

The Behaviour of 3,3-Pentamethylenediaziridine in Reactions with Transition Metal Compounds

Pedro Faria dos Santos Filho*, Heloise de Oliveira Pastore and Adalberto Antonio Bellini

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13081 Campinas, SP, Brasil

Received: april 27, 1992; may 10, 1992.

A 3,3-pentamethylenediaziridina, **1**, reage com alguns cloretos de metais de transição, à temperatura ambiente, formando complexos nos quais o heterociclo funciona como ligante de dois elétrons. Nestes complexos o sistema anelar do heterociclo é preservado e isto independe da estereoquímica ao redor do metal ou da natureza do mesmo. Por outro lado, na reação de **1** com $\text{RhCOCl}(\text{PPh}_3)_2$ ocorre inicialmente uma adição oxidativa do heterociclo ao composto de ródio(I) que resulta, finalmente, na decomposição do heterociclo.

3,3-Pentamethylenediaziridine, **1**, reacts with some transition metal chlorides at room temperature giving complexes in which the heterocycle acts as a two electron ligand. In these complexes the ring system is preserved regardless of the nature of the metal or its stereochemistry. On the other hand, in the reaction of **1** with $\text{RhCOCl}(\text{PPh}_3)_2$ the first step is an oxidative addition of the heterocycle to the rhodium(I) compound followed by heterocyclic decomposition.

Key words: diaziridine; coordination; oxidative addition.

Introduction

Diaziridines have been described in the literature since 1959¹ but only in the seventies was their reactivity with other organic substrates developed. In these reactions, we can find open chain products as well as products in which the ring system is retained². Among all these studies on diaziridines, only a few involve transition metal compounds. Beck and Danzer³, in 1974, were the first in this field to study reactions of tungsten and molybdenum carbonyls with 3,3-pentamethylenediaziridine **1**. In these reactions they observed the formation of iminic and cyclic carbamoylic complexes resulting from the rupture of the ring system. In the same article, the authors derived some data on a complex obtained in the reaction of **1** with nickel and cobalt chlorides. Although they did not fully characterize these products, they believed that the ring system of **1** was maintained. Ten years later, Sosnovsky and Lukszo⁴ isolated a complex in which **1** was coordinated to a platinum atom in a *cis* configuration. This kind of complex is of great importance in view of its similarity with *cis*-platinum, which has good anticancer activity. Using N-monosubstituted diaziridines we observed that they coordinate to palladium dichloride *via* the more basic nitrogen atom, affording a mixture of diastereomeric complexes which can be distinguished by NMR spectroscopy⁵. These compounds and that obtained by Sosnovsky and Lukszo⁴ are the only ones described in the literature in which the ring system of the heterocycle is preserved after complexation.

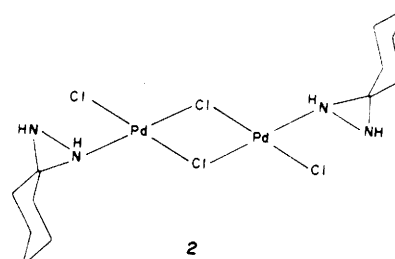
In the presence of stoichiometric amounts of silver and mercury oxides as well as potassium permanganate or dichromate, the diaziridines are dehydrogenated giving the corresponding diazirines⁶. Unfortunately, we do not know the mechanistic aspects involved in diazirine formation.

As far as we know the above considerations are the only known aspects of the diaziridines behaviour in reactions involving transition metal compounds.

Results and Discussion

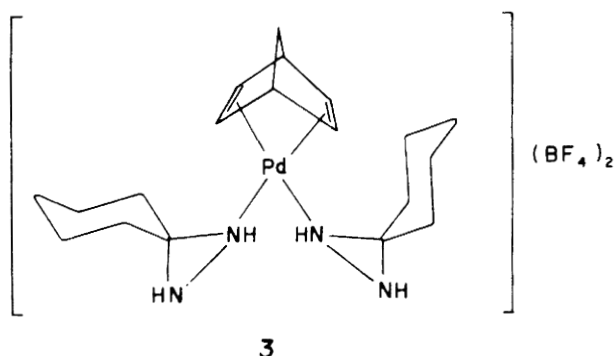
1 - Reactions of **1** with Transition Metal Chlorides

Diaziridine **1** reacts with bis(benzonitrile)palladium dichloride in benzene at room temperature giving the complex bis(palladium-*trans*-chloro-3,3-pentamethylenediaziridine) dichloride, **2**, in 86% yield. The ¹³C-NMR data show



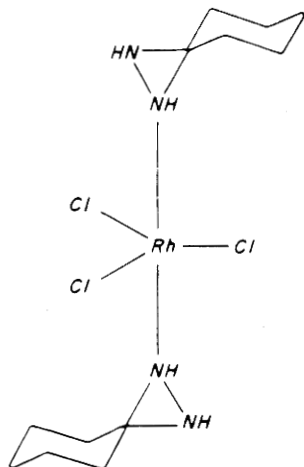
that after coordination to the metal all the nuclei of the heterocycle are deshielded. This suggests that the electronic density at the non-coordinated nitrogen is reduced, inhibiting the formation of polynuclear complexes, in which the heterocycle would act as a bridge between two metal atoms. The elemental analysis confirms the presence of only one diaziridine per palladium atom.

On the other hand, heterocycle **1** reacts in acetonitrile with (norbornadiene)palladium dichloride, in the presence of silver tetrafluoroborate at room temperature, to afford in 75% yield an air stable yellow complex which is insoluble in common organic solvents. In the IR spectrum this complex shows two bands attributed to Pd-N at 479 and 472 cm⁻¹ and only one band at 342 cm⁻¹ assigned to the terminal Pd-Cl. The N-H is observed at 3210 cm⁻¹. The elemental analysis indicates two molecules of **1** per palladium atom. These data suggest that the product formed in this reaction has the structure **3**.



As with other diaziridine-palladium(II) compounds⁽⁵⁾, complexes **2** and **3** are stable at room temperature and may be stored for long periods of time without any sign of decomposition. This clearly shows that the stereochemistry around the metal does not affect the stability of the complexes.

In order to verify the effect of the oxidation state of the metal atom in the reaction of **1** with transition metal chlorides, the reaction with rhodium trichloride was studied. Again, we observed the coordination of two molecules of **1** to the rhodium atom giving the complex **4**.



Based on these results we can state that **1** forms stable complexes with Co(II), Ni(II), Pd(II), Pt(II) and Rh(III) chlorides. This shows that neither the nature of the metal atom, the geometry of the complex (tetrahedral, square planar or bipyramidal trigonal) nor the stereochemistry around the metal atom (*cis* or *trans*) affect the stability of the complex; in all of them the ring system is retained after coordination. This shows that, although there is a strain energy in this heterocycle, these transition metal chlorides are not able to promote the rupture of the ring system. On the other hand, as we can see in the ¹³C-NMR spectrum of complex **2**, besides diminishing the basicity of the non-coordinated nitrogen atom, the coordination to the metal causes an electronic deshielding at the carbon atom of the heterocycle. This deshielding may facilitate nucleophilic attack on this atom and this effect may be used to promote reactions of the coordinated heterocycle with other nucleophilic substrates. Although the nucleophilic attack on the carbon atom of the diaziridine ring system has been shown to be difficult, its coordination to transition metal atoms may prove to be useful, in the future, to facilitate reaction with other organic substrates in the development of new catalytic systems for organic synthesis.

2 - Reactivity of **1** with RhCOCl(PPh₃)₂

The reaction of **1** and RhCOCl(PPh₃)₂, in a mixture of chloroform/methanol 3:2 v/v at room temperature, yields a yellow complex which shows bands in the IR spectrum at 2218 and 1980 cm⁻¹, attributed to the Rh-H and Rh-CO stretchings, respectively. The spectrum also presents bands due to the PPh₃ ligands. In the ¹H-NMR spectrum of this complex we observe two multiplets at -4.28 and 7.42 ppm. These data suggest structure **5** for the complex, obtained according to scheme 1.

We believe that the first step in this reaction is an oxidative addition of **1** to the rhodium(I) compound involving the rupture of a N-H bond and giving the rhodium(III) intermediate **6**. This intermediate may eliminate HCl forming intermediate **7** which shows a diazirine bound to the rhodium atom. It is known that diazirines bound to certain transition metals are easily decomposed, eliminating molecular nitrogen and the corresponding carbene⁶. In this way **7** could eliminate cyclohexylcarbene, forming **8**, which then loses molecular nitrogen forming complex **9**. In the presence of oxygen, cyclohexylcarbene is converted to cyclohexanone as described by Shur et al⁷.

According to the proposed mechanism the first step is an oxidative addition involving the rupture of a N-H bond. When a mixture of chloroform/methanol is the solvent, this reaction occurs at room temperature. On the other hand, when benzene is used, the reaction occurs only at reflux temperature. This shows that the presence of methanol, forming a hydrogen bond with the heterocycle, may assist the rupture of the hydrogen atom bound to the nitrogen and cause the reaction to occur at room temperature. It is important to note that only in the presence of methanol does this reaction occur at room temperature.

A complex like **7**, having a diazirine bound to a transition metal, was already proposed as an intermediate in the decomposition of 3,3-pentamethylenediazirine^{7,8}. This indicates that, for some metals, this kind of complex is not stable and easily eliminates nitrogen and the corresponding carbene. This is in agreement with the proposed mechanism in the sense that once **7** is formed it rapidly eliminates cyclohexylcarbene. To our knowledge this is the first example of an oxidative addition re-

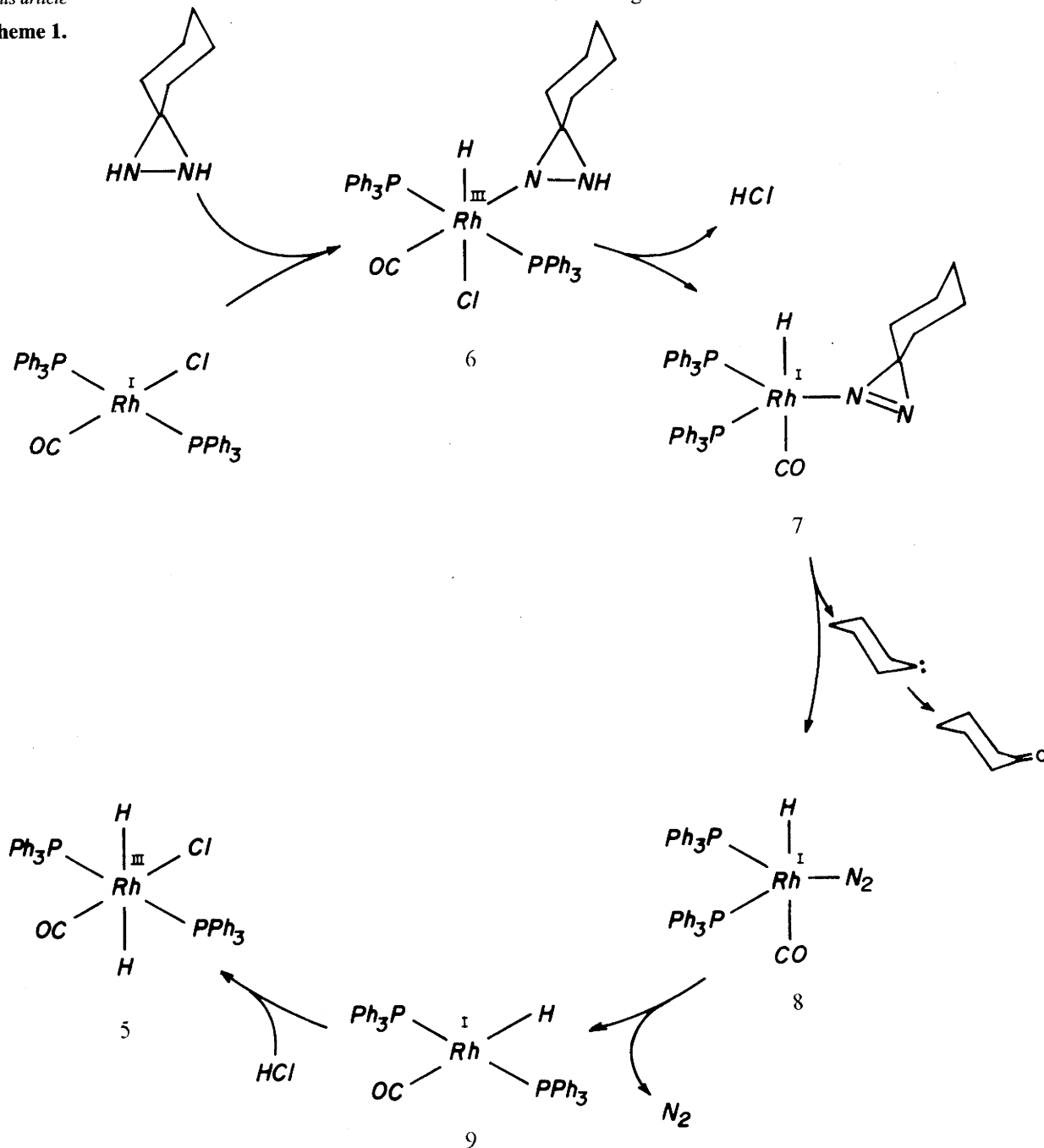
action involving the rupture of one N-H bond of a diaziridine molecule.

We can summarize our knowledge about the behavior of 3,3-pentamethylenediaziridine in the reactions with transition metal compounds in the following table:

Type of Reaction	Rupture ³	Coordination ^{*,3}	Oxidation ⁶	Oxidative addition [*]
Metal:	Mo (0) W(0)	Co(II), Ni (II) Pd (II), Pt (II) Rh (III)	HgO, Ag ₂ O, KMnO ₄ , K ₂ Cr ₂ O ₇	Rh (I)

* This article

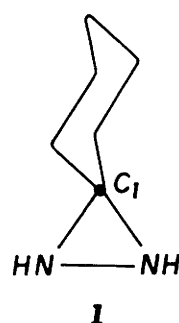
Scheme 1.



Based on this table, it seems that rupture of the ring system and oxidative addition are favored by transition metals in low oxidation states and that they depend on the other ligands bound to the metal center. It is important to note that the decomposition of **1**, producing nitrogen and cyclohexylcarbene, in the presence of RhCOCl(PPh₃)₂, occurs only in stoichiometric amounts. All efforts to catalyze this reaction by the presence of RhCOCl(PPh₃)₂ have failed. It seems that the intermediate RhHCO(PPh₃)₂ does not react with **1** giving the oxidative addition product. This indicates that the oxidative addition of HCl to intermediate **9** is faster than that of **1** and in this way the coordinatively saturated complex **5** is formed.

Finally, we believe that these results can help us in developing new catalytic methods of organic synthesis involving **1** and other organic substrates.

Table 1.



	$\delta_{\text{C}}(\text{d}_6\text{-DMSO})$	IR (Nujol) cm^{-1}				
		C_1	$\text{V}_{\text{N-H}}$	$\text{V}_{\text{Pd-Cl}_1}$	$\text{V}_{\text{Pd-Cl}_2}$	$\text{V}_{\text{Pd-N}}$
1	58,7	3210	-	-	-	
2	61,4	3240	342	308; 245	475	

Experimental

NMR spectra were recorded on a BRUKER W-80 spectrometer. IR spectra were measured on a JASCO IR 700 spectrometer. Elemental Analysis were performed on a Perkin-Elmer 2400 CHN Elemental Analyser.

Bis(palladium- -chloro -trans -3 , 3-pentamethylenediaziridine) dichloride, 2

To a round-bottomed flask containing benzene (25 ml) bis(benzonitrile)palladium dichloride (0.56g, 1.45mmol) was added. To this solution the heterocycle **1** (0.16g, 1.45mmol) was slowly introduced. The reddish-brown solution was kept at room temperature for 2h under stirring. Light petroleum ether (b.p. 40-60°C) (30 ml) was added and the light yellow solid which precipitated was filtered off and washed with additional light petroleum ether (20 ml). The product was recrystallised from chloroform-light petroleum ether and dried under vacuum, yield 86%, m.p. 172-174°C (decomp.); $\nu_{\text{max}}(\text{Nujol})$: 3240, 885, 810, 565, 475, 342, 308 and 245 cm^{-1} . $\delta_{\text{H}}(\text{d}_6\text{-DMSO})$ 1.55(10H, m, CH_2) and 2.60 (2H, broad, NH); $\delta_{\text{C}}(\text{d}_6\text{-DMSO})$ 61.4, 34.3, 32.9, 24.4 and 23.5 (found C, 24.90; H, 4.10; N, 9.50. $\text{C}_{12}\text{H}_{24}\text{Cl}_4\text{N}_4\text{Pd}_2$ requires C, 25.00; H, 4.16; N, 9.72%)

Norbornadiene-bis(3,3-pentamethylenediaziridine)palladium tetrafluoroborate, 3

To a round-bottomed flask containing dry acetonitrile (20 ml) (norbornadiene)palladium dichloride (0.10g, 0.38 mmol) and silver tetrafluoroborate (0.15g, 0.76 mmol) were added, under argon. After 5 min. the precipitated silver chloride was filtered off. To the filtrate the heterocycle **1** (0.085g, 0.76 mmol) was slowly added and the solution was kept under argon at room temperature for 2h while stirring. The solvent was evaporated and the light yellow solid obtained was washed twice with ether (10 ml) and dried under vacuum, yield 75%, m.p. 149-150°C (decomp.); $\nu_{\text{max}}(\text{KBr})$: 3225, 3100, 2970, 2890, 1640, 1450, 1380, 1200, 1100-1020, 885, 840 and 475 cm^{-1} . (Found C, 38.30; H, 5.30; N, 9.50. $\text{C}_{19}\text{H}_{32}\text{B}_2\text{F}_8\text{N}_4\text{Pd}$ requires C, 38.26; H, 5.37; N, 9.40%)

Bis(3,3-pentamethylenediaziridine)rhodium trichloride, 4

Rhodium trichloride (0.30g, 1.15mmol) was added to methanol (20 ml) in a round-bottomed flask, followed by a slow addition of heterocycle (**1**) (0.26g, 2.30mmol). The solution was kept at room temperature for 3h under stirring. The solvent was evaporated and the orange colored solid obtained was washed twice with light petroleum ether and dried under vacuum, yield 85%, m.p. 250°C; $\nu_{\text{max}}(\text{KBr})$: 3182, 2852, 1221, 880, and 828 cm^{-1} . (Found C, 33.50; H, 4.61; N, 13.09. $\text{C}_{12}\text{H}_{20}\text{Cl}_3\text{N}_4\text{Rh}$ requires C, 33.78; H, 4.69; N, 13.13%)

Dihydridecarbonylchlorobis(triphenylphosphine)rhodium(III), 5.

To a round-bottomed flask containing a mixture of chloroform/methanol 3:2 v/v (20ml) chlorobis (triphenylphosphine)carbonylrhodium(I) (0.069g, 0.10mmol) was added. To this solution the heterocycle **1** (0.011g, 0.10mmol) was slowly introduced. The solution was kept at room temperature for 48h while stirring. The solvent was evaporated and ether (10 ml) was added to the yellow mass obtained. The yellow solid which separated was filtered off and recrystallised from chloroform-light petroleum ether (b.p. 40-60°C), yield 70%, m.p. 182-183°C; $\nu_{\text{max}}(\text{KBr})$ 3048, 2218, 1980, 1477, 1432, 572 and 344 cm^{-1} . $\delta_{\text{H}}(\text{CDCl}_3)$ -4.28(2H, m) and 7.42(30H, m). (Found C, 64.20; H, 4.60. $\text{C}_{37}\text{H}_{32}\text{ClOP}_2\text{Rh}$ requires C, 64.22; H, 4.63%)

Careful distillation of the ether left a residue which was identified as cyclohexanone, by comparison of its IR and ^{13}C -NMR spectra with that of an authentic sample.

Acknowledgments

Financial support of this work by FAPESP and CNPq is gratefully acknowledged.

References

- E. Schmitz, *Angew. Chem.* **71**, 127 (1959); H.J. Abendroth and G. Henrich, *Angew. Chem.* **71**, 283 (1959); S.R. Paulsen, *Angew. Chem.* **72**, 781 (1960).
- E.S. Gubnitskaia, Z.T. Semashko, *J. Gen. Chem. USSR* **46**, 1165 (1976); E.S. Gubnitskaia and V.S. Parkhomenko, *J. Gen. Chem. USSR* **50**, 1213 (1980); M. Komatsu, N. Nishikaze, M. Sakamoto, Y. Oshiro and T. Agawa, *J. Org. Chem.* **39**, 3198 (1974).
- W. Beck and W. Danzer, *J. Organomet. Chem.* **73**, C56 (1974); W. Danzer, W. Beck and M. Keubler, *Z. Naturforsch.* **31B**, 1360 (1976).
- G. Sosnovsky and J. Lukszo, *J. Cancer Res. Clin. Oncol.* **107**, 217 (1984).
- P. Faria dos Santos Filho and H.O. Pastore, *J. Chem Research (S)* 326 (1989).
- H. Kato and M. Ohta, *Bull. Chem. Soc. Jpn.* **35**, 2048 (1962); R. F.R. Church and M.J. Weiss, *J. Org. Chem.* **35**, 2465 (1970); S. R. Paulsen, *Angew. Chem.* **72**, 781 (1960).
- P. Faria dos Santos Filho and H.O. Pastore, *J. Mol. Catal.* **58**, L1 (1990).
- V.B. Shur, I.A. Tikhonova, G.G. Aleksandrov, Yu. T. Struchkov, M.E. Vol'pin, E. Schmitz and K. Jahmish, *Inorg. Chim. Acta* **44**, L275 (1980).