Reactions of Olefin Complexes with Nitrene Precursors. Synthesis of Triazoline and Aziridine Complexes of Palladium(II); Crystal and Molecular Structure of *trans*-Dichlorobis(11-phenyl-9,10,11-triazabicyclo[6.3.0]undec-9-ene-*N*⁹)palladium–Chloroform(1/2) *

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By reaction at 70 °C of phenyl azide with a suspension of $PdCl_2$ and *cis*-cyclo-octene, the complex $[PdCl_2\{N{=}N{-}N(Ph){-}CH{-}CH{-}(CH_2)_5{-}CH_2\}_2]{\cdot}2CHCl_3$ has been isolated, and its crystal and molecular structure determined. This compound crystallizes in triclinic space group $P\bar{1}$ with $a = 9.258(2)$, $b = 10.702(3)$, $c = 11.156(2)$ Å, $\alpha = 113.94(3)$, $\beta = 99.60(2)$, $\gamma = 104.87(3)°$, and $Z = 1$. The metal lies on a symmetry centre and the complex configuration is *trans* planar. The chloroform molecules are hydrogen bonded to the co-ordinated chloride ions. The reaction of phenyl azide with *cis*-cyclo-octene at 70 °C in the absence of $PdCl_2$ leads to the corresponding anil, *N*-cyclo-octylideneaniline, $PhN{=}C{-}(CH_2)_6{-}CH_2$. Preformed $[\{PdCl_2(cis\text{-}C_8H_{14})\}_2]$ reacts with phenyl azide in cyclo-octene at 70 °C to give $[PdCl_2\{N(Ph){-}CH{-}CH{-}(CH_2)_5{-}CH_2\}_2]$. By comparison, $[\{PdCl_2[PhN{=}C{-}(CH_2)_6{-}CH_2]\}_2]$ has been synthesized from the reaction of $[PdCl_2(PhCN)_2]$ with *N*-cyclo-octylideneaniline.

Studies on the catalytic activity of metals in organic synthesis have recently received increasing attention. Owing to our interest in the reactivity of the metal–nitrogen bond,[1,2] we have previously studied the transformation of nitrene precursors such as nitrosobenzene,[3] phenyl azide,[4] and primary amines [5] catalysed by transition-metal complexes in the presence of carbon monoxide or dioxygen. We report here a study on the reactivity of phenyl azide with olefins in the presence of palladium(II) derivatives.

Experimental

Phenyl azide was distilled under vacuum (0.1 mmHg) at room temperature before use, from a hydrocarbon solution (ICN Pharmaceuticals Inc.). Palladium(II) chloride was a commercial product (Engelhard S.p.A.). *cis*-Cyclo-octene was distilled under nitrogen, stored under nitrogen, and chromatographed on alumina under nitrogen prior to use.

I.r. spectra were taken on Beckman 4210 and Nicolet MX-1 FT-IR spectrophotometers. Hydrogen-1 n.m.r. spectra in $CDCl_3$ were recorded on a Bruker WP-80 instrument, with $SiMe_4$ as internal standard.

$[\{PdCl_2(cis\text{-}C_8H_{14})\}_2]{\cdot}0.33CH_2Cl_2$.—Palladium(II) chloride (1.0 g) and *cis*-cyclo-octene (6 cm³) were left under a nitrogen atmosphere at 55 °C for 5 h with magnetic stirring. The yellow-orange complex was filtered off, washed with n-hexane, crystallized from methylene chloride–n-hexane, by filtering off some unreacted $PdCl_2$, and dried *in vacuo* (yield 0.69 g, 43%), m.p. = 180—185 °C (decomp.), non-conductor in nitrobenzene (Found: C, 32.5; H, 4.7; Cl, 27.1. Calc. for $C_{16}H_{28}Cl_4Pd_2{\cdot}0.33\ CH_2Cl_2$: C, 32.5; H, 4.8; Cl, 27.5%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ = 6.22 (qnt, =CH), 2.30—2.37 (br m, CH_2), 1.2—2(br m, CH_2), and 5.31 (CH_2Cl_2). I.r. spectrum: $\nu_{max.}$ at 355m, 302m, and 276w cm⁻¹ (Pd–Cl) in Nujol, confirming the presence of chlorine bridges.

$[PdCl_2\{N{=}N{-}N(Ph){-}CH{-}CH{-}(CH_2)_5{-}CH_2\}_2]$.—$PdCl_2$ (0.1 g, 0.563 mmol) and *cis*-cyclo-octene (10 cm³) were left under a nitrogen atmosphere at 45 °C for 3 h, with magnetic stirring. A solution of phenyl azide (0.346 g, 2.91 mmol) in cyclo-octene (2 cm³) was added, and the temperature was raised to 70—75 °C. After 6.5 h the heating was stopped and the suspension was left to cool overnight. The golden-yellow complex was filtered off, washed repeatedly with n-hexane, crystallized twice from methylene chloride–n-hexane, and dried for many hours *in vacuo* (yield 0.1 g, 20.7%), m.p. = 136 °C (Found: C, 52.0; H, 5.9; N, 12.6. Calc. for $C_{28}H_{38}Cl_2N_6Pd$: C, 52.9; H, 6.0; N, 13.2%).

The complex is isolated with some solvent of crystallization, which can be eliminated only by prolonged drying *in vacuo*. For this reason we have obtained a series of samples with uncertain elemental analyses. However, the exact composition of the product has been determined unambiguously by *X*-ray structural analysis. The crystals employed for the *X*-ray determination were obtained by slow diffusion of n-hexane into a chloroform solution of the complex. They were rapidly dried *in vacuo* (15 mmHg), and contain 2 mol of chloroform per mol of complex.

I.r. spectrum (significant bands): $\nu_{max.}$ at 1 580ms, 1 160s, 1 140s, 750s, and 345w cm⁻¹ (Pd–Cl), in Nujol. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ = 4.4 (br m, CH), 1—2 (br m, CH_2), and 5.3 (CH_2Cl_2).

In the mother-liquor of the reaction *ca.* 50% of the initial azide was detected [quantitative analysis by i.r. spectroscopy

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* *Supplementary data available* (No. SUP 56014, 6 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.
Non-S.I. unit employed: mmHg ≈ 134 Pa.

Table 1. Atomic positional parameters with their e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.000	0.000	0.000	C(4)	0.278 9(6)	−0.057 2(5)	−0.490 3(4)
Cl	−0.225 1(1)	−0.064 1(1)	−0.169 3(1)	C(5)	0.382 8(5)	−0.069 0(4)	−0.376 8(4)
Cl(1)	−0.204 0(2)	−0.420 6(2)	−0.503 6(2)	C(6)	0.296 7(5)	−0.141 6(4)	−0.304 2(4)
Cl(2)	−0.045 7(2)	−0.459 2(2)	−0.289 4(2)	C(7)	0.175 3(5)	−0.083 7(4)	−0.250 3(4)
Cl(3)	−0.376 5(2)	−0.546 2(2)	−0.363 7(2)	C(8)	0.240 4(4)	0.077 6(3)	−0.147 0(3)
N(1)	0.127 1(3)	0.118 1(3)	−0.072 1(3)	C(11)	0.265 8(4)	0.451 2(3)	−0.071 4(3)
N(2)	0.137 9(3)	0.248 7(3)	−0.039 7(3)	C(12)	0.205 2(4)	0.539 1(4)	0.017 3(4)
N(3)	0.234 2(3)	0.305 2(3)	−0.095 8(3)	C(13)	0.239 3(5)	0.683 4(4)	0.041 6(4)
C	−0.205 8(6)	−0.419 4(5)	−0.348 7(5)	C(14)	0.331 5(5)	0.737 2(4)	−0.024 3(4)
C(1)	0.278 6(4)	0.193 1(3)	−0.197 3(3)	C(15)	0.394 0(5)	0.649 7(4)	−0.110 9(4)
C(2)	0.187 0(5)	0.149 1(4)	−0.344 4(4)	C(16)	0.364 3(4)	0.506 2(4)	−0.134 9(4)
C(3)	0.267 1(6)	0.092 0(4)	−0.453 2(4)	H	−0.1933	−0.3046	−0.2773

on the ν(N_3) band at 2 120 cm^{-1}]. The solution was evaporated at room temperature *in vacuo* (15 mmHg) for 4 h. Column chromatography of the residue on silica, eluting with n-hexane and toluene, gave an oily mixture. By treating the mixture with n-hexane a very small amount of a yellow powder was obtained, which showed an i.r. spectrum identical to that of the palladium–aziridine complex (see later). By evaporating to dryness the n-hexane solution, an organic compound was obtained which was recognized as *N*-cyclo-octylideneaniline,[6] by its i.r. spectrum [$\nu_{max.}$ at 1 680w cm^{-1} (C=N) in Nujol] and hydrogen-1 n.m.r. spectrum [$\delta(CH_2) = 2.35$ and 1.60 (br multiplets), in $CDCl_3$]. The same reddish oily compound was obtained when phenyl azide (0.33 g) and *cis*-cyclo-octene (12 cm^3) were allowed to react under nitrogen at 70—75 °C for 7 h. Under these conditions, 60% of the initial azide was converted. Work-up of the reaction mixture as described above gave an organic material with identical i.r. and hydrogen-1 n.m.r. spectra. Its composition was confirmed by mass spectrometry and elemental analyses.

$[PdCl_2\{N(Ph)\text{–}CH\text{–}CH\text{–}(CH_2)_5\text{–}CH_2\}_2]$.—To a quantity of $[\{PdCl_2\,(cis\text{-}C_8H_{14})\}_2]$ (0.8 g, 1.39 mmol) a solution (22 cm^3) of phenyl azide (0.838 g, 7.04 mmol) in *cis*-cyclo-octene was added under a N_2 atmosphere. The suspension was left at 70 °C for 6 h, with magnetic stirring, and then left to cool overnight. The ochre-yellow insoluble material was filtered off from the red solution and crystallized from methylene chloride. By slow addition of n-hexane an ochre-yellow precipitate was obtained, which was shown by its i.r. spectrum and elemental analyses to be a mixture of a palladium–olefin complex contaminated by a nitrogen-containing product. Further addition of n-hexane to the solution yielded the pale yellow *trans*-dichlorobis(9-phenyl-9-azabicyclo[6.1.0]nonane)palladium(II) which was filtered off and washed with acetone, m.p. = 206 °C (Found: C, 57.2; H, 6.3; N, 4.8. Calc. for $C_{28}H_{38}Cl_2N_2Pd$: C, 58.0; H, 6.6; N, 4.8%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ = 3.4 and 3.75 (m, aziridine ring H), 2—2.5 and 1.8—1.9 (br m, CH_2). I.r. spectrum (significant bands): $\nu_{max.}$ at 1 625s, 1 590m, 1 070w, 1 020w, 735ms, 695ms, and 343w cm^{-1} (Pd–Cl), in Nujol.

By slow addition of n-hexane to the initial red solution, large quantities of the palladium–aziridine complex were obtained, while excess of n-hexane gave a yellow precipitate whose nature was not clarified, although it contains triazoline and cyclo-octene as ligands (i.r. and ^1H n.m.r. evidence). The final solution was evaporated to dryness and the residue chromatographed on silica. By eluting with toluene and ethanol, a further amount of the palladium–aziridine complex was obtained together with *N*-cyclo-octylideneaniline which was identified from its i.r. and mass spectra. The total yield of the aziridine complex was 0.25 g (31%).

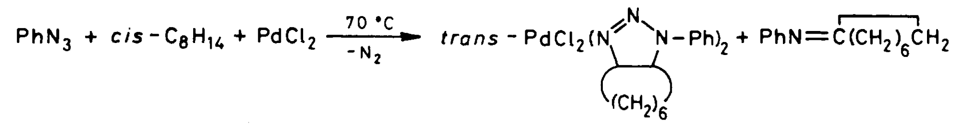
$[\{PdCl_2[PhN{=}C\text{–}(CH_2)_6\text{–}CH_2]\}_2]$.—The complex $[PdCl_2(PhCN)_2]$ (0.095 g, 0.248 mmol) and *N*-cyclo-octylideneaniline (0.05 g, 0.248 mmol) in CH_2Cl_2 (2 cm^3) were refluxed for 2 h. An ochre residue was filtered off. The brown solution was evaporated to *ca.* half-volume. By adding n-hexane a brown precipitate was obtained, m.p. = 149 °C (Found: C, 44.8; H, 5.1; N, 3.9. Calc. for $C_{28}H_{38}Cl_4N_2Pd_2$: C, 44.4; H, 5.0; N, 3.7%). I.r. spectrum (significant bands): $\nu_{max.}$ 1 590m, 1 025w, 940w, 800—790w, 760w, 690m, 345s, and 314w cm^{-1} (Pd–Cl). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ = 1.45 and 2.3 (br m, CH_2).

In the mother-liquor the presence of free PhCN was demonstrated. The same complex (analytical and spectroscopic evidence) was obtained when this reaction was conducted with a 2 : 1 mol ratio of *N*-cyclo-octylideneaniline to $[PdCl_2(PhCN)_2]$.

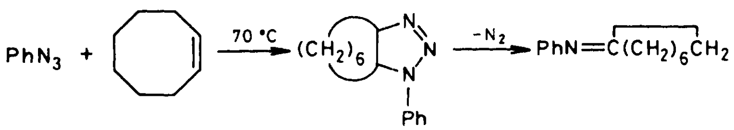
Crystallography.—Crystal data. $C_{30}H_{40}Cl_8N_6Pd$, $M = 874.72$, triclinic, space group $P\bar{1}$, $a = 9.258(2)$, $b = 10.702(3)$, $c = 11.156(2)$ Å, $\alpha = 113.94(3)$, $\beta = 99.60(2)$, $\gamma = 104.87(3)$°, $U = 929$ Å^3, $Z = 1$, $D_c = 1.563$ g cm^{-3}, $F(000) = 444$, $\mu(Mo\text{-}K_\alpha) = 11.03$ cm^{-1}, Mo-K_α radiation ($\lambda = 0.710\ 69$ Å), crystal size 0.15 × 0.2 × 0.3 mm.

Data collection was performed on a Enraf–Nonius CAD-4 automatic diffractometer. Following preliminary photographic studies, accurate unit-cell data and the crystal orientation matrix were determined from least-squares refinement of the setting angles of 25 reflections with $9.5 < \theta < 13°$. Intensity data were collected in the range $3 \leqslant \theta \leqslant 25°$ by the ω-scan technique: scan width, $\Delta\omega = 1.80 + 0.35 \tan\theta$. The intensity of three reflections chosen as standards was monitored every hour during the data collection and showed a small decrease in the scattering power of the crystal (maximum about 7% evaluated on F_o). Three orientation standards were checked after every 200 reflections: if the estimated standard deviations (e.s.d.s) of the *h,k,l* values for any orientation reflection exceeded 0.12 a new orientation matrix was calculated by recentring 22 reference reflections. The intensities of 3 236 unique reflections were measured of which 2 854 had $I \geqslant 3\sigma(I)$ and were used in the structure solution and refinement. Data were corrected for Lorentz, polarization, and decay effects and for absorption. The latter correction was performed by an empirical method based on a set of ψ scans of reflections having χ values near 90°.[7] The minimum value of the relative transmission coefficients was 0.859.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares down to $R[=\Sigma(F_o - k|F_c|)/\Sigma F_o]$ and R' $\{=[\Sigma w_{h,k,l,}(F_o - k|F_c|)^2/\Sigma w_{h,k,l}F_o^{\,2}]^{\frac{1}{2}}\}$

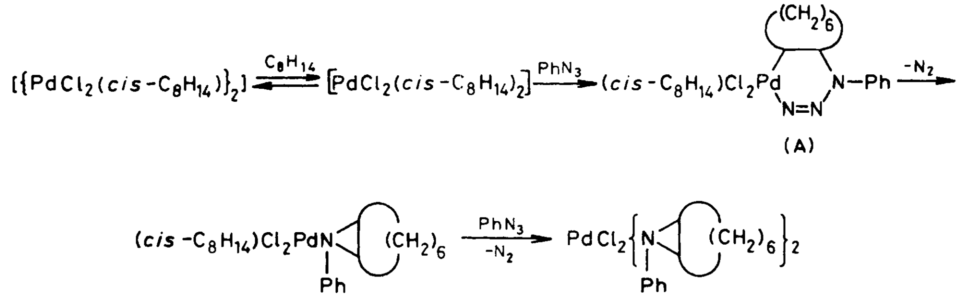


(1)



(2)

$$PdCl_2 + cis\text{-}C_8H_{14} \longrightarrow [\{PdCl_2(cis\text{-}C_8H_{14})\}_2] \xrightleftharpoons{C_8H_{14}} [PdCl_2(cis\text{-}C_8H_{14})_2] \qquad (3)$$



(A)

(4)

values of 0.039 and 0.054 respectively. The hydrogen-atom contributions were included in the final cycles of the refinement. Although many of the H atoms were detected in a Fourier difference map they were introduced in calculated positions and not refined.

A weighting scheme of the form $w_{h,k,l} = \sigma^{-2}(F_o)$ was employed where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (iI)^2]^{\frac{1}{2}}/Lp$ and i, an 'ignorance factor,' was equal to 0.05. Scattering factors and anomalous dispersion factors were taken from ref. 8. The final Fourier difference map showed residual peaks of 0.45 e Å^{-3} close to palladium and chloroform chlorine atoms. All the computations were carried out with a PDP11/34 computer using the Nonius Structure Determination Package (SDP).[9] Final atomic co-ordinates are given in Table 1.

Results and Discussion

Synthesis of the Complexes.—By reaction of phenyl azide with *cis*-cyclo-octene in the presence of palladium(II) chloride, the yellow-orange *trans*-dichlorobis(11-phenyl-9,10,11-triazabicyclo[6.3.0]undec-9-ene)palladium(II) has been obtained [equation (1)]. From the mother-liquor of the reaction, small amounts of an aziridine complex (see later) were also obtained.

As far as we know, this is the first example of a complex having a neutral triazoline as a ligand. The presence of *N*-cyclo-octylideneaniline in the mother-liquor was demonstrated. The triazoline complex proved to be rather stable, and it decomposed only upon reflux in toluene, to give however palladium metal and a complex mixture of organic products, as shown by thin-layer chromatography and by mass spectrometry. One of the products was *N*-cyclo-octylideneaniline. When the complex was heated under nitrogen at 70 °C in cyclo-octene for 6 h, and then left to cool overnight, no reaction was observed, which means that the triazoline complex is not an intermediate leading to the aziridine derivative (see later) by loss of dinitrogen. The reaction of the triazoline complex with triphenylphosphine in toluene at reflux gave *cis*-[$PdCl_2(PPh_3)_2$] and a mixture of organic products, from which *N*-cyclo-octylideneaniline was isolated by column chromatography. The thermal reaction between phenyl azide and *cis*-cyclo-octene gives the corresponding anil, *N*-cyclo-octylideneaniline [equation (2)], but not the corresponding aziridine, 9-phenyl-9-azabicyclo[6.1.0]nonane.[6] This reaction probably proceeds *via* the intermediate formation of the corresponding triazoline,[10] which is unstable at the temperature employed in the reaction. In the presence of palladium(II), this intermediate is trapped by co-ordination of N(9) to the metal centre, which prevents the subsequent loss of dinitrogen.

The reaction of phenyl azide with *cis*-C_8H_{14} to give the anil is not appreciably modified by the presence of $PdCl_2$. The metal atom thus does not manifest any catalytic activity in this reaction. *cis*-Cyclo-octene reacts with palladium(II) chloride to give the corresponding olefinic complex [equation (3)]. In the presence of excess of cyclo-octene, the isolable dimeric species is probably in equilibrium with the monomeric bis(olefinic) complex, although the equilibrium should be largely shifted to the left.[11]

It is difficult to decide which is the reactive species towards phenyl azide. When preformed [{$PdCl_2$(*cis*-C_8H_{14})}$_2$] was treated with phenyl azide in cyclo-octene the aziridine complex, *trans*-dichlorobis(9-phenyl-9-azabicyclo[6.1.0]nonane)palladium(II), was obtained [equation (4)]. This seems to suggest that when uncomplexed palladium(II) chloride is present in the reaction medium [equation (1)] it rapidly co-ordinates the triazoline slowly formed outside the co-ordination sphere of the metal. On the other hand, in the absence of uncomplexed $PdCl_2$ [equation (4)] the triazoline is not able to displace the olefin from the metal and it decomposes to the anil.

Under these conditions the preferred reaction at the metal centre should become attack of the azide on the co-ordinated olefin to give an intermediate such as (A), which by subsequent loss of dinitrogen gives the final aziridine complex. This finds some support from the isolation of a metallocycle derivative, obtained by the attack of phenyl azide on carbon monoxide co-ordinated to osmium.[12] However, the reaction of a nitrene species RN, formed outside the co-ordination sphere of the metal, with the bound alkene cannot be excluded, and in any case it is hazardous to propose a mechanism for such a complex reaction, which gives the products in low yields.

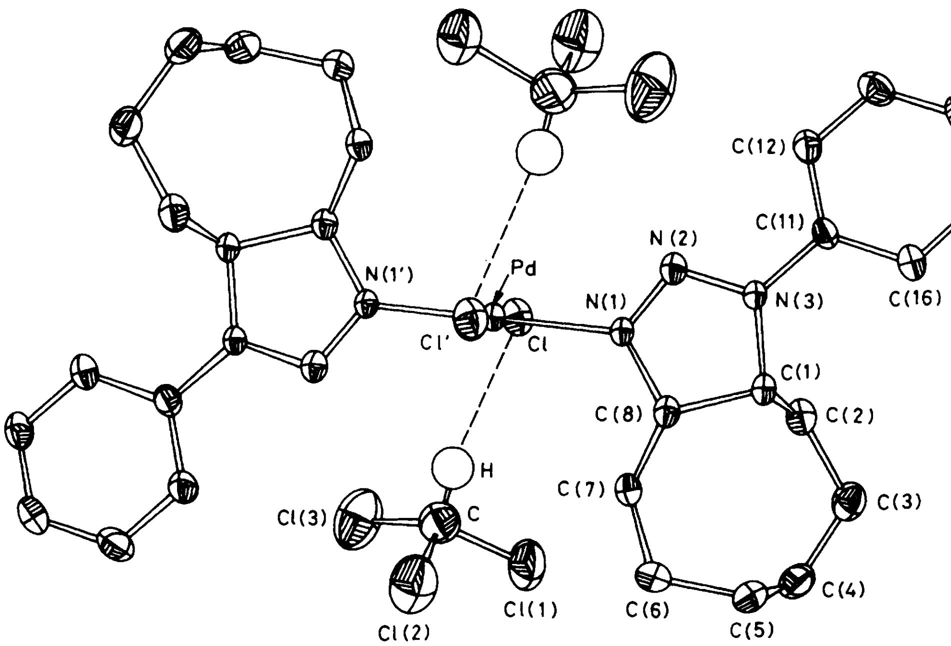
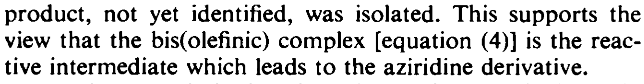


Figure. ORTEP view of *trans*-dichlorobis(11-phenyl-9,10,11-triazabicyclo[6.3.0]undec-9-ene)palladium(II)–chloroform (1/2). Thermal ellipsoids are drawn at 30% probability

By reaction of [{PdCl$_2$(*cis*-C$_8$H$_{14}$)}$_2$] with phenyl azide in chlorobenzene and without excess of the olefin, another product, not yet identified, was isolated. This supports the view that the bis(olefinic) complex [equation (4)] is the reactive intermediate which leads to the aziridine derivative.

In order to exclude that the anil was the organic ligand in the presumed aziridine complex, we have prepared a derivative of *N*-cyclo-octylideneaniline according to equation (5).



$$2[\mathrm{PdCl_2(PhCN)_2}] + 2\mathrm{PhN{=}\overline{C(CH_2)_6CH_2}} \longrightarrow [\{\mathrm{PdCl_2[PhN{=}\overline{C{-}(CH_2)_6{-}CH_2}]}\}_2] + 4\mathrm{PhCN} \quad (5)$$

The anil derivative showed i.r. and ^{1}H n.m.r. spectra substantially different from those observed for the aziridine complex.

Crystal and Molecular Structure of the Complex [PdCl$_2$-{N=N–N(Ph)–CH–CH–(CH$_2$)$_5$–CH$_2$}$_2$]·2CHCl$_3$.—The structure of the complex consists of discrete molecules of [PdCl$_2$-{N=N–N(Ph)–CH–CH–(CH$_2$)$_5$–CH$_2$}$_2$] packed in space group $P\bar{1}$; since the metal atom lies on the centre of symmetry chosen as the cell origin, the independent unit is half a molecule and a strictly planar *trans* conformation is imposed on the complex. Cavities left in the packing are occupied by ordered clathrated chloroform molecules, two per molecule of complex; as will be shown below, there appears to be an interaction, *via* a hydrogen bond, between the two species. Relevant bond distances, angles, and conformational parameters are listed in Table 2. An overall view of the complex is shown in the Figure; the particular projection has been chosen so as to show the orthogonality between the planes defined by the atoms of the inner co-ordination sphere [Pd,Cl,N(1)] and those of the 1,2,3-triazacycle.

The Pd–Cl bonds [2.298(1) Å] can be compared with the range of distances in *trans*-dichloropalladium complexes previously reported, 2.24 [13] to 2.30(2) Å; [14] a value statistically coincident with the present one has been found in *trans*-[PdCl$_2$(PhNO)$_2$].[15] The Pd–N(1) bond length [2.001(2) Å] also falls in the range observed for Pd–N(sp^2) distances, 1.961(11) [16] to 2.03(1) Å.[17] In *trans*-[PdCl$_2$(PhNO)$_2$] the Pd–N distance is 1.994(2) Å. The bond angles at the metal atom deviate slightly from 90° probably due to the packing forces.

The ligand consists of two fused rings. The N-substituted triazapentane ring exhibits quite a pronounced delocalization of the π system, involving the phenyl substituent. This can be appreciated when the covalent radius of nitrogen is computed from the mean length (1.49 Å) of the two C(sp^3)–N(sp^2) bonds C(8)–N(1) and C(1)–N(3): the covalent radius of nitrogen is then 0.72 Å, in good agreement with the bond length of 1.45 Å reported for hydrazine.[18] The N(1)–N(2) bond length [1.266(3) Å] is typical of a double bond (see ref. 19 and references therein); the N(2)–N(3) [1.331(3) Å] and N(3)–C(11) [1.412(3) Å] bonds are significantly shorter than single bonds although longer than double bonds. However, the phenyl ring does not show any significant deviation from D_{6h} symmetry as a result of the conjugation with the π system of the triazacycle.

The triazacyclopentane moiety deviates from planarity in a way that can be described in terms of the best plane passing through N(1),N(2),N(3),C(1) (see Table 3); atom C(8) is then 0.37 Å above this plane. The plane so defined makes a dihedral angle of 88° with the one passing through Pd,Cl,N(1); the almost perfect orthogonality between the two planes allows some degree of interaction between the π system on the ligand and donor orbitals on the metal atom. The fact that in the present complex, as well as in *trans*-[PdCl$_2$(PhNO)$_2$], the Pd–N bond does not have pure σ character is supported by the recent structure determination of a palladium(II) complex of the macrocyclic ligand 3,3,7,7,11,11,15,15-octamethyl-1,-9-dithia-5,13-diazacyclohexadecane:[20] in the latter the interactions of palladium with nitrogen belonging to secondary amine groups have a mean length of 2.09 Å.

The cyclo-octane moiety shows the effects of the strain which is inherent in saturated medium-sized rings. Although a considerable amount of work has been done on these systems, dealing with the calculation of strain energy and with

Table 2. Bond distances (Å) and angles (°)

Pd–Cl	2.298(1)	C(5)–C(6)	1.517(5)	N(1)–N(2)–N(3)	110.7(2)	C(1)–C(2)–C(3)	115.4(3)
Pd–N(1)	2.001(2)	C(6)–C(7)	1.514(5)	N(2)–N(3)–C(1)	112.2(2)	C(2)–C(3)–C(4)	117.4(3)
N(1)–N(2)	1.266(3)	C(7)–C(8)	1.514(4)	N(3)–C(1)–C(8)	98.2(2)	C(3)–C(4)–C(5)	116.2(3)
N(1)–C(8)	1.489(3)	N(3)–C(11)	1.412(3)	C(8)–N(1)–N(2)	111.1(2)	C(4)–C(5)–C(6)	115.7(3)
N(2)–N(3)	1.331(3)	C(11)–C(12)	1.371(4)	N(2)–N(3)–C(11)	120.5(2)	C(5)–C(6)–C(7)	116.4(3)
N(3)–C(1)	1.482(3)	C(12)–C(13)	1.393(4)	C(1)–N(3)–C(11)	126.7(2)	C(6)–C(7)–C(8)	114.0(3)
C(1)–C(8)	1.540(4)	C(13)–C(14)	1.379(5)	N(3)–C(11)–C(12)	120.3(3)	C(7)–C(8)–C(1)	119.7(2)
C(1)–C(2)	1.529(4)	C(14)–C(15)	1.370(5)	N(3)–C(11)–C(16)	119.1(3)	N(1)–C(8)–C(7)	111.0(2)
C(2)–C(3)	1.526(5)	C(15)–C(16)	1.389(4)	C(11)–C(12)–C(13)	119.5(3)	N(3)–C(1)–C(2)	110.7(2)
C(3)–C(4)	1.517(5)	C(16)–C(11)	1.399(4)	C(12)–C(13)–C(14)	120.3(3)	Cl(1)–C–Cl(2)	108.9(2)
C(4)–C(5)	1.527(6)			C(13)–C(14)–C(15)	119.9(3)	Cl(1)–C–Cl(3)	112.2(3)
C–Cl(1)	1.726(5)	C–H	1.12	C(14)–C(15)–C(16)	120.8(3)	Cl(2)–C–Cl(3)	108.9(3)
C–Cl(2)	1.744(5)	H · · · Cl	2.48	C(15)–C(16)–C(11)	118.7(3)	C–H · · · Cl	165
C–Cl(3)	1.730(5)						

Torsional angles (°) within the cyclo-octane moiety

C(2)–C(1)–C(8)–C(7)	26.5	C(2)–C(3)–C(4)–C(5)	−66.0	C(5)–C(6)–C(7)–C(8)	−59.2
C(8)–C(1)–C(2)–C(3)	−94.7	C(3)–C(4)–C(5)–C(6)	102.3	C(6)–C(7)–C(8)–C(1)	76.3
C(1)–C(2)–C(3)–C(4)	70.4	C(4)–C(5)–C(6)–C(7)	−50.8		

Table 3. Weighted least-squares planes in the form $Ax + By + Cz + D = 0$

(*a*) Equations of planes through selected groups of atoms

Plane	Atoms	*A*	*B*	*C*	*D*
1	Pd,Cl,N(1)	0.5371	−0.5948	−0.5982	0.000
2	N(1),N(2),N(3),C(1)	−0.6702	0.0794	−0.7380	0.0094
3	C(11),C(12),C(13),C(14),C(15),C(16)	−0.6373	0.0662	−0.7678	−0.0111

(*b*) Distances (Å × 10^3) of selected atoms from planes

Plane	
2	C(1) 24(3), N(1) −28(3), N(2) 48(3), N(3) −44(3), C(8) −365(3), C(11) −6(4), Pd −9(0)
3	C(11) 13(3), C(12) −1(4), C(13) −11(4), C(14) 11(4), C(15) 2(4), C(16) −14(4), N(3) 6(3), C(1) 141(3), C(8) −247(3)

(*c*) Angles (°) between selected pairs of planes

1—2	88.0	2—3	2.7

indirect structural studies, mainly by n.m.r. spectroscopy, very few definitive *X*-ray structural results have been reported so far (see ref. 21 and references therein). The amount of strain in the present ring can be appreciated from the angles at each carbon atom (mean C–C–C 116.5°); as an effect of this strain, the mean C–C bond length is slightly shorter (1.52 Å) than expected. These results agree nicely with those found for cyclo-octane-1,5-diol.[21] The conformation of the cyclo-octane ring is quantitatively described in Table 2, where the eight torsion angles are reported. The conformation around the C(1)–C(8) bond is synperiplanar (*sp*) (θ = 26.5°) as in the parent cyclo-octene, and the sequence of conformation angles observed here (*sp*, *ac*, *ac*, *ac*, *sc*, *sc*, *ac*) (*ac* = anticlinal, *sc* = synclinal) probably describes also the conformation of the unsaturated hydrocarbon, starting from the double bond.

In the final difference Fourier a peak of 0.4 e Å^{-3} is observed in the proximity of the carbon atom of the $CHCl_3$ clathrated molecule; the distance from the carbon atom and the quite regular pattern of angles this vector makes with C–Cl bonds are appropriate for the hydrogen atom of chloroform. This peak lies 2.48 Å from the chlorine atom bonded to palladium and since a van der Waals interaction between chlorine and hydrogen atoms would be *ca.* 2.8—2.9 Å, there is good evidence for a hydrogen bond connecting the chloroform molecules to the complex; the C–H · · · Cl interaction is roughly linear (165°) as can be appreciated from the Figure.

Conclusions

Although the palladium derivatives employed here have not shown any catalytic activity in the reaction of phenyl azide with *cis*-cyclo-octene, nevertheless, the metal is able to direct the reaction of the azide with the co-ordinated olefin. In fact the aziridine is formed within the co-ordination sphere of the metal, while in the absence of palladium, *N*-cyclo-octylideneaniline is the product of the reaction. Moreover the metal centre stabilizes by co-ordination of 11-phenyl-9,10,11-triazabicyclo[6.3.0]undec-9-ene, preventing the subsequent loss of dinitrogen. Other attempts to find transition-metal complexes able to catalyze the reaction of phenyl azide with olefins have been unsuccessful. Derivatives such as $[\{RhCl(olefin)_2\}_2]$ decompose during the reaction, and work is in progress to stabilize with the appropriate ligand the presumed reactive intermediate.

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