Reactions of Isocyanide Complexes of Palladium(II) and Platinum(II) with Azetidine: Synthesis of Acyclic Diaminocarbene Derivatives and *X*-Ray Structure of $[PdCl(PMe_2Ph)(CH_2CH_2CH_2NH)\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}]Cl\cdot CH_2Cl_2$†

Roberta Bertani and Mirto Mozzon
Centro di Chimica Metallorganica degli Elementi di Transizione, C.N.R., Via F. Marzolo 9, 35131 Padova, Italy
Franco Benetollo
Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R. Corso Stati Uniti, 4, 35020 Padova, Italy
Gabriella Bombieri
Istituto di Chimica Farmaceutica e Tossicologia, Universita' di Milano, Viale Abruzzi, 42, 20131 Milano, Italy
Rino A. Michelin*
Istituto di Chimica Industriale, Facolta' di Ingegneria, Universita' di Padova, Via F. Marzolo, 9, 35131 Padova, Italy

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Azetidine reacts in tetrahydrofuran (thf) at room temperature or below with the co-ordinated RNC ligand in each of the neutral *cis*-$[MCl_2(PPh_3)(CNR)]$ [M = Pd or Pt; R = C_6H_4OMe-*p* or Bu^t) and cationic *trans*-$[MCl(PPh_3)_2(CNC_6H_4OMe\text{-}p)]BF_4$ (M = Pd or Pt) complexes to form the corresponding derivatives containing the acyclic diaminocarbene moiety $M{-}C(NCH_2CH_2CH_2)NHR$. Azetidine reacts also with the bis(isocyanide) complexes *cis*-$[PdCl_2(CNR)_2]$ (R = Bu^t or C_6H_4OMe-*p*) converting one (R = Bu^t) or two (R = C_6H_4OMe-*p*) isocyanide ligands into acyclic carbenes. The isocyanide complexes *cis*-$[MCl_2(PMe_2Ph)(CNC_6H_4OMe\text{-}p)]$ (M = Pd or Pt) react in thf with 2 equivalents of azetidine to afford the cationic acyclic diaminocarbene complexes $[MCl(PMe_2Ph)(CH_2CH_2CH_2NH)\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}]Cl$ containing a metal-co-ordinated azetidine ligand. In contrast to the reactions of the three-membered heterocycle aziridine with isocyanide ligands which lead to five-membered cyclic carbenes, the corresponding reactions of azetidine give no evidence of six-membered diaminocarbenes. The carbene complexes have been characterized by their elemental analyses, i.r., ^1H, and ^{31}P n.m.r. spectra and in a few cases by their ^{13}C n.m.r. and mass spectra. The structure of $[PdCl(PMe_2Ph)(CH_2CH_2CH_2NH)\{C(NCH_2CH_2CH_2)NH\text{-}C_6H_4OMe\text{-}p\}]Cl\cdot CH_2Cl_2$ was determined by *X*-ray diffraction: space group $P2_1/n$, $a = 24.849(4)$, $b = 10.174(2)$, $c = 11.895(2)$ Å, $\beta = 91.85(3)°$, $R = 0.054$ ($R' = 0.059$) for 3 734 observed reflections. The geometry around Pd is a distorted square with the diaminocarbene ligand *trans* to chloride. The Pd–C(sp^2) distance is 1.990(6) Å and the bond lengths within the carbenoid system indicate extensive electronic delocalization.

Electrophilic isocyanide ligands in certain transition-metal complexes can be converted into cyclic carbenes by different synthetic procedures.[1–4] Recently we reported that the highly strained three-membered heterocycles YCH_2CH_2 (Y = NH, S, or O) undergo spontaneous (Y = NH or S) or Cl^--catalyzed (Y = O) ring opening upon attack on Pt^{II}- and Pd^{II}-co-ordinated isocyanide ligands to afford five-membered cyclic diamino-, aminothio-, and amino-oxocarbenes.[5] The reactions have been shown to be influenced either by the nucleophilicity of the entering heterocycle or both the nature of the isocyanide and the metal centre. Aziridine proved to be the most reactive among the three-membered heterocycles investigated.

Closely related to this class of organic nucleophiles, the four-membered ring of azetidine $HNCH_2CH_2CH_2$ is known to be less strained than aziridine and, consequently, the ring opening of azetidine occurs much less easily than that of aziridine.[6] On the other hand, azetidine is a stronger nucleophile ($pK_a = 11.2$) compared to aziridine ($pK_a = 8.4$) suggesting that it would react faster than aziridine with metal-activated isocyanide ligands.[7] Should azetidine behave like aziridine, six-membered cyclic diaminocarbenes will form upon reaction with isocyanides.

Here we report on the reactions of a number of isocyanide complexes of Pd^{II} and Pt^{II} with azetidine and discuss the spectroscopic and structural characterization of the new carbene compounds formed.

Experimental

General.—All reactions were carried out in oven-dried glassware under a nitrogen atmosphere. Tetrahydrofuran (thf) was distilled from solutions of sodium–benzophenone. All other solvents were of reagent-grade purity and used without further purification. The ^1H and ^{13}C n.m.r. spectra of the complexes were obtained on a Bruker AM-400 spectrometer, ^{31}P n.m.r. spectra on a Varian FT-80A spectrometer, i.r. spectra on a Perkin-Elmer 983 spectrophotometer, and fast atom bombardment (f.a.b.) mass spectra on a VG ZAB 2F instrument operating with a xenon-atom beam energy of 8 keV (1.28×10^{-16} *J*). Melting points (uncorrected) of the compounds were determined in air on a hot-plate apparatus. Elemental analyses were performed by the Department of Analytical

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† Azetidine[azetidin-1-yl(*p*-methoxyanilino)methylene]chloro(dimethylphenylphosphine)palladium chloride–dichloromethane(1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Chemistry of the University of Padua. Azetidine, thietane, and oxetane were commercially available products used as received.

Starting Complexes.—The starting isocyanide complexes were prepared according to literature procedures which are outlined in refs. 5 and 8.

cis-[PdCl$_2$(PPh$_3$){C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$OMe-*p*}] (**1**).—To a suspension of *cis*-[PdCl$_2$(PPh$_3$)(CNC$_6$H$_4$OMe-*p*)] (0.330 g, 0.57 mmol) in thf (10 cm^3) was added azetidine (0.058 cm^3, 0.86 mmol) and the reaction mixture stirred at 0 °C to give a clear solution. The stirring was then continued while the temperature of the bath was allowed to rise slowly to room temperature. After 10 min, an i.r. spectrum of the solution did not reveal any band at 2 215 cm^{-1} due to ν(C≡N) of the starting isocyanide complex but showed the ν(C=N) at 1 562 cm^{-1} of the carbene complex. The stirring was then prolonged for 10 h. The white precipitate formed during this time was filtered off, washed with n-hexane (3 × 5 cm^3), and dried under vacuum. The product was recrystallized from CH$_2$Cl$_2$–n-hexane. Yield 0.358 g (98%).

In a separate experiment this compound was prepared by adding *cis*-[PdCl$_2$(PPh$_3$)(CNC$_6$H$_4$OMe-*p*)](0.660 g, 1.14 mmol) to a stirred solution of [NH$_3$(CH$_2$CH$_2$CH$_2$Cl)]Cl (0.212 g, 2.28 mmol) previously treated with a 1.5 mol dm^{-3} n-hexane solution of LiBu^n (1.6 cm^3, 2.5 mmol) at 0 °C in thf (20 cm^3). The reaction mixture was allowed to reach room temperature, giving a clear solution. After 1 h a white product started to precipitate. After 12 h it was filtered off, washed with n-hexane, and recrystallized from CH$_2$Cl$_2$–n-hexane. Yield 0.215 g (30%).

cis-[PdCl$_2$(PPh$_3$){C(NCH$_2$CH$_2$CH$_2$)NHBu^t}] (**2**).—This compound was prepared as described for (**1**) starting from *cis*-[PdCl$_2$(PPh$_3$)(CNBu^t)] (0.325 g, 0.62 mmol) and azetidine (0.050 cm^3, 0.74 mmol) in thf (10 cm^3). An i.r. spectrum of the solution recorded after 15 min did not show ν(C≡N) at 2 229 cm^{-1} of the starting isocyanide complex but the presence of ν(C=N) at 1 560 cm^{-1} of the carbene complex. Yield 0.223 g (62%).

cis-[PtCl$_2$(PPh$_3$){C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$OMe-*p*}] (**3**).—This compound was prepared as described for (**1**) starting from *cis*-[PtCl$_2$(PPh$_3$)(CNC$_6$H$_4$OMe-*p*)] (0.308 g, 0.46 mmol) and azetidine (0.038 cm^3, 0.56 mmol) in thf (10 cm^3). After 5 h an i.r. spectrum of the solution showed that almost all the starting complex had reacted and the carbene complex was formed, as indicated by the absence of ν(C≡N) at 2 206 cm^{-1} and the presence of ν(C=N) at 1 559 cm^{-1}. Yield 0.200 g (60%). Mass spectrum [m/z (relative intensity, probable assignment)]: 718(1.5, M^+), 683(16.6, $[M-\mathrm{Cl}]^+$), 648(39.3, $[M-2\mathrm{Cl}]^+$), 456(11.3, $[M-\mathrm{PPh_3}]^+$), 386(11.4, [Pt{C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$OMe}]$^+$), 328{3.0, [Pt(CNC$_6$H$_4$OMe)]$^+$}, 183(100.0, C$_{12}$H$_8$P$^+$).

cis-[PtCl$_2$(PPh$_3$){C(NCH$_2$CH$_2$CH$_2$)NHBu^t}] (**4**).—This compound was prepared as described for (**1**) starting from *cis*-[PtCl$_2$(PPh$_3$)(CNBu^t)] (0.611 g, 1.0 mmol) in thf (20 cm^3) and azetidine (0.090 cm^3, 1.33 mmol). After 8 h of reaction an i.r. spectrum of the solution did not show the ν(C≡N) stretching of the starting isocyanide at 2 219 cm^{-1}, while ν(C=N) at 1 562 cm^{-1} of the carbene complex was present. Yield 0.567 g (85%).

trans-[PdCl(PPh$_3$)$_2${C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$OMe-*p*}]BF$_4$ (**5**).—This compound was prepared as described for (**1**) starting from *trans*-[PdCl(PPh$_3$)$_2$(CNC$_6$H$_4$OMe-*p*)]BF$_4$ (0.305 g, 0.34 mmol) and azetidine (0.028 cm^3, 0.41 mmol) in thf (15 cm^3). An i.r. spectrum of the solution run after 15 min did not reveal any ν(C≡N) at 2 210 cm^{-1}, but showed ν(C=N) at 1 563 cm^{-1} of the final product. Yield 0.256 g (80%).

trans-[PtCl(PPh$_3$)$_2${C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$OMe-*p*}]BF$_4$ (**6**).—This compound was prepared as described for (**1**) starting from *trans*-[PtCl(PPh$_3$)$_2$(CNC$_6$H$_4$OMe-*p*)]BF$_4$ (0.325 g, 0.33 mmol) and azetidine (0.033 cm^3, 0.49 mmol) in thf (15 cm^3). An i.r. spectrum of the solution taken after 5 h did not display ν(C≡N) at 2 207 cm^{-1}, but showed ν(C=N) at 1 562 cm^{-1} of the final product. Yield 0.214 g (63%).

cis-[PdCl$_2$(CNBu^t){C(NCH$_2$CH$_2$CH$_2$)NHBu^t}] (**7**).—To a solution of *cis*-[PdCl$_2$(CNBu^t)$_2$] (0.115 g, 0.44 mmol) in thf (10 cm^3) was added azetidine (0.065 cm^3, 0.96 mmol) at 0 °C. A white precipitate immediately formed. An i.r. spectrum of the solution showed the presence of only one ν(C≡N) absorption at 2 209 cm^{-1} while the starting bis(isocyanide) complex showed ν(C≡N) at 2 230 and 2 247 cm^{-1} in thf solvent. An absorption of medium intensity at 1 562 cm^{-1} corresponding to ν(C=N) was also observed. The ice-bath was removed and stirring was continued for 10 h. The solid product was filtered off, washed with n-hexane (2 × 5 cm^3), and dried under vacuum. It was redissolved in CH$_2$Cl$_2$–MeOH and precipitated with n-hexane–acetone. Yield 0.151 g (86%).

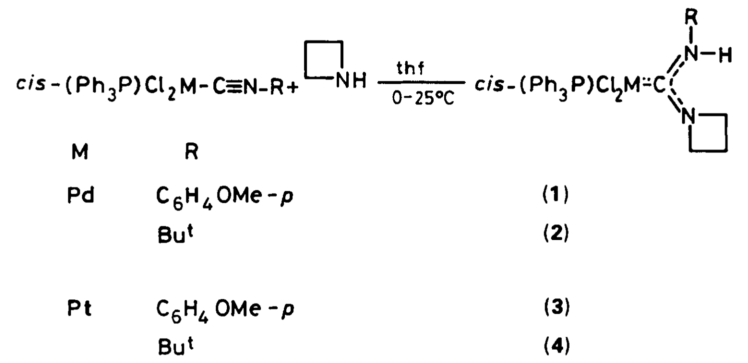
trans-[PdCl$_2${C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$OMe-*p*}$_2$] (**8**).—This compound was prepared as described for (**7**) starting from *cis*-[PdCl$_2$(CNC$_6$H$_4$OMe-*p*)$_2$] (0.333 g, 0.75 mmol) and azetidine (0.112 cm^3, 1.65 mmol) in thf (10 cm^3). After 30 min an i.r. spectrum of the solution showed the presence of only one ν(C≡N) absorption at 2 213 cm^{-1} together with a band at 1 562 cm^{-1} corresponding to ν(C=N). Stirring was continued until no band at 2 213 cm^{-1} was present (*ca.* 6 h). Yield 0.350 g (83%). Mass spectrum [m/z (relative intensity, probable assignment)]: 575(1.0, M^+), 522(2.5, $[M-\mathrm{Cl}]^+$), 487(4.7, $[M-2\mathrm{Cl}]^+$), 296(6.5, [Pd{C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$MeO}]$^+$, 239{2.0, [Pd(CNC$_6$H$_4$OMe)]$^+$}, and 183(100.0, C$_{12}$H$_8$P$^+$).

[MCl(PMe$_2$Ph)(CH$_2$CH$_2$CH$_2$NH){C(NCH$_2$CH$_2$CH$_2$)NH-C$_6$H$_4$OMe-*p*}]Cl [M = Pd (**9**) or Pt (**10**)].—These compounds were prepared similarly as described for (**1**) starting from *cis*-[MCl$_2$(PMe$_2$Ph)(CNC$_6$H$_4$OMe-*p*)] (0.5 mmol) and azetidine (0.067 cm^3, 1 mmol) in thf (30 cm^3) at 0 °C. The products were washed with acetone and recrystallized from CH$_2$Cl$_2$–Et$_2$O: (**9**), yield 0.210 g (75%); (**10**), yield 0.229 g (71%).

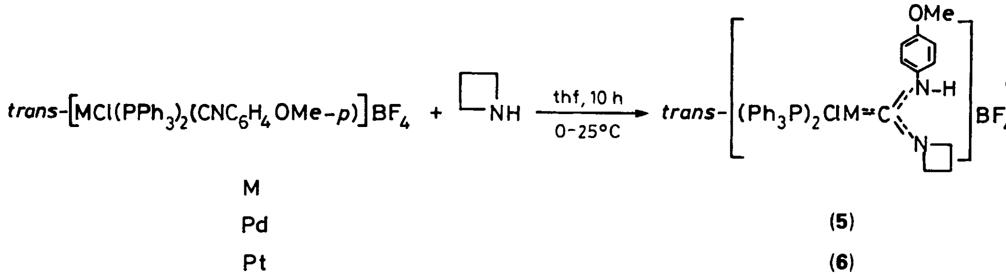
trans-[PtBr(PPh$_3$)$_2${C(NCH$_2$CH$_2$CH$_2$)NHC$_6$H$_4$OMe-*p*}]BF$_4$ (**11**).—The complex *trans*-[PtCl(PPh$_3$)$_2$(CNC$_6$H$_4$OMe-*p*)]BF$_4$ (0.633 g, 0.65 mmol) was added to a stirred solution of [NH$_3$(CH$_2$CH$_2$CH$_2$Br)]Br (0.143 g, 0.65 mmol) previously treated with azetidine (0.037 g, 0.65 mmol) at 0 °C in thf (20 cm^3). The reaction mixture was allowed to reach room temperature, giving a clear solution, and then a second equimolar amount of azetidine was added. After 3 h a white product started to precipitate. After 20 h it was filtered off, washed with n-hexane, and recrystallized from CH$_2$Cl$_2$–n-hexane. Yield 0.228 g (32%).

Crystal Structure Analysis of Complex (**9**)·CH$_2$Cl$_2$.—C$_{22}$H$_{32}$Cl$_2$N$_3$OPPd·CH$_2$Cl$_2$, M = 647.73, monoclinic, a = 24.849(4), b = 10.174(2), c = 11.895(2) Å, β = 91.85(3)°, U = 3 005.6(9) Å^3, space group $P2_1/n$, Z = 4, D_c = 1.43 g cm^{-3}, crystal size 0.18 × 0.20 × 0.24 mm, μ(Mo-K_α) = 9.5 cm^{-1}.

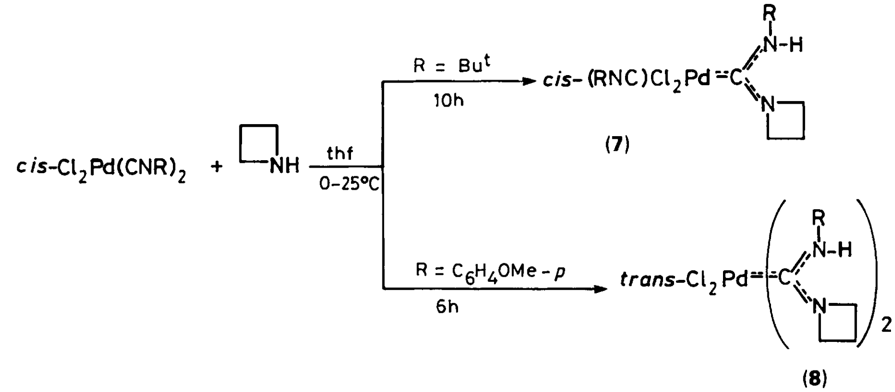
θ—2θ Scan, 2 $\theta_{\max.}$ = 50. 6 354 Reflections were measured, with a Philips PW1100 diffractometer, using Mo-K_α radiation (graphite monochromator); 3 734 observed reflections with $I \geqslant 3\sigma(I)$. The intensity data were corrected for Lorentz



(1)



(2)



(3a)

(3b)

polarization effects but not for absorption. The structure was solved by the heavy-atom method and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were detected from difference maps, but they were introduced in calculated positions (d_{C-H} = 0.95 Å and U_{iso} = 0.07 Å^2) except those of NH groups which were refined isotropically. All the calculations were performed by using the program SHELX 76;[9] PLUTO[10] and ORTEP[11] were used for drawings. Scattering factor data were taken from ref. 12. The final R, R' values were 0.054, 0.059 respectively, with weights of $w = 1/[\sigma^2 F_o + 0.002\,2331 F_o^2]$; goodness of fit S = 1.26. The final atomic positional parameters are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

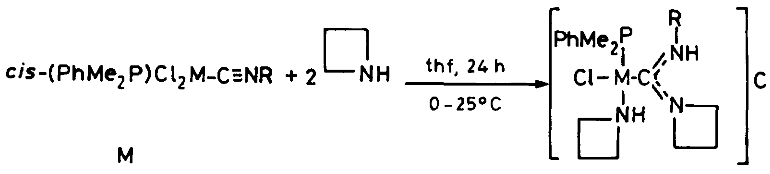
Results and Discussion

Synthesis and Characterization of the Compounds.—The isocyanide ligands and their metal complexes which have been investigated in this work are shown in equations (1)—(4). These isocyanide complexes have been previously reported[5,13] to display values of $\Delta\nu = \nu(C{\equiv}N)_{co\text{-}ord} - \nu(C{\equiv}N)_{free} > 70$ cm^{-1} indicating that the isocyanide carbon is a potentially reactive electrophilic centre[14] towards nucleophiles to give carbene complexes.[7]

Azetidine (1.2—1.5 equiv.) reacts in thf with the RNC ligand in each of the neutral and cationic isocyanide complexes shown in equations (1) and (2) to afford the diaminocarbene complexes (**1**)—(**4**) and (**5**) and (**6**), respectively.

The bis(isocyanide) complexes *cis*-[$PdCl_2(CNBu^t)_2$] and *cis*-[$PdCl_2(CNC_6H_4OMe\text{-}p)_2$] react with 2 equivalents of azetidine under experimental conditions analogous to those used for the monoisocyanide derivatives [equations (3a) and (3b)].

These reactions proceed differently depending on the nature of the RNC ligand. When R = Bu^t only one isocyanide ligand is converted into a carbene group by reaction with azetidine [compound (**7**), equation (3a)]. On the other hand, when R = C_6H_4OMe-*p*, the reaction proceeds stepwise through the rapid formation of a monocarbeneisocyanide complex, which



M	
Pd	(9)
Pt	(10)

R = C_6H_4OMe-*p*

is slowly converted into the final bis(carbene) product (**8**) [equation (3b)]. The intermediate mixed carbeneisocyanide complex was not isolated from the reaction mixture, but was detected in solution (see Experimental section).

The observed trend in reactivity of isocyanide ligands with azetidine agrees well with the generally observed higher reactivity of aryl isocyanides with respect to alkyl analogues[7] and also parallels that found for the analogous reactions with aziridine.[5]

Finally, the neutral isocyanide complexes *cis*-[$MCl_2(PMe_2Ph)(CNC_6H_4OMe$-*p*)] (M = Pd or Pt) react in thf with 2 equivalents of azetidine affording the cationic acyclic diaminocarbene complexes (**9**) and (**10**) according to equation (4). In these reactions, azetidine displaces a chloride ion from the metal to give cationic derivatives containing a co-ordinated azetidine ligand.

In contrast to the reactions of the three-membered heterocycles thi-irane and oxirane with isocyanides, the four-membered heterocycle $\overline{YCH_2CH_2CH_2}$ (Y = S, thietane; Y = O, oxetane) either alone or in the presence of Cl^- ions fails to convert the isocyanide group in complexes of Pd^{II} and Pt^{II} into the aminothio- and amino-oxy-carbene ligand, respectively.

Complexes (**1**)—(**10**) are isolated from the reaction mixture as white, air-stable solids, soluble in CH_2Cl_2 but insoluble in Et_2O and n-hexane. They gave satisfactory C, H, and N elemental analyses (Table 1) and were characterized by i.r. (Table 1), ^1H and ^{31}P n.m.r. (Table 2) spectroscopy. Furthermore compound (**9**) was structurally characterized by an *X*-ray diffraction study, and for complexes (**1**), (**9**), and (**10**) the ^{13}C n.m.r. spectra are reported (Table 3).

The i.r. spectra (Nujol mull) show ν(C=N) as a strong absorption in the range 1 552—1 568 cm^{-1} and medium to strong (NH) absorptions in the range 3 178—3 389 cm^{-1} as also found for complexes of Pd^{II} and Pt^{II} with cyclic[4b,5] and acyclic diaminocarbenes.[15] The presence of two medium-to-weak (MCl) bands in the range 284—326 cm^{-1} is indicative of a *cis* stereogeometry for complexes (**1**)—(**4**) and (**7**).[5,14] The *trans* geometry of complexes (**5**) and (**6**) has been confirmed by their ^{31}P n.m.r. spectra.

The ^{31}P n.m.r. spectra indicate the presence of two diastereoisomeric forms in *ca.* 1.5:1 ratio for compound (**9**) and 3.5:1 ratio for (**10**) based on integration of the signals. The two isomers may arise from different spatial arrangements of the two methyl groups of the co-ordinated PMe_2Ph ligand due to restricted rotation either about the metal–phosphorus bond or the metal–carbene bond.

The protons of the diaminocarbene complexes (**1**)—(**8**) display ABCDEF-type ^1H n.m.r. spectra at 400 MHz.

Compound (**1**) shows four separate multiplets in the range δ 4.91—3.43, one for each proton of the two NCH_2 groups and a complex multiplet centred at δ 2.14 for the CH_2 protons. Each NCH signal (see Table 2) is a doublet (J_{gem} = 9.3 Hz) split by coupling with the vicinal *cis* proton [$J(H^2H^4) = J(H^6H^4)$ = 9.3 Hz; for proton labelling see Table 2] and by the vicinal *trans* proton [$J(H^2H^3) = J(H^6H^3)$ = 6.2 Hz]. The *J* values were obtained by iterative computer modifications of relevant coupling constants leading to a good simulated spectrum. With the aid of double-resonance experiments it was possible to identify the geminal protons. Irradiation of the signal at δ 4.91 led only to a sharpening of the signal at δ 4.17, and irradiation of the signal at δ 3.98 results again in a sharpening of the signal at δ 3.43.

Compounds (**2**)—(**4**) show six separate signals one for each proton of the azetidine ring. For these complexes it is observed that the four NCH_2 resonances fall in the ranges δ 4.75—2.99, 4.70—3.46, and 4.18—2.65, respectively. Also for compound (**2**), double-resonance experiments were carried out to identify the geminal protons. Irradiation of the signal at δ 4.75 leads to a sharpening of the resonance at δ 3.94. Similarly, irradiation of the signal at δ 3.70 results in a sharpening of the multiplet at δ 2.99. Also for (**2**)—(**4**), iterative computer modifications led to good simulated spectra with *J*(HH) values reported in Table 2. The observed coupling constants are in good agreement with those reported for metal-free azetidine.[6]

All the other complexes reported in this work display different ^1H n.m.r. patterns. Thus complexes (**5**)—(**7**) show only three signals for the NCH_2 protons with integration ratios of 1:1:2 in the ranges δ 3.84—3.24, 3.77—3.22, and 4.91—4.03, respectively. Compound (**8**) shows only two signals integrating 1:1 for the NCH_2 protons at δ 4.49 and 3.48.

The two protons of the central CH_2 group of azetidine always appear upfield with respect to the NCH_2 resonances (δ 2.65—1.56).

The ^1H n.m.r. spectra at 400 MHz of compounds (**9**) and (**10**) display complex multiplets due to NCH_2 resonances of the carbene and of the metal-co-ordinated azetidine in the range δ 4.42—3.92. The central CH_2 protons of the carbene-bound azetidine appear as quintets at δ 2.61 and 2.28 for (**9**) and 2.65 and 2.00 for (**10**) while the central CH_2 protons of the metal-co-ordinated azetidine appear as two broad multiplets at δ 2.38 and 2.10 for (**9**) and as a broad multiplet at 2.31 for (**10**). The presence of two diastereoisomers for (**9**) and (**10**) is confirmed by the pattern of the methyl groups of PMe_2Ph. Each diastereoisomer gives rise to a doublet of doublets for the methyl resonance by coupling with the phosphorus atom of the phosphine ligand (Table 2).

Finally, the NH resonances of the carbene ligand of complexes (**1**)—(**10**) appear as broad signals in the range δ 5.04—7.72. The observed $^3J(PtH)$ coupling constant values (*ca.* 90 Hz) in the ^1H n.m.r. spectra of compounds (**3**), (**4**), and (**10**) are in agreement with those previously reported for carbene complexes showing the NH proton *trans* to the platinum(II) centre.[16] The magnitude of $^3J(PtH)$ confirms that the carbene complexes are acyclic, since a cyclic carbene would have the amino proton *cis* to the metal and, consequently, it would display a lower $^3J(PtH)$ value.[16]

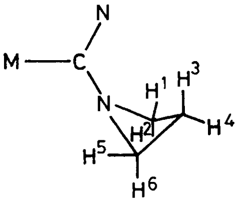
The aminocarbene proton does not undergo H/D exchange with D_2O in CD_2Cl_2 solvent. Furthermore, attempts to deprotonate the carbene nitrogens in complexes (**1**), (**3**), (**5**), and (**6**) with $LiBu^n$ (1.2 equivalents) were unsuccessful, the starting material being recovered unchanged after 12 h of stirring in thf at room temperature. The lack of reactivity of the NH proton in such complexes contrasts with that reported for the carbene complexes *trans*-[$MBr(PPh_3)_2$-

Table 1. Analytical data and characteristic i.r. bands for the complexes (**1**)—(**11**)

Compound	Analyses[a]/%				I.r.[c]/cm^{-1}		
	C	H	N	M.p.[b]/ °C	ν(C=N)	ν(NH)	ν(M–Cl)
(**1**) *cis*-$[PdCl_2(PPh_3)\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}]\cdot0.7CH_2Cl_2$	51.75 (51.75)	4.45 (4.45)	4.05 (4.05)	228—231	1 560s	3 222m	290w, 313w
(**2**) *cis*-$[PdCl_2(PPh_3)\{C(NCH_2CH_2CH_2)NHBu^t\}]$	52.85 (53.85)	5.40 (5.40)	4.75 (4.85)	219—220	1 560s	3 239m	295w, 311w
(**3**) *cis*-$[PtCl_2(PPh_3)\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}]\cdot0.5CH_2Cl_2$	46.75 (46.55)	3.95 (3.95)	3.50 (3.70)	246—247	1 552s	3 249m	284w, 309w
(**4**) *cis*-$[PtCl_2(PPh_3)\{C(NCH_2CH_2CH_2)NHBu^t\}]$	45.75 (46.70)	4.95 (4.65)	4.20 (4.20)	193—195	1 558s	3 265m	290w, 316w
(**5**) *trans*-$[PdCl(PPh_3)_2\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}]BF_4$	59.55 (59.85)	4.80 (4.70)	2.90 (2.95)	168—170	1 564s	3 264m	274m
(**6**) *trans*-$[PtCl(PPh_3)_2\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}]BF_4$	55.20 (55.30)	4.40 (4.30)	2.65 (2.70)	220—221	1 565s	3 290m	311m
(**7**) *cis*-$[PdCl_2(CNBu^t)\{C(NCH_2CH_2CH_2)NHBu^t\}]\cdot CH_2Cl_2$	34.55 (34.60)	5.65 (5.60)	8.70 (8.65)	300	1 568s	3 178m	297w, 326w[d]
(**8**) *trans*-$[PdCl_2\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}_2]$	47.30 (47.35)	5.10 (5.05)	9.80 (10.05)	223—225	1 561s	3 183m	272w
(**9**) $[PdCl(PMe_2Ph)(CH_2CH_2CH_2NH)\{C(NCH_2CH_2CH_2)NHC_6H_4\text{-}OMe\text{-}p\}]Cl$	46.25 (46.95)	5.40 (5.75)	7.15 (7.45)	138—139	1 563s	3 340m[e]	277m
(**10**) $[PtCl(PMe_2Ph)(CH_2CH_2CH_2NH)\{C(NCH_2CH_2CH_2)NHC_6H_4\text{-}OMe\text{-}p\}]Cl$	39.35 (40.55)	4.95 (4.75)	6.15 (5.85)	155—156	1 560s	3 389m	285m
(**11**) *trans*-$[PtBr(PPh_3)_2\{C(NCH_2CH_2CH_2)NHC_6H_4OMe\text{-}p\}]BF_4$	52.05 (52.45)	4.15 (4.10)	2.55 (2.60)	195—197	1 562s	3 281m	

[a] Calculated values in parentheses. [b] All complexes decompose on melting. [c] Nujol mull; s = strong, m = medium, and w = weak. [d] ν(C=N) 2 231s cm^{-1}. [e] In CH_2Cl_2 solution.

Table 2. Proton[a] and $^{31}P\text{-}\{^1H\}$[b] n.m.r. data for the carbene complexes



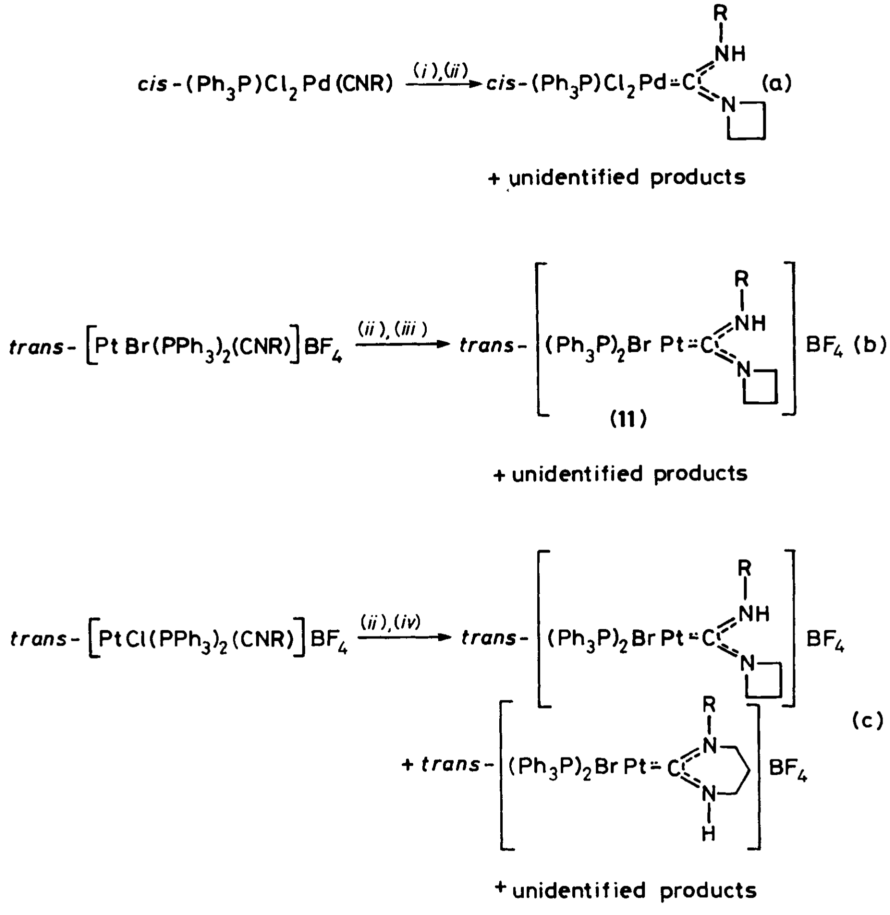
Compound	δ(NCH$_2$)[c]	δ(CH$_2$)	δ(NH)	δ(Other)	δ(P)
(**1**)	4.91(m), 4.17(m), 3.98(m), 3.43(m)	2.14(m)	6.53(br)	3.84(s)[d]	26.76(s)
(**2**)	4.75(m), 3.94(m), 3.70(m), 2.99(m)	2.19(m), 1.66(m)	7.72(br)	1.53(s)[e]	24.69(s)
(**3**)	4.70(m), 4.16(m), 3.89(m), 3.46(m)	2.23(m), 2.11(m)	6.35(br), ^3J(PtH) 90	3.84(s)[d]	8.48(s), ^1J(PtP) 4 080
(**4**)	4.18(m), 3.66(m), 3.04(m), 2.65(m)	2.35(m), 2.18(m)	5.14(br), ^3J(PtH) 99	1.38(s)[e]	6.48(s), ^1J(PtP) 3 425
(**5**)	3.84(m), 3.66(m), 3.24(m)	1.80(m), 1.57(m)	7.68(br)	3.77(s)[d]	20.77(s)
(**6**)	3.77(m), 3.65(m), 3.22(m)	1.56(m)	7.66(br)	3.79(s)[d]	17.11(s), ^1J(PtP) 2 654
(**7**)	4.91(m), 4.42(m), 4.03(m)	2.44(m)	5.04(br)	1.64(s)[e], 1.51(s)[e]	
(**8**)	4.49(m), 3.48(m)	1.92(m)	7.55(br)	3.81(s)[d]	
(**9**)	4.15(m), 4.37(m)[f], 4.27(m)[f]	2.61(qnt), 2.28(qnt) 2.38(m)[f], 2.10(m)[f]	6.60(br), 6.39(br)[g] 8.06(d), ^3J(HP) 8.4[f] 7.94,[f,g] ^3J(HP) 8.9	3.81(s)[d], 3.78(s)[d,g] 1.52(d), ^2J(HP) 11.1 [g,h], 1.43(d), ^2J(HP)11.1[g,h] 1.62(d), ^2J(HP) 11.1[h], 1.38(d), ^2J(HP) 11.8[h]	2.48(s)[g], 1.28(s)
(**10**)	4.21(m), 4.05(m) 4.42(m)[f], 4.29(m)[f], 3.92(m)[f]	2.65(qnt), 2.00(qnt) 2.31(m)[f]	7.67(br), ^3J(PtH) 98 7.81(d)[f], ^3J(HP) 8.0, ^2J(PtH) 80	3.78(s)[d], 3.77(s)[d,g] 1.54(d), ^2J(HP) 11.0[g,h], 1.50(d), ^2J(HP) 11.1[g,h] 1.64(d), ^2J(HP) 11.4[h,i]	−19.83[g], ^1J(PtP) 3 260 −18.54, ^1J(PtP) 3 897
(**11**)	3.86(t), 3.27(t)	1.62(qnt), ^3J(HH) 7.6	7.86(s), ^3J(PtH) 92	3.86(s)[d]	15.44, ^1J(PtP) 2 632

[a] Spectra in CD_2Cl_2; proton chemical shifts are reported with reference to $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as +5.32; J in Hz; s = singlet, t = triplet, qnt = quintet, m = multiplet, br = broad. [b] In CD_2Cl_2; 85% H_3PO_4 as external reference. [c] The following coupling constants were obtained from iterative computer modifications of relevant coupling constants leading to a good simulated spectrum: for (**1**), $J_{gem} = J(H^2H^4) = J(H^6H^4) = 9.3$; $J(H^2H^3) = J(H^6H^3) = 6.2$; for (**2**), $J_{gem} = J(H^2H^4) = J(H^6H^4) = 9.0$; $J(H^2H^3) = J(H^6H^3) = 6.5$; for (**3**), $J_{gem} = J(H^2H^4) = J(H^6H^4) = 9.2$; $J(H^2H^3) = J(H^6H^3) = 6.1$; for (**4**), $J_{gem} = J(H^2H^4) = J(H^6H^4) = 8.9$; $J(H^2H^3) = J(H^6H^3) = 6.8$ Hz. [d] δ(OMe). [e] δ(Bu^t). [f] Protons of metal-co-ordinated azetidine. [g] More abundant isomer. [h] δ(PMe). [i] The second signal of PMe is partially masked by the signal at δ 1.50.

Table 3. Carbon-13 n.m.r. spectral data for complexes (**1**) and (**9**)—(**11**)[a]

Compound	$C_{carbene}$	C_6H_4	OMe	NCH_2	CH_2	PMe
(**1**)	187.2(d) ^2J(PC) 3.8	158.2, 134.7, 132.6, 131.7 128.7, 128.6, 125.4, 114.1	55.8	55.4 54.3	15.7	
(**9**)[b]	192.3(d),[b] ^2J(PC) 5.9; 192.9(d), ^2J(PC) 6.1	157.7, 130.8, 130.3, 128.7, 128.6, 124.6, 124.2, 114.1	55.7	54.9, 54.2 52.5(d),[c] ^3J(PC) 26.0 51.9(d),[c] ^3J(PC) 26.0	23.3,[c] ^4J(PC) 3.8; 15.9	14.6(d), ^1J(PC) 35.0; 14.3(d), ^1J(PC) 32.8
(**10**)[b]	170.0(d), ^2J(PC) 7.7, ^1J(PtC) 1 371	157.9, 134.0, 131.1, 131.0, 130.0, 128.5, 125.7, 113.8	55.7	55.3, 54.2 52.5(d),[c] ^3J(PC) 23.5, 52.1(d),[c] ^3J(PC) 23.0	23.2,[c] ^4J(PC) 2.5 15.3	13.7(d), ^1J(PC) 42.9
(**11**)	174.9, ^2J(PC) 7.5, ^1J(PtC) 1 534	158.3, 134.9, 132.1, 129.0, 128.9, 124.1, 114.0	55.8	55.1 52.3	14.5	

[a] Spectra run in CD_2Cl_2 as solvent; chemical shifts reported with reference to $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as +53.8 p.p.m.; J in Hz. [b] Resonances refer to the more abundant isomer. [c] CH_2 protons of azetidine co-ordinated to the metal.



Scheme. R = C_6H_4OMe-*p*. (*i*) $[NH_3(CH_2CH_2CH_2Cl)]Cl$ + LiBu; (*ii*) thf, 0 °C; (*iii*) $[NH_3(CH_2CH_2CH_2Br)]Br$ + azetidine; (*iv*) $[NH_3(CH_2CH_2CH_2Br)]Br$ + LiBu

$\{\overline{CN(R)CH_2CH_2NH}\}]BF_4$ (M = Pd or Pt, R = aryl)[4b] and $[Fe(\eta\text{-}C_5H_5)(CO)_2(\overline{COCH_2CH_2NH})]$,[17] which are readily deprotonated by $LiBu^n$ or NaH to give the imino complexes $M\text{–}\overline{CN(R)CH_2CH_2N}$: and $M\text{–}\overline{COCH_2CH_2N}$:, respectively, whose nitrogens react with electrophiles.

The ^{13}C n.m.r. spectra (Table 3) of complexes (**1**), (**9**), and (**10**) show the carbene carbon signals in the range 170.0—192.9 p.p.m., as expected for diaminocarbene compounds of Pt^{II} and Pd^{II} [18] with a coupling constant ^1J(PtC) = 1 371 Hz for (**10**). The NCH_2 resonances of the *carbene*-bound azetidine appear in the range 54.2—55.4 p.p.m. and the assignments have been confirmed by comparison of the $^{13}C\text{-}\{^1H\}$ with the corresponding coupled ^{13}C spectra. The assignment of the NCH_2 signals of the *metal*-co-ordinated azetidine is based on the presence of ^3J(PC)(26 and 23 Hz, see Table 3) for (**9**) and (**10**); ^3J(PC) are generally larger than ^2J(PC).[19]

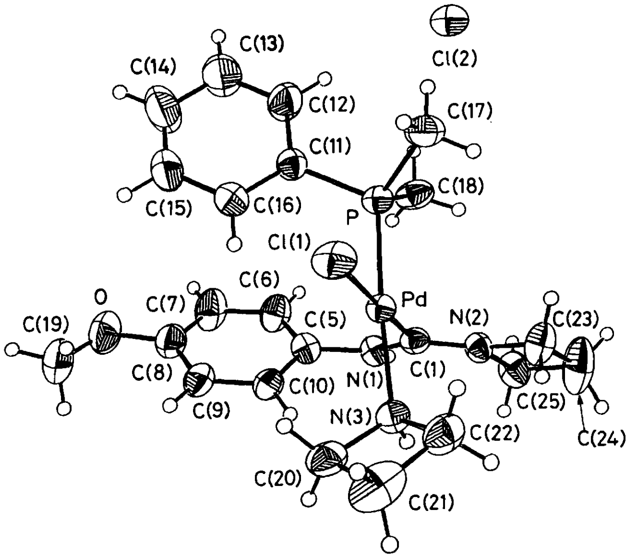
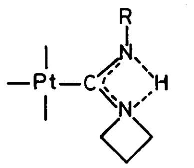


Figure 1. Perspective view of the asymmetric unit of complex (**9**). The ellipsoidal boundaries are at the 40% probability level

Spectroscopic and structural data (see below) indicate that the reactions of azetidine with isocyanide complexes of Pd^{II} and Pt^{II} lead to the formation of acyclic carbene derivatives, with no evidence of cyclic species. Attempts to synthesize six-membered cyclic carbenes are summarized in the Scheme.

The reactions (a)—(c) take advantage of similar reactions reported for 3-halogenopropylammonium salts and a base with carbonyl ligands to give six-membered cyclic carbenes.[20] As for isocyanide ligands, the reactions (a)—(c) lead to a poorly defined mixture of products, consisting mostly of the acyclic carbene derivatives. Thus, the spectral data for the carbene products derived from reactions (a) and (b) show that these complexes are acyclic as compared with the spectroscopic data for compounds (**1**) and (**6**). In one case (c) only, the observed coupling of the aminocarbene proton with ^{195}Pt [$^3J(PtH)$ 46.4 Hz][16] suggests that a cyclic carbene derivative could have been formed together with the acyclic parent complex [$^3J(PtH)$ 95.0 Hz].

As for the mechanism of reactions (1)—(4), it is likely that they proceed by nucleophilic attack of azetidine on the isocyanide carbon and subsequent NH transfer to the imino nitrogen as proposed in several mechanistic studies of nucleophilic attack of anilines on co-ordinated isocyanides.[7]



Structure of Complex (**9**)·CH_2Cl_2.—The structure consists of $[PdCl(PMe_2Ph)(\overline{CH_2CH_2CH_2N}H)\{C(\overline{NCH_2CH_2CH_2})NH\text{-}C_6H_4OMe\text{-}p\}]^+$ cation and Cl^- anion units and CH_2Cl_2 solvent molecules. The co-ordination geometry around Pd^{II} is a distorted square. (The deviations from the best mean plane through the co-ordinated atoms are P −0.004(2), Cl(1) 0.006(2), C(1) 0.063(6), and N(3) −0.046(6) Å with the Pd atom 0.0492(6) Å from this plane.) The diaminocarbene ligand bound to Pd *via* C(1) is *trans* to chloride: the co-ordination is completed by one phosphorus atom from PMe_2Ph and the azetidine nitrogen.

A perspective view of the complex cation showing its conformation and the atom numbering scheme is displayed in Figure 1, while significant bond distances and angles are in Table 5. The Cl(1)–Pd–C(1) angle is 179.0(2)° while P–Pd–N(3) is 175.8(2)°. This bending is related to the steric bulk of the carbenoid ligand which is strongly bound to palladium(II) [Pd–C(1) 1.990(6) Å]. This is readily apparent by comparison with the expected Pd–C(sp^2) distance of 2.05 Å based on the sum of the σ covalent radii {1.31 (Pd^{II}) + 0.74 Å [C(sp^2)]}.[21] The Pd–C(carbene) bond length is also comparable to the corresponding distance for the diaminocarbene ligand in $[PdCl\{C(NEt_2)NHMe\}\{Et_2NCH_2CH_2C(O)\}]$ [2.010(5) and 2.020(5) Å for two independent molecules],[22] where the carbene moiety is *trans* to the amino nitrogen of the bidentate β-aminoacyl ligand. In addition it is in agreement with the Pd–C(carbene) bond lengths of 1.953(8) and 1.972(10) Å reported for the methylamino(methoxy)carbene ligands in *cis*-dichlorobis[methylamino(methoxy)carbene]palladium,[23] where the two carbenes are *trans* to chlorides as in the present structure, and is within the range of 1.95—2.08 Å observed in a variety of platinum diaminocarbene complexes.[4b,24] In the acyclic carbene ligand the C(1)–N(1) bond length [1.334(8) Å] is significantly longer than the C(1)–N(2) bond length [1.298(8) Å] and the N(2)–C(23) and N(2)–C(25) bond lengths of 1.465(9) and 1.475(9) Å, respectively, are shorter than N(3)–C(22) [1.520(9) Å] and N(3)–C(20) [1.507(9) Å] in the azetidine directly bound to the metal atom. This suggests that some degree of electron delocalization is extended also to the N(2)–C(23) and N(2)–C(25) bonds. However, the most

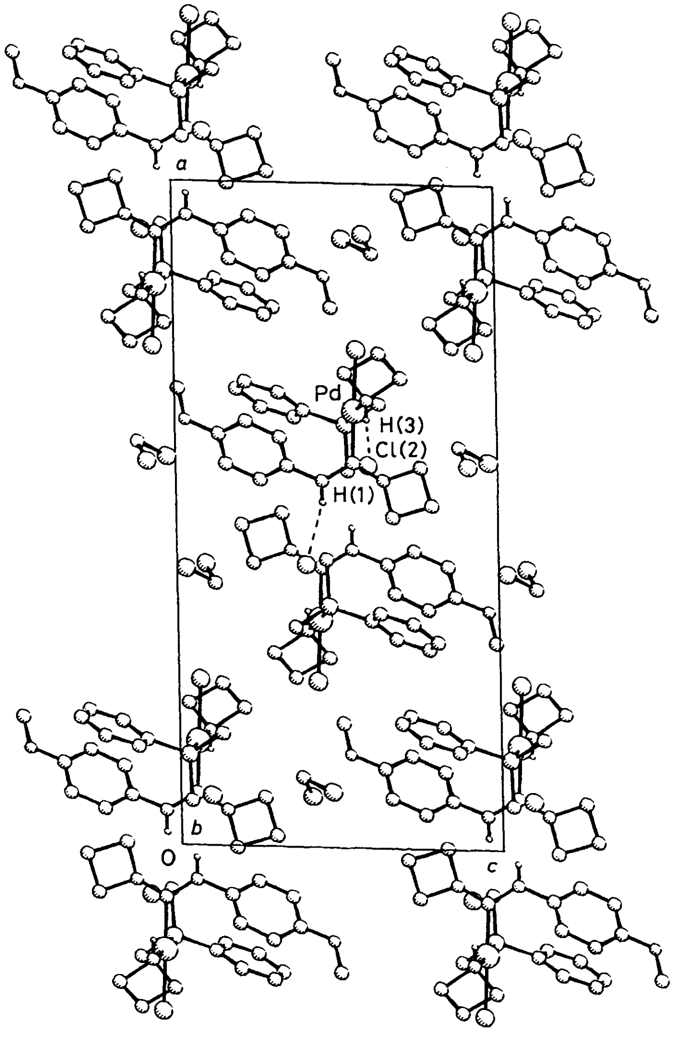


Figure 2. Cell contents of complex (**9**) viewed down *b*

Table 4. Atomic co-ordinates ($\times 10^4$) of complex (**9**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	6 574.8(2)	7 670.9(4)	5 578.4(4)
P	6 369.5(6)	5 536(1)	5 293(1)
Cl(1)	7 501.1(6)	7 142(2)	5 670(2)
Cl(2)	5 752.2(7)	1 583(2)	5 982(2)
N(3)	6 745(2)	9 654(5)	5 964(5)
H(3)	6 449(28)	10 073(72)	5 949(59)
O	6 408(3)	8 058(7)	318(5)
N(1)	5 515(2)	8 233(5)	4 545(4)
H(1)	5 201(22)	8 282(46)	5 949(59)
N(2)	5 535(2)	8 165(5)	6 447(4)
C(1)	5 792(2)	8 090(6)	5 517(5)
C(5)	5 736(2)	8 229(6)	3 462(5)
C(6)	5 523(3)	7 438(8)	2 622(6)
C(7)	5 750(4)	7 419(9)	1 574(7)
C(8)	6 200(3)	8 186(8)	1 365(6)
C(9)	6 400(3)	8 998(7)	2 200(6)
C(10)	6 165(3)	9 035(7)	3 234(5)
C(11)	6 577(3)	4 887(6)	3 969(5)
C(12)	6 468(4)	3 566(8)	3 695(7)
C(13)	6 619(5)	3 053(9)	2 674(9)
C(14)	6 886(5)	3 850(9)	1 922(9)
C(15)	6 994(4)	5 125(9)	2 193(8)
C(16)	6 842(3)	5 657(7)	3 209(7)
C(17)	6 691(3)	4 486(7)	6 331(6)
C(18)	5 672(3)	5 094(7)	5 355(8)
C(19)	6 879(4)	8 732(9)	113(8)
C(20)	7 145(3)	10 419(7)	5 297(6)
C(21)	7 444(4)	10 828(11)	6 357(8)
C(22)	7 084(3)	9 947(8)	7 020(6)
C(23)	5 737(3)	8 136(9)	7 618(6)
C(24)	5 162(4)	8 452(14)	7 956(8)
C(25)	4 979(3)	8 508(8)	6 729(6)
Cl(3)	839(2)	3 477(4)	4 734(3)
Cl(4)	765(2)	746(5)	4 101(4)
C(26)	1 050(5)	2 247(12)	3 815(10)

Table 5. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Pd–P	2.255(2)	Pd–Cl(1)	2.363(2)
Pd–N(3)	2.109(5)	Pd–C(1)	1.990(6)
P–C(11)	1.799(7)	P–C(17)	1.799(8)
P–C(18)	1.795(7)	N(3)–C(20)	1.507(9)
N(3)–C(22)	1.520(9)	O–C(8)	1.37(1)
O–C(19)	1.38(1)	N(1)–C(1)	1.334(8)
N(1)–C(5)	1.417(8)	N(2)–C(1)	1.298(8)
N(2)–C(23)	1.465(9)	N(2)–C(25)	1.475(9)
C(5)–C(6)	1.38(1)	C(5)–C(10)	1.378(9)
C(6)–C(7)	1.38(1)	C(7)–C(8)	1.39(1)
C(8)–C(9)	1.37(1)	C(9)–C(10)	1.38(1)
C(11)–C(12)	1.41(1)	C(11)–C(16)	1.38(1)
C(12)–C(13)	1.39(1)	C(13)–C(14)	1.39(1)
C(14)–C(15)	1.36(1)	C(15)–C(16)	1.39(1)
C(20)–C(21)	1.50(1)	C(21)–C(22)	1.51(1)
C(23)–C(24)	1.53(1)	C(24)–C(25)	1.52(1)
Cl(3)–C(26)	1.75(1)	Cl(4)–C(26)	1.72(1)
N(3)–Pd–C(1)	89.6(2)	Cl(1)–Pd–C(1)	179.0(2)
Cl(1)–Pd–N(3)	91.1(2)	P–Pd–C(1)	89.1(2)
P–Pd–N(3)	175.8(2)	P–Pd–Cl(1)	90.2(1)
Pd–P–C(18)	116.7(2)	Pd–P–C(17)	112.1(3)
Pd–P–C(11)	114.6(2)	C(17)–P–C(18)	103.4(4)
C(11)–P–C(18)	104.4(3)	C(11)–P–C(17)	104.5(3)
Pd–N(3)–C(22)	118.0(4)	Pd–N(3)–C(20)	120.7(4)
C(20)–N(3)–C(22)	88.7(5)	C(8)–O–C(19)	117.3(7)
C(1)–N(1)–C(5)	125.7(5)	C(23)–N(2)–C(25)	94.8(5)
C(1)–N(2)–C(25)	134.3(6)	C(1)–N(2)–C(23)	130.2(6)
N(1)–C(1)–N(2)	118.6(5)	Pd–C(1)–N(2)	119.3(4)
Pd–C(1)–N(1)	122.1(4)	N(1)–C(5)–C(10)	120.2(6)
N(1)–C(5)–C(6)	120.7(6)	C(6)–C(5)–C(10)	119.2(6)
C(5)–C(6)–C(7)	120.2(7)	C(6)–C(7)–C(8)	120.4(8)
O–C(8)–C(7)	116.0(7)	C(7)–C(8)–C(9)	118.8(7)
O–C(8)–C(9)	125.2(7)	C(8)–C(9)–C(10)	120.6(7)
C(5)–C(10)–C(9)	120.8(6)	P–C(11)–C(16)	121.4(5)
P–C(11)–C(12)	119.7(5)	C(12)–C(11)–C(16)	118.9(7)
C(11)–C(12)–C(13)	120.5(8)	C(12)–C(13)–C(14)	119.5(9)
C(13)–C(14)–C(15)	120(1)	C(14)–C(15)–C(16)	121.5(9)
C(11)–C(16)–C(15)	119.8(7)	N(3)–C(20)–C(21)	91.0(6)
C(20)–C(21)–C(22)	89.3(7)	N(3)–C(22)–C(21)	90.4(6)
N(2)–C(23)–C(24)	87.2(6)	C(23)–C(24)–C(25)	90.5(7)
N(2)–C(25)–C(24)	87.4(6)		

prominent electron-delocalization effect is present in the N(1)–C(5) bond length [1.417(8) Å] adjacent to C(1)–N(1) [1.334(8) Å] of the carbenoid moiety. The two azetidine moieties show slightly different conformations, that being more closer to planarity [the deviations from its best mean plane range from −0.020(14) to 0.009(9) Å] which is bound to the carbene ligand [*i.e.* N(2), C(23), C(24), C(25)], and is also quasi-coplanar to the N(1)–C(1)–N(2) plane [dihedral angle 174.4(5)°]. In the other azetidine moiety [*i.e.* N(3), C(20), C(21), C(22)] the deviations from the best mean plane range from −0.067(11) to 0.036(8) Å indicating a twisted ring conformation. The extensive bonding within the N(1)–C(carbene)–N(2) system may be compared with the values quoted for the diaminocarbene complexes of Pd^{II} (1.294—1.340 Å)[23,25] and also of Pt^{II} (1.30—1.37 Å).[24] The second azetidine, which is characterized by normal values of the bond distances and angles, close to those reported for L-azetidine-2-carboxylic acid[26] which has a similar twisted molecular conformation [deviations from the best mean plane range from −0.067(11) to 0.036(8) Å], is quasi-perpendicular to the co-ordination plane [dihedral angle 88.2(3)°].

The phenyl ring of the carbene ligand is rotated with respect to the N(1)–C(1)–N(2) plane by 127.7(5)° (dihedral angle). The Pd–N(3) bond length of 2.109(5) Å observed for azetidine is similar to the Pd–N bond distances of the mutually *trans* β-amino group of the bidentate β-aminoacyl ligand and diethylamino ligand in the compound $[PdCl\{Et_2NCH_2CH_2C(O)\}(NHEt_2)]$ [Pd–N 2.11(1) and 2.09(1) Å, respectively].[27] The value of the Pd–Cl(1) distance in complex (**9**) [2.363(2) Å] is close to the values reported for other palladium(II) complexes having chloro ligands *trans* to a diaminocarbene moiety (Pd–Cl 2.36—2.39 Å).[23,28] The Pd–P distance of 2.255(2) Å is comparable to the values of 2.238(1) Å reported for *cis*-dichloro-[2,3-bis(dimethylamino)cycloprop-2-enylidene](tri-n-butylphosphine)palladium[29] and somewhat longer than the value of 2.214(2) Å found for a Pd–P *trans* to a nitrogen in $[Pd(C_{10}H_8N)\{Ph_2PC[C(O)OEt][=C(O)NHPh]\}]$ ($C_{10}H_8N$ = quinolin-8-ylmethyl).[30] In the co-ordination sphere there is a short intramolecular contact between the proton of the azetidine ligand and the palladium [Pd ··· H(3) 2.57(7) Å] comparable to Pd ··· H [2.42(8) Å] found in *trans*-$[PdCl_2(NHMe_2)_2]$.[31] The crystal packing shown in Figure 2 is characterized by the presence of clathrated CH_2Cl_2 solvent molecules and by short intermolecular contacts among the chloride anions and two carbene and azetidine protons ligands which can be considered as hydrogen bonding: N(3)–H(3) 0.85(7), N(3) ··· Cl(2) 3.154(6), H(3) ··· Cl(2) 2.32(7) Å, N(3)–H(3) ··· Cl(2) 168(6)°; N(1)–H(1) 0.78(6), N(1) ··· $Cl(2^I)$ (I $1-x$, $1-y$, $1-z$) 3.196(5), H(1) ··· $Cl(2^I)$ 2.43(5) Å, N(1)–H(1) ··· $Cl(2^I)$ 165(4)°.

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