Reactions of (Chloromethyl)platinum(II) Derivatives with Nucleophiles. Formation of (Dimethylamino)carbene Complexes Using *N,N,N′,N′*-Tetramethylmethanediamine as Nucleophile and the X-ray Crystal and Molecular Structures of *cis*-[$(Ph_3P)Pt(CH_2NMe_3)Cl_2$], *cis*(*C,P*)-[$(Ph_3P)Pt(CH_2CH_2C(O)NMe_2)Cl$], and *trans*(*As,CH₂*)-[$(Ph_3As)Pt(CHNMe_2)(CH_2NHMe_2)Cl$]$PF_6$

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Reaction, in chloroform solution, of $(COD)Pt(CH_2Cl)Cl$ (**5**) with $Me_2NCH_2NMe_2$ in the presence of 1 equiv (vs **5**) of a monodentate ligand L (L = Ph_3P, (*p*-$MeOC_6H_4)_3P$, (*p*-$FC_6H_4)_3P$, Et_3P, Ph_3As) gives the (dimethylamino)carbene complexes *cis*-[$LPt(CHNMe_2)Cl_2$] (**1a**−**e**) via the cyclic ylide intermediates [$LPt(CH_2NMe_2CH_2NMe_2)Cl$]Cl (**2a**−**e**). Major byproducts of the reaction are the (trimethylammonio)methyl ylide complexes *cis*-[$LPt(CH_2NMe_3)Cl_2$] (**11a**−**e**). With L = Ph_3As, carbene product **1e** is accompanied by a second carbene complex, *trans*(*As,CH₂*)-[$(Ph_3As)Pt(CHNMe_2)(CH_2NHMe_2)Cl$]Cl (**25**). When the reaction with L = Ph_3P is carried out in acetonitrile, the amide chelate [$(Ph_3P)Pt(CH_2CH_2CONMe_2)Cl$] (**24**) is formed in addition to **1a** and **11a**. A deuterium labeling experiment indicates that formation of **24** involves condensation of a CH_2Cl (or derived) moiety with a molecule of solvent. The structures of complexes **11a** and **24**, and of the hexafluorophosphate analogue (**26**) of complex **25**, have been confirmed by X-ray crystallographic analyses. Carbene complex **1a**, along with other products, is also obtained upon reaction of **5** and Ph_3P (1:1) with dimethylamine. Formation of **1a** in this case can proceed via two pathways, one involving cyclic ylide species **2a** as intermediate and the other the N-protonated (dimethylamino)methyl complex *cis*-[$(Ph_3P)Pt(CH_2NHMe_2)Cl_2$] (**20**). The mechanistic pathways involved in formation of carbene complexes **1a**−**e** and **25**, ylide complexes **2a**−**e** and **11a**−**e**, and (dimethylamino)methyl complex **20** are discussed. It is suggested that formation of the ylide complexes and **20** proceeds via initial attack of amine at platinum and that carbene formation proceeds via platinum(IV) carbene hydride intermediates.

Introduction

Halomethyl complexes of transition metals have attracted increasing attention in recent years as precursors to a wide range of products formed by replacement of the halogen by nucleophilic species.[1] We have reported preparative routes[2] to a series of both mono- and bis(chloromethyl)platinum(II) derivatives, and we, and others, have described replacement reactions of certain of these derivatives involving nitrogen,[3] phosphorus,[4] oxygen,[3,5] and sulfur[6] nucleophiles. The present study was suggested by the reported[7] formation of the [(dimethylamino)carbene]platinum(II) complex **1a** via decomposition of the cyclic ammonium ylide complex **2a** (Scheme 1). The latter was obtained[7] by reaction of $(Ph_3P)_3Pt$ with the Mannich salt [Me_2NCH_2]Cl. Decomposition of **2a** was suggested[7] to proceed, as outlined in Scheme 1, via displacement of the coordinated dimethylamino group by the chloride counterion followed by fragmentation of the resulting intermediate (**3a**) to release the Mannich cation which then abstracts hydride from the accompanying fragment (**4a**) to give

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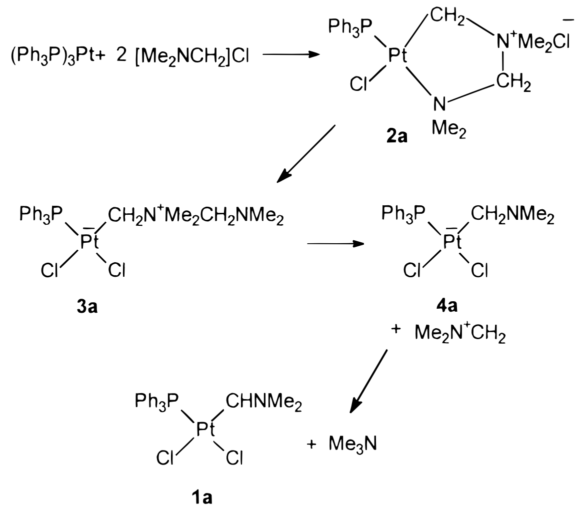
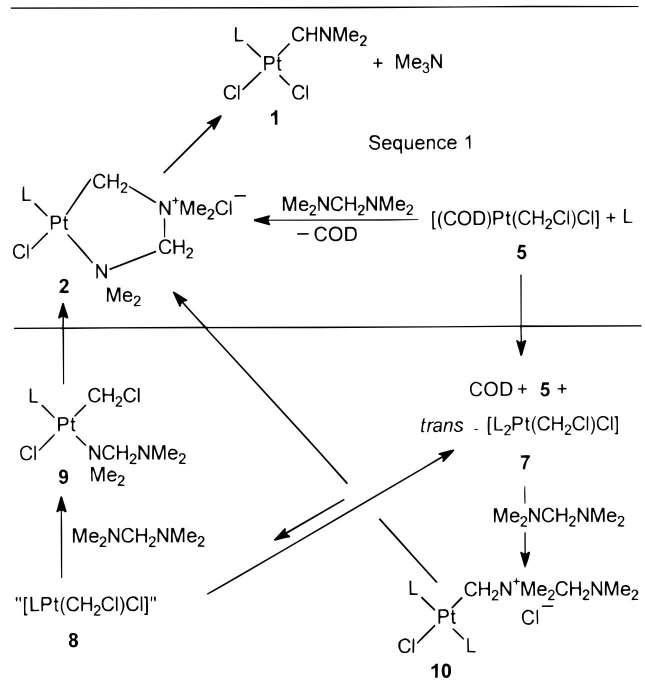
Scheme 1



Scheme 2



trimethylamine and the carbene complex, **1a**. It occurred to us that it might be possible to generate complexes of type **2a**, and consequently (dimethylamino)carbene complexes, by reaction of (chloromethyl)platinum(II) complexes with *N*,*N*,*N*′,*N*′-tetramethylmethanediamine. Formation of **2a** and analogues by reactions of this type might conceivably proceed via initial attack of the diamine at platinum or at carbon. There are a number of reports of the formation of cyclic ylide complexes from (halomethyl)metal or related derivatives and potentially bidentate ligands, in particular those with phosphorus, arsenic, or sulfur donor atoms.[6,8]

Consideration of potential (chloromethyl)platinum(II) precursor complexes for reaction with $Me_2NCH_2NMe_2$ led us to investigate the approach outlined in Scheme 2. Sequence 1 envisages starting from the known[2] complex [(COD)Pt(CH_2Cl)Cl] (**5**; COD = 1,5-cyclooctadiene). It has been observed[6] that complex **5** does not react with the diamine $Me_2NCH_2CMe_2CH_2NMe_2$ ($CDCl_3$, room temperature, 12 h), although the bis(sulfide) $MeSCH_2CEt_2CH_2SMe$ does react slowly (days at room temperature) to give the cyclic sulfonium ylide complex **6**. It was therefore anticipated that $Me_2NCH_2NMe_2$ would not react with **5** alone, at least under relatively mild conditions. However, it seemed possible that addition to the reaction mixture of 1 equiv (vs **5**) of a monodentate ligand (L in Scheme 2) capable of displacing COD from **5** would produce a mixture containing at least a trace of reactive species **8**, which might be, for example, the dimer [LPt(CH_2Cl)Cl]$_2$,[9] [LPt(CH_2Cl)Cl(η^2-COD)], or [LPt(CH_2Cl)Cl(solvent)], in equilibrium. Reactive intermediate **8** could then give the desired cyclic ammonium ylide complex **2** via attack of $Me_2NCH_2NMe_2$ at platinum to give species **9** followed by internal displacement of chloride from the chloromethyl group. Alternatively, reaction might proceed by initial replacement of the chloride of the chloromethyl group in [L_2Pt(CH_2Cl)Cl] (**7**; Scheme 2) by $Me_2NCH_2NMe_2$ to give intermediate **10**[10] followed by intramolecular displacement of ligand L. Given the bulky nature of $Me_2NCH_2NMe_2$, it seemed unlikely that reaction at the chloromethyl group of **7** could proceed via an S_N2-like process. However, attack at carbon would be feasible if preceded by either dissociation of the alkyl chloride (to give a reactive four-coordinate cationic carbene species) or migration of chloride from carbon to platinum (to give a five-coordinate, neutral carbene intermediate).[11]

Results and Discussion

Reactions with L = PPh$_3$. (a) Initial Studies. The feasibility of proposed sequence 1 (Scheme 2) was first explored by monitoring the reaction of equimolar quantities of [(COD)Pt(CH_2Cl)Cl] (**5**), PPh_3, and $Me_2NCH_2NMe_2$ in $CDCl_3$ at ambient temperature in air. ^{1}H and ^{31}P NMR spectra[12] (Tables 1 and 2) run immediately after mixing showed that all of the phosphine had reacted with the COD complex to give *trans*-[$(Ph_3P)_2$Pt(CH_2Cl)Cl][2] (**7a**), so that the solution now contained **5**, **7a**, the diamine, and free COD in a 0.5:0.5:1:0.5 mol ratio, respectively (see Chart 1 for the structures of all compounds discussed in this paper). Over the course of several hours the growth of new NMR signals attributable to the cyclic ammonium ylide complex **2a** could be

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(9) Dimeric complexes of the type [LPt(Ph)Cl]$_2$ have been obtained by treating [(COD)Pt(Ph)Cl] with bulky phosphine ligands, while less sterically demanding monodentate ligands give the bis(phosphine) derivatives *trans*-[L_2Pt(Ph)Cl] with no detectable (by NMR) dimeric product, even with a deficiency of ligand, L (Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 3607−3611).

(10) The species **10** (Scheme 2, L = PPh_3) is a likely intermediate in the formation of cyclic ammonium ylide complex **2a**[7] in the preparation outlined in Scheme 1.

(11) Although the mechanism is presently unknown, our finding[3] that *trans*-[$(R_3P)_2$Pt(CH_2Cl)Cl] (R = Et, cyclohexyl) can be converted cleanly to *trans*-[$(R_3P)_2$Pt(CH_2OMe)Cl] may suggest that initial attack at carbon is feasible.

(12) ^{1}H and ^{31}P NMR data are collected in Tables 1 and 2, respectively.

Table 1. ^{1}H NMR Data

(a) Pt−CH Protons

compd	δ_H	$^{3}J_{P-H}$, Hz	$^{2}J_{Pt-H}$, Hz
1a	9.82 (d, 1H)	4.0	22
1b	9.83 (d, 1H)	4.0	20
1c	9.84 (d, 1H)	3.6	20
1d	10.58 (d, 1H)	4.1	42
1e	10.09 (s, 1H)		*a*
2a	3.21 (br s, 2H)	*a*	53
2b	3.21 (d, 2H)	2.5	*a*
2c	3.26 (d, 2H)	2.5	*a*
2e	3.37 (s, 2H)		*a*
7a	3.03 (t, 2H)	8	52
7b	2.97 (t, 2H)	9	*a*
7c	2.89 (t, 2H)	8	56
7d	3.69 (t, 2H)	8.8	56
7e	3.17 (s, 2H)		59.6
11a	3.63 (d, 2H)	4.6	75
11b	3.62 (d, 2H)	4.4	*a*
11c	3.63 (d, 2H)	4.4	*a*
11d	3.91 (d, 2H)	3.7	72
11e	3.62 (s, 2H)		81
14	3.47 (d, 2H)	4.4	77
16	10.41 (br, 1H)	*a*	26
17	10.09 (br, 1H)	*a*	28
18	3.47 (d, 2H)	4.8	52
21	4.02 (d, 2H)	2.5	50
24	1.34 (m, 2H)	*a*	77
25	11.09 (s, 1H)		48
	~3 (br m, 2H)		*a*
26	10.37 (s, 1H)		48
	3.29 (d, 2H)[b]		57

(b) *N*-Methyl Protons

compd	δ_H	J_{Pt-H}, Hz	compd	δ_H	J_{Pt-H}, Hz
1a	2.85 (s, 3H)		**11a**	2.76 (s, 9H)	
	3.52 (s, 3H)	12	**11b**	2.79 (s, 9H)	
1b	2.89 (s, 3H)		**11c**	2.83 (s, 9H)	
	3.52 (s, 3H)	9.5	**11d**	3.22 (s, 9H)	
1c	2.96 (s, 3H)		**11e**	2.57 (s, 9H)	
	3.55 (s, 3H)	9.5	**14**	2.56 (s, 6H)	
1d	3.48 (s, 3H)		**16**	2.61 (s, 3H)	
	3.81 (s, 3H)	11		3.04 (s, 3H)	20
1e	2.85 (s, 3H)		**17**	2.75 (dd, 6H)[d]	32
	3.56 (s, 3H)	10.1		3.00 (s, 3H)	
2a	3.27 (d, 6H)[c]	22		3.50 (s, 3H)	9.6
	3.40 (s, 6H)		**18**	2.87 (dd, 6H)[e]	30
2b	3.23 (s, 6H)	*a*	**19**	2.74 (dd, 6H)[f]	24
	3.41 (s, 6H)		**21**	2.88 (d, 6H)[g]	24
2c	3.31 (br s, 6H)	*a*	**24**	2.97 (br s, 6H)	
	3.47 (s, 6H)		**25**	2.93 (s, *n*H)[h]	*a*
2e	3.29 (s, 6H)	*a*		3.22 (s, *n*H)[h]	*a*
	3.43 (s, 6H)		**26**	2.87 (s, 3H)	
				2.96 (d,[i] 6H)	
				3.21 (s, 3H)	11

(c) NCH_2N and NCH_2O Protons

compd	δ_H	J_{Pt-H}, Hz	compd	δ_H	J_{Pt-H}, Hz
2a	4.97 (br s, 2H)	27	**2e**	4.99 (s, 2H)	33
2b	4.97 (br s, 2H)	*a*	**14**	4.33 (s, 2H)	
2c	5.16 (br s, 2H)	*a*	**21**	3.67 (d, 2H)[j]	39

[a] Obscured or not resolved. [b] s after D_2O exchange ($^{3}J_{NH-H}$ = 5.6 Hz). [c] $^{4}J_{P-H}$ = 3.5 Hz. [d] $^{4}J_{P-H}$ = 4.0 Hz; $^{3}J_{NH-H}$ = 5.6 Hz. [e] $^{4}J_{P-H}$ = 3.5 Hz; $^{3}J_{NH-H}$ = 6.2 Hz. [f] $^{4}J_{P-H}$ = 3 Hz; $^{3}J_{NH-H}$ = 4 Hz. [g] $^{4}J_{P-H}$ = 2.8 Hz. [h] Singlets superimposed on broad resonances. [i] s after D_2O exchange ($^{3}J_{NH-H}$ = 5.2 Hz). [j] J_{P-H} = 1.2 Hz.

Table 2. ^{31}P NMR Data

compd	δ_P	$^{1}J_{Pt-P}$, Hz	compd	δ_P	$^{1}J_{Pt-P}$, Hz	compd	δ_P	$^{1}J_{Pt-P}$, Hz
1a	8.35	4044	**7a**	27.40	3155	**14**	13.57	4395
1b	3.88	4044	**7b**	23.22	3103	**16**	17.71	2613
1c	5.92	4069	**7c**	24.53	3177	**17**	7.66	3344
1d	10.17	3747	**7d**	16.0	2793	**18**	15.53	4141
2a	10.63	4047	**11a**	13.56	4407	**19**[a]	3.90	3524
2b	5.79	4065	**11b**	9.18	4410	**21**	14.25	4368
2c	8.45	4099	**11c**	11.25	4410	**24**	16.12	4125
			11d	4.33	4115			

[a] Cf. ref 16.

observed. After 1 day, (dimethylamino)carbene complex **1a** could be detected. Essentially complete disappearance of signals due to the starting COD complex, the initially generated bis(phosphine) complex, and the ylide complex required about 10 days at ambient temperature. At this stage, the major platinum-containing species present in solution was the carbene complex **1a**, but this was accompanied by a significant quantity of the more polar product **11a,** which was separated from **1a** and accompanying byproducts by preparative TLC. Its formulation as the trimethylammonium ylide complex **11a** has been confirmed by an X-ray crystal structure analysis (see below). Trimethylamine, liberated in the course of the conversion of **2a** into **1a**, is presumably the source of the Me_3N moiety in **11a**. Since this complex was not obtained from the decomposition of pure **2a**,[7] it must form via reaction of trimethylamine with COD complex **5**, bis(phosphine) complex **7a**, or some species (e.g. **8**) derived therefrom. The relative amounts of **11a** formed could be reduced by using excess diamine in the reaction, although a concomitant increase in the amounts of other byproducts was observed (see later). Interestingly, the overall rate of reaction did not change appreciably with increasing amine concentration.[13]

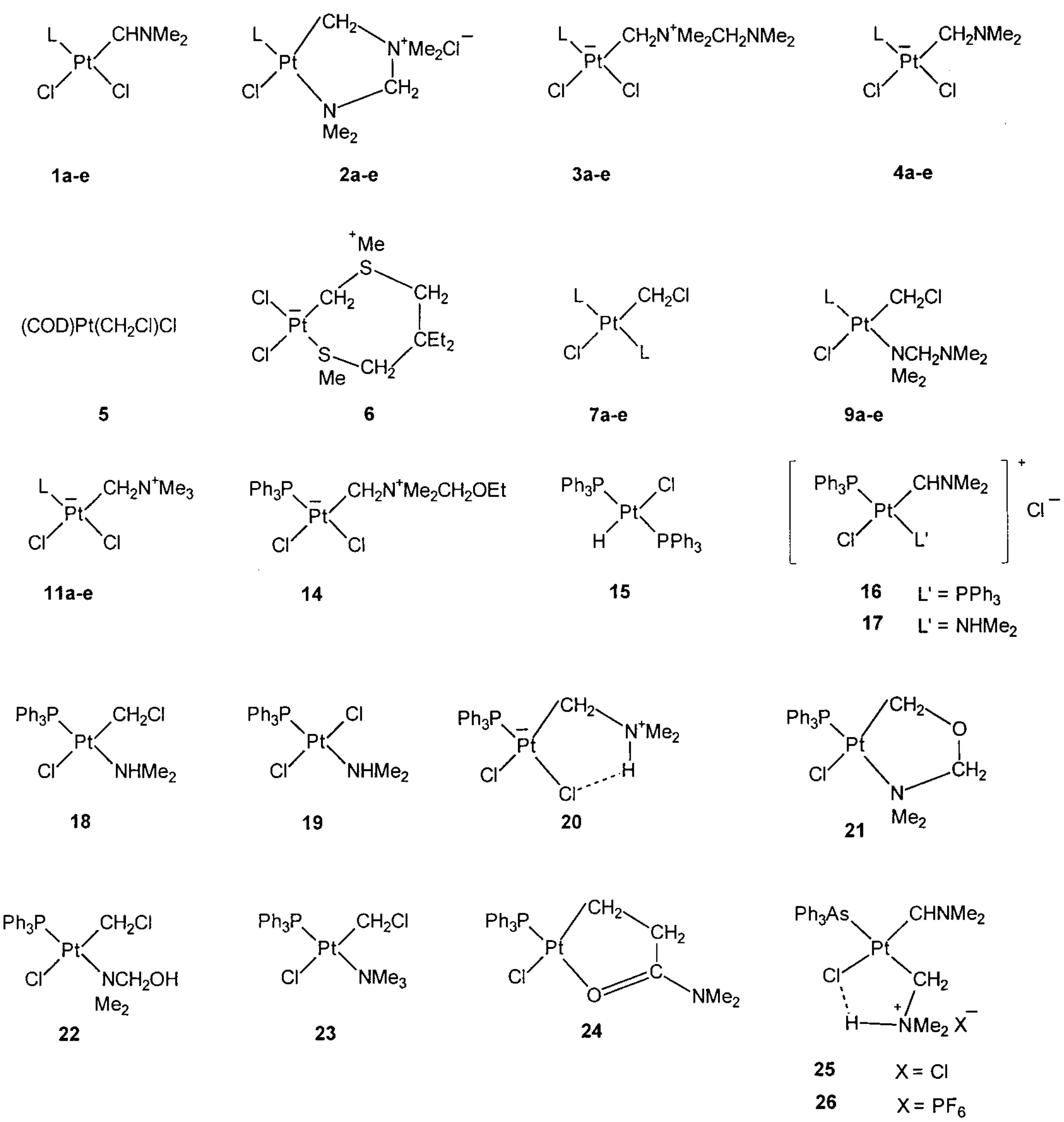
While essentially complete conversion of starting materials to products **1a** and **11a** required more than 1 week at ambient temperature, the reaction time could be reduced to a few hours by heating the $CDCl_3$ solution to 60−65 °C, although a somewhat higher proportion of (trimethylammonio)methyl complex **11a** was obtained under these conditions. On a preparative scale, with heating, yields of **1a** and **11a** of 60−65% and 15−20%, respectively, could be obtained when the solvent was relatively dry. When $CHCl_3$ stabilized with 0.75% of ethanol was used as solvent, products **1a** and **11a** were accompanied by the dimethyl(ethoxymethyl)ammonium ylide complex **14**, which could be prepared, in good yield, by allowing a solution containing equimolar quantities of COD complex **5**, PPh_3, and an authentic sample of $EtOCH_2NMe_2$ to stand at ambient temperature.[14]

(b) Minor Products, and Use of $NHMe_2$ instead of $Me_2NCH_2NMe_2$. Small quantities of various byproducts, the relative amounts presumably depending on the purity of the solvent, were usually detected in the reaction solutions. Thus, the hydride complex *trans*-

(13) Surprisingly, excess diamine did not appear to hinder conversion of **2a** into **1a**, although one would expect liberated Mannich cation to be trapped with the resulting formation of a complex such as $[(Ph_3P)Pt(\eta^2\text{-}CH_2NMe_2)Cl]$ (**12**). The last was the product initially expected from reaction[7] of $(Ph_3P)_3Pt$ with $[Me_2NCH_2]Cl$, since the nickel analogue had been obtained by this route. Indeed, preparative TLC of solutions containing **2a** gave fractions containing a component the NMR spectra of which would be consistent with structure **12** or the related dimer **13** (see Experimental Section). This compound, upon standing in $CDCl_3$, was slowly converted into carbene complex **1a**.

(14) Solutions of **14** show no sign of decomposition, even upon heating to 60−65 °C, to give carbene complex **1a** and EtOMe. Such a reaction would be analogous to the formation of **1a** and trimethylamine from cyclic intermediate **2a** via **3a** (Scheme 1).

Chart 1[a]



[a] Legend: **a**, L = Ph_3P; **b**, L = $(4\text{-}MeOC_6H_4)_3P$; **c**, L = $(4\text{-}FC_6H_4)_3P$; **d**, L = Et_3P; **e** L = Ph_3As.

$[(Ph_3P)_2Pt(CH_2Cl)H]$ (**15**), which can be formed[15] from chloromethyl complex **7a** in the presence of water, was often detected. In addition, *cis*- and, occasionally, *trans*-$[(Ph_3P)_2PtCl_2]$, presumably resulting[15] from further reaction of **15**, and $(COD)PtCl_2$ were found. Occasionally, ^1H NMR spectra of the solutions from reaction of COD complex **5** with PPh_3 and $Me_2NCH_2NMe_2$ showed one or two weak low-field signals (δ 10.41, 10.13) characteristic of carbene complexes, in addition to that of the major product **1a**. Formation of these byproducts was more pronounced in reactions where excess diamine was employed. The signal at δ 10.41 can be ascribed to the bis(phosphine) complex *trans*-$[(Ph_3P)_2Pt(CHNMe_2)Cl]Cl$ (**16**), which is also obtained when carbene complex **1a** is treated with 1 equiv of PPh_3, while the signal at δ 10.13 corresponds to the dimethylamine analogue *trans*(*N,P*)-$[(Ph_3P)(HNMe_2)Pt(CHNMe_2)Cl]Cl$ (**17**). Complex **17** can be generated in solution by addition of dimethylamine to **1a** in $CDCl_3$. Evaporation of the solvent leads to partial decomposition of **17** and regeneration of **1a**, while preparative TLC gives only **1a**.

In some cases, the first product detected, after the initial rapid formation of bis(phosphine) complex **7a**, showed NMR signals consistent with its formulation as the chloromethyl dimethylamine complex **18**. When such a solution was allowed to stand until formation of the main products, **1a** and **11a**, was complete, the NMR signals due to **18** had disappeared. The resulting solution then showed, inter alia, weak signals assignable to *trans*-$[(Ph_3P)(HNMe_2)PtCl_2]$[16] (**19**), which was isolated by preparative TLC. When dimethylamine, most conveniently added as the CO_2 adduct, was reacted with equimolar quantities of **5** and PPh_3 in $CDCl_3$, formation of **18** proceeded largely to completion over a few hours at ambient temperature. When the resulting solution was allowed to stand, slow disappearance of **18** was observed over a period of 10 days. During that time, new signals ascribable to several products developed. These included, not unexpectedly, hydride complex **15** and

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amine phosphine complex **19**, and also the known cyclic ylide species **2a**, carbene complex **1a**, and (trimethylammonio)methyl complex **11a**. However, we were unable to find any signals that could be ascribed to a complex containing a $PtCH_2NMe_2$ moiety, e.g. species **12** or **13**.[13] At the end of the reaction, **1a**, **11a**, **15**, and **19** were recovered by preparative TLC. The formation of **2a** in this reaction probably involves the participation of formaldehyde, formed by reaction[15] of chloromethyl complex **7a** (or **18**)[17] with traces of water in the solvent.

Attempts to isolate **18** were unsuccessful due to its instability (see Experimental Section). However, the results of these investigations revealed that formation of **1a** from **18** proceeds via at least one further route in addition to that via **2a**. When **18** was generated in $CDCl_3$ and this solution was added to a large volume of hexane, the major product in the resulting gummy precipitate was **20**, which contains the novel N-protonated (dimethylamino)methyl ligand. The latter moiety is characterized by proton signals at δ 2.63 (6H, d, J = 5.6 Hz) and 2.70 (2H, m), both of which are coupled (COSY) to a broad peak at δ 8.15 (1H, N*H*). When solutions of **20** in $CDCl_3$ were left at ambient temperature, slow, and apparently clean, conversion to carbene complex **1a** was observed. The material obtained in the attempted precipitation of **18** (above) accounted for less than half of that expected. When the supernatant was evaporated and the residue redissolved in $CDCl_3$, ^1H and ^{31}P NMR spectra indicated that the solution contained largely **18** along with small amounts of bis(phosphine) complex **7a** and hydride **15**. When this solution was allowed to stand, slow decomposition of **18** was again observed, but a new major product was now generated. This proved to be stable to preparative TLC, and NMR (^1H, ^{13}C, and ^{31}P) data and elemental analysis are consistent with its formulation as **21**, which contains a chelating ((dimethylamino)methoxy)methyl ligand. This product could arise via condensation of formaldehyde with dimethylamine complex[18] **18** to give the dimethyl(hydroxymethyl)amine complex **22** followed by intramolecular displacement on the chloromethyl group.

Since the above results indicate that the fate of dimethylamine chloromethyl complex **18** depends critically upon the reaction conditions, a further series of experiments was performed. (i) When **18** was generated in $CDCl_3$ using 1 equiv of dimethylamine (some **5** and **7a** present), followed by the addition of paraformaldehyde and standing at ambient temperature, cyclic complex **21** was formed as a major product. (ii) When **18** was generated as in (i), but using 2 equiv of dimethylamine (little or no **5** or **7a** present), addition of paraformaldehyde resulted in initial significant formation of cyclic intermediate **2a**, with the eventual major product being carbene complex **1a**. (iii) When **18** was generated using excess dimethylamine, the solvent evaporated, and the resulting gum pumped under vacuum, then the major species detected by NMR was (dimethylammonio)methyl complex **20**. Upon standing, gradual conversion into **1a** was observed as before. These experiments clearly demonstrate that, in the reactions with dimethylamine, there are two pathways leading to carbene complex **1a**, one via cyclic intermediate **2a** and a second via **20**. Possible mechanisms are discussed later.

(c) Preliminary Mechanistic Considerations. Further studies were carried out with a view to obtaining some insight into the mechanism of formation of cyclic ammonium ylide complex **2a** in our original reaction. Thus, no reaction was detected when $CDCl_3$ solutions of either COD complex **5** plus diamine or bis(phosphine) complex **7a** plus diamine were allowed to stand for several days at ambient temperature. However, addition of **5**, or of [(COD)$PtCl_2$], to the latter solution resulted in reaction to give intermediate **2a** and then products **1a** and **11a**, as before. These results appear to rule out any mechanism of formation of **2a** involving initial nucleophilic displacement on the chloromethyl groups of complexes **5** or **7a**, since such a C−N bond-forming step would be expected to be irreversible under the reaction conditions employed. Indeed, reaction via initial attack at platinum would be consistent with the observed formation of complex **18** in the reaction with dimethylamine. However, direct displacement by the bulky diamine of either COD, from **5**, or PPh_3, from **7a**, is expected to be very unfavorable, as borne out by the lack of any observable reaction in the experiments described above.[19] The observation that **5**, or [(COD)$PtCl_2$], promotes the reaction suggests that these complexes act as acceptors of a phosphine ligand from **7a**, thereby facilitating what would otherwise be an energetically unfavorable step. This could involve formation of a reactive species (**8**, L = PPh_3; Scheme 2) having the type of structure indicated in the introductory section, via reversible dissociation[20] of a phosphine from **7a**, followed by attack on the reactive species by the diamine to give **9a**. This is consistent with the observation that the overall reaction rate does not change with increasing concentration of the diamine. In the absence of a scavenger for PPh_3, attack of the diamine on **8** apparently cannot compete with return of the phosphine. Subsequent conversion of **9a** to cyclic ylide complex **2a**, e.g. by attack of the free end of the coordinated diamine on the chloromethyl group, must be relatively fast.

Formation of (trimethylammonio)methyl product **11a** could then involve reaction of trimethylamine with **8**

(17) The amount of hydride **15** formed in these reactions, and its relatively rapid appearance, may indicate that **18** is the major source. Formation of **15** from bis(phosphine) complex **7a** alone was very slow.[15]

(18) Condensations involving formaldehyde and coordinated amines are well-known. See e.g.: Bottomley, G. A.; Clark, I. J.; Creaser, I. I.; Engelhardt, L. M.; Geue, R. J.; Hagen, K. S.; Harrowfield, J. M.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; See, A. J.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Aust. J. Chem.* **1994**, *47*, 143−179.

(19) It has been reported that addition of PPh_3 to (COD)$PtCl_2$ under an atmosphere of CO, or to (COD)$PtMe_2$ in the presence of amines, leads to *cis*-[(Ph_3P)Pt(CO)Cl_2][9] or *cis*-[(Ph_3P)(amine)$PtMe_2$] (see: Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1988**, *342*, 269−280) presumably via trapping of η^1-COD intermediates, formed upon initial reaction of the phosphine, by CO or amine, respectively. A similar pathway in the present case would be expected to lead to cyclic intermediate **2a** via species **9a**. However, slow addition of PPh_3 (5 min) to a solution of **5** and $Me_2NCH_2NMe_2$ in $CDCl_3$ did not result in an observable increase in the rate of formation of **2a**, the only detectable initial products being bis(phosphine) complex **7a** and free COD.

(20) Initial reversible dissociation of phosphine is believed to be involved in various reactions of complexes of the type *trans*-[L_2Pt(R)X] (L = phosphine). See e.g.: (a) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110−2116. (b) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795−1803. (c) Brainard, R. L.; Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481−1490. (d) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148−156. (e) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356−3362. (f) Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784−4794.

(L = PPh_3) to give intermediate **23**. Conversion of the latter to **11a** effectively requires migration of the Me_3N ligand from platinum to carbon, with concomitant displacement of chloride, which migrates to platinum. This type of mechanism[21] has been proposed for the formation of the rhodium(III) ylide complex [(η^5-C_5H_5)Rh(PMe_3)(CH_2PMe_3)I]I from [(η^5-C_5H_5)Rh(PMe_3)$_2$-(CH_2I)]I and related reactions. Formation of (dimethyl-(ethoxymethyl)ammonio)methyl complex **14** from Me_2-NCH_2OEt presumably proceeds similarly, and indeed, an alternative mode of formation of cyclic intermediate **2a** could involve the sequence **9a** → **3a** → **2a**. Formation of **20** from chloromethyl dimethylamino complex **18** may proceed similarly. Migration of dimethylamine is significantly slower than that of trimethylamine,[22] probably due to a combination of the lower steric bulk of the former amine and the possibility of its forming a hydrogen bond to the neighboring Cl in **18**.[23]

(d) Reaction in Acetonitrile. In the earlier work[7] carbene complex **1a** was obtained by heating a solution of cyclic ammonium ylide complex **2a** in acetonitrile. We have therefore briefly investigated the use of this solvent in our reaction. Monitoring by ^1H and ^{31}P NMR spectroscopy indicated that the reaction in CD_3CN was complete within 2 h at temperatures in the range 60−70 °C but that major products **1a** and **11a** were accompanied by a third significant product (**24**). These three products were isolated from a preparative-scale reaction in CH_3CN, and the structure of **24** was established by X-ray crystallographic analysis (see below). Although we have not undertaken studies of the mechanism of formation of **24**, we have observed that the product obtained from CD_3CN solution contains the deuterated moiety $-CH_2CD_2C(O)NMe_2$, suggesting that its formation involves coupling of a $-CH_2Cl$ (or derived) fragment with a molecule of solvent.

Reactions with L = (4-MeOC$_6$H$_4$)$_3$P and (4-FC$_6$H$_4$)$_3$P. The aryl phosphines (4-$MeOC_6H_4$)$_3$P and (4-FC_6H_4)$_3$P were found to behave similarly to PPh_3, giving initially the *trans*-bis(phosphine) complexes **7b**,**c** followed by the cyclic ammonium ylide intermediates **2b**,**c** and then the corresponding carbene complexes **1b**,**c** along with the (trimethylammonio)methyl derivatives **11b**,**c**. While the reactions of all three arylphosphines proceeded at very similar overall rates, it was observed (^{31}P NMR) that the ratio of carbene complex to trimethylammonio complex formed in these reactions decreased in the order (4-FC_6H_4)$_3$P > PPh_3 > (4-$MeOC_6H_4$)$_3$P. The differences are small, but they do suggest that the rate of formation of intermediate **2** increases relative to its rate of decomposition in the same order, viz. (4-FC_6H_4)$_3$P > PPh_3 > (4-$MeOC_6H_4$)$_3$P. Presumably, formation of **2b,c** proceeds, as discussed above for **2a**, via short-lived intermediates **9b,c**.

Reactions with L = Et$_3$P and Ph$_3$As. Further investigations of the preparation of (dimethylamino)carbene derivatives via sequence 1 (Scheme 2) provided examples where either the formation of cyclic intermediate **2**, or its breakdown to carbene complex **1**, is significantly slower than found for the arylphosphine derivatives.

The former situation was encountered for L = PEt_3. In this case, the ligand was most conveniently introduced as the previously described chloromethyl complex **7d**.[15] Thus, a solution containing COD complex **5**, **7d**, and $Me_2NCH_2NMe_2$ in $CDCl_3$ showed no sign of reaction on standing at ambient temperature for up to 3 days. However, upon heating at 55 °C the reaction proceeded to produce a mixture containing **1d** and **11d**. The slower reaction in this case might be rationalized if it proceeds through cyclic intermediate **2d**, formed via initial attack of the diamine at platinum to give **9d**, since this would require breaking of a relatively strong bond to PEt_3[24] in **7d**.

The relatively stable cyclic ammonium ylide complex **2e** was formed when equimolar quantities of **5**, Ph_3As, and $Me_2NCH_2NMe_2$ were left at ambient temperature in $CDCl_3$. As with the arylphosphine ligands, rapid initial reaction gave the bis(arsine) complex **7e**. Subsequent formation of cyclic complex **2e** proceeded more rapidly than that of the aryl phosphine analogues **2a**−**c**, being complete within 1 day at ambient temperature. Complex **2e** showed little sign of decomposition over a few days at this temperature, but decomposition could be induced by heating at 55 °C. When decomposition of **2e** was complete, the ^1H NMR spectrum of the resulting solution showed two low-field resonances (δ 11.09 and 10.09) characteristic of protons attached to carbene C atoms. Preparative TLC of this solution gave two major products, the less polar of which proved to be the desired carbene complex, **1e**. The ^1H NMR spectrum of the more polar product (**25**) showed, in addition to the carbene proton resonance at δ 11.09 and signals due to coordinated Ph_3As, a broad D_2O-exchangeable signal (δ 10.0, NH) and two sharp peaks (δ 2.93 and 3.22, NMe's) superimposed on broad, overlapping resonances.[25] Since the polarity of this material, and the broadened signals in its proton spectrum, suggested an ionic species, presumably a chloride salt, it was subjected to ion exchange with excess KPF_6. The resulting product gave a sharp ^1H NMR spectrum, consistent with its formulation as **26**. This structure was confirmed by an X-ray crystallographic study (see below).

Further investigation of the reaction with Ph_3As led to the following observations. (i) When a solution of **5**, Ph_3As, and $Me_2NCH_2NMe_2$ (1:1:2) in $CDCl_3$ was heated from the outset, the resulting product mixture included the (trimethylammonio)methyl complex **11e**. (ii) The bis(arsine) complex **7e** reacts with $Me_2NCH_2NMe_2$ at ambient temperature in the absence of COD complex **5** to give cyclic species **2e** plus free Ph_3As. The rate of formation of **2e** was somewhat slower than what was found for the reaction in the presence of **5**, requiring more than 1 day to reach completion. The reactivity of **7e** contrasts with that of the PPh_3 analogue **7a**. If initial

(21) Werner, H.; Hofmann, L.; Feser, R.; Paul, W. *J. Organomet. Chem.* **1985**, *281*, 317−347.

(22) The presumed intermediate **23** has not been detected.

(23) For recent examples of hydrogen bonds involving four-membered rings, see: Petrucci, M. G. L.; Lebuis, A.-M.; Kakkar, A. K. *Organometallics* **1998**, *17*, 4966−4975. For a recent survey of crystal structures involving hydrogen bonds between metal-bound chlorine and hydrogen donors, including H−N groups, see: Aullon, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *Chem. Commun.* **1998**, 653−654.

(24) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; pp 120−121.

(25) Sometimes an additional weak low-field signal was observed at δ 10.0 (superimposed on the D_2O-exchangeable signal). This was probably due to the presence of some *trans*(*As,N*)-[(Ph_3As)($HNMe_2$)-Pt($CHNMe_2$)Cl]Cl (cf. phosphine analogue **17**).

Table 3. Summary of Principal Dimensions (Å, deg) for 11a, 24 and 26

				Compound **11a**			
Pt1−C1	2.041(7)	C1−N1	1.569(8)	C1−Pt1−Cl1	89.3(2)	Cl1−Pt1−P1	172.72(6)
Pt1−Cl1	2.3495(18)	C2−N1	1.475(9)	C1−Pt1−Cl2	178.0(2)	Cl2−Pt1−P1	86.20(7)
Pt1−Cl2	2.387(2)	C3−N1	1.509(10)	C1−Pt1−P1	95.7(2)		
Pt1−P1	2.2169(18)	C4−N1	1.419(10)	Cl1−Pt1−Cl2	88.86(8)	C3−N1−C1−Pt1	−154.8(6)
				Compound **24**			
Pt1−C3	2.057(10)	C1−C2	1.513(14)	C3−Pt1−Cl1	169.5(3)	C1−C2−C3	112.1(8)
Pt1−Cl1	2.387(2)	C1−N1	1.316(12)	C3−Pt1−O1	81.6(4)	C1−O1−Pt1	117.8(6)
Pt1−O1	2.052(8)	C1−O1	1.321(11)	C3−Pt1−P1	91.5(3)	C2−C1−O1	115.1(8)
Pt1−P1	2.209(2)	C2−C3	1.530(14)	Cl1−Pt1−O1	87.9(2)	C2−C3−Pt1	110.2(7)
		C4−N1	1.435(14)	Cl1−Pt1−P1	98.98(9)	C4−N1−C1−O1	−2.3(17)
		C5−N1	1.460(11)	O1−Pt1−P1	173.1(2)	C5−N1−C1−O1	176.5(10)
				Compound **26**			
Pt1−As1	2.4313(12)	C1−N2	1.489(17)	As1−Pt1−Cl	178.9(4)	N2−C1−Pt1	114.6(8)
Pt1−C1	2.053(10)	C3−N2	1.537(16)	As1−Pt1−C5	91.8(4)	N6−C5−Pt1	132.1(12)
Pt1−C5	1.929(16)	C4−N2	1.448(18)	As1−Pt1−Cl1	92.38(9)	C3−N2−C1−Pt1	168.3(9)
Pt1−Cl1	2.366(4)	C5−N6	1.24(2)	C1−Pt1−C5	87.1(6)	C4−N2−C1−Pt1	−67.7(13)
		C7−N6	1.43(2)	C1−Pt1−Cl1	88.7(4)	C7−N6−C5−Pt1	−1(2)
		C8−N6	1.492(19)	C5−Pt1−Cl1	175.3(4)	C8−N6−C5−Pt1	−177.3(11)

attack of the diamine takes place at Pt (to give **9e**) rather than at C, this would be consistent with the expected greater lability of Pt−As versus Pt−P bonds.[24] (iii) Reaction of **5**, Ph_3As, and diamine proceeds in C_6D_6 at a rate similar to that found in $CDCl_3$, suggesting that the slow step in the formation of **2e** does not involve ionization of the C−Cl bond (or indeed of the Pt−Cl bond) in bis(arsine) intermediate **7e**. This is consistent with reaction via initial attack of diamine at Pt rather than C. (iv) The relative stability of the arsine-containing cyclic intermediate **2e** allowed us to investigate the influence on its rate of formation of different initial concentrations of $Me_2NCH_2NMe_2$. Thus, no increase in the rate of formation of **2e** was observed when $CDCl_3$ solutions prepared using the same initial quantities of **5** and Ph_3As were treated with 2, 4, 8, or 16 equiv of the diamine, suggesting that the rate-determining step(s) in the formation of **2e** does(do) not involve participation of the diamine. When these solutions were heated at 55 °C, decomposition of **2e** to carbene complexes **1e** and **25** was observed as before. However, ^1H NMR spectra of the resulting solutions indicated that the ratio of **1e** to **25** decreases with increasing diamine concentration. Indeed, at the highest diamine concentration employed, the carbene proton signal for **1e** was no longer detectable.

X-ray Crystallographic Studies. **(a) *cis*-Dichloro[(trimethylammonio)methyl](triphenylphosphine)platinum(II) (11a)**. A view of the molecule is shown in Figure 1. Principal dimensions for this complex (and for complexes **24** and **26** discussed below) are listed in Table 3, and full details are given in the Supporting Information. The chlorine ligands are cis in an approximately square-planar platinum coordination sphere. A tetrahedral distortion is shown by the displacement of the coordinating atoms from the least-squares plane through Pt(1), Cl(1), Cl(2), P(1), and C(1). This distortion and the Pt−P−C angle (95.7(2)°) reflect a steric interaction between the bulky triphenylphosphine and (trimethylammonio)methyl ligands. It is interesting to compare the platinum−ligand bond lengths for this complex with those reported[7] for the structurally related carbene complex **1a**. The Pt−P bond lengths are essentially identical (2.2169(18) and 2.220(2) Å, respectively), as are the Pt−Cl bond lengths for the Cl trans to P (2.3495(18) and 2.345(3) Å, respectively). Not surprisingly, the Pt−C distance in **11a** (2.041(7) Å) is

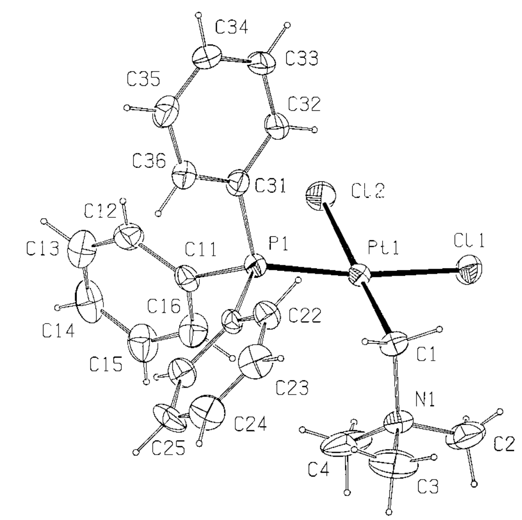


Figure 1. View of **11a** with the numbering scheme. Phenyl ring C atoms are labeled C*i*1−C*i*6 (*i* = 1−3). Thermal ellipsoids are drawn at the 30% probability level.

longer than that in **1a** (1.96(1) Å), reflecting, in part, the difference between Pt−C(sp^3) and Pt−C(sp^2) σ-bonds. Some contribution to the shortening of the Pt−C bond in **1a** relative to that in **11a** may come from dπ→pπ back-bonding in the former. This contribution may be reflected in the relative lengths of the Pt−Cl bonds trans to C in the two complexes (2.347(3) and 2.387(2) Å, respectively), with the shorter bond in **1a** arising from decreased repulsion between chlorine ligand lone pair electrons and Pt d electrons[26] due to Pt→C π donation. All other bond angles and lengths are in the expected ranges.

(b) *cis*(*C,P*)-Chloro[2-(dimethylcarbamoyl)ethyl-*C,O*](triphenylphosphine)platinum(II) (24). A view of the molecule is shown in Figure 2. The X-ray analysis establishes the presence of the chelating $-CH_2CH_2C(O)NMe_2$ ligand and the trans disposition of the phosphine ligand with respect to the coordinated carbonyl oxygen. The coordination about platinum is essentially square planar with some deviation of the in-plane angles from the ideal 90° (O(1)−Pt(1)−C(3) = 81.6(4)° and P(1)−Pt(1)−Cl(1) = 98.98(9)°). The conformation adopted by the chelate ring is best described as an envelope with

(26) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.

Table 4. Summary of Crystal Data, Data Collection, Structure Solution, and Refinement Details

	11a	24	26
	(a) Crystal Data		
formula	$C_{22}H_{26}Cl_2NPPt$	$C_{23}H_{25}ClNOPPt$	$C_{24}H_{31}AsClN_2PPtPF_6·0.82CH_2Cl_2$
molar mass	601.40	592.95	867.58
color, habit	colorless, needle	colorless, plate	colorless, plate
cryst size, mm	0.39 × 0.14 × 0.11	0.41 × 0.15 × 0.01	0.42 × 0.31 × 0.20
cryst syst	orthorhombic	triclinic	triclinic
a, Å	9.8281(16)	7.9253(16)	8.7724(16)
b, Å	27.674(4)	8.9490(19)	10.3240(17)
c, Å	16.750(3)	16.763(8)	18.441(3)
α, deg	90	92.37(2)	76.309(15)
β, deg	90	97.42(3)	84.86(2)
γ, deg	90	111.127(14)	86.967(15)
V, Å^3	4555.8(12)	1094.7(6)	1615.3(5)
space group	$Pbca$	$P\bar{1}$	$P\bar{1}$
Z	8	2	2
F(000)	2336	576	841
d_{calcd}, g cm^{-3}	1.754	1.799	1.784
μ, mm^{-1}	6.472	6.617	5.680
	(b) Data Acquisition[a]		
temp, K	294(1)	294(1)	294(1)
unit cell rflns (θ range), deg	8.8−11.9	5.8−11.9	9.5−17.5
max. θ for rflns, deg	26.93	26.88	25.01
hkl range of rflns	0−12; 0−35; 0−21	−10 to +9; 0−11; −21 to +21	−10 to +10; 0−12; −20 to +21
decay in 3 std rflns	0.5	8.6	12.6
no. of rflns measd	4965	4743	6138
no. of unique rflns	4965	4743	5743
R_{int}			0.018
no. of rflns with $I > 2\sigma(I)$	2491	3374	4137
abs cor type	ψ scans	ψ scans	Gaussian
min, max abs cor	0.3514, 0.4970	0.3609, 0.9167	0.1724, 0.3707
	(c) Structure Solution and Refinement[b]		
refinement on	F^2	F^2	F^2
soln method	Patterson heavy atom	Patterson heavy atom	Patterson heavy atom
H-atom treatment	riding	riding	riding
no. of variables in least squares	247	255	434
weights k^c	$(0.0361P)^2$	$(0.0651P)^2$	$(0.1002P)^2 + 2.8184P$
R, R_w, GOF	0.037, 0.073, 0.90	0.044, 0.104, 1.00	0.061, 0.164, 1.05
density range in final Δ-map, e Å^{-3}	−0.961, 1.151	−2.199, 2.636	−0.766, 1.979
final shift/error ratio	0.002	0.002	0.027

[a] Data collection on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 67 Å). [b] All calculations were done on a Dell Inspiron 3200 laptop computer with the NRCVAX system of programs (Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384−389) for refinement with observed data on F or with SHELXL-97 (G. M. Sheldrick, 1997) for refinement with all data on F^2. [c] $w = 1/(\sigma^2 F_o^2 + k)$; $P = (F_o^2 + 2F_c^2)/3$.

C(3) as the flap. The dihedral angle between the Pt(1)−O(1)−C(1)−C(2) segment and the coordination plane is only 7.64(0.58)°. The framework atoms of the carbamoyl group show no significant deviation from planarity. Bond lengths and all other bond angles are in the expected ranges.

(c) *trans*(*As,CH₂*)-Chloro[(dimethylamino)methylene][(dimethylammonio)methyl](triphenylarsine)platinum(II) Hexafluorophosphate (26). Analysis of the structure of **26** was complicated by disorder in the orientations of the phenyl groups of the arsine ligand, for which two conformations were found, and by the presence of solvent dichloromethane in the crystal lattice. In addition, significant degradation of the crystal took place in the course of data collection (see Table 4). The structure consists of discrete four-coordinate cations and hexafluorophosphate anions. A view of the cation, which depicts only the major conformation found for the arsine ligand, is shown in Figure 3. The coordination sphere of the cation is close to square planar, and the analysis confirms the presence of a protonated (dimethylamino)methyl ligand trans to the arsine. The conformation adopted by the former ligand allows the formation of a hydrogen bond to the neighboring chlorine ligand (N(2)···Cl(1) = 3.064(11) Å, N(2)−H = 0.91 Å, Cl(1)···H = 2.39 Å, N(2)−H···Cl(1) = 130°). The carbene ligand shows negligible deviation from planarity, and the dihedral angle between the carbene plane and the coordination plane (87.79(49)°) is within the range found for other platinum(II) carbene complexes.[7]

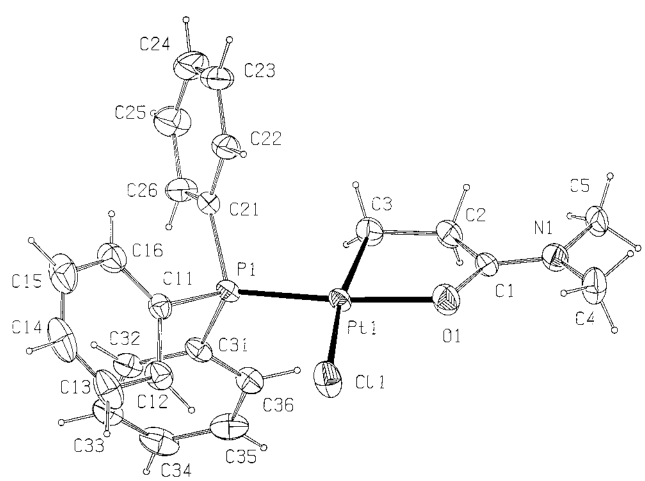


Figure 2. View of **24** with the numbering scheme. Phenyl ring C atoms are labeled C*i*1−C*i*6 (i = 1−3). Thermal ellipsoids are drawn at the 30% probability level.

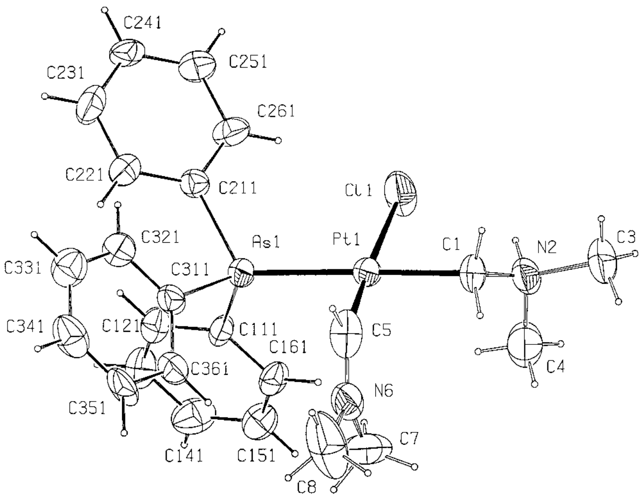
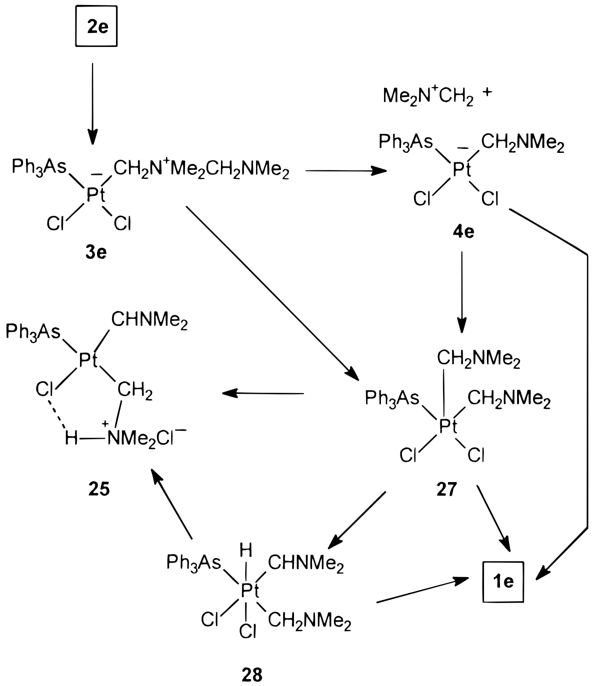


Figure 3. View of the cation of **26** with the numbering scheme. Phenyl ring C atoms are labeled C*i*1−C*i*6 (*i* = 1−3). Thermal ellipsoids are drawn at the 30% probability level. Only the major conformation found for the phenyl groups is shown.

Scheme 3



As expected, the Pt(1)−C(5) (carbene) bond (1.929(16) Å) is shorter than the Pt(1)−C(1) (aminomethyl) bond (2.053(10) Å), although the comparison is complicated by the different trans ligands (Cl and As respectively). The platinum−carbene distance is similar to that found for **1a** (1.96(1) Å),[7] as are the trans Pt−Cl distances (Pt(1)−Cl(1) = 2.366(4) vs 2.347(3) Å in **1a**). The considerable shortening of the C(5)−N(6) bond (1.24(2) Å) compared to C(1)−N(2) (1.489(17) Å) reflects substantial double-bond character in the former, as found also for **1a** (carbene C−N = 1.25(1) Å).

Mechanism of Formation of Carbene Complexes 1. (a) From Cyclic Species 2. Possible mechanisms of formation of **1e** and **25** are outlined in Scheme 3. Formation of simple carbene product **1e** may proceed in a manner similar to that suggested in Scheme 1 for the Ph_3P analogue. Alternatively, reaction of the Mannich cation with anionic species **4e** could involve electrophilic attack at platinum (oxidative addition) to give the platinum(IV) intermediate **27**. Indeed, formation of **27** might proceed via direct 1,3-migration of the $[NMe_2CH_2]^+$ fragment in intermediate **3e** from nitrogen to platinum. This would be more consistent with the observed ineffectiveness of excess diamine in trapping the Mannich cation[27] or even in having a significant retarding effect on the conversion of cyclic intermediate **2a** into carbene complex **1a**. Conversion of **27** into final products, **25** and **1e**, could involve net proton abstraction by one of the two $-CH_2NMe_2$ moieties in **27** from the methylene group of the other and 1,2-elimination of Me_3N, respectively. Formation of carbene derivatives by the latter type of mechanism is well-known for early transition metals.[28]

A preferable alternative mode of decomposition of intermediate **27** would involve an α-H shift to give the Pt(IV) carbene hydride species **28**.[29] Formation of **1e** would then simply require reductive elimination of Me_3N, while **25** would result from elimination of HCl. Analogous modes of reaction have been proposed by others for various Pt(IV) complexes. Thus, decomposition of platina(IV)cyclobutane derivatives can proceed via an initial α-H shift to the metal to give a Pt(IV) carbene hydride species with subsequent reductive elimination involving the hydride.[30] An α-H shift from the CH_2NMe_2 moiety may be particularly favorable, since the resulting carbene species should be relatively stable.[31] Reductive elimination of HCl from Pt(IV) complexes (and the reverse reaction) is well-known[32] and believed often to entail removal (or addition) of H^+ and Cl^- in two separate steps. The observed increase in the amount of **25** formed relative to **1e** with increasing excess of diamine could then be accounted for by an increase in the rate of H^+ abstraction from **28**. It is interesting that no product analogous to **25** has been observed in the reactions involving phosphine ligands. This might be rationalized by considering that intermediates analogous to **28**, but containing a phosphine ligand instead of Ph_3As, should be subject to readier reductive elimination of Me_3N due to the higher trans effect of phosphines relative to arsines.

(b) From (Dimethylammonio)methyl Complex 21. A mechanism similar to that proposed in (a) above can be envisaged for the conversion of **20** into carbene complex **1a**, viz. a 1,3-proton shift from N to Pt to generate a Pt(IV) hydride intermediate,[33] an α-H shift from the resulting CH_2NMe_2 moiety to give a Pt(IV) carbene dihydride, and reductive elimination of H_2 to give **1a**. Alternatively, an α-H shift might precede

(27) The possibility of liberating Mannich cation is indicated by the formation of small amounts of **12**/**13**(?)[13] in the presence of excess diamine, or upon TLC of the cyclic ylide complex **2a**.

(28) Feldman, J.; Schrock, R. R. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1991; Vol. 39, pp 1−74.

(29) Complexes of this type, containing late transition metals in high oxidation states, have been postulated as reactive intermediates in several processes. See: Alias, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *Organometallics* **1998**, *17*, 4124−4126 and references therein.

(30) (a) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149−194. (b) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241−2290.

(31) Cf. formation of $Pt^{IV}CHNMe_2$ complexes by oxidative addition of $[Me_2NCHCl]Cl$ to Pt(II) precursors: Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 1030−1038.

(32) See e.g.: Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966−4968 and references therein.

proton attack at Pt. Some precedent for such a pathway is provided by the reported[34] formation of a Pt(II) alkoxycarbene hydride complex from a Pt^{II}[CH(Me)OEt] precursor.

Experimental Section

Spectral data were acquired as follows: ^{1}H and ^{13}C NMR spectra, Varian UNITY 400 or Gemini 200 ($CDCl_3$ solution, residual proton resonance at δ 7.24 and carbon resonance at δ 77.0 as references); ^{31}P NMR spectra, Varian UNITY 400 ($CDCl_3$ solution unless indicated otherwise, phosphorus resonance of triphenylphosphine in $CDCl_3$ at δ −5.31 as external reference). ^{1}H NMR data required for the discussion and ^{31}P NMR data are collected in Tables 1 and 2, respectively. ^{13}C and additional ^{1}H NMR data are given below. Elemental analyses were determined by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. Preparative-scale thin-layer chromatography (TLC) was performed on Kieselgel G (Merck) using MeOH/CH_2Cl_2 (3:97) as eluting solvent. Reactions were carried out without precautions to exclude air or moisture unless otherwise indicated.

Crystal data and details of data collection, structure solution, and refinement are summarized in Table 4.

Reactions of [(COD)Pt(CH_2Cl)Cl] (5) with PPh_3 and $Me_2NCH_2NMe_2$. (i) NMR-Scale Reactions in $CDCl_3$ (0.75 mL). (a) A solution containing **5** (12.9 mg, 0.033 mmol), PPh_3 (8.1 mg, 0.031 mmol), and $Me_2NCH_2NMe_2$ (4.4 μL, 0.032 mmol) was left at ambient temperature. Monitoring by ^{1}H and ^{31}P NMR spectroscopy showed immediate formation of bis(phosphine) complex **7a** and subsequent formation of cyclic ylide complex **2a** and then the final products carbene complex **1a** and (trimethylammonio)methyl complex **11a**. The concentration of **2a** reached a maximum after about 1 day, and complete conversion to final products required about 10 days.

(b) When this experiment was repeated with heating at 60−65 °C for 3 h, reaction to give **1a** and **11a** was complete but the relative amount of the latter was greater (see (c) for a similar experiment).

(c) Three solutions were made up, each containing **5** (9.7 mg, 0.025 mmol) and PPh_3 (6.6 mg, 0.025 mmol). Two equivalents (7.0 μL) of $Me_2NCH_2NMe_2$ was added to tube 1 and 8 equiv (28.0 μL) to each of tubes 2 and 3. The first two were left at ambient temperature, and the last was heated at 65 °C for 4 h. Complete reaction for tubes 1 and 2 required a time similar (ca. 10 days) to that found in experiment a. After 1 day, when cyclic intermediate **2a** was the major complex present, the ^{31}P NMR spectrum of tube 2 showed, inter alia, a weak signal at δ 8.41 corresponding to a (dimethylamino)methyl complex.[13] After 10 days, tube 1 contained **1a**, **11a**, and **17** (relative peak heights in ^{31}P NMR spectrum 7.7:1.8:1, respectively) and tube 2 contained **1a**, **17**, **16**, and **11a** (6.1:2.6:1:1). Reaction was complete in the heated tube, tube 3, which contained **1a**, **17**, **16**, and **11a** (2.9:1.1:1:1).

(ii) Preparative-Scale Reactions. (a) COD complex **5** (570.4 mg, 1.47 mmol), PPh_3 (385.4 mg, 1.47 mmol), and $Me_2NCH_2NMe_2$ (0.50 mL, 3.6 mmol) were dissolved in $CHCl_3$ (40 mL, freshly distilled from P_2O_5 under nitrogen), and the resulting solution was heated at reflux for 2 h and then left overnight at ambient temperature under nitrogen. Preparative TLC gave two major fractions, the less polar of which contained carbene complex **1a** (536.9 mg, 0.917 mmol, 62.4% yield). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.6 ($^1J_{Pt-C}$ = 1136 Hz), 50.96 ($^3J_{Pt-C}$ = 70 Hz), 48.40 ($^3J_{Pt-C}$ = 70 Hz). The more polar fraction contained (trimethylammonio)methyl complex **11a** (163.2 mg, 0.271 mmol, 18.5% yield). Crystallization of this material from dichloromethane/acetone (1:3) gave colorless needles, one of which was selected for X-ray crystallographic examination.

(b) When similar reactions were carried out in $CHCl_3$ stabilized with 0.75% of EtOH, products **1a** and **11a** were accompanied by a new species, **14** (see below), which is slightly less polar than **11a**.

(c) A solution of COD complex **5** (63.2 mg, 0.163 mmol), PPh_3 (37.2 mg, 0.142 mmol), and $Me_2NCH_2NMe_2$ (28.0 μL, 0.204 mmol) in freshly distilled chloroform (5 mL) was left for 4 h at ambient temperature to allow partial buildup of **2a** and then subjected to preparative TLC. Three fractions were recovered. The most polar (14.6 mg) was essentially pure **2a**: that of intermediate polarity (6.5 mg) also contained essentially a single component which showed δ_P 8.41 ($^1J_{Pt-P}$ = 4144 Hz) and δ_H 4.83 ($^2J_{Pt-H}$ = 56 Hz, $^3J_{P-H}$ = 3.7 Hz, Pt−CH_2) and 2.88 (s, NMe_2), suggesting a structure such as **12** or **13**.[13] The least polar fraction (50.6 mg) consisted of a mixture from which [(COD)$PtCl_2$] (10.3 mg), hydride **15** (14.7 mg), the phosphine dimethylamine complex **19** (4.3 mg), and starting complex **5** (7.6 mg) were recovered by further chromatography. Upon standing in solution in $CDCl_3$, the fraction of intermediate polarity slowly gave carbene complex **1a** (10−15% over 4 days).

(d) COD complex **5** (162.0 mg, 0.417 mmol), PPh_3 (101.0 mg, 0.380 mmol), and $Me_2NCH_2NMe_2$ (70 μL, 0.51 mmol) were dissolved in CH_3CN (20 mL, freshly distilled from CaH_2), and the resulting solution was heated at 60−70 °C for 2.5 h. Preparative TLC gave three major products: most polar, **11a** (42.9 mg); intermediate polarity, **1a** (126.2 mg); least polar, the new compound **24** (26.4 mg after crystallization from dichloromethane/diethyl ether (1:3); crystal suitable for X-ray structure determination). The Pt−CH_2CH_2− moiety shows δ_H (200 MHz) 1.34 (apparent dt, $^2J_{Pt-H}$ = 77 Hz) and 2.57 (apparent t, $^3J_{Pt-H}$ = 52 Hz).

(e) A similar experiment performed in CD_3CN gave the same three products, but **24** now contained the −$CH_2CD_2CONMe_2$ moiety (^{2}D NMR resonance at δ 2.57).

Reaction of Carbene Complex 1a with PPh_3. Addition of PPh_3 (7.5 mg, 0.026 mmol) to a $CDCl_3$ solution of carbene complex **1a** (12.3 mg, 0.021 mmol) gave *trans*-chloro[(dimethylamino)methylene]bis(triphenylphosphine)platinum(II) chloride (**16**), which was obtained as colorless needles (18.9 mg) upon crystallization from dichloromethane/diethyl ether (1:3). A ^{1}H NMR spectrum of the crystalline material indicated the presence of 1−2 equiv of water. Anal. Calcd for $C_{39}H_{37}Cl_2NP_2$-Pt·1.5H_2O: C, 53.55; H, 4.61; N, 1.60. Found: C, 53.44; H, 4.63; N 1.61.

Reaction of Carbene Complex 1a with $(Me_2NH)_2CO_2$. Addition of an excess of the amine adduct to a $CDCl_3$ solution of carbene complex **1a** resulted (^{1}H and ^{31}P NMR spectra) in its rapid, and clean, conversion into the dimethylamine complex **17**. When this solution was evaporated in vacuo and the residue redissolved in $CDCl_3$, the NMR spectra indicated the presence of both **1a** and **17**. Preparative TLC of this mixture gave only **1a**.

Reaction of [(COD)Pt(CH_2Cl)Cl] (5) with PPh_3 and Me_2NCH_2OEt. Me_2NCH_2OEt[35] (4.6 μL, 0.033 mmol; contained ca. 20% of $Me_2NCH_2NMe_2$) was added to a solution of **5** (12.9 mg, 0.033 mmol) and PPh_3 (8.2 mg, 0.031 mmol), in $CDCl_3$. Monitoring by ^{1}H and ^{31}P NMR spectroscopy showed, after the initial generation of bis(phosphine) complex **7a**, growth of signals corresponding to cyclic intermediate **2a** and products **1a**, **11a**, and **14**. After 1 day, relative peak heights in the ^{31}P

(33) Models for this 1,3-proton shift may be provided by the N−H···X−Pt^{II} (X = Cl, Br) and N−H···Pt^{II} species formed from certain organoplatinum−amine complexes in the presence of HX. See: (a) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484−5493. (b) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916−9924.

(34) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848−849.

(35) Heaney, H.; Papageorgiou, G.; Wilkins, R. F. *J. Chem. Soc., Chem. Commun.* **1988**, 1161−1163.

NMR spectrum were 8.7:7.5:2.5:1 for **7a**, **11a** + **14**, **2a**, and **1a**, respectively. After standing for a further 3 days, the solution was heated at 55 °C for 8 h to drive the reaction to completion. At this stage integration of the ^{1}H NMR spectrum indicated that the major products **1a**, **11a**, and **14** were present in a ratio of ca. 3:2:4, respectively. *cis*-Dichloro[((ethoxymethyl)-dimethylammonio)methyl](triphenylphosphine)platinum(II) (**14**; 5.7 mg), was isolated by preparative TLC, as a band of intermediate polarity between **1a** and **11a**, and purified by crystallization from dichloromethane/hexane (1:3). Anal. Calcd for $C_{24}H_{30}Cl_2NOPPt$: C, 44.66; H, 4.68; N, 2.17. Found: C, 44.73; H, 4.74; N 2.10.

Reactions of [(COD)Pt(CH$_2$Cl)Cl] (5) with PPh$_3$ and (Me$_2$NH)$_2$CO$_2$. (i) COD complex **5** (11.9 mg, 0.031 mmol), PPh_3 (8.1 mg, 0.031 mmol), and dimethylammonium dimethylcarbamate (2.3 mg, 0.017 mmol) were dissolved in 0.75 mL of $CDCl_3$. A ^{31}P NMR spectrum, run after 1 h, showed two major peaks assignable to **7a** and **18**: after 1 day, signals ascribable to **1a**, **2a**, and **11a** had appeared. The solution was left until the signal from **18** (and **2a**) had disappeared (a further 9 days), at which stage two further ^{31}P signals, due to hydride complex **15** and *trans*-[(Ph$_3$P)(Me$_2$NH)PtCl$_2$] (**19**), were present. Samples of all four products, **1a**, **11a**, **15**, and **19**, were recovered by preparative TLC.

(ii) The previous reaction was repeated on a larger scale (**5** (45.3 mg), PPh_3 (31.0 mg), and the amine adduct (11.4 mg) in 2 mL of $CDCl_3$). After 5 h, when the solution contained (^{31}P NMR spectrum) mainly the dimethylamine complex **18**, it was added dropwise to hexane (30 mL) in an attempt to precipitate **18**.

A ^{31}P NMR spectrum of the precipitate (23 mg) showed no signal corresponding to **18**, but rather two major signals at δ 15.21 ($^1J_{Pt-P}$ = 4564 Hz) and 6.1 ($^1J_{Pt-P}$ = 3985 Hz). Preparative TLC of this material gave a fraction which contained largely the major component (**20**, δ_P 15.21), while the other main component decomposed on the plates. ^{1}H NMR and ^{31}P NMR spectra of the TLC fraction showed relatively weak signals ascribable to carbene complex **1a** in addition to those of **20** (δ_H 2.63 (6H, d, J = 5.6 Hz, NMe$_2$), 2.70 (2H, m, CH$_2$N), 7.25−7.80 (15H, aromatic H), 8.1 (1H, br, NH)). Spectra run subsequently, over several days, showed a steady increase in the strength of the signals for **1a** relative to those for **20**, with complete conversion requiring more than 1 week at ambient temperature.

The filtrate was evaporated in vacuo to give a white residue (51 mg), the ^{31}P NMR spectrum of which showed a major signal corresponding to **18** and minor signals for bis(phosphine) complex **7a** and hydride **15**. When this solution was allowed to stand at ambient temperature for 3 days, the signal for **18** disappeared and was replaced mainly by signals at δ 14.25 (**21**) and 6.1 ($^1J_{Pt-P}$ = 3985 Hz) (cf. precipitate). Preparative TLC of this mixture gave **21** (19 mg) as the only isolable product, the other major component decomposing on the plate. Crystallization of **21** from dichloromethane/hexane gave an analytical sample (δ_C 92.67 (J_{Pt-C} = 26 Hz, J_{P-C} = 3.2 Hz), 66.88 (J_{Pt-C} = 800 Hz, J_{P-C} = 3.2 Hz), 45.33 (J_{P-C} = 2.4 Hz)). Anal. Calcd for $C_{22}H_{25}ClNOPPt$: C, 45.48; H, 4.34; N, 2.41. Found: C, 45.13; H, 4.40; N, 2.27.

(iii) Two $CDCl_3$ solutions were prepared, each containing **5** (9.7 mg, 0.025 mmol) and PPh_3 (6.6 mg, 0.025 mmol). One (solution A) or two (solution B) equivalents of dimethylamine (as the CO_2 adduct) was added to these solutions. After 3 h at ambient temperature ^{1}H and ^{31}P NMR spectra indicated that chloromethyl dimethylamine complex **18** was the major platinum-containing species present in both solutions. Solution A also contained small amounts of COD complex **5** and bis(phosphine) complex **7a**, while solution B contained no more than traces of these complexes. Excess solid paraformaldehyde (2 mg) was added to each solution, and the mixtures were shaken at intervals and monitored by ^{1}H and ^{31}P NMR spectroscopy over a period of 12 days. After this time solution A showed significant ^{31}P signals corresponding to carbene complex **1a**, *cis*-[(Ph$_3$P)$_2$PtCl$_2$], chelate complex **21**, (dimethylammonio)methyl complex **20**, and hydride **15**. One day after the addition of paraformaldehyde solution B gave strong signals ascribable to cyclic ylide intermediate **2a**, while after 12 days ^{31}P signals corresponding mainly to **1a** and ylide complex **11a** were observed.

(iv) A $CDCl_3$ solution was prepared as for solution B in (iii). After 3 h, when essentially all of the starting platinum complex had been converted into **18**, the solution was evaporated and the residual gum was pumped for 6 h at 0.05 mmHg. The gum was then redissolved in $CDCl_3$. The major species present was **20**, with the main byproducts being cyclic ylide complex **2a** and hydride **15**. Upon standing for 7 days the signals corresponding to **2a** and **20** shrank while those for carbene complex **1a** appeared and grew.

Reactions of [(COD)Pt(CH$_2$Cl)Cl] (5) and Me$_2$NCH$_2$NMe$_2$ with (*p*-FC$_6$H$_4$)$_3$P or (*p*-MeOC$_6$H$_4$)$_3$P. NMR-scale reactions of these two phosphines proceeded very similarly to that described above for PPh_3. Thus, immediately after mixing, signals for the bis(phosphine) complexes **7b**,**c** dominated the ^{31}P NMR spectra. Over the next few hours, resonances due to cyclic intermediates **2b**,**c** appeared, followed by those from the final products, carbene complexes **1b**,**c** and (trimethylammonio)methyl complexes **11b**,**c**, with complete conversion requiring more than 1 week. The intermediates were identified only on the basis of their NMR spectra. The products, **1b**,**c** and **11b**,**c**, were isolated by preparative TLC. For comparison purposes, **5** (0.033 mmol) was reacted with equimolar quantities of $Me_2NCH_2NMe_2$ and each of PPh_3, (*p*-FC$_6$H$_4$)$_3$P, and (*p*-MeOC$_6$H$_4$)$_3$P. After 2 days at room temperature the solutions were heated at 55 °C for 4 h to ensure that the decomposition of cyclic intermediates was complete (^{31}P NMR spectra). Relative peak heights in the ^{31}P NMR spectra at this stage were 2.5:1, 1.7:1, and 4.2:1 for **1a**:**11a**, **1b**:**11b**, and **1c**:**11c**, respectively. Preparative TLC gave **1a** (13.7 mg), **11a** (4.2 mg), **1b** (14.2 mg), **11b** (4.3 mg), **1c** (13.7 mg), and **11c** (1.8 mg). Crystals of *cis*-dichloro[(dimethylamino)methylene][tris(4-methoxyphenyl)phosphine]platinum(II) (**1b**) obtained from dichloromethane/hexane contained (^{1}H NMR) 0.5−1 mol equiv of dichloromethane. Anal. Calcd for $C_{24}H_{28}Cl_2NO_3PPt\cdot0.75CH_2Cl_2$: C, 40.22; H, 4.02; N, 1.89. Found: C, 40.15; H, 4.11; N, 1.87. *cis*-Dichloro[(dimethylamino)methylene][tris(4-fluorophenyl)phosphine]platinum(II) (**1c**), obtained similarly, also contained dichloromethane. Anal. Calcd for $C_{21}H_{19}Cl_2F_3NPPt\cdot0.1CH_2Cl_2$: C, 39.12; H, 2.99; N, 2.16. Found: C, 38.97; H, 3.06; N, 1.97.

Reaction of [(COD)Pt(CH$_2$Cl)Cl] (5) with *trans*-[(Et$_3$P)$_2$-Pt(CH$_2$Cl)Cl] (7d) and Me$_2$NCH$_2$NMe$_2$. No reaction was observed (^{1}H NMR spectra) when a solution of **5** (10.7 mg, 0.028 mmol), **7d** (12.6 mg, 0.024 mmol), and diamine (6.8 μL, 0.050 mmol) was kept at room temperature for 3 days. The solution was then heated to 55 °C. After 1 day, the reaction appeared to be complete and peaks for two major species, **1d** and **11d**, were evident in the ^{1}H NMR spectrum. Preparative TLC gave **1d** (8.2 mg) and **11d** (4.8 mg). Crystallization of **1d** from chloroform gave white needles. Anal. Calcd for $C_9H_{22}Cl_2NPPt$: C, 24.50; H, 5.03; N, 3.17. Found: C, 24.57; H, 5.06; N, 3.04.

Reactions of [(COD)Pt(CH$_2$Cl)Cl] (5) with AsPh$_3$ and Me$_2$NCH$_2$NMe$_2$. (i) When **5** (8.5 mg, 0.022 mmol), $AsPh_3$ (6.7 mg, 0.022 mmol), and diamine (3.1 μL, 0.023 mmol) were dissolved in $CDCl_3$, bis(arsine) complex **7e** was formed rapidly. Upon standing at ambient temperature, resonances for the cyclic species **2e** appeared in the ^{1}H NMR spectrum, with complete conversion requiring about 1 day. Since no further reaction was apparent during the next 2 days, the solution was heated at 55 °C for 6 h, after which time the signals arising from **2e** were replaced by those for carbene complexes **1e** and **25**. Preparative TLC gave **1e** (3.8 mg) and **25** (5.0 mg). Crystallization of the former from dichloromethane/hexane gave *cis*-dichloro[(dimethylamino)methylene](triphenylarsine)-platinum(II) (**1e**). Anal. Calcd for $C_{21}H_{22}AsCl_2NPt$: C, 40.08; H, 3.52; N, 2.23. Found: C, 39.96; H, 3.72; N, 2.14. A solution of **25** in CH_2Cl_2 was shaken with excess KPF_6 in H_2O to give **26**, which was recovered from the organic layer and crystallized from $CHCl_3$/hexane (3/1). This provided crystals suitable for X-ray analysis. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.74 ($^1J_{Pt-C} = 1243$ Hz), 50.79 ($^3J_{Pt-C} = 80$ Hz), 48.55 ($^3J_{Pt-C} = 100$ Hz), 46.89 ($^3J_{Pt-C} = 40$ Hz) and 44.01 ($^1J_{Pt-C} = 791$ Hz).

(ii) When the reaction outlined in (i) was repeated (0.025 mmol scale) but with heating at 55 °C from the outset, complete decomposition of cyclic intermediate **2e** required ca. 10 h. Preparative TLC gave carbene complex **1e** (8.0 mg) and the more polar (trimethylammonio)methyl complex **11e** (6.2 mg) as the major products.

(iii) Reaction i was also repeated (0.033 mmol scale) using C_6D_6 as solvent. As before, essentially complete conversion into **2e** was observed within 24 h, although some of this product deposited as a gum.

(iv) A series of four reactions was carried out in $CDCl_3$ on a 0.025 mmol scale (in **5** and arsine) but using 2, 4, 8, and 16 equiv of diamine, and formation of cyclic product **2e** was monitored. Reaction took place at essentially the same rate in all four samples. After standing for 2 days, to ensure that formation of **2e** was complete, the samples were heated at 60 °C for 6 h to promote its decomposition. Monitoring by ^1H NMR spectroscopy showed the formation of the two carbene complexes **1e** and **25** and indicated that the relative amount of the former decreases with increasing diamine concentration.

(v) Reaction i was carried out on a 0.050 mmol scale, and after 1 day, when formation of **2e** was complete, the solvent was evaporated in vacuo. The resulting gum was triturated with acetone (1.5 mL) to give a solution from which crystalline material began to deposit almost immediately. After standing overnight, the supernatant was removed and the crystals were washed successively with acetone, diethyl ether, and pentane and dried in vacuo. This gave essentially pure *trans*(*C,Cl*)-chloro[(dimethyl((dimethylamino)methyl)ammonio))methyl-*C,N*](triphenylarsine)platinum(II) chloride (21.9 mg). Anal. Calcd for $C_{24}H_{31}AsCl_2N_2Pt$: C, 41.87; H, 4.54; N, 4.07. Found: C, 41.57; H, 4.72; N, 3.85.

Reaction of *trans*-[$(Ph_3As)_2Pt(CH_2Cl)Cl$] with $Me_2NCH_2NMe_2$. The bis(arsine) **7e** was obtained by reaction of **5** (19.4 mg, 0.050 mmol) with Ph_3As (32.3 mg, 0.105 mmol) in CH_2Cl_2. Crystallization from CH_2Cl_2/pentane (1:3) gave feathery crystals of *trans*-bis(triphenylarsine)chloro(chloromethyl)-platinum(II) (**7e**; 43.0 mg). Anal. Calcd for $C_{37}H_{32}As_2Cl_2Pt$: C, 49.79; H, 3.61. Found: C, 49.88; H, 3.74. Monitoring of a $CDCl_3$ solution of **7e** (8.9 mg, 0.010 mmol) and diamine (2.0 μL, 0.014 mmol) by ^1H NMR showed the development of resonances arising from cyclic species **2e**. Complete conversion required 1−2 days.

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Supporting Information Available: Lists of fractional coordinates, calculated hydrogen coordinates, anisotropic thermal parameters, and interatomic distances and angles for **11a**, **24**, and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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