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Abstract

Since their first synthesis by Hückel (1937) and the first systematic exploration by Trofimenko (1970), interest in poly(1H-pyrazol-1-yl)methanes (bis, tris and tetrakis) has increased dramatically. This review focuses on the synthesis and reactivity of these ligands and contains 541 different structures and 271 references. After a brief historical introduction, the synthesis, reactivity, and nature of the coordinated metals are described along with some properties of these compounds, particularly the complete set of X-ray molecular structures. All of the formulae are represented to show the extraordinary richness of poly(1H-pyrazol-1-yl)methanes and to promote the use of the already known poly(1H-pyrazol-1-yl)methanes in coordination chemistry and the design of new ligands with the reported procedures.

Keywords	Pyrazoles Pyrazolylmethanes bis(1H-pyrazol-1-yl)methanes tris(1H-pyrazol-1-yl)methanes tetrakis(1H-pyrazol-1-yl)methanes Metal ligands X-ray structures
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Suggested reviewers	Antonio Otero, James GARDINIER, Daniel REGEL, Glenn Yap, Claudio Pettinari

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scheme 1.docx [Figure]

scheme 2.docx [Figure]

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Dear Professor Lever:

Please find enclosed a new revised version of our manuscript, "*The organic chemistry of poly(1H-pyrazol-1-yl)methanes*". We would like to thank you again for giving us the opportunity to revise and improve our manuscript and also for the promptness of your response.

- Graphical abstract has been modified following your comments.
- "it should be remarked" has been deleted in two occasions.
- All suggestions about spacing (p 21), unnecessary words (p 13), improved grammar (p 13) and corrections of mistakes as center dot (p 18) have been followed.
- The conclusions have been completed with new proposals in NMR of other nuclei as well as solid-state NMR. A more encouraging sentence about the study of the unexpected compounds is incorporated.
- All structures are in the corresponding figures or schemes:
 - 20 is in scheme 4.
 - 38-41 are in scheme 7; 325 s in scheme 8; 326-330 are in schemes 9; 331-333 are in scheme 10 and 334-336 are in scheme 11.
 - Compound 104 has been deleted in figure 11.
 - 365-368 are in scheme 14
 - 507 and 508 are in scheme 18 (reaction conditions are included in the text).
 - 480-489 are in figure 19; 490-492 are in scheme 15; 493-494 are in scheme 16 and 495-496 are in scheme 17.
- Compound 483 and 484 have been reordered in Figure 19; scheme 19 has been modified in order to improve the identification of the structures.
- Caption of figure 28 has been corrected.

We are confident that this new version will fit the valuable considerations you have passed on to us.

Sincerely

H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og				

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
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Metals coordinated by poly(pyrazol-1-yl)methanes

The organic chemistry of poly(1*H*-pyrazol-1-yl)methanes

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Dedicated to Sebastián Juliá Arechaga for his pioneering contribution to the title compounds

Keywords:

Pyrazoles

Pyrazolylmethanes

Bis(1*H*-pyrazol-1-yl)methanes

Tris(1*H*-pyrazol-1-yl)methanes

Tetrakis(1*H*-pyrazol-1-yl)methanes

Metal ligands

X-ray structures

A B S T R A C T

Since their first synthesis by Hückel (1937) and the first systematic exploration by Trofimenko (1970), interest in poly(1*H*-pyrazol-1-yl)methanes (bis, tris and tetrakis) has increased dramatically. This review focuses on the synthesis and reactivity of these ligands and contains 541 different structures and 271 references. After a brief historical introduction, the synthesis, reactivity, and nature of the coordinated metals are described along with some properties of these compounds, particularly the complete set of X-ray molecular structures. All of the formulae are represented to show the extraordinary richness of poly(1*H*-pyrazol-1-yl)methanes and to promote the use of the already known poly(1*H*-pyrazol-1-yl)methanes in coordination chemistry and the design of new ligands with the reported procedures.

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Abbreviations:

AIBN: azobisisobutyronitrile

CAN: Ceric ammonium nitrate

DFT: Density functional theory

GIAO: Gauge-including atomic orbital

HBTU: 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate

HSAB: Hard and soft acids and bases

LiHMDS: Lithium hexamethyldisilazane

PBE0: Perdew, Burke, Ernzerhof functional

PTC: phase transfer catalysis

QTAIM: Quantum theory of atoms in molecules

6-31G(d,p): A double z Pople basis set

6-311++G(d,p): A triple z Pople basis set

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1. Introduction

The extraordinary success of polypyrazolylborate anions (mainly the trispyrazolylborates, the famous scorpionates) [1–5] prompted Trofimenko to explore the isosteric, but neutral, poly-1-pyrazolylmethanes [6]. Even prior to the development of the scorpionates, these ligands had great success in their own right amongst organometallic chemists. This success led to a large number of reviews on their coordination chemistry and some aspects of their synthesis and organic reactivity were reported [7–18].

There is an important review on the design of heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane bearing stereogenic centers [19]. The present publication is the first attempt to summarize the rich chemistry of poly(1*H*-pyrazol-1-yl)methanes from an organic chemistry point of view. This review covers the literature up to the end of September 2016.

A foreword: the IUPAC names the unsubstituted pyrazol-1-yl derivatives as di-, tri- and tetra- and the C-substituted pyrazol-1-yl derivatives as bis-, tris- and tetrakis-, thus when the substituents

on the pyrazole ring are not defined, the more general names will be used.

2. Synthesis

2.1. Historical accounts

This section covers the preparation of poly(1*H*-pyrazol-1-yl)methanes from other structures such as 1*H*-pyrazoles, di(1*H*-pyrazol-1-yl)ketones and 1,1'-sulfinylbis(1*H*-pyrazoles). The preparation of new poly(1*H*-pyrazol-1-yl)methane ligands from poly(1*H*-pyrazol-1-yl)methanes will be discussed in the reactivity section with a few exceptions (Fig. 1).

The first example of the preparation of a poly(1*H*-pyrazol-1-yl)methane was in 1937 when Walter Hückel (the brother of Erich Hückel) and Horst Bretschneider reported the preparation of tri(1*H*-pyrazol-1-yl)methane (**1**) by reacting the potassium salt of pyrazole with chloroform. They obtained **1** in 34% yield after purification by sublimation, m.p. 106 °C (the authors reported that sodium pyrazolate did not react with chloroform) [20]. Not until 1970 was the field explored again, when Trofimenko [21], by analogy to scorpionates, prepared a large series of bis-(1*H*-pyrazol-1-yl)methanes, **2–13**, together with two tris(1*H*-pyrazol-1-yl)methanes, **1** and **14**, and the tetra(1*H*-pyrazol-1-yl)methane **15**. This seminal paper also described complexes of **1** with Ni(II), Co(II), Fe(III), Cr(0), Mo(0), W(0), Mn(I), and Mo(I), and complexes of **14** with Mo(0) and Mo(I). New complexes of **1** with Rh(II), Co(I), and Ru(II) and of **14** with Co(II) were reported three years later [22].

Figure 1 here

The parent compounds **2** and **15** melt at 83–84 °C and 146–147 °C, respectively. Neutral pyrazoles, their sodium and potassium salts and polyhalogenoalkanes (CH₂Br₂, CH₂I₂) were used to provide yields between 34 and 82% (the new synthesis of **1** was not reported).

Bis(1*H*-pyrazol-1-yl)methanes with mono- or di-substitution on the central carbon atom, **5–13**, were prepared by another procedure (Scheme 1) that uses acetals of aldehydes and ketones.

Scheme 1 here

Thé and Peterson described a new and important procedure (Scheme 2) starting from di(1*H*-pyrazol-1-yl)methanone [23,24].

Scheme 2 here

This procedure was used to prepare the following compounds: **5**, **9**, **10**, **11**, **12**, **13** and **16–19**. The authors pointed out that benzophenone, acetophenone, hexafluoroacetone, hexachloroacetone and 2-methylcyclohexanone did not react (Fig. 2).

Figure 2 here

It is worth noting that di(1*H*-pyrazol-1-yl)methanone is an azolide, a class of compounds of relative fragility, particularly towards hydrolysis [25].

Around 1977, Sebastián Juliá became interested in the reactivity of dichlorocarbene, generated from chloroform under PTC conditions, on CC double bonds [26,27] and he was interested in ascertaining what would happen with a pyrazole formal C=C bond. Previously, in 1969 Jones and Rees had already studied the reaction of 3,4,5-trimethyl-1*H*-pyrazole with chloroform and with sodium trichloroacetate [28]. The reaction (Scheme 3) afforded complex mixtures in which tris(3,4,5-

trimethyl-1*H*-pyrazol-1-yl)methane (**20**) was identified. The authors reported that the compound decomposed upon treatment with picric acid. In the case of 1*H*-benzimidazole, a mixture of three compounds was formed including tri(benzimidazol-1-yl)methane [29].

Scheme 3 here

In the same year, de Angelis *et al.* [30] repeated (PTC, CHCl₃, NaOH) the reaction shown in Scheme 3 and isolated only the most abundant derivatives (Scheme 4). The trispyrazolylmethane **20** was isolated in 63% yield after purification.

Scheme 4 here

Juliá *et al.* published five papers [31–35] in which the preparation of the following poly(1*H*-pyrazol-1-yl)methanes using phase transfer catalysis conditions was described: **1–3**, **14**, **15**, **19** and **21–34** (Fig. 3). The 4,4'-dibromo, **26**, and 4,4'-dinitro, **27**, derivatives were prepared from 4-bromo- and 4-nitro-1*H*-pyrazole, respectively, by reaction with CH₂Cl₂. The mixed compounds **24** and **25** were prepared from mixtures of pyrazole and 4-substituted pyrazoles (yielding mixtures of **2/24/26** and **2/25/27**) and by bromination and nitration of **2** (to afford **26** and **25/27**, respectively) [35]. The latter procedure will be discussed in the reactivity section. In cases where the two tautomers of a pyrazole are different, three isomers of bis(pyrazol-1-yl)methanes are obtained with the statistical product distribution corresponding to a two-step mechanism involving the *N*-CH₂Cl intermediate. The yields obtained were 3(5)-methyl-1*H*-pyrazole **21** (27%), **22** (50%), **23** (23%) and 3(5)-amino-1*H*-pyrazole **28** (40%), **29** (47%), **30** (13%), *i.e.* $(a + b)^2$ with $a = 52\%$ and $b = 48\%$ in the case of the methyl derivative and $a = 63\%$ and $b = 37\%$ in the case of the amino pyrazole. However, in the case of **31** only the less crowded derivative was obtained.

Non-symmetrical compounds **32**, **33** (56%) and **34** (44%) were obtained by the two-step method shown in Scheme 5 [34].

Figure 3 here

Scheme 5 here

Besides the methods already described, the only real improvement was the replacement of the fragile azolide (Scheme 2) by sulfoxides to prepare bis(pyrazol-1-yl)methanes (Scheme 6).

Scheme 6 here

This method was introduced by Thé, Peterson and Kiehlmann in 1973 [36] to prepare **12**, **16** and **18** and it was used by Reger *et al.* in 2004 [37] to prepare compounds **35**, **36** and **37** (Fig. 4).

Figure 4 here

Finally, addition of 1*H*-pyrazoles to activated CC triple bonds catalyzed by zinc chloride afforded bis(1*H*-pyrazol-1-yl)methanes monosubstituted on the central carbon (Scheme 7) [38].

Scheme 7 here

With a few exceptions, the poly(1*H*-pyrazol-1-yl)methanes have been prepared by one of the methods that are summarized in Tables 1 to 5.

2.2. By nucleophilic substitution of polyhalogenoalkanes

All of the structures obtained by this method, from **42** to **122**, will be represented first and the synthetic procedures are summarized in Table 1, including some structures described in the historical accounts section. The first column includes the polyhalogenated derivative; the second column the synthetic methodology; the third column the products obtained; the fourth the coordinated metals; and the fifth column contains the references. The references are provided in chronological order.

Figure 5 here

Table 1

Synthesis of poly(1*H*-pyrazol-1-yl)alkanes by nucleophilic substitution of polyhaloalkanes under phase transfer catalysis conditions.

Polyhaloalkane	Method	Products	Complexes	Ref.
CH ₂ Cl ₂	A	2	Pd(II)	[39]
PhCHCl ₂		19	Pd(II)	[39]
CH ₂ I ₂		42-44	Pd(II)	[40]
CH ₂ Br ₂		45-47	Zn(II)	[41]
CH ₂ Cl ₂		48	Sn(IV) Zn(II) Cd(II) Hg(II)	[42,43]
CHCl ₃		14, 21, 49-53		[44]
CH ₂ Cl ₂		2		[45]
CHCl ₃		1		[46]
CHCl ₃		54		[47]
			Cu(I)	[48]
			Ni(II) Cu(II)Zn (II)	[49]
CHCl ₃	B	55		[50]
CH ₂ Br ₂		57, 58	Co(II) Ni(II) Cu(II) Zn(II)	[51]
			In(III) Pb(II)	
CH ₂ Cl ₂		1, 54-56		[52]
Br ₂ CHCOOH		59, 60	Mn(I) Re(I)	[53]
			Pd(II) Pt(II) Au(III)	[54]
Br ₂ CHCOOH		61	Fe(II) Zn(II)	[55]
			Sn(IV)	[56]
CH ₂ Br ₂		62-66	Cr(0) Mo(0) W(0)	[57]
CH ₂ Br ₂		2, 3		[58]
CH ₂ Cl ₂	C	67	Zn(II)	[59]
CH ₂ Cl ₂		68		[60]
CH ₂ Br ₂		69-71	W(0)	[61]
Ph ₂ CCl ₂		72	Ag(I)	[62]
Ph ₂ CCl ₂		72-74	Cu(I) Cu(II)	[63]
CH ₂ Cl ₂		75-80	Zn(II)	[64,65]
CHCl ₃		81, 82	Cu(I)	[66]
CH ₂ Br ₂		48, 84, 85	Cu(II)	[67]
CH ₂ Cl ₂		86	Ag(I) Cu(I)	[68]
CH ₂ I ₂		87	Ag(I) Cu(I)	[68]
PhCHBr ₂	D	88	Ag(I) Cu(I)	[68]
CH ₂ Br ₂	B	89-93^a		[69]

<i>p</i> -CF ₃ -aryl	B	94-96		[70]
CH ₂ Cl ₂		71	Cu(I)	[71]
CHCl ₃		97, 98	Cu(I)	[72]
CHCl ₃		83		[73]
CH ₂ Cl ₂		3, 71, 99, 100	Cu(II)	[74]
		99	Li(I) Cu(I) Ag(I)	[75]
		2, 3, 71, 99	Cu(II)	[76]
CHCl ₃		101, 102	Tc(I)	[77]
CHCl ₃		49, 81, 82	Cu(II)	[78]
CH ₂ Br ₂		109	Pd(II)	[79]
<i>p</i> -CF ₃ -phenol	E	103		[80]
(CHBr ₂) ₂	B	89, 104		[81]
CH ₂ Cl ₂		105-109	Fe(II) Fe(III) Mn(II) Ni(II)	[82]
CHCl ₃		110-112		[83]
CHCl ₃		113		[84]
(CHBr ₂) ₂	B	89, 91, 92, 114-117		[85]
CHCl ₃		118	Mg(II) Ca(II) Sr(II) Ba(II)	[86]
CH ₂ Br ₂	F	119		[87]
CHCl ₃		120, 121	Mg(II) Y(II)	[88]
ArCF ₃	G	122		[89]

A KOH/MeCN. **B** KOH/DMSO. **C** Et₃N/toluene reflux. **D** NaH/DMF/80–100 °C. **E** NaH/THF reflux. **F** *t*-BuOK/THF reflux. **G** from 3,5-dimethylpyrazole, LiHMDS and the anion of N,N'-bis(2-(trifluoromethyl)phenyl)formamidine.

^a Compounds **91** and **93** were also prepared from terephthalaldehyde according to Scheme 1.

2.3. From aldehydes, ketones and their acetals

In a similar way to the previous section, the structures are shown first, from **123** to **143**, and then the results are summarized in Table 2, with similar columns.

Figure 6 here

Table 2

Synthesis of poly(1*H*-pyrazol-1-yl)methanes from aldehydes, ketones and their acetals catalyzed by ZnCl₂ or by *p*-toluensulfonic acid (*p*-TsOH) as described in Scheme 1.

Method	Products	Complexes	References
A, B	19, 123-125		[90]
A	126-132		[91]
B	9		[92]
B	133		[93]
B	134		[94]
B	12, 13		[95]
B	11		[96]
B	72, 135	Pd(0) Pd(II)	[97]
B	136	Ag(I)	[98]
B	19	Ag(I)	[62]
B	137	Ag(I)	[62]
B	138, 139	Re(I)	[99]

B	140	Cu(I)	[100]
B	141, 142	Fe(II)	[101]
B	143	Zn(II)	[102]

A From the aldehyde. **B** From the acetal.

2.4. From bis(1H-pyrazol-1-yl)ketones

As in the previous sections, the structures, from **144** to **224**, are shown first and the corresponding data are summarized in Table 3, with similar columns.

Figure 7 here

Table 3

Synthesis of poly(1H-pyrazol-1-yl)alkanes from di(pyrazol-1-yl)ketones and the appropriate carbonyl compound, catalyzed by CoCl₂, as described in Scheme 2.

Products	Complexes	References
144-150		[36]
72		[36]
19, 151	Rh(I)	[103]
152, 153	Pd(II) Pd(III)	[104]
136	Pt(IV)	[105]
154-156	Pt(II)	[106]
157-161	Co(II) Cu(II)	[107,108]
162	Ni(II)	[109]
163	Zn(II)	[110]
157, 158, 164-167	Zn(II) Pd(II) Pt(II)	[111,112]
168-171		[113]
172-174	Co(II) Zn(II) Ni(II)	[114]
175-177	Mn(I)	[115]
178	Pt(II) Re(I)	[116]
179		[117]
19, 151, 164, 180, 181	Ru(II)	[118]
182	Zn(II) Re(I)	[119]
183, 184	Cu(II)	[120]
185-189	Ni(II) Pd(II)	[121]
190		[122]
191	Na(I) Mg(II) Zn(II)	[123]
192	Zn(II)	[124]
193	Ag(I)	[125]
194-196	Ag(I)	[126]
71, 197-202	Cu(II)	[76]
157, 158, 191, 203-205	Ti(IV) Zr(IV)	[127]
206-208	Mo(0) Mo(I) W(0) W(I)	[128]
209, 210	Pd(II) Co(II) Ni(II) Zn(II) Ag(I)	[129–131]
211, 212	Ag(I) Pd(II)	[132]
91, 92, 214, 215	Pd(II) Zn(II) Cu(II)	[133]
216, 217	Zn(II)	[134]
213		[135]

218	Zn(II)	[136]
219	Ca(II)	[137]
220-224	Ag(I)	[138]

2.5. From sulfinylbis(1H-pyrazol-1-yl) derivatives

As in the previous sections, the structures, from **225** to **293**, are shown first and the corresponding data are summarized in Table 4, with similar columns.

Figure 8 here

Table 4

Synthesis of poly(1H-pyrazol-1-yl)methanes from sulfinylbis(1H-pyrazol-1-yl) derivatives and the appropriate aldehyde, catalyzed by CoCl₂ or by pyridine, as described in Scheme 6.

Products	Complexes	References
1, 14, 35, 54-56	Mn(I)	[52]
91, 178, 225^a	Pt(II) Re(I)	[116]
226	Re(I)	[139]
81, 82^a	Cu(I)	[66]
227	Re(I)	[140]
182	Ni(II) Pd(II)	[121]
228-231	Ni(II) Fe(II) Co(II) Mn(II) Cu(II) Zn(II) Ru(II) [Pd(II)-Ru(II)] ^d	[141–145]
192	Zn(II)	[124]
232-234	Ag(I)	[126]
235-241, 242-244^b	Co(II)	[146]
245-250	Cr(III)	[147]
153, 157, 245, 251-253		[148]
254-260^b		
261-263^c	Cu(I)	[149]
264-267^b	Pd(II)	[150]
264-267	Pd(II) Ru(II) Ir(III) [Ir(III)-Pd(II)] ^d	[151]
214, 268-272	Ag(I)	[152]
273	Zn(II) Mo(VI)	[153]
274-279	Rh(I)	[154]
280-282	Ag(I)	[155]
283^b		[156]
284	Cu(II)	[157]
285, 286	Ag(I)	[158]
287-289	Pt(IV)	[159]
290-292	Cr(III)	[160]
293	Zn(II)	[161]

^a A catalyst was not used. ^b *In situ* formation of the sulfinylbis(1H-pyrazol-1-yl) derivative. ^c Pyridine as catalyst. ^d A heterobimetallic complex was reported.

2.6. By addition of 1H-pyrazoles to CC triple bonds

As in the previous sections, the structures, from **294** to **324**, are shown first and the corresponding data are summarized in Table 5, with similar columns.

Figure 9 here

Table 5

Synthesis of poly(1H-pyrazol-1-yl)alkanes by addition of 1H-pyrazoles to CC triple bonds as described in Scheme 7.

Method	Products	Complexes	References
ZnCl ₂ as catalyst	38-41		[38]
Lewis acids as catalyst	294-306		[162]
Metals as catalyst, best Ag(I)	307-324	Pd(II)	[163]

2.7. Rare methods

The methods that do not belong to any of the preceding cases and that have seldom been used are collected in this section. This includes the pyrolysis of di(1H-pyrazol-1-yl)methanone to afford **15** and the reactions included in Schemes 8–11 (Table 6).

Scheme 8 here
Scheme 9 here
Scheme 10 here
Scheme 11 here

Table 6

Rare methods to prepare poly(pyrazol-1-yl)alkanes.

Starting material	Method	Products	Complexes	References
14	Scheme 8	325 (See Scheme 8)		[164]
di(1H-pyrazol-1-yl)methanone	Pyrolysis	15		[36]
3(5)-arylpyrazole	Scheme 9	54, 326-328		[165]
3(5)-arylpyrazole	Scheme 9	329, 330		[166]
1-trimethylsilylpyrazole	Scheme 10	331, 332		[167]
sulfinylbis(1H-pyrazol-1-yl)methane	Scheme 10	333		[168]
2,5-bis-(3,5-dimethylpyrazol-1-yl-methyl)pyrrole	Scheme 11	334-336	Pd(II)	[169]

In addition, an unexpected reaction between an α,α' -disubstituted cyclopentanone with 1,1,3,3,-tetramethoxypropane afforded **337** [170] (Fig. 10).

Figure 10 here

2.8. Comparative methods for the preparation of simple derivatives

The different methods used to prepare bis-, tris- and tetrakis-derivatives of 1*H*-pyrazole and 3,5-dimethyl-1*H*-pyrazole are listed in Table 7.

Table 7

Yields in the synthesis of characteristic poly(pyrazol-1-yl)methanes.

Compound	Halide	Method ^a	Yield (crude)	Yield (purified)	Reference
2 (di)	CH ₂ Br ₂	autoclave 150 °C (2 h)	46.5%		[21]
	CH ₂ Cl ₂	Liquid-liquid PTC/K ₂ CO ₃	93%		[33]
	CH ₂ Cl ₂	Liquid-liquid PTC/K ₂ CO ₃		79%	[35]
	CH ₂ Cl ₂	Liquid-liquid PTC/K ₂ CO ₃	92%		[39]
	CH ₂ Cl ₂	Solid-liquid PTC/KOH	97%		[171]
	CH ₂ Cl ₂	Liquid-liquid PTC/NaOH	98%		[45]
	CH ₂ Br ₂	KOH/DMSO	82%		[67]
3 (bis)	CH ₂ I ₂	Reflux in THF ^b	82%		[21]
	CH ₂ Cl ₂	Solid-liquid PTC/K ₂ CO ₃	89%		[30]
	CH ₂ Br ₂	KOH/DMSO	92%		[67]
1 (tri)	CHCl ₃	Reflux in C ₆ H ₆ ^b		34%	[20]
	CHCl ₃	Reflux in THF ^b	^c	^c	[21]
	CHCl ₃	Liquid-liquid PTC/K ₂ CO ₃	72%	62%	[33]
	CHCl ₃	Reflux in THF ^b	43%		[104]
	CHCl ₃	Solid-liquid PTC/K ₂ CO ₃	47%		[46]
	CHCl ₃	Liquid-liquid PTC/Na ₂ CO ₃	63%		[52]
	CHCl ₃	Liquid-liquid PTC/Na ₂ CO ₃		60%	[172]
14 (tris)	CHCl ₃	Reflux in THF ^b	17%		[21]
	CHCl ₃	Solid-liquid PTC/K ₂ CO ₃	62%	42%	[31]
	CHCl ₃	Liquid-liquid PTC/Na ₂ CO ₃	65%		[172]
	CHCl ₃	Solid-liquid PTC/K ₂ CO ₃	41%		[173]
15 (tetra)	CCl ₄	Reflux in THF ^b	12%		[21]
	CCl ₄	Liquid-liquid PTC/K ₂ CO ₃		20%	[31]
325 (tetrakis)	----	From 14 (Scheme 8)	27%		[164]

^a The parent pyrazole was used except where indicated. ^b potassium salt of the parent pyrazole was used. ^c not reported

3. Reactivity

In this section new poly(1*H*-pyrazol-1-yl)methane ligands are described, unless their reactivity is characteristic of these compounds and not typical of pyrazoles or of general organic compounds.

N-Substituted azoles can be considered as pseudohalogens [174,175] since they are also good leaving groups and they undergo analogous reactions. The reaction depicted in Scheme 12 is reversible and the 1-pyrazolyl residues of **1** can be replaced by other nucleophiles, including other pyrazoles [165]. Related to this is the report that tris(3,4,5-trimethyl-1*H*-pyrazol-1-yl)methane (**20**)

decomposes upon treatment with picric acid [28].

Scheme 12 here

3.1. Reactivity of the pyrazole ring

3.1.1. Ring atoms

Electrophilic substitution at carbon occurs easily at position 4 of the pyrazole ring. This fact permitted the introduction of a wide variety of substituents in the ring. For instance, bromination of **2** afforded the 4,4'-dibromo derivative **26** while nitration afforded a mixture of the 4-nitro and 4,4'-dinitro derivatives **25** and **27**, respectively. This finding shows that while the 4-bromo substituent does not deactivate the other pyrazole ring the 4-nitro group reduces the reactivity of the other half of the pyrazole [35]. Bromination of **3** produced **338** [176], iodination of **2** and **3** afforded the 4,4'-diiodo derivatives **84** and **85** [67] and the tetra-4-iodo and tetra-4-nitro derivatives of **89** have also been prepared, **104** and **339** [69,85] (Fig. 11). However, reaction of **2** with FSO₃Me led to a mixture of mono- and dimethyl pyrazolium derivatives, **340** and **341** [35], by quaternization of the N-2.

Figure 11 here

The Vilsmeier–Haack reaction (POCl₃/DMF) has been used to prepare **342** from **3**, with **342** subsequently transformed into the imine **343** by reaction with aniline [177] (Fig. 12).

Figure 12 here

A widely used reaction is the preparation of 5-lithio derivatives of pyrazolylmethanes as intermediates in the synthesis of an extensive series of 5-substituted pyrazolylmethanes. These studies were initiated by Katritzky in his synthesis of 5-monosubstituted bis(1*H*-pyrazol-1-yl)methanes **344**–**349** [39]. Lithiations in position 5 were performed with *n*-BuLi in hexane at low temperature followed by addition of carbonyl compounds and anhydrides as the electrophiles. This methodology was used to prepare **350**, **351** and **352** from **2** by reaction with chlorodiphenylphosphine and chlorotrimethylsilane, respectively [178–180] (for **352** see also ref. [181]), **353** from **1** [182] by reaction with methyl iodide and **354** and **355** from **26** using, in this case, LDA as the base and chlorotrimethylsilane and *tert*-butylisocyanate as the respective electrophiles [179] (Fig. 13).

Figure 13 here

3.1.2. Substituents on the pyrazole ring

Classical reactions of the pyrazole side-chains have been reported in several publications. For instance, basic hydrolysis of **119** to **356** [87], oxidation of diphosphines **350** and **351** to phosphine sulfides **357** and **358** with elemental S₈ [180], or reductions of ester groups, such as the preparation of compounds **359**–**361** from **42** (a 3,3'-CO₂Et derivative) (Scheme 13) [40]. Compound **328** reacted with 1,3,5-tribromomethylbenzenes to yield the cage compounds **362** and **363** [165,183].

Scheme 13 here

Bispyrazolylmethanes with reactive halogens in the ring have been transformed into new useful structures. The 4,4-diiodo derivatives **84** and **85** were transformed into the acetylenic derivatives **364–365** by a palladium-catalyzed coupling [Pd(PPh₃)₂Cl₂] with 2-methyl-but-3-yn-2-ol in pyridine and reaction with KOH led to the elimination of acetone to give **366–367** (Scheme 14) [184]. The boronic acid **368** was prepared from **355** by reaction with B(OEt)₃ after a Br-Li exchange with *t*-BuLi in THF at –78 °C [179].

Scheme 14 here

3.2. Reactivity of the central C

3.2.1. The CH₂ and the CH

This is probably the most interesting reaction of bis- and tris-pyrazolylmethanes and it has been used to prepare a wide range of derivatives through lithium or potassium salts of carbanions, owing to the relatively high acidity of the central CH₂ or CH groups. Alkyl groups, electron-deficient alkenes, chlorotrimethylsilanes, chlorotriarylstannanes, carbonyl compounds, imines and diimines, isocyanates, isothiocyanates, nitriles, acid derivatives, CO₂ and CS₂ have been used as electrophiles. Metalation of the CH₂ and CH groups is always in competition with metalation in position 5 of the pyrazole ring (see section 3.1.1). The chemoselectivity and consequently the preparation of the desired isomer requires a careful choice of reaction conditions in terms of the combination of base/solvent, the use of kinetic (CH₂) vs thermodynamic conditions (C-5) (temperature and reaction time) and the nature of the electrophile (HSAB principle).

Katritzky employed compound **2** to prepare compounds **5**, **137** and **369–377** [39] and he showed how the reaction conditions modify the selectivity. Metalation with *n*-butyllithium at room temperature followed by addition of the electrophile led to substitution in the CH₂ when alkyl halides were used as the electrophile but, surprisingly, carbonyl compounds reacted at C-5. However, substitution at C-5 was achieved using LDA as the base, with inverse addition (addition of base at the end) at –10 °C or the use of *n*-BuLi at –78 °C for metalation and reaction with the electrophile at 0 °C.

Wagner used the latter conditions (*n*-BuLi at 0 °C) to prepare **378** from **188** [121] and **379** from **190** by reaction with methyl iodide [122], while Reger prepared compounds **380–387** [185] by reaction of the appropriate trispyrazolylmethane with a variety of electrophiles and using *n*-BuLi, LiHMDS and K⁺tBuO[–] as the bases. Similarly, on using *n*-BuLi as the base in THF at –70 °C Otero prepared compounds **388** [186], **389–394** [187] and **395–398** from **3** [188] and **399–405** from **3** and **99** [189] using aldehydes, isocyanates, isothiocyanates and carbodiimides as electrophiles.

Compound **406** was prepared from **1** [190] using MeLi in THF followed by treatment with chlorotrimethylsilane. Subsequent treatment with potassium *tert*-butoxide followed by formaldehyde gave compounds **380** and **407** [191] and the use of LDA followed by addition of allylbromide and formaldehyde provided compounds **408**, **409** and **410** from the mono-substituted **60** and **411**, respectively [192].

Compound **412** was prepared from **350** [178] and compounds **413** and **414** from **2** [179] by reaction with chlorotrimethylsilane using *n*-BuLi as the base in the first case and LDA in the second. Compounds **415–418** were prepared from **3**, **69**, **70** and **71** [193], respectively, by reaction with chlorotrimethylstannane and a series of amidinate salts. Compounds **419–421** were obtained from **3** [194] by reaction with carbodiimides and using *n*-BuLi as the base.

A large series of acid derivatives were obtained on applying this methodology. For example, the anion **422** [75] and the acid **61** [55] were prepared from **99** and other carboxylic and dithioic acids, **423** and **424** were prepared similarly [195] using CO₂ and CS₂ as the electrophiles and *n*-BuLi as the base in THF. Similarly, the esters **425–428** and the carboxylic acids **429–431** [82] were obtained by reaction of derivatives **105–107** and **109** with ethyl chloroformate and CO₂, respectively, and **432** [59], **433** [60] and **434** [196] were prepared from **67**, **68** and **47**, respectively, again by reaction with CO₂. Lithium salts of sulfonic acids **435** [48], **436** [197] and **437** [48] were prepared from **1**, **56**, and **54** by reaction with SO₃.NMe₃ under similar conditions. Finally, **438** [198] was prepared from **1** and cyanuric chloride as the electrophile (Fig. 14).

Breher and Mountford reported a study of the anions formed by removing a proton from the central CH of trispyrazolylmethanes [199]. Zwitterionic structures were obtained by reaction of **1** with Mg{N(SiMe₃)₂}₂, Ca{N(SiMe₃)₂}₂(THF)₂ and Cd{N(SiMe₃)₂}₂. The corresponding Zn derivatives could not be prepared directly but by deprotonation with *n*-BuLi followed by addition of ZnCl₂. These zwitterionic structures contain a free pyramidal carbanion and a cationic moiety.

Figure 14 here

In a series of papers Otero *et al.* employed compound **3** to prepare the lithium salts of ligands **439** [200], **440** and **441** [201,202] by metalation with *n*-BuLi in THF and allowed these ions to react with 6-mono- and disubstituted fulvenes. Protonation with ammonium chloride afforded the free bases, which can exist in three tautomeric forms, namely 1', 2' and 5' cyclopentadienyl. However, the NMR spectra showed the presence of two isomers in solution and these were characterized as 1' and 2' derivatives. However, after crystallization only isomer 2' of **440** and **441** was present in the solid [201,202], as revealed by X-ray diffraction (Fig. 15). Similarly, reaction with (1*R*)-(–)-myrtenal produced enantiomerically pure **442** [203].

Figure 15 here

3.2.2. The C-substituents

The introduction of a functional group on the CH₂ is key for the derivatization and preparation of a large variety of pyrazolylmethanes by several known reactions. For example, reaction of the acid **60** with 4,4'-tellurinylbis(methoxybenzene) afforded **443**, a telluroxane-supported coordination ligand [204]. Hydrolysis of **40** and **41** afforded the acids **444** and **445** [205]. Reaction of the carboxylic acid **60** with amines afforded the amides **446** and **447** [206] and **448** [82], and esterification of **59** and **60** with ethanol produced **449** and **450** [54] (Fig. 16).

Figure 16 here

Reduction of lithium carboxylate **60** with (CH₃)₂S·BH₃ in THF led to C–CH₂OH derivative **451** [207,208]. The terminal OH of **451**, **380** and **384** has been transformed to prepare several derivatives of bis- and trisazolylmethanes. Deprotonation with NaH in THF followed by alkylation reactions gave compounds **452** [185], **453–455** [209], **456** [210], **457** and **458** [211], **459** [212] and **460** [213],

acylation reactions with methylsulfonyl chloride in the presence of trimethylamine gave compounds **461** [192] and **462** [214], sulfonylation gave compound **463** [215], and silylation gave compound **464** [190] (Fig. 17).

Figure 17 here

From **456**, compounds **465-469** were prepared by radical addition of the appropriate iodoalkane to the double bond [210] followed by reduction with Bu₃SnH, in both reactions in the presence of AIBN (Fig. 18).

Some hydroxymethyl derivatives have been transformed in immobilized compounds such as **470**, **471** [191] and **472** [192] using the adequate supported alkyl halide and NaH in the first reaction and KO^tBu/CsF/18-crown-6 in the second as the bases. **462** was copolymerized with methyl methacrylate using AIBN as the radical initiator to give **473** [214] (Fig. 18).

Figure 18 here

The use of alkylation agents with various halogens has permitted the synthesis of complex structures bearing several units of di- and tripyrazolylmethane. For example, from bis-, tris-, tetrakis- and hexakisbromomethylbenzenes, compounds **474-476** [216,217], **477-479** [218-220], **480** [221], **481** [222] and **482** [221] were prepared, and compound **483** was produced from 1-iodo-3,5-bisbromomethylbenzene [213]; in all cases NaH was used as the base. Compounds **484** and **486-488** were obtained by a wide variety of oxidative Cu-catalyzed (Cu(OAc)₂) coupling reactions of alkynes with **460** and **483** and by Pd-catalyzed (Pd(PPh₃)₂Cl₂) coupling reactions of aryl iodide **483** with alkynes **460** and **485** [213]. Finally, reaction with cyanuric chloride provided compound **489** [198] (Fig. 19).

Figure 19 here

Otero used this approach, namely acylation of the hydroxymethyl group with (*R*)-(-)-acetylmandelic acid chloride in the presence of pyridine, for the resolution of racemic (*R,S*)-**492** (Scheme 15) to obtain enantiomerically pure ligand (*R*)-**492** [186].

Scheme 15 here

Other well-known reactions have been used for the derivatization of azolylmethanes. For example, ligands **493** and **494** were obtained by hydrogenation of **180** and **181** using a Pd/C catalyst [118] (Scheme 16).

Scheme 16 here

Deprotonation of **3** by with *n*-BuLi and addition of two equivalents of dimethylcarbodiimide

provided the ligand **496** [195]. The reaction occurs through amidinate **495** and involves a double [1,3]-sigmatropic rearrangement of the methyl groups in the second step (Scheme 17).

Scheme 17 here

The hydroquinones **185**, **186**, **189** and **190** were oxidized to quinones **497**, **498**, **500** and **501** [121] and **499** and **502** were similarly prepared from **378** and **379**, respectively, with CAN in acetonitrile/water [122] (Fig. 20).

Figure 20 here

The dithio compound **192** was reduced by LiAlH_4 to thiol **503** [124] and compound **232** was transformed into ligands **504–506** by condensation of the amine with the appropriate aldehydes followed by reduction *in situ* with NaBH_4 [147] (Fig. 21).

Figure 21 here

Reaction of the amino group of aminomethyl derivatives is another interesting method to prepare new derivatives with interesting structures as ligands. In this regard, Reger *et al.* carried out the series of reactions represented in Scheme 18 to prepare **507**, **508** and **509** – once again secondary amines were prepared by reaction with the aldehyde and reduction with NaBH_4 [99,223]. Compound **510** was prepared by reaction of **507** with α,α' -dibromo-*p*-xylene and also by reaction with terephthalaldehyde followed by reduction with sodium borohydride.

Scheme 18 here

Similarly, Comba prepared compound **507** from **138**. Compound **507** was reacted with dibenzylketone and paraformaldehyde to prepare compound **511** [224], while reaction with a TTF-derived acyl chloride gave compound **512** [225]. Santos reported a series of reactions starting from **507**; reaction with glycolic acid and HBTU in DMF produced **513** [209] and this was subsequently reduced to **514** with LiAlH_4 and, finally, alkylation with 1-chloro-2-methoxyethane in the presence of K_2CO_3 and KI in ethanol provided **515** [209] (Fig. 22).

Figure 22 here

Compounds **516** and **517** were prepared from **333** [168] by alkylation with MeI in acetonitrile and acylation with 1*H*-pyrazole-1-carbothioyl chloride, respectively (Fig. 23); the latter compound was obtained as a by-product in the preparation of **333**.

Figure 23 here

Gardinier reported the transformation of **94** into the diethylamino **518** and bromo **519** derivatives by alkylation with ethyl iodide and diazotization with *tert*-butylnitrite, respectively [70].

Holliday described the preparation of **520** by Stille coupling starting from **103** with the appropriate tributylstannylthiophene [226] and Wagner described the preparation of **521** [151] from **265** by a sequence of oxidation with CAN and reaction with 4-*n*-butylpyridine. Finally, Laguna reported **522** by propargylation of **157** in the presence of K₂CO₃ (Fig. 24) [227].

Figure 24 here

Higgs and Carrano reported the sequence shown in Scheme 19 to prepare a series of multidentate, N₂SS* and N₂S, **168–171**, **523–530**, ligands bearing different substituents at the pyrazole and benzene rings [113]. The sequence involves the preparation of a thiocarbamic acid O-ester from the phenol, a pyrolytic Newman–Kwart rearrangement to obtain the isomeric thiocarbamic ester and finally cleavage of this group by either base hydrolysis (KOH) or reduction (LiAlH₄).

Scheme 19 here

The ether **531** was formed by bubbling O₂ at –80 °C through a solution of the radical shown in Scheme 8 [164]. Starting from **1**, the trimethylsilyl derivative **406** was prepared together with two carbosilanes to provide the first and second generation dendritic structures **532** and **533** [228]. Reduction (H₂/Pd/C) of **307** afforded the phenethyl derivative **534** [163]. The quaternary salts with different counteranions, **535** and **536**, were prepared from **211** and **212** by reaction with benzyl halides [132]. Derivatives **141** and **142** were deprotected under basic conditions (K^tBuO, O₂ and KOH respectively) to afford the free NH-pyrazole **537** [101]. Aniline **538** was prepared from **285** and **286**, respectively, by basic hydrolysis (KOH) and copper-catalyzed amination of the aryl halide with aqueous ammonia [158] (Fig. 25).

Figure 25 here

Trofimenko reported an interesting rearrangement, the conversion of **2** into 4,4'-dipyrazole by thermolysis at 200 °C; he proposed that this compound was formed through a carbonium-type rearrangement (Scheme 20) [21].

Scheme 20 here

A series of Flash Vacuum Pyrolysis experiments (FVP) have been reported concerning the simplest compounds **1** and **2**. The results are represented in Scheme 21. Besides the fact that both compounds interconvert, the most interesting compounds are 1,1'-dipyrazole and pyrimidine [229].

Scheme 21 here

4. Poly(1*H*-pyrazol-1-yl)methanes as ligands in organometallic chemistry

Poly(1*H*-pyrazol-1-yl)methanes have a wide range of applications as ligands in organometallic chemistry. A description of the structures of these complexes is beyond the scope of this review and has been provided elsewhere [7-16]. However, it seemed useful to include the metals used for coordination with each pyrazolylmethane. The complexes described in section 2 are collected in

Tables 1–6 and the compounds described in section 3 are collected in Table 8.

Only two tetrakis, the tetra **15** and tetrakis **325**, have been reported. We carried out a search with SciFinder® and found that compound **15** forms three kinds of complexes: **a**, **b** and **c** (compound **325** is too difficult to prepare and it has not been used as a ligand) (Fig. 26).

Figure 26 here

The most common complexes are of type **a** (B [21], Mo [230], Ru [231], Pd [104] and Pt [105]), but there is an example of type **b** (bimetallic with Mo and Re [230]) and another one of type **c** (Ru [231]).

Table 8

Reported complexes of ligands described in the reactivity section.

Compound	Complexes	References
3, 8, 69-71	W(0)	[61]
60	Ti(IV) Zr(IV) Hf(IV) Ta(IV)	[9]
246-250	Cr(III)	[147]
350	Pd(II) Pt(II)	[178–180]
356	Cu(II) Co(II)	[87]
354	Pd(II)	[180]
359, 360	Cu(I)	[165,183]
388	Y(III) Lu(III)	[232]
390, 392, 393	Nd(III) Sm(III)	[233]
390, 392, 393	Sc(III) Y(III) Lu(III)	[234]
394	Nd(III)	[235]
396, 399	Zn(II)	[236]
400-405	Al(III)	[189]
408	Mn(I) Re(I)	[192]
419	Li(I) Ti(III) Zr(III)	[194]
420	Li(I)	[194]
424	Ti(IV) Zr(IV) Hf(IV)	[9]
438	Ag(I) Cu(II) Zn(II) Ru(II)	[198]
439	Li(I) Zr(III)	[200]
439, 440	Sc(III) Y(III)	[201,202]
439, 441	Nd(III) Sm(III) Y(III) Lu(III)	[237]
440, 441	Y(III) Lu(III)	[232]
441	Ti(IV)	[203]
443	Te(IV)	[204]
444	Mn(0) Re(0)	[205]
445, 446	Cu(II)	[206]
449	Nb(III)	[207]
449	Pd(II)	[54]
453-455, 509, 510	Re(I) Tc(I)	[209]
457, 458	Fe(II) Zn(II), Ni(II), V(IV) Pd(II)	[211]
459	Ag(I) [Ru(III) on terpyridine]	[212]
461	Mn(I) Re(I)	[192]
462, 473	Mn(I) Re(I) Cu(II)	[214]
463	Cu(II)	[238]
464	Mo(0) Ti(II) Pd(II) Cr(III)	[190,215]

466	Cu(II) Ni(II) Co(II) Fe(II)	[210]
470	Ni(II)	[191]
474	Ag(I)	[216]
477-479	Cd(II)	[218]
478	Ag(I)	[219]
478, 479, 481	Mn(II)	[220]
480	Ag(I) Cd(II)	[221]
481	Ag(I)	[222]
492	Ti(IV) Zr(IV)	[186]
494	Ru(II)	[118]
495	Li(I)	[194]
498, 499	Pd(II)	[121]
501	Pd(II)	[122]
503	Zn(II)	[124]
507	Cu(I)	[223]
509	Cu(I) Cu(II)	[223]
510	Cu(I)	[223]
511	Fe(II) Zn(II) Ni(II) Co(II) Cu(II)	[224]
512	Re(I)	[225]

5. Spectroscopy

5.1. X-ray crystallography

A search in the Cambridge Structural Database (CSD) found 164 hits. All of these structures are summarized in Table 9 ordered by number and the references are indicated; more than one reference indicates multiple reports. Most of the references in this table have previously appeared in the literature as methods for the synthesis or reactivity of polypyrazolylmethanes; however, no less than 20 references are exclusively dedicated to crystallography.

Based on the structure determined for **15** and using ^1H NMR spectroscopy (together with lanthanide shift reagents), dipole moment, molecular mechanics (MM2) and semiempirical calculations (MNDO) were carried out on the conformational space of di- (**2**), tri- (**1**) and tetrapyrazolylmethane (**15**) [239]. The potential surfaces (Fig. 27) thus obtained were compared with experimental results in solution (by NMR and using dipole moments) and in the solid state (by crystallography using the already known structures of **1** and **2** and by determining the structure of **15**). The conformation of pyrazolylmethanes results from the balance of two effects: the repulsion between the lone pairs of the N2 nitrogen atoms and the steric repulsions between H5 hydrogen atoms. Compound **2** shows the absolute minimum at $\varphi\text{A}/\varphi\text{C} = 93.6/90.8$, while compound **1** shows two preferred conformations ($\varphi\text{A}/\varphi\text{B}/\varphi\text{C} = 136.9/-163.0/-96.5$; and $\varphi\text{A}/\varphi\text{B}/\varphi\text{C} = 134.2/-154.4/86.8$) in a 2:1 ratio. Compound **15** has an approximate S4 axis such that the four N1 atoms form a distorted tetrahedron. This situation is dramatically modified in the presence of metals.

Figure 27 here

Table 9. Reported X-ray diffraction of poly(1*H*-pyrazol-1-yl)methanes (for the CSD codes see the Supporting Information)

Number	reference	Number	reference	Number	reference
1	[240,241]	153	[242]	335	[169]
2	[227,243]	158	[107]	337	[170]
3	[244]	168	[113]	338	[176]
9	[243]	172	[114]	341	[79,83]
11	[96]	178	[116]	356	[87]
12	[95]	179	[117]	358	[180]
13	[95]	182	[153]	362	[183]
14	[245,246]	183	[120]	368	[179]
15	[239]	184	[120]	380	[198,247,248]
20	[86]	185	[121]	388	[186]
27	[249]	187	[121]	390	[187]
31	[250]	188	[121]	392	[187]
47	[196]	189	[121]	395	[194]
48	[42]	190	[122]	396	[188]
49	[78]	193	[125]	400	[189]
54	[251]	196	[126]	401	[189]
58	[252]	210	[131]	406	[190]
59	[53]	215	[133]	408	[192]
60	[56,253]	217	[137]	409	[192]
61	[55]	219	[134]	430	[82]
64	[57]	230	[145]	431	[82]
68	[60]	231	[145]	432	[59]
71	[254]	235	[146]	433	[60]
72	[63]	236	[146]	434	[196]
74	[63]	237	[146]	435	[197]
81	[66]	238	[146]	435	[49]
82	[66]	239	[146]	438	[198]
83	[73]	240	[146]	440	[202]
85	[176]	241	[146]	441	[201]
92	[133]	242	[146]	442	[185,202]
94	[68,15]	245	[148]	443	[204]
96	[70]	257	[148]	444	[205]
97	[72]	261	[149]	445	[205]
98	[72]	262	[149]	446	[206]
99	[74,255]	263	[149]	448	[82]
100	[74]	264	[150]	450	[54]
103	[80]	265	[150]	453	[256]
104	[79,83]	266	[151]	457	[211]
106	[82]	267	[257]	459	[212]
109	[79]	274	[154]	460	[213]
110	[83]	275	[154]	461	[192]
111	[83]	276	[258]	462	[214]
112	[83]	283	[156]	463	[238]
114	[85]	284	[157]	467	[210]
118	[86]	293	[136]	474	[218,259]
120	[88]	325	[164]	477	[167]
121	[88]	331	[167]	479	[217,230]
122	[89]	332	[167]	481	[213]
143	[102]	334	[169]	486	[213]

490	[186]	516	[168]	524	[113]
492	[186]	517	[168]	538	[158]
498	[121]	520	[226]	539	[260]
502	[122]	521	[151]	540	[260]
511	[224]	522	[227]	541	[260]
512	[225]	523	[113]		

5.2. NMR spectroscopy

The most interesting publications on the NMR spectroscopy of poly(1*H*-pyrazol-1-yl)methanes dealt with the fluxional behavior of the complexes. Regarding the ligands themselves, most papers describe NMR (¹H in the past, ¹H and ¹³C nowadays) as an analytical tool to identify the compounds or to assign positional isomers. These data can be found in the cited references. However, to illustrate the usefulness of NMR spectroscopy, the available data on the properties of the parent compounds are reported in Table 10.

Table 10

NMR data for parent poly(1*H*-pyrazol-1-yl)methanes, chemical shifts in ppm and coupling constants in Hz

	Di 2	Tri 1	Tetra 15
¹ H [TMS]	CDCl ₃ [33] 6.30 (H1) 7.50 (H3') 7.61 (H5') 6.30 (H4') ³ J _{3'4'} = 1.70 ³ J _{4'5'} = 2.45 ⁴ J _{3'5'} = 0.45 DMSO- <i>d</i> ₆ [35] 6.50 (H1) 7.62 (H3') 8.05 (H5') 6.36 (H4')	CDCl ₃ [261]* 8.45 (H1) 7.65 (H3') 7.55 (H5') 6.35 (H4') ³ J _{3'4'} = 1.6 ³ J _{4'5'} = 2.5 ² J _{H1N1'} = -1.2 ³ J _{H1N2'} = 1.4 ² J _{N1'H5'} = 4.5 ² J _{N2'H3'} = 13.0 ³ J _{N1'H3'} = 8.8 ³ J _{N1'H4'} = 6.2 ³ J _{N2'H4'} = 1.2	CDCl ₃ [31] 7.7 (H3') 7.5 (H5') 6.3 (H4')
¹³ C [TMS]	CDCl ₃ [32] 140.6 (C3') 129.5 (C5') 107.0 (C4') 65.1 (C1)	CDCl ₃ [261]* 141.8 (C3') 129.6 (C5') 107.3 (C4') 83.2 (C1) CDCl ₃ [262] ¹ J _{C3'H3'} = 188.4 ¹ J _{C4'H4'} = 179.9 ¹ J _{C5'H5'} = 191.7 ³ J _{C5'H1} = 2.5	CDCl ₃ [32] 142.3 (C3') 132.3 (C5') 107.1 (C4') 95.8 (C1)
¹⁵ N [CH ₃ NO ₂]	CDCl ₃ [263] -170.7 (N1') -77.4 (N2')	CDCl ₃ [261] -170.0 (N1') -79.0 (N2') CDCl ₃ [264]* -169.5 (N1') -76.8 (N2') ¹ J _{N1'N2'} = -13.0	CDCl ₃ [259] -167.2 (N1') -77.1 (N2')

		$^1J_{N1'C1} = 18.0$ $^1J_{N1'C5'} = 13.0$ $^1J_{N2'C3'} = -0.5$ $^1J_{N1'C3'} = 1.3$ $^2J_{N1'C4'} = 5.9$ $^2J_{N2'C1'} = 7.8$ $^2J_{N2'C4'} = -2.3$	
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* ^{15}N doubly labeled **1**.

Only review papers that deal with pyrazoles, including pyrazolylmethanes, less common nuclei, for instance ^{15}N , and some interesting and less common results will be discussed here.

Comparative papers include a ^{13}C NMR study of polyphenyl-, poly-*N*-azolyl- and poly-*N*-benzazolylmethanes [32]; a review on substituent effects on the ^{15}N NMR parameters of azoles [263]; a theoretical multinuclear NMR study of pyrazolylborates that includes for comparative purposes the parent pyrazolylmethanes **2**, **1** and **15** [264]; and an experimental and theoretical (GIAO/DFT) study of the pyrenyl derivative **213** [265].

In 1973, Thé and Peterson described an example of anisochrony of pyrazole rings in the ^1H NMR study of compounds **13**, **17** and **18** in CDCl_3 [24]. The assignment of H3 and H5 was based on the criterion that $^3J_{45} > ^3J_{34}$. When the cyclohexane ring was unsubstituted (**13**) the pyrazole rings were enantiotopic but when there is a methyl group, either at the 3' or 4' positions, **17** and **18**, respectively, the pyrazole substituents became diastereotopic. GIAO/DFT/6-311++G(d,p) + PCM (CHCl_3) calculations, carried out for this review, allow all of the signals to be assigned (Fig. 28). In the case of **13**, the inversion of the cyclohexane ring made the two pyrazole rings equivalent but the inversion of the ring in the case of **17** and **18** transformed the equatorial (eq) Me group to the much less stable axial (ax) position and, therefore, the pyrazolyl rings remained diastereotopic with their concomitant anisochronous signals.

Figure 28 here

{1-[Bis(4-carboxy-3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-3,5-dimethyl-1*H*-pyrazole-4-carboxylate} sodium dihydrate **113** was studied by SSNMR spectroscopy. The ^{13}C CPMAS spectrum showed some splittings that were rationalized using GIAO/B3LYP/6-311++G(d,p) calculations [84].

Three papers reported ^{15}N NMR data of pyrazolylmethanes. In a review of substituent effects on the ^{15}N NMR parameters of azoles [263] the chemical shifts of N1 and N2 of compounds **1**, **14** and **15** were reported. Compound **1** was prepared doubly-labeled with ^{15}N and this allowed the measurement and determination of the absolute sign of the ^1H - ^{15}N , ^{13}C - ^{15}N and ^{15}N - ^{15}N coupling constants [261]. The ^{15}N chemical shifts of the ligands **438** and **486** were reported by Pettinari *et al.* [198].

6. Computational studies

These studies concern several aspects of pyrazolylmethanes, particularly conformational analyses that are related both to crystallography [239] and NMR spectroscopy [239]. DFT calculations on the different conformations of compound **1** and their interconversion pathways have been carried out and related to the binding abilities toward Ag(I) and Cu(I) [266]. Although the paper is mainly devoted to pyrazolylborates, a conformational analysis was carried out on **2**, **1** and **15** for comparative purposes: for **15** two minima were found, the most stable of which has S_4 symmetry and the least stable a D_2 symmetry [264]. The di(1*H*-pyrazol-1-yl)methane (**2**) has been studied theoretically [PBE0/6-31+G(d,p)] and its IR spectrum measured and compared with the calculated one [267]. A QTAIM investigation of compound **293** was carried out based on its X-ray structure [268].

7. Properties other than complexes

The antifungal properties of several bis(1*H*-pyrazol-1-yl)methanes (**19**, **123–132**) have been reported [91]. The moderate properties of **2** and **3** as carbonic anhydrase activators have been described [269]. A more complete study of the same activity of compounds **1** and **14** was reported by Supuran *et al.*; these compounds show good activatory properties [270].

Selective membranes were built up using tris(3-*iso*-propyl-1*H*-pyrazol-yl-methane) (**56**) in a poly(vinyl chloride) matrix and these membranes were selective for Cu(II). Other pyrazolylmethanes, including **15**, were less effective [271].

8. Conclusions

A wide range of synthetic methods and numerous useful reactions open up access to almost any desired structure with the exception of the still rare tetrakis(1*H*-pyrazol-1-yl)methanes. This review should help the coordination chemist to select the best approach for a ligand related to a known example or to prepare less common structures. The list of metals coordinated to different ligands allows the reader to ascertain the structures that are known and those that are not, thus pointing to future lines of research.

Two major challenges should be addressed: chirality and applications. Although there are some contributions concerning the use of chiral ligands, a greater advance is necessary in the preparation of chiral ligands and complexes. Some pioneering contributions on the use of this class of complex as catalysts for polymerization and fixation of carbon dioxide have already been described. This should be an appropriate field to expand the potential of complexes with polypyrazolylmethanes. Furthermore, in materials chemistry several applications could be envisaged: the preparation of dendrimeric structures bearing pyrazolylmethanes on the periphery and the use of pyrazolylmethanes to prepare nanoparticles.

The complete collection of X-ray structures is a source of structural information that has not been sufficiently explored and the scarcity of theoretical studies is surprising. Some unexpected reactions warrant further study and give an appealing entry into considering future work, such as those that yield compounds **325** (Scheme 8), **337** (Fig. 10), **348** and **349** (Fig. 13), **533** as well as the rearrangement of **2** (Fig. 25).

Future multinuclear NMR spectroscopy should be extended to other nuclei such as ¹⁷O and the coordinated metals of Table 8. It is also expected that solid-state NMR will develop considerably, especially to cover ¹H and ²H nuclei.

In order to facilitate the search for a particular ligand, in the Supporting Information the structures are represented by families: pz-CH₂-pz (75); pz-CHR-pz (259); pz-CRR'-pz (63); pz-CH-pz,pz (34); pz-CR-pz(pz) (45); (pz)pz-C-pz(pz) (2); poly[pz-CHR-pz; pz-CR-pz(pz)] (63 derivatives).

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Fig. 1. First synthesized pyrazolylmethanes.

Fig. 2. Products obtained with the Thé and Peterson methodology.

Fig. 3. Products synthesized by Juliá *et al.*

Fig. 4. Products synthesized by Reger *et al.*

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R = Et, R¹ = H, **69**
 R = Me, R¹ = Et, **70**
 R = *i*-Pr, R¹ = H, **71**

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R = Me, R¹ = H, **73**
 R = R¹ = Me, **74**

R¹, R³, R⁴, R⁶, R⁷, R⁹, R¹⁰, R¹² = H; R², R⁵, R⁸, R¹¹ = OC₁₀H₂₁, **75**
 R¹, R³, R⁶, R⁷, R¹⁰, R¹² = H; R², R⁴, R⁵, R⁸, R⁹, R¹¹ = OC₁₀H₂₁, **76**
 R¹, R², R⁴, R⁵, R⁸, R⁹, R¹⁰, R¹¹ = OC₁₀H₂₁, R³, R⁶, R⁷, R¹² = H; **77**
 R¹-R⁶, R⁸-R¹¹ = OC₁₀H₂₁, R⁷, R¹² = H; **78**
 R¹-R¹² = OMe, **79**
 R¹-R¹² = OC₁₀H₂₁, **80**

81

R = *t*-Bu, R¹ = *i*-Pr, **82**
 R = Ph, R¹ = Me, **83**

R = H, R¹ = I, **84**
 R = Me, R¹ = I, **85**

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R = H, **87**
 R = Ph, **88**

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92

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Fig. 5. Compounds collected in Table 1.

Fig. 6. Compounds collected in Table 2

Fig. 7. Compounds collected in Table 3

R = *t*-Bu, 251 R = H, 253
R = Mes, 252 R = Ph, 254 R = Mes, 256

R = Ph, 257
R = *t*-Bu, 258
R = Mes, 259

Fig. 8. Compounds collected in Table 4.

Fig. 9. Compounds collected in Table 5

Fig. 10. Unexpected cyclopentanone obtained by Yurovskaya *et al.*

Fig. 11. Compounds prepared by quaternization and electrophilic aromatic substitution.

Fig. 12. Compounds prepared by Vilsmeier-Haack reaction.

Fig. 13. Compounds prepared from 5-lithio derivatives.

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$R^1 = \text{Me}$, **381**

$R^1 = \text{SiMe}_3$, **382**

$R^1 = \text{CH}_2\text{Ph}$, **383**

$R^1 = \text{CH}_2\text{OH}$, **384**

$R^1 = \text{Me}$, **385**

$R^1 = \text{SiMe}_3$, **386**

$R^1 = \text{CH}_2\text{OH}$, **387**

388

$R = \text{Ph}$, $E = \text{O}$, **389**

$R = \text{Ph}$, $E = \text{S}$, **390**

$R = t\text{-Bu}$, $E = \text{O}$, **391**

$R = t\text{-Bu}$, $E = \text{S}$, **392**

$R = s\text{-Bu}$, $E = \text{O}$, **393**

$R = (\text{S})\text{-Ph}(\text{Me})\text{CH}$, $E = \text{O}$, **394**

395

$R = \text{Me}$, $R^1 = \text{Et}$, $R^2 = t\text{-Bu}$, **396**

$R = t\text{-Bu}$, $R^1 = \text{Et}$, $R^2 = t\text{-Bu}$, **397**

$R = \text{Me}$, $R^1 = R^2 = i\text{-Pr}$, **398**

$R = t\text{-Bu}$, $R^1 = R^2 = i\text{-Pr}$, **399**

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401

402

R = Me, R¹ = H, **415**
 R = Et, R¹ = H, **416**
 R = Me, R¹ = Et, **417**
 R = *i*-Pr, R¹ = H, **418**

R¹ = R² = *i*-Pr, **419**
 R¹ = R² = Cy, **420**
 R¹ = Et, R² = *t*-Bu, **421**

R = *t*-Bu, **422**
 R = Me, **423**
 R = Ph, **424**

R = Ph, **425**
 R = *o*-PhOMe, **426**
 R = *o*-PhOiPr, **427**
 R = Adamantyl, **428**

R = Ph, **429**
 R = *o*-PhOMe, **430**
 R = *o*-PhOiPr, **431**

Fig. 14. Reactivity of the central C atom.

Fig. 15. Compounds prepared by Otero *et al.*

Fig. 16. Derivatives of carboxylic acids.

Fig. 17. Simple derivatization of the hydroxymethyl group.

Fig. 18. Fluorous and polymer supported derivatives of the hydroxymethyl group.

Fig. 19. Polyderivatization of the hydroxymethyl group.

Fig. 20. Oxidation to quinones **497-502**.

Fig. 21. Bispyrazolylmethanes prepared by reduction.

Fig. 22. Substituted aminomethyl derivatives

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Fig. 23. Substituted thio-derivatives.

Fig. 24. Compounds obtained by Gardinier, Holliday, Wagner and Laguna.

Fig. 25. Miscellaneous reactions of bispyrazolymethanes.

Fig. 26. Coordination complexes of tetrapyrzolylmethane **15**.

Fig. 27. The MM2 potential energy surface of di(*1H*-pyrazol-1-yl)methane (**2**)

Fig. 28. The three cyclohexyl derivatives. In normal characters the experimental results of Thé and Peterson [22]; in italics the calculated values (the signal of the Me in **18** was not reported).

Scheme 1. Synthesis of bis(1*H*-pyrazol-1-yl)methane mono and disubstituted on the central C atom.

Scheme 2. The Thé and Peterson methodology.

Scheme 4. The de Angelis result.

Scheme 5. Synthesis of non-symmetrical bis(1*H*-pyrazol-1-yl)methanes.

Scheme 6. The synthetic utility of 1,1'-sulfinylbis(1*H*-pyrazoles).

Scheme 7. Bis(pyrazol-1-yl)methanes obtained by addition to triple bonds.

Scheme 8. The unusual transformation of a trispyrazolylmethane into a tetrakispyrazolylmethane.

Scheme 9. An example of trans-pyrazolylation.

Scheme 10. Preparation of polypyrazolylalkanes from 1-trimethylsilylpyrazole.

Scheme 11. Oxidation of 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole and reduction to **336**.

Scheme 12. The arenology principle.

Scheme 13. Reactivity of pyrazole side-chains.

Scheme 14. Modifications on the pyrazole ring.

Scheme 15. Resolution of racemic (R,S)-492.

Scheme 16. Hydrogenation of **180** and **181**.

Scheme 17. Transformation of intermediate amidinate **495**.

Scheme 18. Preparation of aminomethyl derivatives.

Scheme 19. Preparation of multidentate, N₂SS* and N₂S ligands.

Scheme 20. Thermal rearrangement of bispyrazolylmethane **2**.

Scheme 21. FVP experiments.

The organic chemistry of poly(1*H*-pyrazol-1-yl)methanes

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The supporting information summarizes all polypyrazolymethanes cited in the text. They have been organized following increased-complexity criteria:

1. Bispyrazolymethanes not substituted at the central carbon; pz-CH₂-pz.
2. Bispyrazolymethanes substituted at the central carbon; pz-CHR-pz.
3. Bispyrazolymethanes di-substituted at the central carbon; pz-CRR'-pz.
4. Trispyrazolymethanes not substituted at the central carbon; pz-CH-pz,pz.
5. Trispyrazolymethanes substituted at the central carbon; pz-CR-pz,pz.
6. Tetrakispyrazolymethanes; pz,pz-C-pz,pz.
7. Polypyrazolymethanes; structures having two and three bispyrazolymethanes moieties and two, three and four trispyrazolymethanes moieties.

Each section begins with the unsubstituted structure, i.e. bis(pyrazol-1*H*-yl)methane, followed by compounds bearing: one substituent in one ring, one substituent in each ring (first, position 3), two substituents in each ring (order: 3,4; 3,5; 4,5) and finally 3,4,5-trisubstituted.

When a general formula is used to represent a large number of compounds, using R, R¹..., aliphatic ones are placed the first, followed by aromatic and heterocyclic ones, and finally compounds having groups linked by bonds different to C-C. CIP rules have been used to obtain the resulting order.

pz-CH₂-pz

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339

340

R = NO₂, **25**
R = Br, **24**

344

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R = CH₃, **21**
R = CH₂OH, **359**
R = CH₂Br, **360**
R = CH₂CH(CO₂C₂H₅)₂, **361**
R = CO₂Et, **42**
R = CF₃, **86**
R = 2-pyridyl, **58**
R = NH₂, **28**

R = CH₃, **48**
R = ethynyl, **366**
R = NO₂, **27**
R = Br, **26**
R = I, **84**

364

R = CH₃, **23**
R = CO₂C₂H₅, **44**
R = NH₂, **30**
R = Si(CH₃)₃, **352**
R = PPh₂, **350**
R = P(S)Ph₂, **357**

R = CH₃, **22**
R = CO₂C₂H₅, **43**
R = NH₂, **29**
R = 2-pyridyl, **57**

45

46

R = CH₃, **3**
R = C₂H₅, **69**
R = CH(CH₃)₂, **71**
R = C(CH₃)₃, **99**
R = adamantyl, **109**
R = CF₃, **87**
R = Ph, **105**
R = o-CH(CH₃)₂Ph, **107**
R = o-OCH₃Ph, **106**
R = 2,6-(OCH₃)₂Ph, **108**

R¹, R³, R⁴, R⁶, R⁷, R⁹, R¹⁰, R¹² = H; R², R⁵, R⁸, R¹¹ = OC₁₀H₂₁, **75**
R¹, R³, R⁶, R⁷, R¹⁰, R¹² = H; R², R⁴, R⁵, R⁸, R⁹, R¹¹ = OC₁₀H₂₁, **76**
R¹, R², R⁴, R⁵, R⁸, R⁹, R¹⁰, R¹¹ = OC₁₀H₂₁, R³, R⁶, R⁷, R¹² = H; **77**
R¹, R⁶, R⁸, R¹¹ = OC₁₀H₂₁, R⁷, R¹² = H; **78**
R¹, R¹² = OCH₃, **79**
R¹, R¹² = OC₁₀H₂₁, **80**

R = C(CH₃)₃, R¹ = CH(CH₃)₂, **100**
R = CO₂H, R¹ = CH₃, **356**
R = CO₂CH₃, R¹ = CH₃, **119**
R = Ph, R¹ = SCH₃, **62**
R = p-OCH₃-Ph, R¹ = SCH₃, **63**
R = SCH₃, R¹ = C(CH₃)₃, **64**
R = SCH₃, R¹ = p-OCH₃-Ph, **65**

pz-CHR-pz

R = CH₃, **5**
 R = C₂H₅, **6**
 R = CH₂CH₂Ph, **534**
 R = CH₂CO₂H, **444**
 R = CH₂CO₂CH₃, **40**
 R = CH₂CO₂Na, **38**
 R = CH₂Ph, **137**
 R = CH(CH₃)₂, **7**
 R = CH₂NH₂, **507**
 R = CH₂NHCH₂Ph, **509**
 R = CH₂N=CHPh, **508**
 R = CH₂SPh, **200**
 R = COCH₃, **369**
 R = CO₂H, **59**
 R = CO₂C₂H₅, **449**
 R = Ph, **19**
 R = *p*-NH₂-phenyl, **538**
 R = *o*-NH₂-phenyl, **493**
 R = *p*-acetamidophenyl, **285**
 R = *o*-OH-phenyl, **157**
 R = 2,5-(OH)₂-phenyl, **185**
 R = 3,4-(OH)₂-phenyl, **264**

R = 2-OH,3-C(CH₃)₃,5-CH₃-phenyl, **168**
 R = 2-OH,3,5-[C(CH₃)₃]₂-phenyl, **203**
 R = 2,5-(OH)₂,3-C(CH₃)₃-phenyl, **186**
 R = *o*-OCH₃-phenyl, **164**
 R = 2,5-(OCH₃)₂-phenyl, **188**
 R = *o*-NO₂-phenyl, **180**
 R = 2-SH,3-C(CH₃)₃,5-CH₃-phenyl, **169**
 R = *o*-(SPh)phenyl, **197**
 R = *p*-Br-phenyl, **286**
 R = *p*-I-phenyl, **282**
 R = *m*-I-phenyl, **281**
 R = *o*-I-phenyl, **280**
 R = *p*-(1-imidazolyl)phenyl, **211**
 R = 9-anthracenyl, **143**
 R = 4-pyridyl, **209**
 R = 3-pyridyl, **218**
 R = 2-pyridyl, **153**
 R = 3(5)-1-H-pyrazolyl, **537**
 R = 3-(1-CH₂Ph-pyrazol-1-yl), **141**
 R = 2-(1-CH₃-1H-imidazolyl), **152**
 R = 2-thienyl, **132**
 R = SiC(CH₃)₃, **413**

244

R = Ph, R¹ = R³ = CH₃, R² = R⁴ = H, **124**
 R = Ph, R¹ = R⁴ = CH₃, R² = R³ = H, **125**
 R = *p*-Cl-Ph, R¹ = R³ = CH₃, R² = R⁴ = H, **130**
 R = *p*-Cl-Ph, R¹ = R⁴ = CH₃, R² = R³ = H, **131**
 R = *o*-Cl-Ph, R¹ = R³ = CH₃, R² = R⁴ = H, **128**
 R = *o*-Cl-Ph, R¹ = R⁴ = CH₃, R² = R³ = H, **129**

182

R = H, **503**
 R = SCH₃, **192**

261

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273

139

163

R = CH₂COOH **445**
 R = CH₂CO₂CH₃, **41**
 R = CH₂CO₂Na, **39**
 R = cyclohexyl, **166**
 R = CH₂OH, **451**
 R = CH₂SPh, **201**
 R = COOH, **60**
 R = COOCH₃, **411**
 R = COOC₂H₅, **450**
 R = Ph, **151**
 R = *p*-COOH-phenyl, **184**
 R = *m*-COOH-phenyl, **183**
 R = *o*-NH₂-phenyl, **494**
 R = *o*-NO₂-phenyl, **181**
 R = *o*-OH-phenyl, **158**
 R = 2-OH,3-C(CH₃)₃,5-CH₃-phenyl, **162**
 R = 2-OH-3,5-[C(CH₃)₃]₂-phenyl, **191**
 R = 3,4-(OH)₂-phenyl, **266**
 R = 4-OH-3-OCH₃-phenyl, **193**
 R = *o*-OCH₃-phenyl, **165**
 R = 2,5-(OCH₃)₂-phenyl, **236**

R = *o*-F-phenyl, **206**
 R = *o*-SH-phenyl, **159**
 R = *o*-(SCH₃)-phenyl, **224**
 R = *o*-(SPh)-phenyl, **198**
 R = *o*-Cl-phenyl, **207**
 R = *o*-Br-phenyl, **208**
 R = ferrocenyl, **167**
 R = quinolin-8-yl, **290**
 R = 1-pyrenyl, **213**
 R = 4-pyridyl, **210**
 R = 3-pyridyl, **219**
 R = 2-pyridyl, **246**
 R = 2-(6-CH₃-pyridyl), **247**
 R = 2-furanyl, **291**
 R = 2-thienyl, **292**
 R = 2-(1-CH₃-1H-imidazolyl), **248**
 R = 2-(1,4,5-(CH₃)₃-1H-imidazolyl), **249**
 R = 2-(1-CH₃-1H-benzo[d]imidazolyl), **250**
 R = SnAr₃, **415**

R = CH₃, R¹ = C₂H₅, R² = C(CH₃)₃, **396**
 R = CH₃, R¹ = R² = CH(CH₃)₂, **398**
 R = C(CH₃)₃, R¹ = C₂H₅, R² = C(CH₃)₃, **397**
 R = C(CH₃)₃, R¹ = R² = CH(CH₃)₂, **399**

R¹ = R² = CH₃, **495**
 R¹ = C₂H₅, R² = C(CH₃)₃, **421**
 R¹ = R² = CH(CH₃)₂, **419**
 R¹ = R² = cyclohexyl, **420**

R = C(CH₃)₃, R¹ = H, **441**
 R = Ph, R¹ = H, **440**
 R = R¹ = Ph, **439**

R = n-C₅H₁₁, **505**
 R = Ph, **504**
 R = ferrocenyl, **506**

R = s-C₄H₉, E = O, **393**
 R = (S)-Ph(CH₃)CH-, E = O, **394**
 R = C(CH₃)₃, E = O, **391**
 R = C(CH₃)₃, E = S, **392**
 R = Ph, E = O, **389**
 R = Ph, E = S, **390**
 R = 1-naphthyl, E = S, **404**
 R = 1-fluorenyl, E = O, **405**

R = CH₃, **423**
 R = C(CH₃)₃, **422**
 R = Ph, **424**

R = adamantyl, R¹ = OC₂H₅, **428**

R = Ph, R¹ = OH, **429**

R = Ph, R¹ = OC₂H₅, **425**

R = *o*-OCH₃-Ph, R¹ = OC₂H₅, **426**

R = *o*-OCH₃-Ph, R¹ = OH, **430**

R = *o*-OCH(CH₃)₂-Ph, R¹ = OH, **431**

R = *o*-OCH(CH₃)₂-Ph, R¹ = OC₂H₅, **427**

R = *o*-OCH₃-Ph, R¹ = NHCH(CH₃)₂, **448**

432

223

R = NH₂, **173**

R = OC₂H₅, **172**

174

433

434

8

222

417

pz-CRR¹-pz

- R = R¹ = CH₃, **9**
 R = Me, R¹ = C₂H₅, **10**
 R = Me, R¹ = CH₂CH₂Ph, **295**
 R = Me, R¹ = *n*-C₆H₁₃, **294**
 R = Me, R¹ = CH₂Ph, **296**
 R = Me, R¹ = CH₂Cl, **154**
 R = Me, R¹ = CHCl₂, **156**
 R = Me, R¹ = Ph, **300**
 R = Me, R¹ = *p*-OCH₃-Ph, **302**
 R = Me, R¹ = 2,5-(OCH₃)₂-phenyl, **378**
 R = Me, R¹ = *p*-Cl-Ph, **301**
 R = Me, R¹ = 3-thienyl, **303**
 R = R¹ = C₂H₅, **11**
 R = R¹ = CH₂Cl, **155**
 R = Ph, R¹ = CH₂Ph, **376**
 R = Ph, R¹ = COPh, **377**
 R = R¹ = Ph, **72**
 R = Ph, R¹ = 2-pyridyl, **35**
 R = *p*-Br-Ph, R¹ = 2-pyridyl, **176**

n = 1, **16**
 n = 2, **12**
 n = 3, **13**

R = 3-CH₃, **17**
 R = 4-CH₃, **18**

36

177

297

298

337

299

304

305

375

379

499

502

473

- R = R¹ = R² = CH₃, **145**
 R = R¹ = CH₃, R² = Ph, **133**
 R = R¹ = Ph, R² = CH₃, **73**
 R = R¹ = Ph, R² = C(CH₃)₃, **135**
 R = Ph, R¹ = 2-pyridyl, R² = Ph, **260**

n = 1, **146**
 n = 2, **147**

148

R = CH₃, R¹ = *n*-C₆H₁₃, **306**
 R = Ph, R¹ = 2-pyridyl, **175**

241

$R = R' = \text{CH}_3$, **149**
 $R = \text{CH}_3$, $R' = 2,5\text{-di-CH}_3\text{Ophenyl}$, **239**
 $R, R' = \text{cyclobutyl}$, **150**
 $R = \text{CH}_2\text{OH}$, $R' = \text{COOCH}_3$, **409**
 $R = \text{COOH}$, $R' = \text{CH}_2\text{CH=CH}_2$, **408**
 $R = \text{COOH}$, $R' = \text{CH}_2\text{OH}$, **410**
 $R = R' = \text{Ph}$, **74**

pz-CH-pz,pz

R = H, **1**
R = CH₃, **31**
R = CH(CH₃)₂, **56**
R = C(CH₃)₃, **55**
R = Ph, **54**
R = 2,4,6-trimethylphenyl, **97**
R = 2-thienyl, **118**

328

R = H, **362**
R = CH₃, **363**

R = 2,4,6-trimethylphenyl, **98**

353

R = R' = CH₃, **14**
R = CH₃, R' = CF₃, **110**
R = R' = CH(CH₃)₂, **81**
R = C(CH₃)₃, R' = CH₃, **49**
R = C(CH₃)₃, R' = CH(CH₃)₂, **82**
R = adamantyl, R' = CH₃, **120**
R = R' = CH₂OCH₃, **101**
R = Ph, R' = CH₃, **83**

R = R² = R⁵ = adamantyl, R¹ = R³ = R⁴ = Me, **121**
R = R³ = R⁵ = CF₃; R¹ = R² = R⁴ = Me, **111**
R = R² = R⁵ = CF₃; R¹ = R³ = R⁴ = Me, **112**

326

327

330

rac-329

R = CH₃, **20**
R = CH₂OCH₃, **102**

R = CH(CH₃)₂, **50**
R = C(CH₃)₃, **51**
R = Ph, **52**
R = *p*-(CH₃)₂CH-Ph, **53**

113

pz-CR-pz,pz

R = CH₂OH, **380**
R = CH₂OCH₃, **453**
R = CH₂OCH₂CH₃, **454**
R = CH₂O(CH₂)₂CH₃, **455**
R = CH₂OCH₂CH=CH₂, **456**
R = propargyloxymethyl, **460**
R = CH₂OSi(CH₃)₃, **464**
R = *p*-NH₂-phenyl, **94**
R = *p*-NHEt-phenyl, **95**
R = *p*-NEt₂-phenyl, **518**
R = *o*-NH₂-phenyl, **96**
R = *p*-OH-phenyl, **103**
R = *p*-Br-phenyl, **519**
R = S⁻, **331-3**
R = SCH₃, **516**
R = SO₃⁻Li⁺, **435**
R = SO₃⁻TBA⁺, **435**
R = Si(CH₃)₃, **406**

459

520

470

517

463

283

Rf = CF₃(CF₂)_n
n = 4, **465**
n = 6, **466**
n = 8, **467**
n = 10, **468**
n = 12, **469**

R = H, R¹ = *p*-C(CH₃)₃-phenyl, **452**
R = H, R¹ = 4-pyridyl, **457**
R = Ph, R¹ = 4-pyridyl, **458**

R = CH₃, R¹ = Ph, **381**
R = CH₃, R¹ = C(CH₃)₃, **385**
R = CH₂Ph, R¹ = Ph, **383**
R = CH₂OH, R¹ = Ph, **384**
R = CH₂OH, R¹ = C(CH₃)₃, **387**
R = SO₃⁻Li⁺, R¹ = CH(CH₃)₂, **436**
R = SO₃⁻Li⁺, R¹ = Ph, **437**
R = Si(CH₃)₃, R¹ = C(CH₃)₃, **386**
R = Si(CH₃)₃, R¹ = Ph, **382**

471

335

407

pz,pz-C-pz,pz

15

325

poly(pz-CHR-pz; pz-CR-pz,pz)

R = H, **89**
R = (3 or 5)-CH₃, **90**
R = 4-NO₂, **341**
R = 4-I, **104**

n = 1, R = H, **136**
n = 1, R = 3,5-(CH₃)₂, **140**
n = 4, R = H, **277**
n = 5, R = H, **278**

R = H, **91**
R = 3,5-(CH₃)₂, **92**
R = (3 or 5)-CH₃, **93**
R = 3,5-(CH₃)₂,4-NO₂, **117**
R = 3,5-(CH₃)₂,4-I, **115**
R = 4-CH₂Ph, **225**
R = 4-NO₂, **116**
R = 4-I, **114**

178

189

500

2,2', **268**
2,3', **269**
2,4', **270**
3,3', **271**
3,4', **272**
4,4', **214**

279

510

276

274

227

275

511

37

R = H, **348**
R = CH₃, **349**

482

532

533

Table 1. CSD codes for poly(1*H*-pyrazol-1-yl)methanes

Number	CSD name	Number	CSD name	Number	CSD name
1	IZANOM	153	CURPAI	335	DOLXIN
2	PAPHOD	158	RIBNUL	337	LAQDUE
3	PAPHUJ	168	OHAXOK	338	EFOPIZ
9	TEMWIR	172	ESUFON	341	TECYUX
11	QAPKUN	178	NAKFIP	356	SOQGAI
12	QEJJUK	179	FOMGUK	358	ELEMEN
13	QEJJOE	182	MIMBOB	362	FOPHAU
14	CICYES	183	NICGAI	368	QIXCEH
15	JEHRET	184	NICGUC	380	URAWOA
20	DUDFAL	185	TIXSEZ	388	SUSBUE
27	TACGIN	187	TIXSOJ	390	FUPWET
31	TUYZEU	188	TIXRUO	392	FUPWIX
47	ESIYIO	189	TIXSUP	395	NICSEY
48	ZASHIK	190	YUJBEL	396	XIZWEJ
49	TUJKIT	193	IGECED	400	TOXPAZ
54	AKUSAA	196	BUPCIZ	401	TOXPED
58	POWQIB	210	RAVGOM	406	XAGLOH
59	ABUBEE	215	MINBES	408	KETHEX
60	JAWNEB	217	JUGBUK	409	KETHOH
61	XELQUA	219	YUQXIT	430	SEMGOI
64	CAKWAN	230	IJASUI	431	SEMGUO
68	QAFWEA	231	IJATAP	432	LUSTUO
71	MITKIK	235	UJUXUT	433	QAFWIE
72	ATOBOA	236	UJUXAZ	434	ESIYOU
74	ATOBUG	237	UJUZEF	435	NEVWAO
81	SEFKUK	238	UJUYII	435	HOPREL
82	SEFLAR	239	UJUXIH	438	ESIWUZ
83	MIXVAR	240	UJUYAA	440	MIMFIY
85	EFOPOF	241	UJUYUU	441	DOFCOR

92	MINBAO	242	UJUZAB	442	TIRSET
94	HIXLIK	245	FUXYAZ	443	NEVPIP
96	HIXLOQ	257	FUXXUS	444	IGUWEN
97	XIVVAA	261	ISUPOC	445	IGUWAJ
98	XIVVEE	262	ISUPUI	446	YAMLOP
99	ISIKAW	263	ISUQAP	448	SEMKIG
100	NIXRAO	264	DAFPIL	450	FUHZAK
103	YAHKOJ	265	DAFPUX	453	YOHLAK
104	TECZAE	266	WEQFAB	457	IJEPUI
106	SEMHAV	267	ABANOI	459	CEDPOR
109	GUTPIV	274	VILBOJ	460	GASBIM
110	ZEQBEE	275	VILBUP	461	KETJAV
111	ZEQBII	276	HADZET	462	TIZMIZ
112	ZEQBOO	283	COVTOY	463	OGIWAD
114	YULWIN	284	FACWEO	467	USUGUL
118	DUFDFUF	293	LORGUW	477	QUTCEN
120	ZONXAD	325	LUNYID	479	QUTCIR
121	ZONXEH	331	QOGCEU	481	ACUCUW
122	HUDGAQ	332	QOGBOD	484	GASBOS
143	LISYET	334	DOLXEJ	486	GASBUY
490	SUSCAL	516	COKXUX	524	OHAYAX
492	SUSBOY	517	COKYEI	538	TUYWUH
498	TIXSID	520	YAHFOE	539	QEPTAI
502	YUJBIP	521	WEQFEF	540	QEPTUC
511	GIFMUF	522	NEXMOT	541	QEPVAK
512	YITDOW	523	OHAXUQ		

Poly(pyrazolyl)methanes are extraordinary ligands: complexes with 40 metals are known

A historical overview of the preparation of these polydentate systems is gathered

A comprehensive survey of the preparation of the main structures is included

Numerous ways for derivatization at the ring, bridge and chains are reported

NMR, X-Ray and computational studies of poly(pyrazolyl)methanes are also included