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Multinuclear NMR solution studies on complexes of hexakis(pyrazol-1-yl)benzene (hpzb) with Ag(I)

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This paper is dedicated to Professor Usón for his outstanding contribution to organometallic chemistry

Abstract

The reaction of the polydentate N-donor ligand hexakis(pyrazol-1-yl)benzene (hpzb) with AgSbF₆/PPh₃ or AgClO₄PPh₃ in a 1:1 ratio leads to the complexes [Ag(PPh₃)(hpzb)]SbF₆ (1) or [Ag(PPh₃)(hpzb)]ClO₄ (3). When two or three equivalents of the silver derivatives are used the species [Ag(PPh₃)₂]X are formed in addition to 1 or 3. In the case of SbF₆⁻ the remaining Ag⁺ competes with AgPPh₃⁺ for coordination to hpzb and the derivative [Ag(hpzb)]SbF₆ (2) is also obtained, while in the case of ClO₄⁻ the insoluble salt AgClO₄ is formed. The same reactions performed with hpzb⁻¹⁵N₁₂ confirmed the presence of the N-donor ligand in 1–3. At room temperature a Ag–P dissociation process is observed for all the derivatives containing Ag–PPh₃ fragments. Complexes 1–3 show in solution an intramolecular argentotropic shift that makes the six pyrazolyl rings of the hpzb ligand equivalent on the ¹H NMR time scale. When the amount of counteranion present in solution is sufficiently high, an intermediate of lower coordination number (stabilized with the anion) is observed for complexes 1 and 3 in the low temperature ³¹P NMR spectra in addition to the three-coordinated species. This intermediate is more stable in the case of ClO₄⁻ due to the higher coordinating ability of this anion. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silver; N-donor ligands; Dynamic behaviour; Pyrazole; Phosphine

1. Introduction

The coordination chemistry of N-donor ligands has received a great deal of interest in recent decades [1]. The use of ligands containing N-substituted pyrazoles is very common [2], with the three main types of derivatives being polypyrazolylborates (scorpionates), polypyrazolylmethanes **A** (see Scheme 1) and polypyrazolylazines (such as pyridines, pyrimidines and s-triazines). On the other hand, polypyrazolylbenzenes have seldom been used. Only the (pyrazol-1-yl-methyl) derivatives of type

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B ('coelenterands') [3-19] and (pyrazol-1-yl)benzenes of type **C** containing two [20-24], three [25] or four [26] pyrazolyl rings have been studied as ligands (see Scheme 1).

However, hexakis(pyrazol-1-yl)benzene (hpzb), a member of the 'propellene' class of ligands that we have studied systematically [27–32], has very seldom been used previously (see Scheme 2) [33].

In a previous work, we have described the coordination chemistry of hpzb with different metallic fragments of Pd, Pt and Cu [33]. The use of these metals gives rise to mono- or dinuclear derivatives. In only one case was it possible to obtain a trinuclear complex. We decided to explore the behaviour of this ligand in the reaction with silver fragments. It is well known that silver–phosphine

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complexes [34–51], not only homoleptic species but also with other types of ligands, exhibit a rich dynamic behaviour involving Ag–P and/or Ag–N bond rupture in intra- or intermolecular processes. Some of the complexes reported contain pyrazolyl-derived ligands [42,43,45,46]. On the basis of the information presented above, the main goals of our work were as follows: (i) to analyse the possibility of obtaining silver complexes with different nuclearities, (ii) to study the fluxional behaviour of the new complexes obtained and (iii) to compare the results with those previously obtained with other metallic fragments.

2. Experimental

2.1. General comments

Manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Acetone-d₆ was degassed before use. AgSbF₆ and PPh₃ were used as purchased from Aldrich. Other starting materials were prepared as reported in the literature: AgClO₄PPh₃ [52],¹ hpzb [30]. ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹⁹F NMR spectra were recorded on a Varian Unity 300 spectrometer. ¹⁵N{¹H} NMR spectra were recorded on a Bruker DRX 400 spectrometer, Inverse Gated and gs-HMBC experiments were carried out to assign the ¹⁵N signals. Chemical shifts (ppm) are given relative to TMS (¹H and ¹³C), H₃PO₄ (³¹P), CFCl₃ (¹⁹F) and external CH₃NO₂ (¹⁵N). For variable temperature spectra the probe temperature $(\pm 1 \text{ K})$ was controlled by a standard unit calibrated with a methanol reference. Mass spectra (position of the peaks in Da) were recorded on a VG BIOTECH Quattro spectrometer (University of La Coruña) using the FAB⁺ technique and *m*-nitrobenzylic alcohol as matrix.

2.2. Sample preparations

2.2.1. $AgSbF_6/PPh_3/hpzb$

A solution of $[Ag(PPh_3)](SbF_6)$ (0.048 M, 2.0 ml) was prepared in a Schlenk tube from $AgSbF_6$ (32.87 mg, 95.9×10^{-3} mmol) and PPh₃ (25.18 mg, 96×10^{-3} mmol) in acetone-d₆ and the solution was stirred for 1 h.

Three solutions were prepared in the corresponding NMR tubes (tubes 1–3) from hpzb (3.5 mg, 7.38×10^{-3} mmol) and the corresponding volumes of the [Ag(PPh₃)](SbF₆) solution (0.048 M): tube 1 (1:1), 0.154 ml, 7.36×10^{-3} mmol; tube 2 (2:1), 0.307 ml, 14.71 × 10⁻³ mmol and tube 3 (3:1), 0.461 ml, 22.13 × 10⁻³ mmol). Additional quantities of acetone-d₆ were added to make up a volume of 0.5 ml in each tube. ¹⁹F NMR (acetone-d₆, 282 MHz, 193 K): tube 1, $\delta = -122.8$ (six broad lines, 6F, $J_{F^{-121}Sb-F} = 1953$ Hz) ppm; tube 3, $\delta = -123.1$ (six broad lines, 6F, $J_{F^{-121}Sb-F} = 1977$ Hz) ppm. The significant broadening of the signals makes the chemical shift and coupling constant values somewhat inaccurate. Partially overlapped signals corresponding to the coupling with ¹²³Sb were also observed.

2.2.2. AgClO₄/PPh₃/hpzb

The ligand hpzb (5.3 mg, 11.07×10^{-3} mmol) was introduced into three NMR tubes (4–6). The corresponding amounts of [Ag(PPh₃)]ClO₄ were then added: tube 4 (1:1), 5.2 mg, 11.07×10^{-3} mmol; tube 5 (2:1), 10.4 mg, 22.15×10^{-3} mmol; tube 6 (3:1), 15.6 mg, 33.22×10^{-3} mmol. 0.5 ml of acetone-d₆ was also added to each tube.

3. Results and discussion

Schlenk techniques were used in the first reactions carried out with hpzb and silver centres. After several reactions, we realised that the product ratio depended to a large extent on the experimental conditions and manipulations of the product mixture. As a consequence, we decided to carry out these reactions 'in situ' in NMR tubes, using acetone- d_6 as solvent, in order to identify the resonances of the products in the absence of any post-reaction manipulation.

The reactions carried out are indicated in the following equations:

$$1 \text{AgSbF}_{6} + 1 \text{PPh}_{3} + 1 \text{hpzb} \rightarrow [\text{Ag}(\text{PPh}_{3})(\text{hpzb})]\text{SbF}_{6}(1)$$
(1)

¹ Safety note: perchlorate salts of metal complexes with organic ligands are potentially explosive.

$$x \operatorname{AgSbF}_{6} + x \operatorname{PPh}_{3} + \operatorname{Ihpzb} \rightarrow \mathbf{I} + [\operatorname{Ag(hpzb)}]\operatorname{SbF}_{6}(\mathbf{2}) + [\operatorname{Ag(PPh}_{3})_{2}]\operatorname{SbF}_{6}$$
(2)
$$1 \operatorname{AgClO}_{4}\operatorname{PPh}_{3} + \operatorname{Ihpzb} \rightarrow [\operatorname{Ag(PPh}_{3})(\operatorname{hpzb})]\operatorname{ClO}_{4}(\mathbf{3})$$
(3)

$$AgCIO_4PPn_3 + Inpzb \rightarrow 3 + AgCIO_4$$

$$+ [Ag(PPh_3)_2]ClO_4$$
(4)

where x = 2, 3

3.1. Reactions of hpzb with AgSbF₆/PPh₃

For all the stoichiometries studied these reactions gave products that were soluble in the NMR solvent. The reaction products in Eqs. (1)-(4) show very broad signals in the ³¹P NMR spectra at room temperature and coupling between silver and phosphorus was not observed in any case. This fact indicates a relatively fast bond dissociation Ag-PPh₃ [34,35,37,41,42,45-47,49,50] in solution in relation to the NMR time scale. Consequently, in Eq. (2) a phosphine exchange process is possible at this temperature and low temperature ${}^{31}P$ NMR spectra were therefore recorded to obtain further structural information. The $P{^{1}H}$ NMR spectrum of complex 1, obtained according to Eq. (1), clearly shows at 233 K a pair of doublets due to a single PPh₃ group coupled to the two silver isotopes ${}^{1}J_{P^{-109}Ag} = 745$ Hz, ${}^{1}J_{P^{-107}Ag} = 648$ Hz) (see Table 1). The ratio ${}^{1}J({}^{109}Ag - {}^{31}P)/{}^{1}J({}^{107}Ag - {}^{31}P)$ is consistent with the ¹⁰⁹Ag/¹⁰⁷Ag gyromagnetic ratio. The same situation was found for all the Ag-P coupling constants in our derivatives and, from now on, only the ${}^{1}J_{P-107}_{Ag}$ values will be specified in the text. These results indicate that, at this temperature, a P-Ag bond dissociation process is slow enough for coupling constants to be observed. The ¹H NMR spectra (see Table 2) exhibit the three resonances expected for only one type of pyrazole and significant changes were not observed on lowering the temperature down to 193 K. On the basis of these data it is reasonable to propose that, with this reactant ratio, a complex of stoichiometry [Ag(PPh₃)(hpzb)]SbF₆ (1) is selectively formed and that this exhibits an argentotropic shift [42] extended to the six pyrazole rings of the

Table 1				
$P{^{1}H} NMR$	data for	complexes	1 - 3 in	acetone-d ₆

Table 2	
H NMR data for complexes $1-3$ in acetone-d ₆ at 233 K	

Complex	H_4	H ₃	H ₅
1 2 3	6.41 (pt) 6.57 (pt) 6.43 (bs)	7.42 (t) ${}^{3}J_{34} = 2,2$ 7.82 (d) ${}^{3}J_{34} = 2,0$	7.82 ^a 8.03 (d) ${}^{3}J_{45} = 2,4$

Reactions made with a $Ag^+/hpzb$ ratio of 3:1. Ph signals appear in the region 7.5–7.7 (1 and 2), 7.4–7.8 (3).

^a Overlapped.

ligand, which become identical on the NMR time scale. The ¹⁹F NMR spectra show six broad lines corresponding to the coupling of six equivalent F nuclei to ¹²¹Sb (I = 5/2), $J_{F^{-121}Sb} = 1953$ Hz. The lines corresponding to the coupling with ¹²³Sb (I = 7/2) were partially overlapped and could not be observed clearly. From these data we conclude that in solution the SbF₆⁻ anion does not interact with the silver centre in a sufficiently strong manner to allow differentiation between the F atoms.

When the reaction was performed using a 2:2:1 or 3:3:1 ratio of reactants (AgSbF₆:PPh₃:hpzb, Eq. (2)), the $P{^{1}H}$ NMR (233 K) spectra showed the presence of a new pair of doublets that was shown to correspond to the complex $[Ag(PPh_3)_2]SbF_6 ({}^{1}J_{P-{}^{107}Ag} = 493 \text{ Hz})$. The resonance assigned to 1 was also present but this became broader and gave larger Ag-P coupling constants as the amount of silver was increased. Importantly, a new set of pyrazole resonances also appeared in the ¹H NMR spectra, indicating the formation of a second complex (2) bearing hpzb but not PPh₃. In principle, complex 2 might be formulated as $[Ag_x(hpzb)(SbF_6)_x]$. A simple mass balance based on the integration of the ³¹P and ¹H NMR spectra concludes that $x \sim 1$ and, as a consequence, 2 can be formulated as $[Ag(hpzb)SbF_6]$. In a similar way to 1, complex 2 exhibits the aforementioned argentotropic behaviour that made the six pyrazole rings of the ligand identical. The ratio of the pairs of resonances, both in ¹H (1 and 2) and ³¹P NMR (1 and [Ag(PPh₃)₂]SbF₆) spectra, varies with the two ratios of

Complex	Reactant ratio (Ag ⁺ /hpzb)	Temperature (K)	δ (ppm)	$J_{{ m P}{-}^{109}{ m Ag}}$ (Hz)	$J_{{ m P}_{-}{}^{107}{ m Ag}}$ (Hz)
1	1:1	233	17.1 (2d)	745	648
1	2:1	233	17.2 (2bd)	754	652
1	3:1	233	16.8 (2bd)	772	669
1a	3:1	193	17.2 (2bd)	750	652
1b	3:1	193	15.3 (vb)	ca.850	ca.740
3	1:1	233	16.6 (vb)	724	630
3	2:1	233	16 (vb)		
3	3:1	233	15.3 (vb)		
3a	3:1	193	16.0 (2d)	750	650
3b	3:1	193	14.1 (2d)	767	667

2bd = two broad doublets, vb = very broad.

reactants studied (Eq. (2), $\chi = 2$ or 3), with an increasing amount of **2** and the diphosphine complex observed when more silver is present in the solution. A pattern similar to that found for the 1:1:1 reaction was obtained in the ¹⁹F NMR spectrum at 193 K — once again ruling out the existence of strong Ag–SbF₆ interactions.

The behaviour observed for the $AgSbF_6/PPh_3/hpzb$ system is consistent with the existence of the equilibrium depicted in Eq. (5).

$$2[Ag(PPh_3)]SbF_6 \rightleftharpoons AgSbF_6 + [Ag(PPh_3)_2]SbF_6$$
(5)

In the reaction with the 1:1:1 reactant ratio the above equilibrium does not take place to a great extent, possibly because the $Ag(PPh_3)^+$ group is coordinated to the hpzb ligand and only complex 1 is formed. However, when a higher Ag⁺-PPh₃/hpzb ratio is used the formation of dinuclear or trinuclear derivatives seems to be less favoured, possibly because of the repulsion between two cationic species. In this case, equilibrium (5) operates and leads to the formation of the diphosphino derivative [Ag(PPh₃)₂]SbF₆ and Ag⁺ cations, which compete with $Ag(PPh_3)^+$ for coordination of the hpzb ligand to form complex 2. Consequently, it seems that the higher stability of the [Ag(PPh₃)₂]SbF₆ complex compared to that of the expected dinuclear derivatives prevents the formation of the dinuclear species under these conditions. The observation of 1 and 2 as separate species in the ¹H NMR spectrum indicates that, although the intramolecular process of argentotropism is present, an intermolecular exchange between the two complexes apparently does not take place on the NMR time scale.

Mass spectrometry (FAB⁺) provides some supplementary information on these complexes. The solids obtained by evaporation of the reaction solutions, for both 1:1:1 and 3:3:1 reactant ratios, gave essentially the same mass spectra and the following fragments were detected: $AgPPh_3(hpzb)SbF_6$, 1080 Da: $AgPPh_3(hpzb)^+$, 845 Da; $AgPPh_3^+$, 369 Da: $Ag(hpzb)^+$, 581 Da; $Ag(PPh_3)_2^+$, 631 Da. These data indicate a facile interconversion between the species shown in Eq. (5) under the conditions in the mass spectrometer and also support the proposal that complexes 1 and 2 are mononuclear in nature. The existence of a fragment containing a SbF₆ group possibly indicates that a weak interaction with the silver centre takes place.

The most informative data concerning the coordination mode of the silver centres is the P-Ag coupling constant. According to bibliographic data the ${}^{1}J_{P-107}{}_{Ag}$ coupling constants are inversely proportional to the coordination number of the silver atom [35,40,47,50,51,53] and increase with decreasing Ag-P distances [38]. The value of ${}^{1}J_{P-107}{}_{Ag}$ = 648 Hz found for complex **1** (obtained from Eq. (1)) is not very different to that observed in species' where the AgPPh₃

is bonded to two pyrazolato groups (565 or 590 Hz) [42] or to phen (579 Hz) [50]. Consequently, in complex 1 the fragment AgPPh₃ will be bonded to two pyrazole groups. One possible reason for the slightly higher value found for **1** is the less basic character of the pyrazole groups in hpzb compared with the reported ligands, a situation that could strengthen the Ag-P bond. The slight increase in the value of J_{P-Ag} observed for 1 when the AgP:hpzb ratio is changed from 1:1 to 3:1 (see Table 1) could be explained in terms of the increasing participation of a species of lower coordination number. The fact that dicoordinate 'N-Ag-P' species have been reported [42a] must be taken into account in this context. If we consider the possible mechanism for the aforementioned intramolecular argentotropism process, which would essentially involve an N,N metalotropic shift (see Scheme 3), we find that this species could be an intermediate of type b, formed after transient decoordination of one pyrazole group, which could in turn be stabilised by an interaction with the counteranion. The increase in the anion concentration when the AgPPh₃:hpzb ratio increases would imply a higher participation of this intermediate in the process and, consequently, in the weighed averaged J_{Ag-P} . In order to ascertain whether the two species could be observed separately, low temperature (193 K) $P{^{1}H}$ NMR spectra were recorded in the tube with a metal:hpzb ratio of 3:1. The resonances of 1 decoalesced and signals corresponding to two species containing AgPPh₃ groups were observed. The major component at 17.2 ppm (approximately 61%) had a ${}^{1}J_{P-{}^{107}Ag}$ value of 652 Hz and for the minor species (signals very broad and partially overlapped), which appeared at higher field, the ${}^{1}J_{P-107}Ag$ was approximately 740 Hz. This observation supports the participation of 'dicoordinated' species of type **b**, which exhibit higher J_{Ag-P} coupling constants.

In order to confirm these results and to unambiguously establish that the pyrazole rings are coordinated to the silver centres in complexes **1** and **2**, the reaction depicted in Eq. (2) was carried out with hpzb $-^{15}N_{12}$ in a 2:2:1 ratio. The same results as for the non-labelled ligand were obtained. At 233 K the P{¹H} NMR spectrum shows a complicated pattern of signals for **1**



due to coupling with ¹⁵N. The two doublets due to $[Ag(PPh_3)_2]SbF_6$ are not coupled with ¹⁵N according with the absence of hpzb in this complex. In the ${}^{1}H$ NMR spectrum the corresponding $J_{H^{-15}N}$ coupling constants for the resonances of 1 and 2 could be determined (see Table 3). Two signals at -70.8 (=N-) and -183.3 ppm (>N-, ${}^{1}J15_{N}-15_{N}=13.0$ Hz) were observed in the ${}^{15}N-{}^{1}H$ NMR spectrum of the free hpzb (solvent, CDCl₃). Complex 1 exhibits resonances at -81.2 (br) and -184.6 (${}^{1}J15_{N}-15_{N} = 12.2$ Hz) while complex 2 shows signals at -93.4 (br) and -186.4 ppm $({}^{1}J15_{N}-15_{N}=11.0$ Hz). The signals at lower field are broad in each case. This observation is understandable when we consider that coordination has a greater influence on the chemical shift of the =N- signal, and that both resonances must correspond to the average of the six pyrazoles.

3.2. Reactions of hpzb with AgClO₄PPh₃

These reactions evolved in a similar way to those with $AgSbF_6/PPh_3$ but, in this case, $AgClO_4$ is insoluble in the NMR solvent (acetone- d_6) and hence certain differences were observed. When the reaction was carried out with а reactant ratio of 1:1, complex $[Ag(PPh_3)(hpzb)]ClO_4$ (3) was formed exclusively and the six pyrazole groups were equivalent in the ¹H NMR spectrum (even at low temperature). Broad signals appeared in the $P{^{1}H}$ NMR spectrum even at 193 K. When x (Eq. (4)) was increased up to a value of 2 or 3, signals corresponding to only one type of pyrazole ring (3) were observed. In these reactions, precipitation of AgClO₄ was detected and the concomitant formation of [Ag(PPh₃)₂]ClO₄ occurred in solution. The precipitate was identified as AgClO₄ by redissolving the salt by addition of PPh3. The formation of the complex [Ag(PPh₃)₃]ClO₄ [35,54] was observed and this product was characterised by its $P{^{1}H}$ NMR spectrum.²

The formation of $[Ag(PPh_3)_2]ClO_4$ in Eq. (4) indicates that an equilibrium similar to that shown in Eq. (5) is also operating (see Eq. (6)):

$$2AgClO_4PPh_3 \rightleftharpoons AgClO_4 + [Ag(PPh_3)_2]ClO_4$$
(6)

² P{¹H} NMR at 193 K in acetone-d₆: $\delta_{ppm} = 11.66$, ¹J_{P-109Ag} = 366 Hz, ¹J_{P-107Ag} = 318.6 Hz.

Table 3			
NMR spectra	of compounds	$^{15}N_{12}$ -(1-3) in	acetone-d ₆ at r.t.

In this case, the lack of solubility of $AgClO_4$ prevents competition between Ag^+ and $Ag(PPh_3)^+$ for coordination of hpzb and a complex similar to **2** is not formed in this reaction.

The $P{^{1}H}$ NMR spectra of the products resulting from the reactions with 2:1 or 3:1 reactant ratios were registered at 233 K and very broad signals were observed (besides [Ag(PPh₃)₂]ClO₄). However, at 193 K two pairs of doublets were observed that were broadened only slightly and these correspond to two new derivatives: $\delta = 16.0 \ (^{1}J_{P^{-107}Ag} = 650)$ and $\delta = 14.1$ $({}^{1}J_{P-107Ag} = 668)$ in a 43/57 ratio (for the 1:3 reaction) (see Fig. 1). The signals with larger coupling constants can be assigned to the intermediate of type b. When these intermediates were detected (reactions 3:1) and both anions compared, it was noticeable that the intermediate with ClO₄ (i) exhibits a smaller J_{P-Ag} (differences in J_{P-Ag} that depend on the distinct coordinating ability of the anion have been described [36,39]), (ii) is present in a higher ratio with respect to the species of type a (see Scheme 3) and (iii) the interchange process between the two species has a higher activation energy. All these data can be explained in terms of the greater coordinating ability of ClO₄⁻ with respect to SbF_6^- , which results in stronger coordination in the intermediate and, as a consequence, the stabilisation of this species.

The results of the reactions of $hpzb^{-15}N_{12}$ with AgClO₄PPh₃ in different ratios led to the same conclusions as deduced with the system Ag⁺/PPh₃/SbF₆⁻.

The ${}^{13}C{}^{1}H$ NMR spectra of 1–3 (see Table 4) are in agreement with the previous proposals.

4. Conclusions

Complexes $[Ag(PPh_3)(hpzb)](SbF_6)$ (1) and $[Ag(PPh_3)(hpzb)](ClO_4)$ (3) were synthesised as single products in the reactions between hpzb and silver centres with metal/PPh_3/hpzb ratios of 1:1:1. Whereas di- and trinuclear complexes have been prepared with hpzb and other metallic fragments such as CuPPh_3⁺, the reactions performed with 2 or 3 silver centres per ligand led only to mononuclear derivatives — probably because the disproportion reaction of the Ag(PPh_3)⁺ fragment gives rise to the highly stable species

Complex	H_4	H ₃	H ₅
$\frac{{}^{15}N_{12}{-}1}{{}^{15}N_{12}{-}2}}{{}^{15}N_{12}{-}3}$	6.27 (m) 6.54 (m) 6.37 (m)	^a 7.76 (ddd), ${}^{2}J_{\rm HN} = 12.0, {}^{3}J_{\rm HN} = 9.3, {}^{3}J_{\rm H3H4} = 2.2$	7.45 (m) 7.98 (dd), ${}^{2}J_{HN} = 5.4$, ${}^{3}J_{H4H5} = 2.6$ 7.73 (dd), ${}^{2}J_{HN} = 5.1$, ${}^{3}J_{H4H5} = 2.7$

^a Overlapped signals.



Fig. 1. ${}^{31}P$ NMR spectrum in acetone-d₆ at 193 K corresponding to the result of the reaction of AgClO₄PPh₃ with hpzb in 3:1 ratio. For **3a** and **3b**, see Scheme 3.

Table 4 $^{13}C\{^1H\}$ NMR data of complexes 1–3 in acetone-d_6 at r.t.

Complex	hpzb				PPh ₃		
	C ₄	C ₃	C ₅	C (benzene)	Ortho	Meta	Para
1	107.8	142.6	133.6	137.5	134.1 (d), ${}^{2}J_{\rm CP} = 15.1$	129.7 (d), ${}^{3}J_{\rm CP} = 8.5$	131.5
2	108.4	144.8	135.3	139.7	134.0 (d), ${}^{2}J_{\rm CP} = 11.3$	129.6 (bs)	131.5
3	109.5	145.2	136.1	139.6	135.2 (d), ${}^{2}J_{\rm CP} = 12.4$	130.6 (bs)	132.3

Unless specified the signals are singlets.

 $[Ag(PPh_3)_2]^+$ and Ag^+ . The Ag^+ cation is able to compete with $Ag(PPh_3)^+$ in the coordination of hpzb when the counteranion does not precipitate as the corresponding silver salt (SbF_6^-) and, as a result, the derivative [Ag(hpzb)]SbF₆ is formed. The reactions performed with the hpzb $-^{15}N_{12}$ ligand confirmed the presence in 1-3 of the N-donor ligand. At room temperature an Ag-P dissociation process is observed for all the derivatives containing Ag-PPh₃ fragments. In solution complexes 1-3 show an intramolecular argentotropic shift that makes the six pyrazolyl rings of the hpzb ligand equivalent in the ¹H NMR time scale. An intermediate of lower coordination number is observed in the argentotropic process for complexes 1 and 3 in the low temperature ³¹P NMR spectra when the amount of the counteranion present in solution is sufficiently high. This intermediate is more stable in the case of ClO_4^- than for SbF_6^- , which is in accordance with the higher coordination ability of the former ion. Differences in the energy barrier of the argentotropic process between the two complexes can also be ascribed to the higher coordination ability of the ClO_4^- anion when compared with SbF_6^- .

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