

A Series of Pyrazole Adducts and Pyrazolato Derivatives of Platinum(II) Containing Various Chelating Phosphines as Ligands: Characterization, ^1H and ^{31}P $\{^1\text{H}\}$ NMR Spectra

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New pyrazolato derivatives of platinum(II) are isolated, $(L-L)\text{Pt}(\text{pz})_2$, A, $[L-L = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3, \text{ or } 4$), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$, $(\text{Ph}_2\text{AsCH}_2)_2$ or *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$; $\text{pzH} = \text{pyrazole}$, 3,5-dimethyl-, 3,5-bis(trifluoromethyl)-, or 3,5-dimethyl-4-nitro-pyrazole] by reaction of $(L-L)\text{PtCl}_2$ with pyrazole and potassium hydroxide in methanol. By protonation of A with fluoboric acid the corresponding pyrazole adducts, $[(L-L)\text{Pt}(\text{pzH})_2][\text{BF}_4]_2$, B, are obtained when pzH is 3,5-dimethylpyrazole. The properties of the compounds are discussed on the basis mainly of the NMR evidence; ^{31}P data are related to the dimension of the $\text{Pt}-\text{P}-\text{C}$ ring ($n = 1-4$) and to the trans-influence of the pyrazolato and pyrazole ligand.

Introduction

During our investigations on the azole derivatives of metals, we reported preparation and properties of various pyrazole adducts of platinum, palladium [1], rhodium [2], and gold [3], as well as pyrazolato derivatives of the same elements. While studying the reactivity of some of these species it was found that the platinum complexes are very useful intermediates: indeed, from the ionic compounds $[(L-L)\text{Pt}$

(3,5-dimethylpyrazole-*N*) $_2][\text{BF}_4]_2$,* new polynuclear hydrides such as $[(\text{dppe})_2\text{Pt}_2\text{H}_3][\text{BF}_4]$ and $[(\text{dppe})_3\text{Pt}_3\text{H}_x][\text{BF}_4]$ were obtained [4], while from the bis-pyrazolato derivatives a series of heteropolynuclear compounds were isolated by reaction with suitable Lewis acids, e.g. $(\text{dppe})\text{Pt}\{\mu-(3,5-\text{Me}_2\text{-pz-}N,N')\}_2\text{ZnX}_2$, or $[(\text{dppe})\text{Pt}(\mu-3,5-\text{Me}_2\text{-pz-}N,N')_2]_2\text{Zn}][\text{BF}_4]_2$ [5].

Owing to the versatility of this type of platinum complexes and to their interest as ligands [5, 6], the preparation was undertaken of an extended series of derivatives in which both the chelating ligand and the pyrazole (or pyrazolato) moiety are systematically changed.

Experimental

Analyses, selected infrared data, molecular weight determinations and conductivities are reported in Table I; ^1H , ^{31}P , and ^{19}F NMR data are given in Table II. All the compounds were prepared according to the general pattern here reported.

Compounds of Type A

$(L-L)\text{PtCl}_2$, pyrazole, and potassium hydroxide (1:2:2 molar ratio) were refluxed in methanol solution (ca. 100 ml for 0.75 g of the platinum compound) for a few minutes. The concentrated methanol solution afforded a precipitate, which was extracted with dichloromethane. The analytical sample was obtained upon addition of diethyl ether. The yields are reported in Table I.

*A general bidentate ligand is indicated by L-L. $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ is abbreviated dppm ($n = 1$), dppe ($n = 2$), dppp ($n = 3$), dppb ($n = 4$). $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ is indicated by dppae, *cis*- $\text{Ph}_2\text{PCH}=\text{CHPh}_2$ by dppet. A general pyrazole is indicated by pzH, unsubstituted pyrazole by PzH; in a substituted pyrazole substituents and positions are given: e.g. 3,5-dimethylpyrazole is 3,5-Me $_2$ pzH.

TABLE I. Analytical and Other Data for the New Compounds.

Compound	M.p. °C ^a	Analyses ^b			Yield ^c %	Infrared data ^d	Other data ^e
		C	H	N			
1	dec. > 165 m.p. 260	55.13 55.1	4.90 5.08	6.92 6.94	60 ^f	1510s	M.W. 623 ^g CHCl ₃ (806) Not electrolyte in acetone
2	215	44.43 44.46	4.22 4.02	5.64 5.93	90	3300s,br 1575s	Λ = 156 (MeOH, 17 °C, 8 × 10 ⁻⁴ molar)
7	dec. > 290	43.37 43.23	2.72 2.60	5.51 5.60	72	1530m 1510m	
8	dec. > 290	48.88 49.5	4.08 4.13	9.24 9.62	79	1530s	
9	dec. > 220 m.p. 250	53.07 54.08	4.67 4.75	6.56 7.00	82	1510s	M.W. 778 CHCl ₃ (817)
10	256	44.76 45.17	4.08 3.97	5.62 5.85	97	3300s,br 1575s	M.W. 920 CHCl ₃ (957) Λ = 153 (MeOH, 17 °C, 7 × 10 ⁻⁴ molar)
11	270-85 dec.	55.90 55.72	5.00 5.01	6.80 7.02	80	1515s	M.W. 810 C ₆ H ₆ (797)
12	dec. > 285 m.p. ca. 300	45.73 45.67	4.57 4.32	5.37 5.76	95	3305s,br 1570s	Λ = 122 (MeOH, 17 °C, 5 × 10 ⁻⁴ molar)
13	dec. > 240 m.p. 258	55.81 56.24	5.48 5.18	6.65 6.90	66	1520s	M.W. 758 CHCl ₃ (811)
14	261-263	43.20 43.69	4.26 4.29	5.23 5.22	86	3265s,br 1575s	M.W. 907 CHCl ₃ (1072) Λ = 146 (MeOH, 17 °C, ca. 5 × 10 ⁻⁴ molar)
15 ^h	dec. > 270 m.p. 280	38.89 38.73	3.54 3.57	5.05 4.75	92	1520s	M.W. 1200 CHCl ₃ (1177)
15 ⁱ	<i>idem</i>	37.94 37.9	3.24 3.52	4.31 4.59	67	1520s	Not electrolyte in CH ₂ Cl ₂
16	dec. > 180 m. 198	52.26 52.26	4.68 4.59	6.76 6.77	70	1510m	
17	255-260	41.92 41.93	3.62 3.92	5.30 5.35	93	3300s,br 1575m	Λ = 160 (MeOH, 17 °C, ca. 5 × 10 ⁻⁴ molar)

^aDecomposition is generally gradual. ^bFound/calculated; data from the Microanalytical Laboratory of the University of Milan. ^cAll the compounds were crystallized from CH₂Cl₂/Et₂O but 2 from MeOH/Et₂O. ^dNujol mull; only N-H stretching and ring breathing modes are here reported. ^eMolecular weight by osmometry in the solvent indicated. ^fBy deprotonation of 2 the yield was 78%. ^gLow value owing to clathrated solvent. ^hFrom ether, see text. ⁱFrom CH₂Cl₂/Et₂O; it contains ½ CH₂Cl₂.

TABLE III. ¹J(¹⁹⁵Pt-³¹P) for (L-L)PtX₂ compounds.

Compound	(L-L) = dppe		(L-L) = dppm	
	¹ J(Pt-P)	lowering	¹ J(Pt-P)	lowering
(L-L)PtCl ₂	3610		3078	
(L-L)Pt(3,5-Me ₂ pz) ₂	3300	310	2744	334
(L-L)Pt(3,5-Me ₂ pzH) ₂ ²⁺	3320	290	2836	242
(L-L)PtMe ₂	1794	1826	1434	1644

Compounds of the Type B

Compound A was suspended in methanol and treated with a slight excess of fluoboric acid (50% aqueous solution) at room temperature. The resulting

solution was evaporated to dryness, the residue was extracted with dichloromethane to afford the analytical sample by addition of diethyl ether, with the yield indicated in the Table I.

TABLE II. Nuclear Magnetic Resonance Data.

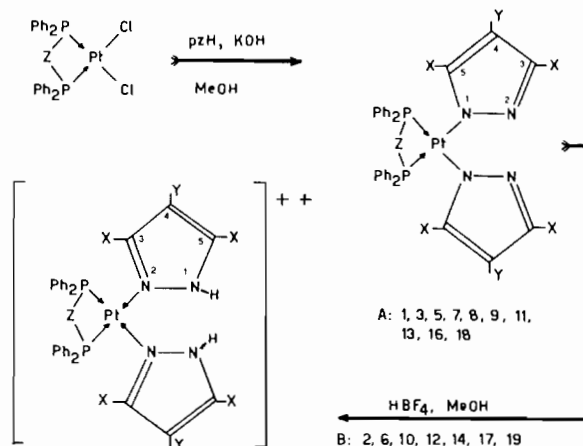
Compound ^a	Proton (or fluorine) data		Pyrazole ring ^a , τ values and J(PtH), Hz										31P data	
	Chelating ligand, τ													
	Phenyl ring	CH ₂	1	3	J	4	J	5	J	6	J	6	J	6
1	(dppm)Pt(3,5-Me ₂ pz) ₂ · ½Et ₂ O ^b	2.2-2.7m	5.74 ^c		7.95 ^d		4.38s	7	8.16s ^d		-61.0	2744		
2	[(dppm)Pt(3,5-Me ₂ pzH) ₂] [BF ₄] ₂	2.2-2.7m	4.88 ^e	-1.6s ^f	7.62s ^d		4.14s,br		8.11s ^d		-58.6	2836		
3	(dppe)Pt(Pz) ₂ ^g	2.0-2.8m	7.5-8.0m,br		3.20 ^d	9	4.05 ^t	7	h		+32.9	3122		
4	[dppe] ₂ Pt ₂ (Pz) ₂] [BF ₄] ₂ ^g	2.2-3.2m	7.1-7.6m		3.44s,br		4.04s,br		3.44br		+33.5	3176		
5	(dppe)Pt(3,5-Me ₂ pz) ₂ ^g	2.1-2.7m	7.5-7.9m		8.12s	4	4.54s,br	9	8.25s	4	+33.0	3300		
6	[(dppe)Pt(3,5-Me ₂ pzH) ₂] [BF ₄] ₂ ^g	ca. 2.40m	7.0-7.5m	-1.4s ^f	8.19s	5	4.27s,br		7.89s,br		+35.7	3320		
7	(dppe)Pt(3,5-(CF ₃) ₂ pz) ₂ ^j	2.0-2.6m	7.0-7.8m		-60.8s ^k		3.53s	8	-57.9s ^k	9	+37.8	3296		
8	(dppe)Pt(3,5-Me ₂ -4-NO ₂ pz) ₂	2.2-2.8m	7.0-7.7m		7.69s				7.87s	6	+32.1	3120		
9	(dpet)Pt(3,5-Me ₂ pz) ₂ · 2H ₂ O	2.2-2.9m	1		8.45s		4.50s	5	8.00s		+37.2	3161		
10	[(dpet)Pt(3,5-Me ₂ pzH) ₂] [BF ₄] ₂ · ½CH ₂ Cl ₂	1.9-2.9m	1	-1.1s ^f	8.50s		4.14s		7.75s		+44.3	3359		
11	(dppp)Pt(3,5-Me ₂ pz) ₂	2.0-3.0m	7.0-8.0m		8.20s ^d		4.90s	8	8.25s ^d		-13.3	2883		
12	[(dppp)Pt(3,5-Me ₂ pzH) ₂] [BF ₄] ₂	2.0-2.7m	6.5-7.2br	-1.4s ^f	7.88s ^d		4.54s,br		7.98s ^d		-16.1	3111		
13	(dppb)Pt(3,5-Me ₂ pz) ₂	2.17-3.0m	7.0-8.0m,br		8.43s	m	4.9s	8	8.12s		+1.2	2998		
14	[(dppb)Pt(3,5-Me ₂ pzH) ₂] [BF ₄] ₂ · CH ₂ Cl ₂	0.9-2.4m	7.85-8.15m,br	-1.17s ^f	7.85s ^d		4.5s	m	8.06s ^d		+1.5	3205		
15	[(dppb)Pt(3,5-Me ₂ pz) ₂] Cdl ₂ · ½CH ₂ Cl ₂	2.1-3.1m	6.5-7.7br		7.78s		4.8s,br		8.22s		-1.9	3017		
16	(dpase)Pt(3,5-Me ₂ pz) ₂	2.2-2.8m	7.4-8.0m		8.04 ^d		4.58		8.17 ^d		+29.8	3078		
17	[(dpase)Pt(3,5-Me ₂ pzH) ₂] [BF ₄] ₂ · ½CH ₂ Cl ₂	2.1-2.8	6.7-7.7m	-1.34s	8.12 ^d		4.53		8.34 ^d		+38.1	3266		
18	(dase)Pt(3,5-Me ₂ pz) ₂	1.8-2.3m	ca. 7.25m	-1.61s	7.93 ^d		4.30		8.02 ^d		-	-		
19	[(dase)Pt(3,5-Me ₂ pzH) ₂] [BF ₄] ₂	1.9br	ca. 7.1br		7.98 ^d		4.17		8.24 ^d		-	-		

^aThe abbreviations are explained in the footnote to be found in the Introduction. For the numbering of the pyrazole substituents see Figures 4 and 5. ^bEt₂O signals at 8.80t and 6.55q, with J = 7 Hz. ^cJ(P-H) = 10 Hz, ³J(Pt-H) = 57 Hz. ^dThese assignments could be exchanged. ^eJ(P-H) = 11.5 Hz, ³J(Pt-H) = 57 Hz. ^fProton exchange upon treatment with D₂O. ^gData from reference 1. ^h5-CH of the pyrazolato overlaps with aryl signals. ⁱ¹³J(H-H) = 2 Hz. ^j(CD₃)₂CO solvent. ^k¹⁹F NMR, against internal CCl₃F. ^l-CH= protons overlap with aromatic protons. ^mEvidence for coupling to ¹⁹⁵Pt, but J cannot be measured.

Results and Discussion

The preparation of the two series of the complexes, A and B, was carried out generally according to the following reaction Scheme.

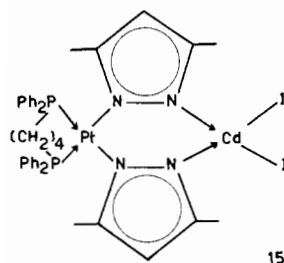
The adducts *B* were obtained directly by protonation with fluoboric acid when pz^- was the 3,5-dimethylpyrazolato anion. Such a reaction is generally reversible, e.g. treatment of the compound 2 with potassium hydroxide in methanol afforded the compound 1. Unexpected results were obtained when a differently ring-substituted pyrazole was employed. So the compound 3 reacted with fluoboric acid yielding the pyrazolato-bridged binuclear species 4, $[(\text{dppe})\text{Pt}(\mu\text{-Pz-}N,N')_2\text{Pt}(\text{dppe})][\text{BF}_4]_2$, as already described [1]. In the same conditions the bis(tri-



Compound	1,2	3	5,6	7	8	9,10	11,12	13,14	16,17	18,19
X =	CH ₃	H	CH ₃	CF ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃
Y =	H	H	H	H	NO ₂	H	H	H	H	H
Z =	CH ₂	(CH ₂) ₂	(CH ₂) ₂	(CH ₂) ₂	(CH ₂) ₂	CH=CH	(CH ₂) ₃	(CH ₂) ₄	(CH ₂) ₂	(CH ₂) ₂
E,E =	P,P	P,P	P,P	P,P	P,P	P,P	P,P	P,P	P,As	As,As

fluoromethyl)derivative 7 underwent a cleavage of the Pt–N bond, affording an aquo or a hydroxo-bridged complex, e.g. $[(\text{dppe})_2\text{Pt}_2(\text{OH})_2][\text{BF}_4]_2$ [7].

The ability of the bis(pyrazolato)platinum(II) derivatives to act as ligands through the uncoordinated nitrogen atoms has been previously ascertained [5] when the chelating ligand was $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$; now formation of an adduct was attempted only in the case of the complex 13 which gave 15 upon reaction with cadmium(II) iodide:



The compound 15 can be isolated from diethyl ether; if it is crystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, a dichloromethane clathrate is isolated, as it is often the case with molecules, like the present ones, having bulky or scarcely flexible ligands.

All the compounds are air-stable, colourless solids (but 8 is yellow); they were identified through analyses, conductivity measurements, infrared (Table I) and ^1H , ^{19}F , and $^{31}\text{P}\{^1\text{H}\}$ spectra (Table II).

The infrared spectra support the formulae proposed. The compounds of the type *B* show strong N–H stretching vibrations in the 3300 cm^{-1} region, and very strong and broad absorptions at ca. 1050 cm^{-1} , typical of the BF_4^- anion with tetrahedral symmetry. In the derivative of the 3,5-bis(trifluoro-

methyl)pyrazole, 7, a weak band at 3125 cm^{-1} reveals the presence of a heterocyclic ring, while very strong absorptions centered at 1255 and 1120 cm^{-1} are ascribed to C–F stretching vibrations.

The proton, phosphorus [8, 9, 10], and fluorine spectra (Table II) were recorded, generally in CDCl_3 solution. Besides supporting the structures proposed, they make possible certain observations and allow some conclusion to be reached, namely:

1) The observed values of $^1J(^{195}\text{Pt}-^{31}\text{P})$, 2.7–3.4 kHz, rule out the presence of a system containing a platinum-carbon bond, such as $\text{P}\rightarrow\text{Pt}-\text{C}=\text{CH}-\text{NH}-\text{N}=\text{CH}$ or $\text{P}\rightarrow\text{Pt}-\text{CH}-\text{CH}=\text{N}-\text{N}=\text{CH}$, the latter arising from the isomerization of the heterocyclic ring. Indeed a phosphine *trans*- to a carbon ligand would require a much lower value of 1J . Consequently, in all the cases reported here the pyrazole, or the pyrazolato ligand, coordinates to the platinum atom through nitrogen, as already suggested by us [1] for the compounds 5 and 6 on the basis of the $^4J(^{195}\text{Pt}-^1\text{H})$ values.

2) The new complexes containing the $\text{Pt}-\text{P}(\text{C})_n-\text{P}$ ring are mononuclear for $n = 1-4$, a point which is confirmed by the available molecular weight determinations. In the case of the *dppm* complexes 1 and 2, i.e. of a ligand with a marked tendency to bridge rather than to chelate, additional evidence of the mononuclear nature of the complex was reached through the NMR spectra. For example, in the case of 1 the resonance of the $\text{P}-\text{CH}_2-\text{P}$ protons appears as a triplet ($^1J(\text{P}-\text{H}) = 10\text{ Hz}$) flanked by satellites in a 1:4:1 ratio (coupling to only one ^{195}Pt ; $^3J(\text{Pt}-\text{H}) = 57\text{ Hz}$), as expected in the hypothesis of chelation. A more complicated pattern is predictable for a $-\text{Pt}\leftarrow\text{P}-\text{CH}_2-\text{P}\rightarrow\text{Pt}-$ system: the NMR spectra of

species of this type have been reported many times and discussed in detail [11]. Furthermore the ^{31}P chemical shift (-61 ppm from H_3PO_4) shows that the diphosphine is more shielded than the free ligand. A similar increase in shielding has been previously observed in other cases where the dppm acts as a chelating (e.g.: $(\text{dppm})\text{PtCl}_2$, -64.3 [8]; $(\text{dppm})\text{-PdCl}_2$, -57.3 [12]) rather than a bridging ligand ($(\text{dppm}_2)\text{Pd}_2\text{Cl}_2$, -2.5 ppm [12]).

3) The displacement of the ^{31}P chemical shift upon coordination, $(\Delta P = \delta_{\text{COMPLEX}} - \delta_{\text{LIGAND}})$ increases with the number of members in the $\text{Pt-P-(C)}_n\text{-E}$ ring along the series $n = 1, 3$, and 4 ($\text{E} = \text{P}$), while the compounds with $n = 2$ ($\text{E} = \text{P}$, or As) show the biggest values of ΔP . This fact is in line with the previous observations carried out on $(\text{L-L})\text{PtCl}_2$ and on $(\text{L-L})\text{PtR}_2$ ($\text{R} = \text{Me}$, or Et) complexes [8, 9]. The point can be verified by inspection of Fig. 1 which contains data concerning pyrazolato, pyrazoles, chloro, and alkyl derivatives of platinum.

4) In both type of compounds, *A* and *B*, the same factors are active on the ^{31}P chemical shifts. Indeed, if the δ_{P} of the pyrazolato derivatives, *A*, are plotted against the corresponding values of the pyrazole adducts, *B*, the points lie on the bisecting line (Fig. 2). The same conclusion can be reached if δ_{LIGAND} is plotted against δ_{COMPLEX} for either type *A* or type *B* complexes (Fig. 3): all the points but two lie on a straight line. These two points concern the compounds 9 and 10, i.e. $(\text{dpet})\text{Pt}(3,5\text{-Me}_2\text{pz})_2$ and $[(\text{dpet})\text{Pt}(3,5\text{-Me}_2\text{pzH})_2][\text{BF}_4]_2$, resp., which alone contain a rigid chelating ligand, *cis*- $\text{Ph}_2\text{PCH=CHPh}_2$.

5) In both the series of complexes *A* and *B* the

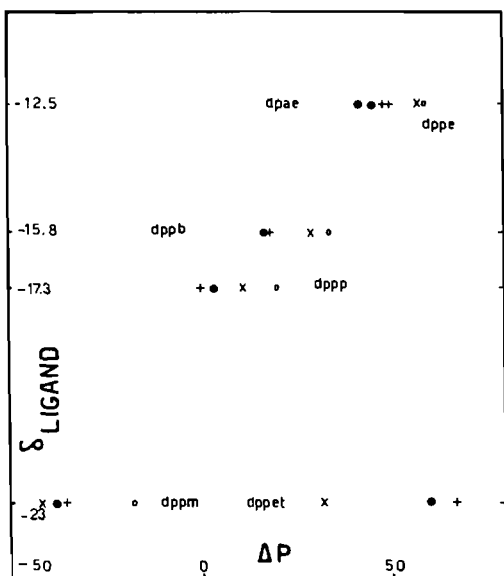


Fig. 1. $\Delta P = \delta_{\text{P}}(\text{complex}) - \delta_{\text{P}}(\text{Ligand})$ against δ_{P} of the ligand: ● dipyrazolate (A), + dipyrazole (B), x dichloro, and ○ dimethyl derivatives of the formula $(\text{L-L})\text{PtX}_2$. Data from this work and from the references [8–10].

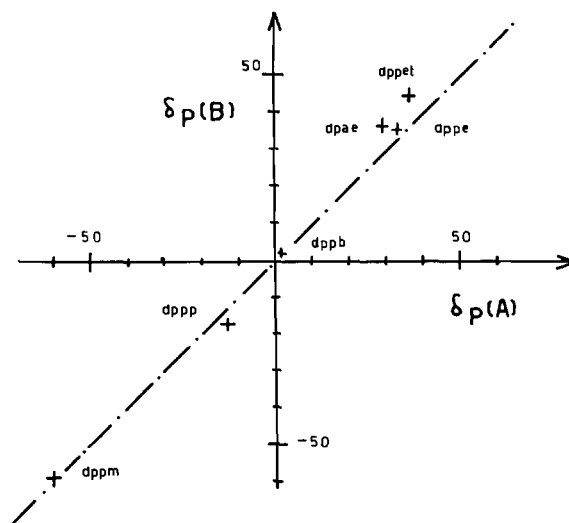


Fig. 2. Values of the ^{31}P chemical shifts of the pyrazolato derivatives, $\delta_{\text{P}}(\text{A})$, against the values of the corresponding protonated compounds, $\delta_{\text{P}}(\text{B})$.

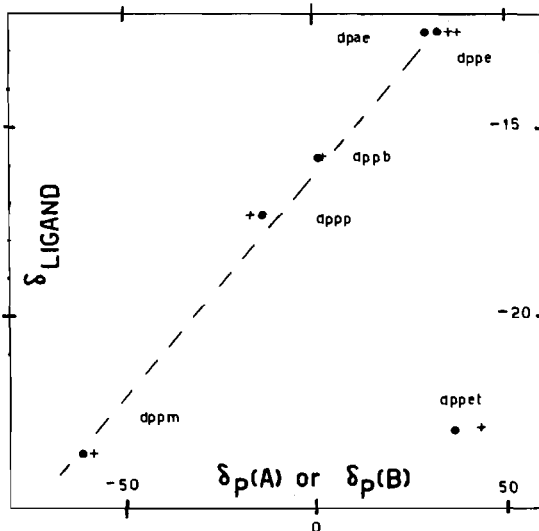


Fig. 3. Values of the ^{31}P chemical shifts of the ligands, δ_{LIGAND} versus the chemical shift of the pyrazolato (●) or the pyrazole (+) complexes, $\delta_{\text{P}}(\text{A})$ or $\delta_{\text{P}}(\text{B})$ respectively.

platinum–phosphorus coupling constants, $^1\text{J}(\text{Pt-P})$, are found in the range $3.0\text{--}3.3$ kHz for all the compounds, with the exception of the dppm derivatives 1 and 2. The range observed is in line with the values previously reported for the Pt-P coupling *trans* to other *N*-bonded ligands, e.g. $(\text{dppe})\text{Pt}(\text{NHCOCH}_3)(\text{CH}_3)$, 3322, or $(\text{dppe})\text{Pt}(\text{CH}_3)(\text{NO}_2)$, 3345 Hz, [8]. The lower values observed for the dppm derivatives, 1 and 2, 2744 and 2836 resp., are likely to be due to the strain connected with a four-membered Pt-P-C-P ring. This conclusion is better evidenced if, in the place of the absolute values of $^1\text{J}(\text{Pt-P})$, its lowering on going from the dichloro- to the dimethyl-derivatives of the $(\text{dppm})\text{Pt}$ and of the $(\text{dppe})\text{Pt}$ moieties

TABLE IV. Comparison of the Proton Magnetic Resonance Data of the Pyrazole or Pyrazolato Ligands.

Compound of the type	E=P Z=CH ₂	E=P Z=(CH ₂) ₂	E=P Z=CH=CH	E=As Z=(CH ₂) ₂	E=P Z=(CH ₂) ₃	E=P Z=(CH ₂) ₄
	Resonances of the 4-H (τ units)					
A	1 4.38	5 4.54	9 4.50	16 4.58 4.53	11 4.90	13 4.90
B	2 4.14	6 4.27	10 4.14	17 4.30 4.17	12 4.54	14 4.50
difference (A - B)	0.24	0.23	0.36	0.28 0.36	0.36	0.40
	Resonances of the methyl groups (τ units)					
A	1 7.95 8.16	5 8.12 8.25 ^a	9 8.00 8.45		11 8.20 8.25	13 8.12 8.43
B	2 7.62 8.11	6 7.89 8.19 ^a	10 7.75 8.50		12 7.88 7.98	14 7.85 8.05
difference (A - B)	0.33 0.05	0.23 0.06	0.25 -0.05		0.32 0.27	0.27 0.38

^aThis band is flanked by two satellites due to coupling with ¹⁹⁵Pt (natural abundance 33%).

is considered (Table III). The values of ¹J(Pt-P) in the complexes A and B suggest, therefore, that both pyrazole and pyrazolato ligands have a moderate *trans*-influence, bigger nevertheless than that of the chloro group. Changes of the substituents on the azole rings produce small changes on ¹J(Pt-P): 3122, 3300, 3296 and 3120 Hz for the compounds 3, 5, 7, and 8, respectively.

A few other comments can be made on the part of the ¹H NMR spectra relative to the pyrazole moieties, namely:

6) The proton chemical shift of the 4-H is sensitive to the nature of the group attached to the neighbouring carbon atoms, *i.e.* C-3 and C-5, and to the size of the Pt-P-(C)_n-P ring. (a) The first effect is most evident in the series of the compounds A where Z = CH₂CH₂, E = P, and Y = H. This 4-H was found to resonate at 4.54, 4.05, or 3.53 τ when X was methyl (5), hydrogen (3), or trifluoromethyl (7), respectively. This trend has no parallel in either the chemical shifts or the coupling constants connected with the phosphorus nuclei, so that it must be considered as a local effect of the substituents on the pyrazole ring. (b) The other effect, *i.e.* the size of the Pt-P-(C)_n-P ring, is evident when the derivatives of the same pyrazolato (*i.e.* 3,5-Me₂pz) are considered. In the compounds of the type A where X = CH₃, the τ values of 4-H is *ca.* 4.5 when the ring is five-membered, and lies at lower (4.38) or at higher field (4.90) when the ring is smaller or larger. A similar, though less marked, trend is detectable in the 4-H shifts of the corresponding complexes of the type B, while no such a behaviour is evident in the chemical shifts of the methyl groups, both in A and B type of compounds.

7) Protonation of an A-type compound to give the corresponding B-type species causes a lowering of the chemical shifts of all the 4-H protons and of nearly all the 3- or 5-methyl protons. The lowering, *ca.* 0.20–0.40 ppm (Table IV) is fairly constant only for the 4-H protons, which are directly bound to the ring which is protonated. The methyl groups become

more deshielded upon protonation when near to the protonated nitrogen than when near to the platinum atom, as seen in the couples of compounds 1 and 2 or, better, 5 and 6, where the assignment of the signals is checked by the presence of the satellite bands.

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