Synthesis, Characterization and Dynamic Behavior of (π-Allyl)palladium Complexes with Polydentate Nitrogen Ligands, Evidence of a Dissociative Mechanism

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New examples of the fluxional behavior of (η^3-allyl)palladium complexes are described. Variable-temperature experiments and line-shape analysis of two (η^3-allyl)palladium complexes containing 2-(1*H*-pyrazol-1-yl)azine ligands were performed in order to determine the activation free energies, enthalpies and entropies of the process. A dissociative mechanism pointing to a selective Pd-N cleavage is proposed on the basis of these results and NOE experiments above and below the coalescence temperature.

The synthesis and catalytic reactivity of (η^3-allyl)palladium complexes have been widely studied[1]. For instance, the catalytic allylation is a process of synthetic interest[1e–h]. When a chiral group, for example a chelating nitrogen or a phosphorus-nitrogen ligand, is involved, relatively high enantiomeric excesses are obtained[2]. There is a growing interest in understanding the solution structures[3] and the fluxional behavior[4] of allylpalladium compounds as they may be related with the catalytic results. Some of us reported recently[5a] on the stabilization of PF_6^- hydrolysis intermediates by the [2-methylallylpalladium]$^+$ fragment. This unsaturated species may be stabilized in solutions of coordinating solvents such as acetone and reacts with different polypyrazolylmethane and borate ligands to give cationic complexes with interesting fluxional properties[5b,c]. The fluxionality phenomena are very common in palladium(II) chemistry and, in many cases, the dynamic behavior is explained as a result of preliminary ligand dissociations enabling different processes to occur[6]. For instance, in complexes with N-donor chelating ligands, the Pd–N bond breaking is at this moment an accepted path to explain different interconversion processes. In this paper we study the fluxional behavior of new allyl complexes containing asymmetric N-donor ligands. In this case, the equivalence of the two halves of the allylic group would be an indication of a fluxional process and, if a dissociative mechanism was found, the selectivity towards the Pd–N bond cleavage could be explored. Another aim in our work was to investigate if the study of NOE effects between the allylic group and the ligand could be a way to test the existence of a Pd–N bond cleavage.

Results and Discussion

In this paper we report on the preparation and dynamic behavior of (2-methylallyl)palladium complexes with asymmetric ligands such as 2-(1*H*-pyrazol-1-yl)pyridine (PzPy) and 2-(1*H*-pyrazol-1-yl)pyrimidine (PzPm). The new complexes [Pd(η^3-2-Me-C_3H_4)PzPy]Tf (**1**) and [Pd(η^3-2-Me-C_3H_4)PzPm]Tf (**2**) (Tf = $CF_3SO_3^-$, Scheme 1) were prepared by treatment of the dimer complex [Pd(η^3-C_4H_7)Cl]$_2$ with $AgCF_3SO_3$. The addition of the ligands to the filtered solutions allowed the isolation of complexes **1** and **2**.

Complexes **1** and **2** were characterized by their NMR spectra, elemental analyses and MS FAB. ^{1}H-NMR and ^{13}C-NMR spectra of **1** and **2** (Tables 1–2) at 293 K were assigned by comparison with the spectra of the ligand and with several related complexes[7]. Coordination with the (η^3-allyl)palladium fragment results in a downfield shift of all signals in the ^{1}H-NMR spectra of both complexes. This deshielding was always larger than that observed with related ruthenium complexes[7c]. This positive contribution was attributed to ligand-to-metal σ donation.

The increased electron deficiency of the heterocyclic rings produces an increase in the ^{1}H,^{1}H coupling constants[8]. Similar deshieldings were observed in the ^{13}C-NMR spectra except for C-2. This effect may be ascribed to the increased steric compression of this carbon atom as a result of the complexation[9]. In contrast to the asymmetric environment

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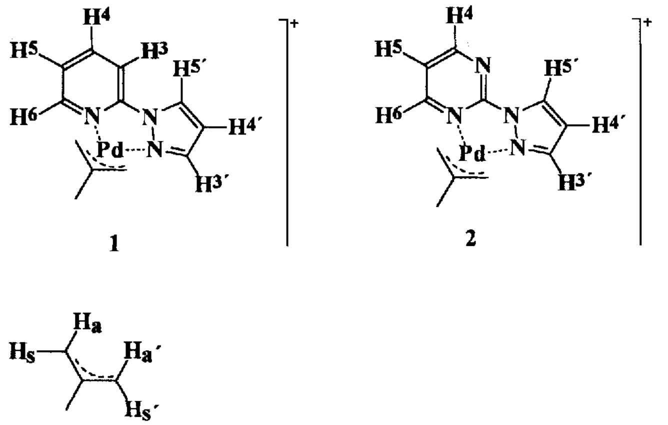
Scheme 1. Structure of complexes **1** and **2** showing the numbering of the heterocyclic rings and the allyl group. In both complexes Ha' and Hs' are located close to the pyrazole ring



of the allylic fragment in **1** and **2** (see Scheme 1), the ^{1}H-NMR spectra for these complexes show only one singlet for both *syn* and another singlet for both *anti* allylic protons at 293 K. In addition, 4-H and 6-H of the pyrimidinyl group are apparently equivalent in **2** at this temperature.

Similarly, in the ^{13}C-NMR spectra the 1- and 3-allylic carbon atoms of **1** and **2** and C-4 and C-6 of the pyrimidine fragment in **2** are equivalent. The NMR spectra at 193 K show important differences. In the ^{1}H-NMR spectra of **1**, signals assigned to *syn* and *anti* allyl protons are split. *anti* Hydrogen atoms appear as two singlets at 3.51 and 3.31 while *syn* protons appear as an AB systems at 4.44 and 4.42 with a J_{AB} = 3.2 Hz. No couplings with the allylic methyl group were detected.

In the ^{1}H-NMR spectra of **2** at 193 K H_{anti} appears as two singlets at 3.50 and 3.37 while H_{syn} appears as an AB system at 4.56 and 4.53 with a J_{AB} = 2.5 Hz.

The assignment of H_{syn} and H_{anti} of the same part of the allyl group was performed by a COSY experiment at this temperature, showing the correlation between the most deshielded H_{syn} and the most shielded H_{anti}. This coupling constant is very small and was not observed in the 1D-NMR spectra. Irradiation of the 6-H frequency in the pyridine and pyrimidine ring produces a NOE in the most shielded H_{syn}. This permits the differentiation of both H_{syn} and subsequently both H_{anti}.

Finally, 4-H and 6-H of the pyrimidine nucleus are no longer equivalent, and they assigned by comparison with related complexes and by NOE difference spectroscopy at this temperature (irradiation of the H_{syn} produces a NOE in the signal of 6-H).

The ^{13}C-NMR spectra at low temperature (193 K) show two terminal allylic carbon atoms clearly different for **1** and **2**.

Table 1. ^{1}H-NMR spectra of 2-(1*H*-pyrazol-1-yl)pyridine (PzPy), 2-(1*H*-pyrazol-1-yl)pyrimidine (PzPm) and complexes **1** and **2** (δ values, *J*, Hz; solvent: [D$_6$]acetone)

Compound	Temp.		3-H	4-H	5-H	6-H	3'-H	4'-H	5'-H	H_s	$H_{s'}$	H_a	$H_{a'}$	CH_3
PzPy	293 K	δ	8.00	7.96	7.31	8.44	7.75	6.52	8.61		---		---	---
		J	8.3 1.7 1.1	8.3 6.7 1.8	6.7 4.9 1.8	4.9 1.7 1.0	1.0	2.6 2.1	2.7 0.7					
1	293 K	δ	8.32	8.42	7.67	8.88	8.34	6.99	9.03	4.44		3.43		2.26
		J	6.6	9.1 7.6 1.7	6.9 5.5 1	5.5 1		2.9 2.2	2.9					
1	193 K	δ	8.33	8.43	7.67	8.83	8.37	7.05	9.12	4.42	4.44	3.51	3.31	2.21
		J	8.6	8.5 7.5 1.6	6.6 5.6 0.9	5.3 0.9	2.0	2.9 1.9	2.9	3.2	3.2			
PmPz	293 K	δ	-----	8.75	7.21	8.75	7.83	6.51	8.60		-----		-----	-----
		J		4.8	4.7	4.8	1.5	2.5 1.5	2.8					
2	293 K	δ	-----	9.23	7.80	9.23	8.40	7.00	8.89	4.53		3.43		2.25
		J		5.1	5.1	5.1	1.5	3.0 1.7	3.0 0.5					
2	193 K	δ	-----	9.26	7.88	9.34	8.51	7.07	9.03	4.53	4.56	3.50	3.37	2.20
		J		5.5 2.1	5.1	5.5 2.1	1.6	2.7 1.9	2.7	2.5	2.5			

Table 2. ^{13}C-NMR spectra of 2-(1*H*-pyrazol-1-yl)pyridine (PzPy), 2-(1*H*-pyrazol-1-yl)pyrimidine (PzPm) and complexes **1** and **2** (δ values, solvent: [D$_6$]acetone)

Compound	Temp.		C-2	C-3	C-4	C-5	C-6	C-3'	C-4'	C-5'	C	CH_2	CH_2	CH_3
PzPy	293 K	δ	152.4	112.8	139.9	122.5	149.1	143.8	108.6	127.7	-----	-----	-----	---
1	293 K	δ	149.9	113.7	143.8	125.3	153.4	147.3	112.1	131.5	136.1	61.4	61.4	23.7
1	193 K	δ	149.3	113.3	143.5	124.9	153.2	146.7	111.8	131.2	135.8	63.3	59.5	23.3
PzPm	293 K	δ	---	-----	158.8	118.6	158.8	143.6	108.6	129.0	-----	-----	-----	-----
2	293 K	δ	154.4	-----	162.9	122.1	162.9	148.6	112.3	132.2	136.2	62.1	62.1	23.3
2	193 K	δ	154.4	-----	162.5	121.6	162.5	147.0	112.2	132.0	135.8	63.5	60.6	23.6

Variable-temperature experiments allow us to determine the coalescence temperature of the split signals at 193 K. Complex **1** showed two coalescence points for the allylic hydrogen atoms (H_{syn} at 243 K and H_{anti} at 280 K) while in the case of complex **2** three coalescences were observed: two for the allylic hydrogen atoms (H_{syn} at 216 K and H_{anti} at 230 K) and one for the pyrimidine 4-H and 6-H (268 K).

^{1}H-NMR spectra of compound **2** at various temperatures are represented in Figure 1.

The calculated activation free energies[10] at the coalescence ($\Delta G^{\ddagger}_{T}$) and the corresponding coalescence temperatures are compiled in Table 3. The $\Delta G^{\ddagger}_{T}$ values were calculated independently by two methods, using the Δν of the frozen spectrum and the width at half height of the signal at the coalescence.

Both chemical shifts and coalescence temperatures show a strong dependence on the solvent polarity. However, the

Figure 1. Variable-temperature spectra of complex **2**; i) aromatic region, ii) allylic region

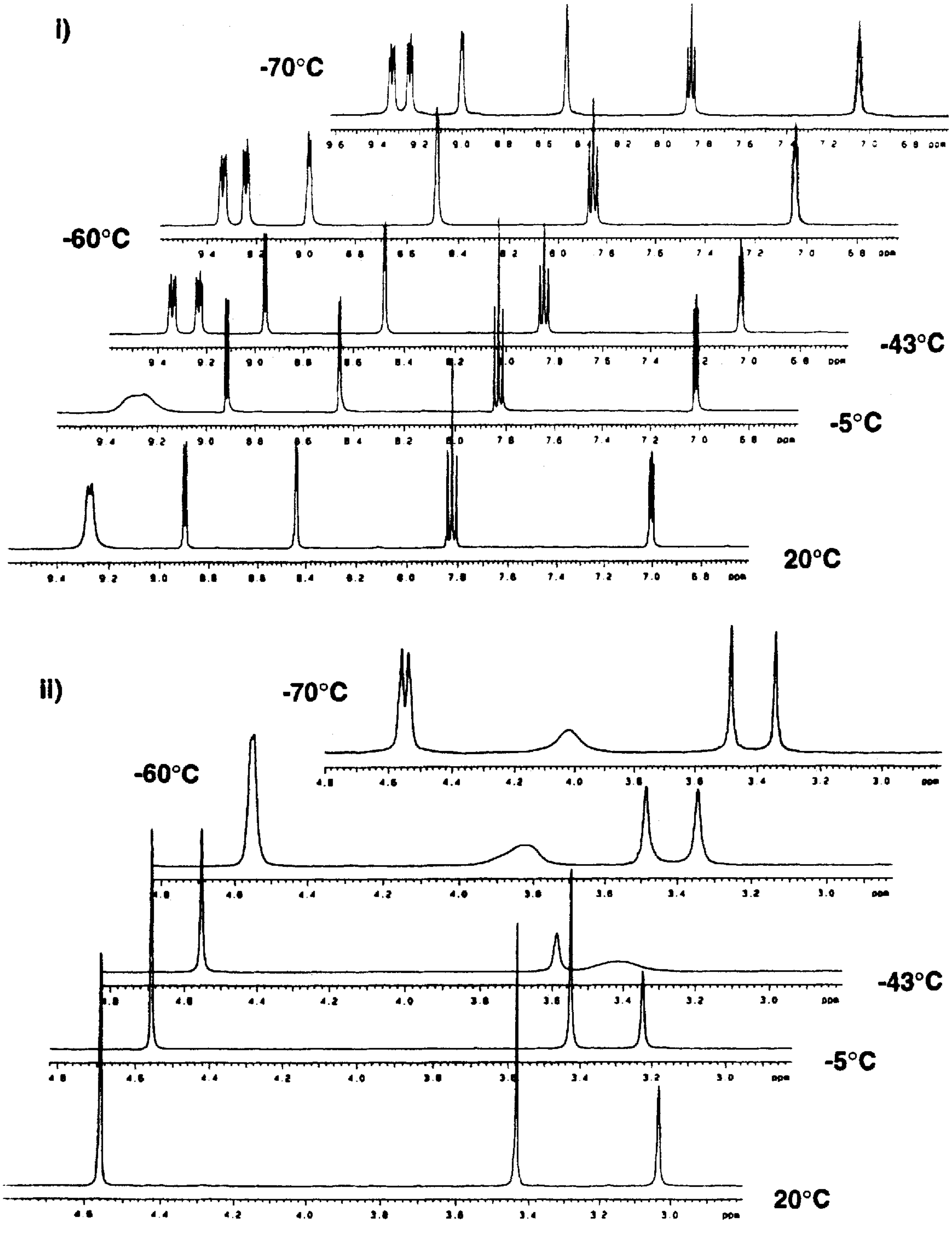


Table 3. Activation free energies and related parameters for the coalescence resonances

Coalescence Resonances [a]	Tc [b] (K)	$\Delta G_T^{\ddagger}$ [c] (kJ mol^{-1})	W* [d]	$\Delta G_T^{\ddagger}$ [e] (kJ mol^{-1})
Complex **1** H_{syn}	243	53.2	16.3	51.8
Complex **1** H_{anti}	280	57.0	46.0	57.6
Complex **2** H_{syn}	216	46.7	5.5	47.8
Complex **2** H_{anti}	230	47.2	39.5	47.3
Complex **2** 4-H,6-H	268	56.3	40.0	55.4

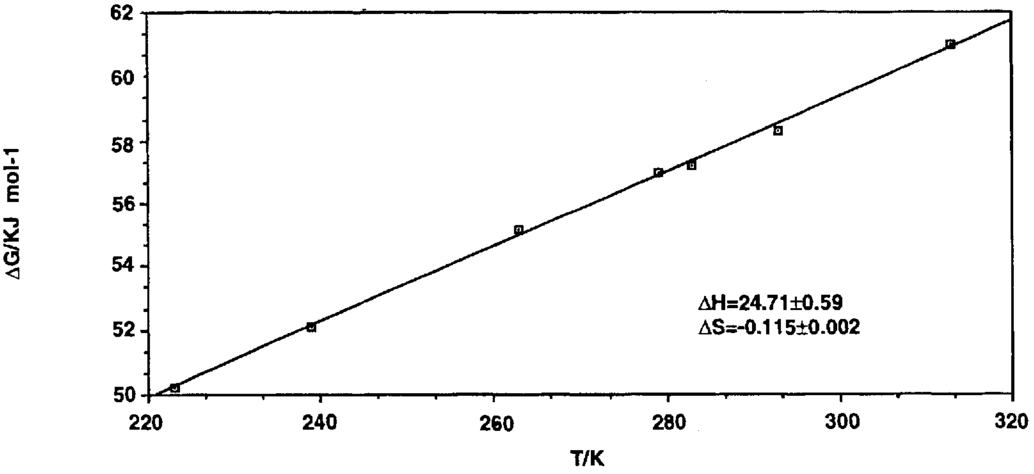
[a] Determined in [D_6]acetone solutions. – [b] Coalescence temperatures. – [c] Activation free energies at the coalescence temperatures calculated according to $\Delta G_T^{\ddagger} = aT[9.972 + \log(T/\Delta\nu)]$ ($a = 1.914 \times 10^{-2}$). – [d] W^* = Width at half height at the coalescence. – [e] Activation free energies at the coalescence temperatures calculated according to $\Delta G_T^{\ddagger} = aT[9.972 + \log(T/W^*)]$ ($a = 1.914 \times 10^{-2}$).

calculated activation free energies are always very similar and do not substantially depend on the solvent polarity.

Line-shape analysis using DNMR4[11] was performed for complex **1** showing a good agreement with the calculated energies at the coalescence.

ΔH^{+} and ΔS^{+} were calculated by plotting ΔG^{+} as a function of the temperature (Figure 2, $r^2 = 0.998$).

Figure 2. ΔG^{+} as a function of T for compound **1** using DNMR4



ΔG^{+} (kJ mol^{-1}) = 24.7 + 0.115 T; ΔH^{+} (kJ mol^{-1}) = 24.7 ± 0.6; ΔS^{+} (J K^{-1} mol^{-1}) = −0.115 ± 0.002.

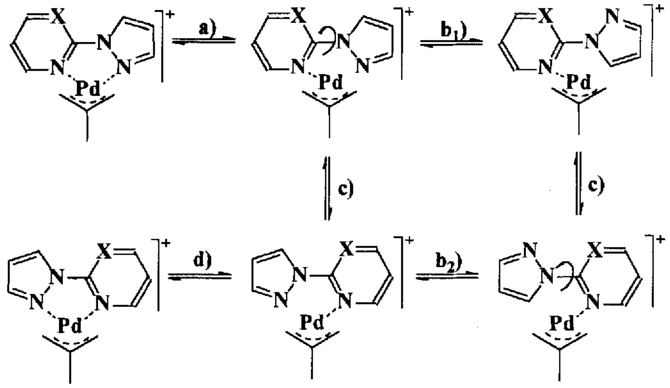
Several mechanisms were proposed for the isomerization or *syn-syn/anti-anti* interchange of (η^3-allyl)palladium complexes[12]. A simple rotation of the allyl ligand in its plane about the axis containing the metal center was often proposed[13] to account for some isomerizations in complexes of metals such as Mo, W, Fe. However, this mechanism is not widely accepted for square-planar palladium complexes, and orbital considerations estimated a high activation barrier in square-planar geometries[12b]. This rotation would be apparently the most facile process in a possible pentacoordinate intermediate[14]. A pentacoordinate activation state may also give rise to an isomerization by two consecutive Berry pseudorotations[12b,15]. Dissociative pathways were also proposed to explain similar phenomena, with monodentate ligands such as amines[5b,16], $SnCl_3$[17], CO[18], as well as macrocycles[19], polyenes[20] and also chelate N-donor ligands[4]. In an elegant study of (η^3-allyl)palladium-nitrogen chelate complexes where the π-allyl part is non-symmetric, Gogoll and coworkers[4e] explained the dynamic behavior by cleavage of a Pd-N bond to give a tricoordinate palladium intermediate. A Pd-N bond cleavage was also proposed by Pregosin and coworkers[3b] to occur in allylic complexes with N-donor chelating ligands.

We demonstrated by means of NOE experiments performed at 313 K (above the coalescence temperature) and 193 K (below the coalescence temperature) that a dissociative mechanism is also operative in complexes **1** and **2**.

In both complexes, at 193 K, irradiation at the frequency of both H_{syn} produces a NOE in H_{anti} but also in 3′-H of the pyrazole ring and 6-H of the pyridine and pyrimidine rings. Irradiation of H_{anti} produces a NOE with the geminal H_{syn} exclusively (3.51 ↔ 4.42 and 3.31 ↔ 4.44 for **1**, 3.5 ↔ 4.53 and 3.37 ↔ 4.56 for **2**). This effect was explained in the case of other allylpalladium complexes by the bending of the *anti* proton (30°) out of the allyl plane and away from the metal[3]. However, at 313 K, irradiation at H_{syn} and H_{anti} frequencies produces a NOE in 3′-H of the pyrazole ring, 6-H of the pyridine and pyrimidine rings but also in 4-H of the pyrimidine ring and even in 5′-H of the pyrazole ring in both complexes. This fact, together with the equivalence of 4-H and 6-H in the pyrimidine ring, confirms the dissociative mechanism and the internal ligand rotation. The observation in the case of complex **1** of a NOE between the allylic H_{syn} and H_{anti} with 5′-H of the pyrazole ring and not with 3-H of the pyridine ring shows that dissociation of the pyrazole N-2 metal bond is more favorable than dissociation of the pyridine N-1 metal bond. In complex **2** dissociation of the pyrimidine N-1 metal bond may also occur. Pregosin et al. working with an allylic complex containing the ligand $(CH_3)_2NCH_2NC_5H_4$ detected a selective cleavage of the pyridine N-1 metal bond[3b]. This cleavage must be related with the availability of the nitrogen lone pair and correlate with the basicity of the heterocycle (pyridine, pK_a = 5.2; pyrimidine, pK_a = 1.1; pyrazole, pK_a = 2.52)[22].

The whole process may be explained as depicted in Scheme 2 according to the following steps: a) dissociation of a Pd–N bond; b) internal ligand rotation; c) isomerization of the tricoordinate[21] intermediate and ligand rotation around the remaining Pd–N bond, d) reformation of the Pd–N bond. Steps b) and c) may be inverted.

Scheme 2. Proposed mechanism for the interchange process referred to the dissociation of the pyrazole ring



Scheme 2 illustrates only the decoordination of the pyrazole group and is applicable to both complexes (X = CH for **1**, X = N for **2**). Successive steps a), c) and d) explain the equivalence of the allylic ends. Step b_1) is necessary to account for the observed NOE effect between the allylic protons and 5′-H of the pyrazole ring. For complex **2** the decoordination of the pyrimidine ring also takes place and the mechanism would be similar to that illustrated in Scheme 2.

The dissociative mechanism is also supported by two other facts: a) the slightly negative value calculated for $\Delta S^{\neq}$ is in favor of a mechanism without participation of a pentacoordinate intermediate and b) the activation free energies found for **1** and **2** resemble the values described by Gogoll for similar complexes[4e].

Finally, we must emphasize that a η^3-η^1-η^3 mechanism although it may explain some of the observed phenomena, it may neither account for the 6-H,4-H interchange of the pyrimidine ring nor for the commmented NOE effects.

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Experimental

All reactions were performed by using standard Schlenk techniques under dry oxygen-free nitrogen. Solvents were distilled from the appropriate drying agents and degassed before use. – Elemental analyses: Perkin-Elmer 2400 microanalyzer. – IR spectra: Perkin-Elmer PE 883, Nujol mulls between CsI plates. – Mass spectra: VG Autospec instrument with FAB technique and nitrobenzyl alcohol as matrix. – ^{1}H- and ^{13}C-NMR spectra: Varian Unity 300, samples in [D$_6$]acetone (3 mg in 0.7 ml). Chemical shifts (ppm) were referenced to the acetone signal (2.05 ppm) in all cases. – COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 μs, relaxation delay 1 s, number of scans 4, number of increments 512. – NOE-difference spectra: acquisition time 3.27 s, pulse width 18 μs, relaxation delay 4 s, irradiation power, 5–10 dB, number of scans 120. For variable-temperature spectra, the probe temperature was controlled (±1 K) by a standard unit calibrated with a methanol reference. Samples were allowed to equilibrate for 10 min at each temperature before recording of the spectra. – Line-shape analysis was carried out by the DNMR4 program[11] with a PC computer. – 2-(1*H*-Pyrazol-1-yl)pyridine and 2-(1*H*-pyrazol-1-yl)pyrimidine were prepared from 2-chloropyridine and 2-chloropyrimidine by phase-transfer-catalysis in the absence of solvent[23].

2-(1H-Pyrazol-1-yl)pyridine: A mixture of pyrazole (1.362 g), potassium *tert*-butoxide (4.489 g) and aliquat 336 (0.6 g) was stirred at 120 °C for 30 min. 2-Chloropyridine (1.25 g) was added at 120 °C and the reaction mixture was stirred at this temperature for 72 h. Extraction with dichloromethane (50 ml), removal of the solvent from the extract and ball-to-ball distillation of the residue afforded 2.3 g (80%) of 2-(1*H*-pyrazol-1-yl)pyridine, m.p. 39 °C (ref.[24] 38–40 °C).

2-(1H-Pyrazol-1-yl)pyrimidine: A mixture of pyrazole (204 mg), potassium *tert*-butoxide (0.6 g) and aliquat 336 (0.08 g) was stirred at 120 °C for 30 min. 2-Chloropyrimidine (0.515 g) was added at 120 °C and the reaction mixture was stirred at this temperature for 1 h. Extraction with dichloromethane (50 ml), removal of the solvent from the extract and flash chromatography of the residue on silica gel using ethyl acetate as the eluent afforded 400 mg (90%) of 2-(1*H*-pyrazol-1-yl)pyrimidine, m.p. 67–68 °C (ref.[6a] 68–70 °C).

[Pd(η^3-C_4H_7)(μ-Cl)]$_2$ was prepared as described in ref.[25].

{Pd(η^3-C_4H_7)}(PyPz)CF_3SO_3 (**1**): To a solution of [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (99 mg, 0.25 mmol) in 20 ml of acetone $AgCF_3SO_3$ (129 mg, 0.50 mmol) was added. The solution was stirred at room temp. for 4 h and the resulting suspension was filtered off. Then PyPz (73 mg, 0.50 mmol) was added to the filtrate. After stirring for 60 min a colorless solution had formed which was evaporated to dryness. The solid was purified by dissolving it in dichloromethane and layering the resulting solution with diethyl ether in a Schlenk tube. Yield: 187 mg (82%). – MS (FAB); *m/z*: 306 [M – $CF_3SO_3^+$]. – $C_{13}H_{14}F_3N_3O_3PdS$ (455.55): calcd. C 34.26, H 3.10, N 9.22; found C 34.49, H 3.12, N 9.12.

{Pd(η^3-C_4H_7)}(PmPz)CF_3SO_3 (**2**): The complex was prepared similarly to the PyPz derivative. Yield: 126 mg (55%). – MS (FAB); *m/z*: 307 [M – $CF_3SO_3^+$]. – $C_{12}H_{13}F_3N_4O_3PdS$ (456.54): calcd. C 31.54, H 2.85, N 12.27; found C 32.18, H 2.92, N 12.29.

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[1] [1a] R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, **1985**. – [1b] J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer Verlag, New York, **1980**. – [1c] J. P. Collman, L. S. Hegedeus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, **1987**. – [1d] P. W. Jolly, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 283–295. – [1e] B. M. Trost, T. R. Verhoeven, *Comprehensive Organometallic Chemistry*, vol. 8 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**, pp. 799–938. – [1f] G. Consiglio, R. M. Waymounth, *Chem. Rev.* **1989**, *89*, 257. – [1g] M. Sawamura, H. Nagata, H. Sakamoto, Y. Ito, *J. Am. Chem. Soc.* **1992**, *114*, 2586–2592.

[2] [2a] T. Hayashi in *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), VCH Publishers, New York, **1993**, pp. 325–365 and references therein. – [2b] T. Hayashi, A. Yamamoto, *Tetrahedron Lett.* **1988**, *29*, 669. – [2c] T. Hayashi, A. Yamamoto, Y. Ito, E. Nishyoka, H. Miura, K. Yanagi, *J. Am. Chem. Soc.* **1989**, *111*, 6301–6311. – [2d] P. Matt, A. Pfaltz, *Angew. Chem. Int. Ed.*

Engl. **1993**, *32*, 566–568. – [2e] B. M. Trost, D. L. Van Vranken, C. Bingel, *J. Am. Chem. Soc.* **1992**, *114*, 9327–9343. – [2f] J. M. Brown, D. I. Hulmes, P. J. Guiry, *Tetrahedron* **1994**, *50*, 4493–4506.

[3] [3a] A. Albinati, C. J. Ammann, P. S. Pregosin, H. Rüegger, *Organometallics* **1990**, *9*, 1826–1833. – [3b] A. Albinati, R. W. Kunz, C. J. Ammann, P. S. Pregosin, *Organometallics* **1991**, *10*, 1800–1806.

[4] [4a] K. Vrieze, P. W. N. M. van Leeuwen, *Prog. Inorg. Chem.* **1971**, *14*, 1–64 and references cited therein. – [4b] J. W. Faller, M. J. Incorvia, M. E. Thomsen, *J. Am. Chem. Soc.* **1969**, *91*, 518–519. – [4c] D. L. Tibbetts, T. L. Brown, *J. Am. Chem. Soc.* **1970**, *92*, 3031–3034. – [4d] A. Gogoll, H. Greenberg, *Magn. Reson. Chem.* **1993**, *31*, 954–959. – [4e] A. Gogoll, J. Örnebro, H. Grennberg, J. E. Bäckvall, *J. Am. Chem. Soc.* **1994**, *116*, 3631–3632. – [4f] D. G. Brown, P. K. Byers, A. J. Canty, *Organometallics* **1990**, *9*, 1231–1235. – [4g] A. J. Canty, H. Jin, A. S. Roberts, P. R. Traill, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1995**, *489*, 153–159. – [4h] C. Breutel, P. S. Pregosin, R. Salzmann, A. Togni, *J. Am. Chem. Soc.* **1994**, *116*, 4067–4068. – [4i] P. S. Pregosin, R. Salzmann, A. Togni, *Organometallics* **1995**, *14*, 842–847.

[5] [5a] R. Fernández-Galán, B. R. Manzano, A. Otero, M. Lanfranchi, M. A. Pellinghelli, *Inorg. Chem.* **1994**, *33*, 2309–2312. – [5b] F. A. Jalón, B. R. Manzano, A. Otero, M. C. Rodríguez-Pérez, *J. Organomet. Chem.* **1995**, *494*, 179–185. – [5c] S. Trofimenko, *J. Am. Chem. Soc.* **1970**, *92*, 5118–5126.

[6] J. A. Casares, S. Coco, P. Espinet, Y.-S. Lin, *Organometallics* **1995**, *14*, 3058–3067 and references therein.

[7] [7a] P. J. Steel, E. C. Constable, *J. Chem. Research (S)* **1989**, 189 *(M)* **1989**, 1601–1611. – [7b] M. Bruix, J. de Mendoza, J. Elguero, *Tetrahedron* **1987**, *43*, 4663–4668. – [7c] P. J. Steel, E. C. Constable, *J. Chem. Soc., Dalton Trans.* **1990**, 1389–1396.

[8] H. Günther, *NMR Spectroscopy*, John Wiley & Sons, New York, **1980**.

[9] E. Breitmeier, W. Voelter, *Carbon 13 NMR Spectroscopy. High Resolution Methods and Applications in Organic Chemistry and Biochemistry*, 3rd ed., VCH, Weinheim, **1987**.

[10] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, **1982**.

[11] [11a] G. Binsch, *J. Am. Chem. Soc.* **1969**, *91*, 1304–1309. – [11b] D. A. Kleier, G. Binsch, *J. Magn. Reson.* **1970**, *3*, 146–160.

[12] [12a] P. M. Maitlis, P. Espinet, M. J. H. Russell, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds.; Pergamon Press, Oxford, **1982**, *6*, 385–454. – [12b] K. Vrieze in *Dynamic Nuclear Magnetic Resonance Spectroscopy*, L. M. Jackman and F. A. Cotton, Eds. Academic Press, New York, **1975**, pp. 441–487.

[13] [13a] J. W. Faller, M. J. Incorvia, *Inorg. Chem.* **1968**, *7*, 840–842. – [13b] J. W. Faller, D. A. Haitko, *J. Organomet. Chem.* **1979**, *149*, C19–C23. – [13c] J. W. Faller, M. A. Adams, *J. Organomet. Chem.* **1979**, *170*, 71–80. – [13d] R. Benn, A. Rufinska, G. Schroth, *J. Organomet. Chem.* **1981**, *217*, 91–104. – [13e] P. K. Baber, S. Clamp, N. G. Connelly, M. Murray, J. B. Sheridan, *J. Chem. Soc. Chem. Commun.* **1986**, 459–460. – [13f] A. D. Horton, A. C. Kemball, M. J. Mays, *J. Chem. Soc., Dalton Trans.* **1988**, 2953–2958.

[14] T. Boschi, U. Belluco, T. Toniolo, R. Favez, R. Roulet, *Inorg. Chim. Acta* **1979**, *23*, 37.

[15] [15a] B. Crociani, F. Di Bianca, A. Giovenco, T. Boschi, *Inorg. Chim. Acta* **1987**, *127*, 169–182. – [15b] S. Hansson, P.-O. Norrby, M. P. T. Sjögren, B. Åkerman, M. E. Cuccilito, F. Giorjuno, A. Vitagliano, *Organometallics* **1993**, *12*, 4940–4948.

[16] [16a] J. W. Faller, M. J. Incorvia, *J. Organomet. Chem.* **1969**, *19*, P13–P16. – [16b] J. W. Faller, M. J. Mattina, *Inorg. Chem.* **1972**, *11*, 1296–1307.

[17] C. Amman, P. S. Pregosin, H. Rüegger, M. Grassi, A. Musco, *Magn. Reson. Chem.* **1989**, *27*, 355–359.

[18] M. Grassi, S. V. Meille, A. Musco, R. Pontellini, A. Sironi, *J. Chem. Soc., Dalton Trans.* **1989**, 615–621.

[19] [19a] G. Hunter, A. McAuley, T. W. Whitcombe, *Inorg. Chem.* **1988**, *27*, 2634–2639. – [19b] S. Liu, C. R. Lucas, M. J. Newlands, J.-P. Charland, *Inorg. Chem.* **1990**, *29*, 4380–4385.

[20] D. J. Mabbott, B. E. Mann, P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* **1977**, 294–299.

[21] [21a] D. L. Thorn, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090. – [21b] G. Alibrandi, L. M. Scolaro, R. Romeo, *Inorg. Chem.* **1991**, *30*, 4007–4013.

[22] A. R. Katritzky Ed., *Handbook of Heterocyclic Chemistry*, Pergamon Press, Oxford **1985**.

[23] A. Loupy, N. Philippon, P. Pigeon, H. Galons, *Heterocycles* **1991**, *32*, 1947–1953.

[24] M. A. Khan, J. B. Poyla, *J. Chem. Soc. (C)* **1970**, 85–91.

[25] [25a] W. T. Dent, R. Long, A. J. Wilkinson, *J. Chem. Soc.* **1964**, 1585. – [25b] Y. Tatsuno, T. Yoshida, *Inorg. Synth.* **1979**, *19*, 220–221.

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