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# Synthesis and characterization of rhodium complexes [Rh(Az)(L)Cl] (Az = 2,2-dimethyl-3-phenyl-3-allylaziridine; L = $C_2H_4$, CO, or $PPh_3$). Crystal and molecular structure of [Rh(Az)(CO)Cl]

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## Abstract

2,2-Dimethyl-3-phenyl-3-allylaziridine (Az) reacts with Cramer's complex [{Rh($C_2H_4$)$_2$Cl}$_2$] to give [Rh(Az)($C_2H_4$)Cl]. This new complex is transformed by carbon monoxide into [Rh(Az)(CO)Cl], which can be also prepared starting from [{Rh($CO_2$)Cl}$_2$]. The crystal and molecular structure of this carbonyl species has been fully solved by X-ray diffraction, providing the first example of a complex with bidentate aziridine. The ethylene complex reacts with one equivalent of triphenylphosphine to give [Rh(Az)($PPh_3$)Cl]. A second equivalent of phosphine does not create a monodentate aziridine, but displaces this ligand. Similar behaviour is observed with the carbonyl complex which gives free aziridine and *trans*-[Rh(CO)($PPh_3$)$_2$Cl].

## Introduction

The chemistry of aziridines, three-membered nitrogen heterocycles, has received continuous study, due to the potential reactivity [1] and use in therapy [2] of these compounds, for example in AIDS treatment [3]. More recently, their coordination chemistry has been developed in two main directions: the first deals with the use of aziridines as substrates in catalytic reactions, e.g. the work of Alper *et al.* [4]; the second concerns transition metal complexes for selectively targeting hypotoxic tumour cells [5]. However, most work concerns the simplest member of the series, namely ethylenimine (**1**).

Our interest in the synthesis and reactivity of substituted aziridines, specially those bearing unsaturated groups on one of the carbon atoms [6], prompted us to examine their applications in coordination chemistry. Such unsaturated aziridine

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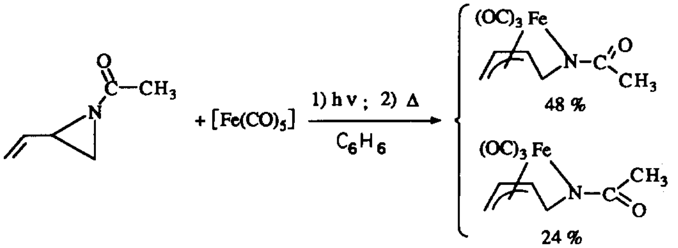
transition-metal complexes have been scarcely mentioned in the literature. The light-induced reaction of 2-vinylaziridines with pentacarbonyliron to give a mixture of stereoisomer iron complexes (eq. 1) [7], and the rearrangement of the 1,3-butadienyl-*N*-tosylaziridine in the presence of $[Pd(PPh_3)_4]$ to give a vinylpyrrolidine derivative (eq. 2) [8] have been described.



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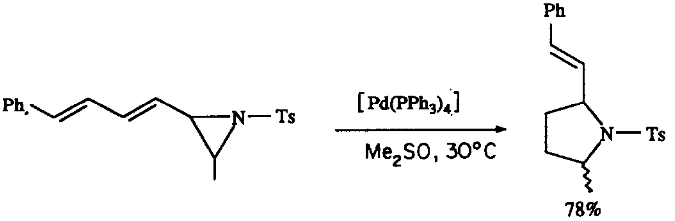

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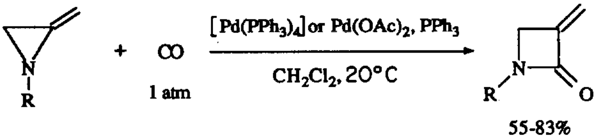
The carbonylation reactions of unsaturated *N*-substituted aziridines, also catalysed by palladium complexes, to produce azetidinones (eq. 3) [4b], (eq. 4 [9]) have also been reported.



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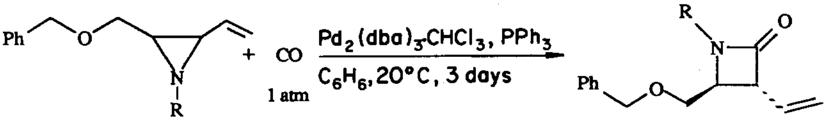

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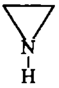
In the present work, the choice of allylaziridine (**2**) (Az) was dictated by the possibility of formation of a hybrid bidentate ligand with two coordination sites, the hard nitrogen atom and the soft double bond allowing chelation.

We first examined rhodium, because of its nuclear spin ($I = 1/2$) and its activity in various catalytic reactions [4].



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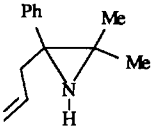


**2**

## Results and discussion

Cramer's complex, $[\{Rh(C_2H_4)_2Cl\}_2]$, is the best precursor for ligand-substitution reactions because of the lability of volatile ethylene. When 2 equiv. of aziridine **2** are added to a suspension of $[\{Rh(C_2H_4)_2Cl\}_2]$ in toluene, gas is evolved and a yellow precipitate is formed. Elemental analysis of this solid is consistent with the formula $[Rh(Az)(C_2H_4)Cl]$ (**3**). The infrared spectrum (Nujol mull) exhibits $\nu$(NH) at 3150 $cm^{-1}$, a strong bathochromic shift in comparison with the free ligand ($\nu$(NH) = 3250 $cm^{-1}$). This is a good indication of the bonding of the NH group to the metal. The C=C stretching band of the free Az ($\nu$(C=C) = 1645 $cm^{-1}$) decreases to 1449 $cm^{-1}$ in the complex, as expected for a double bond coordinated to a metallic centre.

The protons of the ethylene ligands give rise to a doublet in the $^1H$ NMR spectrum at $\delta$ 3.41 ppm ($^2J$(Rh–H) = 1.6 Hz). The olefinic protons of the aziridine are strongly shielded, changing from $\delta$ 4.90 ($CH_2$) and 5.70 ppm (CH) in the free Az to a multiplet ranging from $\delta$ 3.0 to 3.16 ppm in the complex, consistent with coordination of the allylic double bond to the rhodium. Another remarkable feature of the spectrum is the strong deshielding of one of the methyl groups, corresponding to a disposition of this substituent on the same side of the aziridine plane as the metal.

The $^{13}C\{^1H\}$ NMR spectrum is consistent with these results, the resonances of the carbon atoms of the double bond shifting upon coordination from $\delta$ 117.5 ($=CH_2$) and 140.5 ppm ($=CH-$) to 54.7 and 74.9 ppm, respectively, and split by coupling with rhodium ($^1J$(C–Rh) = 15 Hz for $=CH_2$ and 12.5 Hz for $=CH-$). The carbon atoms of the ethylene appear as a doublet at $\delta$ 68.7 ppm ($^1J$(C–Rh) = 10.5 Hz).

All these data are consistent with an olefinic rhodium(I) complex containing one molecule of aziridine **2** acting as a bidentate chelating ligand, but there is no clear indication of the relative positions of the ligands.

In order to explore this, the complex **3** was dissolved in dichloromethane and kept under 1 atm of carbon monoxide for 1 h. A new orange complex **4** was isolated from the reaction mixture. Elemental analysis is consistent with the formula [Rh(Az)(CO)Cl]. The same complex was prepared from $[\{Rh(CO)_2Cl\}_2]$ and 2 equiv. of aziridine **2**.

The infrared spectrum of the resulting solid (Nujol mull) is quite intriguing, since two $\nu$(NH) (3280 and 3180 $cm^{-1}$) and two $\nu$(CO) (2020 and 2000 $cm^{-1}$) bands are observed in the solid state. In $CCl_4$ solution there is only one NH (3180 $cm^{-1}$) and one CO (2015 $cm^{-1}$) stretching band. The relatively high value of $\nu$(CO) may mean that the nitrogen atom is *trans* to the carbonyl ligand, as it compares well with the values observed by Maisonnat *et al.* [10] for [Rh(CO)LL′] (L = 2,6-dimethylpyridine; L′ = $PMe_3$, $\nu$(CO) = 1979 $cm^{-1}$; $PMe_2Ph$, $\nu$(CO) = 1981 $cm^{-1}$). The $^1H$ and $^{13}C\{^1H\}$ NMR spectra are comparable to those of complex **3**. The carbonyl resonance appears in the $^{13}C\{^1H\}$ NMR spectrum as a doublet at $\delta$ 183.9 ppm ($^1J$(C–Rh) = 69 Hz), a normal value.

The carbonyl complex **4** differs from the olefin congener **3**, being more air- and moisture-stable, and more soluble in common organic solvents, allowing the formation of single crystals suitable for an X-ray diffraction study.

Most structural studies of aziridine complexes [5,11,12], relate to the simplest aziridine, **1**, the metal stabilizing the highly reactive ethylenimine. The first structure determination was of a rhodium(III) complex, *trans*-$[Rh(C_2H_4NH)_4I_2]I$ [11], the second of platinum(II) complexes, *cis*- and *trans*-$[Pt(C_2H_4NH)_2Cl_2]$ [12] and the most recent of a cobalt(III) species *trans*-$[Co(C_2H_4NH)_4(NO_2)_2]Br \cdot 2H_2O \cdot LiBr$ [5].

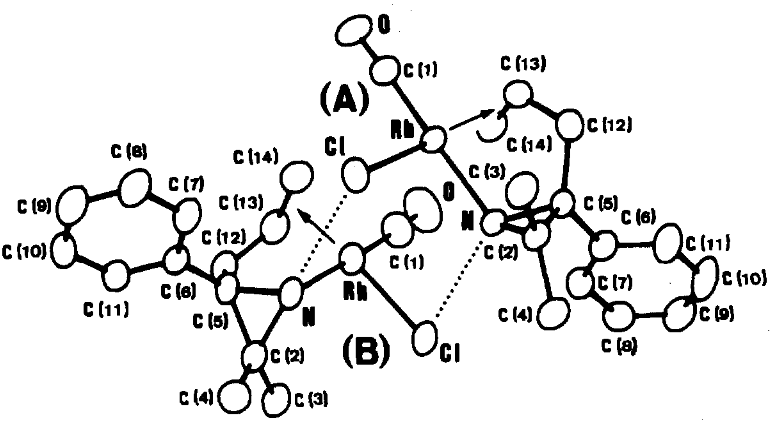
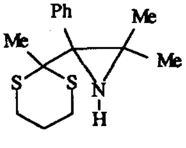


Fig. 1. ORTEP representation of the two independent molecules of the complex [Rh(Az)(CO)Cl] (4) with atomic lettering and numbering. Hydrogen contacts are drawn with dotted lines.

Complex **4** has two different molecules of [Rh(Az)(CO)Cl] in the unit cell as shown in Fig. 1 [13]. The two distinct molecules in the solid state explain the abnormal splitting observed for the NH and CO stretching bands in the infrared spectrum. Selected bond distances and angles are listed in Table 1.

Figure 1 clearly demonstrates the bidentate character of the allylaziridine and shows the relative positions of the ligands around the rhodium: each hard donor is in the *trans*-position to a soft one, according to the antisymbiotic rule of Pearson [14], nitrogen atom *trans* to CO and chloro *trans* to the double bond. Such behaviour has been observed for other rhodium complexes with hybrid P,N ligands [15]. There are weak hydrogen interactions between the chlorine atom of one molecule and the hydrogen atom of the NH group of the other molecule N–H ··· Cl (see Table 1 and Fig. 2). The coordination polyhedron formed by the nitrogen atom, the carbon atom of the carbonyl and the midpoint M* of the C=C double bond is substantially square planar, more distorted in molecule **A** than in molecule **B**. The double bond is nearly perpendicular to the mean coordination plane (8° between the C=C axis and the normal to the plane) as expected for a olefinic $\pi$-bound ligand. The dihedral angle between the latter plane and the plane of the aziridine ring is 50.3° for molecule **A** and 54.5° for **B**. Such an arrangement is dictated by the distorted tetrahedral geometry around the nitrogen atom, as can be seen from Table 1. The distances between the rhodium and its closest neighbours Cl, N, C(12) and C(13) are in the range generally observed for rhodium(I) complexes.

Judging by 2,2-dimethyl-3-phenyl-3-(2′-methyl-1′,3′-dithiane)-aziridine (**5**) [16], which is very similar to the allylaziridine **2**, for which detailed structural data are not to hand, distances in the ring only change slightly on complexation. The



**5**

Table 1

Bond lengths (Å) and angles (deg) with e.s.d.s in parentheses

| | Molecule A | Molecule B |
|---|---|---|
| Rh-Cl | 2.347(2) | 2.370(2) |
| Rh-N | 2.093(4) | 2.092(5) |
| Rh-C(1) | 1.824(7) | 1.817(8) |
| Rh-M*[a] | 2.010(7) | 2.014(7) |
| Rh-C(13) | 2.131(7) | 2.140(6) |
| Rh-C(14) | 2.122(7) | 2.122(7) |
| C(1)-O | 1.137(8) | 1.136(11) |
| N-C(2) | 1.504(7) | 1.493(7) |
| N-H(N) | 0.97(3) | 0.97(4) |
| N-C(5) | 1.505(7) | 1.491(7) |
| C(2)-C(3) | 1.518(7) | 1.509(8) |
| C(2)-C(4) | 1.502(8) | 1.501(9) |
| C(2)-C(5) | 1.506(8) | 1.491(8) |
| C(5)-C(6) | 1.504(7) | 1.508(8) |
| C(6)-C(7) | 1.385(8) | 1.383(8) |
| C(7)-C(8) | 1.386(8) | 1.393(8) |
| C(8)-C(9) | 1.349(10) | 1.355(10) |
| C(9)-C(10) | 1.362(10) | 1.376(9) |
| C(10)-C(11) | 1.373(10) | 1.383(9) |
| C(11)-C(6) | 1.368(9) | 1.371(9) |
| C(5)-C(12) | 1.530(8) | 1.505(8) |
| C(12)-C(13) | 1.495(9) | 1.515(10) |
| C(13)-H(C13) | 0.97(4) | 0.97(4) |
| C(13)-C(14) | 1.386(9) | 1.389(10) |
| C(14)-H1(C14) | 0.97(4) | 0.97(3) |
| C(14)-H2(C14) | 0.97(2) | 0.97(4) |
| Cl-Rh-N | 92.7(1) | 90.5(1) |
| Cl-Rh-C(1) | 91.3(2) | 93.2(3) |
| Cl-Rh-M* | 170.9(2) | 172.7(2) |
| N-Rh-C(1) | 175.2(2) | 175.7(3) |
| N-Rh-M*[a] | 82.7(2) | 83.2(2) |
| C(1)-Rh-M*[a] | 93.7(3) | 93.0(3) |
| Cl-Rh-C(13) | 152.5(2) | 155.9(2) |
| Cl-Rh-C(14) | 168.6(2) | 164.3(2) |
| N-Rh-C(13) | 81.6(2) | 81.3(2) |
| N-Rh-C(14) | 84.6(2) | 85.9(2) |
| C(1)-Rh-C(13) | 96.0(3) | 94.5(3) |
| C(1)-Rh-C(14) | 90.9(3) | 91.1(3) |
| C(13)-Rh-C(14) | 38.0(2) | 38.0(3) |
| Rh-C(1)-O | 175.5(6) | 176.5(7) |
| Rh-N-C(2) | 129.2(3) | 125.8(3) |
| Rh-N-H(N) | 116(3) | 120(3) |
| Rh-N-C(5) | 113.8(3) | 114.5(3) |
| C(2)-N-H(N) | 110(3) | 108(3) |
| C(2)-N-C(5) | 60.1(3) | 59.9(4) |
| H(N)-N-C(5) | 117(3) | 114(3) |
| N-C(2)-C(3) | 115.8(4) | 114.6(5) |
| N-C(2)-C(4) | 115.5(4) | 117.3(5) |
| N-C(2)-C(5) | 60.0(3) | 60.0(4) |
| C(3)-C(2)-C(4) | 113.9(5) | 113.4(5) |
| C(3)-C(2)-C(5) | 122.6(5) | 120.8(5) |
| C(4)-C(2)-C(5) | 117.9(4) | 120.1(5) |

Table 1 (continued)

| | Molecule A | Molecule B |
|---|---|---|
| N-C(5)-C(2) | 59.9(3) | 60.1(4) |
| N-C(5)-C(6) | 118.8(4) | 118.6(4) |
| N-C(5)-C(12) | 110.6(4) | 112.5(5) |
| C(2)-C(5)-C(6) | 120.1(4) | 118.4(5) |
| C(2)-C(5)-C(12) | 119.2(4) | 119.1(4) |
| C(6)-C(5)-C(12) | 115.7(5) | 116.2(4) |
| C(5)-C(6)-C(7) | 123.0(5) | 123.7(5) |
| C(5)-C(6)-C(11) | 119.0(5) | 118.7(5) |
| C(7)-C(6)-C(11) | 117.9(5) | 117.5(5) |
| C(6)-C(7)-C(8) | 120.3(6) | 121.0(6) |
| C(7)-C(8)-C(9) | 120.9(6) | 120.4(6) |
| C(8)-C(9)-C(10) | 118.8(6) | 119.4(6) |
| C(9)-C(10)-C(11) | 121.4(8) | 120.1(6) |
| C(10)-C(11)-C(6) | 120.7(6) | 121.6(5) |
| C(5)-C(12)-C(13) | 112.5(5) | 113.1(5) |
| C(12)-C(13)-C(14) | 122.7(5) | 122.5(6) |
| C(12)-C(13)-Rh | 107.3(4) | 108.2(4) |
| C(12)-C(13)-H(C13) | 119(3) | 109(3) |
| C(14)-C(13)-Rh | 70.6(4) | 70.3(4) |
| C(14)-C(13)-H(C13) | 116(3) | 126(3) |
| Rh-C(13)-H(C13) | 107(3) | 111(3) |
| C(13)-C(14)-Rh | 71.3(4) | 71.7(4) |
| C(13)-C(14)-H1(C14) | 119.(3) | 123(3) |
| C(13)-C(14)-H2(C14) | 118(3) | 121(3) |
| Rh-C(14)-H1(C14) | 108(3) | 107(3) |
| Rh-C(14)-H2(C14) | 113(4) | 112(3) |
| H1(C14)-C(14)-H2(C14) | 117(4) | 112(4) |
| *Hydrogen contacts* | | |
| N(A)...Cl(B) 3.302(5) | N(B)...Cl(A) | 3.427(5) |
| H(NA)...Cl(B) 2.39(3) | H(NB)...Cl(A) | 2.72(5) |
| N(A)-H(NA)...Cl(B) 157(4) | N(B)-H(NB)...Cl(A) | 131(4) |

[a] M* is the midpoint of the C(13)-C(14) bond.

N-C(2) and N-C(5) distances range from 1.465(3) and 1.480(3) Å in **5** to 1.504(7) and 1.505(7) Å for the ligand **2** in complex **A** and 1.493(7) and 1.491(7) Å in **B**, respectively. The C(2)-C(5) distance in the ring is 1.499(3) Å in **5** and 1.506(8) Å in molecule A and 1.491(8) Å in molecule B of **4**. Contrary to what is observed for the complexes of ethylenimine **1** [5], complexation is accompanied by a shortening of the C-C bond. The C(13)-C(14) distance (1.386(9) Å in **A** and 1.389(10) Å in **B**) is longer that the usual C=C double bond (1.337 Å) [17], as expected of its coordination to the rhodium.

Having determined the structure by X-ray measurements, we tried to obtain the monodentate mode by addition of a good donor such as triphenylphosphine, which is known to displace coordinated olefins easily.

The addition of 1 equiv. of triphenylphosphine to the olefinic complex **3** gives the corresponding phosphine complex [Rh(Az)(PPh$_3$)Cl] (**6**). This complex has been characterized in the infrared spectrum by a slight shift of $\nu$(NH) (3160 cm$^{-1}$) and in the $^{31}$P{$^1$H} NMR spectrum by a doublet ($\delta$ 52.8 ppm, $^1J$(P-Rh) = 163 Hz).

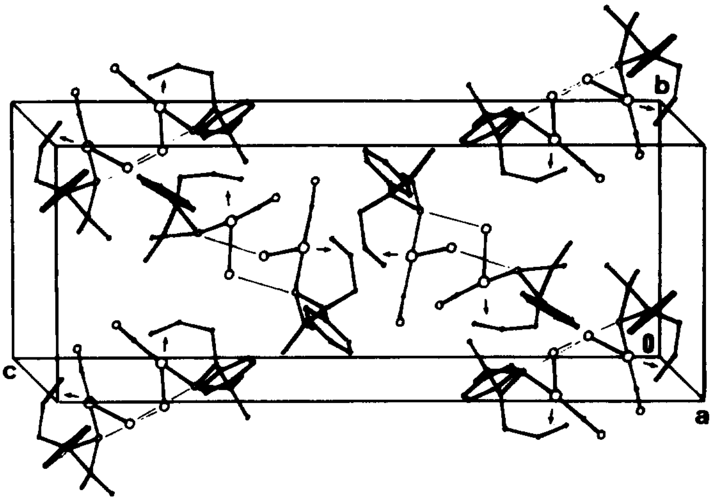
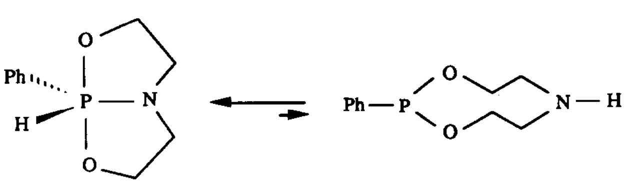


Fig. 2. Molecular packing of the complex [Rh(Az)(CO)Cl] (4) in the unit cell. Hydrogen contacts are drawn with thin lines.

Addition of a second equivalent of triphenylphosphine induces the displacement of the aziridine ligand, without any evidence for a monodentate intermediate.

A similar reaction was carried out with the carbonyl complex **4**. When 2 equiv. of phosphine are added per rhodium, free aziridine **2** is detected and the complex *trans*-$[Rh(PPh_3)_2(CO)Cl]$ (**7**) is formed, as proved by infrared spectroscopy ($\nu$(CO) = 1966 $cm^{-1}$) and $^{31}P\{^1H\}$ NMR spectroscopy ($\delta = +29.2$ ppm, $^1J$(P–Rh) = 129.4 Hz; literature [18]: $\nu$(CO) = 1962 $cm^{-1}$; $\delta = +28.9$ ppm, $^1J$(P–Rh) = 129.4 Hz).

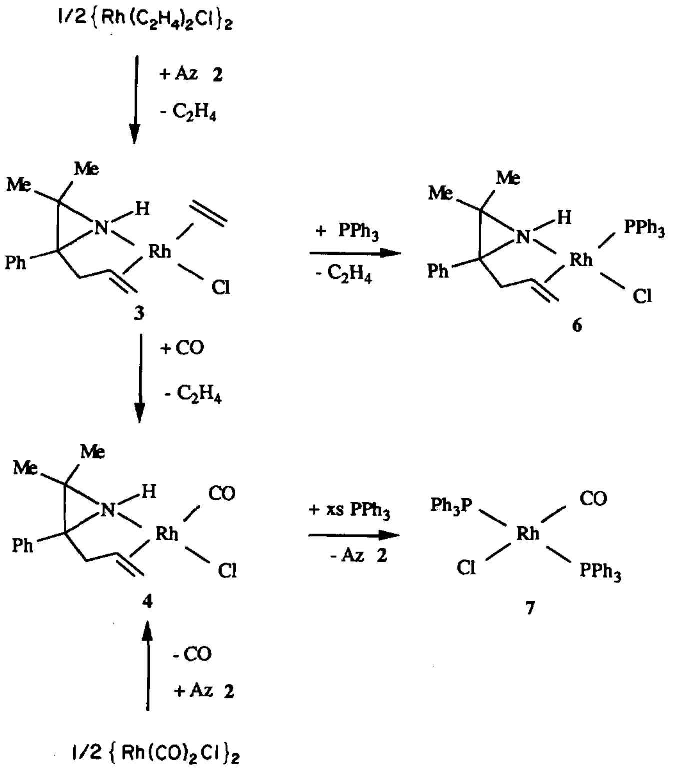
The reactions described in this paper are summarized in Scheme 1. All attempts to force monodentate behaviour of **2** have failed. Such a feature has already been observed for another hybrid ligand, the cyclic aminophosphonite **8a**, which always acts as a chelating ligand in rhodium(I) complexes [19]. Nevertheless, the aminophosphonite is monodentate in cobalt [20] and palladium [21] complexes. We plan a study of allylic aziridine in the presence of these two metals.



**8b**

**8a**

Some preliminary experiments have already been carried out using complex **4** for the catalytic hydroformylation of styrene. In our experimental conditions, the activity and the selectivity do not show any special features, but an interesting property of this system is that it does not need the addition of an amine to be active. We are currently developing some catalytic applications of our aziridine complexes, and the results will appear in a further paper.



Scheme 1.

## Experimental

All the experiments have been carried out under an argon atmosphere by standard Schlenk tube technique. All solvents have been dried by standard methods and distilled under argon before use. The starting materials, allylaziridine **2** [6], Cramer's complex [22], and [$\{Rh(CO)_2Cl\}_2$] [23], have been prepared according to literature methods. Spectroscopic measurements have been performed with the following equipment:

IR: Perkin-Elmer 597 and FT-IR 1725 X (Nujol mull or film between KBr plates)

$^{1}H$ and $^{13}C$ NMR: Bruker AC 200 ($^{1}H$, 200.13 MHz; $^{13}C$, 50.32 MHz, TMS as external standard)

$^{31}P$ NMR: Bruker WH 90 (36.43 MHz, $H_3PO_4$ 85% in $D_2O$ as external/internal standard, in a coaxial capillary tube).

Elemental analyses were obtained from the Service d'Analyse du Laboratoire de Chimie de Coordination and from the Service Central d'Analyse du CNRS in Solaize.

Figure 3 gives the atom numbering for the description of NMR spectra. Note that this scheme differs from that used in the nomenclature and from that used in the structural determination.

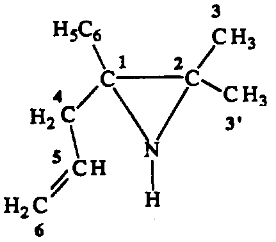


Fig. 3. Numbering scheme of the carbon atoms for NMR spectra.

### *[Rh(Az)($C_2H_4$)Cl] (3)*

A solution of aziridine **2** (385 mg, 2.1 mmol) in toluene (5 ml) was added dropwise to a suspension of [{Rh($C_2H_4$)$_2$Cl}$_2$] (400 mg, 1.03 mmol) in the same solvent (10 ml). Gas evolved and a yellow solid was precipitated within a few minutes. The precipitate was filtered off, washed with toluene and dried *in vacuo*. Yield: 351 mg (50%). Anal. Found: C, 50.76; H, 6.41; N, 3.67. $C_{15}H_{21}ClNRh$ (353.70) calc.: C, 50.94; H, 5.98 N, 3.96%. IR (KBr pellet): $\nu$(NH) 3150; $\nu$(C=C) 1645 $cm^{-1}$. NMR ($CDCl_3$) $\delta(^1H)$ 0.98 (s, 3H, H3); 1.70 (s, 1H, NH); 1.98–2.12 (m, 2H, H4); 2.07 (s, 3H, H3'); 3.03–3.16 (m, 3H, H5 + H6); 3.41 (d, $^2J$(H–Rh) = 1.6 Hz, 4H, $C_2H_4$); 7.05–7.33 (m, 5H, Ph). $\delta(^{13}C)$ 23.3 (C3); 23.7 (C3'); 38.6 (C4); 49.0 (C2); 54.7 (d, $^1J$(C–Rh) = 15.1 Hz, C6); 54.9 (C1); 68.7 (d, $^1J$(C–Rh) = 10.5 Hz, $C_2H_4$); 74.9 (d, $^1J$(C–Rh) = 12.6 Hz, C5); 122.8; 126.0; 127.5; 128.8; 140.6 (Ph).

### *[Rh(Az)(CO)Cl] (4)*

A solution of aziridine **2** (480 mg, 2.56 mmol) in toluene (5 ml) was added dropwise to a red suspension of [{Rh(CO)$_2$Cl}$_2$] (500 mg, 1.28 mmol) in the same solvent (10 ml). Gas evolved and the colour turned yellow. After 1 h, the solution was evacuated to dryness and the solid was then dissolved in dichloromethane (2 ml). Hexane (20 ml) was added and the yellow-orange precipitate formed was filtered off, dried *in vacuo* and washed with hexane. Yield: 835 mg (92%). Anal. Found: C, 47.37; H, 5.08; N, 4.05. $C_{14}H_{17}ClNORh$ (353.64) calc.: C, 47.55; H, 4.85; N, 3.96%. IR (Nujol mull, $cm^{-1}$): $\nu$(NH) 3180, 3280; $\nu$(CO) 2020, 2000. IR ($CCl_4$ solution): $\nu$(NH) 3180; $\nu$(CO) 2015; $\nu$(C=C) 1447 $cm^{-1}$. NMR ($CDCl_3$): $\delta(^1H)$ 0.96 (s, 3H, H3); 1.85 (s, 3H, H3'); 2.50 (d, $^2J$(4–4') = 15.8 Hz, 1H, H4); 2.91 (s, 1H, NH), 3.13 (dd, $^2J$(4–4') = 15.8 Hz, $^3J$(4'–5) = 5.5 Hz, 1H, H4'); 3.44–3.51 (m, 2H, H6); 4.29–4.43 (m, 1H, H5); 7.22–7.40 (m, 5H, Ph). $\delta(^{13}C)$ 23.1 (C3); 23.3 (C3'); 38.3 (C4); 49.2 (C2); 52.9 (d, $^1J$(C–Rh) = 13.7 Hz, C6); 53.4 (C1); 73.9 (d, $^1J$(C–Rh) = 13.6 Hz, C5); 126.2; 127.7; 128.9; 140.1 (Ph); 183.9 (d, $^1J$(C–Rh) = 69.3 Hz, CO).

### *[Rh(Az)($PPh_3$)Cl] (6)*

A solution of triphenylphosphine (115 mg, 0.44 mmol) in dichloromethane (4 ml) was added to a solution of [Rh(Az)($C_2H_4$)Cl] (165 mg, 0.44 mmol) in the same solvent (6 ml). The solution turned immediately from yellow to red and gas evolved. The solution was then evacuated to dryness *in vacuo*, giving a yellow-orange solid. Yield: 250 mg (97%). IR (Nujol): $\nu$(NH) = 3160 $cm^{-1}$. NMR ($CDCl_3$): $\delta(^1H)$ 0.98 (s, 3H, H3); 1.24 (s broad, 1H, NH); 1.54–1.98 (m, 2H, H4); 2.09 (s, 3H, H3'); 2.48–2.59 (m, 2H, H6); 2.57–2.98 (m, 1H, H5). $\delta(^{13}C)\{^1H\}$ 23.5 (C3); 23.6

(C3′); 38.5 (C4); 44.5 (d, $^1J$(C–Rh) = 16 Hz, C6); 47.9 (C2); 53.3 (C1); 62.4 (d, $^1J$(C–Rh) = 16 Hz, C5); 126.3–134.6 (m, Ph). ($CH_2Cl_2$): $\delta(^{31}P)$ +52.8 (d, $^1J$(P–Rh) = 163.2 Hz).

Table 2

Structure determination summary

| | |
|---|---|
| *Crystal data* | |
| Formula | $C_{14}H_{17}ClNORh$ |
| Colour, habit | Orange–red, parallelepiped |
| Crystal size (mm) | 0.500 × 0.150 × 0.125 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ (No. 14) |
| Unit cell dimensions | $a = 10.649(2)$ Å<br>$b = 10.784(2)$ Å, $\beta = 99.89(1)°$<br>$c = 26.823(3)$ Å |
| Volume (Å$^3$) | 3034.4(9) |
| $Z$ | 8 |
| Formula weight | 353.65 |
| Density (calc.) (g cm$^{-3}$) | 1.548 |
| Absorption coefficient (mm$^{-1}$) | 1.20 |
| $F(000)$ | 1424 |
| *Data collection* | |
| Diffractometer used | Enraf–Nonius CAD4 |
| Radiation | Mo-$K_\alpha$ ($\lambda = 0.71073$ Å) |
| Temperature (K) | 293 |
| Monochromator | Highly oriented graphite crystal |
| $2\theta$ range (deg) | 3.0–48.0 |
| Scan type | $\omega - 2\theta$ |
| Scan range | $(0.80 + 0.35 \tan\theta)°$ |
| Scan speed | Variable: 0.92–5.49°/min in $\omega$ |
| Standard reflections: | |
| Intensities | 3 measured every 2 h |
| Orientations | 3 checked every 400 reflections |
| Index ranges | $0 \le h \le 12$, $0 \le k \le 12$, $-30 \le l \le 30$ |
| Reflections collected | 5031 |
| Independent reflections | 4760 ($R_{av} = 0.022$ on $I$) |
| Observed reflections | 3123 [$I > 3\sigma(I)$] |
| *Solution and refinement* | |
| Solution | Direct methods |
| Refinement method | Full-matrix least-squares |
| Quantity minimized | $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ |
| Hydrogen atoms | Riding model, isotropic $U$ |
| Weighting scheme | $w = 1/[\sigma^2(F_o) + 0.001062F_o^2]$ |
| No. of parameters refined | 349 |
| Final $R$ indices | $R = 0.033$, $R_w = 0.043$ |
| Goodness of fit | 0.99 |
| Largest and mean $\Delta/\sigma$ | 0.009, 0.001 |
| Data-to-parameter ratio | 8.9 : 1 |
| Largest difference peak (e Å$^{-3}$) | 0.50 on Rh(B) atom |

### *Crystallography*

Orange-red crystals of the complex [Rh(Az)(CO)Cl] (**4**) suitable for an X-ray diffraction study, were obtained as thin needles by slow evaporation from a solution of 100 mg of **4** in a mixture of 2 ml of dichloromethane and 20 ml of hexane.

Table 3

Atomic coordinates and equivalent isotropic or isotropic temperature factors ($Å^2 \times 100$) with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| Rh(A) | 0.80561(4) | 0.53550(4) | 0.43748(2) | 4.39(8)[a] |
| Cl(A) | 0.9538(1) | 0.5926(2) | 0.38619(6) | 5.5(3)[a] |
| C(1A) | 0.8926(6) | 0.3926(6) | 0.4562(2) | 6(1)[a] |
| O(A) | 0.9419(5) | 0.2998(5) | 0.4653(2) | 9(1)[a] |
| N(A) | 0.6917(4) | 0.6913(4) | 0.4164(2) | 4.1(8)[a] |
| H(NA) | 0.639(4) | 0.687(5) | 0.3832(9) | 6.0 |
| C(2A) | 0.7154(5) | 0.8246(5) | 0.4316(2) | 4.3(9)[a] |
| C(3A) | 0.8518(5) | 0.8571(6) | 0.4544(2) | 6(1)[a] |
| C(4A) | 0.6514(6) | 0.9188(5) | 0.3945(2) | 6(1)[a] |
| C(5A) | 0.6322(5) | 0.7449(5) | 0.4586(2) | 4.4(9)[a] |
| C(6A) | 0.4904(5) | 0.7650(5) | 0.4500(2) | 5(1)[a] |
| C(7A) | 0.4070(5) | 0.7040(6) | 0.4127(2) | 5(1)[a] |
| C(8A) | 0.2768(6) | 0.7238(6) | 0.4076(2) | 6(1)[a] |
| C(9A) | 0.2288(6) | 0.8027(7) | 0.4385(3) | 7(2)[a] |
| C(10A) | 0.3109(7) | 0.8632(7) | 0.4750(3) | 9(2)[a] |
| C(11A) | 0.4401(6) | 0.8443(6) | 0.4812(3) | 7(1)[a] |
| C(12A) | 0.6895(6) | 0.6856(6) | 0.5092(2) | 6(1)[a] |
| C(13A) | 0.7224(6) | 0.5521(6) | 0.5040(2) | 6(1)[a] |
| H(C13A) | 0.781(4) | 0.513(5) | 0.531(2) | 6.0 |
| C(14A) | 0.6490(6) | 0.4729(6) | 0.4701(3) | 6(1)[a] |
| H1(C14A) | 0.571(3) | 0.504(5) | 0.450(2) | 6.0 |
| H2(C14A) | 0.652(5) | 0.385(1) | 0.478(2) | 6.0 |
| Rh(B) | 0.66223(4) | 0.40710(5) | 0.31580(2) | 5.32(9)[a] |
| Cl(B) | 0.5467(1) | 0.5957(2) | 0.30424(6) | 6.1(3)[a] |
| C(1B) | 0.5490(7) | 0.3355(8) | 0.3505(3) | 8(2)[a] |
| O(B) | 0.4827(6) | 0.2863(6) | 0.3730(2) | 12(2)[a] |
| N(B) | 0.7954(4) | 0.4763(4) | 0.2739(2) | 4.6(8)[a] |
| H(NB) | 0.855(4) | 0.540(4) | 0.288(2) | 6.0 |
| C(2B) | 0.7771(5) | 0.4858(6) | 0.2176(2) | 5(1)[a] |
| C(3B) | 0.6415(6) | 0.4672(7) | 0.1911(2) | 7(1)[a] |
| C(4B) | 0.8443(7) | 0.5895(6) | 0.1957(3) | 7(1)[a] |
| C(5B) | 0.8516(5) | 0.3808(5) | 0.2440(2) | 4.4(9)[a] |
| C(6B) | 0.9941(5) | 0.3797(5) | 0.2463(2) | 4.3(9)[a] |
| C(7B) | 1.0796(5) | 0.4328(5) | 0.2851(2) | 5(1)[a] |
| C(8B) | 1.2102(6) | 0.4300(6) | 0.2847(3) | 6(1)[a] |
| C(9B) | 1.2561(6) | 0.3736(6) | 0.2464(3) | 7(1)[a] |
| C(10B) | 1.1724(6) | 0.3199(6) | 0.2076(3) | 6(1)[a] |
| C(11B) | 1.0427(5) | 0.3244(5) | 0.2077(2) | 5(1)[a] |
| C(12B) | 0.7886(6) | 0.2562(5) | 0.2453(2) | 6(1)[a] |
| C(13B) | 0.7345(6) | 0.2346(5) | 0.2933(3) | 6(1)[a] |
| H(C13B) | 0.667(4) | 0.173(4) | 0.286(2) | 6.0 |
| C(14B) | 0.7995(7) | 0.2679(6) | 0.3408(3) | 7(1)[a] |
| H1(C14B) | 0.882(3) | 0.308(5) | 0.346(2) | 6.0 |
| H2(C14B) | 0.783(5) | 0.226(5) | 0.371(1) | 6.0 |

[a] Equivalent isotropic *U* defined as one-third of the trace of the $U_{ij}$ tensor.

Details of crystal data, measurement of intensities and data processing are summarized in Table 2.

An empirical absorption correction [24] based on $\Psi$-scans was made and the transmission factor ranged from 0.85 to 1.00. Fractional atomic coordinates and thermal parameters are given in Table 3. Programs used were MOLEN [25], SHELX-86 [26] and SHELX-76 [27].

Supplementary material includes all atomic parameters, anisotropic temperature factors, a complete list of bond distances and angles, least-squares planes equations, deviations of atoms therefrom and dihedral angles between them (6 pages) and tables of observed and calculated structure factors (14 pages).

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