Multinuclear NMR study of Au(I), Pd(II) and Ag(I) pyrazole complexes to investigate the coordination mode

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Dedicated to Professor José Elguero on his 70th anniversary
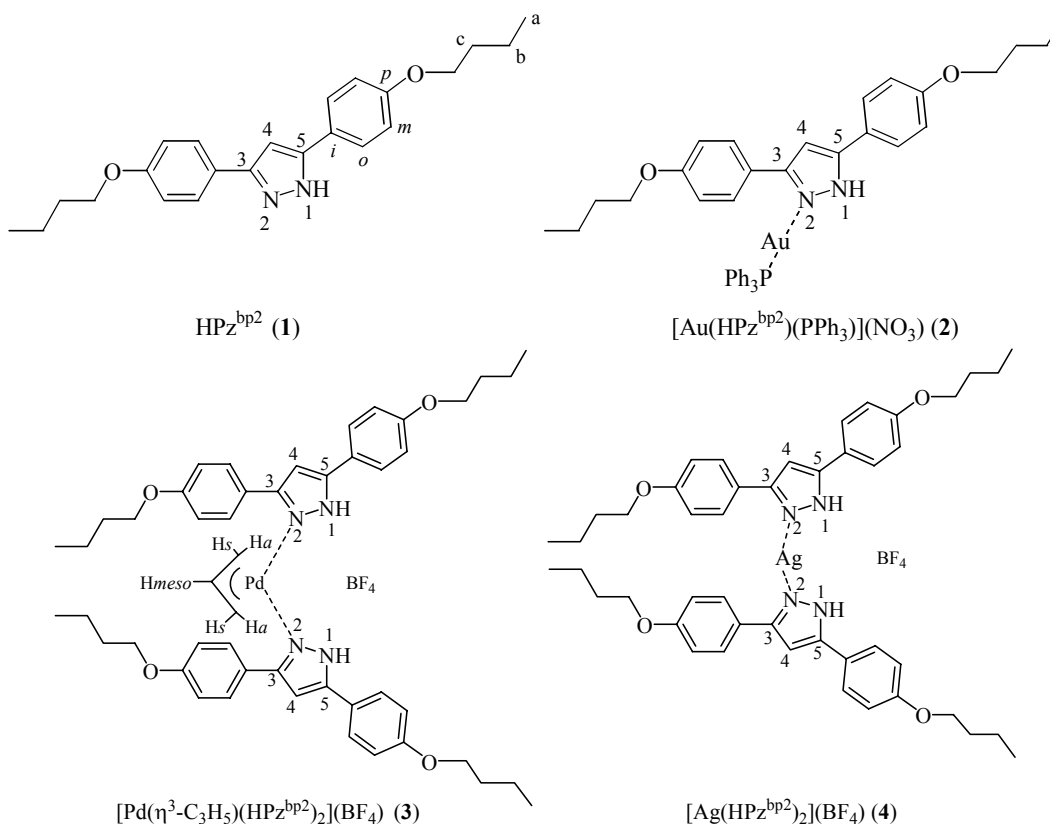**Dedicated to Professor Pedro Molina on his 60th anniversary**

Abstract

The coordination effects induced on the ^{1}H-, ^{13}C-, and ^{15}N- NMR chemical shifts of the 3,5-di-(4-butoxyphenyl)-1H-pyrazole, HPzbp2 (**1**) have been quantified for the following complexes:- $[Au(HPz^{bp2})(PPh_3)](NO_3)$ (**2**), $[Pd(\eta3-C_3H_5)(HPz^{bp2})_2](BF_4)$ (**3**) [or $Pd(\eta3-C_3H_5)(^{15}N_2-HPz^{bp2})_2](BF_4)$ ($^{15}N_2$-**3**)], and $[Ag(HPz^{bp2})_2](BF_4)$ (**4**), in solution and in the solid state. ^{15}N-CPMAS NMR proved to be the most useful tool for establishing the coordination site. The increase in the nitrogen-shielding on metal-complexation owing to changes in the paramagnetic shielding term is about −55 ppm.

Keywords: Pyrazole ligands, gold, palladium, silver, CPMAS NMR

Introduction

3,5-Disubstituted pyrazoles with long-chain substituents HpzR^2 show mesomorphic properties, and their coordination behavior with metals has recently received much attention in view of their possible applications.[1–3]

We have performed a multinuclear ^{1}H-, ^{13}C-, and ^{15}N- NMR study of several gold(I)-, palladium(II)-, and silver(I)- derivatives (**2–4**) of 3,5-di-(4-butoxyphenyl)-1H-pyrazole, HPz^{bp2} (**1**)[1] previously reported by us,[3,4] in order to investigate whether the chemical shift effects induced by the metals could be used as criteria to establish the coordination site.

HPz^{bp2} (**1**)

[Au(HPz^{bp2})(PPh$_3$)](NO$_3$) (**2**)

[Pd(η^3-C$_3$H$_5$)(HPz^{bp2})$_2$](BF$_4$) (**3**)

[Ag(HPz^{bp2})$_2$](BF$_4$) (**4**)

Results and Discussion

The preparation of the HPz^{bp2} (**1**) [or ^{15}N$_2$-HPz^{bp2} (**^{15}N$_2$-1**)] was accomplished in quantitative yield by reaction of the corresponding 1,3-bis-(4-butoxyphenyl)propane-1,3-dione (**5**) with hydrazine hydrate [or ^{15}N$_2$–hydrazine sulfate] in ethanol.

The complexes were obtained by standard methods from the 3,5-di-(4-butoxyphenyl)-1*H*-pyrazole HPz^{bp2} (**1**). When **1** was treated with [Au(NO$_3$)(PPh$_3$)] in a 1:1 molar ratio, [Au(HPz^{bp2})(PPh$_3$)](NO$_3$) (**2**) was formed. The ionic complex [Pd(η^3-C$_3$H$_5$)(S)$_2$]BF$_4$ (S = acetone), prepared *in situ*, reacted with HPz^{bp2} (**1**) [or ^{15}N$_2$-HPz^{bp2} (**^{15}N$_2$-1**)] in the same solvent in a 1:2 molar ratio to yield [Pd(η^3-C$_3$H$_5$)(HPz^{bp2})$_2$](BF$_4$) (**3**) [or Pd(η^3-C$_3$H$_5$)(^{15}N$_2$-HPz^{bp2})$_2$](BF$_4$) (**^{15}N$_2$-3**)]. Finally, addition of AgBF$_4$ to a THF solution of **1**, in a molar ratio 1:2, afforded [Ag(HPz^{bp2})$_2$](BF$_4$), (**4**).

The ^{1}H-, ^{13}C-, and ^{15}N- NMR spectra were obtained in DMSO-d_6, CDCl$_3$ or CD$_2$Cl$_2$ solutions, and the chemical shifts and coupling constants are reported in Tables 1–3. The ^{15}N-NMR chemical shifts referenced to external nitromethane were obtained by 2D- (^{1}H–^{15}N) gs–HMBC and 2D (^{1}H–^{15}N) gs–HMQC experiments, save for the cases of the labeled derivatives ^{15}N$_2$-HPz^{bp2} (**^{15}N$_2$-1**) and [Pd(η^3-C$_3$H$_5$)(^{15}N$_2$-HPz^{bp2})$_2$](BF$_4$) (**^{15}N$_2$-3**) where the data were determined by the Inverse Gated ^{1}H-Decoupling Technique.[5]

Solid state ^{13}C- and ^{15}N- NMR experiments were achieved by using the CPMAS sequence; in the ^{13}C- NMR the non- quaternary suppression sequence (NQS) was applied to identify the

quaternary carbon atoms C-3, C-5, C-*ipso*, and C-*para*.[6] In ^{15}N- NMR, solid ammonium chloride was used as reference and the chemical shift data were transformed to external nitromethane through the equation: $\delta\,(NO_2CH_3) = \delta(NH_4Cl) - 338.1$ ppm.[7]

When analyzing the NMR parameters reported in Table 1 for ^{1}H- NMR, Table 2 for ^{13}C-NMR, and Table 3 for ^{15}N- NMR, the most relevant features are as follows.

Coordination with silver(I) does not affect the ^{1}H- NMR chemical shifts, while in the case of palladium(II), coordination induces an upfield shift of ~ –0.16 ppm on the H-4, H-*ortho* and H-*meta* protons; with gold(I) only a downfield shift on the H-4 and H-*ortho* protons, of about +0.16 ppm, was observed.

Table 1. ^{1}H- NMR chemical shifts (δ in ppm) and coupling constants (J in Hz). In brackets are the coordinative chemical-shift effects

Compd.	[a]CH$_3$	[b]CH$_2$	[c]CH$_2$	O–CH$_2$	H- *meta*	H- *ortho*	H- 4	N-H	Solvent
(1)	0.99 (t) $^3J= 7.4$	1.51 (m) $^3J= 7.5$	1.79 (m) $^3J= 7.0$	3.99 (t) $^3J= 6.5$	6.94 (m)	7.63(m)	6.68 (s)	10.0	CDCl$_3$
	0.92 (t) $^3J= 7.4$	1.42 (m) $^3J= 7.5$	1.68 (m) $^3J= 7.0$	3.95 (t) $^3J= 6.5$	6.97 (m)	7.58(m)	6.91 (s)	13.08	DMSO-d$_6$
(2)	0.99 (t) $^3J= 7.4$	1.51 (m) $^3J= 7.5$	1.79 (m)	4.0 (t) $^3J= 6.5$	6.95 (m) [+0.01]	7.82 (m) [+0.19]	6.82 (s) [+0.14]	a	CD$_2$Cl$_2$
(**[15]N$_2$-3**)[b]	0.99 (t) $^3J= 7.4$	1.50 (m) $^3J= 7.4$	1.78 (m)	3.93 (t) $^3J= 6.7$	6.82 (m) [-0.12]	7.40 (m) [-0.23]	6.54 (t) $^3J=^3J=$ 3.4 [-0.14]	11.86(m) $^1J=$ 106.5 $^2J=$ 4.2	CDCl$_3$
(4)	1.00 (t) $^3J= 7.4$	1.52 (m) $^3J= 7.5$	1.81 (m) $^3J= 7.1$	3.98 (t) $^3J= 6.5$	6.87 (m) [-0.07]	7.60 (m) [-0.03]	6.69 (s) [+0.01]	11.86	CD$_2$Cl$_2$

[a] Not detected.
[b] 3.19 (H$_{anti}$, d, $^3J = 12.3$), 3.93 (H$_{syn.}$, br.), 5.71(H$_{meso}$, m, $^3J_s = 6.2$, $^3J_a = 12.3$).
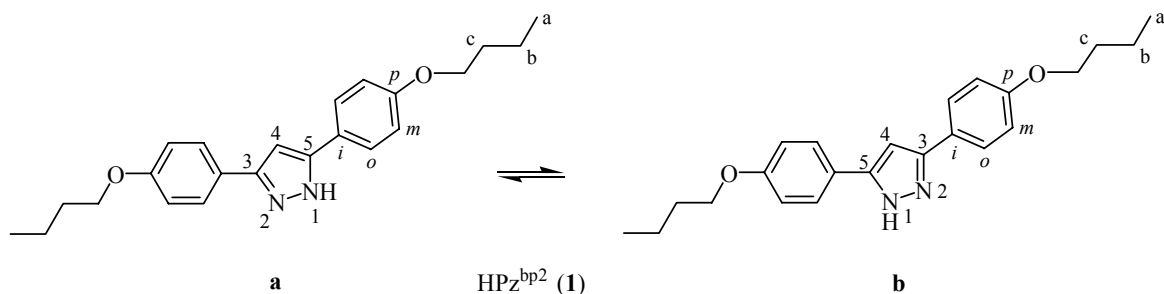
In solution, the ^{13}C- NMR data for C-3 and C-5 of HPz- (**1**) cannot be compared with those of the corresponding complexes because a mean value of 148.5 ppm, corresponding to the two degenerate forms **a** and **b** in fast exchange equilibrium, is observed at 300 K.[8] The coordination effect on C-4 decreases when going from gold [+3.1 ppm] to palladium [+2.7 ppm] and to silver [+2.1 ppm] and the coupling constant value ^1J (C-4, H-4) increases with coordination [~ 5 Hz]. Although to a lesser extent, a similar effect takes place on C- *ortho*.

However, the ^{13}C- CPMAS NMR of the pyrazole **1** presents two distinct values for C-3 and C-5 (150.3 and 144.4 ppm) as well as for the carbon atoms which correspond to the two 4-butoxyphenyl groups, meaning that the tautomeric equilibrium between forms **a** and **b** is frozen—in agreement with its X-ray structure.[1] In this way the metal- interaction effects could be evaluated: on C-4, the coordination induces a similar effect in the three complexes [~ +4 ppm],

on C-3 the effect is smaller for gold- [$+1.2$ ppm] than for palladium- and silver- [$\sim +4$ ppm]-complexes and, finally, δC-5 is almost unaltered.

Table 2. ^{13}C- NMR chemical shifts (δ in ppm) and coupling constants (J in Hz)

Compound	^{a}CH$_3$	^{b}CH$_2$	^{c}CH$_2$	O-CH$_2$	C-*syn* C-*anti*	C-*meso*	Solvent
(1)	13.8 $^1J = 124.7$ $^2J=^3J= 4.1$	19.2 $^1J= 124.2$	31.3 $^1J= 126.1$	67.7 $^1J= 142.4$ $^2J=^3J=4.1$			CDCl$_3$
	14.4 15.4	20.1 20.7	32.7 33.5	67.5 68.3			CPMAS
(2)	14.2 $^1J = 124.8$ $^2J=^3J= 4.0$	19.8 $^1J= 127.1$	31.8 $^1J= 125.6$	68.5 $^1J= 142.8$ $^2J=^3J= 4.2$			CD$_2$Cl$_2$
	13.4 14.2	18.6 19.3	30.0 31.9	66.2 69.1			CPMAS
(3)	13.8 $^1J = 125.0$	19.2 $^1J= 125.1$	31.3 $^1J= 125.1$	67.8 $^1J= 143.1$	62.1 $^1J= 158.9$	117.1 $^1J= 164.3$	CDCl$_3$
	14.0	19.5	31.6	67.5	59.0	118.2	CPMAS
	15.1	20.3	32.9	68.2 68.8	60.8 62.1 63.5		
(4)	14.2 $^1J = 124.9$ $^2J = ^3J = 3.9$	19.8 $^1J = 125.3$	31.9 $^1J = 125.5$	68.5 $^1J = 142.9$ $^2J = ^3J = 4.1$			CD$_2$Cl$_2$
	13.8 14.9	18.5 19.6	31.4	67.9			CPMAS

a   HPz^{bp2} (**1**)   b

For the phenyl groups, the C- *para* and C- *meta* are nearly unaffected, and the C- *ortho* signals are shifted downfield [$+2.8$ to $+1.5$ ppm]: the C-*ipso* carbons move upfield upon coordination [Au > Pd > Ag]. Metal complexation also shifts upfield the carbon atoms of the butoxy chains (See Table 2).

Table 3. ^{13}C- NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for ring-carbons. In brackets are the coordinative chemical shift effects

Compound	C-para	C-meta	C-ortho	C-ipso	C-3	C-4	C-5	Solvent
(1)	159.0	114.6	126.8	124.0	148.5	98.6	148.5	CDCl$_3$
	$^3J=^3J=9.0$	$^1J=159.4$	$^1J=158.3$			$^1J=173.2$		
		$^3J=4.6$	$^3J=7.5$					
	158.8	111.3	125.6	123.2	150.3	96.7	144.4	CPMAS
	159.5	117.9		125.6				
(2)	161.0	115.5	129.0	122.6	150.7 ^{a}	101.7	146.0 ^{a}	CD$_2$Cl$_2$
	$^3J=^3J=9.1$	$^1J=160.7$	$^1J=163.4$			$^1J=179.0$		
		$^3J=4.6$	$^3J=7.1$			[+1.1]		
	158.3	109.0	127.4	119.6	151.5	101.3	143.6	CPMAS
	159.7	110.2	[+1.8]	120.0	[+1.2]	[+4.6]	[-0.8]	
		117.3	128.4	[-4.6]				
		117.9	[+2.8]					
(3)	159.7	114.5	128.5	120.0	155.0	101.3	146.4	CDCl$_3$
	160.0	$^1J=160.5$	$^1J=158.0$	$^3J=^3J=7$		$^1J=177.1$		
	$^3J=^3J=8.9$	$^3J=3.5$	$^3J=7.0$	.3		[+2.7]		
		115.1	127.1	124.3 ^{a}				
		$^1J=160.7$	$^1J=158.2$					
		$^3J=3.2$	$^3J=7.0$					
	158.8	114.0	128.0	119.7	154.5	99.2	144.7	CPMAS
	159.6	114.7	[+2.4]	120.6	[+4.2]	[+0.6]	[+0.3]	
	160.0			123.3	155.3	100.2	145.8	
				[-3.2]	[+5.0]	[+3.5]	[+1.4]	
(4)	160.8	115.6	127.0	122.6	153.0 ^{a}	100.7	148.4 ^{a}	CD$_2$Cl$_2$
		$^1J=160.8$	$^1J=158.6$			$^1J=177.2$		
		$^3J=4.6$	$^3J=7.1$			[+2.1]		
	160.0	114.8	125.6	119.8	153.1	100.9	145.0	CPMAS
		115.4	127.1	124.5	[+2.8]	[+4.2]	[+0.6]	
			[+1.5]	[-2.3]	155.1			
					[+4.8]			

^{a} Broad signal.

The splittings observed for the NMR carbon signals at the solid state can be explained as due to the presence of several independent molecules in the asymmetric unit and intermolecular packing effects.[9]

The ^{15}N- CPMAS NMR chemical shifts presented in Table 4 are the most useful ones for determining the coordination effects on the HPz^{bp2} (1) ligand. The 3,5-di-(4-butoxyphenyl)-1H-

pyrazole, HPz^{bp2} (**1**) gives two signals at -183.6 and -98.0 ppm (these are different from the value of -143.5 ppm found in CDCl$_3$ solution) indicating that the exchange between the **a** and **b** tautomers is blocked. The chemical shift of the pyrazole N-2, that bonds to the metal, changes by about -55 ppm; this effect can be compared to that observed when pyrazole derivatives are protonated, *i.e.*, -111.6 ppm for *N*-methylpyrazole.[10] As expected the coordination with the metal does not significantly affect the chemical shift value of N-1.

A recent attempt to use ^{15}N- NMR studies in solution to probe the nature of electronic metal–ligand interactions in some organoplatinum complexes containing azines resulted in similar coordination effects [~ -54 ppm] on the nitrogen which binds the metal.[11]
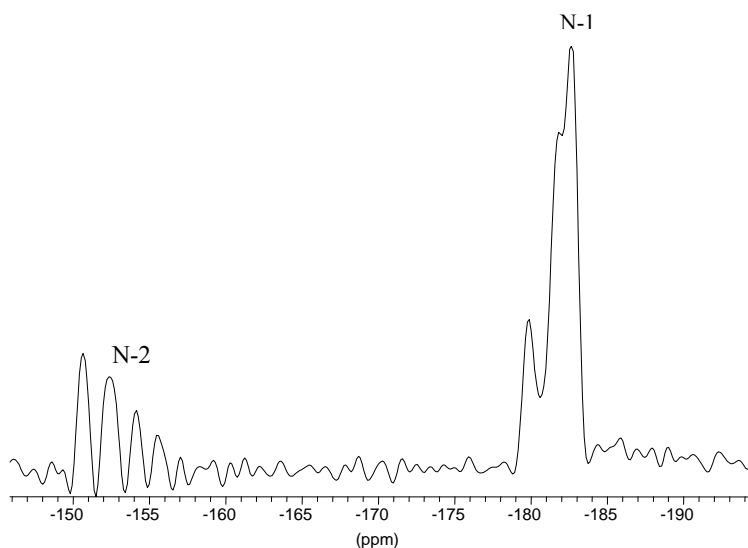

Figure 1. ^{15}N- CPMAS NMR chemical shifts of [Pd(η^3-C$_3$H$_5$)(^{15}N$_2$-HPz^{bp2})$_2$](BF$_4$) (**^{15}N$_2$-3**).

The ^{15}N- CPMAS NMR data for the compound **^{15}N$_2$-3** deserve special comment because it shows three different signals for N-1 and four signals for N-2, owing to spin–spin couplings between ^{15}N–^{19}F and ^{15}N–^{105}Pd.[12] The corresponding spectrum of **3** shows only two pairs of signals for each nitrogen. As we have already described, this derivative crystallizes in the monoclinic space-group *P*21/*n* as three Pd(η^3-C$_3$H$_5$)(^{15}N$_2$-HPz^{bp2})$_2$]$^+$ species,[3] showing different dihedral angles between the phenyl and pyrazole groups which are associated through BF$_4^-$ groups in the asymmetric unit. Each BF$_4^-$ group is bonded through strong N-H$^{...}$F hydrogen-bonds, with two N-H pyrazole groups bridging two neighboring complexes. Probably the splitting of around 40 Hz observed for N-1 corresponds to the coupling between ^{15}N- and ^{19}F-through the hydrogen-bond (N-H$^{+...}$F-BF$_3$) in compound **3** in the solid state, even though there are no literature data for such types of coupling.[13]

Table 4. ^{15}N- NMR chemical shifts (δ in ppm). In brackets are the coordination effects on the chemical shifts

Compound	N-1	N-2	Solvent
(^{15}N$_2$-1)	−143.5	−143.5	CDCl$_3$
(^{15}N$_2$-1)	−183.6	−98.0	CPMAS
(2)	^{a}	−156.0 [−58.0]	CD$_2$Cl$_2$
	-179.8 [+3.8]	^{a}	CPMAS
(^{15}N$_2$-3)	−188.2 [−4.6] $^1J_{N-1,N-2}$= 8.0	−157.4 [−59.4]	CDCl$_3$
	−180.0/−181.8/−182.8 [+3.6] / [+1.8]/ [+0.8]	−150.6 / −152.2/−154.0 / −155.4 [-52.6] / [-54.2]/[−56.0] / [−57.4]	CPMAS
(3)	−179.9/−182.5 [+3.7] / [+1.1]	−151.4/−154.7 [−53.4] / [−56.7]	CPMAS
(4)	−185.0 [−1.4]	−152.0 [−54.0]	CD$_2$Cl$_2$
	−188.0 [−4.4]	−149.0 [−51.0]	CPMAS

^{a} Not detected.

Conclusions

Although the data obtained from our study are limited, they demonstrate the advantages of ^{15}N-NMR (over ^{1}H- and ^{13}C- NMR) chemical- shift effects induced by metal coordination, to provide a connection between trends in coordination shifts and metal bonding. The negative coordination shifts of all metal-bound nitrogen atoms in the complexes [Au(HPz^{bp2})(PPh$_3$)](NO$_3$) (2), [Pd(η^3-C$_3$H$_5$)(HPz^{bp2})$_2$](BF$_4$) (3) and [Ag(HPz^{bp2})$_2$](BF$_4$) (4) parallel the effects induced by alkylation or protonation of a nitrogen lone-pair.

Experimental Section

Synthesis. The commercial starting materials [AuCl(PPh$_3$)], [Pd(η^3-C$_3$H$_5$)(μ-Cl)]$_2$, and [AgBF$_4$] were used as supplied. Commercial solvents were dried prior to use. Melting points were determined on a microscope hot-stage apparatus and are uncorrected. R.T. denotes room temperature.

HPz^{bp2} (1). To a mixture of 4-butoxyacetophenone (3.84 g, 0.02 mol) and ethyl 4-butoxybenzoate (6.67 g, 0.03 mol) in dimethoxyethane (80 mL), 60% NaH (2.00 g, 0.05 mol) was carefully added. After refluxing for 3 h the mixture was cooled at room temperature, poured into water (150 mL) and acidified with dilute HCl. The product was extracted with diethyl ether, and the combined extracts dried over Na$_2$SO$_4$ and then filtered. Evaporation of the solvent gave the 1,3-bis-(4-butoxyphenyl)propane-1,3-dione (5) (5.53 g, 0.015 mol, 75%).

To a suspension of the crude 1,3-dione (**5**) (737 mg, 2 mmol) in EtOH (50 mL) was added an excess of 98% hydrazine monohydrate (112 mg, 2.2 mmol), and the mixture was heated at reflux for 3 h. Then the solution was allowed to cool to R.T. and kept overnight at 4°C. The precipitate was removed by filtration and dried in vacuum, giving the 3,5-di-(4-butoxyphenyl)-1*H*-pyrazole (**1**). Yield 620 mg, 1.7 mmol, 85%. M.p. 183.7-184.5 °C, mol. formula $C_{23}H_{28}N_2$, mol. wt. 364.48.

^{15}**N$_2$-HPz^{bp2} (^{15}N$_2$-1).** To a suspension of the crude 1,3-dione (**5**) (501 mg, 1.36 mmol) in EtOH (65 mL) was added an excess of labeled ^{15}N$_2$-hydrazine sulfate (249 mg, 1.89 mmol) dissolved in 1.6 mL of 10% aq. NaOH and the mixture heated at reflux for 22 h. The reaction mixture was filtered, the insoluble salts washed with $CHCl_3$, and the filtrate allowed to cool at R.T. and kept overnight at 4°C. The precipitated product, ^{15}N$_2$-3,5-di-(4-butoxyphenyl)-1*H*-pyrazole (^{15}**N$_2$-1**). Yield 267 mg, 0.73 mmol, 54%, was isolated by filtration and dried in vacuum.

[Au(HPz^{bp2})(PPh$_3$)](NO$_3$) (2). AgNO$_3$ (34 mg, 0.20 mmol) was added under nitrogen to a solution of [AuCl(PPh$_3$)] (100mg, 0.20 mmol) in acetone (25 mL). After stirring for 2 h in darkness, the solution was filtered through a plug of Celite and the solvent was evaporated. Compound **1** (HPz^{bp2}, 73 mg, 0.20 mmol) was added to a solution of the obtained product in dichloromethane, and the mixture stirred for 5 h at RT. The solvent was removed under vacuum to provide an oil, from which a white solid was isolated by addition of dichloromethane and hexane. This solid **(2)** was crystallized (dichloromethane/hexane). Yield 88 mg, 0.10 mmol, 50%. Mol. formula $C_{41}H_{43}AuN_3O_5P$, mol. wt. 884.74.

[Pd(η^3-C$_3$H$_5$)(HPz^{bp2})$_2$](BF$_4$) (3). AgBF$_4$ (0.18 mmol) was added under nitrogen to a solution of [Pd(η^3-C$_3$H$_5$)(μ-Cl)]$_2$ (33 mg, 0.09 mmol) in freshly distilled acetone (15 mL). After stirring for 6 h in darkness, the solution was filtered through a plug of Celite and cooled with an ice bath. The pyrazole **1** (HPz^{bp2}, 131 mg, 0.36 mmol) was then added and the mixture stirred for 5 h. The solvent was removed under vacuum and the white product crystallized (dichloromethane/diethyl ether). Yield 69 mg, 0.07 mmol, 40%. Mol. formula $C_{49}H_{61}BF_4N_4O_4Pd$, mol. wt. 963.26.

The compound [Pd(η^3-C$_3$H$_5$)(^{15}N$_2$-HPz^{bp2})$_2$](BF$_4$) (^{15}**N$_2$-3**) was prepared in a similar way starting from the labeled compound ^{15}**N$_2$-1**.

[Ag(HPz^{bp2})$_2$](BF$_4$) (4). AgBF$_4$ (19 mg, 0.10 mmol) was added under nitrogen to a solution of HPz^{bp2} (71 mg, 0.20 mmol) in 10 mL of dry THF. After 24 h of stirring, the solvent was evaporated in vacuum, giving an oil from which a white solid was isolated after addition of dichloromethane and pentane. The product was crystallized from dichloromethane/hexane. Yield 37 mg, 0.04 mmol, 40%. Mol. formula $C_{49}H_{56}AgBF_4N_4O_4$, mol. wt. 923.63.

NMR parameters. Solution spectra were recorded on a Bruker DRX-400 spectrometer at 300 K (9.4 T, 400.13 MHz for ^{1}H-, 100.61 MHz for ^{13}C- and 40.56 MHz for ^{15}N-), using the appropriate solvent. Chemical shifts (δ in ppm) are given from external TMS for ^{1}H- and ^{13}C-, and external nitromethane (0.00 ppm) for ^{15}N- NMR. Coupling constants (*J* in Hz) are accurate to ±0.2 Hz for ^{1}H and ±0.6 Hz for ^{13}C- and ^{15}N- NMR. The assignments are based on NMR experiments with pulse field gradients: (^{1}H–^{1}H) gs-COSY, (^{1}H–^{13}C) gs-HMQC, (^{1}H–^{13}C) gs-HMBC, and (^{1}H–^{15}N) gs-HMBC.[5]

Solid-state ^{13}C- (100.73 MHz) and ^{15}N- (40.59 MHz) CPMAS-NMR spectra were obtained with a Bruker WB-400 spectrometer at 300 K with a wide-bore 4-mm DVT probe-head at rotational frequencies of *ca*. 5–10 kHz. Samples were carefully packed in ZrO_2 rotors, and the standard CPMAS pulse sequence and NQS technique (Non-Quaternary Suppression to observe only the quaternary C-atoms) were employed.[5]

Acknowledgements

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