethyl groups of $[Pt(CH_2Cl)_2(cod)]$ but, in contrast to the outcome reported above for some other alkylphosphines, in this case the CH_2CH_2 fragment remains attached to the metal rather than being lost as ethylene. Although the mechanism of the reaction remains in doubt, the following observations may be relevant to it. In deuteriochloroform the reaction is so rapid that, when solutions of the reactants are mixed, a ^1H NMR spectrum run immediately contains resonances attributable to only free cod and **21**. When a similar experiment was carried out using only 1 molar equivalent of the phosphine per platinum, ^1H and ^{31}P NMR spectra revealed the presence of only unreacted $[Pt(CH_2Cl)_2(cod)]$, **21**, and free cod. The reaction is slower in perdeuteriobenzene requiring more than a day to reach completion. Phosphorus-31 NMR spectra run during the course of this reaction revealed the presence of three major phosphorus-containing species, **21**, *cis*-$[Pt(CH_2Cl)_2\{P(C_6H_{11})_3\}_2]$ **24**, and the ylide complex **23**. The production of **24** is perhaps unexpected in light of the report [12] that $[PtR_2(cod)]$ (R = Ph or Me) does not react with bulky monodentate tertiary phosphines. A possible mechanism for the formation of **21** is outlined in Scheme 3. The loss of one or other $P(C_6H_{11})_3$ from $[Pt(CH_2Cl)_2\{P(C_6H_{11})_3\}_2]$ is reasonable, given the steric demands of these two *cis*-phosphine ligands and the presence of an alkyl-type ligand *trans* to each of them. A 1,2 shift of a chloride group from CH_2Cl into the co-ordination site available

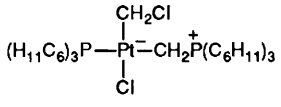
* We proposed earlier [9] that this type of pathway may explain why *cis*-$[PtCl_2\{P(C_6H_{11})_3\}_2]$ acts as an effective catalyst for the conversion of diazomethane into ethylene. Results for the tricyclohexylphosphine derivatives reported here appear to rule out such an explanation. Indeed, a number of (chloromethyl)platinum complexes, including **1** and **12**, catalyse the conversion of diazomethane into ethylene. When $[^2H_2]$diazomethane is used the **1** and **12** recovered do not contain deuterium. It thus appears likely that the catalytic activity arises simply from the presence of a Lewis-acid site in the complex.

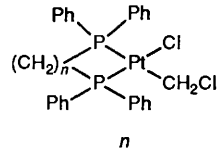
† β-Halide elimination is a well-known [10] process in organopalladium chemistry but we do not know of any examples in platinum chemistry.



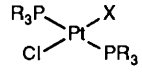
Scheme 2 Possible pathways from complex **1** in $CDCl_3$–$(CF_3)_2CHOH$ to the observed products







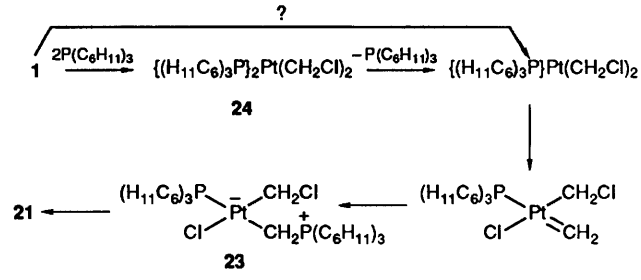
	n
25	2
26	3



	R	X
27	Ph	CH_2Cl
28	Et	CH_2Cl
29	C_6H_{11}	CH_2Cl
30	Ph	H
31	Et	H
32	C_6H_{11}	H
33	Et	Cl
34	Et	CH_2OMe
35	C_6H_{11}	CH_2OMe
36	Ph	Cl

on platinum could then take place, followed by attack of an external phosphine on the resulting carbene. The production of a similar ylidic species by a direct S_N2 attack of a $P(C_6H_{11})_3$ molecule on a bis(chloromethyl) complex appears unlikely. The ylidic intermediate can then suffer a Wagner–Meerwein shift of the ylide fragment to give **21**. A mechanism involving a cationic carbene intermediate is also possible, but in this case migration of (or external attack by) phosphine would have to be faster than migration of CH_2Cl (see Scheme 3) otherwise dichloride and ethylene might be expected to be major products.

In summary, the behaviour of the bis(chloromethyl) complexes suggests that both carbene formation, by ionisation of chloride, and subsequent migration of the remaining CH_2Cl moiety are favoured by the presence of good σ-donating ligands on platinum. In contrast, π-acceptor ligands would be expected to make both of these steps more difficult. Thus, the alkyl

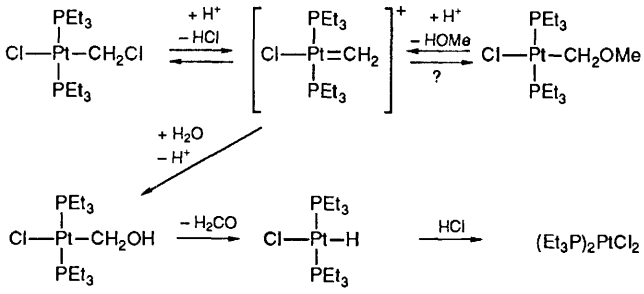


Scheme 3 Possible mechanism for the formation of complex **21**

phosphine complexes form ethylene readily, while their aryl counterparts do so only in more polar media. In the case of $[Pt(CH_2Cl)_2(cod)]$ the olefinic ligand is probably both a weaker σ donor and a stronger π acceptor than the phosphine ligands. Decomposition of **24** gives a unique type of product. Although we cannot discount the possibility that this is formed *via* initial ionisation of a chloride, we suggest that loss of a phosphine is an easier process in this case.

cis-*Chloro(chloromethyl) Complexes.*—All four complexes examined, namely **2**, **18**, **25** and **26**, when pure, survived in solution in deuteriochloroform under vacuum for several months, even in one case **25** in the presence of a drop of water. This stability contrasts sharply with the results reported below for *trans*-chloro(chloromethyl) complexes.

trans-*Chloro(chloromethyl) Complexes.*—The three complexes studied, **27**–**29**, were relatively stable when dissolved in deuteriochloroform from freshly opened vials. However, they all decomposed in solution in moist deuteriochloroform. Monitoring by ^1H and ^{31}P NMR spectroscopy revealed that the tricyclohexylphosphine complex **29** reacted more rapidly than the other two, being converted almost quantitatively into the relatively stable hydride **32** during 3 d. In the course of 4 weeks, appreciable amounts of **27** and **28** were lost (*ca.* 85 and 40% respectively, ^{31}P NMR spectroscopy) giving mainly the corresponding hydrides **30** and **31** together with small quantities of both the *cis* and *trans* dichlorides. In these, and similar experiments, ^1H NMR spectra of the product mixtures did not provide clear evidence for the fate of the 'lost' chloromethyl moiety, although it was suspected that some broad multiplets at about δ 5 arose from oligomeric formaldehyde species. However, formaldehyde was recovered from several of these product mixtures as the 2,4-dinitrophenylhydrazone. The two alkylphosphine complexes are soluble enough in C_6D_6 to allow NMR monitoring of their stability in solution in



Scheme 4 Possible pathways for the formation of complexes **31**, **20** and **33** from **28** and of **28**, **31**, **20** and **33** from **34**

that solvent. Both showed little evidence of decomposition in 1 week. However, addition of a drop of water to each sample induced **29** to decompose to the hydride **32** (*ca.* 25% conversion in 3 d) while **28** gave **31** and finally **33** during several months. When **28** and **29** in C_6D_6 were exposed to water in the presence of 1 molar equivalent of ethyldiisopropylamine the rates of their decomposition were reduced markedly.

Reasoning that hydroxymethyl species are likely intermediates in the production of these hydrides (see Scheme 4 which treats **28** as a representative example), complex **28** was exposed to methanol in deuteriochloroform in the hope that *trans*-[Pt(CH_2OMe)Cl(PEt_3)$_2$] **34** would be formed. However, decomposition proceeded as before, first to hydride and then to the *cis*/*trans* dichlorides. Monitoring the progress of the reaction by ^{31}P NMR spectroscopy failed to reveal signals attributable to **34**. On the assumption that this failure may have resulted from the reaction of any **34** formed with adventitious water and hydrogen chloride, the reaction was repeated in the presence of a scavenger for these two compounds, trimethyl orthoformate. However, reaction of the complex proceeded as before, yielding the hydride and the dichlorides. In addition, the ^1H NMR spectrum showed the presence of dimethoxymethane (from formaldehyde liberated by decomposition of the CH_2Cl group), and peaks which could be ascribed to methyl chloride and methyl formate. We then turned to the more aggressive scavenger dimethylformamide dimethyl acetal. This did, indeed, lead to the formation of the (methoxymethyl) complex **34** in essentially quantitative yield in less than a week. The analogous reaction for the tricyclohexylphosphine derivative **29** gave **35** in 1 d. With **34** now in hand it was possible to evaluate its reactivity towards HCl (*ca.* 0.8 mol equivalent, generated from methanol and acetyl chloride) in deuteriochloroform. Phosphorus-31 NMR spectroscopy revealed that within 1 d, complex **34** suffered substantial conversion into mainly the hydride **31** along with, in progressively smaller amounts, the (chloromethyl) complex **28**, the *cis* dichloride **20**, and *trans* dichloride **33**. This outcome appeared to indicate that the chemical reactivity of the Pt(CH_2OMe) moiety is more akin to that of an acetal than that of a simple ether and is in apparent accord with the mechanism outlined for the decomposition of **34** and **28** in Scheme 4. Certainly our evidence does not rule out a variety of other possible mechanisms, including some based on associative or other dissociative processes. The mechanism suggested has the advantage of simplicity while accounting for the following observations, if carbene formation is rate-limiting. The decomposition is facilitated by a more polar solvent, by the presence of protons in the solution, and of bulky tricyclohexylphosphine ligands in the co-ordination sphere. It may be noted that the formation of a carbene *trans* to a halogen is expected to be more facile than that *trans* to a phosphine.[13]

Experimental

Melting points were determined on a Kofler hot-stage, and are uncorrected. Proton (internal tetramethylsilane reference) and ^{31}P (external 85% H_3PO_4) NMR spectra were recorded for deuteriochloroform solutions (unless otherwise stated) on a Bruker WH-400 spectrometer. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee. Plates for thin-layer chromatography were spread with Kieselgel G (Merck).

Mono(chloromethyl)platinum(II) complexes were prepared from chloro(chloromethyl)(cycloocta-1,5-diene)platinum(II) **2**, and bis(chloromethyl)platinum(II) complexes from bis(chloromethyl)(cycloocta-1,5-diene)platinum(II) **1** in essentially quantitative yield by ligand exchange and were purified by preparative TLC and/or crystallisation unless noted otherwise. Most of the compounds have been prepared earlier[1] but the following have been characterised for the first time: [1,2-*bis*(*diphenylphosphino*)*ethane*]*bis*(*chloromethyl*)*platinum*(II) **3**, colourless crystals from dichloromethane [m.p. >280 °C (change of crystalline form at *ca.* 270 °C)], δ_H* 2.21 (m, 4 H, PCH_2) and 3.96 (dd, 4 H, $PtCH_2$, $^3J_{PH}$ = 7.4 and 2.8, $^2J_{PtH}$ = 48.4), δ_P 43.59 ($^1J_{PtP}$ = 1893 Hz) (Found: C, 48.95; H, 4.25. $C_{28}H_{28}Cl_2P_2Pt$ requires C, 48.55; H, 4.1%); [1,4-*bis*(*diphenylphosphino*)*butane*]*bis*(*chloromethyl*)*platinum*(II) **5**, fine, colourless needles from dichloromethane–pentane [m.p. >280 °C (decomp. from 200 °C)] δ_H 1.79 (br m, 4 H, PCH_2CH_2), 2.51 (vbr s, 4 H, PCH_2), and 3.58 (d, 4 H, $PtCH_2$, $^3J_{PH}$ = 7.9, $^2J_{PtH}$ = 44.8), δ_P 15.77 ($^1J_{PtP}$ = 1913 Hz) (Found: C, 50.15; H, 4.5. $C_{30}H_{32}Cl_2P_2Pt$ requires C, 50.0; H, 4.5%); [1,2-*bis*(*dicyclohexylphosphino*)*ethane*]*chloro*(*chloromethyl*)*platinum*(II) **18**, colourless crystals from dichloromethane–pentane, crumbled on drying [m.p. >280 °C (decomp. from 230 °C)], δ_H 3.78 (t, 2 H, $PtCH_2$, $^3J_{PH}$ = 2.8, $^2J_{PtH}$ = 37), δ_P 56.09 ($^1J_{PtP}$ = 4025) and 63.68 ($^1J_{PtP}$ = 1832 Hz) (Found: C, 44.2; H, 7.15. $C_{27}H_{50}Cl_2P_2Pt{\cdot}0.5CH_2Cl_2$ requires C, 44.3; H, 6.9%); trans-*chloro*(*chloromethyl*)*bis*(*triethylphosphine*)*platinum*(II) **28**, colourless crystals from pentane (at −78 °C) (m.p. 62–68 °C), $\delta_H(C_6D_6)$ 0.96 (18 H, CH_3), 1.80 (12 H, PCH_2) and 3.88 (t, 2 H, $PtCH_2$, $^3J_{PH}$ = 8.5, $^2J_{PtH}$ = 55.6), δ_P 16.0 ($^1J_{PtP}$ = 2793 Hz) (Found: C, 30.05; H, 6.0. $C_{13}H_{32}Cl_2P_2Pt$ requires C, 30.25; H, 6.25%).

In general, the stabilities of complexes (0.05–0.1 mmol) were monitored by ^1H and, for all but **1** and **2**, ^{31}P NMR spectroscopy for solutions in deuteriochloroform in 5 mm tubes which had been sealed under vacuum, or capped with rubber septa under nitrogen, and were kept at ambient temperature in the dark. Approximate relative concentrations of complexes in mixtures resulting from substrate decomposition were estimated only by comparison of relative peak heights in ^{31}P NMR spectra. Acid-free deuteriochloroform refers to material that had been passed through a column of anhydrous potassium carbonate. Head-space gas analyses were carried out with a Varian Aerograph 1200 gas chromatograph [two stainless-steel columns ($\frac{1}{8}$ in × 5 ft), one containing 3% SE-30, the other Porapak Q, in series; nitrogen as carrier gas with a flow rate of 25 cm^3 min^{-1}].

cis-*Bis*(*chloromethyl*) *Complexes.*—*Bis*(*chloromethyl*)(*cycloocta*-1,5-*diene*)*platinum*(II) **1**. Proton NMR spectra of this complex in acid-free deuteriochloroform showed no changes during 1 month. In deuteriochloroform–1,1,1,3,3,3-hexafluoropropanol (9:1) *ca.* one half of the solute **1** decomposed in 3 weeks giving ^1H NMR signals for the complexes[1,9] [PtMe(Cl)(cod)], [Pt(CH_2Cl)Cl(cod)], and [PtEt(Cl)(cod)] and for MeCl (δ_H 3.02, confirmed by spiking). In C_6D_6–$(CF_3)_2CHOH$ (9:1) less than 20% of **1** was lost during 3 weeks to give [PtMe(Cl)(cod)], [Pt(CH_2Cl)Cl(cod)] and MeCl; the head-space gas contained large amounts of CH_4 along with smaller amounts of C_2H_6, C_2H_4 and MeCl.

Chelating Arylphosphine Complexes **3**–**5**.—These three complexes showed no changes in their ^1H and ^{31}P NMR

* For brevity, ^1H resonances for the phenyl rings are not reported for this and other complexes; couplings quoted are observed values.

spectra in acid-free deuteriochloroform (tubes sealed *in vacuo*) during 3 months. When dissolved in $CDCl_3$–$(CF_3)_2CHOH$ (9:1), ^1H and ^{31}P NMR spectra run as soon as possible thereafter contained resonances for only the corresponding dichlorides and, in the ^1H NMR spectra, a signal at δ 5.42 for ethylene.

Monodentate Arylphosphine Complexes **6**, **8** *and* **10**.—Solutions of the first of these in $CDCl_3$ (capped tubes), prepared either from crystalline material[1] or *in situ* by adding PPh_3 (1.9 mol equivalent) to a solution of **1** in that solvent, decomposed very slowly to the dichloride **7** (*ca.* 0.5% formed in 2 weeks, ^{31}P NMR spectroscopy). The *p*-OMe and *p*-F analogues **8** [δ_P 20.8 ($^1J_{PtP}$ = 2001 Hz)] and **10** [δ_P 22.2 ($^1J_{PtP}$ = 1964 Hz)] prepared *in situ* also decomposed slowly to the analogous dichlorides (*ca.* 5% of **9** and 2% of **11** in 1 week, ^{31}P NMR spectroscopy).

Chelating Alkylphosphine Complexes **12**–**14**.—Samples of the last two complexes were prepared *in situ* by dissolving a mixture of **1** and either 1,4-bis(dicyclohexylphosphino)butane or 1,3-bis-(dicyclohexylphosphino)propane (0.9 mol equivalent) in $CDCl_3$ under N_2 (capped tubes). Complex **14** had δ_H 3.86 (d, 4 H, $PtCH_2$, $^3J_{PH}$ = 7.1, $^2J_{PtH}$ = 43 Hz) and δ_P 18.3 ($^1J_{PtP}$ = 1971 Hz): during 10 d the signals due to **14** were replaced by those for the dichloride **17** [δ_P 21.5 ($^1J_{PtP}$ = 3621 Hz)]. Complex **13** had δ_H 3.86 (d, 4 H, $PtCH_2$, $^3J_{PH}$ = 5.7, $^2J_{PtH}$ = 41 Hz) and δ_P 4.1 ($^1J_{PtP}$ = 1909 Hz): within *ca.* 2 weeks the signals due to **13** were replaced by those for **16** [δ_P 8.7 ($^1J_{PtP}$ = 3464 Hz)]. When solid[1] **12** was dissolved in $CDCl_3$ the ^{31}P NMR signal arising from this compound was gradually replaced by one for **15** during 2–3 weeks. After decomposition, analysis of the head-space gases by GC showed the presence of a large amount of ethylene and a minor amount of methane. A sample of **12** prepared *in situ* from **1**, by treatment with the phosphine ligand in $CDCl_3$, decomposed to **15** at essentially the same rate (*i.e.* in the presence of free cod). A sample of solid complex **12** (180 mg) was dissolved in $CDCl_3$ (5 cm^3) and the solution divided among six NMR tubes (5 mm). One was kept (under nitrogen), as a standard, in the dark and its rate of decomposition was compared (^{31}P NMR spectroscopy) with the other five samples which were treated as follows: (*i*) left on the bench (fluorescent/daylight), no rate difference: (*ii*) drop of water added, no rate difference; (*iii*) tetrabutylammonium chloride (4 mol equivalents) dissolved, rate *ca.* double; (*iv*) 1,1,1,3,3,3-hexafluoropropan-2-ol (30 μl) added, decomposition to **15** complete in 1 d; (*v*) exposed to 300 nm light for 15 min, *ca.* 75% decomposition to approximately equal amounts of **15** and **18**.

The Bis(triethylphosphine) Complex **19**.—This complex, which was prepared[1] from the dichloride **20** by treatment with diazomethane, decomposed rapidly (overnight) back to the dichloride when dissolved in $CDCl_3$. The resulting solution contained ethylene (^1H NMR integration indicated 42% of that expected on the basis of stoichiometry in solution, while the presence of a further 45% was calculated to be present in the gas phase assuming that the solubility of ethylene in chloroform is similar to its solubility in chlorobenzene[8]). Ethylene and a trace of methane were detected in the head-space gas by GC.

The Bis(tricyclohexylphosphine) Complex **24**.—When complex **1** and tricyclohexylphosphine (2 mol equivalents) were dissolved in $CDCl_3$ under nitrogen, only the phosphonioethyl complex **21** could be detected[11] by a ^{31}P NMR spectrum run immediately. When this reaction was repeated using C_6D_6, initially at 10 °C, and subsequently at ambient temperature (25 °C), peaks due to **21** were found right from the beginning. However the most prominent peaks appeared at δ 19.4 ($^1J_{PtP}$ = 2774) and 45.2 ($^1J_{PtP}$ = 67.5 Hz), and are assigned to the ylide complex **23**. These peaks gradually decreased in intensity on standing, and finally disappeared after about 1 d at 25 °C. The initial spectrum also showed a prominent signal at δ 19.0 ($^1J_{PtP}$ = 1904 Hz), which disappeared within a few hours at 25 °C, and is ascribed to the *cis*-bis(chloromethyl) complex **24**. After 1 d the major component present was **21**, although several weaker resonances were observed. The overall reaction was less clean in benzene than in chloroform. When the same reaction was monitored by ^1H NMR spectroscopy, signals ascribable to CH_2Cl resonances of **23** and **24** were observed at δ 4.5 ($^3J_{PH}$ = 6.8, $^2J_{PtH}$ = *ca.* 60) and 4.42 ($^3J_{PH}$ = 8.5, $^2J_{PtH}$ = *ca.* 35 Hz) respectively.

cis-*Chloro(chloromethyl) Complexes*.—Solutions of all four complexes **2**, **18**, **25** and **26** in $CDCl_3$ (sealed tubes) were prepared from crystalline material. These showed no evidence (^{31}P NMR spectroscopy) of decomposition during 3 months at ambient temperature. An identical result was obtained for a solution of **25** in $CDCl_3$ containing a drop of water.

trans-*Chloro(chloromethyl) Complexes*.—trans-*Chloro-(chloromethyl)bis(triphenylphosphine)platinum*(II) **27**. This complex[1] gave similar, small, amounts (2–3%, ^{31}P NMR peak heights) of **30** and **7** during 3 weeks, when dissolved in $CDCl_3$ (capped tubes) from a freshly opened vial. This experiment was repeated in the presence of a drop of water. After 4 weeks some **27** (*ca.* 15%, ^{31}P NMR spectroscopy) remained along with the hydride **30** (*ca.* 60%) and the two dichlorides **36** (*ca.* 25%) and **7** (*ca.* 10%).

trans-*Chloro(chloromethyl)bis(tricyclohexylphosphine)-platinum*(II) **29**.—Treatment of complex **1** with tricyclohexylphosphine (2 mol equivalents) in benzene gave **29** which was crystallised from benzene–pentane. It had δ_H 3.63 (t, 2 H, $PtCH_2$, $^3J_{PH}$ = 8.0, $^2J_{PtH}$ = 51.6) and δ_P 19.4 ($^1J_{PtP}$ = 2781 Hz). When a solution of this complex in $CDCl_3$ (from a bottle that had been opened frequently) was sealed under vacuum a ^{31}P NMR signal for the hydride **32** gradually increased in intensity during 4 d. Thereafter no change in ^{31}P NMR spectra was apparent (**29**:**32** *ca.* 3:2, based on peak height). This reaction was repeated with a drop of water added and gave, within 3 d, essentially pure **32**; δ_H −18.82 (t, 1 H, PtH, $^2J_{PH}$ = 12.3, $^1J_{PtH}$ = 1293) and δ_P 39.1 ($^1J_{PtP}$ = 2802 Hz). In C_6D_6, **29** gave ^{31}P NMR signals for only this compound even after 1 week but when a drop of water was present a signal arising from **32** gradually increased in intensity (*ca.* 30% of maximum height during 3 d). When both water (1 drop) and ethyldiisopropylamine (1 mol equivalent) were added to **29** in C_6D_6 only a small amount (< 10%) of **32** was produced in 3 d and some **29** survived for 6 months (**29**:**32**, 4:7, ^{31}P NMR peak height). Exposure of **29** in $CDCl_3$ to MeOH (10 mol equivalents) and $(MeO)_2CHNMe_2$ (5 mol equivalents) gave the (methoxymethyl) derivative **35**, quantitatively, within 1 d. Upon crystallisation from CH_2Cl_2–hexane this trans-*chloro(methoxymethyl)bis-(tricyclohexylphosphine)platinum*(II) gave colourless crystals [m.p. 220–223 °C; δ_H 3.20 (s, 3 H, OMe) and 3.68 (t, 2 H, $PtCH_2$, $^3J_{PH}$ = 6.8, $^2J_{PtH}$ = 67.3); δ_P 21.6 ($^1J_{PtP}$ = 2934 Hz) (Found: C, 55.35; H, 8.7. $C_{38}H_{71}ClOP_2Pt\cdot0.2C_6H_{14}$ requires C, 55.15; H, 8.7%).

trans-*Chloro(chloromethyl)bis(triethylphosphine)platinum*(II) **28**.—(*i*) A solution of complex **28** in $CDCl_3$ from a freshly opened vial was stable (^{31}P NMR spectroscopy) for 7 d but, when the tube was opened and a drop of water added, total decomposition into the hydride **31** and the dichlorides **20** and **33** occurred during the next 7 d (**31**:**20**:**33** *ca.* 1:1:1, ^{31}P NMR spectroscopy). Thereafter, the concentration of the *trans* dichloride **33** increased at the expense of **20** and **31**. The reaction in the presence of water was repeated in a sealed tube. When all the substrate had been consumed (^{31}P NMR spectrum) the tube was opened and the contents were treated with excess of ethanolic 2,4-dinitrophenylhydrazine reagent. Most of the

solvent was then removed *in vacuo* and the residue was partitioned between water and dichloromethane. The material dissolved in the organic layer was subjected to preparative TLC (chloroform–hexane, 1:1) to give formaldehyde 2,4-dinitrophenylhydrazone (identified by TLC and ^{1}H NMR spectral comparison with an authentic specimen).

(*ii*) Complex **28** was also stable in dry C_6D_6 (3 months, ^{1}H and ^{31}P NMR spectra) but decomposed slowly, upon the addition of a drop of water to this solution, giving mainly **31** and **33** (after 10 weeks, **33**:**31**:**28**:**20** 18:16:6:1, ^{31}P NMR peak heights).

(*iii*) Upon repeating the last experiment in the presence of ethyldiisopropylamine (1 mol equivalent) a ^{31}P NMR spectrum run after 7 months showed that **28** had largely survived, the only other peaks present arising from the hydride **31** (*ca.* 5%).

(*iv*) When complex **28** was dissolved in deuteriochloroform containing methanol (10 mol equivalents) and the resulting solution monitored by ^{31}P NMR spectroscopy, conversion into the hydride and dichlorides proceeded at a similar rate to that observed in (*i*) with water added.

(*v*) A similar outcome and rate of reaction was observed when experiment (*iv*) was repeated using trimethyl orthoformate (5 mol equivalents) in addition to the methanol. Proton NMR spectra of the final solution contained resonances arising from dimethoxymethane (δ 3.37 and 4.58), methyl formate (δ 3.77 and 8.11), and methyl chloride (δ 3.02).

(*vi*) Complex **28** reacted cleanly with MeOH–$(MeO)_2CHNMe_2$ (10 and 5 mol equivalents respectively) in $CDCl_3$ (within 1 week) and in C_6D_6 (within 1 month) to give **34**. This methoxymethyl complex was purified by preparative TLC (CH_2Cl_2–MeOH, 397:3) giving a clear gum which failed to crystallise, but which showed only peaks for **34** in its ^{1}H and ^{31}P NMR spectra; δ_H 1.14 (m, 18 H, CH_2CH_3), 1.93 (m, 12 H, PCH_2), 3.31 (s, 3 H, OMe) and 4.12 (t, 2 H, $PtCH_2$, $^3J_{PH}$ = 6.2, $^2J_{PtH}$ = 62.1 Hz), δ_P 18.3 ($^1J_{PtP}$ = 2999 Hz). Complex **34** in $CDCl_3$ was treated with methanol–acetyl chloride (0.8 mol equivalent of each) and gave (^{31}P NMR spectra), after 1 d, mainly the hydride **31** and the chloromethyl complex **28** (**34**:**31**:**28**:**20** 19:17:17:2) and, after 10 d, mainly **28** and the *cis* dichloride **20** (**28**:**20**:**31**:**33**:**34** 54:36:12:6:1, ^{31}P NMR peak heights).

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