# Amine, Imine, and Aminocarbene Complexes of Platinum(II) †

**Ronald J. Cross** * **and Michael F. Davidson**
*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ*
**Mercè Rocamora**
*Departament de Quimica Inorganica, Facultat de Quimica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*

Solutions of the chloride-bridged binuclear platinum complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ (L = $PMe_2Ph$ or $PBu_3$) readily react with the amines $NH_2Ph$, 4-$NO_2C_6H_4NH_2$, 3-$MeOC_6H_4NH_2$, $NHPh_2$, or $NH_2Me$ to produce *trans*-$[PtCl_2(am)L]$ in the presence or absence of phenylethyne. The imines PhCH=NPh, PhCH=NMe, 2-$MeC_6H_4CH$=NPh, or $Ph_2C$=NH also react with $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ to produce the analogous N-bonded imine complexes, but reactions of the amines $NHEt_2$ or $NH_2Bu^t$ with the binuclear compounds lead to additional platinum-containing compounds resulting from ligand redistribution reactions. The complexes of $NH_2Ph$, 4-$NO_2C_6H_4NH_2$, 3-$MeOC_6H_4NH_2$, and $NHPh_2$ react with phenylethyne over several days at ambient temperature to yield aminocarbene complexes *cis*-$[PtCl_2\{C(NR^1R^2)CH_2Ph\}L]$ ($R^1R^2$ = H, Ph; H, $C_6H_4NO_2$-4; H, $C_6H_4OMe$-3; or $Ph_2$). Treatment of the imine complexes or any of the other amine complexes with PhC≡CH, however, led only to decomposition. 2-Aminophenylethyne reacts rapidly with $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ to produce the cyclic carbene complex *cis*-$[PtCl_2\{\overline{CCH_2C_6H_4NH}\}L]$ in only 1 h, and although the amine-*N* complexes were observed in solution as transients they were not isolated. Treatment of the carbene complexes with tertiary phosphine, L, leads to cationic complexes *trans*-$[PtCl\{C(NR^1R^2)CH_2Ph\}L_2]Cl$. Both the uncharged and cationic aminocarbene compounds are less reactive than their alkoxycarbene analogues, and show no reaction with $Cl^-$ and little tendency towards H/D exchange with $CD_3OD$. Hydrogen-1, $^{13}C$, and $^{31}P$ n.m.r. spectroscopic parameters for the complexes are reported and related to the likely solution conformations.

All of the many known carbene complexes of platinum contain one or two heteroatoms (N, O, or S) attached to the carbene carbon.[1] The most convenient synthetic routes usually involve attack of alcohol, amine, or thiol at co-ordinated ethynes, ethynyls, or isonitriles. The majority of the complexes prepared in this manner are cationic, but a few years ago we described a route to uncharged alkoxycarbene complexes by treating halide-bridged binuclear compounds with ethynes and alcohols,[2,3] equation (1) (L = tertiary phosphine, X = Cl or Br, R = alkyl or aryl).

$$[Pt_2(\mu\text{-}X)_2X_2L_2] + 2\ RC{\equiv}CH + 2\ R'OH \longrightarrow 2\ cis\text{-}[PtX_2\{C(OR')CH_2R\}L] \quad (1)$$

Here we describe attempts to modify this reaction to produce uncharged amino- or imino-carbene complexes of platinum by substituting the R'OH of equation (1) by $R'NH_2$ or R'CH=NH. The properties of the aminocarbene complexes obtained from some of the reactions are compared with those of analogous alkoxycarbene materials.

## Results and Discussion

*Amine and Imine Complexes.*—The most notable difference between the amine and imine systems under examination, and those with alcohols previously examined,[2] is the ready formation of amine or imine complexes of platinum(II). Thus treatment of $CHCl_3$ solutions of $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ (L = $PMe_2Ph$ or $PBu_3$) by a variety of amines (am) in the presence of PhC≡CH led first to the formation of *trans*-$[PtCl_2(am)L]$, detected as the sole product by $^{31}P$ n.m.r. spectroscopy. Several such compounds were isolated as yellow, crystalline solids from these reactions, repeated more conveniently in the absence of the ethyne, equation (2). Table 1 lists their salient n.m.r. and i.r. characteristics. Similar derivatives have been made this way before,[4] but no analogous alcohol complexes were isolated or detected during the studies of alkoxycarbenes,[2] presumably due to the low nucleophile strength of oxygen for platinum(II).

$$[Pt_2(\mu\text{-}Cl)_2Cl_2L_2] + 2\ am \longrightarrow 2\ trans\text{-}[PtCl_2(am)L] \quad (2)$$

Reactions of $[Pt_2(\mu\text{-}Cl_2)Cl_2(PMe_2Ph)_2]$ with am = $NH_2Ph$, 4-$NO_2C_6H_4NH_2$, 3-$MeOC_6H_4NH_2$, $NHPh_2$, or $NH_2Me$ were uncomplicated, but those with $NHEt_2$ or $NH_2Bu^t$ were accompanied by a redistribution of neutral ligands. In both of these cases, *cis*-$[PtCl_2(PMe_2Ph)_2]$ was precipitated, and pure *trans*-$[PtCl_2(am)(PMe_2Ph)]$ could be obtained *via* chromatography of the residues. Part of the mixture decomposed on the column (silica gel), presumably $[PtCl_2(am)_2]$ since none was detected. Independent experiments established that the two complexes *trans*-$[PtCl_2(am)(PMe_2Ph)]$ (am = $NHEt_2$ or $NH_2Bu^t$) did not disproportionate on standing in solution, so the ligand scrambling must have resulted from the initial attack of the amines. The reactions with $NH_2Me$ required care to ensure that only one mole of amine per platinum was used, otherwise bis- or tris-amine complexes were produced by chloride elimination.

The single ν(Pt–Cl) band in the i.r. spectra of the amine complexes confirmed the *trans* geometry. Since the *trans* effect order[5] is $PR_3 > Cl^-$ this isomer would be expected as the kinetic product. The lack of any tendency to isomerise, with or without nucleophilic catalysts,[6] suggests that this is also the thermodynamic product. The formations of the amine complexes have been described as equilibria,[4] and this was apparent with

† *Non-S.I. unit employed:* Torr ≈ 133 Pa.

**Table 1.** Spectroscopic parameters for *trans*-[$PtCl_2$(am)($PMe_2Ph$)]

| | $^{31}$P N.m.r. | | $^{1}$H N.m.r. | | | I.r. | |
|---|---|---|---|---|---|---|---|
| am | δ(P)/p.p.m. | $^{1}J_{PtP}$/Hz | δ($PCH_3$)/p.p.m. | $^{2}J_{PH}$/Hz | $^{3}J_{PtH}$/Hz | ν(PtCl)/$cm^{-1}$ | ν(NH)/$cm^{-1}$ |
| $NH_2Ph$ | −23.1 | 3 673 | 1.76 | 12 | 32 | 338 | 3 285, 3 105 |
| $NH_2C_6H_4OMe$-3 | −23.1 | 3 616 | 1.62 | 12 | 33 | 345 | 3 220, 3 260 |
| $NH_2C_6H_4NO_2$-4 | −22.3 | 3 666 | 1.80 | 12 | 33 | 343 | 3 205, 3 240 |
| $NHPh_2$ | −22.2 | 3 709 | 1.72 | 12 | 36 | 340 | 3 190 |
| $NEt_3$ | −22.0 | 3 417 | 1.75 | 12 | 29 | | |
| $NH_2Bu^t$ | −24.0 | 3 474 | 1.78 | 11 | 30 | 337 | 3 210, 3 245 |
| $NH_2Me$ | −23.8 | 3 431 | 1.78 | 11 | 30 | 328 | 3 245, 3 280 |
| $NHEt_2$ | −23.2 | 3 424 | 1.75 | 11 | 29 | 342 | 3 230 |

**Table 2.** Spectroscopic parameters for *trans*-[$PtCl_2$(im)L]

| | | $^{31}$P N.m.r. | | $^{1}$H N.m.r. | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| L | im | δ(P)/p.p.m. | $^{1}J_{PtP}$/Hz | δ($PCH_3$)/p.p.m. | $^{2}J_{PH}$/Hz | $^{3}J_{PtH}$/Hz | δ(N=CH)/p.p.m. | $^{4}J_{PH}$/Hz | $^{3}J_{PtH}$/Hz |
| $PMe_2Ph$ | PhN=CHPh | −25.5 | 3 531 | 1.75 | 11.7 | 31.3 | 8.71 | 13 | 60 |
| $PMe_2Ph$ | PhN=$CHC_6H_4$Me-2 | −24.9 | 3 552 | 1.70 | 11.7 | 31.3 | 9.0 | 13 | 56 |
| $PMe_2Ph$ | MeN=CHPh | −25.9 | 3 407 | 1.80 | 11.3 | 29.3 | 8.70 | 15 | 64[a] |
| $PMe_2Ph$ | HN=$CPh_2$ | −24.9 | 3 455 | 1.75 | 11.7 | 29.3 | | | *b* |
| $PBu_3$ | PhN=CHPh | −7.8 | 3 459 | | | | 8.71 | 12 | 57 |

[a] δ($NCH_3$) 3.36 p.p.m. ($^{4}J_{PH}$ 2.5, $^{4}J_{HH}$ 1.5 Hz). [b] δ(NH) 9.4 p.p.m. (br).

am = $NHPh_2$, a large excess of the amine being needed to complete reaction (3).

$$[Pt_2(\mu\text{-}Cl)_2Cl_2L_2] + 2\,NHPh_2 \rightleftharpoons 2\,trans\text{-}[PtCl_2(NHPh_2)L] \quad (3)$$

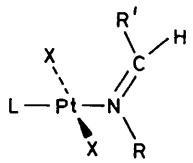
Treatment of the halide-bridged complexes [$Pt_2$(μ-$Cl)_2Cl_2L_2$] by the imines PhCH=NPh, PhCH=NMe, 2-$MeC_6H_4$CH=NPh, or $Ph_2$C=NH led to yellow, crystalline imine (im) complexes [$PtCl_2$(im)L] in analogous manner. The similarity of their appearance and $^{31}$P n.m.r. parameters to those of the amine complexes suggests that these, too, are of *trans* geometry, though in some cases more than one i.r. band was present in the ν(Pt–Cl) region. Spectroscopic parameters are presented in Table 2. Other platinum imine complexes have been synthesised by this method previously.[7]

The proton n.m.r. parameters of these N-substituted imine complexes (**1**) (L = $PMe_2Ph$; R = Ph, R′ = Ph or 2-$MeC_6H_4$; R = Me, R′ = Ph; L = $PBu_3$, R = R′ = Ph) indicate that the organic substituents, R and R′, adopt a *trans* configuration around the double bond. The coupling of the imine hydrogen to $^{31}$P and $^{195}$Pt suggests this arrangement by comparison with related (and sometimes crystallographically characterised) materials.[8] Also, the *ortho* proton(s) of R′ can be identified at δ *ca.* 9.0 p.p.m. This low-field value indicates a close approach to the Pt atom,[7,9] compatible only with the arrangement (**1**).

When deuteriochloroform solutions of the imine complexes *trans*-[$PtCl_2$(im)($PMe_2Ph$)] (im = PhN=CHPh or 2-$MeC_6H_4$CH=NPh) were exposed to the atmosphere for several days, a reversible hydrolysis of the ligand was apparent, equation (4).

$$trans\text{-}[PtCl_2(NPh{=}CHR)(PMe_2Ph)] + H_2O \rightleftharpoons trans\text{-}[PtCl_2(NH_2Ph)(PMe_2Ph)] + RCHO \quad (4)$$

The amine complex produced could be isolated from the reaction mixture, and the aldehydes were detected by n.m.r. spectroscopy. The analogous MeN=CHPh complex hydrolysed to a lesser extent, reaching 40% after 50 d, and no hydrolysis of the HN=$CPh_2$ derivatives was detected at all. We have not established whether the hydrolysis follows ligand release from Pt, or whether it is a reaction of the co-ordinated ligand, though it should be noted that such hydrolyses promoted by $Pd^{II}$ or $Pt^{II}$ have been reported.[10]




(**1**)

The co-ordinated imines are readily replaced by more basic (nucleophilic) imines or amines. Thus PhN=CHPh or PhN=CH(*o*-tolyl) are readily displaced from platinum by MeN=CHPh, $NH_2Ph$, or $NEt_3$.

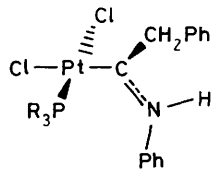
*Aminocarbene Complexes.*—The complex *cis*-[$PtCl_2$\{C(NHPh)$CH_2Ph$\}($PMe_2Ph$)] was isolated in 30% yield as a colourless insoluble solid from mixtures of [$Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2$], $NH_2Ph$, and PhC≡CH in chloroform after 7 d at room temperature. As observed, the first product is the amine complex, and treatment of this with phenylacetylene also led to the carbene complex, equation (5). *cis*-[$PtCl_2$\{C($NHC_6H_4NO_2$-4)$CH_2Ph$\}-

$$trans\text{-}[PtCl_2(NH_2Ph)(PMe_2Ph)] + PhC{\equiv}CH \longrightarrow cis\text{-}[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)] \quad (5)$$

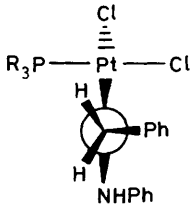
($PMe_2Ph$)], *cis*-[$PtCl_2$\{C($NHC_6H_4OMe$-3)$CH_2Ph$\}($PMe_2$-Ph)], and *cis*-[$PtCl_2$\{C($NPh_2$)$CH_2Ph$\}($PMe_2Ph$)] were similarly obtained from the other relevant amine complexes, and use of [$Pt_2(\mu\text{-}Br)_2Br_2(PMe_2Ph)_2$] or [$Pt_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2$], respectively, with $NH_2Ph$ and PhC≡CH produced *cis*-[$PtBr_2$\{C(NHPh)$CH_2Ph$\}($PMe_2Ph$)] or *cis*-[$PtCl_2$\{C-(NHPh)$CH_2Ph$\} ($PBu_3$)]. Complexes of the more basic amines $NHEt_2$, $NH_2Bu^t$, and $NH_2Me$, on the other hand, failed to

**Table 3.** Spectroscopic data for aminocarbene compounds *cis*-$[PtCl_2\{C(NR^1R^2)CH_2Ph\}L]$

| | | | | | $^1$H N.m.r. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | I.r./cm$^{-1}$ | | | $CH_2Ph$ | | | $PCH_3$ | | |
| $NR^1R^2$ | L | ν(PtCl) | ν(NH) | Solvent | δ/p.p.m. | $^2J_{HH}$/Hz | $^3J_{PtH}$/Hz | δ/p.p.m. | $^2J_{PH}$/Hz | $^3J_{PtH}$/Hz |
| NHPh | $PMe_2Ph$ | 305 | 3 170 | $CDCl_3$– | 4.55 | 14.8 | 0 | 1.25 | 11.5 | 44.6 |
| | | 280 | 3 130 | $CD_3OD$ | 4.29 | | 37 | 1.16 | 11.6 | 46.4 |
| $NHC_6H_4NO_2$-4 | $PMe_2Ph$ | 305 | 3 145 | $CD_3OD$ | 4.60 | 14.0 | 0 | 1.31 | 11.3 | 42.0 |
| | | 280 | | | 4.31 | | 44 | 0.95 | 11.2 | 49.6 |
| $NHC_6H_4OMe$-3 | $PMe_2Ph$ | 305 | 3 180 | $CD_3OD$ | 4.54 | 14.0 | 0 | 1.19 | 11.7 | 45.7 |
| | | 280 | 3 130 | | 4.25 | | 44 | 0.99 | 11.5 | 48.9 |
| $NPh_2$ | $PMe_2Ph$ | 307 | | $CDCl_3$ | 4.57 | 14.7 | 0 | 1.28 | 11.6 | 44.8 |
| | | 283 | | | 4.01 | | 47 | 1.26 | 11.6 | 48.0 |
| NHPh | $PBu_3$ | 305 | 3 180 | $CDCl_3$ | 4.84 | 18.2 | 0 | | | |
| | | 280 | 3 130 | | 4.29 | | 36 | | | |




(2)




(3)

produce carbene complexes, as did the imine complex *trans*-$[PtCl_2(HN{=}CPh_2)(PMe_2Ph)]$: reactions with PhC≡CH took place, but were accompanied by decomposition. The reactions between MeC≡CH and *trans*-$[PtCl_2(NH_2Ph)L]$ likewise failed to yield any carbene complex. The failures may well be the result of low stability of the desired products. It is known that formation of cationic aminocarbene complexes from aminolysis reactions of alkoxycarbene derivatives with $NHEt_2$, $NHPr_2$, or $NH_2Bu^t$ led to decomposition.[11]

A striking property of the aminocarbene complexes formed is their low solubility in common organic solvents. Only the tributylphosphine complex *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ was soluble enough in $CDCl_3$ to allow convenient recording of its n.m.r. spectra. Interestingly, all the complexes appeared to have an enhanced solubility in methanol, so n.m.r. spectra for the others could be obtained in $CD_3OD$ or $CD_3OD$–$CDCl_3$ mixtures;* parameters are listed in Table 3. Most of the spectroscopic features resemble those of related alkoxycarbene compounds.[2,3] Noticeable is the AB quartet of the benzyl $CH_2$ protons ($^2J_{HH}$ *ca.* 14 Hz), with only one of these protons showing appreciable coupling to $^{195}$Pt ($J_{PtH}$ *ca.* 40 Hz). The methyl groups of the $PMe_2Ph$ ligands are also non-equivalent.

The amino proton of the more soluble $PBu_3$ complex is discernible at δ 10.1 p.p.m., indicative of considerable deshielding. The magnitude of its $^3J_{PtH}$ (120 Hz) suggests a *trans* arrangement of the proton and platinum about the C···N partial double bond.[12] The enhanced solubility of *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ in $CDCl_3$–$CD_3OD$ mixtures allowed its $^{13}$C n.m.r. spectrum to be recorded. This revealed the characteristic downfield signal for the carbene carbon at δ(C) 218 p.p.m. ($^2J_{PC}$ 5 Hz), but its $^{195}$Pt satellites were too weak to be detected. The benzyl $CH_2$ signal was at δ 56.4 p.p.m. ($^2J_{PC}$ 60 Hz). Comparisons of all these data with n.m.r. and structural parameters for other carbene complexes suggest that the plane of the carbene ligands lies perpendicular to the platinum(II) square plane to minimise steric interactions, as in structure (**2**), and that the likely arrangement about the benzyl $CH_2$ carbon atom is that shown in structure (**3**).

Reactions of these uncharged aminocarbene complexes show some interesting differences to those of related alkoxycarbene compounds. Treatment of the former with $CD_3OD$ (or even $D_2O$) caused no H–D exchange at the benzyl $CH_2$ group, and no alkoxy carbenes were formed (exchange of NH for ND was, however, apparent). The implications are that the benzyl $CH_2$ protons are less acidic than those of the alkoxycarbene compounds, and that the aminocarbene complexes are more stable than their alkoxycarbene analogues (aminolysis of alkoxycarbene complexes does proceed readily).

Halide ions, $X^-$, are known to react readily with the alkoxycarbene complexes *cis*-$[PtCl_2\{C(OR)R'\}L]$, eliminating RX and producing acyl derivatives.[3] In the present work, treatment of *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ with $[NEt_4]Cl$ markedly increased the solubility of the complex in $CH_2Cl_2$, but the unchanged carbene compound could be recovered quantitatively from the solution. *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ behaved similarly. Hydrogen-1 and $^{31}$P n.m.r. investigation of the chloride-containing solutions revealed minor changes in parameters, but only the single, unchanged carbene complex in solution. Presumably the halide co-ordinates weakly and reversibly to either Pt or the carbene, and behaves in a similar manner to methanol.

Treatment of *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ by $PMe_2Ph$ released $Cl^-$ and produced a new cationic complex, equation (6). Clearly, the cationic aminocarbene compounds

$$cis\text{-}[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)] \xrightarrow{PMe_2Ph} trans\text{-}[PtCl\{C(NHPh)CH_2Ph\}(PMe_2Ph)_2]Cl \quad (6)$$

are also unreactive towards halide (unlike their alkoxy analogues).[3] Hydrogen-1 n.m.r. spectroscopy indicates hindered rotation about the Pt–C bond, as evidenced by the inequivalent phosphine methyl groups. Repeated attempts to crystallise this cationic complex failed, but treatment with $AgClO_4$ allowed ready crystallisation of the perchlorate salt. Treatment with $AgSO_3CF_3$ likewise produced the triflate salt, which curiously revealed apparent equivalence of the phosphine methyl groups, presumably due to chance isochrony of the resonances.

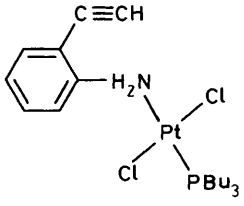
*Cyclic Aminocarbene Complexes.*—The reaction between $[Pt_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$ and 2-$H_2NC_6H_4C{\equiv}CH$ was followed by $^{31}$P n.m.r. spectroscopy in $CDCl_3$ at −50 °C. An immediate reaction took place to produce a new material with δ(P) −4.51 p.p.m. and $^1J_{PtP}$ 3 500 Hz. Comparison with the amine

* The amount of $CD_3OD$ affects the $^1$H n.m.r. parameters: *cf.* references 2 and 12.

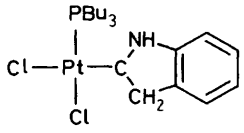
**Table 4.** Physical and analytical data* (%) for *trans*-$[PtCl_2L'(PMe_2Ph)]$ (L' = am or im)

| L' | M.p./°C | C | H | N |
|---|---|---|---|---|
| $NH_2Ph$ | 182—184 | 33.8 (33.8) | 3.4 (3.65) | 2.8 (2.8) |
| $NH_2C_6H_4OMe$-3 | 162—164 | 34.0 (34.2) | 3.9 (3.8) | 2.3 (2.7) |
| $NH_2C_6H_4NO_2$-4 | 183—185 | 31.1 (31.0) | 3.2 (3.2) | 4.9 (4.2) |
| $NHPh_2$ | 125—126 | 41.6 (41.9) | 3.7 (3.9) | 2.1 (2.4) |
| $NH_2Bu^t$ | 137—138 | 30.4 (30.2) | 4.75 (4.65) | 2.9 (2.9) |
| $NH_2Me$ | 125—131 (decomp.) | 24.8 (24.8) | 3.5 (3.7) | 3.2 (3.2) |
| $NHEt_2$ | 90—91 | 30.1 (30.2) | 4.7 (4.65) | 2.9 (2.9) |
| PhN=CHPh | 153—155 | 42.8 (43.1) | 3.5 (3.8) | 2.1 (2.4) |
| MeN=CHPh | 124 | 36.7 (36.7) | 3.6 (3.85) | |
| $PhN{=}CHC_6H_4Me$-2 | 152—153 | 44.2 (44.1) | 3.9 (4.0) | 2.5 (3.3) |
| $HN{=}CPh_2$ | 157—158 | 43.0 (43.1) | 3.3 (3.8) | 2.2 (2.4) |

* Theoretical values given in parentheses.




(4)




(5)

complexes already described suggests this to be the amine complex (**4**). At ambient temperature, however, this compound changed in about 1 h to a new material with δ(P) 2.24 p.p.m. and $^1J_{PtP}$ 3 792 Hz, assigned to the cyclic aminocarbene complex, (**5**). This complex is of low solubility, and is readily isolated as a white, crystalline material. The less soluble dimethylphenylphosphine analogue can be made in similar fashion from $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$ and 2-$H_2NC_6H_4C{\equiv}CH$.

A carbon-13 n.m.r. spectroscopic study of the tributylphosphine complex reveals its carbene carbon resonance at δ 208.7 p.p.m., $^2J_{PC}$ 7 Hz, and its α (benzylic) carbon at δ 54.3 p.p.m., $^2J_{Pt\text{-}C}$ 90.6 Hz. The benzyl $CH_2$ protons are a singlet at δ 4.1 p.p.m., rather than an AB quartet, the change presumably resulting from the geometric restrictions of the cyclic group.

The short formation times for these cyclic complexes, compared to the acyclic carbene complexes, is presumably a result of the chelate effect, since the similarly slow reaction times of 3-$MeOC_6H_4NH_2$ and 4-$NO_2C_6H_4NH_2$ suggest that the process is insensitive to electronic effects of ring substituents. We are unable to say whether the reactions proceed by complete displacement of the co-ordinated $NH_2$ by the ethyne [which would give an isomer of (**4**) which would still be amenable to neighbouring group assistance] or whether it results directly from formation of a pseudo-five-co-ordinate intermediate by ring closure.

*Deprotonation Reactions.*—It was hoped that deprotonation of the aminocarbene complexes might lead to iminoacyl compounds, to enable an investigation of the insertion/elimination behaviour of isocyanide ligands to be made.[13] In addition, deprotonation of the imine complexes described earlier might conceivably lead to the same species after a shift of the co-ordination site, and could thus enable the relationship between these species to be investigated.

Treatment of *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ with $NEt_3$ in MeOH precipitated $[NHEt_3]Cl$, but $^{31}P$ n.m.r. investigation of the platinum-containing residue indicated extensive decomposition leading to many products. Use of NaOEt in ethanol in place of the triethylamine produced a similar range of products, as did $[NBu_4]OH$ in $CH_2Cl_2$. The intractable array of products could have arisen as a result of the bases attacking several sites (metal, carbene carbon, or either of the atoms in the α positions). In an attempt to limit the number of attack sites, the platinum complex was treated with 1,8-bis(dimethylamino)naphthalene ('proton sponge'), known to be a strong base but a poor nucleophile. No reaction took place, however, over 6 d in chloroform.

Treatment of the imine complex *trans*-$[PtCl_2(PhN{=}CHPh)(PMe_2Ph)]$ by bases was equally disappointing. Use of the nitrogen bases $NH_2Ph$ or $NEt_3$ led only to replacement of the imine and formation of the analogous amine complexes (Table 1). Treatment of *trans*-$[PtCl_2(MeN{=}CHPh)(PMe_2Ph)]$ by NaOEt in ethanol, or by proton sponge in chloroform, on the other hand, led to no reaction at all. Thus the indications are that the imine proton is relatively unreactive towards bases, and interconversion of the imine and aminocarbene complexes cannot readily be achieved.

## Experimental

The compounds $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$,[14] $[Pt_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$,[15] and PhN=CHPh[16] were made by literature methods. MeN=CHPh[7] was prepared from $NH_2Me$ and PhCHO in similar manner to PhN=CHPh; $Ph_2C{=}NH$ was purchased from Aldrich Chemical Company. 2-$H_2NC_6H_4C{\equiv}CH$ was prepared from 2-$O_2NC_6H_4CHCHCO_2H$ by literature methods.[17] Amines were distilled prior to use. N.m.r. spectra were recorded on Perkin-Elmer R32 ($^1H$, continuous wave at 90 MHz), or Varian XL100 or Bruker WP200SY ($^1H$, $^{13}C$, $^{31}P$, operating in the Fourier-transform modes) instruments. Hydrogen-1 and $^{31}P$ chemical shifts are relative to $SiMe_4$ and $H_3PO_4$ respectively, those to high field being positive. I.r. spectra were recorded as KBr discs on Perkin-Elmer 530 or 892 instruments.

2-*Methylbenzylideneaniline.*—2-Methylbenzaldehyde (6.42 g, 53.3 mmol) and aniline (4.98 g, 53.6 mmol) were vigorously stirred together, and a viscous, cloudy solution formed in 15 s. This was poured into EtOH–$H_2O$ (9:1, 10 $cm^3$) and stood to form two layers. The denser, brown layer was separated and vacuum distilled (116—122 °C/0.4 Torr) to give the *product* (9.85 g, 60%) as a colourless liquid (Found: C, 85.5; H, 6.9; N, 7.5. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%). $^1H$ N.m.r. (in $CDCl_3$): δ(CH) (imine) 8.61, δ($CH_3$) 2.46 p.p.m.

trans-*Dichloro(dimethylphenylphosphine)(phenylamine)platinum*(II).—To a solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$ (0.52 g, 0.64 mmol) in $CHCl_3$ (50 $cm^3$) under $N_2$ was added $NH_2Ph$ (4 ml). The orange solution changed to yellow-green immediately. The solvent was removed under reduced pressure and the resulting brown oil crystallised from benzene–pentane to afford

**Table 5.** Physical and analytical data[a] (%) for aminocarbene compounds *cis*-$[PtX_2\{C(NR^1R^2)CH_2Ph\}L]$

| X | $NR^1R^2$ | L | M.p./°C | C | H | N |
|---|---|---|---|---|---|---|
| Cl | NHPh | $PMe_2Ph$ | 243—245 | 44.2 (44.1) | 3.6 (3.6) | 1.9 (2.3)[b] |
| Cl | $NHC_6H_4NO_2$-4 | $PMe_2Ph$ | 227—229 | 41.0 (41.0) | 3.6 (3.6) | 4.3 (4.35) |
| Cl | $NHC_6H_4OMe$-3 | $PMe_2Ph$ | 231 | 43.9 (43.9) | 4.1 (4.2) | 1.7 (2.2) |
| Cl | $NPh_2$ | $PMe_2Ph$ | >205 (decomp.) | 49.9 (49.8) | 3.8 (4.2) | 1.7 (1.6) |
| Br | NHPh | $PMe_2Ph$ | >207 (decomp.) | 38.4 (38.2) | 3.6 (3.5) | 1.9 (2.1)[c] |
| Cl | NHPh | $PBu_3$ | 209—212 | 47.3 (47.1) | 6.1 (6.1) | 2.2 (2.1) |

[a] Theoretical values in parentheses. [b] Cl, 12.1 (11.8); P, 5.6 (5.2)%. [c] Br, 22.8 (23.2)%.

yellow crystals of *product* (545 mg, 85%). Analytical data are in Table 4.

Similarly prepared were *trans*-$[PtCl_2(NH_2C_6H_4OMe$-3)$(PMe_2Ph)]$, *trans*-$[PtCl_2(NH_2C_6H_4NO_2$-4)$(PMe_2Ph)]$, *trans*-$[PtCl_2(NH_2Me)(PMe_2Ph)]$ (using a 33% solution of $NH_2Me$ in 'industrial spirit'), *trans*-$[PtCl_2(NHPh_2)(PMe_2Ph)]$ (using an excess of $NHPh_2$ to prevent precipitation of the starting material), *trans*-$[PtCl_2(PhN{=}CHPh)(PMe_2Ph)]$, *trans*-$[PtCl_2$-$(MeN{=}CHPh)(PMe_2Ph)]$, *trans*-$[PtCl_2(PhN{=}CHC_6H_4Me$-2)-$(PMe_2Ph)]$, and *trans*-$[PtCl_2(HN{=}CPh_2)(PMe_2Ph)]$. Data are given in Table 4.

trans-*Dichloro(diethylamine)(dimethylphenylphosphine)platinum*(II).—To a solution of $[Pt_2(\mu$-$Cl)_2Cl_2(PMe_2Ph)_2]$ (1.0 g, 1.24 mmol) in $CHCl_3$ (25 $cm^3$) was added $NHEt_2$ (135 mg, 2.53 mmol). The colour of the solution changed to yellow-green, and solvent was removed after 30 min. Crystallisation of the resultant yellow oil from MeOH–$CH_2Cl_2$ produced white crystals of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (379 mg), identified by comparison of its i.r. and n.m.r. spectra with those of authentic samples. Removal of solvent and redissolution in benzene precipitated more *cis*-$[PtCl_2(PMe_2Ph)_2]$ (67 mg). The benzene solution was then chromatographed on silica gel, leaving a brown band on the column. A yellow eluate afforded *trans*-$[PtCl_2(NHEt_2)(PMe_2Ph)]$ (298 mg, 25%), recrystallised from $Et_2O$–pentane. Analytical data are in Table 4.

Similarly prepared was *trans*-$[PtCl_2(NH_2Bu^t)(PMe_2Ph)]$.

cis-[(*Benzyl*)(*phenylamino*)*carbene*]*dichloro*(*dimethylphenylphosphine*)*platinum*(II).—To a solution of $[Pt_2(\mu$-$Cl)_2Cl_2(PMe_2Ph)_2]$ (1 g, 1.24 mmol) in $CHCl_3$ (100 $cm^3$) under $N_2$ was added $NH_2Ph$ (255 mg, 2.74 mmol) and PhC≡CH (793 mg, 7.8 mmol). The solution was stirred for 7 d at ambient temperatures, during which time it turned brown and precipitated crude *product*, which was isolated by filtration (400 mg, 27%). This was recrystallised from methanol; analytical data are given in Table 5. Removal of solvent from the mother-liquors and dissolution in benzene afforded a small amount of *cis*-$[PtCl_2(PMe_2Ph)_2]$, as a precipitate, before crystals of *trans*-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ were obtained.

Similarly were obtained *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}$-$(PBu_3)]$, *cis*-$[PtCl_2\{C(NHC_6H_4NO_2$-4$)CH_2Ph\}(PMe_2Ph)]$, *cis*-$[PtCl_2\{C(NHC_6H_4OMe$-3$)CH_2Ph\}(PMe_2Ph)]$, *cis*-$[PtCl_2\{C(NPh_2)CH_2Ph\}(PMe_2Ph)]$, and *cis*-$[PtBr_2\{C(NHPh)$-$CH_2Ph\}(PMe_2Ph)]$ {from $[Pt_2(\mu$-$Br)_2Br_2(PMe_2Ph)_2]$}. Analytical data are given in Table 5.

*cis*-$[PtCl_2(\overline{CCH_2C_6H_4NH}$-2$)(PMe_2Ph)]$.—To a solution of $[Pt_2(\mu$-$Cl)_2Cl_2(PMe_2Ph)_2]$ (0.395 g, 0.49 mmol) in $CHCl_3$ (25 $cm^3$) was added 2-$H_2NC_6H_4C{\equiv}CH$ (0.115 g, 0.98 mmol). The colour changed from orange to yellow-green, then back to orange whilst stirring at room temperature was maintained for 1 h. Removal of the solvent and recrystallisation from $CH_2Cl_2$–pentane produced white crystals of the *product* (0.301 g, 60%) (Found: C, 36.6; H, 3.0; N, 2.75. $C_{16}H_{18}Cl_2NPPt$ requires C, 36.9; H, 3.5; N, 2.7%).

Similarly prepared was *cis*-$[PtCl_2(\overline{CCH_2C_6H_4NH}$-2$)$-$(PBu_3)]$ (21%) (Found: C, 40.8; H, 5.45; N, 2.4. $C_{20}H_{34}Cl_2NPPt$ requires C, 41.1; H, 5.9; N, 2.4%).

trans-[(*Benzyl*)(*phenylamino*)*carbene*]*chlorobis*(*dimethylphenylphosphine*)*platinum*(II) *Perchlorate*.—To a suspension of *cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ (211 mg, 0.35 mmol) in $CH_2Cl_2$ (15 $cm^3$) was added $PMe_2Ph$ (50.2 μl, 0.35 mmol) followed immediately by $AgClO_4{\cdot}H_2O$ (95.5 mg, 0.42 mmol). The mixture was protected from light whilst stirred at room temperature for 2 h. AgCl was removed by filtration and the solution was dried over anhydrous $MgSO_4$ prior to removing the solvent by evaporation. Crystallisation from $CHCl_3$–MeOH produced colourless crystals of *trans*-$[PtCl\{C(NHPh)CH_2$-$Ph\}(PMe_2Ph)_2]ClO_4$ (154 mg, 46%), m.p. 200—202 °C (Found: C, 44.8; H, 4.5; N, 1.45. $C_{30}H_{37}Cl_2NO_4P_2Pt$ requires C, 44.95; H, 4.4; N, 1.75%). I.r.: ν(PtCl), 310; ν(NH), 3 250 and 3 200 $cm^{-1}$. $^{31}P$ N.m.r.: δ −10.8 p.p.m. ($J_{PtP}$ 2 489 Hz). $^1H$ N.m.r. (in $CDCl_3$): δ($CH_2$) 3.98 ($^3J_{PtH}$ 40), δ($PCH_3$) 1.57, 1.56 ($^2J_{PH}$ 7.0, 7.0; $^3J_{PtH}$ 29, 31 Hz).

In similar experiments performed in the absence of $AgClO_4$, *trans*-$[PtCl\{C(NHPh)CH_2Ph\}(PMe_2Ph)_2]Cl$ was produced in $CDCl_3$ or $CH_2Cl_2$ solution. The compound remained unchanged over 6 d, but could not be crystallised.

*Reaction of cis*-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ *with Bases*.—To a suspension of the complex (191 mg) in MeOH (20 $cm^3$) was added $NEt_3$ (21.2 mg). The suspension was stirred at room temperature for 27 h, then solvent was removed. Phosphorus-31 n.m.r. spectroscopic examination of the residue indicated the presence of many products, none of which was identified or isolated.

Similar reactions were performed with $[NBu_4]OH$ in $CH_2Cl_2$ and with NaOEt in EtOH, and in these cases also, $^{31}P$ n.m.r. investigation revealed the presence of many compounds.

*Reaction of trans*-$[PtCl_2(PhN{=}CHPh)(PMe_2Ph)]$ *with Amines*.—To a solution of the imine complex (20 mg) in $CDCl_3$ was added one equivalent of $NEt_3$. Phosphorus-31 and $^1H$ n.m.r. spectroscopic investigation indicated the presence in solution of unco-ordinated PhN=CHPh and *trans*-$[PtCl_2(NEt_3)(PMe_2$-$Ph)]$ (identical to a sample prepared from $[Pt_2(\mu$-$Cl)_2Cl_2(PMe_2$-$Ph)_2]$ and $NEt_3$; parameters are given in Table 1). In a similar experiment, co-ordinated PhN=CHPh was displaced by aniline.

## Acknowledgements

We thank Johnson-Matthey for a loan of platinum salts, the S.E.R.C. for a maintenance award (to M. F. D.), and the Ministerio de Educacion y Ciencia, Spain, for a scholarship (to M. R.).

## References


1 F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, 1972, **16**, 487; D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

2 G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1979, 684.

3 G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1979, 690.

4 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 3858; 1957, 2445; H. van der Poel, G. van Koten, D. M. Grove, P. S. Pregosin, and K. A. D. Starzewski, *Helv. Chim. Acta*, 1981, **64**, 1174.

5 F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163.

6 G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185.

7 J. F. van Baar, K. Vrieze, and D. J. Stufkens, *J. Organomet. Chem.*, 1974, **81**, 247.

8 D. Hottentot and C. H. Stam, *Cryst. Struct. Commun.*, 1975, **4**, 421; H. van der Poel, G. van Koten, M. Kokkes, and C. H. Stam, *Inorg. Chem.*, 1981, **20**, 2941; M. R. P. van Vliet, G. van Koten, J. A. M. van Beck, K. Vrieze, F. Muller, and C. H. Stam, *Inorg. Chim. Acta*, 1986, **112**, 77.

9 H. van der Poel, G. van Koten, and K. Vrieze, *Inorg. Chem.*, 1980, **19**, 1145.

10 I. Jardine and F. J. McQuillin, *Tetrahedron Lett.*, 1972, 459.

11 M. H. Chisholm, H. C. Clark, W. S. Johns, J. E. H. Ward, and K. Yasufuku, *Inorg. Chem.*, 1975, **14**, 900.

12 B. Crociani and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 693.

13 G. K. Anderson and R. J. Cross, *Acc. Chem. Res.*, 1984, **17**, 87.

14 A. C. Smithies, P. Schmidt, and M. Orchin, *Inorg. Synth.*, 1970, **12**, 240.

15 G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, 1963, **2**, 246; J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 2787.

16 L. A. Bigelow and H. Eatough, *Org. Synth.*, Coll. vol. 1, 2nd edn., 1967, 80.

17 K. Schofield and J. C. E. Simpson, *J. Chem. Soc.*, 1945, 512; K. Schofield and T. Swain, *ibid.*, 1949, 2393.


*Received* 4*th June* 1987; *Paper* 7/978