Argentotropism in (Pentamethylcyclopentadienyl)iridium Complexes with Pyrazole Ligands: Multinuclear DNMR Experiments

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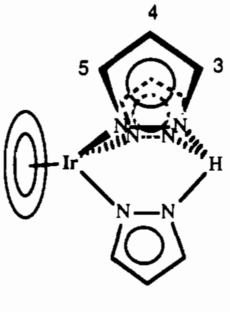
The dynamic behavior of the heterobimetallic compounds [(η^5-C$_5$Me$_5$)Ir(pz)$_3$Ag(PPh$_3$)] (**2**), [(η^5-C$_5$Me$_5$)Ir(μ-pz)$_3${Ag(PPh$_3$)}$_2$]BF$_4$ (**3**), [(η^5-C$_5$Me$_5$)Ir(pz)$_2$ PPh$_3$] (**4**), and [(η^5-C$_5$Me$_5$)Ir(PPh$_3$)(μ-pz)$_2$Ag(PPh$_3$)]BF$_4$ (**5**) has been studied by multinuclear (^{1}H, ^{13}C, ^{15}N, ^{31}P, and ^{109}Ag) NMR. The results demonstrate that argentotropism accounts for the observed spectra of compounds **2** ($\Delta H^\ddagger$ = 8.3 kcal mol^{-1}, $\Delta S^\ddagger$ = −13 eu) and **3** ($\Delta H^\ddagger$ = 7.6 kcal mol^{-1}, $\Delta S^\ddagger$ = −20 eu); in the case of compound **4**, the dynamic behavior is due to a slow rotation about the P–Ir bond, and for compound **5**, the dynamic behavior corresponds to a flipping of the central heteroring Ir(N)$_4$Ag. Several new heteronuclear coupling constants have been determined, some of them [such as $^1J(^{31}\text{P}–^{107(109)}\text{Ag})$ being related to the structure and dynamical properties of the complex.

Introduction

Some years ago we described the prototropism of [(η^5-C$_5$Me$_5$) Ir(pz)$_2$(Hpz)] (**1**).[1]



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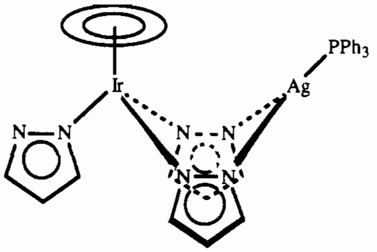
At room temperature, the ^{1}H and ^{13}C NMR spectra of compound **1** show an averaged signal for each group of the three protons (carbons) of positions 3–5. ^{1}H NMR: δ(H$_3$) = 7.63 ppm, δ(H$_4$) = 6.15 ppm, δ(H$_5$) = 7.00 ppm, δ(C$_5$Me$_5$) = 1.52 ppm. ^{13}C NMR: δ(C$_3$/C$_5$) = 139.18, 136.64 ppm, δ(C$_4$) = 104.82 ppm, δ(C$_5$Me$_5$) = 8.54, 88.07 ppm (solvent acetone-d_6). The fact that the three pyrazole rings were equivalent was interpreted as a rapid prototropy between Hpz and (pz)$_2$.



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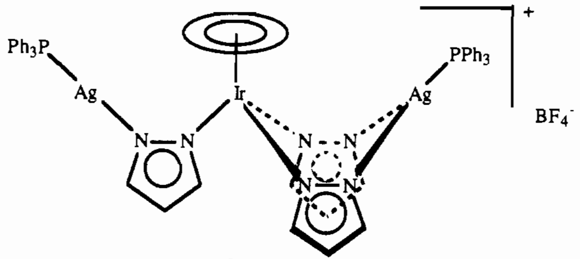

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We report now the behavior of related compounds, [(η^5-C$_5$Me$_5$) Ir(pz)$_3$Ag(PPh$_3$)] (**2**) and [(η^5-C$_5$Me$_5$)Ir(μ-pz)$_3${Ag(PPh$_3$)}$_2$]BF$_4$ (**3**), where a silver triphenylphosphine cation replaces the proton. Compound **2** has been fully characterized by X-ray crystallography.[2] The iridium shows a pseudooctahedral coordination whereas the coordination around the silver is trigonal planar. The six-membered IrN$_4$Ag ring adopts a boat conformation with the bow at Ir and the stern at Ag. The pentamethylcyclopentadienyl ring occupies an axial position whereas the remaining pyrazole is equatorially oriented.

The heterodinuclear complex **2** is obtained with an impurity **4** that was isolated and whose structure was determined; the same happens with the trinuclear complex **3**, but in this case the impurity has structure **5**.

Compounds **2–5** have also been prepared labeled with ^{15}N at both nitrogen positions of each pyrazole. We will describe the multinuclear NMR (^{1}H, ^{13}C, ^{15}N, ^{31}P, ^{109}Ag) experiments at different temperatures.

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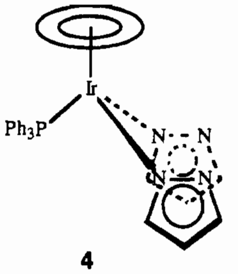
(1) Carmona, D.; Oro, L. A.; Lamata, M. P.; Elguero, J.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1114–1115.

(2) Carmona, D.; Lahoz, F. J.; Oro, L. A.; Lamata, M. P.; Buzarra, S. *Organometallics* **1991**, *10*, 3123–3131.

0020-1669/94/1333-2196$04.50/0



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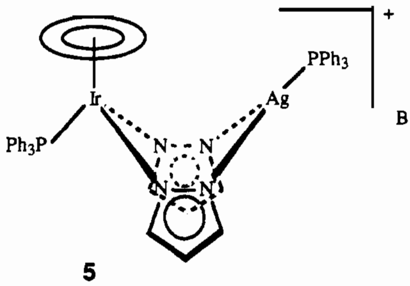
[(η^5-C$_5$Me$_5$)Ir(pz)$_2$PPh$_3$]



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[(η^5-C$_5$Me$_5$)Ir(PPh$_3$)(μ-pz)$_2$Ag(PPh$_3$)]BF$_4$

Experimental Section

1. Chemistry. All solvents were dried over appropriate drying agents, distilled under N$_2$, and degassed before use. All preparations were carried out under nitrogen. The C, H, and N analyses were determined with a Perkin-Elmer 240 B microanalyzer.

(a) Synthesis of [(η^5-C$_5$Me$_5$)Ir(pz)$_2$(PPh$_3$)] (4). To a solution of **1**[1] (788 mg, 1.49 mmol) in 30 mL of CH$_2$Cl$_2$/acetone (1/1, v/v) was added solid PPh$_3$ (390.2 mg, 1.49 mmol). After 5 min of stirring, the precipitation of a yellow solid began. The resulting suspension was stirred for 3 h and then was vacuum-concentrated to *ca.* 5 mL. The precipitation of the complex was completed by addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and air-dried. Yield: 853 mg, 79%. Anal. Calcd. for C$_{34}$H$_{36}$N$_4$IrP: C, 56.42; H, 5.01; N, 7.74. Found: C, 56.43; H, 5.21; N, 7.88.

(b) Synthesis of [(η^5-C$_5$Me$_5$)Ir(PPh$_3$)(μ-pz)$_2$Ag(PPh$_3$)]BF$_4$ (5). To a suspension of **4** (249 mg, 0.34 mmol) in 20 mL of acetone were added 90.2 mg (0.34 mmol) of PPh$_3$ and 67 mg (0.34 mmol) of AgBF$_4$. The resulting solution was stirred for 20 min and then vacuum-concentrated to 2 mL. The addition of diethyl ether led to the precipitation of a yellow solid, which was filtered off, washed with diethyl ether and air-dried. The compound was recrystallized from CH$_2$Cl$_2$/diethyl ether. Yield: 332 mg, 82%. Anal. Calcd for C$_{52}$H$_{51}$N$_4$AgBF$_4$IrP$_2$: C, 52.89; H, 4.35; N, 4.74. Found: C, 53.07; H, 4.48; N, 4.91.

(c) Synthesis of Labeled Compounds. [^{15}N$_2$]pyrazole was prepared from [^{15}N$_2$]hydrazine sulfate according to ref 3. Complexes **2′** and **3′** were prepared as described for the corresponding unlabeled compounds **2** and **3** .[2]

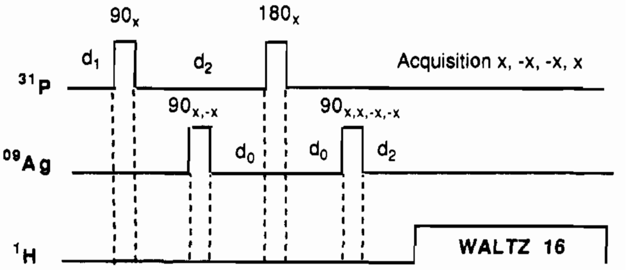
2. NMR Spectroscopy. ^{1}H, ^{13}C, ^{15}N, and ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer (CSIC, Madrid) operating at 299.9, 75.4, 30.4, and 121.4 MHz, respectively, using CDCl$_3$ and acetone-d_6 as solvents. Some preliminary NMR spectra were recorded on a Varian XL-200 spectrometer (University of Zaragoza) operating at 200.0 (^{1}H) and 80.9 MHz (^{31}P).

^{1}H NMR spectra were obtained using tetramethylsilane as internal standard with the following conditions: pulse angle, 77°; acquisition time, 6 s; sweep width, 4000 Hz; data size, 32K.

Proton-decoupled ^{13}C NMR spectra were obtained with WALTZ decoupling and tetramethylsilane as internal standard, using the following conditions: pulse angle, 53°; acquisition time, 0.9 s; sweep width, 16 720 Hz; data size, 32K.

^{15}N NMR spectra were obtained using 4 M ^{15}NH$_4$NO$_3$ in 2 M HNO$_3$ as external reference and the following conditions: pulse angle, 30°; acquisition time, 0.7 s; sweep width, 21 600 Hz; data size, 32K. The homonuclear *J* resolved experiment was carried out with the following conditions: sweep widths, 10 965 Hz for f_2 dimension and 80 Hz in the f_1 dimension, relaxation delay, 2 s; 4096 × 256 points for the table data.

Scheme 1



d$_1$ = recycle delay
d$_2$ = silver/phosphorus coupling evolution delay = 1/2 $^1J(^{109}$Ag-^{31}P)
d$_0$ = evolution delay

^{31}P NMR spectra were obtained with WALTZ decoupling using 85% H$_3$PO$_4$ in D$_2$O as external reference and the following conditions: pulse angle, 50°; acquisition time, 0.8 s; sweep width, 10 000 Hz; data size, 32K.

^{31}P and ^{109}Ag experiments were obtained with a Bruker ARX-300 spectrometer operating at 121.50 MHz (^{31}P) equipped with an inverse triple resonance probe, TBI 5 mm (^{2}H/^{1}H/^{31}P/BB$_{\text{low range}}$ {^{15}N > frequency > ^{187}Os}, and with a third channel necessary for the ^{109}Ag/^{31}P{^{1}H} inverse correlations. The one-dimensional ^{31}P spectra were obtained with WALTZ 16 proton decoupling during the acquisition phase [P_{90} impulsion (^{31}P) 14.5 μs, relaxation delay 4 s, number of scans 128]. Two-dimensional spectra (inverse correlations ^{109}Ag/^{31}P{^{1}H}) were recorded using the sequence depicted in Scheme 1.

The values of the P_{90}(^{31}P) and P_{90}(^{109}Ag) impulsions were 14.5 and 35 μs, respectively. The relaxation time was 2 s, the silver/phosphorus transfer time was 760 μs, and the number of scans was 8. A proton decoupling was carried out during the acquisition time. The ^{109}Ag chemical shifts are refered to a 2 M aqueous solution of AgNO$_3$ (δ(^{109}Ag) = 24 ppm).[4]

Variable-temperature experiments for complexes **2** and **3** were carried out under the same conditions, the temperature being varied in the range 218–328 K for CDCl$_3$ and 188–318 K for acetone-d_6. The kinetic parameters were calculated by experimental line-shape analysis using the appropriate equations for the dynamic processes,[5] considering a 2:1 ratio for the populations of tautomers, and taking into account the temperature dependence of the chemical shifts. By means of the Eyring equation,[4] the values of activation entalphy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ were calculated by least-squares linear regression analysis. Temperature readings were accurate to ±0.5 °C (the thermometer was calibrated against the ^{1}H NMR spectra of methanol, 4% CH$_3$OH in CD$_3$OD).[6]

Results and Discussion

Although some preliminary ^{1}H and ^{31}P NMR results were reported in ref 2, we will describe the whole collection of data regarding compounds **2–5**. We will follow the following sequence: ^{1}H, ^{31}P, ^{13}C, ^{15}N, ^{109}Ag; compounds **2, 3, 4, 5**; room temperature (300 K), low temperature; unlabeled, ^{15}N$_2$-labeled; and, finally, the kinetic studies (DNMR).

^{1}H NMR. The corresponding results are gathered in Table 1.

(a) Compound 2. The spectra of this compound in CDCl$_3$ at 300 MHz were recorded between 293 and 213 K. At room temperature, the signals corresponding to one pyrazole ring are observed at 6.72 (H$_5$, broad singlet) and 5.96 ppm (H$_4$, triplet, J_{34} = J_{45} = 1.7 Hz), whereas that of H$_3$ is overlapped by the triphenylphosphine proton resonances that appear as a complex system between 7.5 and 7.8 ppm. When the temperature is

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(3) Fruchier, A.; Pellegrin, V.; Claramunt, R. M.; Elguero, J. *Org. Magn. Reson.* **1984**, *22*, 473–474.

(4) Granger, P. In *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991; pp 273–288.

(5) Wehrli, F. H.; Marchand, A. P.; Wehrli, S. *Interpretation of ^{13}C NMR Spectra*; Wiley & Sons: New York, 1988; pp 307–323.

(6) Experimental calibration of the probe temperature: $\Delta\delta$ = δ(CH$_3$) − δ(OH) (ppm)/[T (K)]: 2.230 [211], 1.964 [245], 1.864 [257], 1.774 [268], 1.670 [280], 1.570 [291].

Table 1. ^1H NMR Data for Complexes **2–5**

			δ^a				
complex	medium	T, K	C_5Me_5	H_3	H_5	H_4	PPh_3
2	$CDCl_3$	293	1.45 d	*b*	6.72 bs	6.08 t	7.5–7.8 m
		213	1.43 d	*b*	6.72 bs	6.11 bs	
	acetone-d_6	293	1.41 d	7.38 d	6.59 bs	5.96 t	7.5–7.8 m
		183	1.33 d	7.39 bs, 2 pz	6.51 bs, 2 pz	6.07 bs, 2 pz	
				7.49 bs, 1 pz	6.41 bs, 1 pz	5.88 bs, 1 pz	
3	$CDCl_3$	293	1.30 d	*b*	*b*	6.27 bs	7.0–7.8 m
		204	1.27 d	*b*	6.77 bs, 2 pz	6.19 bs, 2 pz	
				8.04 bs, 1 pz	*b*	6.42 bs, 1 pz	
4	$CDCl_3$	293	1.29 d	7.39 d	7.12 d	5.84 t	6.5–8.0 m
	acetone-d_6	293	1.26 d	7.22 d	7.20 d	5.72 t	7.5–7.8 m
		183	1.16 d	7.24 bs	7.24 bs	5.74 bs	
5	acetone-d_6	293	1.35 d	7.49 d	6.78 bs	5.86 t	7.5–7.7 m
		183	1.28 d	*b*	6.65 bs	5.86 bs	

^{a} Key: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet; pz, pyrazole. ^{b} Overlapped by the PPh_3 protons.

lowered, the signals corresponding to the pyrazole protons broaden, but at 213 K the coalescence is still not observed.

The spectra of the same compound in acetone-d_6 at 300 MHz were recorded between 293 and 183 K, every 20 deg. At room temperature, only the signals corresponding to one pyrazole ring are observed at 7.38 (H_3, doublet), 5.96 (H_4, triplet), and 6.59 ppm (H_5, broad singlet) ($J_{34} = J_{45} = 1.8$ Hz); the protons of the triphenylphosphine group appear as a complex system at 7.5 and 7.8 ppm and the methyl groups of the pentamethylcyclopentadienyl moiety at 1.41 ppm (variable quantities, depending on the sample, of impurity **4** are also observed). The protons of the methyl groups of C_5Me_5 exchange slowly with the deuteriums of the solvent, which is very unusual but not without precedent.[7–10] When the temperature is lowered, the signals corresponding to the pyrazole protons broaden and at about 233 K the coalescence is observed. At 183 K two kinds of pyrazoles are observed in a 2:1 ratio. The signals of the "free" pyrazole (that linked by N_1 to Ir) appear at 7.49 (H_3), 5.88 (H_4), and 6.41 ppm (H_5) and those of the two "complexed" pyrazoles (linked to Ir and to Ag) at 7.39 (H_3), 6.07 (H_4), and 6.51 ppm (H_5). The averaged values coincide with the room temperature values, *e.g.* for H_4 $(5.88 + 2 \times 6.07)/3 = 6.01$ to compare with 5.96 ppm. The ^1H–^1H coupling constants of pyrazole rings are 1.8 Hz.

(b) Compound 3. The spectra were recorded at 300 MHz in $CDCl_3$ between 313 and 204 K every 15 deg. At 313 K an averaged spectrum is observed, but since in this case all the pyrazoles are linked to both iridium and silver, the differences in chemical shifts are smaller and the spectrum is not easily interpreted. Proton H_4 appears at 6.27 ppm but protons H_3, H_5, and those of PPh_3 appear in the 7.0–7.8 ppm zone; the methyl groups of C_5Me_5 appear at 1.30 ppm. Lowering the temperature results first in a broadening of the signals (coalescence at about 283 K) and finally in a splitting of the pyrazole signals. At 204 K, two H_4 protons are observed at 6.42 and 6.19 ppm [relative ratio 1:2, which average at $(6.42 + 2 \times 6.19)/3 = 6.27$ ppm].

(c) Compound 4. The room-temperature spectrum of this compound in $CDCl_3$ at 200 MHz shows the signals corresponding to the two pyrazole rings at 7.39 d (H_3), 5.84 t (H_4), and 7.12 ppm d (H_5) [^3J(H–H) ~ 1.8 Hz]. The protons of the triphenylphosphine group appear as a very broad signal from 6.5 to 8.0 ppm, and the methyl groups of the pentamethylcyclopentadienyl moiety appear as a doublet centered at 1.29 ppm [^4J(P–H) = 2.2 Hz]. The spectra of **4** in acetone-d_6 were recorded between 293 and 183 K every 20 deg. At room temperature, only the signals corresponding to one pyrazole ring are observed at 7.22 (H_3, doublet), 5.72 (H_4, triplet), and 7.20 ppm (H_5, doublet) ($J_{34} = J_{45} = 1.8$ Hz) (the assignment of H_3 and H_5 can be interchanged). When the temperature is lowered, the signals corresponding to the pyrazole protons broaden, but even at 183 K the coalescence is not observed.

(d) Compound 5. The spectrum of this compound (200 MHz) in acetone-d_6 at 293 K shows the signals of the pyrazole protons as broad singlets at 7.49 (H_3, doublet), 5.86 (H_4, quartet), and 6.78 ppm (H_5, broad singlet) ($J_{34} = 1.7$, $J_{45} = 1.9$ Hz). The protons of the triphenylphosphine groups appear as a broad signal centered at 7.6 ppm. A doublet at 1.34 ppm [^4J(P–H) = 2.2 Hz] corresponds to the pentamethylcyclopentadienyl protons. At 183 K, the pyrazole and pentamethylcyclopentadienyl signals are only slightly shifted whereas the triphenylphosphine multiplet splits into two different complex multiplets, between 6.5 and 8.0 ppm, one of them corresponding to the phosphine linked to iridium and the other corresponding to the phosphine linked to silver.

^{31}P NMR. The data concerning this nucleus are gathered in Table 2.

(a) Compound 2. The ^{31}P spectrum of this compound in $CDCl_3$ at 121.4 MHz was recorded between 293 and 213 K. At room temperature, a broad doublet centered at 15.71 ppm is observed. Lowering the temperature to 213 K results in two doublets, centered at 15.52 ppm, due to both silver isotopes.

The $^{15}N_2$-labeled derivative, **2′**, shows at 213 K a very interesting spectrum: four quartets centered at 15.62 ppm (the difference from the signal, 15.52 ppm, of the unlabeled compound—Table 2—is too small to assess that it is an isotope effect). The large couplings, identical to those observed for **2**, are due to ^1J couplings with silver isotopes. The fine splitting corresponds to pseudoquartets with frequency differences of 9.1 Hz, but as discussed in ref 7, the real coupling constant is three-halves of the splitting; *i.e.* $^2J(^{31}P\text{–}Ag\text{–}^{15}N) = 13.6$ Hz. This coupling has important consequences regarding the dynamic behavior of **2**.

(b) Compound 3. The only comment to the values of Table 2 is that the signal at 15.55 ppm belongs to phosphorus linked through the silver to two pyrazoles (in compound **2** this signal appears at 15.52 ppm) and that at 19.78 ppm to Ph_3P–Ag–pz. The averaged value, 17.66 ppm, is near the experimental value at room temperature (17.52 ppm).

In the corresponding $^{15}N_2$ derivative **3′** the $^1J(^{31}P\text{–}Ag)$ coupling constants differ slightly from those of Table 2: phosphorus at 15.55 ppm, 574.1 (^{107}Ag) and 661.0 Hz (^{109}Ag); phosphorus at 19.78 ppm, 630.6 (^{107}Ag) and 727.0 Hz (^{109}Ag). Besides, $^2J(^{31}P\text{–}Ag\text{–}^{15}N)$ coupling constants were measured, for the signal at 15.54 ppm, $^2J = 12.8$ Hz, and for that at 19.93 ppm, $^2J = 18.3$ Hz.

(c) Compound 4. The ^{31}P spectrum of this compound in $CDCl_3$ at room temperature shows a narrow singlet at 6.77 ppm due to the phosphine directly linked to iridium. The lowering of the temperature to 213 K only results in a slight shift of the signal but no broadening at all. The corresponding $^{15}N_2$-labeled

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(7) Limbach, H. H. *NMR: Basic Princ. Progr.* **1990**, *23*, 63–164.
(8) Kang, J. W.; Maitlis, M. P. *J. Organomet. Chem.* **1971**, *30*, 127–133.
(9) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2335–2338.
(10) Miguel-García, J. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1472–1473.

Table 2. ^{31}P Chemical Shifts (ppm) and Coupling Constants (Hz) for Complexes **2–5**

complex	medium	*T*, K	$\delta(^{31}PPh_3Ag)^a$	$\delta(^{31}PPh_3)^a$	$^nJ(^{31}P\text{–}Ag)$
2	$CDCl_3$	239	15.71 bd		^1J(P–Ag) = 576
		213	15.52 bd		1J(P–^{107}Ag) = 565
					^1J(P–^{109}Ag) = 653
2′	$CDCl_3$	213	15.62 ddq		^{1}J(P–^{107}Ag) = 564.6
					^1J(P–^{109}Ag) = 652.7
					^2J(P–Ag–^{15}N) = 9.1
3	$CDCl_3$	293	17.52 bd		^1J(P–Ag) = 607
		213	19.78 dd, 1 pz		^1J(P–^{107}Ag) = 635.1
					^{1}J(P–^{109}Ag) = 733.1
			15.55 dd, 2pz		^1J(P–^{107}Ag) = 573.2
					^1J(P–^{109}Ag) = 661.9
3′	acetone-d_6	188	19.93 ddd, 1 pz		^1J(P–^{107}Ag) = 630.6
					1J(P–^{109}Ag) = 727.0
					^2J(P–Ag–^{15}N) = 18.3
			15.54 ddt, 2pz		^1J(P–^{107}Ag) = 574.1
					^1J(P–^{109}Ag) = 661.0
					^2J(P–Ag–^{15}N) = 12.8
4	$CDCl_3$	293		6.77 s	
		213		6.70 s	
4′	$CDCl_3$	213		5.20 t	^2J(P–Ir–^{15}N) = 4.2
5	$CDCl_3$	293	15.0	9.21	^1J(P–Ag) = 600
		213	16.65 dd	9.54 s	^1J(P–^{107}Ag) = 590.1
					^1J(P–^{109}Ag) = 681.6
5′	acetone-d_6	188	16.78 ddt, 2pz	9.30 s	^1J(P–^{107}Ag) = 591.4
					^1J(P–^{109}Ag) = 681.1
					^2J(P–Ag–^{15}N) = 11.3

[a] Key: s, singlet; bs, broad singlet; bd, broad doublet; dd, double doublet; t, triplet; pz, pyrazole.

Table 3. ^{13}C NMR Data for Complexes **2–5**

			δ				
complex	medium	*T*, K	$C_3{}^a$	C_4	$C_5{}^a$	phosphine	Cp
2	$CDCl_3$	328	140.7	104.00	140.13	133.97 (C_o), 129.16 (C_m), 130.68 (C_p), 132.78 (C_i)	8.61 (Me) 87.21 (C)
		213	141.13, 2pz 139.28, 1pz	104.46, 2pz 102.03, 1pz	139.99, 2pz 138.72, 1pz	133.56 (C_o), 129.04 (C_m), 130.70 (C_p), 131.47 (C_i) 131.47 (C_i)	8.62 (Me) 86.65 (C)
3	acetone-d_6	318	143.25	106.87	142.17	134.65 (C_o), 130.20 (C_m), 132.02 (C_p), 132.11 (C_i)	8.88 (Me) 88.68 (C)
		188	144.56, 2pz	107.78, 2pz	142.99, 2pz	134.77, 134.43 (C_o) 130.36, 130.23 (C_m)	8.58 (Me)
			141.53, 1pz	106.45, 1pz	141.30, 1pz	132.07, 132.07 (C_p) 131.57, 130.85 (C_i)	94.71 (C)
4	$CDCl_3$	303	139.93	103.14	138.90	135.28 (C_o), 127.73 (C_m), 130.49 (C_p), *b* (C_i)	8.58 (Me) 94.71 (C)
5	acetone-d_6	318	144.41	106.11	143.89		9.11 (Me) 96.75 (C)

[a] These assignments can be reversed. [b] Obscured.

derivative, **4′**, was recorded at 213 K in $CDCl_3$. At 5.20 ppm a triplet appears with $^2J(^{31}P\text{–}Ir\text{–}^{15}N) = 4.2$ Hz.

(d) Compound 5. The ^{31}P spectrum of this compound in $CDCl_3$ at 293 K shows a very narrow singlet at 9.21 ppm and a very broad doublet at about 15 ppm with a coupling constant of about 600 Hz, which can be used to identify them immediately, as the phosphorus linked only to iridium and that linked both to iridium and to silver, respectively. At 213 K, the P–Ir signal (9.54 ppm) is only slightly shifted whereas the P–Ag signal becomes a very narrow double doublet at 16.51 ppm with $^1J(^{31}P\text{–}^{107}Ag) = 590.1$ Hz and $^1J(^{31}P\text{–}^{109}Ag) = 681.6$ Hz.

In the spectrum of the $^{15}N_2$-labeled compound **5′** recorded in acetone-d_6 at 188 K the following results were observed: 9.3 ppm, singlet (P–Ir), 16.78 ppm, multiplet (P–Ag) [$^1J(^{31}P\text{–}^{107}Ag) = 591.4$, $^1J(^{31}P\text{–}^{109}Ag) = 681.1$ Hz, $^2J(^{31}P\text{–}Ag\text{–}^{15}N) = 11.3$ Hz].

^{13}C NMR. Table 3 contains the data corresponding to this nucleus.

(a) Compound 2. The spectra were recorded in $CDCl_3$ between 328 and 218 K with intervals of 15 deg. The C_5Me_5 signals are independent of the temperature: 8.61 ppm (Me) and 87.21 ppm (ring carbons). On the other hand, the triphenylphosphine signals are best resolved at low temperature. Thus, at 328 K, carbons appear at 132.78 (*ipso*), 133.97 (*ortho*), 129.16 (*meta*), and 130.68 ppm (*para*) with coupling constants of $^1J(^{13}C_i\text{–}^{31}P) = 34.1$, $^2J(^{13}C_o\text{–}^{31}P) = 17.0$, and $^3J(^{13}C_m\text{–}^{31}P) = 10.3$ Hz. The increased resolution observed at 218 K allows determination of the coupling constants involving silver (they are too small to distinguish between both isotopomers): $^2J(^{13}C_i\text{–}Ag) = 3.5$, $^3J(^{13}C_o\text{–}Ag) = 2.2$, and $^4J(^{13}C_m\text{–}Ag) = 1.7$ Hz, as well as $^4J(^{13}C_p\text{–}^{31}P) = 1.7$ Hz.

The study of compound **2** by ^{13}C DNMR was used to determine the activation barrier of the argentotropism. The best signal for this purpose is that of C_4, but the phenomenon is also apparent for C_3 and C_5. At 328 K, three pyrazole carbons are observed: 104.0 (C_4), 140.7 and 140.13 ppm (C_3 and C_5). At 218 K, these signals appear at 102.02 (intensity 1) and 104.46 (intensity 2) (C_4) and at 138.72 and 139.28 (intensity 1) and 139.99 and 141.13 ppm (intensity 2) (C_3 and C_5).

(b) Compound 3. In this case also, the ^{13}C DNMR results were used to determine the activation barrier. The spectra were recorded in acetone-d_6 between 318 and 188 K. At 318 K the following signals are observed: 8.88 (methyl groups of C_5Me_5), 88.68 ppm (ring carbons of C_5Me_5), 132.11 (*ipso*), 134.65 (*ortho*), 130.20 (*meta*), and 132.02 ppm (*para*), $^1J(^{13}C_i\text{–}^{31}P) = 34.9$, $^2J(^{13}C_o\text{–}^{31}P) = 16.9$ and $^3J(^{13}C_m\text{–}^{31}P) = 10.3$ Hz (triphenylphosphine group); 106.87 (C_4), 142.17 and 143.25 ppm (C_3 and C_5) (pyrazoles). At 188 K, the phosphine carbons split into two

Table 4. ${}^{15}N$ NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for Complexes **2** ($CDCl_3$), **3** (Acetone-d_6), **4** ($CDCl_3$), and **5** (Acetone-d_6) (External Reference CH_3NO_2)

		pz—Ir		Ir═(pz)$_2$═AgPPh$_3$		Ir═(pz)$_2$═AgPPh$_3$	
complex	*T*, K	N_1	N_2	N_1	N_2	N_1	N_2
2	213	–165.5 ${}^{1}J({}^{15}N{-}{}^{15}N) = 15.1$	–60.5b	–165.5 ${}^{1}J({}^{15}N{-}{}^{15}N) = 15.1$	–93.1b		
3	188			–170.8 ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.7$	–90.7 ${}^{1}J({}^{15}N{-}{}^{107}Ag) = 31.8$ ${}^{1}J({}^{15}N{-}{}^{109}Ag) = 36.5$ ${}^{2}J({}^{15}N{-}Ag{-}{}^{31}P) = 13.2$	–168.5 ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.5$ ${}^{2}J({}^{15}N{-}N{-}Ag) = 2.8$ ${}^{3}J({}^{15}N{-}NAg{-}{}^{31}P) = 1.7$	–105.2 ${}^{1}J({}^{15}N{-}{}^{107}Ag) = 63.6$ ${}^{1}J({}^{15}N{-}{}^{109}Ag) = 73.8$ ${}^{2}J({}^{15}N{-}Ag{-}{}^{31}P) = 18.5$
4	213	–203.5 ${}^{1}J({}^{15}N{-}{}^{15}N) = 16.4$ ${}^{2}J({}^{15}N{-}Ir{-}{}^{31}P) = 4.2$	–53.7				
5	188			–205.6 ${}^{1}J({}^{15}N{-}{}^{15}N) = 14.0$ ${}^{2}J({}^{15}N{-}N{-}Ag) = 3.2$ ${}^{3}J({}^{15}N{-}N{-}Ag{-}{}^{31}P) = 1.5$	–94.0 ${}^{1}J({}^{15}N{-}{}^{107}Ag) = 31.7$ ${}^{1}J({}^{15}N{-}{}^{109}Ag) = 36.7$ ${}^{2}J({}^{15}N{-}Ag{-}{}^{31}P) = 11.3$		

groups of signals (131.57/130.85, 134.77/134.43, 130.36/130.23, 132.37/132.07), corresponding to a frozen structure **3** (no attempt was made to assign these signals to the two different $AgPPh_3$ groups). The pyrazole carbons appear at 106.45/107.78 (C_4) and at 141.30/142.99 and 141.53/144.56 ppm (C_3 and C_5).

(c) Compound 4. The following signals can be observed: 8.58 (methyl groups of C_5Me_5), 94.71 (ring carbons of C_5Me_5), 103.14 (pyrazoles C_4), 138.90 and 139.93 ppm (pyrazoles, C_3 and C_5). The triphenylphosphine signals appear broadened and thus C_{ipso} cannot be observed; the remaining carbons appear at 135.28 (*ortho*), 127.73 (*meta*), and 130.49 ppm (*para*). The broadening of Ph_3P signals in this acyclic compound should be due to a slow rotation about the phosphorus–iridium bond. No previous reports concerning the P–Ir bond are found in the literature, but the phenomenon is well documented for other metal–PPh_3 bonds: Rh–P,[11] Cr–P[12] and Fe–P.[13]

(d) Compound 5. The spectrum was recorded in acetone-d_6, and the following signals can be observed: 9.11 (methyl groups of C_5Me_5), 96.75 (ring carbons of C_5Me_5), 144.41 and 143.89 (C_3 and C_5 of pyrazoles), and 106.11 ppm (C_4 of pyrazoles). At 318 K, the carbons of $AgPPh_3$ appear as narrow signals whereas those of PPh_3 are broad.

${}^{15}N$ NMR. Due to the low abundance of this isotope only data for enriched compounds were obtained. Chemical shifts and coupling constants were gathered in Table 4.

(a) Compound 2. ${}^{15}N$ spectra of this compound in $CDCl_3$ at 30.41 MHz were recorded between 328 and 213 K. At 328 K, two signals appear at –84.20 (broad singlet) and –169.69 ppm [doublet, ${}^{1}J({}^{15}N{-}{}^{15}N) = 14.8$ Hz], shieldings which correspond to the average of N_2 and N_1 signals, respectively. When the temperature is lowered, the coalescence for N_2 is reached at 243 K. At 213 K, three multiplets can be observed at –60.5, –93.1 (nitrogens linked to silver) and –165.5 ppm (nitrogens linked to Iridium). The signal at –60.5 ppm corresponds to the N_2 nitrogen of the "free" pyrazole. As the signal is broadened, it is not possible to measure coupling constants. The signal at –93.1 ppm corresponds to the same nitrogens of the two "complexed" pyrazoles (linked to Ir and to Ag). As those signals are broadened, it is not possible to measure coupling constants. Finally, the sharp doublet which appears at –165.5 ppm has an averaged shielding which corresponds to the three nitrogens linked to iridium. The coupling constant is due to the coupling between N_1 and N_2.

(b) Compound 3. The ${}^{15}N$ spectra of this compound in acetone-d_6 at 30.41 MHz were recorded between 293 and 188 K. At 293 K, two signals appear at –96.6 (broad singlet) and –171.93 ppm [doublet, ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.5$ Hz]; the chemical shift at –96.6 ppm corresponds to an averaging of the N_2 and N_1 signals respectively [$(-90.7 \times 2) - 105.2)/3 = -95.5$ ppm]. When the temperature is lowered, the coalescence for both nitrogens is reached between 243 and 263 K. At 188 K, four multiplets can be observed at: –90.66, –105.2 ppm in a ratio 2:1 (nitrogens linked to silver) and –170.8, –168.5 ppm in a ratio 2:1 (nitrogens linked to Iridium). The signal at –105.2 ppm is a complex multiplet where it is possible to measure four interesting coupling constants: ${}^{1}J({}^{15}N{-}{}^{107}Ag) = 63.6$ Hz, ${}^{1}J({}^{15}N{-}{}^{109}Ag) = 73.8$ Hz, ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.6$ Hz, and ${}^{2}J({}^{15}N{-}Ag{-}{}^{31}P) = 18.7$ Hz. In the same way, the multiplet at 90.66 ppm has the following constants: ${}^{1}J({}^{15}N{-}{}^{107}Ag) = 32.8$ Hz, ${}^{1}J({}^{15}N{-}{}^{109}Ag) = 36.5$ Hz, ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.7$ Hz and ${}^{2}J({}^{15}N{-}Ag{-}{}^{31}P) = 13.7$ Hz. Multiplets corresponding to N_1 nitrogens appear as doublets: the signal at –170.8 ppm due to two nitrogens with ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.7$ Hz and the signal at –168.5 ppm due to one nitrogen with ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.5$ Hz.

(c) Compound 4. The ${}^{15}N$ spectra of this compound in $CDCl_3$ at 30.41 MHz were recorded between 328 and 213 K. At 213 K two multiplets can be observed: one at –53.7 ppm [doublet, ${}^{1}J({}^{15}N{-}{}^{15}N) = 16.4$ Hz] corresponding to sp^2 nitrogens and the other at –203.5 ppm [doublet of doublets, ${}^{1}J({}^{15}N{-}{}^{15}N) = 16.4$ Hz, ${}^{2}J({}^{15}N{-}Ir{-}{}^{31}P) = 4.3$ Hz] corresponding to nitrogens linked to iridium.

(d) Compound 5. The ${}^{15}N$ spectra of this compound in acetone-d_6 at 30.41 MHz were recorded between 293 and 188 K. At 293 K, two signals appear at –95.9 ppm (broad singlet) and –208.74 ppm [doublet, ${}^{1}J({}^{15}N{-}{}^{15}N) = 15.6$ Hz], which correspond to the average of N_2 and N_1 signals, respectively. At 188 K, the signal at –93.98 ppm is a complex multiplet where it is possible to measure four interesting coupling constants: ${}^{1}J({}^{15}N{-}{}^{107}Ag) = 31.7$ Hz, ${}^{1}J({}^{15}N{-}{}^{109}Ag) = 36.7$ Hz, ${}^{1}J({}^{15}N{-}{}^{15}N) = 14.1$ Hz, and ${}^{2}J({}^{15}N{-}Ag{-}{}^{31}P) = 11.3$ Hz. The signal at –205.56 ppm corresponding to N_1 nitrogens appears as a doublet with ${}^{1}J({}^{15}N{-}{}^{15}N) = 13.9$ Hz. To distinguish between ${}^{1}J({}^{15}N{-}{}^{15}N)$ and ${}^{2}J({}^{15}N{-}{}^{31}P)$ the first one was assigned by means of a 2D *J*-resolved homonuclear experiment.

${}^{109}Ag$ NMR. (a) Compound 2. The ${}^{109}Ag/{}^{31}P\{{}^{1}H\}$ correlation spectrum at 211 K in $CDCl_3$ shows a doublet at 902.8 ppm with a ${}^{1}J({}^{31}P{-}{}^{109}Ag) = 651$ Hz, consistent with the result obtained by ${}^{31}P$ NMR (see Table 2).

(b) Compound 3. Six ${}^{109}Ag/{}^{31}P\{{}^{1}H\}$ correlation spectra corresponding to a solution of this compound in $CDCl_3$ were recorded between 211 and 283 K and another spectrum corresponding to a solution in acetone-d_6 at 211 K was also recorded. At 211 K in $CDCl_3$, two ${}^{109}Ag$ signals are observed, one at 884.3 ppm [${}^{1}J({}^{31}P{-}{}^{109}Ag) = 664$ Hz] and the other at 562.9 ppm [${}^{1}J({}^{31}P{-}{}^{109}Ag) = 731$ Hz]. For each signal two spots are observed with the same position in the f_1 dimension (${}^{109}Ag$) and different positions

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(11) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862–2863.
(12) Jones, W. D.; Feher, F.J. *Inorg. Chem.* **1984**, *23*, 2376–2388.
(13) Hunter, G.; Weakley, T. J. R.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **1987**, 1545–1550.

Table 5. ^{15}N NMR Parameters of Structural Importance

				N₂ couplings, Hz		
position 1	position 2	$\delta(N_1)$	$\delta(N_2)$	$^1J(^{15}N-^{15}N)$	$^1J(^{15}N-^{109}Ag)$	$^2J(^{15}N-Ag-^{31}P)$
CH₃	lone pair	–180.0	–76.5	15.0		
2, Ir(C_5Me_5)pz	lone pair	–165.5[a]	–60.5	**16.1**[b]		**0**[d]
2, Ir(C_5Me_5)(pz)$_2$AgPPh$_3$	AgPPh$_3$ (μ)	–165.5[a]	–93.1	**14.2**[b]	**38**[c]	**13.6**[d]
3, Ir(C_5Me_5)(pz)$_2$AgPPh$_3$	AgPPh$_3$	–168.5	–105.2	13.5	73.8	18.5
3, Ir(C_5Me_5)pzAgPPh$_3$	AgPPh$_3$ (μ)	–170.8	–90.7	13.7	36.5	13.2
4, Ir(C_5Me_5)(PPh$_3$)	lone pair	–203.5	–53.7	16.4		
5, Ir(C_5Me_5)(PPh$_3$)	AgPPh$_3$ (μ)	–205.6	–94.0	14.0	36.7	11.3

[a] Averaged value. [b] Averaged value 15.0 Hz. [c] Signal width of the –93.1 ppm signal, 67 Hz. [d] Averaged value 9.1 Hz.

in the f_2 dimension (^{31}P) due to the ^1J coupling. The signal at $\delta(^{109}Ag)$ = 884.3 ppm corresponds to $\delta(^{31}P)$ = 15.55 ppm while that at $\delta(^{109}Ag)$ = 562.9 ppm corresponds to $\delta(^{31}P)$ = 19.78 ppm. From the ^{31}P chemical shifts and from the ^1J values (Table 2) there is no doubt that the 884.3 ppm signal belongs to the silver atom linked to two pyrazole rings and that at 562.9 ppm to the silver atom linked to only one pyrazole ring. Increasing the temperature produces a broadening of the silver signals, and the correlation spots become less and less intense until they disappear.

In acetone-d_6, the ^{109}Ag chemical shifts are 885.3 and 574.8 ppm.

Discussion of the Data

(1) NMR Parameters (δ and J). (a) ^{1}H. The chemical shifts of the two kinds of pyrazoles of compound **2** (spectrum at 183 K) show that the coordination with silver does not modify the chemical shifts to an important extent (less than 0.2 ppm). An important consequence of this observation is that these Ir–pz–Ag heterocycles behave as if the iridium were at position 1 and the silver at position 2 of the pyrazole ring; *i.e.,* they are 1-iridiapyrazoles using the lone pair at position 2 to coordinate the silver triphenylphosphine.

(b) ^{31}P. The couplings between the phosphorus and the two silver isotopes should be in a ratio close to the magnetogyric ratio of the latter [$\gamma(^{107}Ag)/\gamma(^{109}Ag)$ = 0.867]. The following experimental values in parentheses were found: **2** (564.6/652.7 = 0.865), **3** (630.6/727.0 = 0.867, 574.1/661.0 = 0.868), **5** [CDCl₃ (590.1/681.6 = 0.866), acetone-d_6 (591.4/681.1 = 0.868)].

Limiting our discussion to the ^{109}Ag isotope, we can see that to the situation P—Ag—pz corresponds a ^1J = 733 Hz (compound **3**) and to the situation P—Ag═(pz)$_2$ corresponds a ^1J = 665 Hz (averaged value of compounds **2, 3,** and **5**). It has been established that there is a relationship between ^1J(Ag–P) and the number of phosphorus ligands n (when n increases, ^1J decreases).[14] The situation seems to be the same, when the number of nitrogen ligands increases. It is reasonable to assume that this behavior is related to the P–Ag bond strength; when the silver is coordinated to two pz's, the P—Ag bond weakens. A more thorough analysis of the P—Ag═(pz)$_2$ case shows that ^1J depends on the substituent on the iridium: 653 Hz, compound **2**, where the substituent is pz; 662 Hz, compound **3**, where the substituent is Ph$_3$P–Ag–pz; 682 Hz, compound **5**, where the substituent is Ph$_3$P (note that Ph$_3$P–Ag–pz behaves, as a substituent, intermediately between pz and Ph$_3$P). According to our hypothesis, this shows a slight increase in the P–Ag bond strength. If we further assume that when the P–Ag bond strength increases, the corresponding Ag–N(pz) bond strength decreases, then there should be a decrease in the bond strength on going from **2** to **3**, which could explain why the activation energy for the silver migration decreases in the same direction (see below).

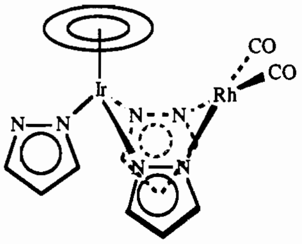
Compound **4′** presents a $^2J(^{31}P-Ir-^{15}N)$ coupling with both pyrazole rings for which there is no precedent in the literature.

(c) ^{13}C. The results obtained on complex **2** at low temperature show how slightly sensitive they are to coordination with silver (a shift of about 2 ppm or less). Coordinated or free, carbons C$_3$ and C$_5$ have very similar chemical shifts. The same occurs in compounds **3** and **5**.

The ^{13}C NMR spectra of the labeled compounds, **2′**–**5′**, do not provide any useful information. Due to slightly broad signals and to the fact that $^{13}C-^{15}N$ coupling constants in pyrazoles are usually small (the largest one, $^1J(C_5-N_1)$, attains only 12 Hz),[3] the spectra are for all purposes identical to those of the unlabeled compounds.

Compound **4**, in which pyrazoles are "classically" linked to iridium, shows that carbons C$_3$ and C$_5$ resonate so closely ($\Delta\delta$ = 1.0 ppm) that their assignment is not possible. This is not an indication of fluxionality (the iridium exchanging rapidly between both positions of a pyrazolate) since the chemical shifts would become not similar but **identical.** Some substituents on the nitrogen have the property to close the gap between $\delta(C_3)$ and $\delta(C_5)$, usually separated by 10 ppm.[15,16] For instance, in dihydrobis(1-pyrazolyl)borate, $\Delta\delta$ = 4.2 ppm.[17]

In order to show that $\delta(C_3) \sim \delta(C_5)$ in all compounds (free or linked to AgPPh$_3$) is due to the iridium, compound **6**,[2] in which no dynamical complication can arise, was studied.



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The spectrum (recorded in CDCl₃; all J values correspond to $^1H-^{13}C$ coupling constants) shows the signals of "free pyrazole" (relative intensities 1) at 102.3 (C$_4$, ^1J = 171.0, ^2J = ^2J = 10.6 Hz), 137.9 (C$_5$, ^1J = 181.7, ^2J = 8.9, ^3J = 4.7 Hz), and 139.2 ppm (C$_3$, ^1J = 178.1, ^2J = ^3J = 6.9 Hz) and those of "μ-coordinated pyrazoles" (relative intensities 2) at 106.6 (C$_4$, ^1J = 177.1, ^2J = ^2J = 9.5 Hz) and 141.3 and 144.1 ppm (C$_3$, ^1J = 181.7, ^2J = ^2J = 6.7 and C$_5$, ^1J = 184.4, ^2J = ^2J = 6.8, ^4J = 2.8 Hz). Positions 3 and 5 with regard to the iridium at position 1 in the monosubstituted pyrazole are clearly distinct; the assignment of the signals is possible using both chemical shifts and coupling constants.[17,18] For the μ-coordinated pyrazoles, the assignment

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(14) Attar, S.; Alcock, N. W.; Bowmaker, G. A.; Frye, J. S.; Bearden, W. H.; Nelson, J. H. *Inorg. Chem.* **1991**, *30*, 4166–4176.

(15) Davies, S. G.; Derome, A. E.; McNally, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2854–2861.

(16) Begtrup, M.; Elguero, J.; Faure, R.; Camps, P.; Estopá, C.; Ilavsky, D.; Fruchier, A.; Marzin, C.; de Mendoza, J. *Magn. Reson. Chem.* **1988**, *26*, 134–151.

(17) Begtrup, M.; Boyer, G.; Cabildo, P.; Cativiela, C.; Claramunt, R. M.; Elguero, J.; García, J. I.; Toiron, C.; Vedsø, P. *Magn. Reson. Chem.* **1993**, *31*, 107–168.

(18) López, C.; Claramunt, R. M.; Sanz, D.; Foces-Foces, C.; Cano, F. H.; Faure, R.; Cayón, E.; Elguero, J. *Inorg. Chim. Acta* **1990**, *176*, 195–204.

is tentative and assumes that position 1 corresponds to nitrogen bonded to iridium. Here the effect of the rhodium atom is more apparent than that of silver triphenylphosphine, but nevertheless, carbons C_3 and C_5 have very similar chemical shifts.

(d) ^{15}N. In all cases, the ratios of $^1J(^{15}N–Ag)$ coupling constants for silver isotopomers correspond to the expected values: **3**, 0.871 and 0.862; and **5**, 0.864.

Table 4 contains a considerable amount of new information regarding ^{15}N NMR spectroscopy. Two types of data from the literature are useful for the following discussion: the chemical shifts of 1-methylpyrazole, $\delta(N_1) = -180.8$ and $\delta(N_2) = -76.5$ ppm,[18] and $^1J(^{15}N–^{15}N) \sim 15$ Hz for the pyrazoles.[3]

To discuss the information obtained from the ^{15}N NMR spectra, the most relevant data were gathered in Table 5. The main problem concerns compound **2** for which, even at 313 K, only averaged values were obtained for $\delta(N_1)$ and $^1J(^{15}N–^{15}N)$ and for $^2J(^{15}N–Ag–^{31}P)$ (from ^{31}P NMR). The value of –165.5 ppm has not been modified since it results from the average of two similar chemical shifts. The $^1J(^{15}N–^{15}N)$ average value of 15.0 Hz has been decomposed into two contributions of 16.1 (one time) and 14.2 (two times) [average $(14.2 \times 2 + 16.1)/3 = 14.8$ Hz], which will be discussed later. $^1J(^{15}N–^{109}Ag)$ cannot be measured on the –93.1 ppm broad signal; however, taking into account that its width is 67 Hz and considering that the couplings with ^{109}Ag are larger than those with ^{107}Ag (*i.e.*, the external branches of the multiplet should belong to the 109 isotopomer), it is possible to divide the 67 Hz into the sum of 38 Hz [$^1J(^{15}N–^{109}Ag)$] + 15 Hz [$^1J(^{15}N–^{15}N)$] + 14 Hz [$^2J(^{15}N–Ag–^{31}P)$]. The last value could be estimated independently considering that the 9.1-Hz coupling constant (measured in ^{31}P NMR) **over three rings** is the average of 13.6 Hz of the two rings linked to $AgPPh_3$ and a coupling of 0 Hz (this is the assumption) of the third ring.

Now it is possible to discuss the five parameters of Table 5. First of all, it is clear that both nitrogens can be described as N_1 and N_2, the iridium being the substituent at position 1.

The N_1 chemical shifts depend mainly on the other substituents of the 1-iridium atom. For Ir–pz, an averaged value of –167.6 ppm (compounds **2** and **3**) is observed whereas, for Ir–P, the value amounts to –204.6 ppm (compounds **4** and **5**). Whether position 2 of the pyrazole is coordinated to $AgPPh_3$ or not has very little effect.

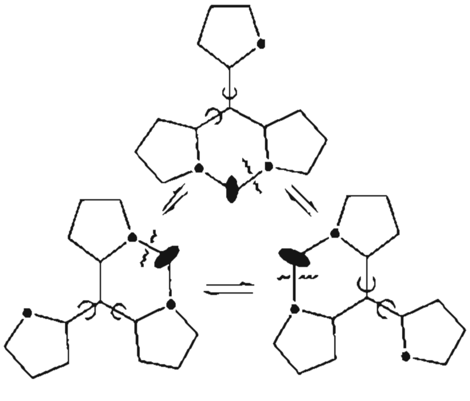
The N_2 chemical shifts are more sensitive but depend mainly on the nature of position 2. If there is a lone pair (compounds **2** and **4**), the signal appears at about –57 ppm. If position 2 is coordinated to $AgPPh_3$, two cases are observed. For a μ-coordination, the signal appears at –92.6 ppm (compounds **2**, **3**, and **5**) whereas, for a single coordination (compound **3**), the signal appears at –105.2 ppm.

$^1J(^{15}N–^{15}N)$ coupling constants are related to $\delta(N_2)$. Excluding compound **2**, the following empirical relationship holds for all compounds including 1-methylpyrazole: $^1J(^{15}N–^{15}N) = 19.6 + 0.06\,\delta(N_2)$, $n = 5$, $r^2 = 0.96$. From the chemical shifts of N_2 in compound **2** (–60.5 and –93.1 ppm), it is possible to estimate the ^1J coupling constants, 15.9 and 14.0 Hz, respectively. The values of Table 3, **16.1** and **14.2**, are a compromise of this calculation and that which results from the averaged value of 15.0 Hz (16.3 and 14.4 Hz, respectively).

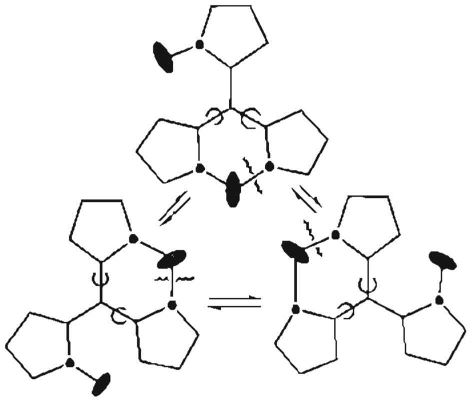
$^1J(^{15}N–^{109}Ag)$ couplings are very sensitive to the mono- or dicoordination of pyrazole and silver or, in other words, to the neutral or cationic character of the complex. For $[(pz)_2AgPPh_3]^+$, a value of 37 Hz is observed (compounds **2**, **3**, and **5**), whereas, for $[pzAgPPh_3]^0$, the value doubles to reach 73.8 Hz.

Thus, both $\delta(N_2)$ and $^1J(^{15}N–^{109}Ag)$ are sensitive to the effect of the coordination. As a matter of fact, the values for compounds **3** and **5** are related by the empirical equation $^1J(^{15}N–^{109}Ag) = -217.8–2.76\,\delta(N_2)$, $n = 3$, $r^2 = 0.95$. Using this equation and the chemical shift of N_2 in compound **2** (–93.1 ppm), a calculated value of 39 Hz is obtained for $^1J(^{15}N–^{109}Ag)$ in good agreement with the value of Table 3.

Scheme 2



Compound 2



Compound 3

Finally, $^2J(^{15}N–Ag–^{31}P)$ depends similarly on the coordination and charge. For μ complexes, $^2J = 12.7$ Hz, and for monocoordinate complexes, $^2J = 18.5$ Hz.

In Table 4 there remain several small couplings which have never been reported previously: $^2J(^{15}N–N–Ag)$ (too small to observe the difference between ^{107}Ag and ^{109}Ag), $^3J(^{15}N–N–Ag–^{31}P)$ (too small to be measured in the ^{31}P NMR spectra), and $^2J(^{15}N–Ir–^{31}P)$ (observed also in the ^{31}P NMR spectrum).

(e) ^{109}Ag. The results obtained for compounds **2** and **3** in $CDCl_3$ show that the signals corresponding to a silver atom linked to a phosphine and two pyrazole rings appear at 902.8 (compound **2**) and 884.3 ppm (compound **3**) while that for a silver atom linked to a phosphine and one pyrazole ring appears at 562.9 ppm (compound **3**), that is more than 300 ppm apart. One signal of compound **3** is insensitive to solvent effects (884.3 and 885.3 ppm) while the other is rather sensitive (562.9 and 574.8 ppm).

(2) Dynamic Phenomena. (a) Compound 2. The quartet observed in ^{31}P NMR of compound **2′** ($^2J = 9.1$ Hz) at 213 K shows that the phosphorus is identically coupled with the **three** pyrazoles (nitrogen of the position 2, $^{15}N–Ag–^{31}P$). Thus, at this temperature, well below the coalescence (experiments carried out at the same frequency, 121.4 MHz, for compounds **2** and **2′**), (i) for the chemical shifts the argentotropy is blocked but (ii) for the coupling constants, there are still three equivalent pyrazoles. In other words, the exchange rate is still sufficiently rapid to transmit the spin information of the third pyrazole ^{15}N to the phosphorus atom, even though most of the time it is linked to only two pyrazoles.

Using the signal of C_4 (14 points in $CDCl_3$), the kinetic parameters were determined:

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(19) Chen, B. C.; von Philipsborn, W.; Nagarajan, K. *Helv. Chim. Acta* **1983**, *66*, 1537–1555.

$$\Delta H^{\ddagger} = 8.28\ (\pm 0.44)\ \text{kcal mol}^{-1}\ (34.6\ \text{kJ mol}^{-1})$$

$$\Delta S^{\ddagger} = -12.8\ (\pm 1.8)\ \text{eu}\ (-54\ \text{J K}^{-1}\ \text{mol}^{-1})$$

(b) Compound 3. The signal of carbon C_4 has been used to determine the barrier. The value at high temperatures, 106.87 ppm, corresponds to the average of those at low temperatures: $(2 \times 107.78 + 106.45)/3 = 107.3$ ppm. Using 8 points, the following kinetic parameters were obtained:

$$\Delta H^{\ddagger} = 7.64\ (\pm 0.40)\ \text{kcal mol}^{-1}\ (32\ \text{kJ mol}^{-1})$$

$$\Delta S^{\ddagger} = -19.8\ (\pm 1.4)\ \text{eu}\ (163\ \text{J K}^{-1}\ \text{mol}^{-1})$$

Using the ^{31}P NMR signals, the values are $\Delta H^{\ddagger} = 7.67$ ($\pm$ 0.43) kcal mol^{-1} and $\Delta S^{\ddagger} = 18.4$ ($\pm$1.7) eu, in excellent agreement with those determined using another nucleus (^{13}C) and another part of the molecule (pyrazole rings).

(c) Compound 4. To explain the broadening of the signals pertaining to the PPh_3 group of this simple compound, the only possibilty is a slow rotation about the P–Ir bond (see the previous discussion and refs 12, 13, and 15).

(d) Compound 5. This compound shows a dynamical behavior which can be observed in ^{31}P NMR. Since the signal of Ph_3P–Ir at 9.21 ppm (293 K) and 9.54 ppm (213 K) is always a very narrow singlet, whereas that of Ph_3P–Ag–$(pz)_2$, at about 15 ppm (293 K) and 16.65 ppm (213 K), changes from a broad doublet to a well-resolved double doublet, there is no doubt that the phenomenon involved is the ^{31}P–$^{107(109)}$Ag bond breaking. This well-known phenomenon has been observed for Ag(hfacac)PPh_3 by Partenheimer and Johnson,[20] for $[(R_3P)_4Ag]^+$ by Muetterties and Alegranti,[21] and by ourselves for [(η^6-*p*-cymene)Ru(μ-pz)$_3$-Ag(PPh_3)].[22] Its activation energy lies in the range of 10–11 kcal mol^{-1},[20-22] that is, higher than the argentotropism of compounds **2** and **3.**

(3) Barriers. Although slightly different and probably related to $^1J(^{31}\text{P–Ag})$ (see discussion in the ^{31}P NMR part), the most remarkable fact is that $\Delta H^{\ddagger}$(**2**) ~ $\Delta H^{\ddagger}$(**3**) when in the first case the migration involves only one $AgPPh_3$ group and in the second two $AgPPh_3$ must migrate in a concerted way. Since the process is intramolecular (reversibility and thermal stability prove this assertion), we proposed the mechanisms shown in Scheme 2.

The origin of the barrier is the breaking of **one** N–Ag bond and the rotation of **one** pz–$AgPPh_3$ group in both cases, this is why $\Delta H^{\ddagger}$ are similar. The differences affect only $\Delta S^{\ddagger}$, which is larger in complex **3** than in complex **2**, probably due to the larger mass of the former.

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(20) Partenheimer, W.; Johnson, E. H. *Inorg. Chem.* **1973**, *12*, 1274–1278.

(21) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386–6391.

(22) Ferrer, J. Ph.D. Thesis, University of Zaragoza, 1992. Carmona, D.; Ferrer, J.; Lamata, M. P.; Oro, L. A.; Limbach, H. H.; Scherer, G.; Elguero, J.; Jimeno, M. L. *J. Organomet. Chem.*, in press.