Journal of Organometallic Chemistry, 263 (1984) 385–393
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION OF SOME *trans*-BIS(2*H*-AZIRINE)PALLADIUM DICHLORIDE COMPLEXES AND THE OPENING OF THEIR AZIRINE RINGS IN BENZENE *

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(Received May 10th, 1983)

Summary

The *trans*-bis(2*H*-azirine)palladium dichloride complexes **2f**, **2g**, **2h** and **2i** are formed in the reaction of $(C_6H_5CN)_2PdCl_2$ with 3-phenyl- (**1f**), 2-phenyl-3-styryl- (**1g**), 2(formyl-*N*-phenylimine)-3-phenyl- (**1h**) and 2-styryl-3-phenyl-2*H*-azirine (**1i**). The cleavage of the azirine rings of these complexes was studied in benzene at room temperature. The complexes **2f** and **2g** form the novel bis(η^2-3-chloro-1-azaallylpalladium) dichloride complexes **3f** and **3g** by rupture of the C–N single bond. **2h** reacts in the same way but the intermediate azaallylic palladium complex rearranges to form the bis(1,5-diazapentadienylpalladium) dichloride complex **5**. **2i** decomposes rapidly upon dissolution to form palladium dichloride and 2,5-diphenylpyrrole as the main products.

Introduction

Since 1977 2*H*-azirines (**1**) are known to form stable complexes with palladium dichloride. Taniguchi and co-workers [2] described the *trans*-palladium dichloride complexes of 3-phenyl- (**2a**), 3-*p*-tolyl- (**2b**), 3-methyl- (**2c**) and 3-unsubstituted-2,2-diphenyl-2*H*-azirine (**2d**). They observed that at room temperature **2c** and **2d** suffer ring opening at the C–N single bond, forming the corresponding indoles. In 1978 Hassner and co-workers [3] reported several other *trans*-bis(2*H*-azirine)palladium dichloride complexes and determined the X-ray structure of the 3-*p*-tolyl-2*H*-azirine complex (**2e**). They reported that these complexes do not decompose in the presence of humid air at room temperature; since the azirines can be regenerated from **2** by treatment with triphenylphosphine, storage in the form of their palladium dichloride complexes is convenient.

* For a preliminary communication see ref. 1.

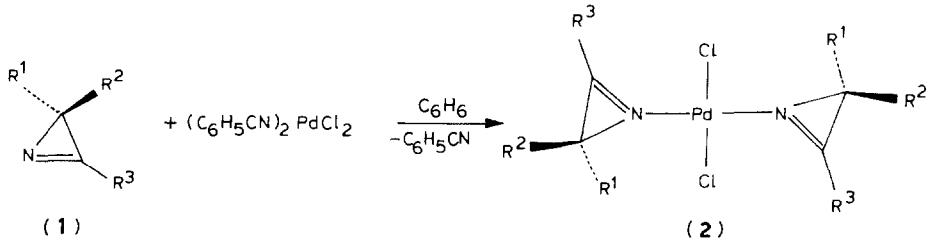
Alper and co-workers [4] described the palladium(0)-catalyzed carbonylation of **1**, during which the C–N single bond is opened and bicyclic β-lactams are formed. We obtained the polymeric palladium dichloride complex of 3,3′-*p*-phenylenebis(2*H*-azirine) which, on reaction with methanol, opens at the C–N double bond to form a polymeric diamine complex [5].

We report here the preparation of the new *trans*-bis(2*H*-azirine)palladium complexes **2f**, **2g**, **2h** and **2i** and the opening of their 2*H*-azirine ring systems in benzene at room temperature to form azaallylic complexes of palladium (**3**) and rearrangement products.

Results and discussion

In the reaction of the 2*H*-azirines **1** with bis(benzonitrile)palladium dichloride in a 2/1 ratio in benzene at room temperature, the *trans*-bis(2*H*-azirine)palladium dichloride complexes **2** are formed in high yields. They are light yellow compounds stable in the solid state [3].

As can be seen in Table 1, the C–N double bond of the azirines is shifted to higher frequencies on complexation with palladium dichloride. The shift of the *exo* double bonds of **2g**, **2h** and **2i** is smaller and not uniform.



(1) (2)

	R^1	R^2	R^3	Ref.
a	C_6H_5	C_6H_5	C_6H_5	2
b	C_6H_5	C_6H_5	C_6H_4-*p*-CH_3	2
c	C_6H_5	C_6H_5	CH_3	2
d	C_6H_5	C_6H_5	H	2
e	H	H	C_6H_4 -*p*-CH_3	3
f	H	H	C_6H_5	*a*
g	H	C_6H_5	$CHCHC_6H_5$	*a*
h	H	$CHNC_6H_5$	C_6H_5	*a*
i	H	$CHCHC_6H_5$	C_6H_5	*a*

a Own work

SCHEME 1

TABLE 1

CN AND CC FREQUENCIES (cm^{-1}) OF THE AZIRINES **1f–1i** AND THEIR PALLADIUM DICHLORIDE COMPLEXES **2f–2i**

	Bond attribution (ν)	1	2	Shift
f	C=N	1740	1770	30
g	C=N	1732	1755	23
	C=C	1615	1600	15
h	C=N	1745	1772	27
	C=N	1633	1642	9
i	C=N	1770	1791	21
	C=C	1720	1740	20

Similar C–N double bond shifts have been reported by Hassner and co-workers [3] for the complexation of 2*H*-azirines to palladium dichloride and are also observed for other Schiff bases upon complexation [6]. The *exo* C–N and C–C double bonds in **2h** and **2i** are also shifted to higher frequencies, showing the electronic deshielding of the entire ligand. The shift of the C–C double bond of **2g** to lower frequencies can be explained by the delocalization of the conjugated π-electrons toward the ring.

In all complexes the azirine is bound to the palladium dichloride through the cyclic nitrogen. This shows that the ring nitrogen is more basic and/or less hindered than the exocyclic nitrogen in **2h**. In contrast, iminoaziridines coordinate to palladium dichloride through their exocyclic imino nitrogen [7].

We obtained the ^1H NMR spectra only of **2f** and **2g** as **2h** and **2i** rearrange upon dissolving in $CDCl_3$. All protons of the azirines in **2f** and **2g** are shifted downfield between 0.23 to 0.63 ppm, according to the distance to the palladium atom, showing the electronic deshielding of the azirines coordinated to the palladium atom. The spectroscopic data show that, on coordination to the palladium atom, the entire 2*H*-azirine is electronically deshielded, strengthening the cyclic C–N double bond and delocalizing electrons from substituents toward the ring system.

The complexes **2f**, **2i** suffer ring opening of the 2H-azirine in benzene at room temperature. For **2f** and **2g** this reaction is slow while **2h** and **2i** react upon dissolution. This is in contrast to the behavior of **2e**, which forms a polymeric material only in refluxing chloroform or benzene [3]. During the reaction of **2f** in benzene at room temperature the C–N double bond frequency at 1770 cm^{-1} diminishes and a new absorption at 1625 cm^{-1} appears, as shown in Fig. 1.

Appearance of N–H absorption at 3200 cm^{-1} and C–Cl absorption at 698 cm^{-1} is also observed. In the ^1H NMR spectrum, the signal of the CH_2 group of **2f** at 2.23 ppm disappears during the reaction in benzene. Two new signals with the same intensity are observed at 1.88 and 2.15 ppm, the first of which is rather broad and is attributed to the N–H proton as it disappears on addition of D_2O. The ^{13}C NMR spectrum shows five close signals in the range of 127.0 to 128.4 ppm and a doublet at 75.4 ppm. These data can be explained by an opening of the C–N single bond of the azirine in **2f**, forming the azaallylic complex **3f** in 90% yield. The reaction is complete in 8 days. As a side-product, 2,5-diphenylpyrazine (**4**) [8] is formed in equivalent amounts.

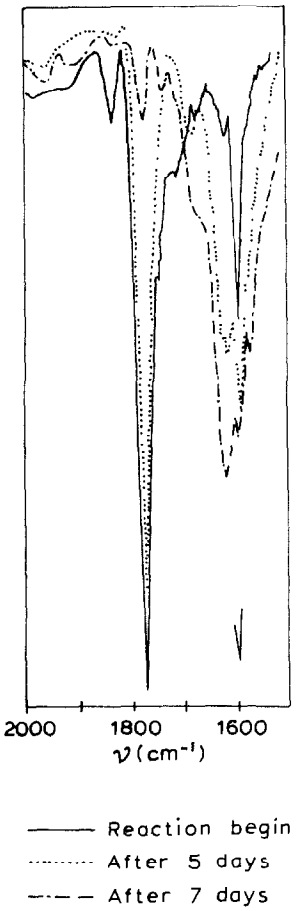
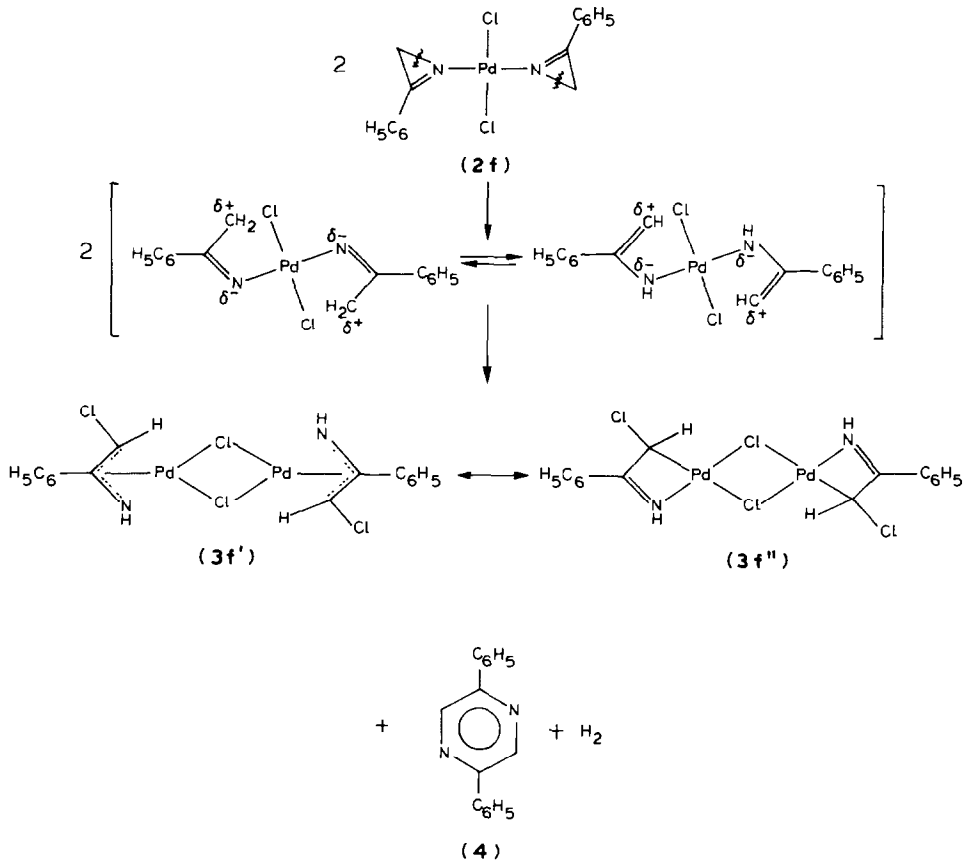


Fig. 1. Reaction of **2f** in benzene at room temperature. Change of IR intensities between 2000 and 1500 cm^{-1}.

Azaallylic complexes of type **3f** are not reported in the literature. The aliphatic proton appears at 2.15 ppm, which means at 1 ppm higher field than in symmetric η^3-allylic complexes [9]. This can be explained by an η^2-coordination of the azaallylic ligand, in agreement with a strong participation of structure **3f''**. This means that the CHCl group bound to palladium is more saturated, explaining the upfield shift. In agreement, the C–N double bond of **3f** at 1625 cm^{-1} appears in the same region as reported for diiminic nickel(II) complexes [10]. On the other hand, the ^{13}C signal of the CHCl group at 75.4 ppm is in the range expected for an allylic terminal carbon, bound to palladium(II) [11]. The new complex **3f** is rather inert and does not react with activated olefins (norbornadiene and dimethyl maleate), nor does it decompose in humid air.

Complex **2g** suffers the same kind of ring opening in benzene. The reaction is complete after four days at room temperature, forming **3g** in 85% yield. The C–N double bond is observed at 1640 cm^{-1}, the N–H and C–Cl bonds at 3250 and 690 cm^{-1}, respectively.



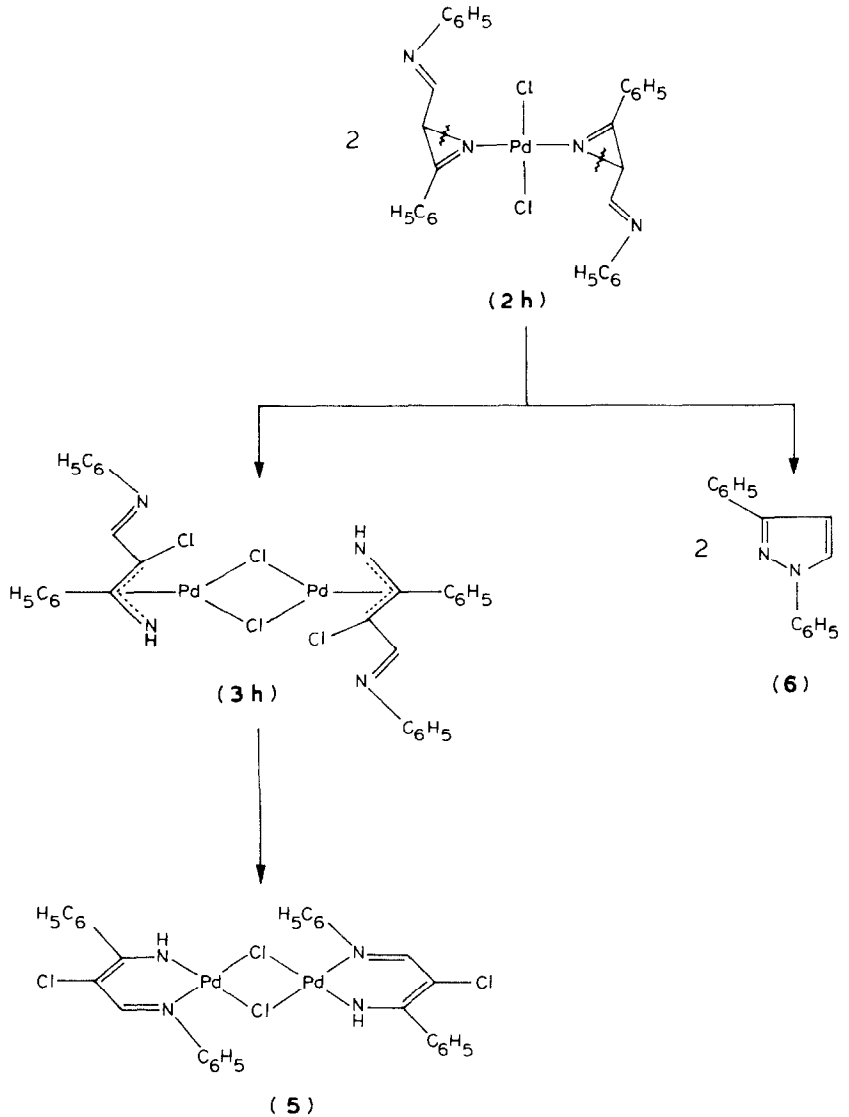
SCHEME 2

Complex **2h** rearranges immediately upon dissolving in benzene at room temperature, forming a new complex in quantitative yield which shows two different absorptions for the palladium–nitrogen bonds at 565 and 520 cm^{-1}. Besides the N–H (3200 cm^{-1}), C–N double bond (1640 cm^{-1}), C–C double bond (1580 cm^{-1}) and C–Cl (680 cm^{-1}) absorptions, we also observed a C–N single bond at 1280 cm^{-1}. These spectroscopic data suggest that the bis(1,4-diphenyl-3-chloro-1,5-diazapentadienylpalladium) dichloride complex **5** is formed. This can be explained by the rupture of the C–N single bond of **2h**, forming an intermediate azaallylic complex **3h** which rearranges to form **5**. As a side-product, 1,3-diphenylpyrazole (**6**) is formed in equivalent amounts. **6** is formed by the rupture of the C–N single bond of the second azirine in **2h** which has been displaced during the formation of **5**. **6** can also be obtained by refluxing **1h** in xylene for 15 h [12].

The rearrangement of **3h** to **5** can be explained by the formation of a stable conjugated 6π system which represents a better ligand for the palladium atom. A similar rearrangement is not observed for **3f** and **3g** because they have no suitable substituent at the carbon atom bound to the palladium. **5** is an inert compound and can be stored in air without decomposition.

The palladium complex **3i** decomposes upon attempted dissolution in benzene at room temperature. Palladium dichloride precipitates quantitatively and several heterocyclic compounds are formed, of which the major product has been identified as 2,5-diphenylpyrrole. The high reactivity of **2i** is due to the presence of the styryl group in position 2 of the azirine **1i**. 2,5-Diphenylpyrrole can also be obtained from **1i** by refluxing in benzene [12].

In the complexes **3f**, **3g** and **5** the azirine has been ring-opened at the C–N single bond but remains complexed to the palladium atom. This result is in agreement with the formulation of Taniguchi and coworkers [2]. As the azirines used by these authors have no hydrogen at the 2-position, azaallylic complexes were not formed. On the other hand the formation of the indoles can only be explained by the rupture



SCHEME 3

of the C–N single bond and insertion of the nitrene into an aromatic C–H bond. The proposed structure of the azaallylic complex is in agreement with the thioallylic complex described by Tanaka and coworkers [13] which also is bound in an η^2-mode.

Experimental

All reactions were carried out in dry solvents without using an inert atmosphere. $(C_6H_5CN)_2PdCl_2$ was prepared as reported by Hartley [14]. The azirines were prepared following methods described in the literature: **1f** [15], **1h** [12] and **1i** [12]. **1g** was prepared in an analogous way as indicated by Hassner and Keogh [16].

The ^1H NMR spectra were taken in $CDCl_3$ with TMS as internal standard using the Varian instruments T-60 and EM-360, while the ^{13}C NMR spectra were performed in $CDCl_3$ with a Varian XL 100. The infrared spectra were obtained as film (liquid) or KBr pellet (solid) with polystyrene film as reference using the Perkin–Elmer instruments 180 and 337. The elemental analyses were made by Dornis u. Kolbe, Mikroanalytisches Laboratorium, Mülheim-Ruhr, West Germany. The melting points were determined with a Mettler FP5 apparatus and are uncorrected.

*Preparation of trans-bis(3-phenyl-2H-azirine)palladium dichloride (**2f**)*

To a solution of $(C_6H_5CN)_2PdCl_2$ (0.766 g, 2 mmol) in benzene (20 ml) was added 3-phenyl-2*H*-azirine (0.468 g, 4 mmol) in benzene (10 ml). The solution was stirred at room temperature for 3 h. The product was precipitated with 50 ml of petroleum ether (b.p. 30–60°C), filtered on a D3 sintered plate and washed with an additional amount of petroleum ether (30 ml). Recrystallization from $CHCl_3$/pentane gave the complex **2f** as yellow crystals, in quantitative yield. It decomposes at 140°C without melting but can be stored at room temperature, in the presence of air, without decomposition. IR(KBr) 1770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.36 (2H, m), 7.68 (3H, m) and 2.23 (2H, s); ^{13}C NMR ($CDCl_3$) δ 166.9 (s), 135.4 (d), 132.3 (d), 129.2 (d), 121.8 (s) and 21.0 (t). (Found: C, 46.70; H, 3.40; N, 6.79; Pd, 25.75. $C_{16}H_{14}N_2PdCl_2$ calcd.: C, 46.71; H, 3.40; N, 6.81; Pd, 25.79%).

*Preparation of trans-bis(2-phenyl-3-stryryl-2H-azirine)palladium dichloride (**2g**)*

2-Phenyl-3-styryl-2*H*-azirine (0.876 g, 4 mmol) in benzene (10 ml) was added to a solution of $(C_6H_5CN)_2PdCl_2$ (0.766 g, 2 mmol) in benzene (20 ml) and the mixture was stirred at room temperature for 3 h. The product was precipitated with 50 ml of petroleum ether (b.p. 30–60°C), filtered on a D3 sintered plate and washed with an additional amount of petroleum ether (20 ml). Recrystallization from $CHCl_3$/pentane gave the complex **2g** in 80% yield as yellow microcrystals. This product is stable at room temperature and can be stored in the presence of air without decomposition. It decomposes at 135°C without melting. IR (KBr) 1755 and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8–6.8 (12H, m) and 3.38 (1H, s). (Found: C, 61.81; H, 4.20; N, 4.40; Pd, 17.25. $C_{32}H_{26}N_2PdCl_2$ calcd.: C, 62.11; H, 4.26; N, 4.45; Pd, 17.28%).

*Preparation of trans-bis[2(formyl-N-phenylimine)-3-phenyl-2H-azirine]palladium dichloride (**2h**)*

To a solution of $(C_6H_5CN)_2PdCl_2$ (0.766 g, 2 mmol) in toluene (20 ml) was added 2(formyl-*N*-phenylimine)-3-phenyl-2*H*-azirine (0.880 g, 4 mmol) in toluene

(30 ml) and the resulting mixture was stirred for 3 h at −10°C. The product was precipitated with 40 ml of petroleum ether (b.p. 30–60°C), filtered on a D3 sintered plate and washed with an additional amount of petroleum ether. The complex **2h** was obtained, in 90% yield, as a yellow powder which is stable at −5°C under argon. Under these conditions, it can be stored for several months without decomposition. **2h** is soluble in chloroform and benzene but, in solution, it rearranges at room temperature in a few minutes. IR (KBr) 1772 and 1642 cm^{-1}. (Found: C, 58.28; H, 3.80; N, 8.95; Pd, 17.25. $C_{30}H_{24}N_4PdCl_2$ calcd.: C, 58.34; H, 3.89; N, 9.07; Pd, 17.18%).

Preparation of trans-bis(2-styryl-3-phenyl-2H-azirine)palladium dichloride (2i)

2-Styryl-3-phenyl-2*H*-azirine (0.876 g, 4 mmol) in benzene (10 ml) was added to a solution of $(C_6H_5CN)_2PdCl_2$ (0.766 g, 2 mmol) in benzene (20 ml) and the mixture was stirred at room temperature for 20 min. After addition of pentane (30 ml) the product was filtered on a D4 sintered plate at 0°C and dried in vacuo. The complex **2i** was obtained in 40% yield as a yellow powder which is stable at −5°C under argon. On dissolving in chloroform **2i** decomposes to palladium dichloride and a mixture of organic compounds. IR (KBr) 1790 and 1740 cm^{-1}. (Found: C, 61.30; H, 4.18; N, 4.30; Pd, 17.70. $C_{32}H_{26}N_2PdCl_2$ calcd.: C, 61.61; H, 4.26; N, 4.55; Pd, 17.28%).

Preparation of bis(2-phenyl-3-chloro-1-azaallylpalladium) dichloride (3f)

A solution of **2f** (0.411 g, 1 mmol) in benzene (20 ml) was stirred at room temperature for 8 days. The complex **3f** was precipitated with petroleum ether (b.p. 30–60°C), filtered on a D3 sintered plate and washed with an additional amount of petroleum ether (30 ml). **3f** was obtained as a yellow powder in 90% yield, which could not be crystallized but is stable at room temperature and can be stored in the presence of air without decomposition; it does not melt up to 250°C. IR (KBr) ν(N–H) 3200, ν(C=N) 1625, ν(C=C) 1580, ν(C–Cl) 698 and ν(Pd–N) 562 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (5H, m), 2.15 (1H, s) and 1.88 (1H, s); ^{13}C NMR ($CDCl_3$) δ 128.4, 128.1, 127.9, 127.3, 127.0 (s and d) and 75.4 (d), (Found: C, 36.10; H, 2.20; N, 4.45; Pd, 34.20. $C_{16}H_{14}N_2Pd_2Cl_4$ calcd.: C, 36.24; H, 2.26; N, 4.53; Pd, 34.30%). In the filtered solution 2,5-diphenylpyrazine (**4**) was identified by its ^1H NMR spectrum.

Preparation of bis(2-styryl-3-phenyl-3-chloro-1-azaallylpalladium) dichloride (3g)

A solution of **2g** (0.615 g, 1 mmol) in benzene (20 ml) was stirred for 4 days at room temperature. The product was precipitated with pentane and filtered on a D3 sintered plate. It was dissolved in chloroform, precipitated again with pentane and dried in vacuo. The complex **3g** was obtained as a yellow powder in 85% yield; it is stable at room temperature in the presence of air but decomposes at 140°C without melting. IR (KBr) ν(N–H) 3250, ν(C=N) 1640, ν(C=C) 1620 and 1600, ν(C=C) 1580, ν(C–Cl) 690, ν(Pd–N) 490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (12H, m). (Found: C, 48.61; H, 3.38; N, 3.60; Pd, 26.70. $C_{32}H_{26}N_2Pd_2Cl_4$ calcd.: C, 48.60; H, 3.29; N, 3.54; Pd, 26.83%).

Preparation of bis(1,4-diphenyl-3-chloro-1,5-diazapentadienylpalladium) dichloride (5)

A solution of **2h** (0.617 g, 1 mmol) in benzene (15 ml) was stirred for 3 h at room temperature. Petroleum ether (30 ml) was added to the solution and a yellow solid

precipitated. The yellow precipitate was filtered on a D3 sintered plate and recrystallized from chloroform/pentane; the complex **5** was obtained as yellow microcrystals in quantitative yield. It is stable at room temperature and can be stored in the presence of air without decomposition. It does not melt up to 250°C. IR (KBr) ν(N–H) 3200, ν(C=N) 1640, ν(C=C) 1580, ν(C–N) 1280, ν(C–Cl) 680, ν(Pd–N) 565 and 520, ν(Pd–Cl) 320 and 315 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (11H, m) and 1.76 (1H, s). (Found: C, 45.70; H, 3.13; N, 7.04; Pd, 25.99. $C_{30}H_{24}N_4Pd_2Cl_4$ calcd.: C, 45.45; H, 3.03; N, 7.07; Pd, 26.76%). The filtered solution was evaporated, giving 1,3-diphenylpyrazole (**6**) as a yellow, dense oil, which was identified by its IR and ^1H NMR spectra.

Acknowledgments

Financial support of this research by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and the Conselho Nacional de Desenvolvimento Científico e Tecnológio (CNPq) is gratefully acknowledged.

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